
The 6th Asian Workshop on Molecular Spectroscopy

November 2-5, 2022 Sapporo, Taipei, Xi'an, and Ulsan
November 3, 4 (Scientific Program)

- New spectroscopic techniques and instruments
- Precision measurements
- Application of spectroscopy to dynamics
- Spectroscopy in the gas phase
- Condensed phase spectroscopy
- Ultrafast spectroscopy
- Theory and analysis



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We are pleased to acknowledge the sponsors for supporting the 6th AWMS (AWMS 2022). The support of the Kou-Share online broadcasting and posters comes from DIENTECH (成都迪恩科技), the Ultrafast Science journal, the PARATERA (并行科技) computing, and the School of Physics, Xi'an Jiaotong University. Please see the this book to learn more about them.



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1. Join our Webex Video conference from the meeting link https://asmeet.webex.com/asmeet-en/j.php?MTID=m634c609a6cf8d9f8193db9afacf12615 Join the Webex Videoconference by meeting number Meeting number (access code): 2514 674 3091 Meeting password: AWMS2022	
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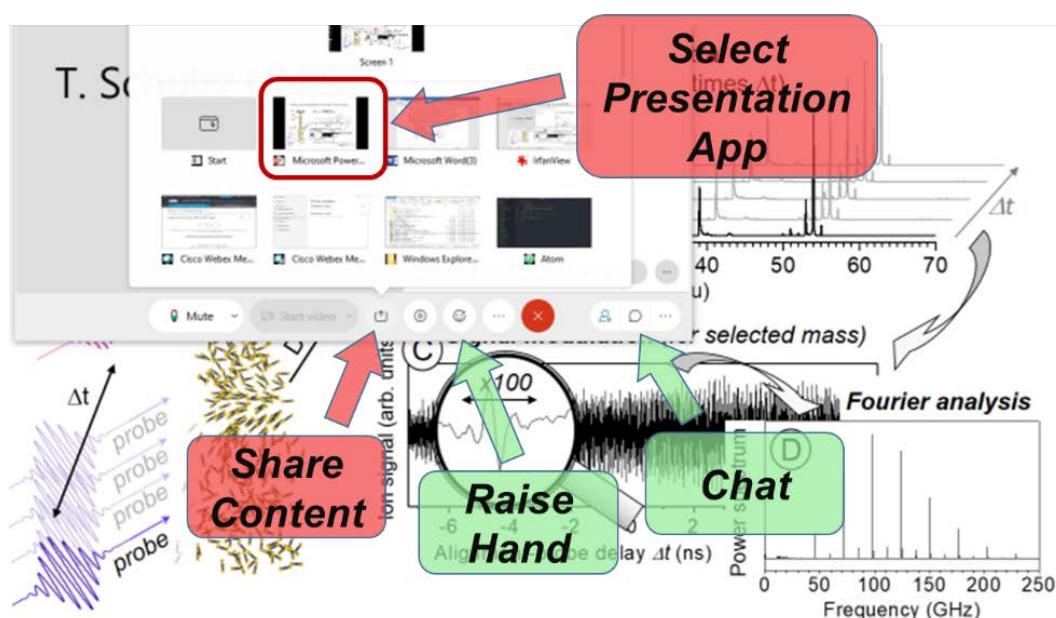
Visit: www.awoms.org or <https://www.koushare.com/topicIndex/i/AWMS2022>

1. If you have not installed Webex, download it at: www.webex.com/downloads.html.
Please take a few minutes to familiarize yourself with the program functions. Refer to the figure on the next page for the location of critical interface elements.
2. Please use your full name to log in the Webex meeting room, so the session Discussion Leader can identify you.
3. Please keep your microphone muted unless you are a session Discussion Leader or the current presenter. Always check the microphone setting when entering the meeting room.
4. A session Discussion Leader speaks first, followed by the presenter. The next presenter can use the function **Reactions**  > **Raise hand**  or type a message in the **chat window** to inform the session Discussion Leader that he / she is online and ready.
5. After a presenter finishes his/her speech, members of the audiences can use **raise hand**  to attract a session Discussion Leader's attention. The session Discussion Leader then calls out the audience member to ask his / her question. At this moment, the audience member should turn on his / her microphone and speak. Questions can also be typed in the **chat window** . In this case, the session Discussion Leader will read the question to the presenter. Each session Discussion Leader can decide how to apportion the Q&A time. After the Q&A time, all questioners should turn off their microphone.
6. Presenters share slides on their computer by starting their presentation software (**Full-Screen!**) and then selecting **Share content**  in the Webex app. The **Share content** dialog box shows thumbnail previews: select the presentation window.
7. The Taipei venue runs a "live stream" for the workshop. Therefore, presenters at the Taipei meeting site do not use the **share content** function and all presenters will speak in the front of the lecture hall as in a regular local conference.
8. For watching presentations from Taipei (live stream mode), audiences can use the **Focus view** function to zoom into the video.
8. Do not record or publish any video or screen-shots without the permission of the presenter.
9. For details about the Webex meeting software, please check the official Cisco Webex website.

Workshop at the Taipei site and other joint meeting rooms

1. Most participants at the Taipei site will attend the workshop in the lecture hall and the audio-visual (AV) equipment in the lecture hall will be integrated into the conference live stream. Participants in the lecture hall can also use their own computer to join the on-line workshop, but the microphone should be always remain turned off. Otherwise, sound-feedback will create an echo loop.
2. For the Q&A time, we must distinguish between local and remote talks. When a session Discussion Leader is at the local site, raise your hand and walk downstage to the side of the presentation stage. Please walk downstage as soon as the Q&A period starts (before the session Discussion Leader calls on you) to avoid delays. Ask your question using the session Discussion Leader's microphone.

When the session Discussion Leader is at a different location, you can use your own computer / phone or the public computer in the meeting room to ask your question. With your own computer / phone, you can use the Webex **Raise hand** function to attract the Discussion Leader's attention and wait for his/her acknowledgement of your question. Once acknowledged, turn on the microphone and speak without delay. We will prepare two public computers at the Taipei site for raising questions: one is in the lecture hall and another is outside the lecture hall. In the lecture hall, you must use the public microphone and walk downstage, otherwise online attendees may not see you. Outside the lecture hall, you can use your own laptop / phone or the public computer; you don't need to appear on the stage of the lecture hall. At any time, you can use the **Chat** function to type your question to a session Discussion Leader. The Discussion Leader will then read your question to the speaker (if time permits).



The Webex user interface

1. We plan to live-stream all presentations via [KouShare](https://www.koushare.com) and leave them accessible for some time after the meeting. Please inform us ahead of time if your presentation contains confidential information that should not be publicly shared.

Please visit: <https://www.koushare.com/topicIndex/i/AWMS2022>



2. Because a traditional poster session is incompatible with the online meeting format, we asked all Poster Presenters to prepare a 3-5-minute video recorded by favorable meeting software (see below brief guidelines). The poster videos/pdf files will be accessible during the meeting days and will remain accessible afterwards for a certain time. ***We strongly encourage all conference participants to look at the posters and to leave comments for each poster.***

To prepare for the poster presentation, please follow roughly the following guidelines:

1. Save a pdf version of your poster (A4 or letter size);
2. Open your favorable meeting software, e.g., zoom, tencent, skype, or others you like, and share the part of the poster you are demonstrating in full screen;
3. Explain your poster within 3-5 mins and record it;
4. Send the recorded video and your pdf version of poster to awms2022xian@126.com with your name and your assigned poster number (see Page xx), for example, P01-Kaito Takahashi.

If the size is too large and cannot be transferred via email attachment, please send the link where the committee can download the files.

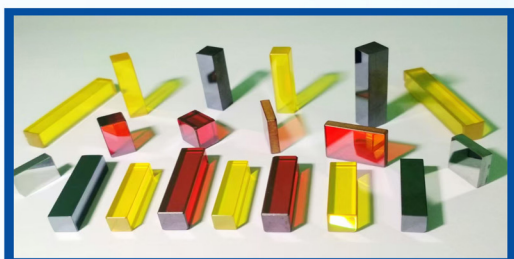
Poster abstracts can be found in the poster part of this book.



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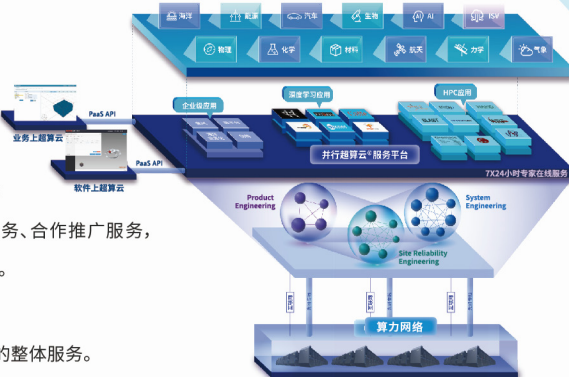
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Time table of the AWMS 2022 program

Nov. 03			Nov. 04		
Xi'an/Taipei Time (UTC+08:00)			Xi'an/Taipei Time (UTC+08:00)		
For Sapporo/Ulsan time (UTC+09:00), please add 1 hour			For Sapporo/Ulsan time (UTC+09:00), please add 1 hour		
			Session 6 discussion leader: Thomas Schultz		
			8:30	8:45	Qian Gou
8:50 9:15 OPENING			8:45	9:00	Carlos Cabezas
Session 1 discussion leader: Takayuki Ebata			9:00	9:15	Weixing Li
9:15	9:30	Xue-Bin Wang	9:15	9:30	Begüm Rukiye Özer
9:30	9:45	Yuki Miyamoto	9:30	9:45	Hyejin Kwon
9:45	10:00	Kaijun Yuan	9:45	10:00	Changseop Jeong
10:00	10:15	Daofu Yuan	10:00 10:15 BREAK		
10:15	10:30	Do Hyung Kang	Session 7 discussion leader: Tetsuya Hama		
10:30 10:45 BREAK			10:15	10:30	Xiaqing Zeng
Session 2 discussion leader: Gao-Lei Hou			10:30	10:45	Isabelle Weber
10:45	11:00	Ayami Hiramoto	10:45	11:00	Prasad Joshi
11:00	11:15	Tao Wu	11:00	11:15	Shu-Yu Lin
11:15	11:30	Shota Saito	11:15	11:30	Min Cheng
11:30	11:45	Yang Liu	11:30 12:30 LUNCH		
11:45	12:00	Yandong Tan	Session 8 discussion leader: Yasuki Endo		
12:00	12:15	I-Yun Chen	12:30	12:45	Arunan Elangannan
12:15 13:00 LUNCH			12:45	13:00	Gang Feng
Session 3 discussion leader: Jer-Lai Kuo			13:00	13:15	Ziqiu Chen
13:00	13:15	Naresh Patwari	13:15	13:30	Jiwen Guan
13:15	13:30	Takayuki Ebata	13:15	13:45	JangHan Kwon
13:30	13:45	Gang Li	13:45	14:00	Makoto Nikaido
13:45	14:00	Chen-An Chuang	14:00 14:15 BREAK		
14:00 14:15 BREAK			Session 9 discussion leader: Tao Yang		
Session 4 discussion leader: Masashi Tsuge			14:15	14:30	You Li
14:15	14:30	Ni-En Sie	14:30	14:45	Jianzhi Xu
14:30	14:45	Chao-Hui Huang	14:45	15:00	Hikaru Tanaka
14:45	15:00	Ying-Hsuan Chen	15:00	15:15	Jia-Lin Chang
15:00	15:15	Takeshi Hasegawa	15:15	15:30	Qin Yang
15:15	15:30	Yaodi Yang	15:30	15:45	Zhongming Jiang
15:30	15:45	Anna A. Simonova	15:45 16:00 BREAK		
15:45 16:00 BREAK			Session 10 discussion leader: Yung Sam Kim		
Session 5 discussion leader: Kaito Takahashi			16:00	16:15	Hong Gao
16:00	16:15	Zhendong Sun	16:15	16:30	Quan Shuai
16:15	16:30	Mingde Li	16:30	16:45	Yen-Chu Hsu
16:30	16:45	Piero Ferrari	16:45	17:00	Yurong Xu
16:45	17:00	Shunli Chen	17:00	17:15	Akira Shimizu
17:00	17:15	Hak-Won Nho	17:15	17:30	Masaaki Baba
FINISH			Concluding		

Meeting Program – Nov. 03 (Thursday)

Times in Xi'an and Taipei (UTC+08:00)

+ 1h for all times in Sapporo and Ulsan

8 : 50 — 9 : 15 Opening remarks

Session 1: Electronic ion; Discussion leader: Takayuki Ebata

- 9 : 15 — 9 : 30** O1 Xue-Bin Wang (Pacific Northwest National Laboratory, USA)
Cryogenic “Iodide-Tagging” Photoelectron Spectroscopy: A Sensitive Probe for Specific Binding Sites of Amino Acids
- 9 : 30 — 9 : 45** O2 Yuki Miyamoto (Okayama University, Japan)
High resolution spectroscopy of buffer gas cooled phthalocyanine
- 9 : 45 — 10 : 00** O3 Kaijun Yuan (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China)
VUV Photochemistry of Hydrogen Sulfide (H₂S)
- 10 : 00 — 10 : 15** O4 Daofu Yuan (Brown University, USA)
Probing dipole-bound electron induced valence orbital polarization using high resolution photoelectron imaging of cryogenically cooled molecular anions
- 10 : 15 — 10 : 30** O5 Do Hyung Kang (KAIST, Republic of Korea)
Real-time Nonadiabatic Electron Dynamics on Non-valence Bound States of Polyatomic Molecular Anions

----- Break -----

Session 2: Detection method; Discussion leader: Gao-Lei Hou

- 10 : 45 — 11 : 00** O6 Ayami Hiramoto (Okayama University, Japan)
Doppler effects in cryogenic buffer gas cell
- 11 : 00 — 11 : 15** O7 Tao Wu (Czech academy of sciences, Czech)
Exploring Lanthanide Circularly Polarized Luminescence by a Raman Optical Activity Spectrometer
- 11 : 15 — 11 : 30** O8 Shota Saito (The University of Tokyo, Japan)
Direct detection of OH radicals in the photolysis of liquid nonanoic acid using laser-induced fluorescence
- 11 : 30 — 11 : 45** O9 Yang Liu (Institute of Physics, Chinese Academy of Sciences, China)
High-power longwave mid-IR frequency combs based on Er-fiber laser driven SESS
- 11 : 45 — 12 : 00** O10 Yandong Tan (University of Science and Technology of China, China)
Quantitative detection of molecules by cavity-enhanced double resonance absorption spectroscopy

12: 00 — 12 : 15 O11 I-Yun Chen (Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan)
Ppt-level NO₂ detection based on quartz-enhanced photoacoustic spectroscopy (QEPAS)

----- Lunch -----

Session 3: Cluster, atmospheric; Discussion leader: Jer-Lai Kuo

13 : 00 — 13 : 15 O12 Naresh Patwari (Indian Institute of Technology Bombay, India)
Hierarchy of π -Stacking Determines the Aggregation Behaviour

13 : 15 — 13 : 30 O13 Takayuki Ebata (National Yang Ming Chiao Tung University, Taiwan)
IR-VUV Spectroscopic Study on the Structure of Pyridine-water Clusters and its Relationship with the Local Structure of Pyridine/Water Mixed Solution

13 : 30 — 13 : 45 O14 Gang Li (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China)
Infrared Spectroscopy of Neutral Atmospheric Clusters

13 : 45 — 14 : 00 O15 Chen-An Chuang (National Yang Ming Chiao Tung University, Taiwan)
Rate coefficient of methyl vinyl ketone oxide + HCl investigated with a quantum cascade laser absorption system

----- Break -----

Session 4: Ice, solvations; Discussion leader: Masashi Tsuge

14 : 15 — 14 : 30 O16 Ni-En Sie (National Central University, Taiwan)
Key Parameters Controlling the Photodesorption Yield in Interstellar CO Ice Analogs

14 : 30 — 14 : 45 O17 Chao-Hui Huang (National Central University, Taiwan)
Chemical Evolution and electron-stimulated desorption of H₂O+CO ice mixture

14 : 45 — 15 : 00 O18 Yen-Chu Hsu (National Central University, Taiwan)
VUV photolysis of N₂O ices

15 : 00 — 15 : 15 O19 Takeshi Hasegawa (The University of Tokyo, Japan)
Infrared multiple-angle resolution spectroscopy of interstellar ice analog in cryogenic environment

15 : 15 — 15 : 30 O20 Yaodi Yang (Tohoku University, Japan)
Overtone spectroscopy of microsolvated protonated methanol

15 : 30 — 15 : 45 O21 Anna A. Simonova (V.E. Zuev Institute of Atmospheric Optics of Siberian Branch of the Russian Academy of Science, Russia)

Semiempirical dimer-based model of the water vapour self-continuum absorption within IR absorption bands

----- Break -----

Session 5: Metal, surface, charge transfer; Discussion leader: Kaito Takahashi

- 16 : 00 — 16 : 15 O22 Zhendong Sun (Shandong University, China)
Adsorption and Dissociation of CO₂ Molecules at Co(0001) Surfaces Probed by Infrared Spectroscopy
- 16 : 15 — 16 : 30 O23 Mingde Li (Shantou University, China)
Ultrafast spectroscopy detection and regulation of excited states and transient intermediates of organic single crystals and nanocrystals
- 16 : 30 — 16 : 45 O24 Piero Ferrari (FELIX Laboratory, The Netherlands)
An octacoordinated Nb atom in the NbAl₈H₈⁺ cluster
- 16 : 45 — 17 : 00 O25 Shunli Chen (Shantou University, China)
Tuning Near-Infrared Photothermal Conversion of Binary and Ternary Charge-transfer Cocrystals by Intermolecular Interactions
- 17 : 00 — 17 : 15 O26 Hak-Won Nho (Ulsan National Institute of Science and Technology, Republic of Korea)
Ultrafast photophysics of a single chain donor-acceptor copolymer

Meeting Program – Nov. 04 (Friday)

Times in Xi'an and Taipei (UTC+08:00)

+ 1h for all times in Sapporo and Ulsan

Session 6: Rotational spectroscopy techniques; Discussion leader: Thomas Schultz

- 8 : 30 — 8 : 45 O27 Qian Gou (Chongqing University, China)
Detection of Pre-Reactive intermediates of Diels-Alder Cycloadditions by
Molecular Rotation Spectra
- 8 : 45 — 9 : 00 O28 Carlos Cabezas (Instituto de Física Fundamental (IFF), Spain)
Identification of New Interstellar Molecules by Rotational Spectroscopy and
Quantum Chemical Calculations
- 9 : 00 — 9 : 15 O29 Weixing Li (Fudan University, China)
Double-proton transfer tunneling over a phenyl ring revealed by broadband
microwave spectroscopy
- 9 : 15 — 9 : 30 O30 Begüm Rukiye Özer (Ulsan National Institute of Science and Technology,
Republic of Korea)
Molecular Beam Spectroscopy with an Infinite Interferometer: Spectroscopic
Resolution and Accuracy
- 9 : 30 — 9 : 45 O31 Hyejin Kwon (Ulsan National Institute of Science and Technology, Republic
of Korea)
2D IR Investigation of the Structure and Dynamics of D₂O Dissolved in CHCl₃
- 9 : 45 — 10 : 00 O32 Changseop Jeong (Chungbuk National University, Korea)
Anisotropic Circular Dichroism Spectroscopy of Jet-cooled Chiral Molecules

----- Break -----

Session 7: Cold chemistry, matrix isolation; Discussion leader: Tetsuya Hama

- 10 : 15 — 10 : 30 O33 Xiaoqing Zeng (Fudan University, China)
Photochemistry of Phosphorus Hydrides Studied by Matrix-isolation
Spectroscopy
- 10 : 30 — 10 : 45 O34 Isabelle Weber (National Yang Ming Chiao Tung University, Taiwan)
Electronic Spectroscopy of PAH Isolated in Solid para-Hydrogen
- 10 : 45 — 11 : 00 O35 Prasad Joshi (National Yang Ming Chiao Tung University, Taiwan)
Production of isoquinolinium (*iso*-C₉H₇NH⁺) and isoquinolinyl radical (*iso*-C₉H₇NH,
1-*iso*-HC₉H₇N, and 3- to 8-*iso*-HC₉H₇N in solid para-hydrogen

11 : 00 — 11 : 15 O36 Shu-Yu Lin (National Yang Ming Chiao Tung University, Taiwan)
Formation of Para-H₂O by Vacuum-UV Photolysis of O₂ in Solid Hydrogen:
Implication to Astrochemistry

11 : 15 — 11 : 30 O37 Min Cheng (Institute of Chemistry Chinese Academy of Sciences,
China)
Spectroscopic study of C₂ in vacuum ultraviolet region

----- Lunch -----

Session 8: Molecular interactions; Discussion leader: Yasuki Endo

12 : 30 — 12 : 45 O38 Arunan Elangannan (Indian Institute of Science, India)
Microwave Spectroscopy and Computational Chemistry: Structure, Bonding and
Dynamics

12 : 45 — 13 : 00 O39 Gang Feng (Chongqing University, China)
Rotational spectroscopic characterization of the non-covalent S- π interactions

13 : 00 — 13 : 15 O40 Ziqiu Chen (Lanzhou University, China)
The Rotationally-resolved Vibrational Spectra of Cyclopropylamine in the Infrared
Region

13 : 15 — 13 : 30 O41 Jiwen Guan (University of Science and Technology of China, China)
Bottom-Up Synthesis of Tetracyclic Polycyclic Aromatic Hydrocarbons through the
Indenyl Radical Self-Reaction

13 : 30 — 13 : 45 O42 JangHan Kwon (Ajou University, Korea)
Cryogenic Ion Spectroscopy of Singly Protonated Peptide DYYVVR for Identifying
Phosphorylation Sites

13 : 45 — 14 : 00 O43 Makoto Nikaido (Tokyo Institute of Technology, Japan)
Ultrafast mode-selective excitation of large-amplitude vibration in
diphenylmethane through impulsive stimulated Raman scattering

----- break -----

Session 9: Theory; Discussion leader: Tao Yang

14 : 15 — 14 : 30 O44 You Li (Jilin University, China)
Constructing spectroscopic accuracy intermolecular potential energy surface by
the physical model with machine learning technique

14 : 30 — 14 : 45 O45 Jianzhi Xu (Xi'an Jiaotong University, China)
Benchmarking calculations of the infrared spectra of cosmic fullerene and its
relatives

- 14 : 45 — 15 : 00 O46 Hikaru Tanaka (Gifu University, Japan)
Theoretical Study on Benzene Using Path Integral Molecular Dynamics Method:
Are the C-H and C-D Bond Lengths in C₆H₆ and C₆D₆ Almost the Same?
- 15 : 00 — 15 : 15 O47 Jia-Lin Chang (National Taichung University of Education, Taiwan)
Interpretation and prediction of the photoelectron spectra of molecules via
computing Franck–Condon factors
- 15 : 15 — 15 : 30 O48 Qin Yang (Institute of Organic Chemistry and Biochemistry, Academy
of Sciences, Czech)
Anharmonic Vibrational Raman Optical Activity of Methyloxirane: Theory and
Experiment Pushed to the Limits
- 15 : 30 — 15 : 45 O49 Zhongming Jiang (Scuola Normale Superiore, Piazza dei Cavalieri,
Italy)
Computational approach to study the vibronic effect in Electronic Linear Dichroism

----- Coffee Break -----

Session 10: Experiment and Theory; Discussion leader: Yung Sam Kim

- 16 : 00 — 16 : 15 O50 Hong Gao (Institute of Chemistry, Chinese Academy of Sciences, China)
High-resolution scattering imaging of the charge transfer processes between spin-
orbit selected Ar⁺(²P_{3/2, 1/2) ion and the neutrals N₂ and H₂}
- 16 : 15 — 16 : 30 O51 Quan Shuai (Dalian Institute of Chemical Physics, Chinese Academy of
Sciences, China)
Mapping partial wave dynamics in scattering resonances by low-energy NO-He
collisions
- 16 : 30 — 16 : 45 O52 Yen-Chu Hsu (National Taiwan University, Taiwan)
Vibrational Predissociation and Intramolecular Vibrational Redistribution of the
C₃Ar van der Waals Complex
- 16 : 45 — 17 : 00 O53 Yu-Rong Xu (University of Science and Technology of China, China)
Saturated absorption spectroscopy of the A-band of O₂
- 17 : 00 — 17 : 15 O54 Akira Shimizu (Kobe University, Japan)
High-resolution laser spectroscopy of S₁←S₀ transition of trans-stilbene
- 17 : 15 — 17 : 30 **Closing Remarks** **Masaaki Baba (Kobe University, Japan)**

Meeting Program – Posters

Because a traditional poster session is incompatible with the online meeting format, we asked all Poster Presenters to prepare a 3-5-minute video recorded by favorable meeting software (see below brief guidelines). The poster videos/pdf files will be accessible during the meeting days and will remain accessible afterwards for a certain time. ***We strongly encourage all conference participants to look at the posters and to leave comments for each poster.***

To prepare for the poster presentation, please follow roughly the following guidelines:

1. Save a pdf version of your poster (A4 or letter size);
2. Open your favorable meeting software, e.g., zoom, tencent, skype, or others you like, and share the part of the poster you are demonstrating in full screen;
3. Explain your poster within 3-5 mins and record it;
4. Send the recorded video and your pdf version of poster to awms2022xian@126.com with your name and your assigned poster number (see below), for example, P01-Kaito Takahashi.

If the size is too large and cannot be transferred via email attachment, please send the link where the committee can download the files.

Poster abstracts can be found in the poster part of this book.

A full list of submitted posters

P01	Kaito Takahashi	Vibrational Spectra from Quantum, semiclassical, and classical pictures
P02	Shuming Bai	The shift between vertical excitation and band maximum in molecular photoabsorption
P03	Jia Li	From State-of-the-art Ab initio Calculations to Spectroscopic and Thermophysical Properties
P04	Yurong Hu	Ab initio potential energy functions, spectroscopy and thermal physics for krypton-contained rare gas dimers
P05	Huu Trong Phan	A neural network potential assisted first-principle exploration of the structure of mono-saccharides
P06	Dong Cao Hieu	Application of neural network potential to assist understanding of Structure of protonated dipeptide of glycine, sarcosine and alanine
P07	Shweta Jindal	Role of efficient structure search in assigning peaks in vibrational spectra
P08	Qian-Rui Huang	Anharmonic vibrational analysis on the near-infrared region of $\text{H}_3\text{O}^+-\text{X}_n$ ($\text{X} = \text{Ar}, \text{N}_2$, and CO , $n = 1-3$)
P09	Rona F. Barbarona	From Dark to Bright: Fermi resonance in astrochemically relevant cyanocontaining complexes
P10	Ha-Quyen Nguyen	A Study on the Fermi-Resonance in protonated amino acids and peptides modulated by intramolecular hydrogen-bond strength
P11	Ekta Arora	Infrared spectra of mono-deuterated pyridines
P12	Po-Jen Hsu	Infrared spectroscopy and theoretical structure analyses of protonated 2,2,2-trifluoroethanol clusters

P13	Chia-I Huang	IR spectroscopy of the C–H stretching region of mono-substituted benzenes cooled in a supersonic jet and the anharmonic analysis
P14	Jun-Ying Feng	Infrared spectra and structures of supersonically cooled (pyrazine) ₂ and (pyrazine) _m –(H ₂ O) _n clusters studied with IR-VUV spectroscopy
P15	Ching-Hua Chang	Gas-phase spectroscopic identification of the chlorovinyl radical
P16	Jie-Ning Yang	Kinetics of Criegee Intermediate Reactions with Nitric Acid Measured by UV Absorption Spectroscopy
P17	Yen-Ru Wu	Kinetics Isotope Effect of the Simplest Criegee Intermediate Reaction with Water Vapor Measured with UV Absorption Spectroscopy
P18	Yen-Hsiu Lin	Absolute cross sections of thermalized methyl vinyl ketone oxide (MVKO) and methacrolein oxide (MACRO) have been measured
P19	Bedabyas Behera	Infrared Characterization of the Intermediates and Products of the Reaction between methyl-substituted Criegee Intermediate CH ₃ CHOO and HC(O)OH
P20	Chun-Kai Chen	Reaction dynamics of (CH ₃) ₂ Cl + O ₂ studied with step-scan time-resolved Fourier-transform infrared emission spectroscopy
P21	Sheng-Lung Chou	A Laboratory-Demonstrated Model that Explains the Galactic Extended Red Emission: Graphene Exposed to Far-ultraviolet Light
P22	Yu-Xuan Wu	The 3D printed Photoacoustic Spectroscopy with T shaped cell for detection of ozone with a 265-nm LED
P23	Zengjun Xiao	A BaGa ₄ Se ₇ crystal based mid-infrared pulsed light source for high resolution spectroscopy in 3.5 -12 μm
P24	Zhaofeng Wang	A 1083 nm Pulsed Laser Source for Helium Resonance Fluorescence Lidar
P25	Dingding Lv	Controlling Double Proton Transfer: The Formic Acid Dimer-Fluorinated Benzenes Complexes Studied by Broadband Microwave Spectroscopy
P26	Tingting Yang	Non-covalent Interactions between Aromatic Heterocyclic and Carboxylic Acid: Rotational Spectroscopy of the Furan-Formic Acid and Thiophene-Formic Acid Complexes
P27	Liuting Wang	Noncovalent interactions between amides and aldehyde: Rotational Spectroscopy of the Formamide-H ₂ CO and 2-azetidinone-H ₂ CO Complexes
P28	Siyu Zou	Change of Binding sites from monohydrate to dihydrate: Rotational studies of 2-ethacrolein-(H ₂ O) ₂
P29	Kaisheng Song	Validating experiments for the reaction H ₂ + NH ₂ - on a full-dimensional accurate PES
P30	Xinyue Zhang	Missing Link in Diels-Alder Reaction: Rotational Imaging Pre-reactive Intermediate of Furan-Maleic Anhydride Cycloaddition Competitive
P31	Tianyue Gao	hydrogen bond and π···π* interaction between isoprene and acrolein: A rotational study
P32	Hao Wang	Chiral Recognition:direct spectroscopic detection of propylene oxide-trifluoromethyl propylene oxide dimer
P33	Xinlei Chen	Concerted vs Stepwise Quantum Tunnelling of Heavy Atom Observed by Microwave Spectroscopy

P34	Jingling Hong	Controlling Double Proton Transfer Tunneling in Formic Acid-Propionic Acid Dimer with a Single Weakly Bound Molecule
P35	Zhuang Liu	Molecular beam density measurement with cavity-enhanced absorption spectroscopy
P36	Mengyi Yu	Cavity-enhanced double resonance spectroscopy of HD
P37	Song Zhang	Spectroscopic determination of single proton transfer on the excited photochromism of Schiff bases
P38	Duoduo Li	Signatures of a Conical Intersection in Nonadiabatic Dynamics of Polyfluoropyridine
P39	Yanmei Wang	Structural Evolution Dynamics and Vibrational Wavepacket Coherence of Excited States in Polyatomic Molecules
P40	Jing Lai	Incorporation of the CH ₂ group promotes indirect-direct bandgap transition of perovskite
P41	Ding Yongqi	Conversion of Dinitrogen and Oxygen to Nitric Oxide Mediated by Triatomic Yttrium Cations: N–N Bond Switch
P42	Shaowen Feng	Photoelectron Spectroscopy of C ₂ O ₃ using a plasma entrainment slow electron velocity-map imaging spectrometer
P43	Gaoming Hu	Photodissociation Spectroscopy and Dynamics of the [O–O ₂] ⁺ Complex
P44	Bong Gyu Jeong	Branching ratio of 1-bromo-3-chlorobenzene cation in various wavelength photodissociation
P45	Jr-Yau Li	Chemical Evolution and electron-stimulated desorption of H ₂ O+CO ice mixture
P46	Chun-Yi Lee	Key Parameters Controlling the Photodesorption Yield in Interstellar CO Ice Analogs
P47	Yen-Yu Hsu	Vacuum ultraviolet photodesorption of hydrogen sulfide
P48	Yi-Xiang, Peng	VUV Photolysis of Methane Ices
P49	Chun-Chi Huang	VUV photoinduced energy transfer in solid CO ices
P50	Pan Jiang	Observation of rotationally dependent fine-structure branching ratios near the predissociation threshold N(² D _{5/2, 3/2})+N(² D _{5/2, 3/2}) of ¹⁴ N ₂
P51	Yufan Ding	A research plan on the reaction mechanism between H ₂ ⁺ and He at low collision energy
P52	Liya Lu	Accurate measurements of the bond dissociation energies of ¹⁴ N ₂ , ¹⁴ N ¹⁵ N and ¹⁵ N ₂
P53	Liyang Ma	vacuum ultraviolet spectra of C ₂ : g ³ Δ _g g-a ³ Π _{uu} and f ³ Σ _g ⁺ --a ³ Π _u
P54	Tonghui Yin	Observation of the new electronic state of C ₂ : 1 ³ Σ _g ⁺
P55	Guo-dong Zhang	State-selected ion-molecule scattering for Ar ⁺ (² P _{3/2,1/2}) + N ₂ at low energy
P56	Yuan-Pin Chang	Accelerated Sulfur Oxidation by Ozone on Surfaces of Single Optically Trapped Aerosol Particles
P57	Guan-Jie Luo&Pei-Hsuan Wu	Kinetics and solvent effect of the color fading reaction of phenolphthalein in alkaline solution studied with a simple and economic device

P58	Kowit Hengphasatporn	Estimation of acid dissociation constants (pKa) of N-containing heterocycles in DMSO and transferability of Gibbs free energy in various solvent conditions
P59	Aniruddha Adhikari	Probing Excited-State Proton Transfer in a Nanoscopic Water Pool
P60	Ye-Jin Choi	Determination of the formation constants for the hydrogen-bonded complex of a photoacid in polar aprotic binary solvent mixtures
P61	In Heo	Corrected Benzene Structure by Mass-Correlated Rotational Raman Spectroscopy
P62	Yujian Li	Formation of Complex Nitrogen-Containing Prebiotic Molecules Induced by Single Photon Ionization
P63	Jia Li	An Accurate Full-Dimensional H ₄ O Potential Energy Surface and Dynamics of Exchange Reaction $\text{H}_2 + \text{H}'_2\text{O} \rightarrow \text{HH}' + \text{HOH}'$
P64	Yue Liang	Characterizing the molecular structure of fluorinated benzaldehyde by rotational spectroscopy

Abstracts for Oral Talks

Cryogenic “Iodide-Tagging” Photoelectron Spectroscopy: A Sensitive Probe for Specific Binding Sites of Amino Acids

Wenjin Cao,¹ Hanhui Zhang,² Qinqin Yuan,¹ Xiaoguo Zhou,² Steven R. Kass,³

Xue-Bin Wang¹

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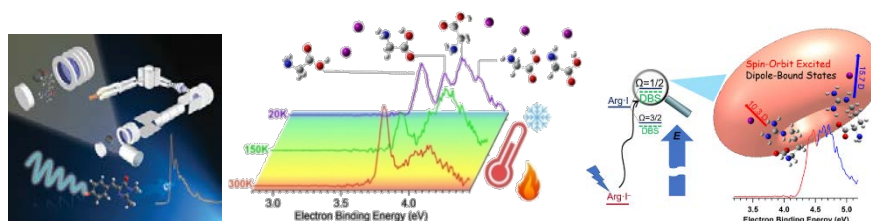
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This presentation showcases applying cryogenic photoelectron spectroscopy coupled with electrospray ionization (ESI) to probe specific binding sites of amino acids (AA) ranging from glycine, various methylated glycine to arginine [1-3]. Multiple isomers of AA·I⁻ complexes were generated from ambient ESI and kinetically isolated in a cryogenic ion trap. Their structures were characterized with temperature-dependent “iodide-tagging” negative ion photoelectron spectroscopy (NIPES) where iodide is used as the “messenger” to interpret electronic energetics and structural information of various AA·I⁻ isomers. Distinct binding sites accessible for I⁻ have been identified. We observed spin-orbit excited dipole-bound states (DBSs) in arginine-iodide complexes (Arg·I⁻). The observed DBSs are bound to the spin-orbit excited I(²P_{1/2}) level of the neutral Arg·I complex in zwitterionic conformations and identified based on the resonant enhancement due to spin-orbit electronic autodetachment from the I(²P_{1/2}) DBS to the I(²P_{3/2}) neutral ground state. This work thus demonstrates a new and generic spectroscopic approach to probe specific binding interactions in biological molecules and further to categorize ion-molecule cluster conformations based on their distinguishable dipole moments.



[1] Hanhui Zhang, Wenjin Cao, Qinqin Yuan, Xiaoguo Zhou, Marat Valiev, Steven R. Kass, and Xue-Bin Wang, “Cryogenic ‘Iodide-Tagging’ Photoelectron Spectroscopy: A Sensitive Probe for Specific Binding Sites of Amino Acids”, *J. Phys. Chem. Lett.* **2020**, *11*, 4346-4352.

[2] Wenjin Cao, Hanhui Zhang, Qinqin Yuan, Xiaoguo Zhou, Steven R. Kass, and Xue-Bin Wang, “Observation of Conformational Simplification upon *N*-Methylation on Amino Acid Iodide Clusters”, *J. Phys. Chem. Lett.* **2021**, *12*, 2780-2787.

[3] Wenjin Cao, Hanhui Zhang, Qinqin Yuan, Xiaoguo Zhou, Steven R. Kass, Xue-Bin Wang, “Observation and exploitation of spin-orbit excited dipole-bound-states in ion-molecule clusters.” *J. Phys. Chem. Lett.*, **2021**, *12*, 11022-11028.

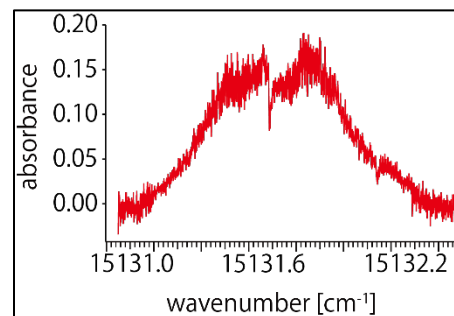
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High resolution spectroscopy of buffer gas cooled phthalocyanine**Yuki Miyamoto, Reo Tobaru, and Ayami Hiramoto***RIIS, Okayama University**miyamo-y@okayama-u.ac.jp*

The buffer gas cooling is a method in which the target species are cooled by collision with inert gas at the desired temperature. Since the principle of cooling is a simple molecular collision, almost any chemical species can be cooled relatively easily and efficiently as long as it has a certain lifetime. Depending on the experimental conditions, it is possible to cool molecules at or above room temperature to cryogenic regions without pre-cooling. Although the speaker is mainly using the buffer gas method to cool molecules for spectroscopy, atoms, ions, and exotic atoms are also cooled by buffer gases for various purposes. Buffer gas cooling has been used as a spectroscopic technique for many years and is not particularly new. The advantages of cooled gas-phase molecules in spectroscopy are their small Doppler width and rotational distribution. Until now, most spectroscopy of cooled molecules has been performed using supersonic jets.

Recently, however, buffer gas cooling has attracted particular attention. This is because buffer gas cooling is widely used as pre-cooling in techniques such as laser cooling of molecules. Research using molecules cooled to cryogenic temperatures is increasingly important, with many proposals in the field of chemistry, fundamental physics and quantum information. Accordingly, buffer gas cooling has been re-evaluated as a cooling method for molecular spectroscopy, and many results have been reported since the 2010s. Compared to the supersonic jet method, the most important feature of the buffer gas cooling method is the small translational velocity in the laboratory frame. This feature is important for further cooling, e.g., by laser cooling. As a spectroscopic technique, the buffer gas is expected to be complementary to the supersonic jet because it can handle molecules that are difficult to handle by the supersonic jet.

The speakers have been developing a spectroscopy system using buffer gas cooling. Recently, we have succeeded in cooling and spectroscopy of a relatively large molecule, Phthalocyanine (Pc). The visible absorption spectrum of Pc is shown in the figure. Pc is a relatively large molecule with a molecular weight of 514, and there have not been many examples of high-resolution spectroscopy of such a molecule. Because the rotational constants of large molecules are small, it is difficult to resolve the lines of rotation. Although we were not able to completely separate the rotational lines in this study, we were able to measure the structure due to the rotational motion. These are the oscillations that look like noise in the figure. By comparing this structure with simulations, it was found that Pc is cooled to below 10 K in both translational and rotational motions. This result shows the potential of buffer gas cooling as a spectroscopic technique, and we look forward to its further development. In this talk, I will present the latest experimental results.

**NOTES**

VUV Photochemistry of Hydrogen Sulfide (H₂S)**Kaijun Yuan**

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Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China*

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Photochemistry plays a significant role in shaping the chemical reaction network in the solar nebula and interstellar clouds. However, even in a simple triatomic molecule photodissociation, determination of all fragmentation processes is yet to be achieved. In the last few years, such goals can be achieved by the recently constructed VUV free electron laser (FEL), at the Dalian Coherent Light Source (DCLS), combined with the VUV source from the table-top lasers. In this talk, we will introduce the photofragment translational spectroscopy (PTS) measurements of the H and S(¹D) atoms from photolysis of H₂S molecules at many wavelengths in the range $122 \leq \lambda \leq 155$ nm. The PTS study shows that only ~25% of H₂S photoexcitation events induced by the general interstellar radiation field (ISRF) would yield SH(X) products; sequential fragmentation to three atoms is the most likely outcome. The high resolution translational spectroscopy measurements from the fragmentation of H₂S excited to selected quantum levels of a Rydberg state of ¹B₁ symmetry at $\lambda \sim 139.1$ nm, provide a comprehensive illustration of the rich dissociation dynamics. Analysis reveals formation of SH(X), SH(A), S(³P) and H₂ partner fragments, and in the case of the diatomic products, inverted internal (vibrational or rotational) state population distributions. The energy disposal can be rationalised in terms of competing homogeneous and heterogeneous (*i.e.* vibronic and rotational level dependent) predissociation pathways.

Reference:

1. J. M. Zhou, Y. R. Zhao, et al., M. N. R. Ashfold*, K. J. Yuan*, X. M. Yang*, *Nat. Commun.* **11**, 1547 (2020).
2. Y. R. Zhao, Z. J. Luo, Y. Chang, et al., M. N. R. Ashfold*, K. J. Yuan*, X. M. Yang, *Nat. Commun.* 2021, 12, 4459. (Featured Article).
3. Y. R. Zhao, J. J. Chen, Z. J. Luo, et al., X. X. Hu*, D. Q. Xie, H. B. Ding*, K. J. Yuan*, X. M. Yang, *J. Phys. Chem. Lett.*, 2022, 13, 9786.

NOTES: This work was supported by the National Natural Science Foundation of China (Grant Nos. 21922306, 22225303). We thank the VUV FEL staff for technique supporting.

Probing dipole-bound electron induced valence orbital polarization using high-resolution photoelectron imaging of cryogenically cooled molecular anions**Dao-Fu Yuan, Yuan Liu, Yue-Rou Zhang, Lai-Sheng Wang***Department of Chemistry, Brown University, USA. daofu_yuan@brown.edu*

Polar molecule with sufficiently large dipole moment could bind an excess electron and form highly diffuse dipole-bound anion. Dipole-bound anions possess noncovalent dipole-bound states (DBSs) just below the detachment threshold by the long-range electron-dipole interaction. The diffuse electron in a DBS is spatially well separated from the valence electrons and is known to have negligible effects on the molecular structure. Electron correlation effects between the distant dipole-bound electron and the valence electrons of the neutral cores are known to be important for the accurate calculation of the binding energies of the dipole-bound electron. The single electron in DBSs could produce oriented intramolecular electric fields. However, how the oriented intramolecular electric field of the dipole-bound electron influences the valence electrons has not been examined. Using our third-generation electrospray ionization - photoelectron spectroscopy (ESI-PES) apparatus, we observed a DBS in deprotonated 4-(2-phenylethynyl)-phenoxide anions. The photodetachment of the dipole-bound electron is observed to accompany a simultaneous shakeup process in valence orbitals in this aromatic molecular anion. This shakeup process is due to configuration mixing as a result of valence orbital polarization by the intramolecular electric field of the dipole-bound electron. This observation suggests that dipole-bound anions can serve as a new platform to probe how oriented electric fields influence the valence electronic structure of polyatomic molecules.

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Real-time Nonadiabatic Electron Dynamics on Non-valence Bound States of Polyatomic Molecular Anions**Do Hyung Kang and Sang Kyu Kim***Department of Chemistry, KAIST, Republic of Korea,**sonar112@kaist.ac.kr*

Non-valence bound state (NBS) is an electronic state of anion where an excess electron is weakly bound in long-range potentials of a neutral molecular core. The NBS plays a critical role as a doorway state to form the valence anions in the electron attachment to a neutral molecule. Despite its importance in atmospheric or astrochemical implications, nonadiabatic electron dynamics on NBS has not been sufficiently studied up to date. In particular, time-resolved aspect of nonadiabatic electron dynamics such as autodetachment and nonradiative relaxation to the valence anion has been still remained beyond the deepest understanding. Herein, we present the nonadiabatic mode-specific electron dynamics studies on dipole-bound state (DBS) and quadrupole-bound state (QBS) of phenoxide anion and its derivatives by the means of picosecond time-resolved photoelectron imaging combined with cryogenically cooled Paul ion trap techniques.

The nonadiabatic autodetachment rates on the vibrational Feshbach resonances of the DBS or QBS were found to be highly influenced on vibrational mode-character of neutral core where the vibrational propensity rule ($\Delta v = -1$) is strictly obeyed [1-2]. By invoking Fermi's golden rule, we directly monitored mode-specific behaviors on the vibrational autodetachment rate originating from the dynamic wobbling of the diffuse dipole-bound or quadrupole-bound electrons by the neutral core vibronic motion. For the case of the largely polarizable neutral core, electron correlation effect between the excess dipole-bound electron and valence orbitals was found to give exceptionally slow autodetachment rate, which cannot be fully described by the Fermi's golden rule [3]. Those real-time autodetachment dynamics studies on DBS and QBS in mode-specific way corroborate that the NBS should be described by the comprehensive binding potentials of long-range electrostatic interactions (charge-dipole or charge-quadrupole) involving the quantum-mechanical electron correlation interaction.

For the dynamic role of the NBS in anion chemistry as a doorway state, we observed competition dynamics between the autodetachment and nonadiabatic relaxation into the valence anions in iodine-substituted phenoxide anions. The energetic hierarchy of the DBS and valence anionic potential energy surface was found to govern the whole nonadiabatic electron dynamics whether the NBS may form the valence anions and then promotes further chemical reactions, or emits the excess electron resulting in the neutral and free electron. Moreover, those competition dynamics revealed mode-specific aspect giving the electron or I⁻ fragment selectively, which can be used for reaction control by the means of active/passive control of anion chemistry [4-5].

- [1] D. H. Kang, S. An, and S. K. Kim, *Phys. Rev. Lett.*, **125**, 093001 (2020)
- [2] D. H. Kang, J. Kim, M. Cheng, and S. K. Kim, *J. Phys. Chem. Lett.*, **12**, 1947-1954 (2021)
- [3] D. H. Kang, J. Kim, and S. K. Kim, *Chem. Sci.*, **13**, 2714-2720 (2022)
- [4] D. H. Kang, J. Kim, and S. K. Kim, *J. Phys. Chem. Lett.*, **12**, 6383-6388 (2021)
- [5] D. H. Kang, J. Kim, H. J. Eun, and S. K. Kim, *J. Am. Chem. Soc.*, **144**, 16077-16085 (2022)

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Doppler effects in cryogenic buffer gas cell

Ayami Hiramoto, Reo Tobaru, and Yuki Miyamoto*Research Institute for Interdisciplinary Science, Okayama University, Okayama, Japan**hiramoto@okayama-u.ac.jp*

Buffer-gas cooling is a universal cooling technique for producing high-density cold molecules [1] and used for a variety of purposes. Hot target molecules are introduced into a cryogenically cooled cell and cooled down to a few K by collision with ultracold buffer gas, such as helium and neon. One application of this technique is using molecules inside a buffer-gas cell for spectroscopy at low temperature [2]. However, although a high-intensity signal is expected in the cell, complicated molecular dynamics would be a drawback for precise spectroscopy. In this study, we performed high-resolution absorption spectroscopy of low- J transitions in $\tilde{A}^2\Pi(0,0,0) - \tilde{X}^2\Sigma^+(0,0,0)$ band of calcium monohydroxide (CaOH). Figure shows the setup of our measurement. The CaOH molecules were produced by laser ablation in a copper cell cooled to $\sim 5\text{K}$ and cooled by helium buffer gas. We probed Doppler effects in a buffer-gas cell using counter-propagating lasers going through inside the cell. The time evolutions of Doppler width and Doppler shift were simulated using a dedicated Monte Carlo simulation and compared with data.

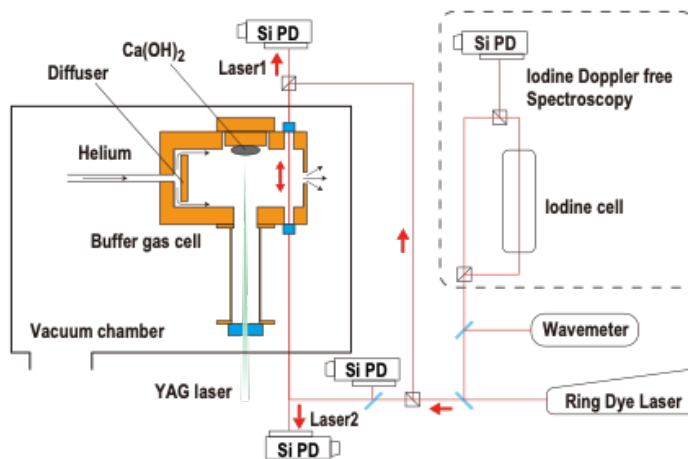


Figure: Experimental setup for absorption spectroscopy of CaOH molecules.
Counter-propagating lasers are injected through the cell.

- [1] N. R. Hutzler, H.-I. Lu, and J. M. Doyle, *Chem. Rev.* **112**, 4803 (2012).
 [2] Y. Takahashi, M. Baba, K. Enomoto, A. Hiramoto, K. Iwakuni, S. Kuma, R. Tobaru, and Y. Miyamoto, *ApJ* **936**, 97 (2022).

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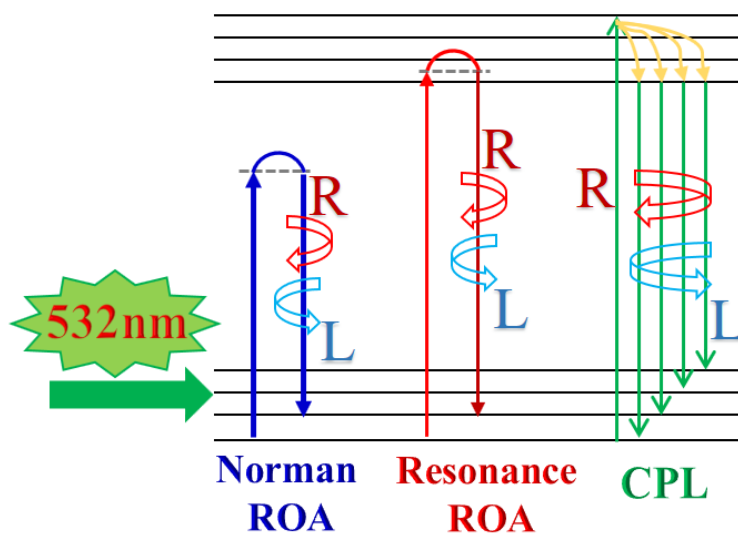
Exploring Lanthanide Circularly Polarized Luminescence by a Raman Optical Activity Spectrometer

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Recently, many studies have appeared in which the Raman optical activity (ROA) instrument with 532 nm laser was found to be convenient for measuring lanthanide circularly polarized luminescence (CPL). The new detection scheme is referred to as ROA-CPL spectroscopy. It is particularly useful when also the vibrational (ROA) itself is detectable as the molecule structure can be examined more reliably. The experiment requires much lower concentrations of the analyte and shorter recording times compared to conventional ROA experiments. Induced lanthanide CPL is applicable to systems lacking usable UV/vis chromophores, and is thus useful in structural studies of various biomolecules.



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NOTES

Direct detection of OH radicals in the photolysis of liquid nonanoic acid using laser-induced fluorescence

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In recent years, photochemical reactions of surfactant organic compounds at sea surface microlayers and atmospheric aerosol interfaces have attracted much attention in the field of atmospheric chemistry. For example, it has been reported that nonanoic acid [$\text{CH}_3(\text{CH}_2)_7\text{COOH}$] at the air-water interface can react with solar UV light ($>295\text{ nm}$), leading to the formation of complex organic compounds that serve as aerosol precursors [1]. Rossignol et al. [1] proposed the OH radical formation [$\text{CH}_3(\text{CH}_2)_7\text{COOH} + h\nu \rightarrow \text{CH}_3(\text{CH}_2)_7\text{CO}\cdot + \cdot\text{OH}$] through photodissociation (C–O bond fission) as a possible photochemical reaction mechanism. Because OH is a strong oxidant that reacts with almost all molecules in the atmosphere and promotes the formation and growth of aerosol particles, it is highly desirable to quantify the photochemical efficiency for the OH formation. However, the mechanisms of the photochemical reactions of nonanoic acid remain poorly understood even in the neat liquid phase, let alone in a monolayer at the air–water interface.

In this talk, we report the development of a new experimental apparatus to detect OH radicals photodesorbed from the liquid nonanoic acid interface [2]. Figure 1 shows a schematic diagram of the photoreaction experiment. Liquid nonanoic acid was introduced into a vacuum chamber and evacuated at the pressure of 1–80 Pa for laser-induced fluorescence. A 213 nm Nd:YAG pulsed laser was used for photolysis. OH radicals desorbed from the interface were excited by a 282 nm pulsed dye laser, and the fluorescence emitted upon de-excitation (315 nm ; $A^2\Sigma, v'=1 \rightarrow X^2\Pi, v'=1$) was detected by a photomultiplier tube. In this study, we successfully quantified the upper limit of the photoreaction cross section of OH radical desorption by comparing the 213 nm photolyses of liquid nonanoic acid and gas-phase acetic acid, because the absorption cross section and quantum yield of OH formation is known for the latter process [3, 4].

The upper limit of the photoreaction cross section for liquid nonanoic acid was determined to be $9.0 \pm 4.1 \times 10^{-22}\text{ cm}^2$ in this study. This value is extremely small ($1.2 \pm 0.8\%$) compared to the photoreaction cross section for gas-phase acetic acid monomer ($7.6 \pm 1.8 \times 10^{-20}\text{ cm}^2$). This may be due to the formation of cyclic dimers by hydrogen bonding of nonanoic acid molecules at the interface, which reduced the efficiency of OH radical formation [2].

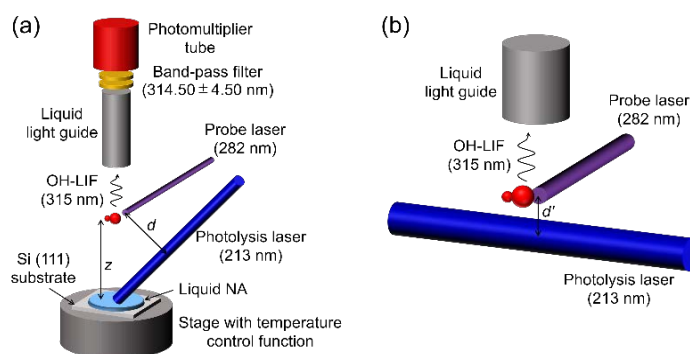


Fig. 1. Schematic diagrams of 213 nm photolysis of (a) liquid- and (b) gas-phase organic molecules and OH radical probing

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High-power longwave mid-IR frequency combs based on Er-fiber laser driven SESS

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Ultrafast sources tunable in the longwave mid-IR range of 7-20 μm have important applications in high-precision spectroscopy because many molecules have absorption signatures in this wavelength range. In this submission, we demonstrate a long-wave mid-IR frequency comb with the average power improved by one order of magnitude. In the new implementation, we derive the pump/signal pulses from a 32-MHz Er-fiber laser that emits 5-W, 290-fs pulses centered at 1.55 μm . A portion of the laser output is coupled into a short piece of optical fiber such that the spectrum is substantially broadened mainly by self-phase modulation (SPM) [Fig. 1(a)]. As we increase the coupled pulse energy into the fiber, the peak wavelength of the rightmost spectral lobe shifts from 1.6 μm to 1.94 μm . To implement SPM-enabled spectral selection (SESS), we then use long-pass optical filters to select the spectral lobe, which results in strong signal pulses tunable in 1.6-1.94 μm . Difference-frequency generation between this signal pulse and the pump pulse at 1.55 μm in GaSe crystal allows us to generate mid-IR pulse tunable in the wavelength range of 7.6-20 μm [Fig. 1(b)], and the maximum power of 58.3 mW centered at 8.9 μm is obtained.

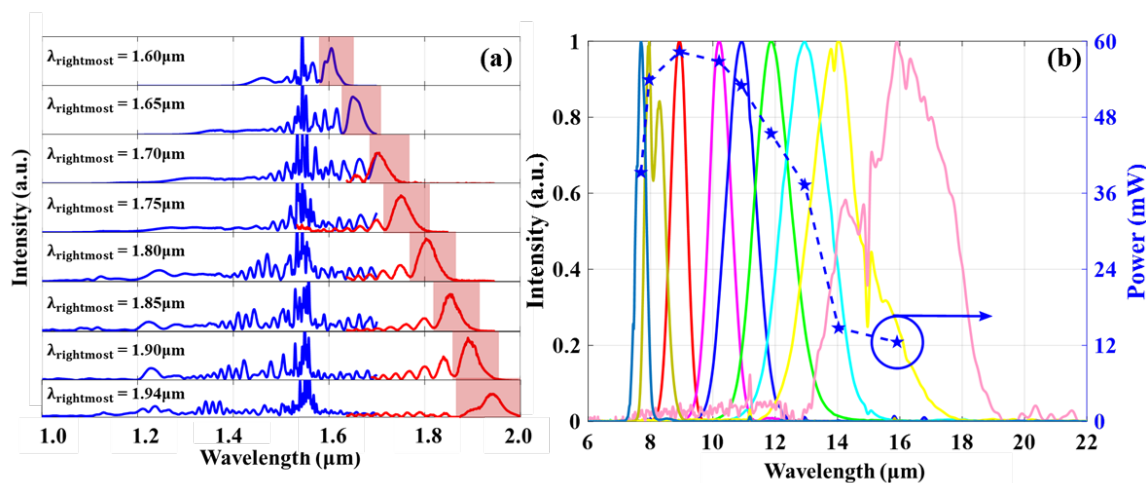


Fig. 1. (a) Spectral broadening with the rightmost spectral lobe peaking in the range of 1.60-1.94 μm . (b) Measured spectra and average power for mid-IR pulses generated in 2-mm GaSe crystal.

NOTES

Quantitative detection of molecules by cavity-enhanced double resonance absorption spectroscopy**Yan-dong Tan, Cun-feng Cheng*, Shui-ming Hu****Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026 China** cfcheng@ustc.edu.cn, smhu@ustc.edu.cn

Cavity enhanced absorption spectroscopy has been widely used in trace gas detection and quantitative analysis of molecular isotopes, including the field of atmospheric environment, industrial pollution monitoring and earth science. In order to further improve the selectivity, we propose a cavity-enhanced double-resonance spectroscopy method. By locking two lasers to a high finesse cavity, we are able to excite and detect molecules through a two-photon process. With the Mid-infrared and NIR-infrared cavity-enhanced double-resonance technique, we demonstrated that the concentration of CO in a gas sample can be measured to 1% accuracy. It is expected that the molecules can be quantitatively detected to a higher precision with a frequency-stabilized and narrow-linewidth Mid-infrared laser source. Our method opens a new route to detect the atmospheric carbon isotopes such as $^{14}\text{CO}_2$.

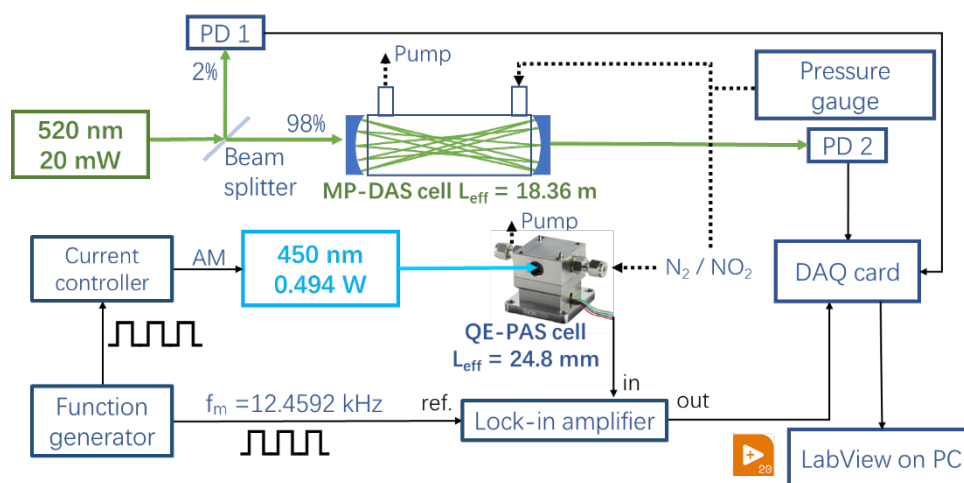
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NOTES

Ppt-level NO₂ detection based on quartz-enhanced photoacoustic spectroscopy (QEPAS)**I-Yun Chen^{*1}, Yu-Xuan Wu^{1,2}, Pei-Ling Luo¹**^{*}iyunchen21@gmail.com¹ Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan² Department of Chemistry, National Taiwan Normal University, Taiwan**Abstract**

Nitrogen dioxide (NO₂) plays an important role in the atmospheric chemistry. In this work, we apply multi-pass direct absorption (MP-DAS) and quartz-enhanced photoacoustic spectroscopy (QE-PAS) to detect the concentration of NO₂. A 520-nm diode laser was coupled to a multi-pass cell with an effective optical path length of 18.4 m for concentration calibration of NO₂. Another 450-nm laser with an averaged optical power of 494 mW was amplitude modulated and sent into the QE-PAS cell. The laser-induced photoacoustic signal collected by the quartz-tuning fork was demodulated by a lock-in amplifier and recorded with a data acquisition board. A detection limit (3 σ) of NO₂ at 1 atm is estimated to be 509 ppbv with a 1-s averaging time based on the MP-DAS system. In addition, by using the QE-PAS system, the detection limit (3 σ) of 211 pptv can be achieved with an average time of 10 s at atmospheric pressure.

**NOTES**

Hierarchy of π -Stacking Determines the Aggregation Behaviour

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The aggregates of phenylacetylene and monofluorinated phenylacetylenes, investigated in the gas-phase using the IR-UV double resonance spectroscopic method in combination with extensive structural search and electronic structure calculations. The aggregation behaviour of phenylacetylene in the gas phase is fundamentally different from benzene, phenol and aniline vis-à-vis their crystal structures. The structures of the three known polymorphic crystals can be reconciled by the formation of supramolecular synthons with acetylenic C–H $\cdots\pi$ interactions, which is preferred over energetically favored aromatic C–H $\cdots\pi$ interactions, which arises due to interaction switching at various levels of aggregation, as shown in Figure 1.¹ On the other hand, substitution of a F atom on the phenyl ring increases the dipole moment, leading to robustness in the formation of a π - π stacked dimer, which propagates incorporating C–H $\cdots\pi$ and C–H $\cdots$ F interactions involving both acetylenic and aromatic C–H groups. The structural evolution of fluorophenylacetylene aggregates is fundamentally different than parent phenylacetylene with differences in the nucleus for the growth of higher clusters.² However, in all the cases, the small gas phase clusters can be hypothesized as “liquid-like clusters” acting as intermediates in the generation of various polymorphic forms.

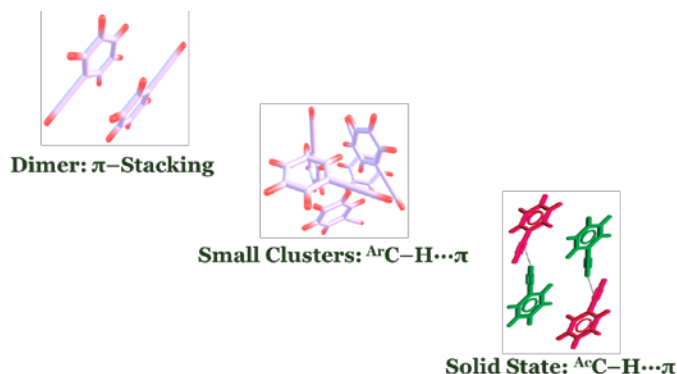


Figure 1. Interaction switching in phenylacetylene aggregates

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NOTES

IR-VUV Spectroscopic Study on the Structure of Pyridine-Water Clusters and its Relationship with the Local Structure of Pyridine/Water Mixed Solution

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Introduction

While Pyd is soluble to water at any concentration, the structure of Pyd/water mixed solution is not fully understood. Recent studies of neutron diffraction and soft X-ray absorption spectroscopy suggested that Pyd is not uniformly mixed with water and some local structure exists in the mixed solution. In the present study, we report the structure of the $(\text{Pyd})_m(\text{H}_2\text{O})_n$ clusters cooled in a supersonic beam by IR spectroscopy in the O-H stretching region and by quantum chemical calculation. We will show that the stable structure of the clusters may explain the local structure of Pyd/water mixed solution.

Experiment

The IR spectra of the $(\text{Pyd})_m(\text{H}_2\text{O})_n$ clusters were measured by IR-VUV spectroscopy and were compared with the calculated IR spectra of the possible isomers obtained by quantum chemical calculations.

Results and discussion

Fig. 1(a) shows the IR-VUV spectrum obtained by monitoring the $(\text{Pyd})_2^+$ cation, which are produced by the fragmentation of $(\text{Pyd})_2(\text{H}_2\text{O})_n$ clusters upon the VUV ionization. Figs. 1(b)-(d) show the harmonic calculated (scaled) IR spectra of the O-H stretching vibrations for the possible clusters contributing the observed IR spectrum obtained at B3LYP+D3/6-311+G(d,p) level calculation. Fig. 2 shows part of the corresponding structures of $(\text{Pyd})_2(\text{H}_2\text{O})_{n=1,2}$. As seen in Fig. 2, major stable isomers contain the π -stacked $(\text{Pyd})_2$. This stable π -stacked $(\text{Pyd})_2$ is also suggested to exist in the Pyd/water mixed solution. We propose that the H-bonding bridge by the water molecules works to increase the stability of the π -stacked $(\text{Pyd})_2$ structure also in the solution.

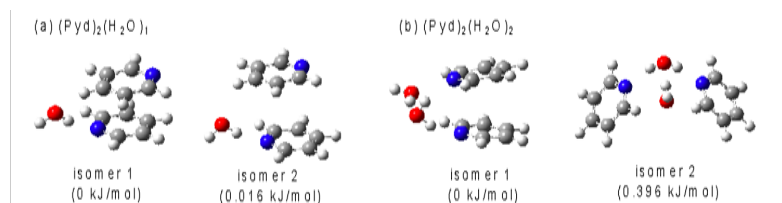


Fig.2 Possible structures of (a) $(\text{Pyd})_2(\text{H}_2\text{O})$ and (b) $(\text{Pyd})_2(\text{H}_2\text{O})_2$.

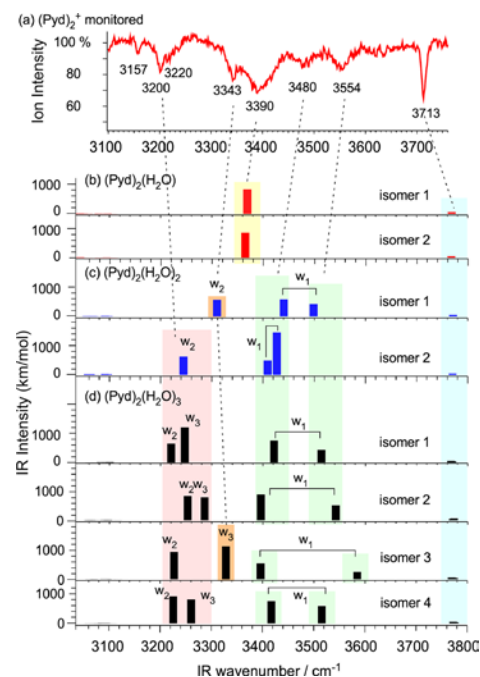


Fig. 1 (a) IR-VUV spectrum observed by monitoring $(\text{Pyd})_2^+$ ion. (b-c) Harmonic IR spectra of the OH stretching vibration of possible isomers of $(\text{Pyd})_2-(\text{H}_2\text{O})_n$.

NOTES

Infrared Spectroscopy of Neutral Atmospheric Clusters

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The formation of atmospheric clusters from molecules in the atmosphere environment is a crucial step towards aerosol nucleation. In order to gain fundamental insights into nucleation and growth mechanism of atmospheric nanoparticles, it is prerequisite to characterize the structures of atmospheric clusters and the chemical components and dynamics of aerosol particles. Over the past several decades, enormous efforts were devoted to the spectroscopic study of charged clusters, which allow easy size-selection and detection. In contrast, neutral clusters have presented major experimental challenges, because the absence of a charge makes it difficult for size-selection and detection. The Dalian Coherent Light Source (DCLS) facility delivers vacuum ultraviolet free electron laser (VUV-FEL) with a continuously tunable wavelength region between 50 and 150 nm and high pulse energy. Inasmuch as clusters with different sizes have different ionization energies, the DCLS facility paves the way for selectively ionizing a given neutral cluster free of confinement, thus facilitating realization of size selectivity. We focused on the studies of the structure and dynamics of neutral atmospheric clusters using the mass-selected infrared spectroscopy based on the DCLS, providing important insights into bonding characteristics, structures, and dynamics of these systems. The unique capabilities of the study of neutral atmospheric clusters based on the DCLS will help to understand aerosol nucleation mechanism at the molecular level.

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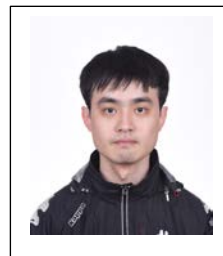
Rate coefficient of methyl vinyl ketone oxide + HCl investigated with a quantum cascade laser absorption system

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Abstract

The reactions between Criegee intermediates and hydrogen chloride might be significant in the atmosphere, particularly in the polluted urban areas, due to their large rate coefficients. Chung et al. have employed step-scan FTIR to record the IR absorption spectra of *syn-trans*-MVKO by photolyzing a gas mixture of (Z)-1,3-diiodobut-2-ene/O₂ with laser light at 248 nm.¹ The sharp Q-branch near 916.0 cm⁻¹ was assigned to be the c-type transition of CH₂ wagging mode (ν₂₅). Following the same synthesis method, we further recorded the high-resolution IR spectrum of *syn-trans*-MVKO in region of 915.5–916.0 cm⁻¹ by employing a tunable cw external-cavity quantum cascade laser coupled with a Herriott cell. The sharp Q-branch near 915.82 cm⁻¹ was found to be suitable for kinetic probe with sufficient sensitivity. By probing the temporal profiles of *syn-trans*-MVKO in the presence of HCl, the rate coefficient of *syn-trans*-MVKO + HCl at 298 K under total pressure of 5.0–9.0 Torr was determined to be $(1.6 \pm 0.1) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, near four times the values for reactions of HCl with CH₂OO and *syn*-CH₃CHOO.^{2,3} Due to larger reaction rate coefficient, the effective first-order rate for the reaction of *syn-trans*-MVKO with HCl is comparable with its reactions with HCOOH or H₂O or the unimolecular decomposition of *syn-trans*-MVKO.^{4,5}

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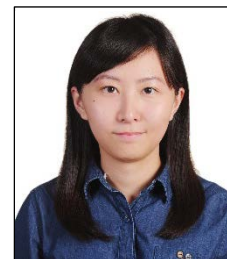
Key Parameters Controlling the Photodesorption Yield in Interstellar CO Ice Analogs

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Guillermo M. Muñoz Caro², Li-Chieh Hsiao¹, Hsien-Chou Lin¹, and Yu-Jung Chen¹

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Abstract –

The abundant CO molecules have been observed in the cold dense clouds and interstellar medium, which is attributed from the irradiation of energetic sources since the thermal desorption is inhibited. The photodesorption of CO ice as a function of deposition temperature has been investigated in previous literature, however, the temperature dependence is not well explained. In this work, the CO ice was deposited at 12.5–25 K and irradiated by ultraviolet (UV) photons. We proposed that the instantaneous photodesorption yield of CO ice is dominated by three temperature dependent parameters, the energy transfer length $L(T)$, the desorption yield contributed by a single ice layer $Y(T)$, and the relative effective surface area $R_A(T)$. Furthermore, the instantaneous photodesorption yields strongly depend on the incident photon intensity of the microwave-discharge hydrogen-flow lamp (MDHL) $W(\lambda)$ as well as the absorption cross section of solid CO ice.

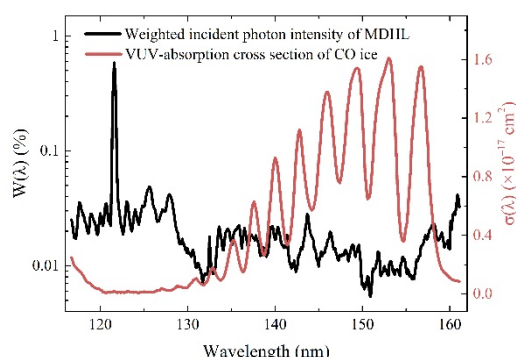


Fig 1. The normalized incident photon intensity of the MDHL and the VUV absorption cross section of CO ice as a function of wavelength.

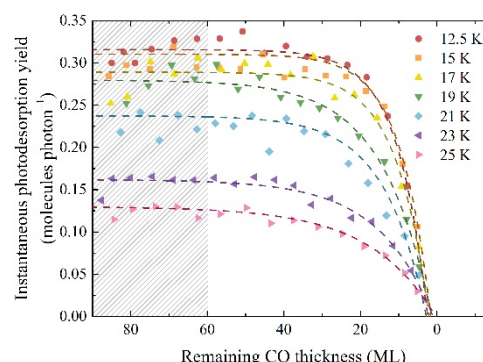


Fig 2. The instantaneous photodesorption yield as a function of remaining CO thickness for CO deposited in the 12.5–25 K range.

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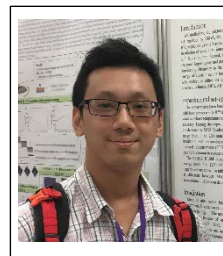
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Chemical Evolution and electron-stimulated desorption of H₂O+CO ice mixture

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Abstract –

Carbon monoxide is the second abundant solid-phase species followed water molecule. We investigated the ice mixture made of first two abundant molecules observed toward the star formation region. Electron with energy in a range of 200-1000 eV are used to simulate the radiolysis processes of primary electron produced by cosmic-ray and X-ray reacting with gaseous molecules. Electron irradiation is separated into several period and infrared (IR) spectra are collected in the between. Products produced under electron irradiation were assigned in the spectra (Figure 1). Also, column densities of parent molecules and abundant products (CO₂, HCO, H₂CO, and CH₃OH) as functions of electron fluence were computed from IR spectra (e.g. CO₂, Figure 2). Cross-sections are computed and compared with previous studies performed with different energetic sources such as vacuum ultraviolet [1] and X-ray [2]. The results of cross-sections will be discussed.

Corresponding with desorption species and electron penetration depth from CASINO [3], more than the qualitative and idea of the desorption-relevant depth (DRD) reported by Dupuy et al., 2020 [4], we quantitatively estimated DRD in the H₂O+CO ice mixtures.

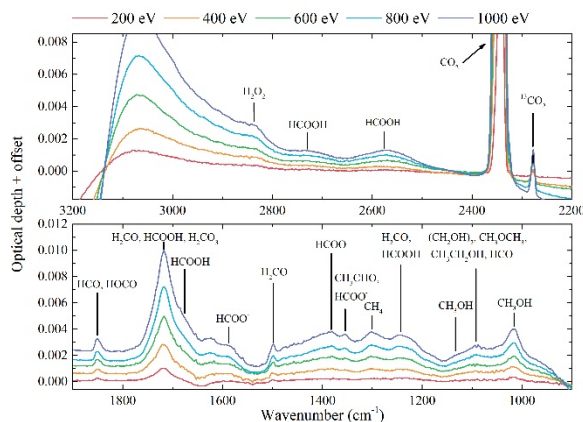


Figure 1. IR spectra with different energy electrons

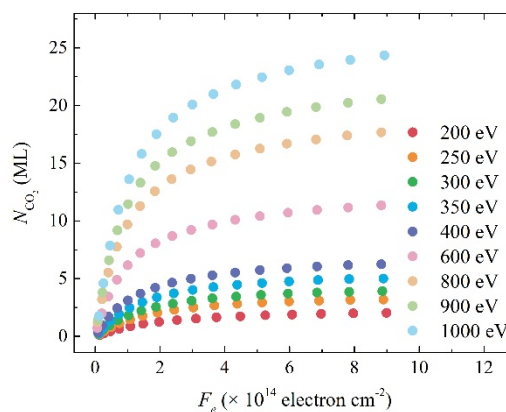


Figure 2. Column density of CO₂ as a function of electron.

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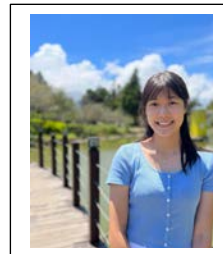
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VUV photolysis of N₂O ices

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N₂O is observed to be one of the most abundant gas molecules in our atmosphere, but only six kinds of molecules that contain N–O bonds have been detected in the cold dense clouds and interstellar medium (ISM). In this work, the N₂O ice is deposited with different ice thicknesses at 13 K and irradiated by the vacuum ultraviolet (VUV) photons to simulate the photon processing in the cold dense clouds and the ISM. The experimental results show that the N₂O ice depletes easily and the depletion cross-section of N₂O ice is initial N₂O thickness dependent. Most of the depleted N₂O molecules form various products, such as O₃, N₂O₃, N₂O₅, etc., and are assigned in figure 1. Among those products, some of them desorb with a linear trend and some of them desorb in the gas phase with a special turning trend, which is shown in figure 2 and is supposed to be influenced by products.

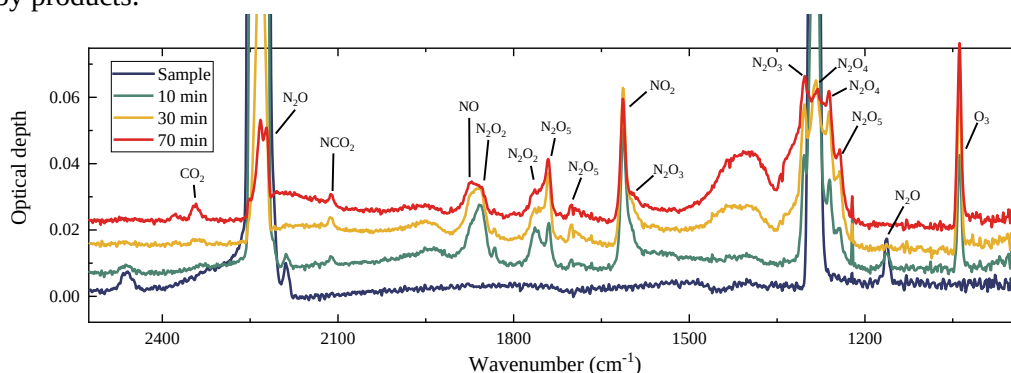
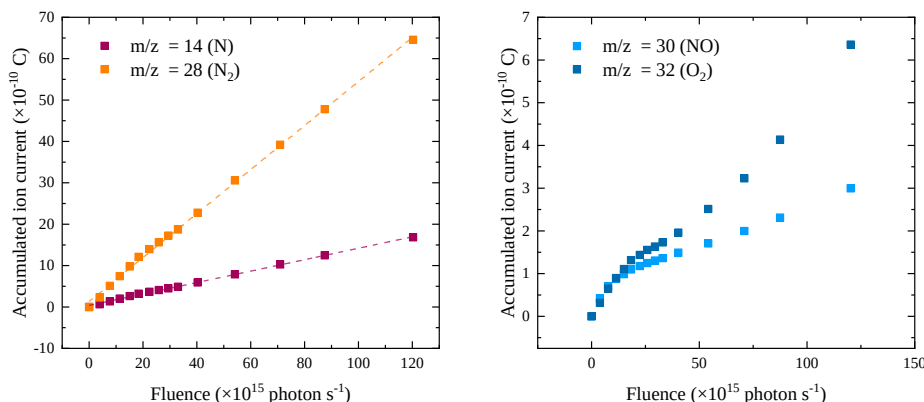


Figure 1. The optical depth of products produced after VUV irradiation.

Figure 2. The accumulated ion current of desorbing N, N₂, O₂ and NO as a function of fluence.

NOTES

Infrared multiple-angle resolution spectroscopy of interstellar ice analog in cryogenic environment

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Interstellar molecular clouds, the birthplaces of stars and planets, have cryogenic environment with temperature as low as 10 K. Infrared (IR) observations suggest that amorphous ice (H₂O) is abundant in the interstellar clouds [1]. The IR spectra of amorphous ice at low temperatures prepared in laboratory experiments show two weak absorption peaks at 3696 cm⁻¹ and 3720 cm⁻¹, which are assigned to the free OH stretching mode of three- and two-coordinated H₂O on the ice surface, respectively (Figure 1). These are called "dangling OH" and reflect the ice surface structure (porosity and specific surface area). However, the absorption cross section for dangling OH is unknown, hindering quantitative understanding of the surface structure and reactions of interstellar ices. In this study, we used infrared multiple-angle incidence-resolved spectroscopy (IR-MAIRS) to experimentally measure the dangling OH peaks in vapor-deposited amorphous ice at 90 K [2, 3]. IR-MAIRS is a recently developed infrared spectroscopic technique to qualitatively measure the molecular orientation of thin film. Oblique incidence transmission measurements and chemometrics (multivariate analysis) are combined to simultaneously obtain spectra of vibrations parallel (IP) and perpendicular (OP) to the thin film [3].

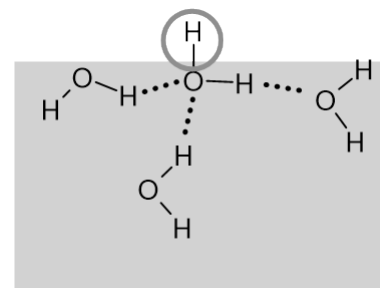


Figure 1. Schematic image of three-coordinate dangling OH.

Figure 2 shows that three-coordinated dangling-OH bonds were found only in OP spectra at 90 K, indicating that three-coordinated dangling-OH bonds oriented perpendicular to the ice surface. Note that the three-coordinated dangling-OH peaks should be invisible to normal-incidence transmission measurements, which observe only the IP vibration without any OP vibration contribution. Based on the IR-MAIRS spectra, the absorption cross section is derived as $1.0 \pm 0.2 \times 10^{-18} \text{ cm}^2$ at 3696 cm⁻¹. The integrated absorption cross section (band strength) of the three-coordinate dangling OH bond is also obtained as $1.4 \pm 0.3 \times 10^{-17} \text{ cm molecule}^{-1}$ at 3710–3680 cm⁻¹, which is more than an order of magnitude smaller than that of the four-coordinate H₂O in the ice ($2.9 \times 10^{-16} \text{ molecules cm}^{-1}$). These findings provide fundamental insights into the relationship between the structure and optical properties of ice surfaces, and aid quantitative understanding of the surface structure of interstellar ices and their laboratory analogs [2, 3].

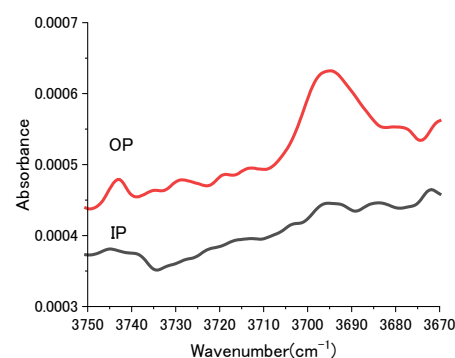


Figure 2. IR-MAIRS spectra of amorphous ice deposited at 90 K.

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NOTES

Overtone Spectroscopy of Microsolvated Protonated Methanol

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Overtone spectroscopy can directly probe highly excited vibrational states, and it is expected to provide rich information on vibrational potential shape, anharmonic coupling, and intramolecular vibrational energy redistribution (IVR). However, because of its extremely low sensitivity (transition intensity), applications of overtone spectroscopy to molecular clusters in the gas phase have been very scarce.¹ In the present study, we observed the OH stretch overtone region of microsolvated protonated methanol, $\text{CH}_3\text{OH}_2^+\text{-X}_n$, ($\text{X} = \text{Ar}$, N_2 , and CO , $n = 1$ and 2). The spectral features were assigned by comparison with the anharmonic vibrational simulations based on the discrete variable representation (DVR) approach.² Impact of weak hydrogen bond (H-bond) formation to OH stretching vibration in the overtone region is discussed.

Fig. 1 shows the observed vibrational spectra of $\text{CH}_3\text{OH}_2^+\text{-X}$ ((a) $\text{X}=\text{Ar}$, (b) $\text{X}=\text{N}_2$, and (c) $\text{X}=\text{CO}$) in the OH stretch overtone region. In $\text{CH}_3\text{OH}_2^+\text{-X}$, the solvent molecule X is H-bonded to one of the OH bonds of CH_3OH_2^+ . In spectrum of (a) $\text{X}=\text{Ar}$, the overtone of the free OH stretch ($2\nu_f$) is seen at around 7000 cm^{-1} . The overtone of the H-bonded OH stretch ($2\nu_1$) appears at $\sim 6450\text{ cm}^{-1}$. The most prominent band at $\sim 5200\text{ cm}^{-1}$ is assigned to a combination band of the OH bend and free OH stretch ($\nu_b + \nu_f$). The dominance of the combination band over the overtone bands has been also observed in protonated water clusters.¹ With the change of the solvent molecule to (b) $\text{X}=\text{N}_2$ and (c) $\text{X}=\text{CO}$, the H-bond becomes stronger, and the further red-shift of $2\nu_1$ occurs. However, the main feature is the combination band. In (c) $\text{X}=\text{CO}$, the band positions of the combination and overtone seem overlapped, and broadened background also appears in this region. Therefore, the assignment of the 5200 cm^{-1} band is not straightforward.

The spectra of the $n=2$ clusters and comparison with the DVR simulations will be shown in the presentation. The anticooperative effect of the H-bond and appearance of IVR with increasing H-bond strength will be also discussed.

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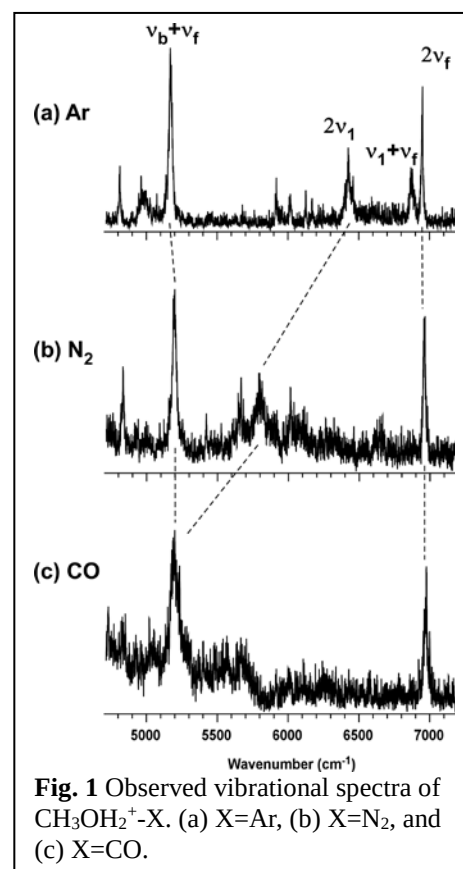


Fig. 1 Observed vibrational spectra of $\text{CH}_3\text{OH}_2^+\text{-X}$. (a) $\text{X}=\text{Ar}$, (b) $\text{X}=\text{N}_2$, and (c) $\text{X}=\text{CO}$.

NOTES

Semiempirical dimer-based model of the water vapour self-continuum absorption within IR absorption bands

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The continuum absorption (or *continuum*) of water vapor is a slightly varying with frequency component of the water vapor absorption spectrum. To date it is considered the nature of the continuum is determined by the physical effects that take place during intermolecular interactions of H₂O molecules. The simplest and most significant case of this is pair collisions, as a result of which, on the one hand, H₂O molecules form short-lived dimers with characteristic absorption spectra [1], and, on the other hand, there are changes in the shape of resonant H₂O line wings at large detuning from their centers that go beyond the impact approximation [2]. It is known that water dimers make the main contribution to the continuum within the IR absorption bands, while the line wings mechanism dominates in the atmospheric windows. However, a rigorous physically based separation of the contributions of each of these mechanisms to the continuum is currently not available. Therefore, semiempirical models are used to reproduce the water vapor continuum absorption spectra for applications. The MT_CKD continuum model, which extends over a wide spectral region from 0 to 20,000 cm⁻¹, has become widely used [3]. However, within the IR bands, the MT_CKD often provides a weak prediction of the magnitude and (or) spectral features of the water vapor continuum, especially at temperatures above atmospheric (see, for example, [4]).

Here, we propose a semiempirical modification of the water dimer model [5] to reproduce the magnitude and spectral features of the water vapor continuum within the IR absorption bands in the frequency region from 50 to 11200 cm⁻¹ (from 200 to 0.89 μm) in a wide temperature range from 280 K to 430 K. The so-called semiempirical dimer-based model describes the continuum as a set of spectra of bound and quasibound water dimers, simulated using the last available spectroscopic information on the transitions of water dimers and the effective equilibrium dimerization constant (characterizing the content of H₂O dimers in the water vapor at temperature *T*) obtained from fitting. The latter was found to be higher than the modern estimates of the physical dimerization constant at the same temperatures. The average deviation of the model from the experimental continuum data at the centers of the IR absorption bands is no more than 15% within the spectral and temperature boundaries of the model. The listed characteristics of the semiempirical dimer-based model provide its advantage when comparing with the earlier continuum models within the absorption bands.

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NOTES

Adsorption and Dissociation of CO₂ Molecules at Co(0001) Surfaces Probed by Infrared Spectroscopy

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The carbon dioxide (CO₂) exists in the air. For protecting ecological environment of the earth on which human beings live from negative impact by extra increasing amount of CO₂ concentration and by the rising of global temperature, many researchers in the past thirty years have always been taking measures to control CO₂ emissions and seeking reaction pathways to convert CO₂ into useful carbon feedstock [1,2]. Although various reduction reactions often have high activation energies and the CO₂ itself is also a stable and almost inert compound, catalytically activating the CO₂ molecules at the surfaces of catalysts has been alternatively proposed. However, the active sites on single crystal Co(0001) catalyst surfaces for CO₂ adsorption in the gas phase and elementary reaction pathways at the molecular level for governing the activation process of CO₂ dissociation have not been studied yet using the technique of Fourier transform infrared spectroscopy.

In our study, the CO₂ adsorptions and dissociations on clean and hydrogen pre-adsorbed Co(0001) single crystal surfaces were studied by using the ultrahigh vacuum-Fourier transform infrared reflection absorption (IRRA) spectroscopy. In the measurements, CO₂ was dosed on the Co(0001) surfaces for 10 min at a few low pressures, and the surfaces were cooled down to temperatures of 110, 125, and 135 K, respectively, then the IRRA spectra of the surfaces were recorded, which are shown in Fig.1. In our experiment, two active sites are recognized for CO₂ dissociation into CO and O, one is the hollow site on the terraces and another is the step (defect) site. Four reaction pathways are found and will be reported. Our results provide experimental evidences for properly understanding the molecular dynamics in active sites and reaction pathways of CO₂ reduction at Co(0001) surfaces and are conducive to the design and synthesis of heterogeneous catalysts.

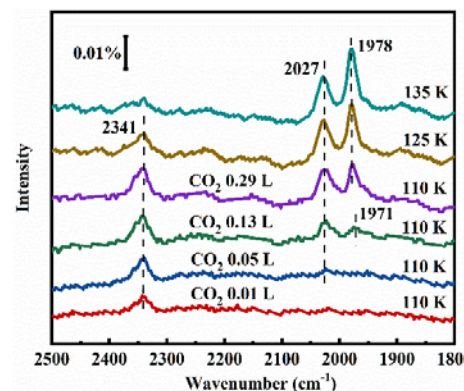


Fig. 1 IRRA spectra of the adsorption and dissociation of CO₂ and CO on Co(0001) surfaces at different CO₂ exposures on Co(0001) surfaces. The spectra were acquired at temperature of 110, 125, and 135 K. Dashed lines indicate the peak positions measured at 110 K for CO₂ exposure 0.13 L.

Acknowledgments: This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 91536105, 1174186, and 11074147), and the Tianshan Scholar Program.

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NOTES

Ultrafast spectroscopy detection and regulation of excited states and transient intermediates of organic single crystals and nanocrystals**Wenbin Chen^a, Guanheng Huang^a, Ye-Tao Chen^a, Jiaying He^a, Xinyi Wen^a, Shaofei Ni^a, Shun-Li Chen^a, Li Dang^{a,b}, Ming-De Li^{a,b}**^a Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Shantou 515063, China^b Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031, China

Ultrafast time-resolved spectroscopy is the most important method to study the reaction mechanism of ultrafast processes induced by light, such as photophysics, photochemistry, photobiology and photodrugs. The excited states of photofunctional materials are energetic active intermediates with a very short lifetime and complicated electronic structure, which make the photophysical and photochemical processes difficult to control. The spatio-temporal detection and regulation of the excited state of photofunctional materials is still in its infancy, which is a hot and difficult topic in the field of photochemistry. Studying complicated photophysical and photochemical processes by ultrafast spectroscopy, tracking and probing excited states and transient intermediates, and obtaining the electronic structures and dynamics of excited states and transient intermediates are the basis for understanding complex photochemical photocontrol mechanisms, but they are difficult to achieve. In practical device design, organic photofunctional materials usually exist in the form of solid samples. However, there are a series of challenges and difficulties in the study of spectral detection and dynamics of excited states and transient intermediates of solid samples, including the light scattering problem of solid samples and the complexity of analyzing spectral signals collected by reflection mode; the interaction between solid sample medium and strong light resulting in nonlinear optical effects; the intermolecular interactions in solid samples leading to more complicated excited state processes; influence of interface and defect on excited state process in solid samples; simulation of excited state of crystal phase and electronic structure of transient intermediate and so on. Therefore, our research group has carried out the exploration of spectral detection and regulation of excited state of organic solid photofunctional materials by using ultrafast spectroscopy, and revealed the internal relationship between excited state property and electronic structure,¹⁻⁷ so as to realize the regulation of excited state and provide the guidance for the design of photofunctional materials.

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NOTES

An octacoordinated Nb atom in the NbAl₈H₈⁺ cluster**Piero Ferrari,^{a,b} Hung Tan Pham,^c Jan Vanbuel,^a Minh Tho Nguyen,^c****Andre Fielicke^d and Ewald Janssens^a**^a*Quantum Solid-State Physics, KU Leuven, Leuven*^b*FELIX Laboratory, Radboud University, Nijmegen, The Netherlands*^c*Department of Chemistry, KU Leuven, Leuven, Belgium*^d*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*

Coordination chemistry is a rich and vibrant field of research, featuring applications ranging from catalysis and medicine to optics and magnetism. Many stable compounds with unprecedented coordination can be understood by the electron counting rules introduced by Langmuir. Those rules for delocalized valence electrons around a central atom prescribe a more stable complex for closed-electronic configurations with 8, 18, 20 or 32 itinerant electrons. In this contribution, we present the discovery of an hydrogenated niobium doped aluminum cluster with a remarkable coordination. The NbAl₈H₈⁺ cluster was formed in a molecular beam and characterized by mass spectrometry and infrared spectroscopy. Density functional theory calculations show the lowest-energy isomer is a high symmetry singlet with the Nb atom placed at the center of a distorted hexagonal Al ring and coordinated by two AlH moieties, therefore exhibiting octacoordination. The unprecedented high symmetric geometry is attributed to the 20 valence electrons; the central Nb atom adheres to the 18-electron rule and two additional delocalized electrons stabilize the hexagonal ring [1].

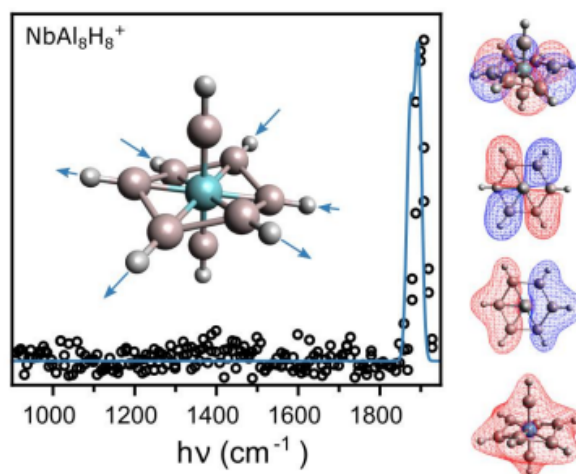


Figure 1. Infrared spectrum of NbAl₈H₈⁺ in the gas phase.

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NOTES

Tuning Near-Infrared Photothermal Conversion of Binary and Ternary Charge-transfer Cocrystals by Intermolecular Interactions

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Organic charge-transfer (CT) cocrystals with tunable energy gaps are attracting candidates for solar photothermal conversion (PTC), but mature design strategies to achieve ideal PTC efficiency are still scarce. Herein, binary and ternary cocrystals were constructed to check the effect of isomeric donor and third component on their PTC efficiencies, respectively. These subtle intermolecular interactions were resolved by single-crystal X-ray diffraction, ultrafast time-resolved transient absorption, and excited-state theoretical calculations.

Our results reveal that, for binary cocrystals, the π - π stacking of cocrystals is conducive to promoting the near-infrared (NIR) light-harvesting ability and the p - π interaction can regulate the nonradiative rotation of $-C(C\equiv N)_2$ groups, resulting in a tunable NIR PTC via the isomeric cocrystals. Under NIR laser irradiation, the PTC efficiencies @808 nm of binary cocrystals can be tuned from 35.85% to 60.53%. For ternary cocrystals, strong π - π stacking interactions facilitate enhanced light capture, while weak $C-H\cdots\pi$ interactions can loosen the molecular stacking and thus facilitate the rotation of $-C(C\equiv N)_2$, which promotes non-radiative transition to achieve efficient PTC performance. The PTC efficiencies @808 nm of ternary cocrystals could be tuned from 59.6% to 87.7%.

With wide absorption spectrum (300-1300 nm) and excellent NIR PTC efficiency (87.7%), the ternary cocrystal (P-P-TCNQ) was further used in a solar-driven interfacial heating evaporation system with a water evaporation rate of up to $1.42\text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. This work provides valid strategies to design high-performance organic cocrystal solar PTC materials by regulating fine intermolecular interactions.

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NOTES

Ultrafast photophysics of a single chain donor-acceptor copolymer**Hak-Won Nho^{a,b}, Won-Woo Park^a and Oh-Hoon Kwon^{*a,b}**

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The mechanism of charge-carrier dynamics in bulk-heterojunction structures remains a fascinating topic for application in photovoltaics more than two decades[1–3]. Understanding the charge-carrier dynamics within the light-harvesting process is essential for optimizing organic photovoltaic devices. In this study, we explored the photophysics in single chains of the top-notch performance conjugated copolymer, PM6, by utilizing the two complimentary femtosecond-resolved spectroscopic techniques, fluorescence-upconversion and transient-absorption spectroscopy[4]. Our observations reveal the ultrafast evolution of intrachain charge-transfer (CT) state and its equilibrium with parent local excited (LE) state on a single chain of PM6. The intrachain CT state diffuses along the PM6 chain and finally transforms into a interchain CT state at a chain folding site. The global analyses of transient-absorption spectra show that interchain CT state bifurcates into forming a long-lived charge-separated state or annihilating within a picosecond. The lifetime of the transient species was simulated by simple one-dimensional diffusion model. Accordingly, the nonexponential relaxation time of the species was found to correlate with the abundance of chain foldings in a single PM6 chain, thus, supporting the formation of interchain CT state.

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NOTES

Detection of Pre-Reactive intermediates of Diels-Alder Cycloadditions by Molecular Rotation Spectra

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The Diels-Alder (DA) reaction, with its rich synthetic diversity, has proven to be one of the most powerful protocols for accessing [4+2] cycloaddition to carbo- or heterocycles, and is recognized as one of the cornerstone reactions that both enabled and shaped the modern organic chemistry.^[1] In this presentation, taking furan as the diene, acrolein and maleic anhydride as the dienophile, the first stages of their DA reactions have been imaged with rotational spectroscopy, which is an ideal tool to characterize, at the molecular level, the nature of molecular complexes.^[2-4] The results have shown that the pre-reactive molecular complexes are stabilized with $\pi \cdots \pi$ stacking, which might be attributed to the selectivity as *endo*- or *exo*- products of such cycloaddition.

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NOTES

IDENTIFICATION OF NEW INTERSTELLAR MOLECULES BY ROTATIONAL SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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The chemical complexity of the interstellar medium (ISM) is demonstrated by detecting more than 270 different chemical species (CDMS¹). The list of observed molecules includes very simple species like methylidyne (CH), the first molecule detected in the ISM or more complex structures like PAHs. The emergence of radio astronomy in the middle of the last century enabled the detection of many new molecules, and, thanks to the increased sensitivity, the detection rate has remarkably increased in the last years. In particular, sensitive line surveys are the best tool to unveil the molecular content of astronomical sources and to search for new molecules. In this context, the GOTHAM² and the QUIJOTE³ line surveys performed using the Green Bank Telescope and the Yebes 40m telescope, respectively, opened a new golden age for astrochemistry with more and 35 molecules detected in 2021.

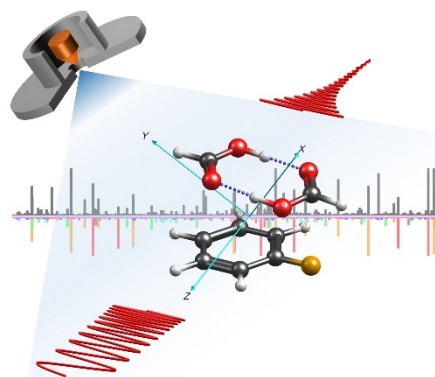
Although some of the discoveries performed with QUIJOTE are based on previous laboratory data available on spectral catalogues, several species have been identified thanks to new *ad-hoc* spectroscopic measurements and quantum chemical calculations. These interstellar molecules detected are transient species that cannot be synthesized through conventional chemical methods and stored in the laboratory. In this talk, some examples of these new interstellar discoveries will be discussed, focusing on the experimental and theoretical methods employed in the identifications.

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B Double-proton transfer tunneling over a phenyl ring revealed by broadband microwave spectroscopy**Weixing Li, Guanjun Wang, Xiaoqing Zeng, Mingfei Zhou***Department of Chemistry, Fudan University, Songhu Rd. 2005, 200438 Shanghai (China)*weixingli@fudan.edu.cn; mfzhou@fudan.edu.cn

Our previous work demonstrated that the measurement of pure rotational spectroscopy of “non-polar” dimer of formic acid can be achieved by means of asymmetric H->D substitution.[1] The concerted double proton transfer of the two hydroxyl hydrogens takes place between two equivalent minima and generates a tunneling splitting of 331.6(5) MHz. In the talk, I will discuss the double proton transfer over a phenyl ring in the complexes of formic acid dimer (FAD) with several phenyl compounds. For example, in the FAD-fluorobenzene complex, the presence of fluorobenzene as a neighboring molecule does not quench the double proton transfer tunneling in the FAD but decreases its tunneling splitting to 267.608(1) MHz.[2] In the FAD-fluorobenzaldehyde complex, the tunneling splitting disappears but generates two non-equivalent isomers. Our spectra show that isotopic substitution at different atomic positions have different influences on the tunneling process. The experiments were carried out by using the newly-built broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer in Shanghai.



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NOTES

Molecular Beam Spectroscopy with an Infinite Interferometer: Spectroscopic Resolution and Accuracy

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Pulse-selection from a stable laser oscillator allows to perform interferometric spectroscopy with an effectively infinite interferometer. This approach removes the dominant resolution limitation for interferometric measurements and allows us to obtain the world's highest resolution scanned interferometric data. Herein, we present mass-correlated rotational Raman spectra [1] with sub-kHz effective resolution over a 500 GHz spectral range. The achieved resolution is several orders-of-magnitude better than that achieved by any preceding rotational coherence spectroscopy or Fourier-transform IR spectroscopy measurements [2] and corresponds to the scanning of km-scale path differences.

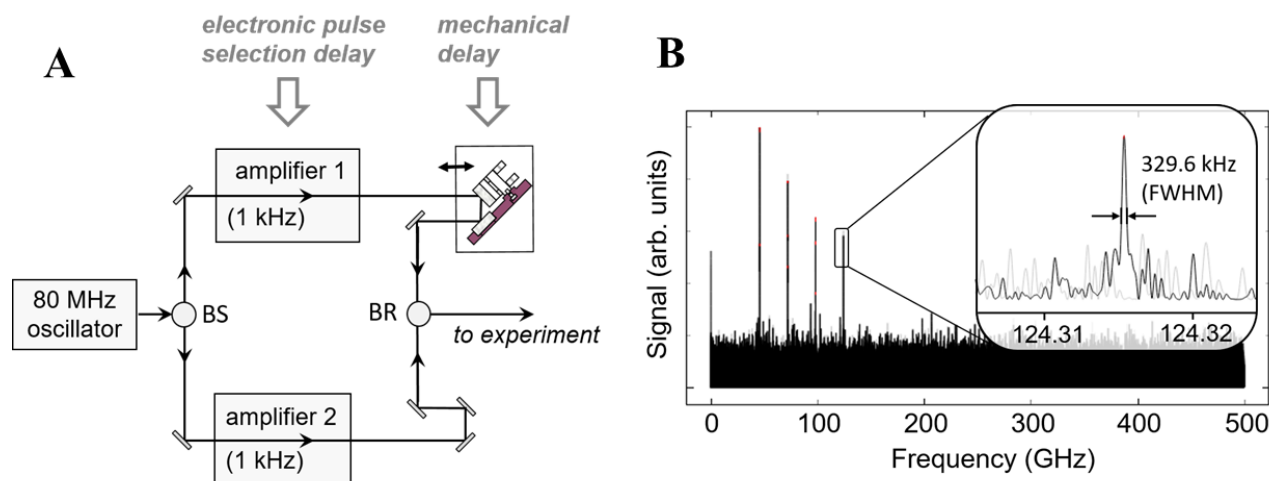


Figure. **(A)** The experimental scheme for the infinite interferometer **(B)** The highest-resolution rotational Raman spectrum obtained with the mass-CRASY technique.

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NOTES

2D IR Investigation of the Structure and Dynamics of D₂O Dissolved in CHCl₃

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D₂O dissolved in CHCl₃ was investigated by two-dimensional infrared (2D IR) spectroscopy to study the structure and dynamics of highly isolated water molecules. The symmetric (ν_s) and asymmetric (ν_a) OD stretch modes of D₂O in CHCl₃ appear at 2740 and 2637 cm⁻¹, respectively. The two modes showed strong cross peaks, and the sign and magnitude of the cross peaks depended on the polarization configuration of the excitation pulses. The coupling between the two modes was found to be -50 cm⁻¹ based on the simple vibrational excitation model, and the energy-level diagram revealing the relationship between the local states and the exciton states is shown in **Figure 1**. The projection angle between the transition dipoles of the two modes obtained from polarization-dependent 2D IR spectra was ~100 degrees. The values of coupling and the projection angle were further reproduced by numerically simulated 2D IR spectra. The two modes also show inter-mode energy transfer on a timescale of ~7 ps with a population relaxation time of ~70 ps.

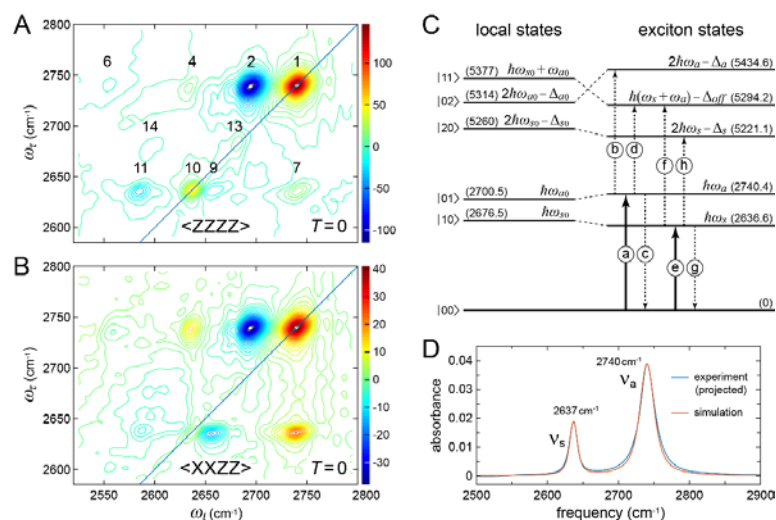


Figure 1. (A and B) Experimental 2D IR spectra collected with (A) <ZZZZ> and (B) <XXZZ> polarization conditions. (C) Energy-level diagram revealing the relationship between the local states and the exciton states. In each state, the letters and the number in parentheses indicate the symbolic expression for the energy level and the numeric value of the state in cm⁻¹, respectively. The numbers in the ket represent the quantum numbers of the ν_s and ν_a in the local states (D) Experimental and simulated linear IR spectra. The experimental linear spectrum is a projected spectrum consisting only of ν_s and ν_a .

NOTES

ANISOTROPIC CIRCULAR DICHROISM SPECTROSCOPY OF JET-COOLED CHIRAL MOLECULES**Changseop Jeong,¹ Jiyeon Yun,¹ Jiyoung Heo,² and Nam Joon Kim^{1,*}**¹ *Department of Chemistry, Chungbuk National University, Korea*² *Department of Biomedical Technology, Sangmyung University, Korea**E-mail: spd2002@naver.com*

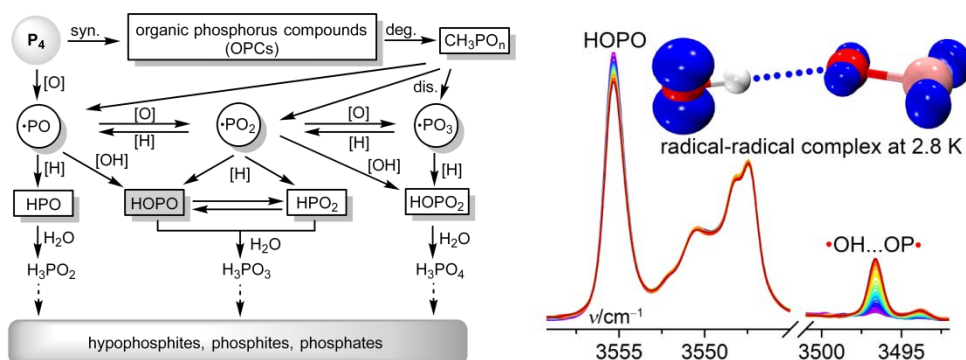
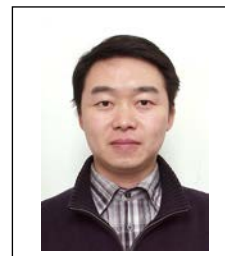
Circular dichroism (CD) spectroscopy is one of the most powerful methods to investigate the structures and reactions of chiral molecules. The CD of molecules with fixed spatial distribution is called anisotropic CD (ACD). ACD spectroscopy has been extensively used to probe the orientation of macromolecules in anisotropic medium. Here, we have obtained the resonant two photon ionization CD (R2PI CD) spectra of (+)- and (–)-Pseudoephedrine ((+)- and (–)-PED) using a dual laser beam R2PI method. It is found that the CD values of the P-, Q-, and R-branch transitions of the origin bands are different from each other. These results are explained by ACD phenomena of jet-cooled molecules undergoing the P-, Q-, and R-branch transitions.

NOTES

Photochemistry of Phosphorus Hydrides Studied by Matrix-isolation Spectroscopy

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As the simplest phosphorus hydride, the diatomic species PH is the parent molecule for phosphinidenes. Similar to the electronic properties of the nitrene analogue NH, PH is highly reactive since it has a triplet ground state. Chemically, PH serves as a transient intermediate in the photochemistry of PH_3 , and it also acts as a biologically relevant phosphorus-bearing species that has been observed in diverse interstellar and circumstellar environments such as Venus, Jupiter, and the carbon star envelope IRC +10216.^[1] Although the spectroscopic properties of PH in the ground and excited states have been extensively explored, its fundamental reactivity remains barely investigated. By combining matrix-isolation spectroscopy (IR and UV-vis) and quantum chemical calculations, the dimerization of PH and its reactions with CO, O_2 , and N_2 were studied. A number of novel phosphorus-containing molecules including P_2H_2 isomers, HPCO/HOCP, HOPO/HPO₂, and HPN₂/PNN have been obtained as the products, and their structures and reactivity have been also disclosed for the first time.^[2]

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Electronic Spectroscopy of PAH Isolated in Solid *para*-Hydrogen

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Diffuse interstellar bands (DIB), narrow absorption features observed from the near IR to the UV, have drawn a lot of interest since their first discovery in 1922. Despite their increasing numbers – over 200 DIB have been catalogued up to today – so far, only two DIB (and a few weaker ones) have been successfully assigned to a specific carrier molecule, the buckminsterfullerene cation, C₆₀⁺.^{1,2} Polycyclic aromatic hydrocarbons (PAH) and especially their cationic, protonated and hydrogenated derivatives are considered particularly promising candidates, but laboratory spectra of these unstable species suitable for comparison to astronomical observations are scarce.

para-Hydrogen matrix isolation spectroscopy has frequently been employed to record the IR spectra of PAH and their protonated and hydrogenated derivatives, prospective carriers of the unidentified infrared bands. The obtained spectra exhibit only small shifts in line positions due to interactions with the matrix host, in line with the ‘softness’ of the quantum solid *para*-H₂. However, despite these promising prospects, electronic spectra of PAH isolated in solid *para*-H₂ have rarely been reported.

To assess the properties of *para*-H₂ as a matrix host for electronic spectroscopy, we present the fluorescence excitation and dispersed fluorescence spectra of several PAH – sumanene, pyrene, coronene, and the 1-hydronaphthyl radical – recorded by *para*-H₂ matrix isolation spectroscopy and compare these to literature data obtained using Ne matrix isolation spectroscopy and jet-expansion methods. In general, the spectra show a good agreement with the reported literature data and vibrational frequencies computed by density functional theory. We observe small but consistent redshifts of 55 cm⁻¹,³ 53 cm⁻¹, 86 cm⁻¹, and 68 cm⁻¹ for the pure electronic transitions to the first excited state for sumanene, pyrene, coronene, and the 1-hydronaphthyl radical, respectively, relative to the reported gas-phase values. Whilst gas-phase spectra of potential DIB carriers will be necessary for an unambiguous identification of specific molecules through comparison with astronomical data, our work suggests that *para*-H₂ matrix isolation spectroscopy can be a useful tool for identifying promising candidates, especially for hydrogenated and protonated PAH which can be efficiently generated during matrix preparation.

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NOTES

Production of isoquinolinium (*iso*-C₉H₇NH⁺) and isoquinolinyl radical (*iso*-C₉H₇NH, 1-*iso*-HC₉H₇N, and 3- to 8-*iso*-HC₉H₇N in solid *para*-hydrogen

Prasad Ramesh Joshi,[†] Masashi Tsuge,[‡] Chih-Yu Tseng,[†] Yuan-Pern Lee^{†,§}

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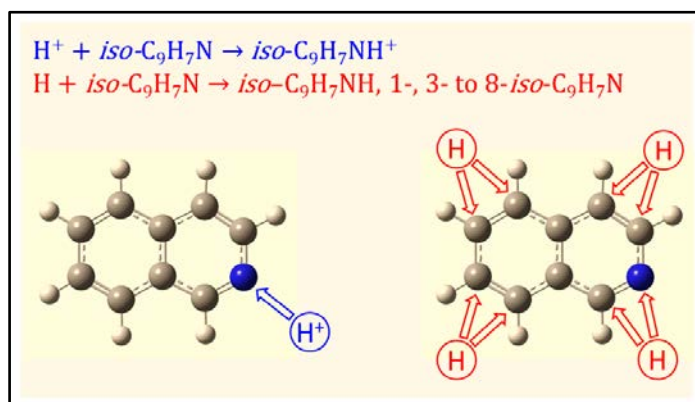
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Abstract

Protonated polycyclic aromatic nitrogen hydrocarbons (H⁺PANH) are prospective carriers of interstellar unidentified infrared (UIR) emission bands from galactic objects, partly because protonation enhances the relative intensities of bands near 6.2, 7.7, and 8.6 μm and partly because the presence of nitrogen atom in the aromatic ring induces a blue shift of the CC-stretching mode so that the spectra of H⁺PANH match better with the 6.2-μm feature in the UIR spectra. We report the infrared (IR) spectra of protonated isoquinoline (2-isoquinolinium cation, *iso*-C₉H₇NH⁺), its neutral counterpart (2-isoquinolinyl radical, *iso*-C₉H₇NH), and another mono-hydrogenated product (6-isoquinolinyl radical, 6-*iso*-HC₉H₇N) produced upon electron-bombardment of a mixture of isoquinoline (*iso*-C₉H₇N) with excess *para*-hydrogen (*p*-H₂) during matrix deposition at 3.2 K. To generate more isomers of hydrogenated isoquinoline, we irradiated *iso*-C₉H₇N/Cl₂/*p*-H₂ matrices at 365 nm to generate Cl atoms, followed by IR irradiation to generate H atoms for reaction via Cl + H₂ (ν = 1) → HCl + H. In addition to *iso*-C₉H₇NH and 6-*iso*-HC₉H₇N observed in electron-bombardment experiments, we identified six additional hydrogenated isoquinoline, 1-, 3-, 4-, 5-, 7-, and 8-*iso*-HC₉H₇N; hydrogenation on all available carbon atoms except the two on the fused ring were observed. Spectral grouping was achieved according to their behaviors after maintenance of the matrix in darkness and on secondary photolysis. The assignments were further supported by comparison of experimental results with vibrational wavenumbers and IR intensities of possible isomers predicted with the B3LYP/6-311++G(d,p) method.



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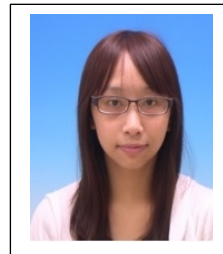
Formation of Para-H₂O by Vacuum-UV Photolysis of O₂ in Solid Hydrogen: Implication to Astrochemistry

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and Yu-Jong Wu^{1,2*}**

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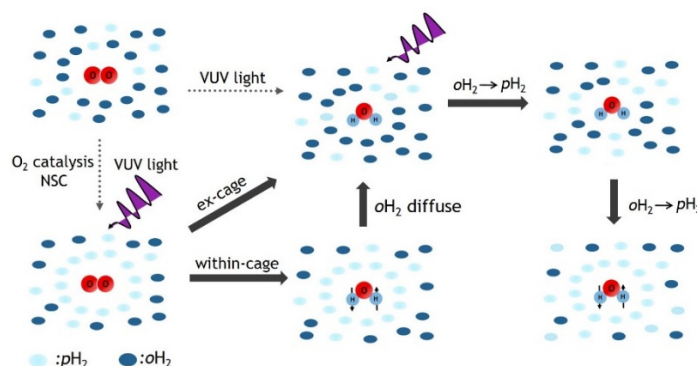
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Abstract

The ortho to para ratio (OPR) of interstellar H₂O smaller than 3 is an important yet unresolved subject in astronomy. We irradiated O₂ embedded in solid normal H₂ (denoted as *n*H₂) at 3 K with either broadband vacuum-ultraviolet (VUV) light or monochromatic light at 121.6 nm and observed IR lines associated with para-H₂O (denoted as *p*H₂O) and non-rotating H₂O-(*o*H₂)_n, but not line associated with ortho-H₂O (denoted as *o*H₂O). After maintaining the matrix in darkness for ~30 h, the intensities of *p*H₂O lines decreased and became nearly completely vanished, while those of non-rotating H₂O-(*o*H₂)_n lines increased and reached to a maximum. After that, the intensities of lines of *p*H₂O and *p*H₂O-*o*H₂ increased continuously, while those of non-rotating H₂O-(*o*H₂) decreased continuously. The later increase in *p*H₂O and *p*H₂O-*o*H₂ is explained by the continuous nuclear-spin conversion from ortho-H₂ (denoted as *o*H₂) to para-H₂ (denoted as *p*H₂) in solid H₂ over time. This continuous conversion from *o*H₂ to *p*H₂ resulted in the conversion of non-rotating H₂O-(*o*H₂)_n to rotating *p*H₂O (and *p*H₂O-*o*H₂) in solid *p*H₂. The observation of the formation and conversion of *p*H₂O in our experiment suggests a plausible route that VUV irradiation of O₂ and H₂ adsorbed on grain surface might be responsible for a smaller OPR of interstellar H₂O.



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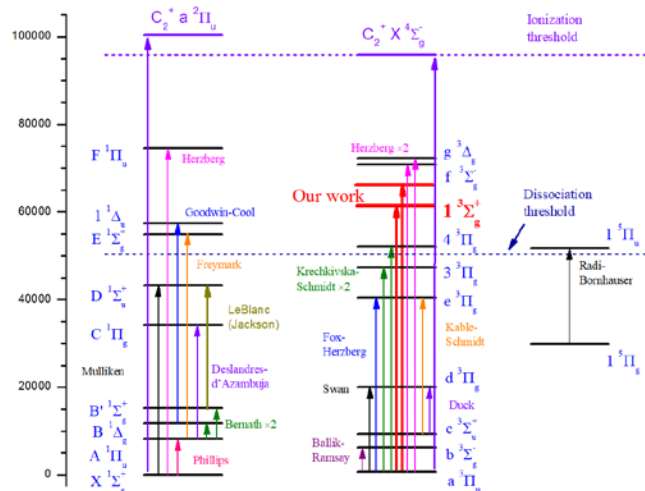
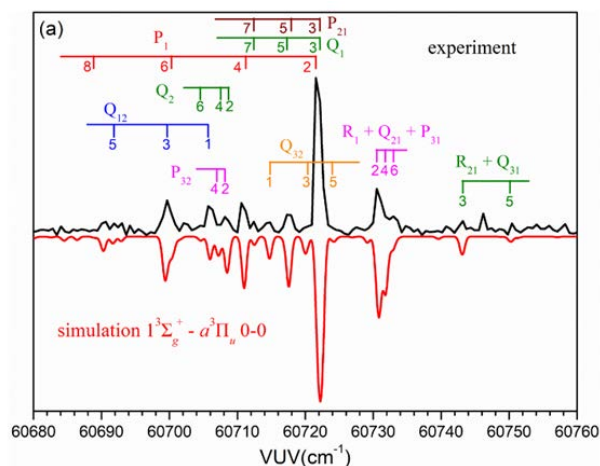
NOTES

Spectroscopic study of C₂ in vacuum ultraviolet regionTonghui Yin, Liying Ma, Min Cheng* and Hong Gao*

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The dicarbon radical, C₂, is one of the most abundant molecules in the universe, and has been widely observed in various energetic environments. The long history of spectroscopic studies for C₂ can be dated back to two centuries ago, which has identified many electronic transition band systems in low energy region,¹ as shown in Fig. 1. However, electronic transitions with upper states above the lowest dissociation threshold are still largely unknown. The only three known absorption band systems in vacuum ultraviolet (VUV) region were identified by Herzberg and coworkers² in 1969 by VUV spectrograph, namely the electronic transitions $F^1\Pi_u(v') \leftarrow X^1\Sigma_g^+(v'')$, $f^3\Sigma_g^-(v') \leftarrow a^3\Pi_u(v'')$ and $g^3\Delta_g(v') \leftarrow a^3\Pi_u(v'')$ (Herzberg-Lagerqvist-Malmberg transitions). Recently in our lab, the spectroscopy of C₂ in VUV region has been systematically studied, by using a tunable high-resolution VUV laser radiation source for the 1+1' (VUV + UV) resonance enhanced multiphoton ionization (REMPI) of the C₂ radicals produced by DC discharge method. Various bands for electronic transitions of C₂ are measured and identified, including those for $g^3\Delta_g$ and $f^3\Sigma_g^-$ states originated from the first excited state of $a^3\Pi_u$ as observed previously by Herzberg et al. Two new transition bands for $1^3\Sigma_g^+$ and $2^3\Sigma_g^-$ states from $a^3\Pi_u$ are observed and identified for the first time, as shown in Fig. 2. The spectroscopic parameters determined for these new states are in good agreement with those predicted by the most recent high level *ab initio* calculations.^{3, 4} The rather astrophysically important $F^1\Pi_u$ state was not observed by us, mainly due to its fast predissociation process. Instead, our study shows that the position of the absorption band $g^3\Delta_g(v'=2) \leftarrow a^3\Pi_u(v''=0)$ exactly overlaps with that of $F^1\Pi_u(v'=0) \leftarrow X^1\Sigma_g^+(v''=0)$. Our study paves the method for systematic investigations of the photoabsorption and photodissociation of C₂ in vacuum ultraviolet region, which has important applications in the field of astrochemistry.

Fig 1. All the currently known one-photon band systems of C₂Fig 2. The measured new transition of $1^3\Sigma_g^+ \leftarrow a^3\Pi_u$

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NOTES

Microwave Spectroscopy and Computational Chemistry: Structure, Bonding and Dynamics

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Abstract –

Microwave spectroscopy has proven to be the most accurate way of determining structure of molecules in the gas phase. What has not been as widely recognized is the application of microwave spectroscopy to infer about bonding, both within a molecule and between molecules. Our group has focused on weakly bound complexes of H₂O and H₂S, as the former is a text-book example for hydrogen **bonding** and the latter was thought to have van der Waals **interactions**. We have recently shown that both (H₂O)₂ and (H₂S)₂ have hydrogen bonds holding them together.¹ We defined a ‘carbon bond’ analogous to the hydrogen bond² and showed that CH₃CN•••CO₂ complex is bound by a carbon bond.³ Though, (H₂O)₂ is a classic example for hydrogen bond, three different large amplitude tunneling motions can break the hydrogen bond and enable each of the four H atoms to be involved in the hydrogen bond.⁴ While the tunneling dynamics in (H₂O)₂ has been investigated extensively, we showed recently how the presence of an argon atom affects this in Ar-(H₂O)₂.⁵ The ground state microwave spectrum of C₆H₆-H₂O was solved 3 decades ago, proving that water forms hydrogen bonds with water.⁶ However, the excited state transitions could not be properly assigned and they were fitted to a free rotor Hamiltonian, with unacceptable residues. Microwave spectra of several similar complexes were fit with a free-rotor model leading to unacceptable residues. We have recently shown that a Hamiltonian including Coriolis interaction can explain the excited state transitions incorrectly assigned as a free rotor, for C₆H₆-H₂O and similar complexes.⁷ This talk will highlight how microwave spectroscopy has been used to infer structure, bonding and dynamics in molecules/molecular complexes.

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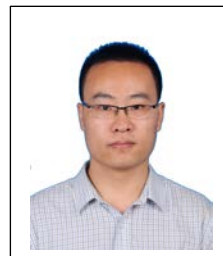
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Acknowledgements

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NOTES

Rotational spectroscopic characterization of the non-covalent S- π interactions**Gang Feng***Chongqing University, Daxuecheng South Rd. 55, 401331, Chongqing, China.**fenggg@cqu.edu.cn*

The sulfur-bearing non-covalent interactions are of great significance for understanding the microscopic mechanisms of molecular recognition, binding and catalysis. We employed high-resolution Fourier transform microwave (FTMW) spectroscopy in combination with quantum chemical computations to characterize and understand the nature of these sulfur non-covalent interactions.[1-6] In this contribution, we will present the structural and energetic details of S- π interactions revealed in the complexes of benzofuran. In the specific, two isomers have been observed for the benzofuran and diethyl disulfide complex, in which diethyl disulfide configures as gauche-gauche-gauche conformation sitting on the face of the benzofuran ring. The lone-pair electrons of the sulfur atom points to the π -electron cloud of the benzofuran with a distance of ~ 3.6 Å, thus indicating a direct interaction between S and aromatic ring. Computations suggest both observed isomers are stabilized by cooperative S $\cdots\pi$, C-H $\cdots\pi$, and C-H $\cdots$ O weak intermolecular interactions with total interaction energies of about 26 kJ mol⁻¹ and is dominated by dispersion.

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NOTES

**THE ROTATIONALLY-RESOLVED VIBRATIONAL SPECTRA OF
CYCLOPROPYLAMINE IN THE INFRARED REGION****Yue Liang¹, Brant Billingham², Bowen Liu¹, Ziqiu Chen¹***1 College of Chemistry and Chemical Engineering, Lanzhou University,
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The infrared spectra of cyclopropylamine (c-C₃H₅NH₂) in the region of 35-600 cm⁻¹ have been measured at room temperature with a resolution of 0.00096 cm⁻¹ using the far-infrared beamline at the Canadian Light Source synchrotron. We report here the results of the rovibrational analysis of the ν_{27} (253.87 cm⁻¹) –NH₂ torsional fundamental and hot bands, as well as the pure rotational analysis of transitions associated with the ground state and higher excited states of the –NH₂ torsional mode between 35 and 60 cm⁻¹. The ongoing assignment and analysis of hot bands and overtones involving higher torsional states will also be discussed.

NOTES

Bottom-Up Synthesis of Tetracyclic Polycyclic Aromatic Hydrocarbons through the Indenyl Radical Self-Reaction**Hong Wang, Jinyang Zhang, Jiwen Guan, Qian Xu, Zhandong Wang***National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China.***Abstract**

Indenyl radical (C_9H_7) is a key precursor for the formation of large polycyclic aromatic hydrocarbon (PAH) and nascent soot at combustion conditions. Herein, we present a direct high-temperature synthesis of tetracyclic PAHs via the elementary recombination reactions of 1-indenyl in a laminar flow tube. Probing by molecular beam sampling coupled with isomer-resolved synchrotron vacuum ultraviolet photoionization mass spectrometry, direct association products and H-elimination products are suggested. Supplemented with the offline gas chromatography–mass spectrometry, four $C_{18}H_{12}$ isomeric products are clearly discriminated. The produced PAHs are identified as chrysene, benzo[a]anthracene and benzo[c]phenanthrene, and 4-vinylpyrene. By performing the corresponding potential energy surface calculations and RRKM/ME kinetic stimulations, we show how these prototypical tetracyclic PAHs can be efficiently formed via a radical-radical reaction mechanism. The versatile routes converting 1-indenyl to the 18- π aromatic PAHs provide a clear view of high-temperature molecular mass growth processes of large-size PAHs that may unravel the formation of more complex PAHs and nascent soot particles in combustion.

NOTES

Cryogenic Ion Spectroscopy of Singly Protonated Peptide DYYVVR for Identifying Phosphorylation Sites

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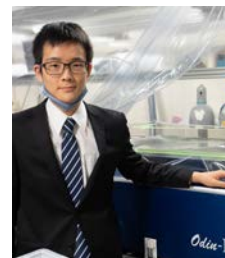
Post-translational modification (PTM) is enzymatic modification of proteins following protein biosynthesis. Phosphorylation of tyrosine is a key post-translational modification of proteins in the propagation of extracellular information to intracellular signal transduction. The role of tyrosine phosphorylation of janus kinase 3 (JAK3) is a switch in regulating its kinase activity within the activation loop of the kinase domain. We applied cryogenic ion spectroscopy (CIS) to singly protonated DYYVVR, a tryptic peptide that contains the two active tyrosine residues (Y980 and Y981) of JAK3 kinase domain and its point mutants (Y980F and Y981F), phosphorylated peptides (pY980, pY981, and pY980pY981). The two tyrosine chromophores showed different UV absorption bands around 35200 cm⁻¹ and 35450 cm⁻¹, respectively. By comparing with the point mutants, the lower electronic band was assigned to the absorption of Y981 and the higher one to Y980. When phosphorylated, the UV absorption of the phosphorylated chromophore shifts to higher energy above 36500 cm⁻¹ but the dephosphorylated chromophore gives the absorption at the same region of wild type peptide. Conformer-specific IR spectroscopy and density functional theory (DFT) calculation was used to tentatively assign the structure of DYYVVR. At least two conformations were found, where Y981 is solvated by the protonated side chain of arginine R984 and orientation of the carboxylic OH of D979 was different between the two. It is demonstrated that CIS can be used to distinguish the two tyrosine chromophores and to locate the phosphorylation site of a kinase domain.

NOTES

Ultrafast mode-selective excitation of large-amplitude vibration in diphenylmethane through impulsive stimulated Raman scattering

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With recent advances in ultrashort laser techniques, many studies have been conducted to control rotational and vibrational wave packets. Among the molecular motions, large-amplitude vibration in the electronic ground state is especially important because such a motion induces large structural change, which may result in a variety of functions in functional molecules like biomolecules. However, there have been few studies on the creation of vibrational wave packets in the electronic ground state of isolated gas systems. Furthermore, most of them deal with simple molecules such as diatomic molecules [1] and biphenyl derivatives [2], in which only one vibrational mode can be excited by ultrashort laser pulses. Here we study diphenylmethane (DPM), which has two large-amplitude vibrational modes, i.e., torsional vibration T (20cm^{-1}) and anti-torsional vibration $\bar{T}$ (16cm^{-1}). With the irradiation of ultrashort laser pulses, both modes should normally be excited through impulsive stimulated Raman scattering (ISRS) because they have similar frequencies and they are both Raman active. In this study, mode-selective excitation of the large-amplitude vibration in DPM has been realized using wave packet interference.

Adiabatically cooled DPM was irradiated by a pair of Ti:Sapphire femtosecond laser pulses (pumps) to excite mode T and $\bar{T}$ through ISRS. 200ns after the irradiation of pump pulses, resonance two-photon ionization (R2PI) spectra were obtained by the irradiation of the doubled output ($\sim 268\text{ nm}$) of the nanosecond dye laser (probe). Then, the populations in $v = 1$ of both vibrational modes were obtained from the hot band area in the R2PI spectra.

Figure 2 shows the change of population in $v = 1$ of mode T and $\bar{T}$ against the double pump interval. These results indicate that the population in $v = 1$ of these modes oscillates with the period of 1.7 ps and 2.1 ps, respectively, as a result of the wave-packet interference. By utilizing the difference in the oscillation periods, selective excitation of mode T and $\bar{T}$ is realized at 3.1 ps and 4.1 ps, as clearly shown in Figure 2.

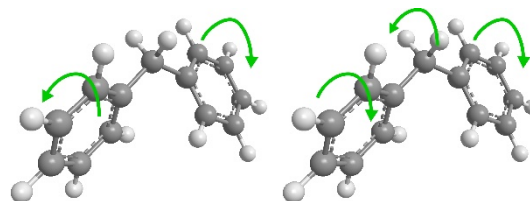


Figure 1 Symmetric and antisymmetric torsional modes, T (left) and $\bar{T}$ (right), of DPM.

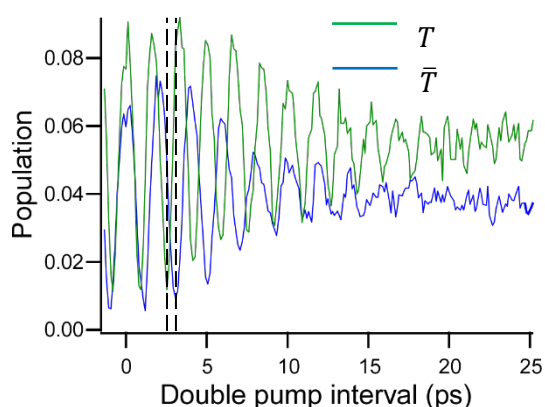


Figure 2 The population in $v = 1$ of mode T (green line) and $\bar{T}$ (blue line) against the double pump interval. When the double pump interval is 3.1 ps (4.1ps), mode T ($\bar{T}$) is selectively excited (dashed line).

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NOTES

Constructing spectroscopic accuracy intermolecular potential energy surface by the physical model with machine learning technique

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The potential energy surface (PES) is one of the prerequisites for nearly all atomic-scale simulations, and the accuracy and efficiency of the intermolecular PES (IPES) determine the accuracy and cost of calculating the corresponding ro-vibration spectrum. In tradition, IPES fitting was based on physically meaningful potential functions (or so-called force fields), such as the multi-dimensional Morse/Long-range (mdMLR) model[1]. These physical models are often limited by their functional forms and only have good numerical accuracy on specific systems. Nowadays, many machine learning (ML) potential models, especially neural network (NN) potentials, have been developed and become more and more popular due to their convenience in the application and better efficiency in high-dimensional function fitting. However, compared to physical IPES models, the general machine learning PES models usually need more fitting points to "learn" the correct asymptotic behavior and have poor extrapolation outside the dataset region.

In this presentation, we will illustrate our recent development of the physics-based machine learning model for intermolecular PES fitting. This model, named MLRNet, combines the neural network model and the MLR function[2]. The physically realistic behavior of the MLR function ensures the MLRNet has meaningful extrapolation at both short and long ranges, and the neural network representation of the MLR function is more flexible and more efficient than the traditional mdMLR model, especially for systems containing non-rigid monomer(s). We test the performance of MLRNet in two Van der Waals systems: the 3-dimensional IPES of CO₂-He including CO₂ anti-symmetric vibration Q₃, and the 6-dimensional IPES of the H₂O-Ar system. The MLRNet achieves higher accuracy than the mdMLR model in both systems and shows physically sensible extrapolation. Moreover, for the 6-D H₂O-Ar system, the MLRNet only needs 1596 trainable parameters which are almost equal 5-D mdMLR model (1509) and half of the PIP-NN model (3501) with similar accuracy.

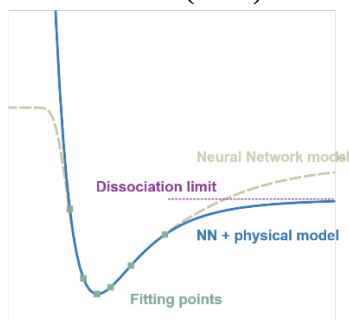


Figure 1: Idea of combining physical model with neural network

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NOTES

Benchmarking calculations of the infrared spectra of cosmic fullerene and its relatives**Jianzhi Xu, Tao Yang, Gao-Lei Hou***

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**Abstract**

Unidentified infrared emission (UIE) bands play important roles in a variety of astrophysical environments. Identification of their exact carriers is of great challenge and remains elusive despite extensive effort over the past 40 years. Fullerenes, including C₆₀ and C₇₀, have been confirmed unequivocally to be UIE carriers in the past 10 years by their characteristic infrared features, first in the young planetary nebula (PN) Tc1 and later in many more astrophysical objects [1, 2]. However, open questions remain regarding that the spectral band intensity ratios as neither fluorescence nor thermal excitation mechanisms can explain the observed facts, and that the carriers of many other UIE features remain unknown [3, 4]. A complete understanding and reliable calculation of the vibrational property of fullerene is thus of significant importance. In this presentation, I will talk our recent progress in tackling those open questions by theoretically studying the previously reported infrared spectra of C₆₀, C₆₀⁺, C₆₀H⁺, C₆₀O⁺, C₆₀OH⁺, C₇₀, and C₇₀H⁺. Our aim is to find out the most reliable and efficient methods that can predict, to a satisfactory extent with the astronomical observation, both the positions and intensities of the infrared features of carbon-containing species, in particular the cosmic fullerene and its relatives.

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NOTES

Theoretical Study on Benzene Using Path Integral Molecular Dynamics Method:
Are the C-H and C-D Bond Lengths in C₆H₆ and C₆D₆ Almost the Same ?

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In many organic molecules, it is known that the C–H bond lengths in H isotopologues are longer than the C–D bond lengths in D isotopologue, due to the anharmonicity of the potential energy curve. Since the zero-point vibrational energy of C–D bond is smaller than that of C–H one, the C–D bond length becomes shorter than the C–H one. In addition, the average bond length (bond length in r_0 -structure) is normally longer than the bond length in equilibrium r_e -structure, which corresponds to the minimum of the potential energy curve.

However, Baba and coworkers recently reported unexpected findings for the C–H and C–D bond lengths in C₆H₆ and C₆D₆ by high resolution spectroscopy [1], that is, the C–H and C–D bond lengths in C₆H₆ and C₆D₆ are almost the same. Hirano *et al.* successfully revealed that the experimentally observed bond lengths are not the raw bond lengths but the projected lengths onto the benzene ring plane by using *ab initio* molecular orbital method [2].

In this study, we have carried out the path integral molecular dynamics (PIMD) simulations, which can represent H/D isotope effects, for C₆H₆ and C₆D₆ to directly estimate the projected C–H and C–D bond lengths. Our PIMD results support the previous explanation by Hirano *et al.* for the experimentally observed fact in C₆H₆ and C₆D₆. More surprisingly, we found that the vibrationally averaged structure of C₆H₆ is “planar but non-flat” [3].

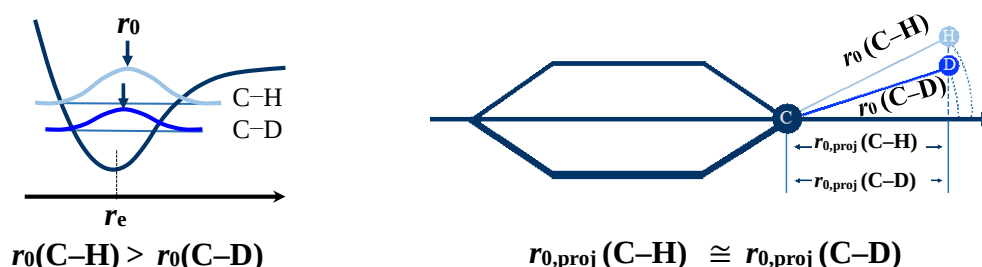


Figure 1. $r_0(\text{C-H})$ and $r_0(\text{C-D})$ bond lengths and the projected bond

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NOTES

Interpretation and prediction of the photoelectron spectra of molecules via computing Franck–Condon factors

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In the past decade, we developed an approach for computing Franck–Condon factors and applied it to interpret and predict the photoelectron spectra of molecules. The harmonic-oscillator model is adopted and the mode-mixing Duschinsky effect is treated explicitly in our model.¹ Our studies provide insights into the vibrational structures of the photoelectron spectra of the molecules investigated, based on the agreement between the experimental and theoretical spectra, such as that for arcolein (Fig. 1).² In addition, we are now constructing a hybrid model of harmonic and anharmonic oscillators for computing Franck–Condon factors, with the hope that the simulated spectra can fit the experimental spectra better. Some preliminary results will be presented in this talk.

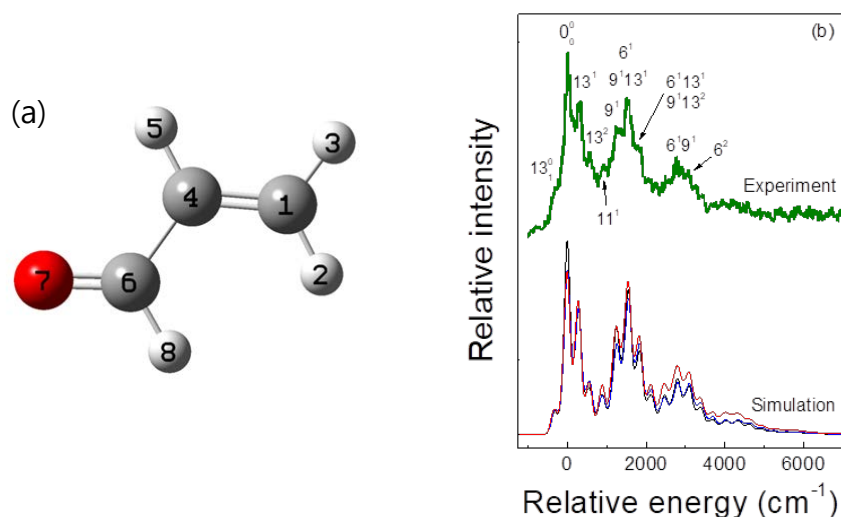


Figure 1. The structure of *trans*-acrolein (a) and the comparison of the simulated photoelectron of *trans*-acrolein with the experimental spectrum (b) reported by Yencha et al.³

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NOTES

Anharmonic Vibrational Raman Optical Activity of Methyloxirane: Theory and Experiment Pushed to the Limits

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Combining Raman scattering and Raman optical activity (ROA) with computer simulations reveals fine structural and physicochemical properties of chiral molecules. Traditionally, the region of interest comprised fundamental transitions within 200-1800 cm^{-1} . Only recently, non-fundamental bands could be observed as well. However, theoretical tools able to match the observed spectral features and thus assist their assignment are rather scarce. We will present an accurate and simple protocol based on a three-quanta anharmonic perturbative approach that is fully fit to interpret the observed signals of methyloxirane within 150-4500 cm^{-1} . An unprecedented agreement even for the low-intensities combination and overtone transitions has been achieved, showing that anharmonic Raman and ROA spectroscopies can be valuable tools to understand vibrations of chiral molecules or to calibrate computational models.

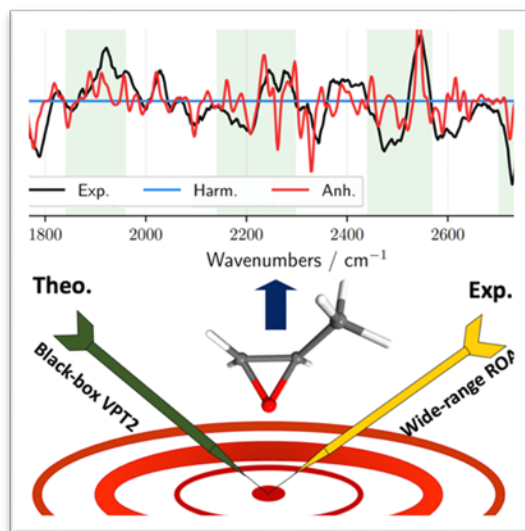


Fig. 1: High agreement between theory and experiment, even for overtones and combinations.

Referencies:

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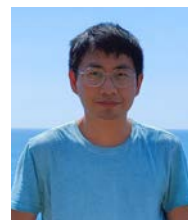
NOTES

Computational approach to study the vibronic effect in Electronic Linear Dichroism

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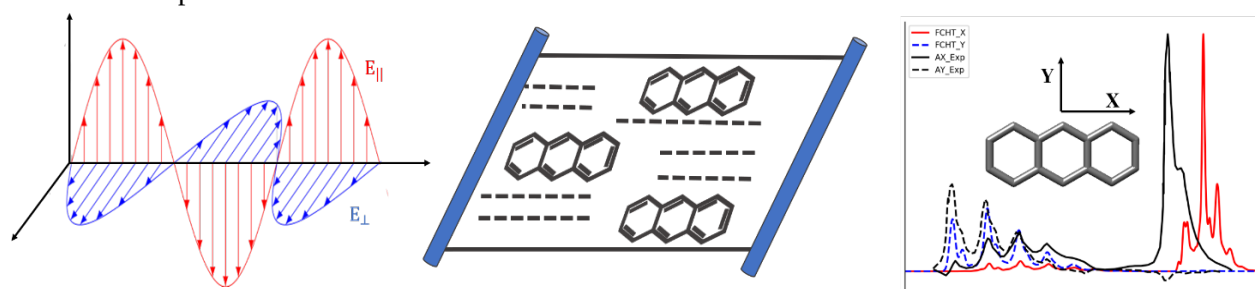
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While the connection between structure and properties is well known, establishing simple rules connecting them is not straightforward, especially as spectroscopic signals are generally an average over random orientations. However, being able to collect precise information on the direction of transition moments from properties such as the electric dipole could help detect easily and understand better subtle structural changes [1], like irregularities in molecular assemblies, deformations related to electronic transitions, or analyze the composition of supramolecular systems such as proteins [2]. Conversely, such knowledge can guide rational designs of molecules to fine-tune their performance, for example in the conception of OLEDs emitters. In light of these possibilities, linear dichroism (LD), which can probe specific components of the electric dipole transition moment of oriented molecules, can offer an invaluable help.

From a theoretical perspective, the prediction of LD spectra presents various challenges, from the modeling of the molecular geometry and orientation in the experimental setup, to the accurate description of the outcome, obtained from the subtraction of two signals oriented parallelly and perpendicularly to the depositing surface. This configuration bears some similarities with circular dichroism, sharing a higher sensitivity related to the lower intensity compared to the standard absorption spectrum. Moreover, the LD technique is more suitable for molecules exhibiting some high degree of symmetry, for which the direction of the transition dipole for the reference, non-deformed structure can be well-established. Both aspects make a pure electronic description of UV-visible LD spectra insufficient, so that the vibrational information needs to be properly included.

In this contribution, we show how the existing framework to compute vibrationally-resolved electronic spectra [3-4] developed in our group was extended to predict linear-dichroism, offering different ways to define the orientation of the molecules. Some of the possibilities offered by our tool and the achievable accuracy will be illustrated with representative test cases.



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NOTES

High-resolution scattering imaging of the charge transfer processes between spin-orbit selected $\text{Ar}^+(\text{}^2\text{P}_{3/2, 1/2})$ ion and the neutrals N_2 and H_2

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Ion-molecule reactions play vital roles in determining the physicochemical properties of interstellar medium, planetary atmospheres and plasma. To study quantum state-to-state ion-molecule scattering dynamics, we have recently built a crossed ion-molecule scattering setup, where the ions can be prepared in selective electronic, vibrational and rotational states by laser photoionization, and the product velocity is measured by the three-dimensional velocity-mapped ion imaging method [1, 2]. In this study, we prepared spin-orbit selected $\text{Ar}^+(\text{}^2\text{P}_{3/2, 1/2})$ ion by using the REMPI method, and the high-resolution scattering images for the prototype charge transfer reactions $\text{Ar}^+(\text{}^2\text{P}_{3/2, 1/2}) + \text{N}_2 \rightarrow \text{Ar} + \text{N}_2^+(\nu)$ and $\text{Ar}^+(\text{}^2\text{P}_{3/2, 1/2}) + \text{H}_2 \rightarrow \text{Ar} + \text{H}_2^+(\nu)$ are obtained, as shown in Figure 1. The features of scattering images show substantial dependence on the specific spin-orbit state of the Ar^+ ion, which indicates that the charge transfer processes are strongly affected by the spin-orbit state of the Ar^+ ion.

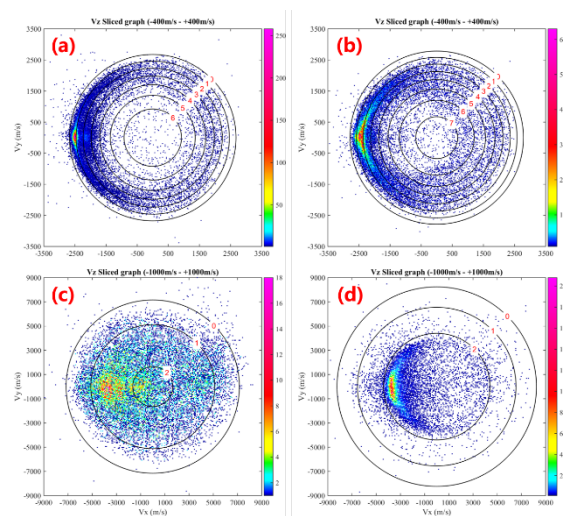


Figure 1 Scattering images for the charge transfer reactions (a) $\text{Ar}^+(\text{}^2\text{P}_{3/2}) + \text{N}_2 \rightarrow \text{Ar} + \text{N}_2^+(\nu)$, (b) $\text{Ar}^+(\text{}^2\text{P}_{1/2}) + \text{N}_2 \rightarrow \text{Ar} + \text{N}_2^+(\nu)$ at the collision energy of 1.588 eV; (c) $\text{Ar}^+(\text{}^2\text{P}_{3/2}) + \text{H}_2 \rightarrow \text{Ar} + \text{H}_2^+(\nu)$ and (d) $\text{Ar}^+(\text{}^2\text{P}_{1/2}) + \text{H}_2 \rightarrow \text{Ar} + \text{H}_2^+(\nu)$ at the collision energy of 0.224 eV. The rings represent the vibrational levels of the product ions N_2^+ and H_2^+ .

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NOTES

Mapping partial wave dynamics in scattering resonances by low-energy NO-He collisions**T. de Jongh^{1#}, Q. Shuai^{1#}, M. Besemer¹, G. Abma¹, S. Kuijpers¹, A. van der Avoird¹, G. C. Groenenboom^{1*}, S. Y. T. van de Meerakker^{1*}**¹Radboud University, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, the Netherlands

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In molecular collisions, resonances occur at specific energies at which the colliding particles temporarily form quasibound complexes. Direct measurements of these complexes are usually difficult. State-to-state low-energy collision experiments with high resolution can serve as an excellent tool for probing the details of the quasibound states. Here we present a joint experimental and theoretical study of low-energy NO-He collisions, that allows us to probe how individual partial waves evolve during the collision. By tuning the collision energies to scattering resonances between 0.2 and 8.5 cm⁻¹, the initial conditions are characterized by a limited set of partial waves. We probed the lowest-lying resonance dominated by *s* and *p* waves only. The highly structured differential cross sections directly reflect the increasing number of contributing waves as the energy is increased.

By preparing NO in a rotationally excited state before the collision and by studying rotational de-excitation collisions, we were able to add one quantum of angular momentum to the system and trace how it evolves. Exploiting the principle of detailed balance, we show that rotational de-excitation collisions probe time-reversed excitation processes with superior energy and angular resolution. Our results are in good agreement with state-of-the-art quantum chemistry calculations at the CCSDT(Q) level.

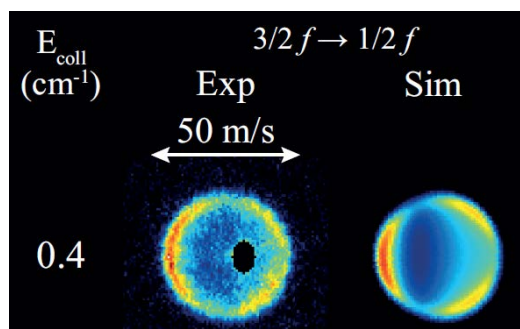


Figure 1: Experimental and simulated velocity map images at the collision energy of 0.4 cm⁻¹ for NO molecules scattered from *j*=3/2 *f* state to *j*=1/2 *f* state in NO-He collisions.

References

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NOTES

Vibrational Predissociation and Intramolecular Vibrational Redistribution of the C₃Ar van der Waals Complex

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Our previous work¹ showed that the Renner effect of the C₃($\tilde{A}$) molecule at the 0 4⁻ 0 and 0 2⁺ 0 levels on the vibrational predissociation (VP) processes of the pertinent C₃Ar levels is small. In this work, seven ro-vibrational levels of the $\tilde{A}$ -state complex lie at 1558-1660 cm⁻¹ above the zero-point level have been studied, where the complex levels associated with a second Renner pair at the 0 8⁻ 0 and 0 4⁺ 0 and the 0 0 2 level of the C₃ molecule, to evaluate the contribution of the Renner effect, energy gap,² vibrational energy to the VP processes. These two Renner pairs have comparable interaction strength, but the energy separations of each pairs are different.³ Their rotationally resolved excitation spectra and emission spectra have been recorded to provide the spectroscopic information and the detailed VP products of the $\tilde{A}$ -state complex. The obtained distributions of the VP fragments versus the excess energies of the fragments can deviate from the predictions of the energy gap law² or momentum gap law.⁴ Combining results from our previous measurements¹ obtained at the low-lying complex levels (340-860 cm⁻¹), we proposed that the effects of vibrational modes, anharmonicities, and energy gap give a primary account of the VP and IVR (intramolecular vibrational redistribution) processes of the $\tilde{A}$ state of the C₃Ar complex. In a collision free system, the energy change involving an IVR process and the VP processes of a weak complex is usually small. In this work, it is found that weak effects such as perturbation, rotational angular momentum, and final state interaction² might change the IVR and VP processes from a primary prediction.

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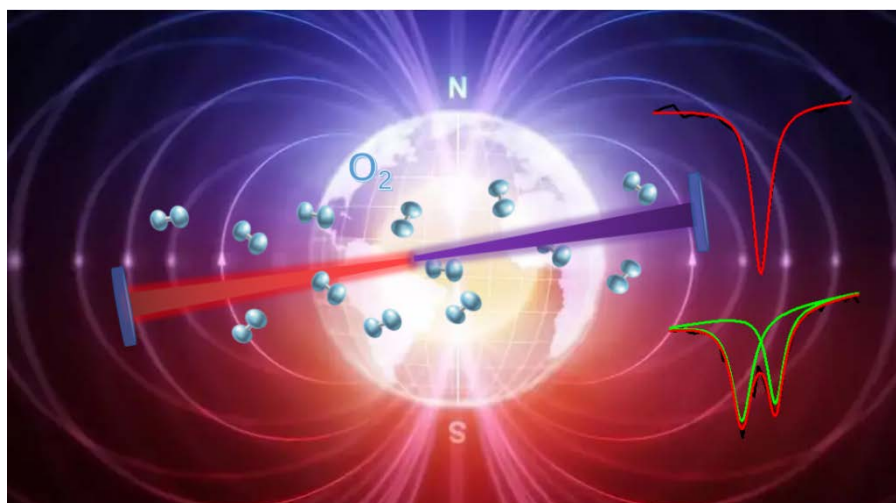
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Saturated absorption spectroscopy of the A-band of O₂**Y.-R. Xu, A.-W. Liu*, Y. Tan, S.-M. Hu***

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The A-band of molecular oxygen, $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-(0,0)$, centered at 13122 cm^{-1} , is one of the most prominent near-infrared characteristic spectra in the Earth's atmosphere, which is also used in satellite sensing of greenhouse atmospheric gases. It is an extremely weak magnetic dipole transition, 10^7 times weaker than a typical electronic dipole transition. The Zeeman splitting at MHz level in the geomagnetic field not only limits the frequency accuracy of these transitions obtained with Doppler spectroscopy measurements^[1], but also introduces a temperature-dependent effect in the atmospheric absorption spectrum at high-altitude^[2]. Here, we present the first saturated absorption spectroscopy of the oxygen A-band lines using comb-locked cavity ring-down spectrometer (CRDS). The positions were determined with an accuracy of a few kHz, two orders more accurate than previous work^[1].



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NOTES

High-resolution laser spectroscopy of $S_1 \leftarrow S_0$ transition of *trans*-stilbene

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We have great interests in the excited-state dynamics of *trans*-stilbene such as *cis-trans* isomerization in the electronically excited state. Zewail et al. [1] reported the results of time-resolved spectroscopy and suggested the nonplanar structure in the S_0 state. In contrast, Pratt et al. [2] concluded that the molecular structure is planar in both S_0 and S_1 states by analyzing the high-resolution spectrum of the $S_1 \leftarrow S_0$ 0_0^0 band. The purpose of this work is the observation of a spectrum with much higher accuracy and determination of the rotational constants. For this purpose, we observed high-resolution fluorescence excitation spectra of the 0_0^0 band and several vibronic bands in the $S_1 \leftarrow S_0$ transition of *trans*-stilbene by crossing a single-mode UV laser beam perpendicular to a molecular beam (Fig.1). For the 0_0^0 band, we determined rotational constants and evaluated rotational temperature as 12 K and line width as 75 MHz. From the obtained rotational constants and inertial defect, it was found S_0 structure is not planar. Additionally, in the S_0 state, we estimated that phenyl rings are rotated approximately ± 10 degrees by using the program we developed. This program compares the observed moment of inertia with the calculated one. On the other hand, theoretical calculation using the WB97XD functional provided the phenyl rings are rotated 14 degrees in the S_0 and 2.4 degrees in the S_1 state. The WB97XD functional evaluates steric repulsion between H atoms by dispersion force potential semi-empirical. This result supports the nonplanar structure revealed by observed rotational constants. Additionally, we are analyzing the vibrational bands such as $0_0^0 + 395\text{ cm}^{-1}$ and $0_0^0 + 788\text{ cm}^{-1}$ bands and also report these results. We found these three observed bands are all *a*-type transition. It is impossible to determine rotational constants *A* from an *a*-type band. So, we try to observe a *b*-type or *c*-type band spectrum. As a future perspective, we are interested in the highly-vibrational levels and spectra of deuterated *trans*-stilbene.

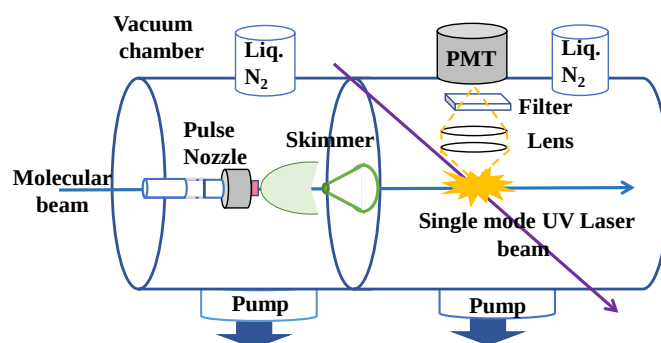


Fig.1 Molecular beam system

[Reference]

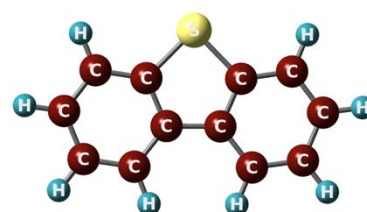
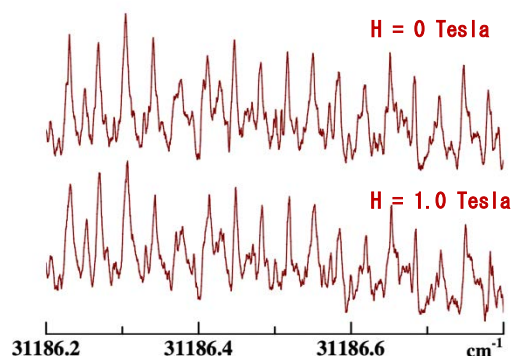
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NOTES

High-resolution Laser Spectroscopy and the Zeeman effect : Dibenzothiophene**Naofumi Nakayama and Masaaki Baba***Molecular Photoscience Research Center, Kobe University, Japan,**baba.masaaki.68e@st.kyoto-u.ac.jp**Conflex Corporation, Tokyo, Japan,**nakayama@conflex.co.jp*

For planar aromatic hydrocarbons, intersystem crossing to the triplet state is expected to be very slow according to El Sayed's rule [1,2]. The fluorescence lifetime in the S_1 state of dibenzothiophene is remarkably shorter compared with the analogous molecules such as dibenzofuran. Pratt et al. suggested that the main fast process was intersystem crossing on the basis of the result of high-resolution laser spectroscopy [3]. We observed the high-resolution spectrum in the external magnetic field in order to confirm the contribution of the triplet state. However, no change has been found in the spectrum up to 1.0 Tesla, indicating that the intersystem crossing is slow and is not the main process for the fluorescence decay in the S_1 state of dibenzothiophene.

Ab initio calculation indicates that the character of the S_1 state is very similar to that of dibenzofuran, and the radiative decay rate is expected to be almost the same. The relatively faster decay is therefore considered to be the result of different internal conversion rate to the ground state. The internal conversion rate is proportional to the level density of the ground state, which drastically increases with the molecular weight. It is suggested that the sulfur atom substitution increases the level density and enhances internal conversion, which is the radiationless transition to the ground state.

**Fig.1 Dibenzothiophene****Fig.2 High-resolution spectra of DBT**

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NOTES

Abstracts for Posters

Vibrational spectra from quantum, semiclassical, and classical pictures

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Infrared spectra have been used in many chemical applications, and theoretical calculations have been useful for analyzing experimental results. For small gas phase molecules, we use the quantum mechanical picture, while for the larger complex systems, such as in the liquid phase, we tend to resort to classical mechanical molecular dynamics methods. However, a systematic understanding of the similarities and differences between the two approaches is not clear. Here we utilized the semiclassical Wigner distribution method to define a connection between the two treatments. In quantum mechanics, the spectra as a function of angular frequency, ω , are given by the Fourier transform of the dipole auto-correlation function

$$I^{QM}(\omega) = \frac{C}{2\pi} \int_{-\infty}^{\infty} dt \langle 0 | e^{i\hat{H}t/\hbar} \hat{\mu} e^{-i\hat{H}t/\hbar} \hat{\mu} | 0 \rangle e^{i\omega t}$$

where C is a constant, $\hat{H}$ and $\hat{\mu}$ are the Hamiltonian and dipole moment operators. $|0\rangle$ is the zero-point vibrational state (ZPS). For the corresponding Wigner treatment, Bose and Makri have recently suggested using the Weyl transform of the $\hat{\rho}_0 \hat{\mu}$

$$P_{\rho_0, \mu_0}^{Wig}(q_0, p_0) = \frac{1}{2\pi\hbar} \int dy e^{(ip_0 y/\hbar)} \left\langle q_0 - \frac{y}{2} \left| \hat{\rho}_0 \hat{\mu} \right| q_0 + \frac{y}{2} \right\rangle$$

From this approach, we can calculate the spectra as

$$I^{Wig}(\omega) = \frac{C}{2\pi} \int_{-\infty}^{\infty} dt \iint dq_0 dp_0 P_{\rho_0, \mu_0}^{Wig}(q_0, p_0) \mu(t; q_0, p_0) e^{i\omega t}$$

Here, the phase space average is used to obtain the auto-correlation function. On the other hand, many previous studies have used the linearized approximation where the Weyl transform of the $\hat{\rho}_0$

$$W_{00}(q, p) = \frac{1}{2\pi\hbar} \int dy \exp\left(\frac{ipy}{\hbar}\right) \phi_0^*\left(q + \frac{y}{2}\right) \phi_0\left(q - \frac{y}{2}\right)$$

is used. Here $\phi_0\left(q - \frac{y}{2}\right)$ is the ZPS. Then we obtain the linearized

$$I^{LWig}(\omega) = \frac{C}{2\pi} \int_{-\infty}^{\infty} dt \iint dq_0 dp_0 W_{0,0}(q_0, p_0) \mu(0; q_0, p_0) \mu(t; q_0, p_0) e^{i\omega t}$$

Lastly, for the classical approach, one will sample the phase space for fixed energy, E_0 , at the ZP energy

$$I^{CM}(\omega) = \frac{C}{2\pi} \int_{-\infty}^{\infty} dt \iint dq_0 dp_0 \delta(H(q_0, p_0) - E_0) \mu(0; q_0, p_0) \mu(t; q_0, p_0) e^{i\omega t}$$

For a 1D harmonic oscillator with a linear dipole moment function (DMF), the quantum and Wigner treatments give nearly the same spectra. On the other hand, the linearized-Wigner underestimates the fundamental transition's intensity by half. Detailed results on more complex systems will be given in the presentation.

NOTES

The shift between vertical excitation and band maximum in molecular photoabsorption

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The absorption spectra of molecules shows that the band maximum is usually redshifted from the vertical excitation. We conducted a throughout analysis of this shift based on low-dimensional analytical and numerical model systems, showing that its origin is rooted in the frequency change between the ground and the excited states. Then we obtained a benchmark of ab initio results for the shift based on a comparison of vertical excitations and band maxima calculated with the nuclear ensemble approach of 28 organic molecules in the Mülheim molecular dataset. The mean value of the shift calculated is 0.11 ± 0.08 eV, and the mean value of the band width is 0.32 ± 0.14 eV.

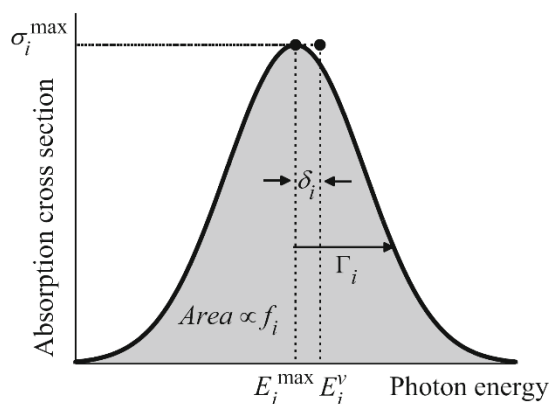


Fig. Schematic illustration of the shift between vertical excitation and absorption band maximum.

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NOTES

From State-of-the-art *Ab initio* Calculations to Spectroscopic and Thermophysical Properties

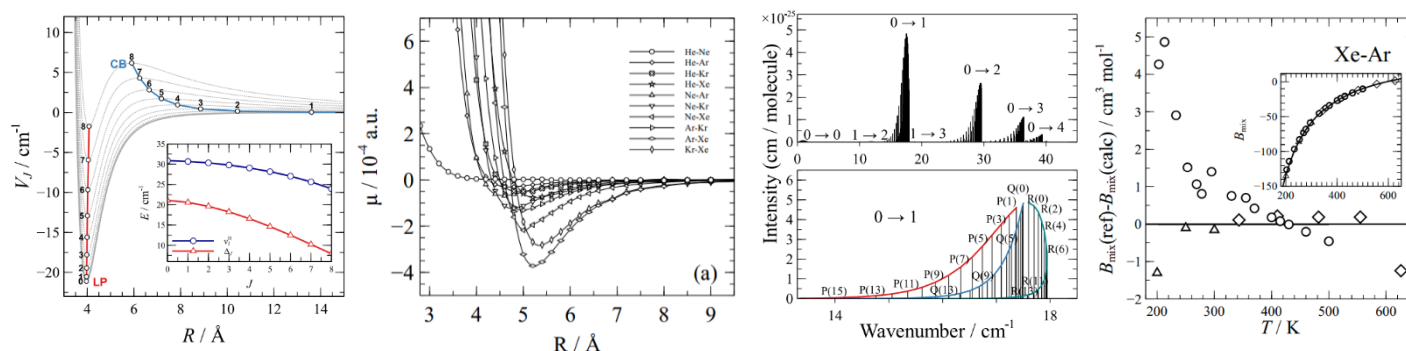
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State-of-the-art potential energy function (PEF) plays a crucial role in determining the spectroscopic and thermophysical properties of matter. In particular, some thermophysical properties of a heteronuclear dimer can only be measured with the same degree of accuracy as the two component pure gases in an experiment, so the values of mixture will be considerably less accurate (by as much as an order of magnitude) than either pure gas. Thus, the better source for these properties will be calculated from accurate *ab initio* PEFs. In this work, we presented the way to obtain spectroscopic and thermophysical properties from state-of-the-art *ab initio* calculations in detail. As examples, the majority interaction energy of Xe-He, Xe-Ne and Xe-Ar dimers are calculated using the CCSD(T) method, which is regarded as a “gold standard” because of its efficiency and accuracy. Contributions from inner nuclear electronic correlation, relativistic effects, and higher-order excitations beyond CCSD(T) are considered as corrections. All these pointwise potential energies are extrapolated to the complete basis set (CBS) limit. For all rare gas dimers, an analytical Morse/long-range (MLR) potential functions, is fitted to *ab initio* data using 13 or 14 parameters: the poorest-quality fit yielded a dimensionless-root-mean-square-deviation ($\overline{d\overline{d}}$) of 1.58. The absorption spectra and thermophysical properties of Xe-He, Xe-Ne and Xe-Ar have been computed and achieved good agreement with the experimental data.



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NOTES

***Ab initio* potential energy functions, spectroscopy and thermal physics for krypton-contained rare gas dimers**

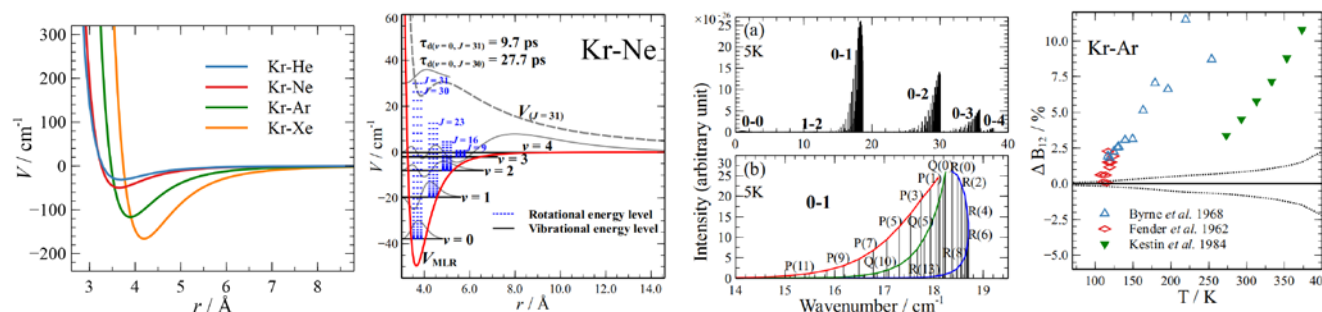
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Three state-of-the-art *ab initio* interatomic potential energy functions (PEFs) for the Kr-Ne, Kr-Ar, Kr-Xe rare gas dimers are presented. These PEFs are based upon extrapolation to complete basis set (CBS) limit results of supermolecular computations at the coupled-cluster level with single, double, and perturbative triple excitations (CCSD(T)) and correlation-consistent basis sets up to sextuple-zeta quality, augmented with mid-bond functions. Core-core and core-valence electron correlation, higher-order coupled-cluster excitations up to perturbative quadruple excitations, CCSDT(Q), and scalar relativistic corrections have also been taken into account. We have employed Morse/Long Range (MLR) potential energy functions (PEFs) to fit the total interaction energies as a function of the internuclear separation, followed by the calculation of spectroscopic parameters, vibrational and rotational energy levels, absorption spectra, and thermophysical properties over an extensive temperature range. Good agreement with experimental data and an empirical potential energy function shows that our *ab initio* MLR PEFs are superior not only to previous PEFs, but also to most empirical PEFs.



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NOTES

A neural network potential assisted first-principle exploration of the structure of mono-sacchrides

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In the last five years, there have been many attempts to investigate the structures of mono-sacchrides via infrared photon dissociation (IRPD) spectra. For example, Tan *et al.* demonstrated that different isomers of lithiated N-Acetyl-D-hexosamine can be differentiated via IRMPD spectra¹, Voss *et al.* investigated the structure of sodiated glucose via the analysis of the energetic preference of conformers calculated using density functional theory (DFT) and IRPD spectra², Rizzo *et al.* examined the structures of the protonated glucosamine system³. While it is well understood that first-principle calculations play a key role in these works to provide links between structural information and experimental spectra, direct exploration of the conformational space is not efficient. In this poster, we report a computational scheme that utilize neutral network potential (NNP) to efficiently search for local minima of sodiated pyranose⁴. For a given pyranose, we can identify nearly 1000 distinct conformers with a diverse structural features and energetic landscape. Furthermore, based on the structures of sodiated pyranose, structures of their lithiated and protonated counter parts can be sample efficiently. With these structural databases, we can check if simulated spectra of low-energy conformers are comparable with experimental IR spectra.

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NOTES

Application of neural network potential to assist understanding of Structure of protonated dipeptide of glycine, sarcosine and alanine

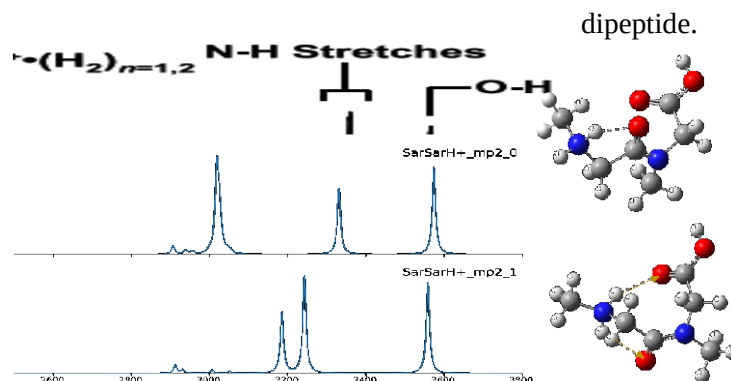
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Three-dimensional structure of small peptides can be probed with gas-phase spectroscopy and infrared photon dissociation (IRPD) spectra of protonated amino acid, di-peptides and tri-peptides were measured in the past 10 years¹⁻⁵. A thorough structural searching with high-level electronic structure methods is essential to extract structural information of peptides from vibrational spectra. Johnson's group studied the influence of methyl groups on the structure of protonated dipeptides of glycine and sarcosine and found conformers with cis form of amide bond¹⁻². In this poster, we report a theoretical study to search stable configurations of nine types of protonated dipeptides derived from glycine, sarcosine, and alanine. With assistance of neutral network potential (NNP), we can identify more than one thousand local minima of these series at the MP2/6-311+G* level. With respect to comparing previous research¹⁻², we believe that our structure database includes several new stable structures in the low energy range (0-40 kJ/mol). The majority of lowest minima are in trans conformation while the cis formers are found to be more stable to two di-peptides. Moreover, the substituting methyl group also affects the torsion angles of these dipeptide.



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NOTES

Role of efficient structure search in assigning peaks in vibrational spectra**Shweta Jindal, Po-Jen Hsu, Jer-Lai Kuo***Postdoctoral researcher, IAMS, Academia Sinica, Taipei, Taiwan; jindal.2292@gmail.com*

Abstract – Exploring the potential energy surface (PES) for minima structures is a resource intensive task due to the increasing cost of the *ab initio* methods and number of distinct conformers as the size increases. Fitting the force fields (FF) using machine learning (ML) to *ab initio* data has gained momentum due to its high accuracy and faster computations. ML-FF is implemented to perform structural searches. Different techniques such as random search with “adding a molecule”, “replacement” of a functional group and “molecular dynamics” simulations are implemented to explore the PES. The replacement technique can help to generate inter-convertible chemically similar databases. Amines and ammonia share a similar chemistry and is a good system to apply our ML-FF to perform a structure search and correlate with the experimentally obtained vibrational spectra.

(Include figures and references in this section)

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NOTES

Anharmonic vibrational analysis on the near-infrared region of $\text{H}_3\text{O}^+-\text{X}_n$ ($\text{X} = \text{Ar}, \text{N}_2$, and CO , $n = 1-3$)

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Abstract – The near-infrared (NIR) vibrational overtone spectroscopy usually contains fruitful information of anharmonicity, including the coupling between different vibrational modes and the vibrational dynamics of high vibration energy levels. With the development of our *ab initio* anharmonic analyses, we have investigated the anharmonic spectral features in the mid-IR region of many different molecule systems in gas-phase; however, there are fewer experimental evidence in the NIR region of these molecules. In the present study, we applied DVR-based anharmonic analysis on the NIR vibrational spectra of $\text{H}_3\text{O}^+-\text{X}_n$ ($\text{X} = \text{Ar}, \text{N}_2$, and CO , $n = 1-3$), in which we use different X to tune the effect of hydrogen bond strength ($\text{H}\dots\text{X}$). We find that the IR intensities in the overtone region are majorly contributed by the combination band of bending and stretching $|b^1, s^1\rangle$ and the stretching overtone $|s^2\rangle$, and we also find the Fermi resonance pattern in these regions, which is very similar to their mid-IR counterparts.

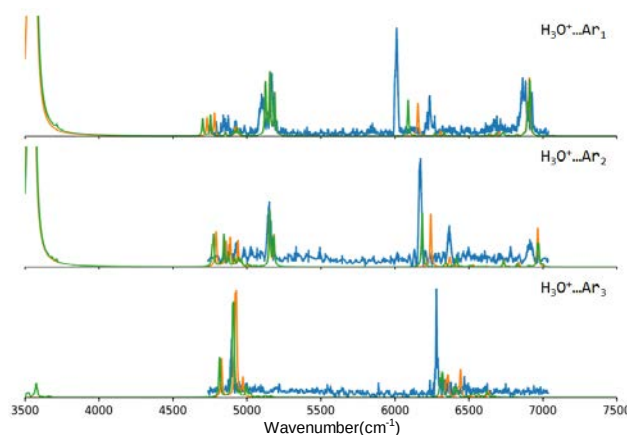


Fig. 1 IRPD spectra (blue) and calculated (DVR-FBR) spectra (orange/green) of $\text{H}_3\text{O}^+-\text{Ar}_n$ ($n = 1-3$). The orange line are calculated at the level of MP2/aug-cc-pVDZ, and the green line are calculated at the level of CCSD/aug-cc-pVTZ.

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NOTES

From Dark to Bright: Fermi resonance in astrochemically relevant cyano-containing complexes

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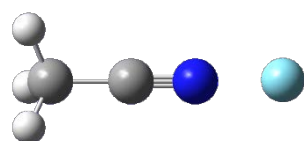
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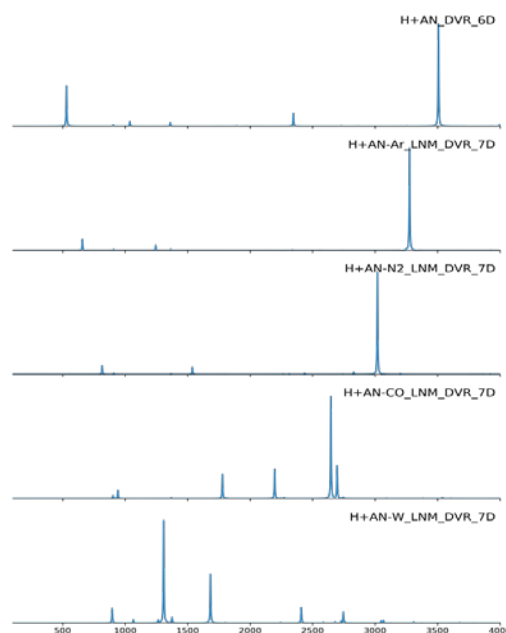


Cyano-containing (–CN) molecules are of increasing interest in the astrochemical environments as many of such molecules bearing this functional group have been detected to be abundant in interstellar and circumstellar media. In this work we explore via *ab initio* anharmonic algorithms the Fermi resonance interaction between relevant modes of vibrations in protonated complexes of acetonitrile with different tagging molecules. The brightened dark states are analyzed in terms of the coupling strengths and energy matching conditions derived from anharmonic vibrational calculations. We aim to provide an insight on the mode couplings of the NH stretching fundamental with its bending overtone and with the CN stretching fundamental.



	Wavenumber (cm ⁻¹)				Ratio
	NH bending overtone	NH stretching fundamental	energy difference	coupling strength	$\frac{\text{coupling strength}}{\text{energy diff}}$
ANH ⁺ Ar	1843	3227	1384	288	0.21
ANH ⁺ N ₂	2025	2968	943	232	0.25
ANH ⁺ CO	2100	2639	539	140	0.26
ANH ⁺ H ₂ O	2634	1455	1179	77	0.07

	Wavenumber (cm ⁻¹)				Ratio
	CN stretching fundamental	NH stretching fundamental	energy difference	coupling strength	$\frac{\text{coupling strength}}{\text{energy diff}}$
ANH ⁺ Ar	2343	3227	884	31	0.04
ANH ⁺ N ₂	2311	2968	657	54	0.08
ANH ⁺ CO	2176	2639	463	92	0.20
ANH ⁺ H ₂ O	2440	1455	985	77	0.08



NOTES

A Study on the Fermi-Resonance in protonated amino acids and peptides modulated by intramolecular hydrogen-bond strength

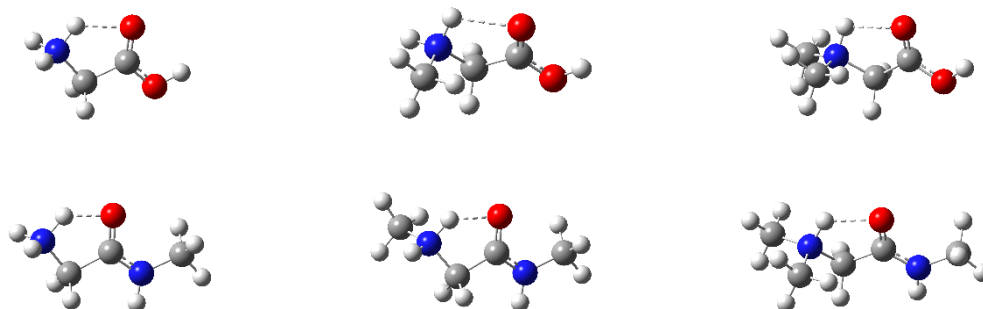
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Gas-phase vibrational spectra of amino acids and small peptides fosters better understanding of their structures. In the past decades, infrared photon dissociation (IRPD) spectra of protonated di-peptides and tri-peptides were measured¹⁻⁴. However, the spectral patterns are not trivial to analyze due to the complexity of the inter-mode coupling of the vibrational motions and the presence of multiple conformers. In 2011, Mark A. Johnson's group reported IRPD spectra of four protonated dipeptides derived from glycine (Gly) and sarcosine (Sar) to explore the structural changes by the replacement of methyl group to hydrogen atom at the N-terminus and at the amide bond^{1,2}. From the experimental spectra, the vibrational signatures of amide group were identified, however, the mysteriously missing peaks of strong intra-molecular hydrogen bonds at around 2800 cm⁻¹ cannot be explained by the harmonic spectra even with multi-conformers. We have found that the mechanism behind those missing peaks is due to Fermi resonance between intra-molecular hydrogen-bond stretching fundamental with overtone of bending-like motions of the methylamine group at N-terminus, resulting in multiple weaker intensity peaks from 2200-2600 cm⁻¹ instead of a strong intense peak at 2800 cm⁻¹. To further understand this phenomenon, we performed a systematic anharmonic study on model systems. The results show that by changing the intramolecular hydrogen-bond strength, we can tune the Fermi resonance window. When the intramolecular hydrogen-bond bond becomes weaker, we can observe a strong intensity peak at its stretching region. The results can be applied to understand vibrational signatures of di- and tri-peptides¹⁻⁴.



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4. S. L. Sherman, et al., J. Phys. Chem. A. (2022) 126:4036-4045

NOTES

Infrared spectra of mono-deuterated pyridines

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Pyridine and deuterated pyridine are widely used as important precursors in many organic as well as biological reactions. Fully deuterated pyridine is also used as an organic solvent in NMR studies. In addition, pyridine and its derivatives are abundantly found in the atmosphere as pyridine is a major byproduct of coal combustion. In the Infrared (IR) spectra of the heterocyclic aromatic compounds between 3000 and 3200 cm^{-1} comprises the CH fundamental bands along with several satellite peaks arising due to extensive Fermi resonance (FR). Theoretical analysis indicates that FR in pyridine occurring between CH stretching fundamentals and bending overtones/combinations of in-plane modes between 1600 to 1300 cm^{-1} [1,2]. In this work, we studied FR in the vibrational spectra of both CH and CD stretching region in mono-deuterated pyridine using quartic potential (QP) and various theoretical methods to solve vibrational Schrodinger equations. We compare numerical solutions from direct diagonalization of the CI matrices[3] with an approximate scheme proposed by Yagi and co-workers.[4] We have given a detailed analysis of the mode couplings and Fermi resonances in both C-H and C-D ($\sim 2200 \text{ cm}^{-1}$). Our analysis reveals that FR originates from coupling between stretching fundamentals and two quanta states of the in-plane bending modes. The roles of three and four quanta combination bands with low-frequency vibrational modes in the FR will also be analyzed.

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NOTES

Infrared spectroscopy and theoretical structure analyses of protonated 2,2,2-trifluoroethanol clusters

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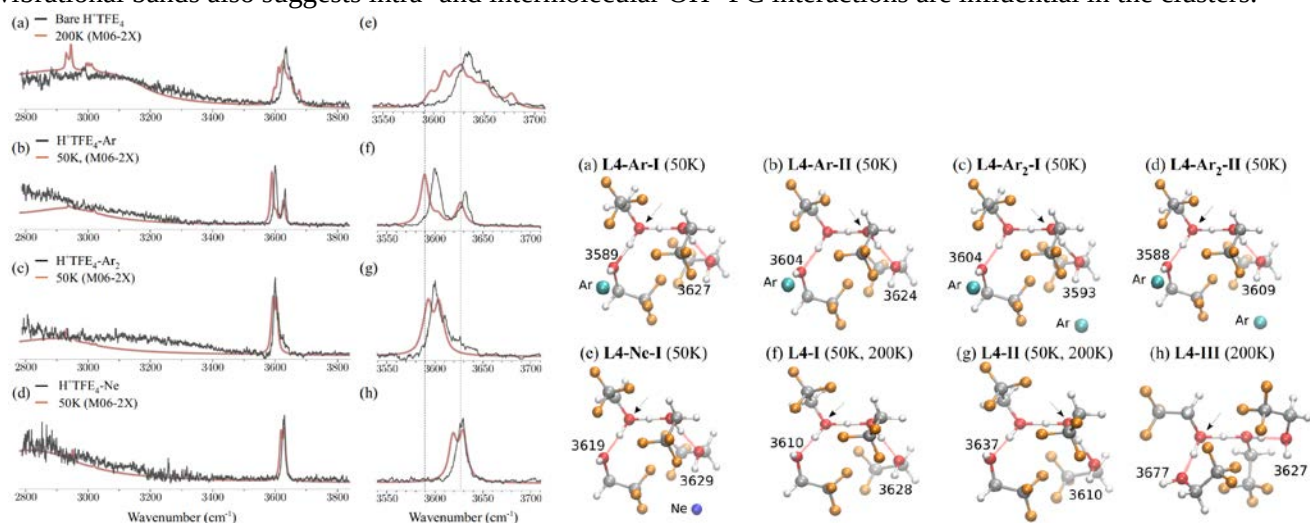
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The development of the hydrogen-bonded (H-bond) structures in the protonated alcohol clusters has been investigated [1-3]. The transition from a linear type to a cyclic type of H-bond network was found in the cluster sizes of 4 and 5 methanol molecules [1]. However, the infrared spectroscopy of the protonated 2,2,2-trifluoroethanol clusters, $H^+(TFE)_n$, $n = 4$ and 5, in the OH/CH stretch region indicates that the linear type structures are the preferential H-bond network irrespective of the temperature of the clusters [4]. To explore the impact of fluorination on the H-bond networks of protonated alcohols, we performed the isomer search for $H^+(TFE)_4$ and $H^+(TFE)_5$ clusters. Our structure search results suggest that the linear type H-bond networks dominate this range of cluster sizes. We obtained a good agreement between the simulated and the experimental infrared spectra with the structure data and the vibrational mode analysis. The analysis of the free OH stretching vibrational bands also suggests intra- and intermolecular $OH\cdots FC$ interactions are influential in the clusters.



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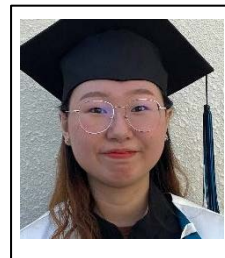
IR spectroscopy of the C–H stretching region of mono-substituted benzenes cooled in a supersonic jet and the anharmonic analysis

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Abstract – We investigated the Fermi-resonance (F-R) of the C–H stretching vibration of mono-substituted benzenes (fluorobenzene, chlorobenzene and bromobenzene) by measuring the IR spectra with IR-vacuum UV (VUV) spectroscopy under jet-cooled gas-phase conditions. The observed spectra were analyzed by 2nd-order vibrational perturbation theory (VPT2) with quadratic potential (QP) at the B3LYP/6-311++G(d,p) level, followed by the vibrational configuration interaction (VCI) method with the same QP. Figure 1 shows the comparison of the observed IR spectra (black) with those obtained by VPT2 (red). The calculated spectra show reasonable agreement with the observed spectra except the appearance of ν_{13} at ~ 3000 cm⁻¹. Figure 2 shows the comparison of the observed spectra with those obtained by the VCI method. In the symposium, we will discuss which overtone or combination band involving the C–H bending vibration is coupled with the C–H stretching fundamentals, and how the coupling varies for different substituents.

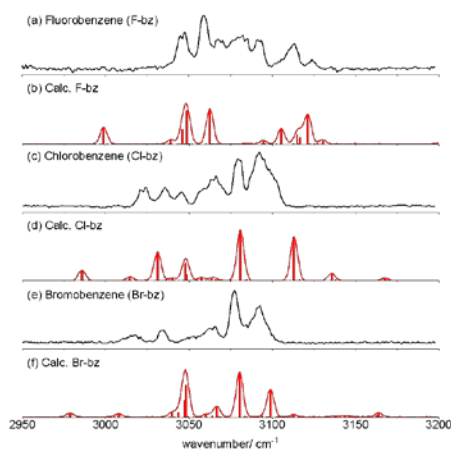


Fig. 1 IR-VUV spectra (black) and calculated (VPT2) spectra (red) of fluorobenzene (a-b), chlorobenzene (c-d), and bromobenzene (e-f).

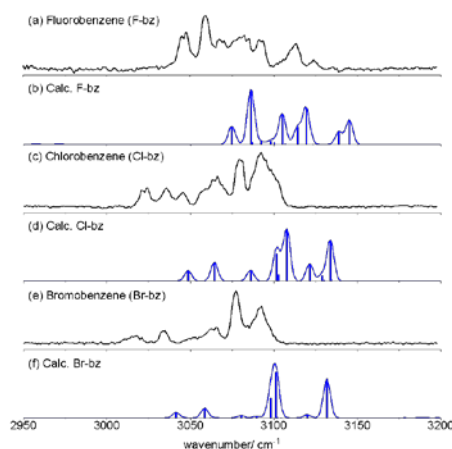


Fig. 2 IR-VUV spectra (black) and calculated (VCI) spectra (blue) of fluorobenzene (a-b), chlorobenzene (c-d), and bromobenzene (e-f).

NOTES

Infrared spectra and structures of supersonically cooled (pyrazine)₂ and (pyrazine)_m-(H₂O)_n clusters studied with IR-VUV spectroscopy

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keywords: Gas-phase spectroscopy



Abstract – In our previous studies, we reported the structures and reactions of pyridine clusters, such as (pyridine)_m-(NH₃)_n, (pyridine)_m-(H₂O)_n, (pyridine)₂, and (pyridine)_n⁺, by measuring their infrared spectra and analyzing them with the help of quantum-chemical calculations.^{1,2,3} In the present work, we studied the structures of pyrazine clusters; (pyrazine)₂ and (pyrazine)_m-(H₂O)_n. We measured the IR spectra of the jet-cooled species in the C–H and O–H stretching regions by the IR–VUV–time-of-flight technique. Figure 1 shows the possible structures of (pyrazine)₂ and (pyrazine)₁(H₂O)_{n=1–3} calculated at the ωb97XD/aug-cc-pVDZ level of theory. We determined the structures of the clusters by comparing the observed IR spectra with those predicted by the anharmonic calculations at the b3lyp/6-311++G(2d,2p) level of theory (Figure 2). The C–H stretching vibrational bands of (pyrazine)₂ are significantly different from that of the monomer. The observed IR spectrum of (pyrazine)₂ (Figure 2(a)) is reproduced by the sum of the π-stacked and planar isomers (Figure 2(e)). We also discuss the structures of (pyrazine)_m-(H₂O)_n.

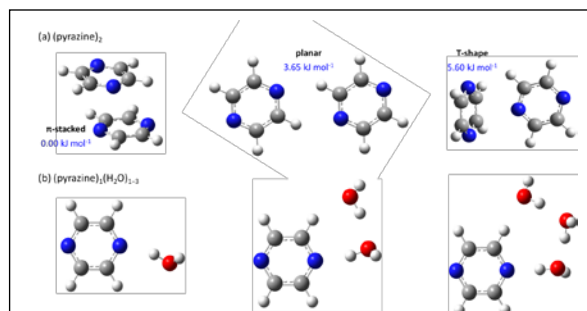


Figure 1 (a) Three most stable structures of (Pyrazine)₂. (b) Most stable structures of (Pyrazine)(H₂O)_{n=1–3}.

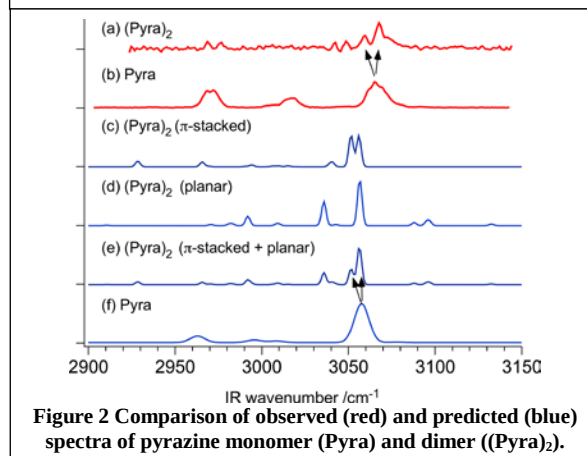


Figure 2 Comparison of observed (red) and predicted (blue) spectra of pyrazine monomer (Pyra) and dimer ((Pyra)₂).

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NOTES

Gas-phase spectroscopic identification of the chlorovinyl radical

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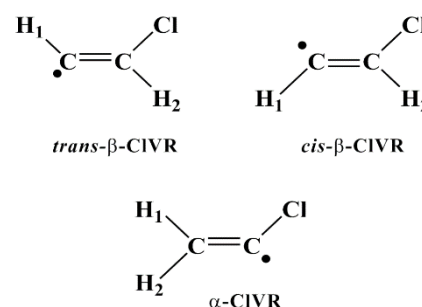


ABSTRACT

The reaction $\text{Cl} + \text{C}_2\text{H}_2$ has been widely investigated experimentally¹ and theoretically.² The addition of the Cl atom to C_2H_2 to form the β -chlorovinyl radical (β -CIVR, $\text{ClH}=\dot{\text{C}}\text{H}$) is one of the initial processes. The β -CIVR has two isomers: *trans*- β -CIVR and *cis*- β -CIVR. There is another chlorovinyl radical isomer, α -CIVR ($\text{H}_2\text{C}=\dot{\text{C}}\text{Cl}$), which is $\sim 15 \text{ kJ mol}^{-1}$ more stable than the other species. Fourier-transform microwave spectra for two isomers, *trans*- β -CIVR and α -CIVR, have been observed in the 4–52 GHz frequency region. The electric discharges of diluted dichloro derivatives of ethylene are used to generate the radicals ($^2\text{A}'$). In the present study, fine and hyperfine components observed for each rotational transitions are fully assigned for two isotopologues (^{35}Cl and ^{37}Cl). Molecular constants, including the electron spin-rotation constants, the Fermi contact constants, the dipole-dipole constants, the nuclear quadrupole coupling constants and the nuclear spin-rotation constants for the two protons and the chlorine nucleus, have been determined precisely. The *cis*- β -CIVR isomer could not be observed in the predicted region although it is speculated to be only $\sim 5 \text{ kJ mol}^{-1}$ less stable than the *trans* isomer.

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NOTES

Kinetics of Criegee Intermediate Reactions with Nitric Acid Measured by UV Absorption Spectroscopy

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Abstract

Criegee intermediates (CIs) can react with atmospheric molecules such as SO₂, water, and organic/inorganic acids and are therefore very reactive species. In this work, we study the reaction kinetics of CIs with HNO₃. In 2016, Forman *et al.* studied the reaction of CH₂OO + HNO₃.¹ The rate coefficient of this reaction is on the order of 10⁻¹⁰ cm³ s⁻¹, which indicates a very fast reaction. However, the reported rate coefficient might have a large uncertainty owing to their experimental method to determine the concentration of HNO₃. Thus, a relatively reliable UV absorption spectroscopy is applied in this work to better determine the concentration of HNO₃. We study the kinetics of HNO₃ reactions with four CIs, which are CH₂OO, (CH₃)₂COO, methyl vinyl ketone oxide (MVKO) and methacrolein oxide (MACRO). The rate coefficients are determined to be $(1.51 \pm 0.45) \times 10^{-10}$, $(3.54 \pm 1.06) \times 10^{-10}$, $(3.93 \pm 1.18) \times 10^{-10}$, and $(3.0 \pm 1.3) \times 10^{-10}$ cm³ s⁻¹ for HNO₃ reactions with CH₂OO, (CH₃)₂COO, MVKO, and MACRO, respectively.

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Kinetics Isotope Effect of the Simplest Criegee Intermediate Reaction with Water Vapor Measured with UV Absorption Spectroscopy

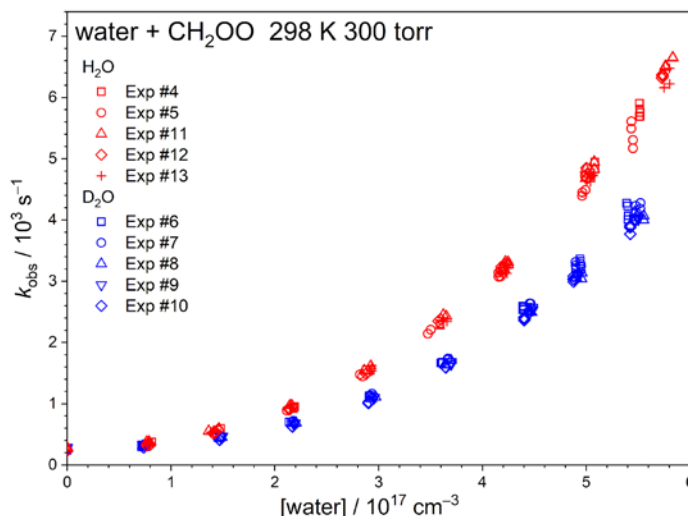
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2. Department of Chemistry, National Taiwan University, Taipei, Taiwan.



Abstract

This work investigates the kinetics of the simplest Criegee intermediate (CH_2OO) reaction with water (H_2O or D_2O) at pressure 300 torr and 600 torr and temperature 298 K. Our result shows that the kinetic isotope effect (KIE, $k_{\text{H}}/k_{\text{D}}$) is around 1.48, which is rather small, considering the large mass ratio between H and D atoms. This indicates that the H tunnel effect is weak. The result is consistent with the literature¹, and the KIE value of this experiment mainly attributes to the kinetic isotope effect that comes from the higher zero point corrected barrier energy caused by deuteration. A weak pressure effect, with a ratio of $k_{600\text{torr}}/k_{300\text{torr}}$ around 1.15, was also found in the reaction of CH_2OO and water. In addition to the normal $\text{CH}_2\text{OO} + 2\text{H}_2\text{O}$ pathway, there is some contribution of $\text{CH}_2\text{OO} + 3\text{H}_2\text{O}$ pathway in our experiment data due to the improvement of the precision of water concentration.



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NOTES

Absolute cross sections of thermalized methyl vinyl ketone oxide (MVKO) and methacrolein oxide (MACRO) have been measured

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Methyl vinyl ketone oxide (MVKO) and methacrolein oxide (MACRO) are Criegee intermediates generated from ozonolysis of isoprene, the most abundant nonmethane volatile organic compound in the atmosphere. Criegee intermediates are strong oxidants which can make an impact on atmospheric chemistry. We measured the absolute UV cross sections of MVKO and MACRO. The absolute absorption cross section represents the interaction between a molecule and a photon. It is a crucial parameter for photochemistry. By measuring the depletion fraction of a 352 nm laser photolysis, the absolute cross sections are determined to be $(3.70 \pm 0.74) \times 10^{-17} \text{ cm}^2$ at peak 371 nm for MVKO and $(3.04 \pm 0.58) \times 10^{-17} \text{ cm}^2$ at peak 397 nm for MACRO. With the measured absolute cross sections, the synthesis yields of MVKO and MACRO can be estimated, which are (0.22 ± 0.10) for MVKO (at 299 K, 30 to 700 Torr), and (0.043 ± 0.019) for MACRO (at 299 K, 500 Torr).

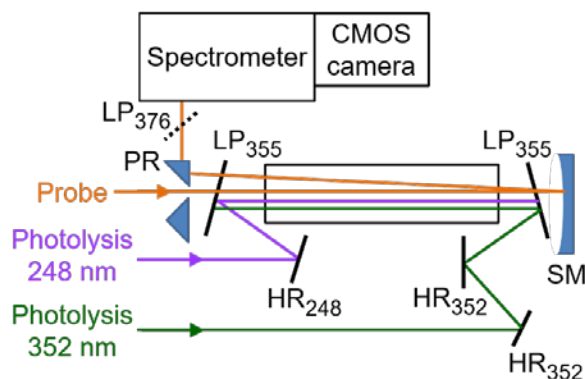


Fig. 1 Experimental Setup. A 248 nm laser was used to photolyze the precursors of Criegee intermediates and the generated Criegee intermediates were photodepleted with a 352 nm laser. Criegee intermediates were measured with a broadband probe light and a spectrometer coupled with a fast CMOS camera.

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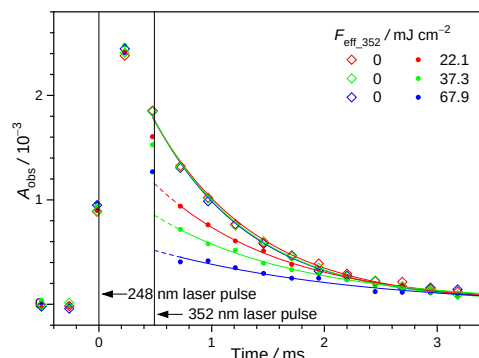


Fig. 2 Time profiles of MACRO under various effective 352 nm laser fluences.

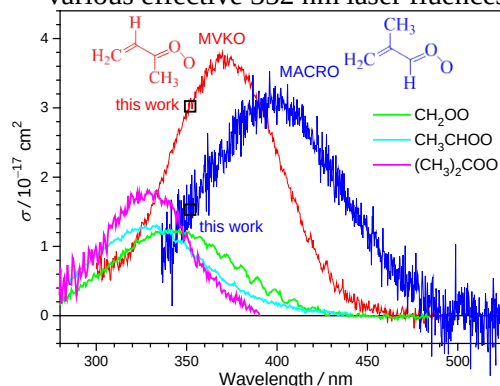


Fig. 3 The absolute cross sections of MVKO and MACRO compared with those of small Criegee intermediates.

NOTES

Infrared Characterization of the Intermediates and Products of the Reaction between methyl-substituted Criegee Intermediate CH_3CHOO and HC(O)OH

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Organic acids play an important role in the acidity of the troposphere. The reactions of Criegee intermediates with organic acids have large rate coefficients¹ and might play a significant role in controlling their concentrations in the atmosphere. These reactions can provide pathways in which alkenes are converted to low-volatility compounds and thus contribute to the formation of secondary organic aerosols (SOA). We investigated the detailed mechanism and kinetics of the reaction of methyl-substituted Criegee intermediate (CH_3CHOO) with HC(O)OH . Theoretical calculations were performed to elucidate the $\text{CH}_3\text{CHOO} + \text{HC(O)OH}$ reaction pathway. We recorded time-resolved absorption infrared spectra of transient species produced upon irradiation at 308 nm of a flowing mixture of $\text{CH}_3\text{CHI}_2/\text{O}_2/\text{HC(O)OH}$ at 298 K. Bands of CH_3CHOO were observed initially upon irradiation; their decrease was accompanied by the appearance of several bands near 847, 890, 934, 1063, 1163, 1190, 1340, 1392, 1427, and 1755 cm^{-1} , assigned to the absorption of hydroperoxyethyl formate [$\text{CH}_3\text{CH}(\text{OOH})\text{OC(O)H}$], HPEF, the adduct of CH_3CHOO and HC(O)OH . Two conformers of HPEF, an open form and an intramolecular hydrogen-bonded form, are identified. We photolyzed a gaseous mixture of $\text{CH}_3\text{CHI}_2/\text{O}_2/\text{HC(O)OH}$ in a static cell and recorded the infrared absorption spectrum in a continuous-scan mode. We observe several new bands at 933, 1045, 1200, 1381, 1790, and 1810 cm^{-1} apart from the bands of CH_3CHI_2 , HC(O)OH , and CH_3CHO . The new bands are assigned to the formic acetic anhydride [$\text{CH}_3\text{C(O)OC(O)H}$, FAA], a dehydrated product of HPEF. Observed infrared spectra of both conformers of HPEF and FAA agree satisfactorily with the scaled harmonic and anharmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVTZ method.

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Reaction dynamics of $(\text{CH}_3)_2\text{CI} + \text{O}_2$ studied with step-scan time-resolved Fourier-transform infrared emission spectroscopy

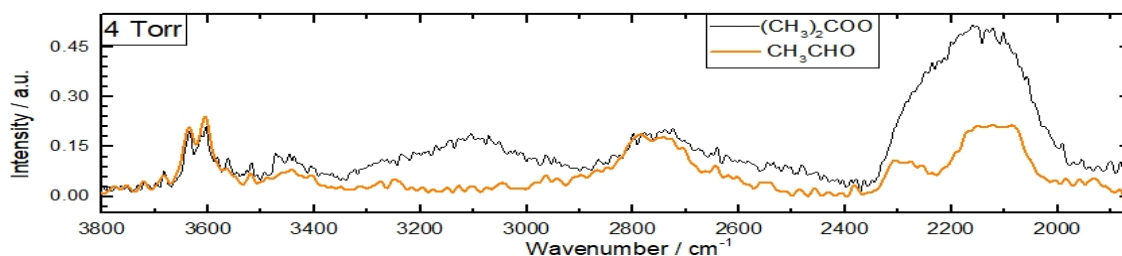
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ABSTRACT

Previous studies on the reaction dynamics of photolysis of diiodomethane[1] and diiodoethane[2] with oxygen have verified the pathways for the production of OH, CO and CO_2 . Since the reaction dynamics of more complicated Criegee intermediates remain unclear, this study will replace CH_2I with $(\text{CH}_3)_2\text{CI}$ and explore the reaction dynamics of $(\text{CH}_3)_2\text{CI} + \text{O}_2$. Infrared emission of the products of this reaction was recorded with a step-scan time-resolved FTIR spectrometer upon irradiation of a flowing mixture of $(\text{CH}_3)_2\text{CI}$ and O_2 (~ 4 Torr) at 248 nm. Possible reaction paths were identified according to predicted potential energy surfaces[3]. At total pressure 4 Torr and irradiation wavelength 248 nm, rotationally resolved lines of CO ($v \leq 3$, $J \leq 25$) in region $1860 - 2300 \text{ cm}^{-1}$ were observed; with CO having averaged vibrational energy of 15 kJ mol^{-1} . In addition, IR emission of H_2CO was observed in region $2600 - 3000 \text{ cm}^{-1}$ and a doublet band was observed in region $2950 - 3650 \text{ cm}^{-1}$, which also appeared in the reaction $\text{CH}_3\text{CHI} + \text{O}_2$. Compared with those of $\text{CH}_2\text{I} + \text{O}_2$, the internal energy of CO is much smaller, consistent with the expectation when two additional methyl moieties are present. Because dimethyldioxirane does not show any pathway to form carboxylic acid, the formation path of CO and CO_2 still need to be confirmed. Our results provide further understanding on the detail dynamics in the reaction of $(\text{CH}_3)_2\text{CI}$ and O_2 .



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NOTES

A Laboratory-Demonstrated Model that Explains the Galactic Extended Red Emission: Graphene Exposed to Far-ultraviolet Light

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Extended red emission (ERE) is a broad feature in spectral region 500–900 nm commonly observed in a wide range of circumstellar and interstellar environments. Although the observational constraints for ERE are well established, definitive identifications of the carriers and associated processes complying these constraints remain unanswered. We report a plausible two-step model involving far-ultraviolet (UV)-irradiated single-layer graphene (SLG), considered as large polycyclic aromatic hydrocarbons, to meet these constraints and supported by laboratory experiments. The far-UV-treated SLG, producing structural defects and graphene quantum dots, showed photoluminescence excitation spectrum extending from far-UV to UV–visible region, hence meeting the requirements of far-UV light and high photon-conversion efficiency. Furthermore, a photoluminescence band shifted from ~585 nm to ~750 nm for high-dose-exposed SLG agrees with the observed red shift of the ERE band in regions under a greater far-UV radiation density.

NOTES

The 3D printed Photoacoustic Spectroscopy with T shaped cell for detection of ozone with a 265-nm LED

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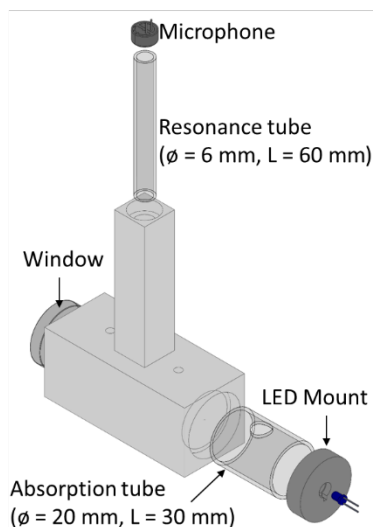
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Abstract

Ozone at ground level is an important air pollutant. It will affect human health when the ozone concentration exceeds 125 ppbv. However, when traffic is very heavy during the rush hour, the ozone concentration is more than the annual average. We would like to perform real-time monitoring of ozone concentration by using the photoacoustic spectroscopy (PAS). We use the 3D printing technique to make the T-shaped cavity of the photoacoustic cell (PAC). The T-shaped cavity consists of two different channels, including a horizontal absorption channel and a vertical resonance channel. The optical power of 265-nm LED is modulated at the reference frequency of 1277 Hz. The modulated light passes the absorption cell of the PAC. The induced acoustic wave will resonate in the resonance channel and it is detected with a microphone. In addition, a resonance circuit is used to improve the signal-to-noise ratio of the acoustic signals. The amplifier signal is demodulated by a lock-in amplifier and recorded by the oscilloscope. In this work, a detection limit of 386 ppbv for ozone detection at 1 atm is achieved. The normalized noise equivalent absorption (NNEA) coefficient of $4.13 \times 10^{-8} \text{ W} \cdot \text{cm}^{-1} \cdot \text{Hz}^{-1/2}$ is obtained.



NOTES

A BaGa₄Se₇ crystal based mid-infrared pulsed light source for high resolution spectroscopy in 3.5 -12 μ m

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Abstract –A BaGa₄Se₇ crystal based mid-infrared pulsed light source for high resolution spectroscopy in 3.5 -12 μ m was demonstrated. For this, we have recently developed a narrow band pulsed near-infrared system with pulse energy more than 10mJ in range of 810-1530nm. The system consists of optical parametric generation (OPG) and optical parametric amplification (OPA) sub-system and injection seeded by a single frequency cw-ECDL and pumped by second harmonic generation of a seeded Nd:YAG laser. For mid-infrared generation, near-infrared idler output of the OPG-OPA system in combination with the fundamental output of a seeded Nd:YAG laser was directed into the BaGa₄Se₇ crystal to proceed efficient difference frequency generation (DFG). Mid-infrared radiation with pulse energies more than 100 μ J and a typical pulse duration of ~5ns was achieved in the 3.5-12 μ m range. We applied this mid-infrared light system on cavity ring down spectroscopy of H₂O absorption lines in the 8 μ m region. A resulting linewidth of 160MHz was obtained in the experimental spectrum. Based on this, the linewidth of the developed mid-infrared system was inferred as 110MHz which is very close to the Fourier-transform limited linewidth of 5ns laser pulses.

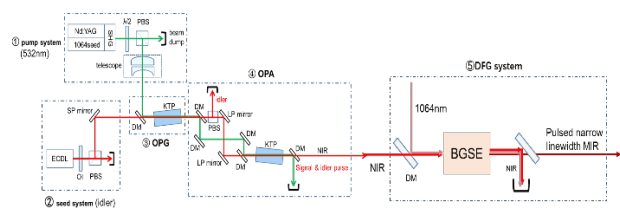


Fig.1. MIR light source setup diagram

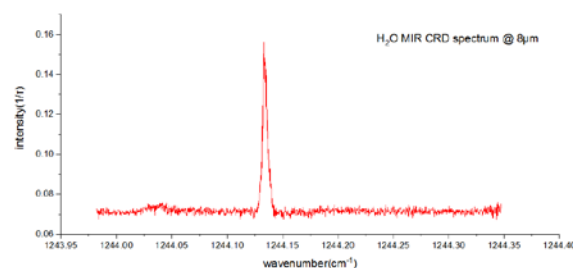


Fig.2. H₂O absorption line at 1244.14cm⁻¹.

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NOTES

A 1083 nm Pulsed Laser Source for Helium Resonance Fluorescence Lidar

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The research of the thermal structure and dynamics of the upper atmosphere is important in practical study of the low earth orbit environment for satellites and the improvement of communication and navigation accuracy. Metastable helium resonance fluorescence (1083.0nm) lidar has proven to be an effective technique for obtaining metastable helium densities in 200-1000 km atmosphere. However, the high energy pulsed laser required for this lidar system is a technical challenge. Here, a 1083 nm pulsed laser source for metastable helium lidar has been developed. The design consists of an optical parametric generation stage with single-frequency seed light injection, followed by high power optical parametric amplification to obtain a high pulse energy output (>100mJ) that meets helium lidar detection requirements. The laser source setup provides a basis for research related to metastable state helium density measurements. (Include figures and references in this section).

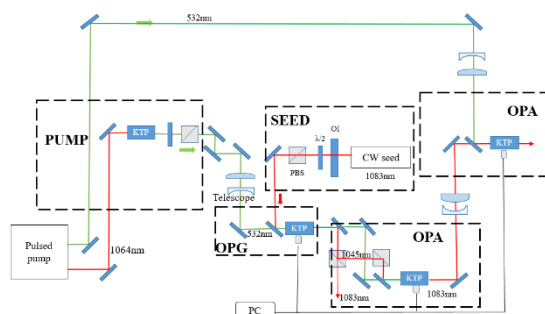


Figure 1: Schematic diagram of the laser system

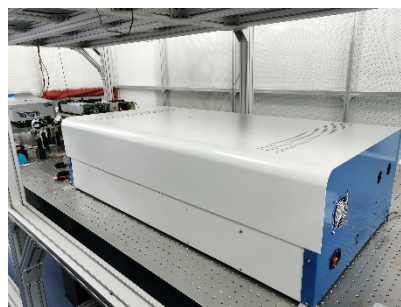


Figure 2: Picture of pulsed 1083nm laser

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NOTES

Controlling Double Proton Transfer: The Formic Acid Dimer-Fluorinated Benzenes Complexes Studied by Broadband Microwave Spectroscopy

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The rotational spectra of the complexes of formic acid dimer (FAD)-fluorinated benzenes were measured by the chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy at Fudan University. The spectra of the complexes have been assigned to the form of π - π stacked structures. For the complex with 1,2,3,5-tetrafluorobenzene, the spectra exhibit splitting which is caused by the symmetric rearrangement of the structure through double proton transfer. But for other complexes, the spectra were assigned to two rigid conformers which could switch to each other via double proton transfer. Compared with the FAD^{1,2}, the double proton transfer rate in the FAD is decreased by complexing with fluorinated benzenes in a controllable manner.

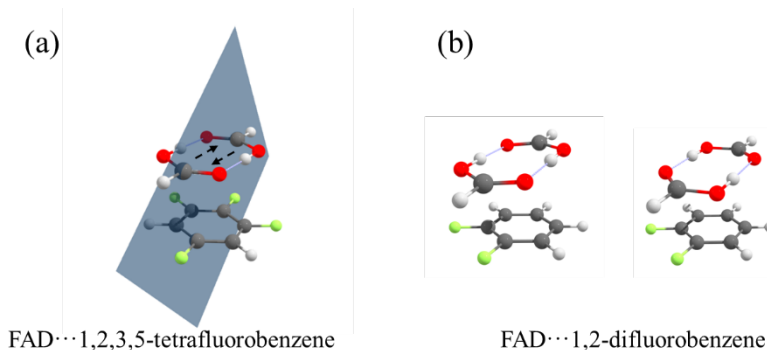


Figure 1. The observed configurations of the FAD...fluorinated benzenes clusters.

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NOTES

Non-covalent Interactions between Aromatic Heterocyclic and Carboxylic Acid: Rotational Spectroscopic studies

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The binary molecular complexes formed between the aromatic heterocycles of furan, thiophene, and thiazole with formic acid were investigated using pulsed-jet Fourier transform microwave spectroscopy complemented with quantum chemical calculations. For the furan-formic acid complex, the observed isomer has a planar configuration characterized by a relatively strong O-H $\cdots$ O and an additional C-H $\cdots$ O hydrogen bonds (Figure 1). Nevertheless, the preferred conformation of the thiophene-formic acid complex was stabilized by a O-H $\cdots$ π and weak C-H $\cdots$ O and C=O $\cdots$ π interactions. Planar configuration stabilized by O-H $\cdots$ N and C-H $\cdots$ O hydrogen bonds features the observed structure of the thiazole-formic acid complex. Information on the NCI, NBO, and SAPT analyses was provided to reveal the nature of the nonbonding interactions between aromatic heterocycles and formic acid.

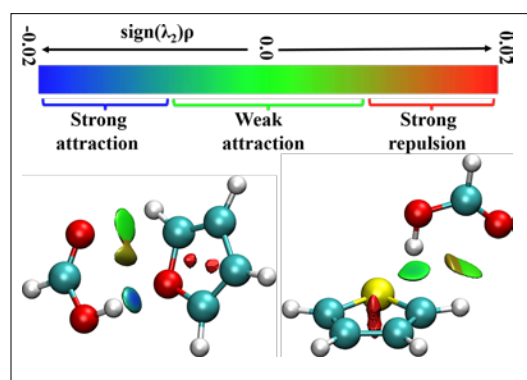


Figure 1 : The NCIs plots of the furan-formic acid and thiophene-formic acid complexes.

Acknowledgments: This work has the support of Chongqing University.

NOTES

Noncovalent interactions between amides and aldehyde: Rotational Spectroscopy of the Formamide-H₂CO and 2-azetidinone-H₂CO Complexes

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The binary intermolecular complexes of amides and formaldehyde can be taken as suitable models to investigate the non-covalent interactions of the peptide with carbonyl group. We investigated the 2-azetidinone-H₂CO and formamide-H₂CO complexes prepared in helium supersonic expansion by using high-resolution microwave spectroscopy and theoretical calculations. The rotational transitions belonging to the most stable isomer of the two complexes were observed and assigned respectively. For each complex, a dominate amide hydrogen bond N—H···O=C and a weaker C—H···O interaction are verified as the main stabilizing forces for both complexes (Figure 1). These two intermolecular linkages maintain a C_s symmetry of the complexes. NBO and SAPT analyses provide quantitative estimation of the non-covalent interactions stabilizing the complexes.

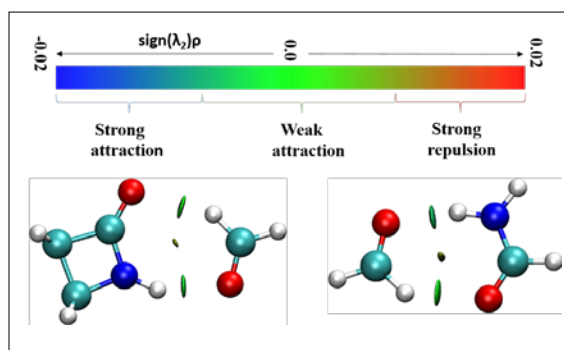


Figure 1 : The NCI plots of the 2-azetidinone- H₂CO (left) and formamide- H₂CO(right) complexes.

Acknowledgments: This work has the support of Chongqing University.

NOTES

Change of Binding sites from monohydrate to dihydrate: Rotational studies of 2-ethacrolein-(H₂O)₂**Siyu Zou, Juncheng Lei, Tianyue Gao, Qian Gou***

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The ethacrolein-(H₂O)₂ hydrates have been investigated by Fourier transform microwave spectroscopy^[1] complemented with quantum chemical calculations. Two isomers of monohydrate were observed in pulsed jet, in which water serves as a proton donor and acceptor forming an O-H...O=C hydrogen bond and a secondary C-H...O-H weak hydrogen bond. Two isomers of the dihydrate were also observed in pulsed jets, which are dominated by the classical O-H...O, O-H...O=C and secondary C-H...O hydrogen bonds. However, the binding sites have been changed from monohydrate to dihydrate. The independent gradient model based on Hirshfeld partition^[2] and Bader's quantum theory of atoms in molecules^[3] were applied to characterize the nature of the non-covalent interactions in the target hydrates.

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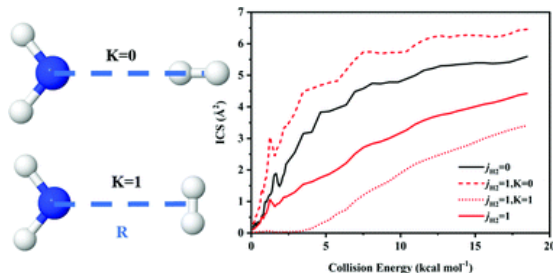
Validating experiments for the reaction $\text{H}_2 + \text{NH}_2^-$ on a full-dimensional accurate PES

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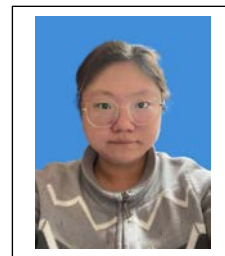
Ion-molecule reactions play key roles in the field of ion related chemistry. As a prototypical multi-channel ion-molecule reaction, the reaction $\text{H}_2 + \text{NH}_2^- \rightarrow \text{NH}_3 + \text{H}^-$ has been studied for decades. In this work, we develop a new globally accurate potential energy surface (PES) for the title system based on hundreds of thousands of sampled points over a wide dynamically relevant region that covers long-range interacting configuration space. The permutational invariant polynomial-neural network (PIP-NN) method is used for fitting and the resulting total root mean squared error (RMSE) is extremely small, $0.026 \text{ kcal mol}^{-1}$. Extensive dynamical and kinetic calculations are carried out on this PIP-NN PES. Impressively, a unique phenomenon of significant reactivity suppression by exciting the rotational mode of H_2 is reported, supported by both the quasi-classical trajectory (QCT) and quantum dynamics (QD) calculations. Further analysis uncovers that exciting the H_2 rotational mode would prevent the formation of the reactant complex and thus suppress the reactivity. The calculated rate coefficients for $\text{H}_2/\text{D}_2 + \text{NH}_2^-$ agree well with the experimental results, which show an inverse temperature dependence from 50 to 300 K, consistent with the capture nature of this barrierless reaction. The significant kinetic isotope effect observed by experiments is well reproduced by the QCT computations as well.

In addition, the H abstraction reactions of a hydroxyl radical with methanol are also of great importance in the interstellar chemistry. The kinetics of the reaction $\text{OH} + \text{CH}_3\text{OH}$ has been measured and calculated extensively by experiments and theories for a long time. We are working on a project aiming to revisit the experimental kinetics by dynamical calculations on a new-fitted full-dimensional accurate PES.

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Missing Link in Diels-Alder Reaction: Rotational Imaging Pre-reactive Intermediate of Furan-Maleic Anhydride Cycloaddition**Xinyue Zhang, Xiao Tian, Jiayi Li, Qian Gou***

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The pre-reactive intermediate of furan-maleic anhydride cycloaddition, a classical Diels-Alder reaction,¹ has been captured in pulsed jets and interpreted by Fourier transform microwave spectroscopy.² The observed intermediate is proven to be molecular complex characterized by π - π^* interactions between furan and maleic anhydride, which connects with the endo channel. The role of carbonyl groups in determining the stability of complexes has been revealed, which is contributable to a more stable pre-reactive intermediate of endo channel with respect to the exo one. The experimental results provide not only an empirical benchmark to the computational models for such molecular complexes with π - π^* interactions, but also an insight into why the endo channel is favored. The pre-reactive intermediates have hitherto been ignored while studying the coordinates of Diels-Alder reactions, generally confined to transition states directly bridging with reactants and products.³ The present study tries to fill the significant void of the van der Waals well as the first stage of Diels-Alder cycloadditions, by outlining the stability of the pre-reactive intermediate and its accurate information on molecular structure and non-covalent interaction.

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NOTES

Competitive hydrogen bond and $\pi \cdots \pi^*$ interaction between isoprene and acrolein: A rotational study

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The rotational spectra of the isoprene-acrolein complex has measured using pulsed jet Fourier transform microwave spectroscopy^[1] and interpreted with complementary quantum chemical calculations. Three plausible conformations are predicted by theoretical calculation, which adopts the trans conformations of both isoprene and acrolein. Only one isomer was observed in pulsed jet. in which the acrolein molecule is located above the plane of the isoprene, dominated by the electrostatic interaction of a classic C-H $\cdots$ O hydrogen. The $\pi \cdots \pi^*$ interaction also contributes to its stabilization. Bader's quantum theory of atoms in molecules^[2] and Independent Gradient Model analysis^[3] were applied and visualized to have a better understanding of the non-covalent interactions in the complex. Symmetry-adapted perturbation theory analysis^[4] suggests that the dominant force gradually transforms from dispersion to electrostatic in stabilizing the titled complex.

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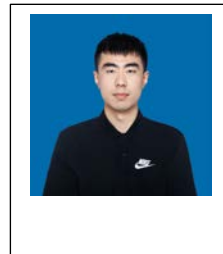
NOTES

Chiral Recognition: Direct Spectroscopic Detection of five isomers of Propylene Oxide-Trifluoromethyl Propylene Oxide Dimer

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The rotational spectrum of propylene oxide-trifluoromethyl propylene oxide dimer has been investigated by pulsed-jet Fourier transform microwave spectroscopy^[1] complemented with quantum chemical calculations. Five isomers have been observed in the pulsed jet, which are mainly connected by hydrogen bonds. Weak C $\cdots$ O tetrel bonds are also found in isomers I and III with strengths of 4.16 kJ mol⁻¹ and 4.11 kJ mol⁻¹, respectively (see Figure 1). According to Bader's quantum theory of atoms in molecules (QTAIM) analysis,^[2] the binding energies of the five dimers are relatively close, ranging from 22.3 to 23.7 kJ mol⁻¹. Among the five isomers observed, interestingly, the isomers I, II, IV and V show a preference for *R*-type trifluoromethyl propylene oxide. Isomers I and III are homochiral dimers, and the other isomers are heterochiral.

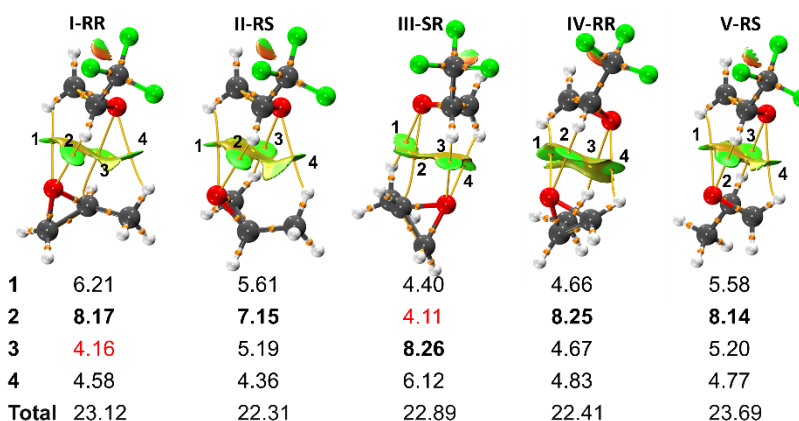


Figure 1 QTAIM analysis of the five observed propylene oxide-trifluoromethyl propylene oxide isomers.

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NOTES

Concerted vs Stepwise Quantum Tunnelling of Heavy Atom Observed by Microwave Spectroscopy

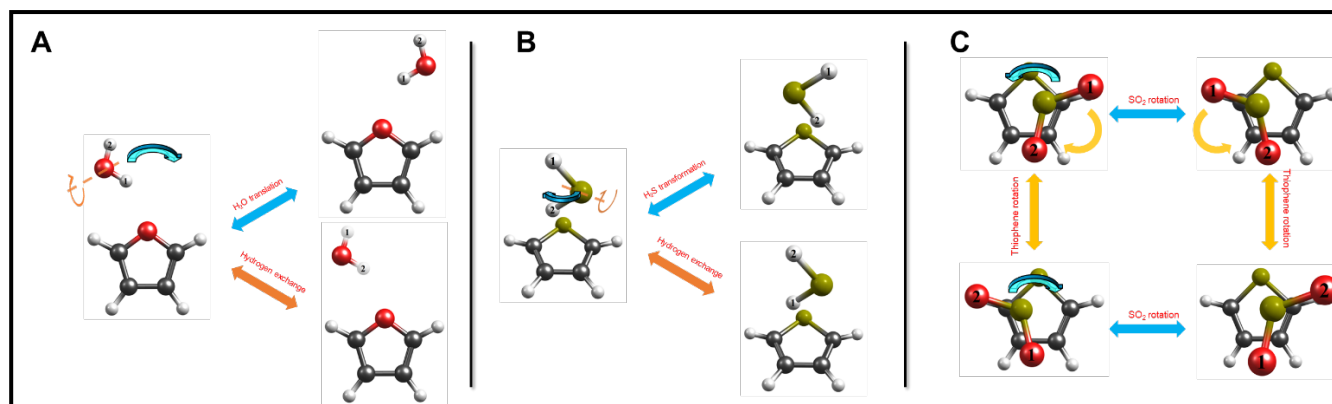
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While quantum tunneling of electron and proton is ubiquitous, the quantum tunnelling of heavy atoms is rarely observed. Furthermore, it is extremely challenging to examine experimentally the quantum tunneling going in a concerted or stepwise manner. Herein, we report the rotational study of several heavy atom tunneling systems in the molecular clusters. Using broadband chirped pulse Fourier transform microwave spectrometer (CP-FTMW), we recorded the pure rotational spectra of furan-water, thiophene-hydrogen sulfide and thiophene-sulfur dioxide complexes. The spectral features of multiple splitting pattern indicate water, hydrogen sulfide and sulfur dioxide undergoing multiple quantum tunneling motions. In the furan-water complex, water molecule, anchored to the furan oxygen through a hydrogen bond, swings as a clock hand while rotating along its C₂ symmetry axis; thiophene-hydrogen sulfide complex shows similar motion except for hydrogen sulfide's location; in the thiophene-sulfur dioxide complex, sulfur dioxide flips on the surface of thiophene which followed by an internal counter rotation of these two molecules. Our finding highlights the potential of rotational spectroscopy to study the multiple tunneling mechanisms of heavy atoms.



NOTES

Controlling Double Proton Transfer Tunneling in Formic Acid-Propiolic Acid Dimer with a Single Weakly Bound Molecule

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Proton transfer along hydrogen bonds plays a significant role in biology and chemistry, such as gene mutations in DNA strands, and this reaction is strongly governed by the quantum tunneling effect. Quantum tunneling rate is considered to be affected by the surrounding environment, but it has been rarely examined experimentally.¹⁻² Microwave spectroscopy is a well-established experimental technique for the study of molecular structure and quantum tunneling effect at the individual molecule level. The tunneling can lift the degeneracy of vibrational states in a symmetric multi-well potential, leading to the splitting of rotational energy levels. Therefore, information about quantum tunneling is encoded in the rotational spectra. Here we utilize the newly constructed chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy within the 2-8 GHz frequency range in our laboratory to measure the pure rotational spectroscopy of formic acid-propionic acid dimer complexed with fluorobenzene and furan, respectively. The results show that the rotational spectra exhibit splitting patterns, which indicates the double proton transfer tunneling in the formic acid-propionic acid dimer. Comparing the results with that of the pure formic acid-propionic acid dimer, we found the neighboring molecules can regulate the tunneling splitting. Furthermore, we extended our study to isotopologue substituted species, in which the substitution depending on the atomic positions can switch on or off the tunneling effect in a controlled fashion. Our results highlight the importance of the surrounding environment of a tunneling system and provide a method to regulate the quantum tunneling process.

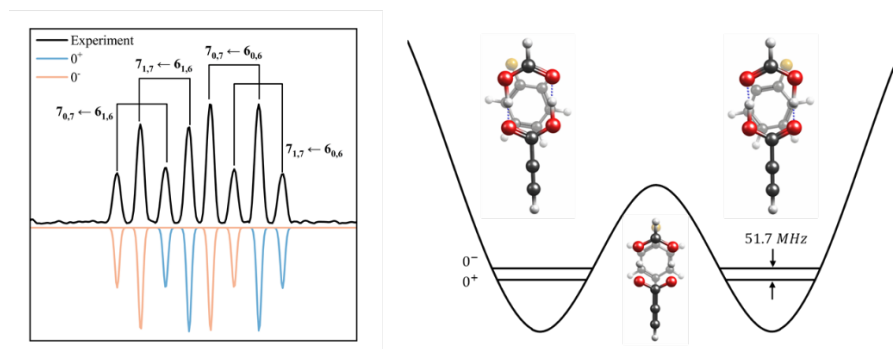


Figure 1: Double proton transfer tunneling in formic acid-propionic acid dimer with fluorobenzene.

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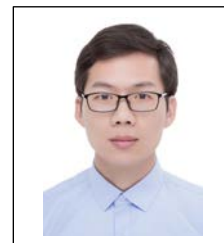
NOTES

Molecular beam density measurement with cavity-enhanced absorption spectroscopy

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Molecular beams have played an important role in chemical physics research^[1, 2]. Beam density is recognized as a crucial element in determining beam properties, reaction rate and differential cross-section in the chemical dynamic experiments^[3]. However, there are few results that present the absolute molecular beam density. Based on the laser locking technique, we are able to measure the cavity-enhanced spectroscopy in a supersonic beam. The CO density in the beam is continuously recorded when the beam is passing the cavity and we have demonstrated that the absolute molecular beam density can be measured. The spectrum of carbon oxide R₂(0) transition is shown in figure 1. It is expected that with the laser locked cavity-enhanced method beam density of other molecules, such as C₂H₂, H₂O, CH₄ and etc., can be measured, which is useful and important for the field of chemical physics research.

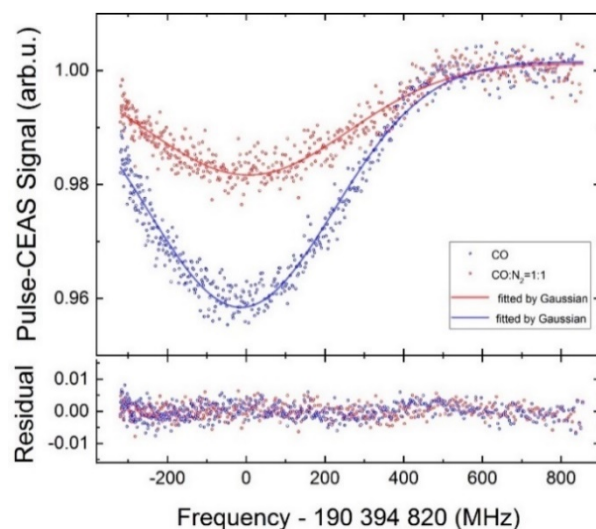


Fig 1. CEAS of carbon oxide R₂(0) transition

References

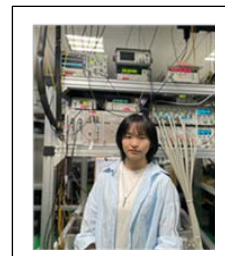
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NOTES

Cavity-enhanced double resonance spectroscopy of HD**M.-Y. Yu, Q.-H. Liu, C.-F. Cheng*, S.-M. Hu***

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The hydrogen molecule is the only molecule that can be both measured and calculated to a high precision. The latest theoretical calculation, by including the relativistic and high-order QED corrections, reaches a fractional accuracy of 7×10^{-10} , which can be used to test the QED theory. To improve the accuracy of molecular hydrogen spectroscopy, we propose a comb-locked cavity-assisted double resonance (COCA-DR) method. By locking two lasers to a high finesse cavity we are able to excite and detect HD molecules sufficiently. A V-type COCA-DR spectroscopy has been measured and the energy of HD has been determined to an accuracy of 26 kHz. We also analyze the uncertainty of the Ξ -type COCA-DR spectroscopy and expect an accuracy of a few kHz. The theoretical and experimental results above indicate that the COCA-DR method allows for a stringent test of the high-order *ab initio* theoretical calculations and can be used to determine the proton-to-electron mass ratio with an accuracy at the ppt level.

Keywords: Precision measurements; Double resonance spectroscopy; Density matrix

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NOTES

Spectroscopic determination of single proton transfer on the excited photochromism of Schiff bases**Ye Wang^{a,b} and Song Zhang^{a,b,*}**

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Photochromism is a reversible photo-induced transformation process of two molecular forms which represent distinct absorption spectra, as well as chemical and physical properties. Taking this feature into account, the molecules with photochromic properties have a vast application in many fields such as molecular switches and memories and have been studied extensively in the past few decades. The photochromism of Schiff bases is usually achieved through an excited state intramolecular proton transfer in a sub-picosecond time scale. Salicylideneaniline is a typical anil and its ultrafast dynamics have acquired extensive investigation in solution and crystalline both experimentally and theoretically.

In this work, the ultrafast dynamics of salicylaldehyde azine were investigated in several solvents with different polarity using steady state spectroscopy and femtosecond transient absorption combined with DFT/TD-DFT calculations. A large Stokes shift indicates the existence of ESIPT in the UV-vis absorption and fluorescence spectra. An ESA and SE bands are observed in ultrafast spectra. ESIPT in the first hundreds femtosecond is determined from decay signals. The lifetime of excited keto tautomer has an obvious decrease trend versus the increase of solvent polarity. DFT/TD-DFT calculations revealed the existence of a barrier in the PES when S1 evolves to its trans keto form through phenol ring rotation. The deactivation of excited keto tautomer is vital in the conversion between the enol and keto stable form. The results open a new standpoint in the field of double proton transfer.

NOTES

Signatures of a Conical Intersection in Nonadiabatic Dynamics of Polyfluoropyridine

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Born-Oppenheimer (BO) approximation is one of the fundamental approximations of atomic and molecular physics. In the BO approximation, the electron and nuclear wave functions are separable because of their different time scales of motion, which makes up the premise for the adiabatic description of chemical reactions^[1,2]. However, the BO approximation loses its effectiveness in some processes. For chemical reactions that occur in electronically excited states, non-adiabatic transitions are not only universal but also essential in many chemical and biological processes. In particular, the minimum energy conical intersection (MECI), in which two adiabatic surfaces cross in at least the two-dimensional coordinate, is accepted widely as the dynamic funnel for such non-adiabatic transitions. MECI is significantly role in nonadiabatic dynamic behavior in terms of molecular structure and chemical reactivity.

The effects of conical intersection on the excited dynamics of polyfluoropyridine are concerned based on ab initial theory of electronic structure, which provides an important insight for photophysical and photochemical reactions. The structures of ground state and excited states of pentafluoropyridine are optimized by several methods, and the energies of the excited states S_1 , S_2 are estimated to be 4.84 eV and 6.69 eV, respectively. The structures of S_1 state and S_2 state are both half-boat structures of out-of-plane distortion with C_s symmetry. Combined with the results of the MECIs and experiments, the potential mechanism is discussed. Majority of transitions follow the $S_2 \rightarrow S_1 \rightarrow S_0$ path involving S_2/S_1 and S_1/S_0 minimum energy conical intersections. The structures of the S_2/S_1 and S_1/S_0 MECIs are boat and half-boat structures, respectively. And their energies are 5.16 eV and 6.39 eV, respectively. Due to the recombination of nuclear arrangement, the relaxation time of pentafluoropyridine is longer than that of benzene. At the same time, due to the intersystem crossing populates to the triplet states, there is a long-lifetime process. We observe that along all crossing geometries, significant ring distortion occurs, which depicts the importance of non-planar motions in the nonadiabaticity of the excited states. This is of enlightening significance for the study of fluoropolymers, especially aromatic molecules containing fluorine^[3,4].

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NOTES

Structural Evolution Dynamics and Vibrational Wavepacket Coherence of Excited States in Polyatomic Molecules

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Molecular structural changes are popular carriers leading to changes in either optical or electrical properties. It is often presented and displayed by the possible accompanied vibrational coherence properties during the conversion processes. Study on vibrational wavepacket coherence can not only help to track the structural evolution dynamics in real time, but also can be used to change the local structure of molecules and improve the conversion of solar energy to chemical energy. In this work, ultrafast spectroscopy, especially time resolved photoelectron spectroscopy, has been used to uncover vibrational wavepacket coherence in the excited-state dynamics of several difluorinated aromatic compounds. Also the ultrafast periodic structural evolution has been captured in real time. Periodic beats in intensity in time-resolved photoelectron kinetic energy spectroscopy were observed clearly and coincidence frequency was obtained to help specify the involved vibration modes. In most cases, there exists a phase shift of π rad between the oscillation components for different PKE regions. Combined with theoretical calculations, the periodic molecular structural evolution dynamics along with the vibrational wavepacket coherence phenomenon are described, the possible physical mechanism of the phase reversal of the photoelectron spectroscopy is elucidated, and the whole nonradiative relaxation processes of the excited states are revealed. These researches have provided deep insights into excited-state photophysics and photochemistry processes and will enhance our understanding of structure-dynamics-function relationships in more complex systems in the future.

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NOTES

Incorporation of the CH₂ group promotes indirect-direct bandgap transition of perovskite

Jing Lai, Zhe Yang, Renlong Zhu, Junjun Tan, Shuji Ye*

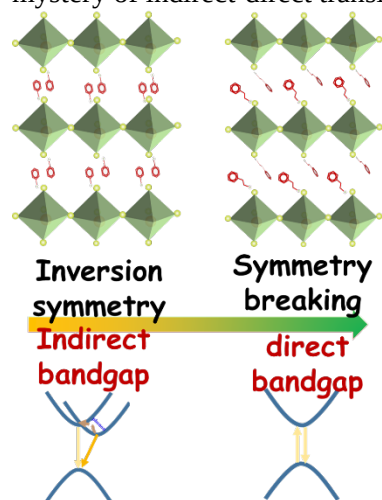
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The origin of slow carrier recombination in organic–inorganic lead halide perovskites has always been controversial, among which the direct–Indirect transition is considered the most likely explanation for this phenomenon. However, there is currently debate over what drives the direct–Indirect transition in perovskites. Herein, we reveal that the carrier recombination dynamics and charge transport properties can be tuned by the incorporation of the CH₂ group. By using the phenyl-based perovskite as a model, we apply sum frequency generation vibrational spectroscopy to determine the orientation of the phenyl group in perovskites. We provide experimental evidence that the organic cations without CH₂ incorporation exhibit opposite orientations, which endows the perovskites with an indirect nature of the band gap. Furthermore, optical pump–THz probe spectroscopy (OPTP) and photoluminescence (PL) spectra show that perpendicular orientation of the organic group results in electronic disorder, which lowers the charge carrier mobility. These findings demonstrate the importance of orientation ordering of the organic group to improve charge carrier dynamics and uncover the mystery of indirect-direct transition in perovskites.



Acknowledgements: This work has the support of National Key Research and Development Program of China (2018YFA0208700, 2017YFA0303500), the National Natural Science Foundation of China (21925302, 21633007, 21873090), Anhui Initiative in Quantum Information Technologies (AHY090000).

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NOTES

Conversion of Dinitrogen and Oxygen to Nitric Oxide Mediated by Triatomic Yttrium Cations: N–N Bond Switch

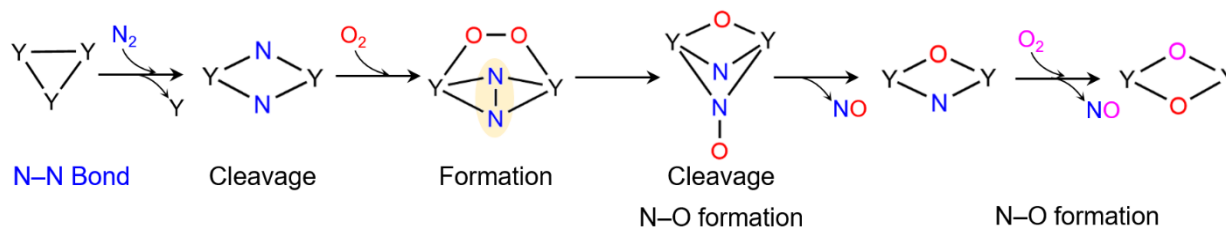
Yong-Qi Ding, Ying Li, Fei Ying, Jing Xie, Jia-Bi Ma*

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The direct coupling of dinitrogen (N_2) and oxygen (O_2) to produce value-added chemicals at room temperature is fascinating but quite challenging because of the inertness of these two molecules. Herein, an interesting reaction pathway is proposed for the oxidation of N_2 by O_2 mediated by all-metal Y_3^+ cations, which begins with the $N\equiv N$ cleavage by Y_3^+ to store electrons in the two N atoms, and then further trigger $O=O$ bond cleave by the change of the bond between two N atoms in $Y_2N_2^+$ to build N–O bond, accompanied by the release of first NO molecule. Then electrons stored in the N atom of the Y_2NO^+ acts as the driving force to activate the second O_2 to form the second N–O bond, which is accompanied by the release of the second NO. The N atom stores electrons in the N_2 activation region, while in the region of N–O bond formation, the electrons stored in N are transferred to further facilitate the $O=O$ bond cleavage. Therefore, the N atom acts as a useful electron reservoir to drive the O_2 activation. It is worth mentioning that the N–N unit acts as a switch, which the operating mechanism is “N–N bond cleavage–formation–cleavage”, to drive the activation of O_2 and the formation of NO molecules in the whole process. Accordingly, a new and versatile N–N switching method for coupling N_2 and O_2 molecules through metal clusters is proposed, which provides a new idea for the direct synthesis of N-containing compounds.



Scheme 1. Key events and mechanisms for the coupling reaction of N_2 with O_2 mediated by Y_3^+ cluster cations.

NOTES

**Photoelectron Spectroscopy of C₂O₃ using a plasma entrainment slow electron
velocity-map imaging spectrometer**

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The weakly-bound CO₂-CO dimer and its derivatives have attracted great interest in fundamental chemistry and interstellar chemistry. Recent theoretical study on C₂O₃ provide a possible explanation to the surprisingly high abundance of molecular oxygen (O₂; hypervolatile species) in cometary comae[1].

Anion slow electron velocity-map imaging spectroscopy is a powerful and convenient technique to characterize the vibrational and electronic structure of neutral radical, clusters, and transient molecules. We have recently constructed an anion slow electron velocity-map imaging spectrometer. We use a plasma entrainment anion source that consists of two perpendicular pulsed beams by a home-made pulsed piezo valve and a pulsed General Valve, respectively. The side General Valve can generate a plasma beam through pulsed discharge. The piezo valve generates main supersonic expansion allowing for reaction with plasma products and efficient jet-cooling. The anions are attracted and deflected by a pulsed electric field, extracted into a time-of-flight (TOF) spectrometer for photoelectrons detachment and imaging. The spectrometer are calibrated by O⁻ photodetachment at 532nm and O₂⁻ photodetachment at 1064nm.

Using this instrument, we have studied the photoelectron spectroscopy of C₂O₃⁻ at different laser wavelengths. The electron affinity (EA) of the produced C₂O₃⁻ is determined to be 1.56(3)eV. In combination with the vibrational analysis of the experimental spectra, the photodetached product is determined as the cyclic dicarbon trioxide (c- C₂O₃), which may play a role of an origin of molecular oxygen in cometary comae.

Acknowledgements: This work has the support of National Natural Science Foundation of China (21827804 and 21773221), the National Key R&D Program of China (2017YFA0303502), the Fundamental Research Funds for the Central Universities of China (WK2340000078).

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NOTES

Photodissociation Spectroscopy and Dynamics of the $[\text{O-O}_2]^+$ Complex

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The spectroscopy, structure and dynamics of reactive chemical intermediates are of great interest to understand the chemical reaction mechanisms. Here, photodissociation spectroscopy and dynamics of $[\text{O-O}_2]^+$ complex, which is isomeric to the ozone cation, has been studied in the 18250-21000 cm^{-1} region using photofragment mass spectrometry method. Two band systems belonging to different electronic transition types, are obtained by recording the photofragment signals of O^+ and O_2^+ , respectively. Analyses on the experimental spectra and the photofragment velocity imaging yield a conclusion of a $[\text{O-O}_2]^+$ complex structure of the spectral carrier. The two excited (pre-)dissociative states correlate to $\text{O} + \text{O}_2^+$ and $\text{O}^+ + \text{O}_2$ product channel, providing necessary information on the reaction pathways of the $\text{O} + \text{O}_2^+ \rightarrow \text{O}^+ + \text{O}_2$ charge transfer reaction.

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NOTES

Branching ratio of 1-bromo-3-chlorobenzene cation in various wavelength photodissociation**Bong Gyu Jeong, Jae Kyu Song and Seung Min Park****Department of Chemistry, Kyung Hee University, Seoul, 02447, Republic of Korea**email: smpark@khu.ac.kr*

The new method for branching ratio based on Rice-Ramsperger-Kassel-Marcus (RRKM) theory with extreme loose transition state (RRKM-eLTS) was adopted to analyze experimental result in photodissociation. The RRKM-eLTS estimated branching ratio without challenging calculation such as structure or frequencies of the transition state. We examined this method through comparison of experimental results that photodissociation of 1-bromo-3-chlorobenzene (3BCB) was selected for branching ratio. The photodissociation channels of 3BCB were described by $3BCB^+ \rightarrow \text{Br-dissociated daughter ion (ClBz}^+) + \text{Br}^\bullet$ and $3BCB^+ \rightarrow \text{Cl-dissociated daughter ion (BrBz}^+) + \text{Cl}^\bullet$. The branching ratio was monitored by a homebuilt tandem time of flight mass spectrometer. Although there was some discrepancy in internal energy between the experimental and calculation results, the RRKM-eLTS is worth to be extended to other diverse systems considering its intuitive and simple nature.

NOTES

Chemical Evolution and electron-stimulated desorption of H₂O+CO ice mixture

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Abstract –

Carbon monoxide is the second abundant solid-phase species followed water molecule. We investigated the ice mixture made of first two abundant molecules observed toward the star formation region. Electron with energy in a range of 200-1000 eV are used to simulate the radiolysis processes of primary electron produced by cosmic-ray and X-ray reacting with gaseous molecules. Electron irradiation is separated into several period and infrared (IR) spectra are collected in the between. Products produced under electron irradiation were assigned in the spectra (Figure 1). Also, column densities of parent molecules and abundant products (CO₂, HCO, H₂CO, and CH₃OH) as functions of electron fluence were computed from IR spectra (e.g. CO₂, Figure 2). Cross-sections are computed and compared with previous studies performed with different energetic sources such as vacuum ultraviolet [1] and X-ray [2]. The results of cross-sections will be discussed.

Corresponding with desorption species and electron penetration depth from CASINO [3], more than the qualitative and idea of the desorption-relevant depth (DRD) reported by Dupuy et al., 2020 [4], we quantitatively estimated DRD in the H₂O+CO ice mixtures.

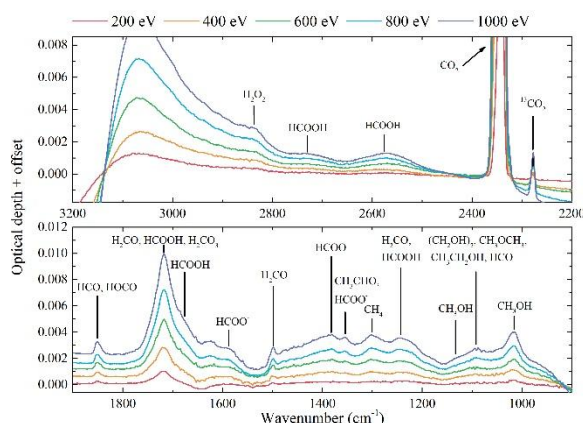


Figure 1. IR spectra with different energy electrons

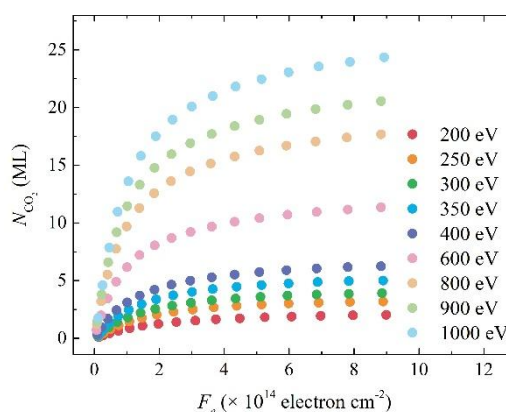


Figure 2. Column density of CO₂ as a function of electron.

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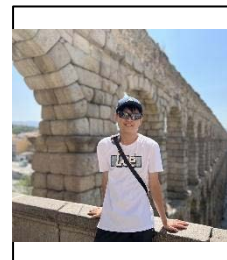
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Key Parameters Controlling the Photodesorption Yield in Interstellar CO Ice Analogs

**Chun-Yi Lee¹, Ni-En Sie¹, Chun-Yi Lee¹, Yun-Ting Cho¹, Chao-Hui Huang¹,
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Abstract –

The abundant CO molecules have been observed in the cold dense clouds and interstellar medium, which is attributed from the irradiation of energetic sources since the thermal desorption is inhibited. The photodesorption of CO ice as a function of deposition temperature has been investigated in previous literature, however, the temperature dependence is not well explained. In this work, the CO ice was deposited at 12.5–25 K and irradiated by ultraviolet (UV) photons. We proposed that the instantaneous photodesorption yield of CO ice is dominated by three temperature dependent parameters, the energy transfer length $L(T)$, the desorption yield contributed by a single ice layer $Y(T)$, and the relative effective surface area $R_A(T)$. Furthermore, the instantaneous photodesorption yields strongly depend on the incident photon intensity of the microwave-discharge hydrogen-flow lamp (MDHL) $W(\lambda)$ as well as the absorption cross section of solid CO ice.

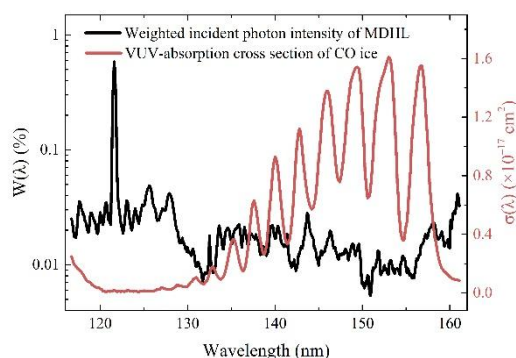


Fig 1. The normalized incident photon intensity of the MDHL and the VUV absorption cross section of CO ice as a function of wavelength.

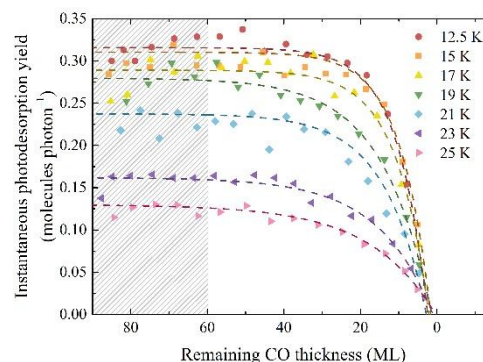


Fig 2. The instantaneous photodesorption yield as a function of remaining CO thickness for CO deposited in the 12.5–25 K range.

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NOTES

Vacuum ultraviolet photodesorption of hydrogen sulfide**Yen-Yu Hsu, Chin-Chi Huang, and Yu-Jung Chen***Department of Physics, National Central University, Jhongli City, Taoyuan County 32054, Taiwan**s108202518@g.ncu.edu.tw***Abstract**

Hydrogen sulfide (H_2S), one of the sulfide-bearing species, can be seen as a precursor of biochemical molecules. In the cold dense clouds where the temperature is near 10 K, the secondary vacuum ultraviolet (VUV) field caused by cosmic rays reacting with molecular hydrogen, is one of the significant energetic sources. Literature has shown the existence of H_2S_x with $x > 1$ and S-polymers as the photoproducts but the photodesorption has not been studied in detail. In this work, we mainly focus on the structural effect on the photodesorption of H_2S ices deposited at different temperatures.

H_2S ices deposited at 13 K and 70 K are irradiated by VUV at 13 K. The results show that the depletion and desorption yield of H_2S ice deposited at 70 K are lower than that deposited at 13 K. However, the amount of desorbing H_2S keeps in $\sim 5\%$ of depleted H_2S ice in the case of depositing at 70 K as well as depositing at 13 K. On the other hand, the H_2S_2 production ratio in the two cases is the same $\sim 34\%$ of depleted H_2S ice. The reason for the lower depletion yield of H_2S ice deposited at 70 K might be explained by the lower energy transfer in the crystalline phase. However, the crystalline phase should have a longer energy transfer distance which can be observed from the turning point of desorption yield. According to sulfur balance and mass spectra obtained during temperature-programmed desorption, the residues of VUV irradiated H_2S ices are mainly S-chain molecules.

NOTES

VUV Photolysis of Methane Ices**Yi-Xiang, Peng, Ni-En, Xie, Chao-Hui, Huang and Yu-Jung, Chen***National central university and a0965261213@gmail.com***Abstract**

Methane ice in the interstellar medium and dense clouds by Lacy et al. (1991). Methane ice with a high abundance of water and carbon monoxide ice in the regions of molecular clouds. The abundance of methane depends on the H/H₂ ratio; if the ratio is high, hydrogenation is the main process, so the abundance of methane ice is higher. In the above regions, the secondary ultraviolet (UV) photon induced by the reactions between cosmic rays and hydrogen molecules is a significant energetic source. When methane ice is exposed to a secondary UV field, a series of photochemistry and photodesorption will occur after absorbing the photons. Therefore, the absorption cross-section of solid methane should be considered.

In this study, the methane ice deposited from 12.5 K to 30 K is irradiated by the UV photons to probe the relation between photodepletion and ice structure. There are two channels for the depleted methane ice. The first channel is the methane desorbing from the ice surface into the gas phase. The other one is that methane dissociated and leads to forming of ethane, propane, and hydrogen photo products. We find that methane's photodesorption trend is similar when it is deposited at temperatures lower than 21 K, while it drops at deposition temperatures higher than 21 K. According to Clusius (1929), the phase transition temperature of methane is 20.4 K, so methane ice transitions from phase II to phase I. The structure affects the efficient energy transfer and leads to the photodesorption amount.

NOTES

VUV photoinduced energy transfer in solid CO ices**Chun-Chi Huang, Ni-En Sie, Chao-Hui Huang, Yu-Jung Chen***huangg7@g.ncu.edu.tw***Abstract –**

Vacuum ultraviolet (VUV) photodesorption is an important non-thermal process, which can explain the abundant gaseous molecules in cold interstellar regions. And furthermore, the secondary VUV field is known as the main energetic source to induce the photodesorption. In the laboratory, the most common light source used to simulate the VUV field is the microwave-discharge hydrogen-flow lamp (MDHL). It provides $\text{H} - \text{H}$ emission (121.6 nm) and molecular H_2 emission bands (140-170 nm). The proportion of $\text{H} - \text{H}$ and H_2 emission bands depends on the operation condition of MDHL, leading to the different photodesorption yields of CO. According to the absorption cross-section of CO ice, CO molecules hardly absorb the $\text{H} - \text{H}$ photons. Thus, the photodesorption yield is assumed to be increased as the proportion of $\text{H} - \text{H}$ is reduced. However, Chen et al. (2014) reported the opposite consequences. It indicates that the photodesorption of CO induced by nonmonochromatic light is complicated. Besides the photodesorption of CO, CO_2 is produced in the ice during the irradiation of CO ices. The absorption cross-sections of CO and CO_2 (fig. 1) have a significant discrepancy in the $\text{H} - \text{H}$ and molecular H_2 emission ranges. Compared to CO, CO_2 absorbs the $\text{H} - \text{H}$ emission much more. This study, based on layered ice structure and a few different configurations of the energy distribution of the light source, will try to demonstrate the effect of CO_2 on the photodesorption of CO, as well as the thickness dependent energy transfer by the double layered ice which ^{13}CO is deposited on CO_2 . The results of this study will be presented in this poster.

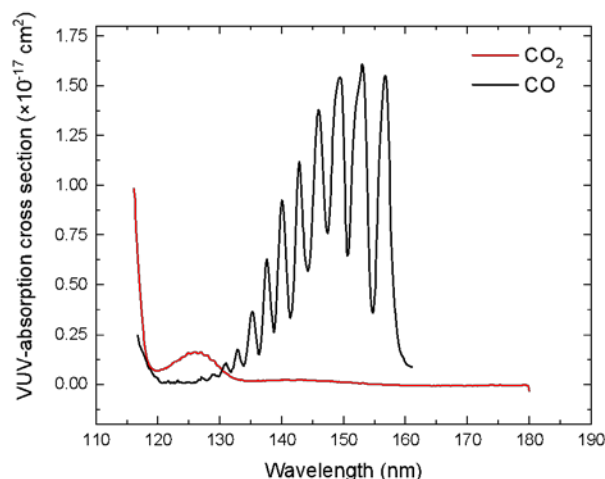


Figure 1. The comparison of absorption cross-sections of solid CO and CO_2 .

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Observation of rotationally dependent fine-structure branching ratios near the predissociation threshold $N(^2D_{5/2, 3/2})+N(^2D_{5/2, 3/2})$ of $^{14}N_2$ **Pan Jiang^{1,2}, Liya Lu^{1,2}, Hong Gao^{1,2*}**¹ Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China² University of Chinese Academy of Sciences, Beijing 100049, China

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Photofragment spin-orbit fine-structure branching ratios have long been predicted to depend on rotational quantum number J' by theory near the dissociation thresholds of several diatomic molecules [1], while this has rarely been observed in any photodissociation experiments yet. Here, we measured the fine-structure branching ratios $N(^2D_{5/2})/N(^2D_{3/2})$ produced in the $N(^2D_{5/2, 3/2})+N(^2D_{5/2, 3/2})$ channel at the $b'^1\Sigma_u^+(v=20)$ state of $^{14}N_2$ by our vacuum ultraviolet (VUV)-pump-VUV-probe time-sliced velocity-mapped ion imaging setup. The strongly rotationally dependent fine-structure branching ratios should be due to the variable contribution of nonadiabatic Coriolis interaction among various dissociative states in the so called “recoupling zone” near the dissociation thresholds as J' increases [2].

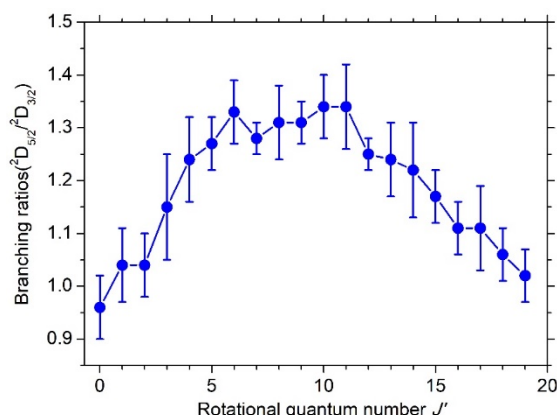


Figure 1 Spin-orbit fine-structure branching ratios $N(^2D_{5/2})/N(^2D_{3/2})$ as a function of the rotational quantum number J' for the $b'^1\Sigma_u^+(v=20)$ state of $^{14}N_2$.

Acknowledgements: This work has the support of the National Natural Science Foundation of China (Grant No. 21973100, 22103090)

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NOTES

A research plan on the reaction mechanism between H_2^+ and He at low collision energy

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In the early universe, there were many ion-molecule reactions. The reaction $\text{HeH}^+ + \text{H} \rightarrow \text{H}_2^+ + \text{He}$ has long been thought to be the first chemical reaction after the Big Bang^[1]. Studying its inverse reaction, i.e. $\text{H}_2^+ + \text{He} \rightarrow \text{HeH}^+ + \text{H}$, will help to build a relevant model to understand the early evolution of the universe. In addition, the proton transfer reaction between H_2^+ ions and He is one of the simplest chemical reactions that can be achieved by theoretical calculations. Investigation of this reaction experimentally will provide deep insights into the proton transfer dynamics. We plan to use our recently constructed ion-molecule cross-beam setup^[2] to investigate it at collision energies below 2 eV, and compare our results with previous theoretical simulations.

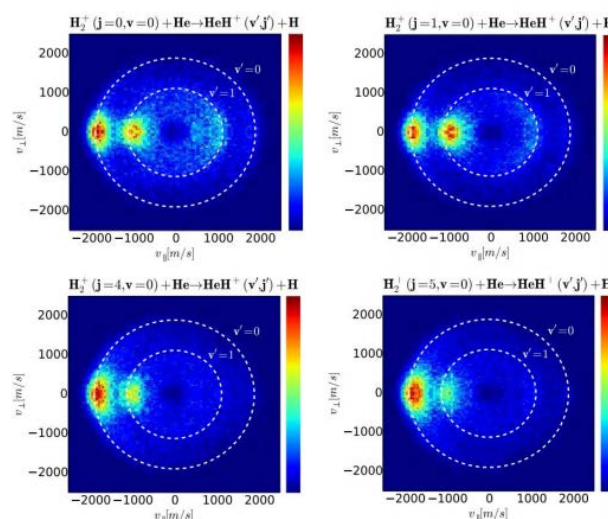


Figure 1: Simulated DCS by Vera et al. ^[3]

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NOTES

Accurate measurements of the bond dissociation energies of

 $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}_2$ **Liya Lu^{1,2}, Pan Jiang^{1,2*}, Hong Gao^{1,2*} (11pt Times bold)**¹Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.² University of Chinese Academy of Sciences, Beijing 100049, China.

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Accurate determinations of bond dissociation energies (BDEs) and the corresponding enthalpies of formation derived from them are of fundamental importance. In this study, we demonstrate a direct experimental scheme for measuring the BDEs of $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}_2$ to an accuracy of a few wavenumbers. A linear fit between squares of the radii of the high-resolution quantum-state-selected velocity-mapped ion(VMI) images and the spectroscopic term energies slightly above the dissociation limit $\text{N}(^2\text{D}_{5/2, 3/2})+\text{N}(^2\text{D}_{5/2, 3/2})$ gives out an accurate measurement of the threshold D_0 for dissociating into the channel $\text{N}(^2\text{D}_{5/2, 3/2})+\text{N}(^2\text{D}_{5/2, 3/2})$. The BDEs of $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}_2$ into the lowest channel $\text{N}(^4\text{S})+\text{N}(^4\text{S})$ are independently determined to be 78688 ± 3 , 78705 ± 4 and 78728 ± 4 cm^{-1} , respectively, which are found to give a consistent value of D_e after considering the zero-point energies for each of the isotopologues [1, 2]. The experimental scheme demonstrated in this study should be generally applicable for precisely determining the BDEs of many other diatomic molecules.

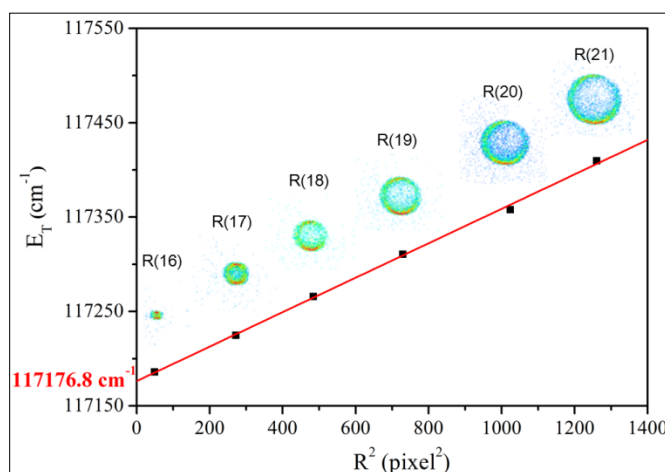


Figure 1: The plot of the squares of the image sizes (R^2) versus the corresponding spectroscopic term energies for $b'^1\Sigma_u^+(v'=20, J') \leftarrow X^1\Sigma_g^+$ of $^{15}\text{N}_2$. The intercept by the red number gives a D_0 value of 117176.8 ± 2.7 cm^{-1} for the channel $\text{N}(^2\text{D}_{5/2})+\text{N}(^2\text{D}_{5/2})$.

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NOTES

The vacuum ultraviolet spectra of C₂: $g^3\Delta_g-a^3\Pi_u$ and $f^3\Sigma_g^--a^3\Pi_u$

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The spectroscopy of C₂ has a long history since its first observation in blue hydrocarbon flames in 1802¹. However, the spectroscopic study of C₂ in VUV region is rare. Recently, we studied the C₂ spectra from 70000 to 75000 cm⁻¹ by discharging 0.5% acetylene in Ar. Following the work of Herzberg et al.², we found higher vibrational levels of the $g^3\Delta_g$ state: $v=2$ through $v=4$ and more absorption bands of the $f^3\Sigma_g^--a^3\Pi_u$ transition. Surprisingly, the $F^1\Pi_u-X^1\Sigma_g^+$ 0-0 band, which is supposed to be the strongest absorption band of C₂, was not observed in the present experiment. This might be due to the fast predissociation process of the $F^1\Pi_u$ state, which supports the recent astronomical observations³. Interestingly, the $g^3\Delta_g-a^3\Pi_u$ 2-0 band and an unknown band are found to be overlapping with the $F^1\Pi_u-X^1\Sigma_g^+$ 0-0 band, which may partially explain the discrepancies found in several previous astronomical observations³⁻⁴.

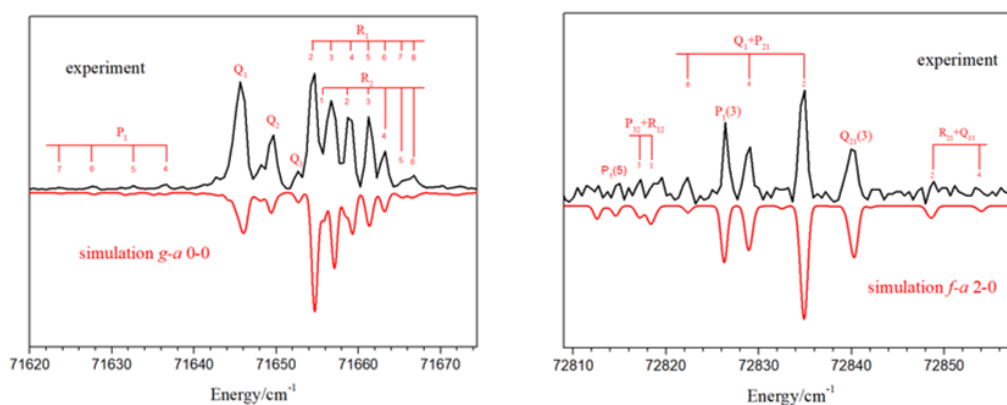


Figure 1 Selected bands of C₂ from 70000 to 75000 cm⁻¹.

Acknowledgements: This work is supported by the National Natural Science Foundation of China (Grant No. 22122308) and Beijing Municipal Natural Science Foundation (Grant No. 8212043).

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Observation of the new electronic state of C₂: $1^3\Sigma_g^+$

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C₂ radical has simple molecular structure, but very complex electronic structure. K. Kirby and B. Liu predicted that C₂ has 62 valence state¹, but only 21 of them have been found so far². Recently, we used C₂H₂ as precursor to produce C₂ radical via pulsed discharge, and obtained C₂ spectra in the wavelength region of 57000-63000 cm⁻¹. A new band system was found, which was assigned as the $^3\Sigma_g^+ - a^3\Pi_u$ band system. The band origin of 0-0 band is 60713.40 cm⁻¹ (7.53 eV), which is in close agreement with the previous theoretical study³.

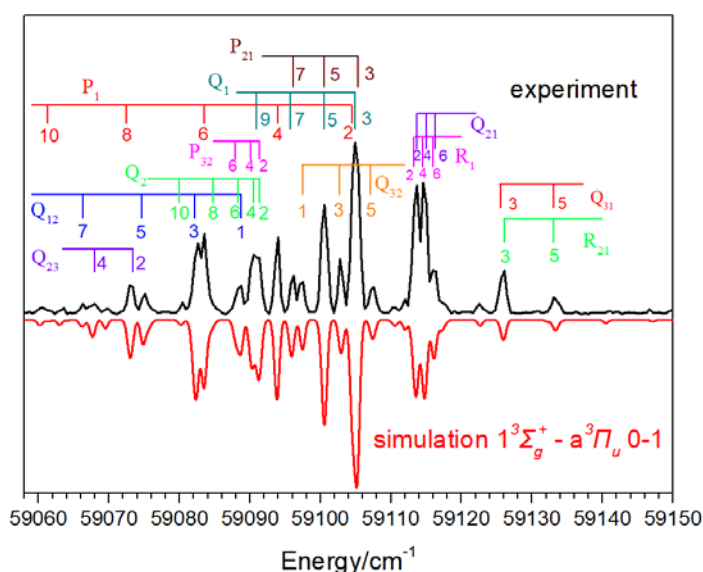


Figure 1: Spectrum of $1^3\Sigma_g^+ - a^3\Pi_u$ 0-1 transition obtained by us.

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NOTES

State-selected ion-molecule scattering for $\text{Ar}^+(\text{}^2\text{P}_{3/2,1/2}) + \text{N}_2$ at low energy**Guo-dong Zhang^{1,2}, Li-chang Guan^{1,2}, Yu-fan Ding^{1,2}, and Hong Gao^{1,2*}***1 Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing China, 100190.**2 University of Chinese Academy of Sciences, Beijing China, 100049.*** honggao2017@iccas.ac.cn*

Studying ion-molecule reactions in gas phase provides insight into the evolution of substances and energy transfer in environments where ions and neutrals coexist, such as interstellar clouds and terrestrial atmospheres^[1,2]. In order to study ion-molecule reaction dynamics on the state-to-state level, we designed a new crossed-beam apparatus, which consists of a state-selected pulsed low kinetic energy ion beam source, a high density neutral molecular beam source and a three-dimensional ion velocity measurement system^[3,4]. We have measured the differential cross sections for both charge transfer and inelastic scattering processes of $\text{Ar}^+(\text{}^2\text{P}_{3/2,1/2}) + \text{N}_2$ at the collision energy range of 0.5-1.6 eV. The obvious difference between the differential cross sections of $\text{Ar}^+(\text{}^2\text{P}_{3/2})$ and $\text{Ar}^+(\text{}^2\text{P}_{1/2})$ indicates that the reaction has distinct spin-orbit dependence, as shown in Figure 1.

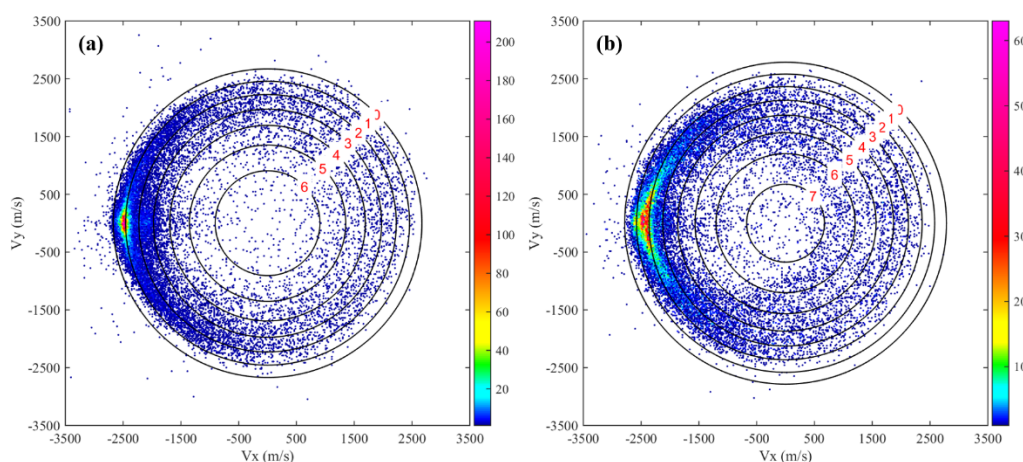


Figure 1: Differential cross sections for the charge transfer processes of (a) $\text{Ar}^+(\text{}^2\text{P}_{3/2}) + \text{N}_2$ and (b) $\text{Ar}^+(\text{}^2\text{P}_{1/2}) + \text{N}_2$ at the collision energy of 1.57 eV.

References

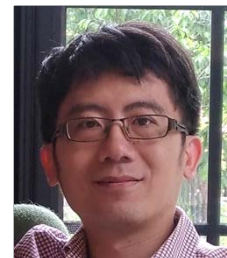
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NOTES

Accelerated Sulfur Oxidation by Ozone on Surfaces of Single Optically Trapped Aerosol Particles

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The sulfur oxidation in mixed sodium thiosulfate/sucrose/aqueous micro-droplets by gaseous ozone is studied in this work [1] via aerosol optical tweezers coupled with Raman spectroscopy [2-3], which can simultaneously determine various physicochemical properties and the heterogeneous reaction kinetics of single optically trapped micro-droplets, allowing for elucidating their complicate interplay. According to the kinetics measurement results at different relative humidities, ozone concentrations and stoichiometries of inorganic and organic solutes, this work finds that a high aerosol ionic strength can accelerate the ozone oxidation of thiosulfate at air-water interfaces, while a high aerosol viscosity prolongs the reaction timescales due to diffusion-limited kinetics. The kinetic multilayer model of aerosol surface and bulk chemistry (KM-SUB) is utilized to investigate the observed heterogeneous kinetics results and to retrieve the surface reaction rate coefficients. The KM-SUB simulations results indicate that the observed kinetics of sulfur oxidation in binary sodium thiosulfate aqueous micro-droplets with high ionic strengths is dominated by interfacial reactions, and the fitted surface reaction rate coefficients increase one order of magnitude when the droplet ionic strength increases around 40 M. Furthermore, this work demonstrated that including the effects of interfacial ion depletion in the kinetics simulations can lead to an excellent agreement with the experimental results, implying its potential role in the interfacial kinetics.

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NOTES

Kinetics and solvent effect of the color fading reaction of phenolphthalein in alkaline solution studied with a simple and economic device

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Abstract

The color fading reaction of phenolphthalein has been found since the 20th century, and many studies¹⁻² have reported its kinetic parameters. However, the experiments usually need a UV-visible spectrometer to measure the absorbance which costs a lot of money and limits its popularity. Herein, a simple photometric device was built to measure the kinetics of the color fading reaction of phenolphthalein in alkaline aqueous solution. The device consisted of a green (centered at 520 nm) light emitting diode (LED), a 10 ml sample vial, a photodiode, and an Arduino UNO microcontroller board. These parts were mounted on a black polylactic acid (PLA) holder which was manufactured by three-dimensional (3D) printing. Adequate sensitivity and dynamic range (linear detection range from 1×10^{-3} to 0.9 in absorbance, base 10) and time resolution (ca. 6×10^{-3} s) have been achieved with this device. The kinetics of the reaction could be studied by the time-resolved absorbance of the pink form of phenolphthalein recorded by the device. The time scale of the forward reaction can be designed to be sub-minute or minutes, depending on the concentration of hydroxide anion $[\text{OH}^-]$. Besides, an experiment was also designed to demonstrate the direct observation of the reversed reaction, of which the time scale is on the order of hours. Evidence of reaching an equilibrium was observed at a condition of higher concentration of phenolphthalein [PhPh] and lower $[\text{OH}^-]$. With the specific experimental design, it could be easier and more interesting to demonstrate the chemical equilibrium. The equilibrium constant could be determined which is comparable with previous works. We also found a significant reduction of the reaction rate constant with adding a minor amount of alcohols. Moreover, alcohol molecules with a larger alkyl group have a stronger solvent effect, revealing the nature of the interaction between the alcohol molecules and phenolphthalein.

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NOTES

Estimation of acid dissociation constants (pK_a) of N-containing heterocycles in DMSO and transferability of Gibbs free energy in various solvent conditions

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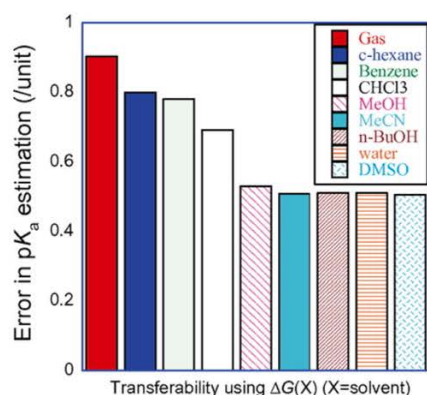
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Abstract

Heterocycles are cyclic organic compounds that include elements other than the carbon atom in the ring and are of great importance in a wide variety of chemistry [1-2]. Especially N-containing heterocycles are essential to life and functional material fields. The acid dissociation constant, pK_a, is a physical quantity indicating the protonation states of molecules in solution at a given pH. The pK_a also shows how a molecule donates or accepts the proton from a counterpart molecule, and thus is a very important index for nucleophilicity in both organic chemistry and biochemistry [3]. However, experimental measurements of pK_a for individual functional groups of complex molecules is sometimes difficult especially when a target compound is slightly soluble or insoluble in a solvent since the detection of the protonation state change for a small amount of solute is difficult. In this study, we theoretically estimated the pK_a of N-containing heterocycles in DMSO by a quantum chemistry method with a polarizable continuum model, which was previously developed for estimating the pK_a of molecules in water. We numerically demonstrate the present scheme, which is also suitable for DMSO solvent as accurately as for water. According to the obtained result, we confirmed the transferability of obtained parameters in calculating pK_a using Gibbs energy in different solvent conditions.



$$pK_a = -\frac{\Delta G(\text{soln}, X)}{RT \ln 10} = \frac{G(\text{HA}, X) - G(A^-, X) - G(H^+, X)}{RT \ln 10}, \quad \text{Eq (1)}$$

$$pK_a = -\frac{s(G(\text{HA}, X) - G(A^-, X) - G(H^+, X))}{RT \ln 10}, \quad \text{Eq (2)}$$

$$pK_a = k(G(A^-, X) - G(\text{HA}, X)) + C_0 = k\Delta G_0 + C_0, \quad \text{Eq (3)}$$

$$k = \frac{s}{RT \ln 10}, \quad C_0 = \frac{sG(H^+, X)}{RT \ln 10}, \quad \text{Eq (4)}$$

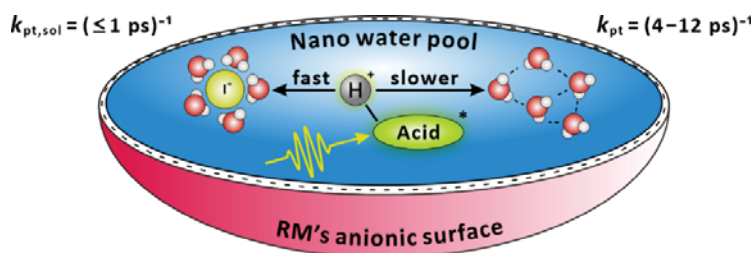
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NOTES

Probing Excited-State Proton Transfer in a Nanoscopic Water Pool**Aniruddha Adhikari, Hak-Won Nho, Oh-Hoon Kwon****Department of Chemistry, College of Natural Sciences, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea**aniruddha@unist.ac.kr***ohkwon@unist.ac.kr*

The phenomenon of proton transfer is of utmost significance in several biochemical processes. One of the strategies employed in studying the phenomenon involves tracking the kinetic behavior of photoacid molecules embedded within model systems such as reverse micelles (RMs) that mimic the microenvironment prevalent in biomacromolecules [1,2]. In this present study, we employed the technique of fluorescence up-conversion to investigate the excited-state proton transfer (ESPT) of a cationic superphotoacid, N-methyl-7-hydroxyquinolium (NM7HQ⁺) within the nanoscopic water pool of an anionic aerosol-OT (AOT), bis(2-ethylhexyl) sulfosuccinate, reverse micelle (RM) [3]. The ultrafast deprotonation step in the ESPT was found to be biphasic in nature, governed by two subpopulations of the water molecules constituting the core of the RM. The core water molecules solvating the iodide counteranion of the photoacid, with their higher basicity than typical water clusters in bulk, resulted in ESPT on a subpicosecond time scale. In contrast, bare water clusters were responsible for the slower ESPT spanning several picoseconds, commensurate with deprotonation times reported for similar photoacids in bulk water.

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NOTES

Determination of the formation constants for the hydrogen-bonded complex of a photoacid in polar aprotic binary solvent mixtures**Ye-Jin Choi, Hak-Won Nho and Oh-Hoon Kwon****Department of Chemistry, College of Natural Sciences, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea***E-mail: ohkwon@unist.ac.kr.**Presenter E-mail: cyj148983@unist.ac.kr.*

The acid-base reaction is an elementary process in chemistry and biology. The hydrogen (H)-bond formation between a proton acceptor and a donor is prerequisite to the reaction. Therefore, identifying and quantifying the formation of H-bonded complexes is a foundation of studying acid-base reactions. The Benesi-Hildebrand method has been widely used to determine the formation constants of H-bonded complexes. This approach determines the formation constants within a limited range of the additive concentration. The additive in a solution is assumed to participate only in forming the complex. If the presence of the additive starts to affect the bulk properties of the solution, the analysis using the Benesi-Hildebrand method becomes unreliable as a spectral shift may also occur due to bulk solvent polarity changes in the solution. In this presentation, we propose a new approach to quantifying weak H-bonded complexes with photoacids to circumvent the limitation of the Benesi-Hildebrand method. In case, a solvent is not conducive to accepting the proton from a photoacid, diffusion-controlled excited-state proton transfer may occur to an additive Brønsted base on the timescale spanning hundreds of picoseconds to nanoseconds. Accordingly, the fractions of the fast, activation-controlled unimolecular process and the much slower bimolecular process represent the equilibrium between the H-bonded complexes and the free acids. We report devising and verifying the new analytical method based on picosecond-resolved fluorescence spectroscopy to quantify the formation of H-bonded complexes and obtain accurate equilibrium constants in a system, where the bulk solvent polarity changes with the concentration of a complexing base.

NOTES

Corrected Benzene Structure by Mass-Correlated Rotational Raman Spectroscopy

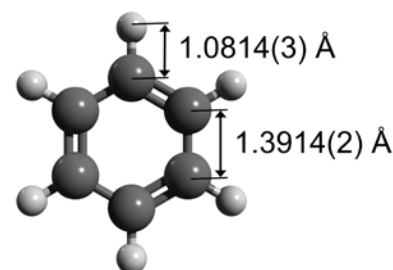
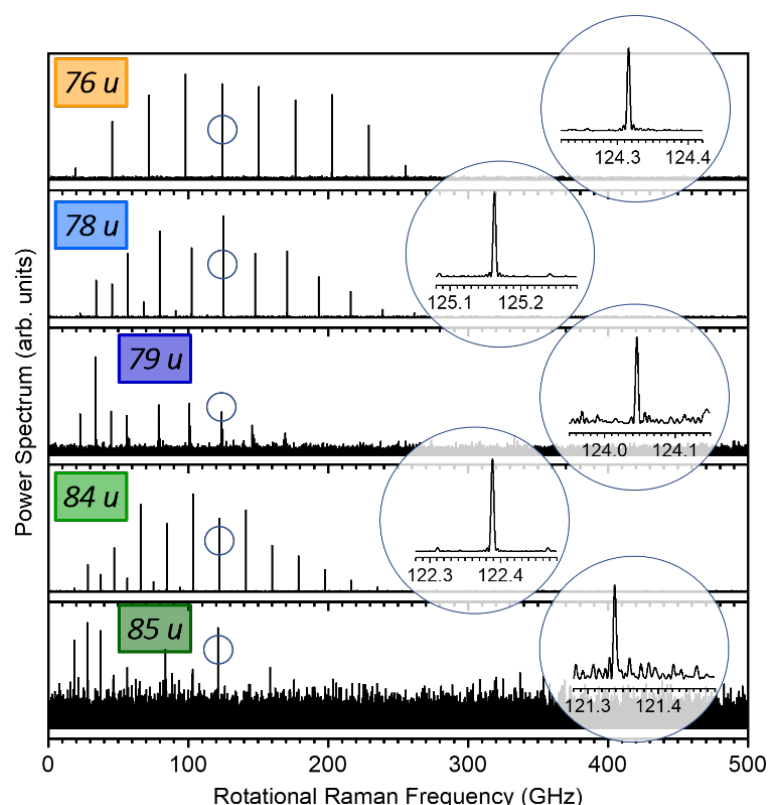
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The high-resolution of rotational Raman spectra for multiple benzene isotopologues were measured by mass-CRASY (mass-correlated rotational alignment spectroscopy) [1]. Mass-CRASY combines the high sensitivity of mass spectroscopy with the high-resolution of rotational spectroscopy [2]. We recently developed a structure fitting program, written by Python, which could calculate structure parameter from these high-resolution rotational data [3]. Equilibrium (r_e) and effective (r_0) bond lengths were estimated from a measured diverse set of isotopically substituted benzenes isotopologues, based on Watson's rovibrational correction terms. Our new geometry corrected new benzene structure and had very good agreement to theoretical and semi-experimental values.



Rotational spectra for CS₂, C₆H₆, ¹³C-C₅H₆, C₆D₆, ¹³C-C₅D₆ from CRASY measurement (left). Benzene equilibrium structure (right)

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Formation of Complex Nitrogen-Containing Prebiotic Molecules Induced by Single Photon Ionization

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More than 270 molecules have been detected in different astronomical environments and meteorite samples. The formation pathways to the complex organic molecules in space are a long-standing astronomical question, which is also closely related to the origin of life. With the aid of state-of-the-art vacuum ultraviolet (VUV)-infrared (IR) spectroscopy and *ab initio* calculations, we reveal a possible way leading to the formation of the nitrogen-containing prebiotic molecules through the ion-molecule reaction of acrylonitrile ($\text{CH}_2\text{CHC}\equiv\text{N}$, AN) clusters. AN is one of the most abundant unsaturated nitriles in space and has been observed in diverse types of extraterrestrial environments. In the study of $(\text{AN})_{2,3}$ ^[1] and $(\text{AN})_{1,2}\text{-NH}_3$ ^[2] clusters, it is found that a new C-N bond is formed in the clusters via the direct addition reaction after 118 nm light ionization. Our recent investigation on the AN-alcohols clusters shows that nitrilium cations and even cyclic amine cations with a peptide bond can be generated through the single-photon ionization-induced sequential Michael addition/cyclization reactions.^[3] While, only the proton transfer reaction can occur in the AN-CH₃SH cluster after 118 nm light ionization. These studies may provide a strong alternative to the interstellar in situ formation of complex prebiotic molecules in space.

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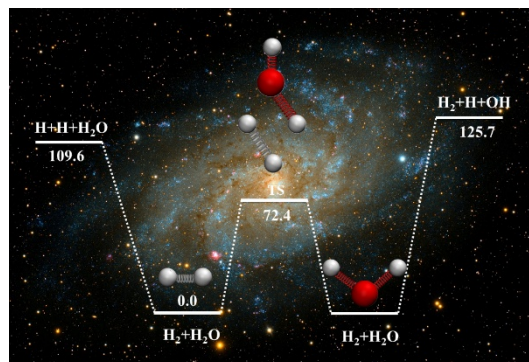
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An Accurate Full-Dimensional H₄O Potential Energy Surface and Dynamics of Exchange Reaction $\text{H}_2 + \text{H}'_2\text{O} \rightarrow \text{HH}' + \text{HOH}'$

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Abstract



H₂O and H₂ are ubiquitous in the universe and their collisions play a crucial role in astrophysical processes. The reaction between the two also provides a prototype for understanding dynamics through four-center transition states. In this work, we adopted the strategy of combining two ab initio methods, CCSD(T)-F12a/AVTZ and MRCI-F12+Qrot/AVTZ, to provide a balanced description for all regions of the configuration space, including one hydrogen exchange channel and two dissociation channels, namely $\text{H}_2 + \text{H}_2\text{O}$, $\text{H} + \text{H} + \text{H}_2\text{O}$, and $\text{H} + \text{OH} + \text{H}_2$. About 40500 points were sampled to cover all dynamically relevant space, and the permutation invariant polynomial-neural network (PIP-NN) method was employed to develop a high-precision full-dimensional potential energy surface (PES), with a total fitting error of 0.055 kcal/mol. Using a quasi-classical trajectory (QCT) method, the reaction dynamics and mode specificity of the hydrogen exchange channel were studied on the PES. It has been found that the stretching mode of H₂, the bending, the symmetric stretching, the asymmetric stretching mode of H₂O, and the translational mode can all promote reactivity. The strongest promotion effect comes from the H-H stretching mode. The Sudden Vector Projection (SVP) model was applied to predict mode specificity effects and rationalize the product energy partitioning. In both cases, the results are generally consistent. Moreover, a detailed analysis of the product angular distributions shows that the sideways scattering is dominant. We are committed to developing not only the reaction PES but also the interaction PES. Currently, we have built a high-accuracy interaction PES for (HF)₃ based on the Δ -Machine Learning Approach.

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NOTES

Characterizing the structures of hydrated benzoyl fluoride by rotational spectroscopy

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The role of fluorine substitution in the synthesis of pharmaceutical compounds and novel materials has been extensively investigated based on its stereoelectronic effects, which have strong influence on the molecular structures and its interactions with surroundings. Here we report the pure rotational spectroscopy of the benzoyl fluoride (*c*-C₆H₅COF)-water complexes, investigated by the chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy within 2-8 GHz frequency range ^[1] in Shanghai. All the rotational transitions belong to benzoyl fluoride, benzoyl fluoride-water, and benzoyl fluoride-water dimer have been assigned. The spectra with splitting patterns indicate the coupling of the internal motions to whole molecular rotation. The rotational spectra of mono-substituted ¹³C isotopologues have also obtained in natural abundance, which can give accurate structural information. Compared with the structures of benzaldehyde and other fluorinated benzaldehyde, the above results of benzoyl fluoride and its hydrated complex are helpful for understanding the effect of fluorine substitution on the intermolecular potentials.

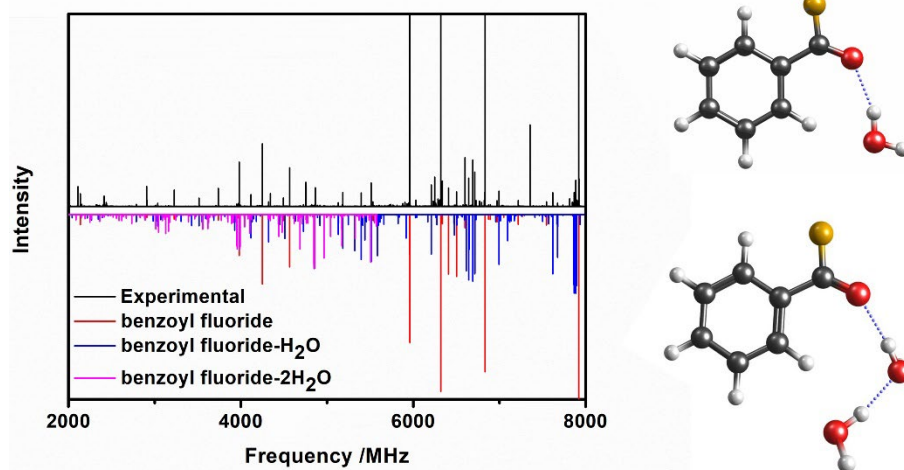


Figure 1. The rotational spectra and structures of benzoyl fluoride-water clusters.

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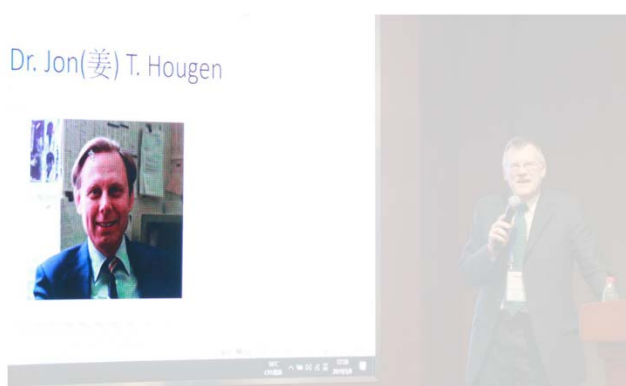
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... because he cared for the future ...

*Written by
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October 2022*

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Approved by the AWMS 2022 organizing committee