The 4th Workshop on Frontier Investigations of Key Species in Atmospheric Chemistry and Astrochemistry

Program Book

Jan. 8, 2025 R210, Science Building II Department of Applied Chemistry National Yang Ming Chiao Tung University

Introduction

This workshop is part of the activities of the NSTC Summit Project "Frontier Investigations of Key Species in Atmospheric Chemistry and Astrochemistry (II)". The project focus on two major research directions:

(A) Key reactions and intermediates in atmospheric chemistry.

(B) Key reactions and species in astrochemistry.

The participants mainly come from the research groups of Prof. Yuan-Pern Lee (NYCU), Prof. Yasuki Endo (NYCU), Prof. Henryk Witek (NYCU), Dr. Jim Jr-Min Lin (IAMS), Dr. Pei-Ling Luo (IAMS), Dr. Jer-Lai Kuo (IAMS), Dr. Yu-Jong Wu (NSRRC), Prof. Yu-Jung Chen (NCU), Prof. Yuan-Pin Chang (NSYSU), Prof. Daniel Harsono (NYU), and Dr. Mao-Chang Liang (IES). The aim of this workshop is to provide an opportunity to share the recent research findings and future plans of each group. We would like to invite all members of these groups to participate in this workshop.

In this one-day workshop, we will have talks from each of the groups.

Session A: each presenter as a full 30 min slot, the talk should be ca. 20 min with a 10 min Q&A period.

Session B: each presenter as a full 20 min slot, the talk should be ca. 10 min with a 10 min Q&A period.

We invite postdoc/RA/student to present in the poster section, which will also include a flash talk session where the poster presenter has the chance to promote their poster.

Speakers

A-1	Yuan-Pin Chang	National Sun Yat-sen University
A-2	Chun-Yi Lee	National Central University
A-3	Daniel Harsono	National Tsinghua University
A-4	Yu-Jong Wu	National Synchrotron Radiation Research Center
B-1	Yen-Hsiu Lin	Academia Sinica
B-2	Chen-An Chung	National Yang Ming Chiao Tung University
B-3	I-Yun Chen	Academia Sinica
B-4	Qian-Rui Huang	Academia Sinica

Sponsored by National Science and Technology Council (NSTC113-2639-M-A49-002-ASP)

Program

09:00~	Registration		
09:30-10:00	A-1 Yuan-Pin Chang (National Sun Yat-sen University)		
	Studying multiphase reactions in microdroplets via single particle		
	spectroscopic platform		
10:00-10:30	A-2 Chun-Yi Lee (National Central University)		
	EUV-induced CO_2 formation on water-covered carbon dust: The role		
	of dust properties in astrochemistry		
10:30-11:00	Coffee break & photo		
11:00-11:30	A-3 Daniel Harsono (National Tsing Hua University)		
	Chemical inventory of planet-forming environment		
11:30-12:00	A-4 Yu-Jong Wu (National Synchrotron Radiation Research		
	Center)		
	From extended red emission to blue luminescence via graphene-based		
	models		
12:00-13:30	Lunch (PI discussion in R323)		
13:30-13:50	B-1 Yen-Hsiu Lin (Academia Sinica)		
	Measurement of the absolute UV photodissociation cross section of		
	anti-CH ₃ CHOO		
13:50-14:10	B-2 Chen-An Chung (National Yang Ming Chiao Tung University)		
	The pressure dependence of the yield of syn-MVKO in the reaction of		
	$(Z)-C_2H_3C(CH_3)I + O_2$ determined with a simultaneous IR/UV dual		
	probe		
14:10-14:30	B-3 I-Yun Chen (Academia Sinica)		
	Measurements of absolute line strengths and determination of band		
	intensity for HO ₂ radical in the OH-stretching v_1 fundamental band		
	near 3 µm		
14:30-14:50	B-4 Qian-Rui Huang (Academia Sinica)		
	Artificial translation modes for efficient anharmonic vibrational		
	analysis of hydrogen-bonded systems		
14:50-15:30	Coffee break		
15:30-16:30	Flash talks for poster presenters		
16:30-20:00	Poster section		
18:00~	Dinner		

Poster Presentations

#	Presenter	Title
P01	Yi-Hsuan Chiu	Spectrally resolved VUV photoinduced energy transfer in layered ices
P02	Shun-Lin Tseng	The mechanisms of pure H_2S ice and H_2O+H_2S ice mixtures under 1 keV electron irradiation
P03	Cheng-Han Tsai	Fourier-transform microwave spectrum of the two conformers of the CHClCHO radical
P04	Yu-Hsuan Chang	Spectral studies of the reaction of the Criegee intermediate CH ₃ CHOO with HNO ₃ using a step-scan Fourier-transform infrared spectrometer
P05	Ssu-Ju Huang	Spectral studies of the reaction of the Criegee intermediate methyl vinyl ketone oxide with HNO ₃ using a step-scan Fourier-transform infrared absorption spectrometer
P06	Jun-Ying Feng	Infrared spectra of protonated glycine $(H^+NH_2CH_2C(O)OH)$ isolated in solid <i>para</i> -H ₂
P07	Ju-Yin Hsu	Formation reaction mechanism and infrared spectra of Criegee intermediate 3-pentene-2-one oxide and its associated precursor and adduct radicals
P08	Tang-Yu, Kao	Rate coefficients of <i>syn-/anti</i> -CH ₃ CHOO with HCl and CH ₃ CHI with O ₂ investigated with an IR/UV dual laser absorption system
P09	Prasad Ramesh Joshi	Introduction of a novel method for H atom generation in solid p - H ₂ and its application in the reaction with acetaldehyde [CH ₃ C(O)H]: An approach to astrochemistry
P10	Hsin-Yu Tang	Electronic states of isoquinoline
P11	Jun-Hao Yu	A study of the protonated nicotine spectrum approached by applying the discrete variable representation technique in protonated-pyridine and N-methylpyrrolidine
P12	Dong Cao Hieu	A study on conformational changes induced by methyl side chains in protonated tripeptides assisted by NNP
P13	Po-Jen Hsu	Hydrogenbondnetworkstructuresofprotonatedmethanol/ethanolmixedclustersprobedbyinfraredspectroscopycombinedwith a deep-learningstructuresamplingapproach
P14	Huu Trong Phan	Unravelling the low-energy conformers of di-saccharides with first-principles accuracy assisted by neural network potentials
P15	Chih-Hao Chin	Radical-molecular reaction dynamics probed using ab initio/RRKM calculations: $CH_2(^1A_1)$ + acetylene
P16	Sheng-Lung Chou	VUV photolysis of silane with nitric oxide in solid neon

Studying multiphase reactions in microdroplets via single particle spectroscopic platform

Y.-P. Chang

Department of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan e-mail: <u>ypchang@mail.nsysu.edu.tw</u>



This study used aerosol optical tweezers coupled with Raman spectroscopy to study various multiphase reactions in optically trapped single microdroplets, such as the interfacial oxidation reaction of droplet thiosulfate and gaseous ozone [1-2] and formation of methanediol in microdroplets exposed to gaseous formaldehyde. The aim is to elucidate the roles of interface and bulk reactions in aerosol chemistry and the complicate interplays between physicochemical properties and chemistry of atmospheric aerosol. The time-resolved Raman spectra of optically trapped single microdroplets, such as droplet radius, refractive index, solute concentrations, pH, ionic strength, diffusivity ... etc. Furthermore, a multi-layer kinetic model dedicated to aerosol chemistry [3] is used to simulate the multiphase reactions on the aerosol surface and bulk reactions. Our results demonstrates that the application of aerosol optical tweezers coupled with Raman spectroscopy can be a versatile tool to elucidate the aerosol reaction kinetics.



Fig. 1. (Left) Schematics of multiphase kinetics model utilized to retrieve the kinetics of interfacial thiosulfate ozonolysis. (Right) The intermolecular interactions between thiosulfate and organics limit the observed reaction kinetics of microdroplets.

References

[1] S.-H. Hsu, F.-Y. Lin, G. G. Huang, Y.-P. Chang, J. Phys. Chem. C 127, 6248 (2023).

4

- [2] T.-C. Hung, F.-Y. Lin, S.-H. Hsu, T. Kasai, Y.-P. Chang, *Environ. Sci. Atmos.* 4, 1398 (2024).
- [3] M. Shiraiwa, C. Pfrang, U. Pöschl, Atmos. Chem. Phys. 10, 3673 (2010).

EUV-induced CO₂ formation on water-covered carbon dust: The role of dust properties in astrochemistry

<u>C.-Y. Lee¹</u>, K.-J. Chuang², Y.-Y. Hsu¹, G. Rouillé², C. Jäger³, Th. Henning⁴, Y.-J. Chen¹

¹Department of Physics, National Central University, Taiwan ²Laboratory for Astrophysics, Leiden Observatory, Leiden University, the Netherlands

³Laboratory Astrophysics Group of the Max Planck Institute for Astronomy at the Friedrich Schiller University Jena, Germany ⁴Max Planck Institute for Astronomy, Germany e-mail: kailee@phy.ncu.edu.tw



The unexpectedly high abundance of CO₂ in interstellar ices, surpassing predictions from gasphase chemistry, points to alternative formation mechanisms. Carbonaceous dust grains, known as scaffolds for interstellar ice formation, may interact with condensed H₂O under energetic irradiation to drive chemical transformations. Previous X-ray studies (Chuang et al. 2023 [1]) demonstrated the formation of CO and CO₂ through oxidation of carbonyl groups at the interface of water ice and amorphous carbon dust.

Building on these findings, this study explores CO_2 production under EUV irradiation, utilizing amorphous carbon (a-¹³C) and hydrogenated amorphous carbon (a-¹³C:H) with varying thicknesses. A key observation is that CO_2 forms prior to CO during irradiation, a phenomenon not documented in earlier X-ray experiments. As shown in Fig. 1, thicker dust layers enhance CO_2 yields due to increased interaction volumes and reactive surface areas, while hydrogenation significantly boosts production efficiency, aligning with results from ion bombardment experiments (Raut et al. 2012 [2]).

These results underscore the pivotal role of carbonaceous dust in CO₂ formation, providing a robust explanation for the substantial solid-phase CO₂ observed in astrophysical environments and highlighting the importance of dust-mediated chemical processes in interstellar ice chemistry.



Fig 1. Left: The evolution of ¹³CO₂ formation during EUV irradiation. Right: The maximum formation of ¹³CO₂ and the formation cross section in varying thicknesses of carbon dust grains. **References**

[1] K.-J. Chuang, C. Jager, N.-E. Sie, et al *ApJ*, **956**, 57 (2023)

[2] U. Raut, D. Fulvio, M. Loeffler, R. Baragiola, ApJ, 752, 159 (2012)

Chemical inventory of planet-forming environment

<u>D. Harsono</u> Institute of Astronomy, Department of Physics, National TsingHua University, Hsinchu, Taiwan e-mail: <u>dharsono@gapp.nthu.edu.tw</u>



A-3

One of the biggest questions in astrophysics and astrochemistry is whether or not the chemical composition of meteorites is inherited from the natal molecular clouds before star formation. There is a line of evidence of chemical inheritance from some volatiles, while some volatiles and refractories from the solar system indicate a complete chemical reset. In the past few years, my collaborators and I have studied the gas-phase water toward a number of protostellar sources to elucidate the water inheritance as traced by the deuteration process. Furthermore, with JWST, we can start to unveil the chemical inventory in the solid phase in addition to the isotopic fractions to understand the chemical changes that may or can take place during the early stages of star and planet formation. I will end by discussing the current and future projects with ALMA and JWST.



Fig. 1. Comparative analysis of the water D/H ratios in Orion protostars and other protostars with comets.

- [1] J. J. Tobin, M. L. R. van't Hoff, M. Leemker, et al., *Nature* **615**, 227 (2023).
- [2] M. K., McClure, W. R. M. Pontoppidan, N. Crouzet, et al., Nat. Astron. 7, 431 (2023).

From extended red emission to blue luminescence via graphene-based models

<u>Y.-J. Wu^{1,2}</u>

¹National Synchrotron Radiation Research Center, Hsinchu, Taiwan
²Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan e-mail: <u>yjwu@nsrrc.org.tw</u>



Understanding the enigmatic luminescence phenomena in astrophysical environments, such as the Extended Red Emission (ERE) and Blue Luminescence (BL), is crucial for unraveling the chemistry of interstellar media. This presentation explores graphene and its derivatives as plausible carriers for these emissions. Laboratory investigations reveal that far-ultraviolet-treated graphene produces structural defects and graphene quantum dots, which satisfy the spectral and efficiency requirements for ERE [1]. Similarly, nitrogendoped graphene demonstrates photoluminescence closely resembling BL observed in the Red Rectangle Nebula [2], highlighting the role of heteroatomic substitutions in altering optical properties. By combining experimental results with astrophysical implications, this study establishes graphene-based materials as compelling models for interstellar luminescence and provides insights into the molecular evolution of cosmic carbonaceous species.

References

S.-L. Chou, W.-B. Shih, M.-Z. Yang, et al., *Astrophys. J.* 944, 18 (2023).
 S.-Y. Lin, S.-L. Chou, T.-P. Huang, et al., *Astrophys. J.* 977, 230 (2024).

Measurement of the absolute UV photodissociation cross section of *anti*-CH₃CHOO

<u>Y.-H. Lin</u>^{1,2}, J. J.-M. Lin^{1,2} ¹Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan ²Department of Chemistry, National Taiwan University, Taipei, Taiwan e-mail: thereistoomuchtrouble@email.com



Absolute photodissociation cross section represents the ability of a molecule interact with a photon, which is crucial for the derivation of the photolysis rate and the absolute concentration of the molecule with absorption spectroscopy.

Generated from the ozonolysis of alkene, Criegee intermediates are important atmospheric oxidants. Many studies focus on methyl Criegee intermediate (CH₃CHOO), which has two conformers: *syn*-CH₃CHOO and *anti*-CH₃CHOO. However, the absolute UV photodissociation cross section of *anti*-CH₃CHOO has not been measured yet.

Our group try to measure this parameter with the photodepletion method in a flow cell system. [1-2] CH₃CHOO is generated by 248 nm photolysis of CH₃CHI₂ and the following reaction of CH₃CHI and O₂. CH₃CHOO is photo-depleted by a 351 nm laser pulse, and the amount of depletion is measured by UV absorption spectroscopy with a 365 nm laser as the probe light and a balanced photodiode as the detector. The probe light and photolysis laser are coupled and decoupled with two 355 nm long pass filters. The reactivity of *anti*-CH₃CHOO with CH₃OH is much higher than that of *syn*-CH₃CHOO. [3] Therefore, we use CH₃OH as a scavenger to extract the signal of *anti*-CH₃CHOO. CH₃CHOO is also generated by the photolysis of CH₃CHI₂ with the 351 nm laser pulse. To determine the fraction of depletion, we control the concentration of O₂ to tune the reaction rate of CH₃CHI with O₂ and fit the time profile of *anti*-CH₃CHOO. The 351 nm laser fluence is measured by a power meter, and calibrated with the measurement of the well-known NO₂ cross section [4]. With the laser flux, the reported unity photodissociation yield [5], and the measured depletion fraction, we can determine the absolute UV photodissociation cross section of *anti*-CH₃CHOO.

- [1] Y.-H. Lin, J. J.-M. Lin, J. Chin. Chem. Soc. 69, 152 (2022).
- [2] Y.-H. Lin, K. Takahashi, J. J.-M. Lin, Phys. Chem. Chem. Phys. 24, 10439 (2022).
- [3] W. Chao, Y.-H. Lin, C. Yin, et al., Phys. Chem. Chem. Phys. 21, 13633 (2019).
- [4] K. Bogumil, J. Orphal, T. Homann, et al., *J. Photochem. Photobiol. A* **157**, 167 (2003).
- [5] M. F. Vansco, H. Li, M. I. Lester, J. Chem. Phys. 147, 013907 (2017).

The pressure dependence of the yield of syn-MVKO in the reaction of (Z)-C₂H₃C(CH₃)I + O₂ determined with a simultaneous IR/UV dual probe

C.-A. Chung¹, T.-Y. Kao¹, Y.-P. Lee^{1,2}

¹Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan. ²Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan. e-mail: bruce84723@email.com

Carbonyl oxides, also known as Criegee intermediates (CIs), play a key role in atmospheric chemistry. Methyl vinyl ketone oxide [C₂H₃C(CH3)OO, MVKO] exists in distinct syn- and anti-conformations, which can be differentiated by their temporal profiles in the UV-Vis and mid-infrared spectral regions. In this study, we utilized a light-emitting diode at 286 nm, an infrared quantum-cascade laser near 11 μ m, and an ultraviolet laser at 335 nm to probe the precursor (Z)-1,3-diiodobut-2-ene, syn-trans-MVKO, and syn-/anti-MVKO, respectively, in the reaction of (Z)-C₂H₃C(CH₃)I with O₂. The absolute yield of syn-MVKO decreased significantly from 77% to 26% as the total pressure increased from 2 to 100 Torr. The relative branching ratio of syn- to anti-MVKO was estimated to be 80:20. In addition, the absorption cross section of the (Z)-C₂H₃C(CH₃)I radical at 286 nm was determined to be $1.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.

cm³



- [1] Y.-H. Lin, Y.-L. Li, W. Chao, et al., *Phys. Chem. Chem. Phys.* 22, 13603 (2020).
- [2] W.-L. Ting, C.-H. Chang, Y.-F. Lee, et al., J. Chem. Phys. 141, 104308 (2014).
- [3] Y.-H. Huang, L.-W. Chen, Y.-P. Lee, J. Phys. Chem. Lett. 6, 4610 (2015).

Measurements of absolute line strengths and determination of band intensity for HO_2 radical in the OH-stretching v₁ fundamental band near 3 µm

<u>I.-Y. Chen</u>^{1, 2}, C.-W. Chang^{1, 3}, P.-L. Luo¹ ¹Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan ²Department of Chemistry, National Taiwan University, Taipei, Taiwan

³Molecular Science and Technology, National Taiwan University, Taipei, Taiwan e-mail: <u>yiyunchen21@gmail.com</u>

In this work, absolute line strengths for hydroperoxyl radical (HO₂) in the fundamental OH-stretching band (v₁) near 3456 cm⁻¹ were first determined by using the synchronized two-color time-resolved dual-comb spectrometer. HO₂ radicals were generated through 351-nm laser photolysis of the flowing gas mixture of Cl₂/CH₃OH/O₂. By simultaneously probing the transitions of HO₂ in both v₁ and v₃ band, the absolute line strengths of the HO₂ v₁ 9_{1,8} \leftarrow 9_{0,9} F_{1,2} and 1_{1,1} \leftarrow 1_{0,0} F₁ transitions near 3456 cm⁻¹ thus can be determined relative to the previously measured accurate line strengths of the v₃ 13_{1,13} \leftarrow 12_{1,12} F_{1,2} transitions at 1122.983 cm⁻¹. The line strengths of the HO₂ v₁ transitions were obtained with an uncertainty of <7%, but those values were approximately 3.3 times of that recommended by the HITRAN database [1]. Moreover, the band intensity of the HO₂ v₁ measured in the range 3434–3472 cm⁻¹ combined with spectral simulation using PGOPHER [2].

- [1] I. E. Gordon, L. S. Rothman, R. J. Hargreaves, et al., J. Quant. Spectrosc. Radiat. Transfer 277, 107949 (2022).
- [2] C. M. Western, J. Quant. Spectrosc. Radiat. Transfer 186, 221 (2017).



Artificial translation modes for efficient anharmonic vibrational analysis of hydrogen-bonded systems

<u>Q.-R. Huang</u>, J.-L. Kuo Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan e-mail: <u>grhuang@gate.sinica.edu.tw</u>

Hydrogen bonds play a pivotal role in defining the vibrational characteristics of molecular systems. In anharmonic vibrational analysis, hydrogen bond formation significantly constrains vibrational motions, leading to pronounced anharmonic couplings between OH/NH stretching and hydrogen-bond stretching motions. While this coupling is straightforward to analyze in smaller systems, for larger systems, normal mode analysis often mixes hydrogen-bond stretching motions with low-frequency backbone vibrational modes. This overlap increases the computational effort required to incorporate such effects into reduced-dimensional analyses. To address this challenge, we propose an innovative approach using artificial translation modes to isolate and represent hydrogen-bond stretching motions. This method effectively captures the essential coupling between OH/NH stretching and low-frequency modes while significantly reducing the computational complexity by minimizing the number of modes required.

- [1] S. Mishra, H. Q. Nguyen, Q.-R., Huang, et al., J. Chem. Phys, 153, 194301 (2020).
- [2] M. Barp, F. Kreuter, Q.-R. Huang, et al., *ChemRxiv* (DOI:10.26434/chemrxiv-2024-47m1r)

Spectrally resolved VUV photoinduced energy transfer in layered ices

<u>Y.-H. Chiu</u>¹, C.-C. Huang¹, Yen-Yu Hsu¹, Chun-Yi Lee¹, G. M. Muñoz Caro², Y.-J. Chen¹ ¹Department of Physics, National Central University, Taoyuan City, Taiwan ²Centro de Astrobiología (INTA-CSIC), Torrejón de Ardoz, Madrid, Spain e-mail: <u>gina.yhchiu@gmail.com</u>



P01

The non-thermal desorption of CO ice driven by vacuum ultraviolet (VUV) photons and cosmic rays has been widely studied over the past few decades. Using tunable, monochromatic synchrotron radiation to irradiate pure CO ice, Fayolle et al. (2011) demonstrated that CO photodesorption is wavelength-dependent. The features between 132 and 160 nm are attributed to vibronic bands in electronic transitions. Building on this, in a study involving N₂/¹³CO layered ice experiments, Bertin et al. (2013) suggested that photodesorption mechanisms are indirect, with energy transfer occurring between molecular species with non-coinciding electronic transition states.

In this study, pure ¹³CO ice and ¹³CO ice layered on Ar, CH⁴, or CH³OH ice are irradiated by tunable, monochromatic synchrotron radiation from the NSRRC. We aim to investigate energy transfer mechanisms through discrepancies in VUV absorption cross-sections among molecular species for the double-layered ice experiments. However, we found that an increased effective surface area enhances the photodesorption yield, while chemical reactions at the ice layer interface inhibit photodesorption. Therefore, the effects of these two factors should be considered when discussing energy transfer using the photodesorption of layered ice. Furthermore, in the pure ice experiments, we aim to determine the energy transfer length for each electronic transition.



Fig. 1. The VUV-absorption cross sections $\sigma(\lambda)$ as a function of wavelength for CO, CH₄, and CH₃OH ices (Cruz-Diaz et al. 2014a, 2014b), along with the VUV spectrum of the beamline BL04C at the NSRRC.

- [1] M. Bertin, E. C. Fayolle, C. Romanzin, et al., Astrophys. J. 779, 120 (2013).
- [2] G. A. Cruz-Diaz, G. M. Muñoz Caro, Y.-J. Chen, et al., A&A, 562, A119 (2014).
- [3] G. A. Cruz-Diaz, G. M. Muñoz Caro, Y.-J. Chen, et al., A&A, 562, A120 (2014).
- [4] E. C. Fayolle, M. Bertin, C. Romanzin, et al., Astrophys. J. Lett. 739, L36 (2011).

The mechanisms of pure H₂S ice and H₂O+H₂S ice mixtures under 1 keV electron irradiation

<u>S.-L. Tseng</u>, C.-Y. Lee, Y.-J. Chen Department of Physics, National Central University, Taiwan e-mail: <u>ninomiyarin0309@gmail.com</u>



Sulfur is integral to prebiotic chemistry in astrophysical settings, yet sulfur-bearing molecules are less prevalent in the interstellar medium (ISM) than theoretical models predict. This discrepancy, often called the "missing sulfur" problem, suggests that sulfur may be sequestered in solid-phase reservoirs, such as ice mantles on dust grains within dense molecular clouds. Among these sulfur species, hydrogen sulfide (H₂S) ranks as the third most abundant, following atomic sulfur (S) and sulfanyl radicals (HS).

Understanding the behavior of H_2S in interstellar ices is crucial, as it influences the chemical pathways leading to more complex sulfur-containing compounds. Studies have shown that H_2S , when subjected to ultraviolet (UV) photoprocessing within H_2O -rich ices, can lead to the formation of species such as H_2S_2 , which further dissociates into various sulfur allotropes up to S_8 . These findings imply that a significant portion of the missing sulfur could reside in the form of polymeric sulfur within dust grains.

This study examines the effects of 1000 eV electron irradiation on pure H_2S ice deposited at varying temperatures, as well as on mixtures of H_2S and water (H_2O) ices. Our objective is to elucidate how deposition temperature and the presence of water influence the depletion of H_2S and the subsequent formation of sulfur-containing products. Insights from this research will enhance our understanding of sulfur chemistry in the ISM and contribute to resolving the sulfur depletion enigma in dense interstellar regions.

- [1] D. E. Anderson, E. A. Bergin, S. Maret, V. Wakelam, Astrophys. J. 779, 141 (2013).
- [2] M. Garozzo, D. Fulvio, Z. Kanuchova, et al., A&A 509, A67 (2010).
- [3] P. Rivière-Marichalar, A. Fuente, G. Esplugues, et al., A&A 665, A61 (2022).

Fourier-transform microwave spectrum of the two conformers of the CHClCHO radical

<u>C.-H. Tsai</u>, Y. Endo National Yang Ming Chiao Tung University, Hsinchu 300, Taiwan. e-mail: <u>hank.sc12@nycu.edu.tw</u>



Chlorine atom plays important roles in reactions in the ozone layer and troposphere. Addition reaction products of chlorine and oxygen atoms on olefins, such as RCHClCH₂ or RCHCH₂O, have attracted much attention. Furthermore, investigations of addition reaction pathways and optimizations of reaction conditions contribute to the discovery of novel chemical transformations, and an LIF spectrum of CHClCHO has been reported on this context.¹ In the present study, pure rotational transitions of CHClCHO have been observed using the Fourier-transform microwave spectrometer in the region of 8 GHz to 34 GHz. Two isomers, trans- and cis-CHClCHO were tried to produce by discharging gaseous mixtures of *trans*- and *cis*-1,2-dichloroethylene with O₂ diluted in Ar, respectively. Nine *a*-type transitions were observed for the trans- $CH^{35}ClCHO$, yielding precisely determined rotational and fine structure constants, in addition to the hyperfine coupling constants of chlorine and two protons, with the standard deviation of the fit only 2.8 kHz. The determined molecular constants show that the unpaired electron of the radical is localized on the out-of-plane π -orbitals of the carbon bonded with Cl. The *cis*-CHClCHO were not observed, even if we used *cis*-1,2-dichloroethylene as a precursor. We think it is due to the fact that the intermediate *cis*-CHClCH is easily transform to *trans*-CHClCH.²

- [1] S. Inomata, I. Bridier, M. Furubayashi, et al., J. Phys. Chem. A 105, 7559 (2001).
- [2] C. Cabezas, C.-H. Chang, J.-C. Guillemin, Y. Endo, Phys. Chem. Chem. Phys. 24, 25099 (2022)

Spectral studies of the reaction of the Criegee intermediate CH₃CHOO with HNO₃ using a step-scan Fourier-transform infrared spectrometer

<u>Y.-H. Chang¹</u>, Y.-P. Lee^{1,2}



 ¹Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu 300093, Taiwan.
 ²Centre for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu 300093, Taiwan.
 e-mail: mowmoww14@gmail.com

The reactions of Criegee intermediates with HNO₃ play a crucial role in the polluted urban atmosphere because of their large reaction rates and the significant concentration of HNO₃. The only experimental study with infrared absorption on the reaction of the simplest Criegee intermediate CH₂OO with HNO₃ by Chung et al. reported three pressuredependent channels: formation of the hydrogen-transferred adduct NO₃CH₂OOH, OH + $H_2C(O)ONO_2$, and $HO_2 + H_2CO + NO_2$ [1]. We recorded time-resolved infrared absorption spectra of transient species and end products in a flowing mixture of CH₃CHI₂/HNO₃/O₂ irradiated at 308 nm at 298 K to initiate the reaction CH₃CHOO + HNO₃. Five bands near 1677.4, 1369.2, 1288.3, 1062.5 and 832.3 cm^{-1} were assigned to the hydrogen-transferred adduct, nitrooxyethyl hydroperoxide (NEHP, NO₃CHCH₃OOH). The observed wavenumbers and relative intensities agree with the anharmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVTZ method, but its conformation could not be definitively assigned because of the similarities in IR spectra of the syn- and anti- conformers. At a later reaction period, absorption bands of H₂O and the end product acetyl nitrate, NO₃C(O)CH₃, were observed at 1793.2, 1732.4 and 1152.6 cm⁻¹. These species were produced from the dehydration of NO₃CHCH₃OOH. No other decomposition channels were observed. We also calculated the potential energy scheme of this reaction system with the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method. Compared with the results by Chung et al. for the reaction $CH_2OO + HNO_3$, we observed the formation of NEHP and the formation of $NO_3C(O)CH_3 + H_2O$ as the only two major channels, indicating that the additional methyl group in NEHP might facilitate rapid quenching to diminish some decomposition channels. We also determined the rate coefficient of the reaction of CH₃CHOO with HNO₃ is about 1.4×10^{-10} cm³ molecule⁻¹ s⁻¹ ¹ which is previously unreported.

References

[1]. C.-A. Chung, C.-W. Hsu, Y.-P. Lee, J. Phys. Chem. A 126, 5738 (2022).



P05

<u>S.-J. Huang</u>¹, Y.-P. Lee^{1,2} ¹Department of Applied Chemistry and Institute of Molecular Science,

National Yang Ming Chiao Tung University, Hsinchu, Taiwan ²Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan e-mail: ssuju1119.sc12@nycu.edu.tw

Methyl vinyl ketone oxide [MVKO, C₂H₃C(CH₃)OO] is an important Criegee intermediate produced from ozonolysis of isoprene, which is the most abundant volatile organic compounds emitted into the atmosphere after methane. The reactions of Criegee intermediates with HNO₃ may compete with those involving water vapor under conditions of significant pollution and moderate relative humidity, potentially leading to the formation of secondary organic aerosols and influencing atmospheric composition.¹ Therefore, the reaction between MVKO and HNO₃ plays a significant role in atmospheric chemistry.

Chung et al. reported three product channels of the reaction $CH_2OO + HNO_3$ using a step-scan Fourier-transform infrared absorption spectrometer.² The relative yields of these three channels were found to be pressure-dependent. In this work, we recorded time-resolved infrared absorption spectra of transient species produced upon irradation at 248 nm of a flowing mixture of (*Z*)-(CH₂I)HC=C(CH₃)I/HNO₃/O₂ at 298 K. Careful analysis revealed that observed new bands could be deconvoluted into the absorption of two distinct products: a slow decay species, the adduct 2-hydroperoxy-2-nitroxybut-3-ene [HPNB, (C₂H₃)(CH₃)C(ONO₂)OOH], and a fast decay species, $C_2H_3CH_3C(O)ONO_2$. Seven bands near 1660, 1378, 1346, 1304, 1100, 1060 and 837 cm⁻¹ were assigned to the absorption of the hydrogen-transferred adduct HPNB according to the predicted IR spectrum using the B3LYP/aug-cc-pVTZ method; the conformation of HPNB could not be definitively determined. Another transient species from the dissociation channel was observed in the early stage of reaction. Two bands at 1683 and 1263 cm⁻¹ were tentatively assigned to $C_2H_3CH_3C(O)ONO_2$, produced from the fission of the O–O bond of internally hot HPNB (HPNB*).

- C. A. Taatjes, D. E. Shallcross, C. J. Percival, *Phys. Chem. Chem. Phys.* 16, 1704 (2014).
- [2] C.-A. Chung, C.-W. Hsu, Y.-P. Lee, J. Phys. Chem. A 126, 5738 (2022).

Infrared spectra of protonated glycine (H⁺NH₂CH₂C(O)OH) isolated in solid *para*-H₂

J.-Y. Feng¹, Y.-P. Lee^{1,2}

¹Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan ²Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan e-mail: <u>yplee@nycu.edu.tw</u>

The interstellar medium (ISM) contains gas and dust, with hydrogen making up about 70%. Organic molecules like water, methane, ammonia, and formaldehyde, believed to be abundant in early Earth's atmosphere, can form life-building components through external energy like collisions or UV radiation.[1,2] Aldehydes, amines, ketones, and sugars observed in the ISM may have played a role in prebiotic chemistry.[3–8] Glycine, the simplest amino acid, was first detected in the ISM by Kuan et al.,[9] supporting the theory that interstellar molecules contributed to life's origins. Cosmic rays ionize hydrogen, forming H_3^+ , which can transfer protons to glycine, creating protonated glycine. Recently, we provided the IR spectrum of protonated glycine isolated in solid *para*-H₂ in the range of 500–3700 cm⁻¹. The conformer of protonated glycine with the least energy has been observed.

- [1] P. Ehrenfreund, S. B. Charnley, Annu. Rev. Astron. Astrophys. 38, 427 (2000).
- [2] S. L. Miller, *BBA* **23**, 480 (1957).
- [3] S. K. Mondal, P. Gorai, M. Sil, et al., Astrophys. J. 922, 194 (2021).
- [4] R. H. Rubin, G. W. Swenson, Jr., R. C. Benson, H. L. Tigelaar, W. H. Flygare, *Astrophys. J.* 169, L39 (1971).
- [5] J. M. Hollis, F. J. Lovas, Anthony J. Remijan, et al. Astrophys. J. 643, L25 (2006).
- [6] D. T. Halfen, V. Ilyushin, L. M. Ziurys, Astrophys. J. 743, 60 (2011).
- [7] C. Bermúdez, B. Tercero, R. A. Motiyenko, et al., *A&A* 619, A92 (2018).
- [8] J. M. Hollis, F. J. Lovas, P. R. Jewell, Astrophys. J. 540, L107 (2000).
- [9] Y.-J. Kuan, S. B. Charnley, H.-C. Huang, et al., Astrophys. J. 593, 848 (2003).

<u>J.-Y. Hsu</u>¹, Y.-P. Lee^{1,2}

¹Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan
²Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan e-mail: hsudiana.sc13@nycu.edu.tw



P07

The five-carbon unsaturated Ciregee intermediate, 3-pentene-2-one oxide $[C_3H_5C(CH_3)OO]$ can be produced through atmospheric ozonolysis of substituted isoprenes, such as 2-methylpenta-1,3-diene or other branched unsaturated alkenes, making it of interest from an atmospheric chemistry perspective. Roy et al. reported a novel reaction scheme to generate 3-pentene-2-one oxide by photolysis of 2,4-diiodopent-2-ene $[CH_3(CHI)=(CH)C(CH_3)I]$ in O_2 .¹ In this study, we followed their method and photolyzed a mixture of 2,4-diiodopent-2-ene and N₂ using an excimer laser at 248 nm. The transient infrared spectra were recorded using a step-scan Fourier-transform infrared absorption spectrometer coupled with a multipass absorption cell. Comparison of observed spectra with calculation results identified (C₃H₅)C(CH₃)I but not (C₃H₅I)C(CH₃), indicating that photolysis of 2,4-diiodopent-2-ene preferentially breaks the allylic C–I bond rather than the vinylic C–I bond.

Upon adding O₂ at 14 Torr, the observed spectrum, which has one intense band near 906 cm⁻¹ and two weaker bands near 959 and 1006 cm⁻¹, matched best with the spectrum of the *tEE* conformer of the 3-pentene-2-one oxide simulated using the PGOPHER program, the simulated spectrum features a single intense O–O stretching band near 911 cm⁻¹ and three less intense bands around 955, 974 and 1016 cm⁻¹. However, a small contribution of other conformers of 3-pentene-2-one oxide could not be definitively excluded. The O–O stretching wavenumber at 906 cm⁻¹ of 3-pentene-2-one oxide is greater than that observed for smaller Criegee intermediates, indicating that the resonance stabilization enhance the O–O bond. The adduct $C_3H_5C(CH_3)IOO$ was also identified. With increasing pressure, the relative yield of 3-pentene-2-one oxide decreased, whereas the relative yield of adduct increased.

References

[1] T. K. Roy, T. Liu, Y. Qian, et al., Chem. Sci. 14, 10471 (2023).

Rate coefficients of *syn-/anti*-CH₃CHOO with HCl and CH₃CHI with O₂ investigated with an IR/UV dual laser absorption system

<u>T.-Y. Kao¹</u>, C.-A. Chung¹, Y.-P. Lee^{1,2}

¹Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu 300093, Taiwan.
²Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu 300093, Taiwan. e-mail: yrr687@gmail.com



Reactions between Criegee intermediates and hydrogen halides play important roles in atmospheric chemistry, particularly in the polluted urban atmosphere. We employed a multi-pass absorption flow cell with four probes to determine the rate coefficient of CH₃CHOO + HCl. Two quantum-cascade infrared lasers near 11 and 7 µm provided temporal profiles of *syn*-CH₃CHOO and a combination of CH₃CHOO and the hydrogentransferred adduct chloroethyl hydroperoxide (CEHP), respectively.[1] A light-emitting diode at 286 nm probed the concentration of the precursor [CH₃CHI₂], hence [CH₃CHI]₀ upon photolysis at 248 nm. The laser light at 351 nm probed the concentration of [CH₃CHOO]. By fitting the observed temporal profiles with a chemical model, we derived rate coefficients of *syn*-CH₃CHOO + HCl and *anti*-CH₃CHOO + HCl at 298 K to be $k_{\text{HCl}}^{\text{syn}}$ = (5.5 ± 1.0)×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ and $k_{\text{HCl}}^{\text{anti}}$ = (3.2 ± 0.7)×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, respectively; listed errors represent 95 % confidence level. The former agrees with the only literature value of $k_{\text{HCl}}^{\text{syn}}$ = (4.77 ± 0.95)×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ at 298 K and ~70 Torr,[2] whereas the latter was previously unreported and is ~5.8 times k_{syn} , demonstrating the conformation-specific reactivity for CH₃CHOO.

We also found that the rate coefficient of the formation reaction $CH_3CHI + O_2 \rightarrow CH_3CHOO + I$, $(3.8\pm0.7)\times10^{-12}$ cm³ molecule⁻¹ s⁻¹, is ~2.5 times smaller than those reported by Howes et al.[3] and Sheps et al.[4] who employed mass spectrometry and UV absorption, respectively.

- [1] Z.-S. Su, Y.-P. Lee, J. Phys. Chem. A 127, 6902 (2023).
- [2] S. Liu, X. Zhou, Y. Chen, et al., J. Phys. Chem. A 125, 8587 (2021).
- [3] N. U. M. Howes, Z. S. Mir, M. A. Blitz, et al., Phys. Chem. Chem. Phys. 20, 22218 (2018).
- [4] L. Sheps, A. M. Scully, K. Au, Phys. Chem. Chem. Phys. 16, 26701 (2014).

Introduction of a novel method for H atom generation in solid *p*-H₂ and its application in the reaction with acetaldehyde [CH₃C(O)H]: An

approach to astrochemistry

P. R. Joshi¹, Y.-P. Lee^{1,2}

¹Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan ²Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan e-mail: prasad.nctu@gmail.com

Hydrogen atom reactions plays vital role in the production of complex organic molecules (COM) in the interstellar medium (ISM). Our research focuses on the generation of radical intermediates via H-atom reactions leading to COM formation. We employed *para*-hydrogen (p-H₂) because it serves as a quantum solid matrix host and a medium for



efficient H atom generation. In the introductory method, H atoms were produced by irradiating CD₃I-doped p-H₂ at 266 nm, generating $^{\bullet}$ CD₃ radicals, which then reacted with H₂ in the dark via tunneling to produce CD₃H and H, ${}^{\bullet}CD_3 + H_2 \rightarrow CD_3H + H$, since the reaction has a barrier of 54 kJ mol⁻¹. The generated H atoms reacted with acetaldehyde [CH₃C(O)H], forming acetyl radical (CH₃•CO) and ketene (CH₂CO) through consecutives H abstractions on the formyl and methyl moieties, as predicted with potential energy diagrams. Compared to a previous established method for H-atom generation using successive UV (365 nm)/IR irradiation on the Cl₂-doped p-H₂, this novel method exclusively produces H atoms in darkness via tunneling, while the previous method generates H atoms during irradiation and only the remnant H atoms are available in darkness. In summary, the formation of the CH3 CO and CH2CO is negligible during irradiation and predominant in the dark with the new method, whereas their formation is major during irradiation and minor in darkness in the previous method. Both, CH₃•CO and CH₂CO are important precursors in the formation of COMs in the ISM.



P09

Electronic states of isoquinoline

<u>H.-Y. Tang</u>¹, I. Weber¹, H. A. Witek¹, Y.-P. Lee^{1,2} ¹ Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan ²Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan e-mail: <u>angelatang1224@gmail.com</u>



Nitrogen analogues of polycyclic aromatic hydrocarbons (PAHs) have been considered [1,2] as potential carriers of the diffuse interstellar bands (DIBs). To identify DIBs and assign them to previously recorded experimental spectra, we are currently working on establishing a computational protocol for accurate simulation of emission and absorption vibronic spectra. As a part of this effort, in the current work we use the TD-B3LYP/cc-PVDZ methodology as implemented in Gaussian 16 program package to study the electronic states of isoquinoline (Fig. 1). Equilibrium geometries of the ground and six low-lying excited singlet and four triplet states were optimized with TD-DFT calculations. It has been found that there is no equilibrium geometry for the second singlet excited state (S₂), owing to the existence of a conical intersection (CI) between the S₁ and S₂ states. We are currently optimizing the geometry of the CI point. Similar phenomenon seems to appear for the T₃/T₄ pair of states. We hope that our efforts will provide a rigorous explanation for the luminescence behavior of isoquinoline.



Fig. 1. Ground state and electronic states of isoquinoline.

- [1] A. L. Mattioda, D. M. Hudgins, C. W. Bauschlicher, et al., *J. Phys. Chem. A* **107**, 1486 (2003).
- [2] I. Weber, J. Langner, H. A. Witek, Y.-P. Lee, J. Phys. Chem. Lett. 15, 10696 (2024).

A study of the protonated nicotine spectrum approached by applying the discrete variable representation technique in protonated-pyridine and N-methylpyrrolidine

J.-H. Yu, Q.-R. Huang, J.-L. Kuo Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan e-mail: <u>opp40111@gmail.com</u>



Nicotine makes us relax and become addicted by the binding between nicotine and nicotinic acetylcholine receptors (nAChRs) Recently, nicotine-containing electronic cigarettes have been widely used with a non-combustible advantage. [1] It is imperative to ask how purer nicotine affects our bodies. Because the protonated site of nicotine affects the interaction with nAChRs, causing an alteration in biological activity, Garrett D. Santis et al. studied protonated nicotine by infrared photodissociation (IRPD) spectroscopy. [2] However, they encounter a puzzle in that the spectrum of water-protonated nicotine clusters has a complicated spectral pattern in the N-H stretching region, although there is only a significant N-H stretching fundamental transition within the harmonic approximation. Therefore, we plan to use the discrete variable representation technique to calculate the spectra, including anharmonic coupling, to assign the origin of this complicated band in the spectrum of nicotine with model systems of protonated-pyridine and N-methylpyrrolidine.

References

- [1] M.-M. Sharon A., G. Julie, J. A Groner, et al., *Pediatrics* 145, e20193997 (2020).
- [2] G. D. Santis, N. Takeda, K. Hirata, et al., J. Am. Chem. Soc. 144, 16698 (2022).

22

A study on conformational changes induced by methyl side chains in protonated tripeptides assisted by NNP

D. C. Hieu^{1,2,3}, P.-J. Hsu¹, J.-L. Kuo¹ ¹ Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, ² Molecular Science and Technology Program, Taiwan International Graduate Program, Academia Sinica, Taipei, 11529, Taiwan ³ International Graduate Program of Molecular Science and Technology (NTU-MST), National Taiwan University, Taipei 10617, Taiwan e-mail: dongcaohieu@gmail.com

Methylated peptides are an adaptable strategy for studying various biological processes, developing new medicinal medications, and improving our understanding of complex biochemical systems. The aided deep-learning neural network potential (DL-NNP) approach can be used to investigate the methylation of protonated tripeptides and how it affects the electronic structure and structural features. Our findings showed that methylation of protonated tri-glycine affects not only the protonated site but also the cis/trans isomers. Furthermore, the low-energy conformers of methylation-tripeptide that have been found are useful in clarifying experimental spectra and providing theoretical predictions for the signature frequency of distinct methylation tri-glycine. Besides, our NNP model training methodology is capable of effortlessly transitioning from a gas-phase model to a solution model (PCM-water technique) with an MAE of less than 3 kJ/mol.





Hydrogen bond network structures of protonated methanol/ethanol mixed clusters probed by infrared spectroscopy combined with a deep-learning structure sampling approach



P.-J. Hsu¹, A. Mizuide², J.-L. Kuo¹, A. Fujii² ¹Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan ²Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan e-mail: pjhsu@gate.sinica.edu.tw

We conducted measurements of the IR spectra of Ar-tagged H⁺(MeOH)₄ and H⁺(EtOH)₄, revealing that the former adopts a linear H-bond structure, whereas the latter displays features characteristic of a cyclic H-bond.¹ However, density functional theory (DFT) calculations suggested that the linear H-bond structure is more stable than the cyclic form in both systems and did not exhibit the characteristic vibration frequency of a double acceptor in a cyclic H-bond network (~3400 cm⁻¹). It was only upon incorporating dispersion corrections that the cyclic structure of H⁺(EtOH)₄ was found to be more stable than its linear counterpart. To elucidate the transition of the H-bond network from a linear to a cyclic configuration with increasing numbers of EtOH molecules, we examined the spectra of Ar-tagged H⁺(MeOH)_m(EtOH)_n clusters (m + n = 4). Additionally, we employed a neural network potential (NNP) through the deep-learning technique to replace DFT in the structure search process.² The local minima identified were subsequently re-optimized using DFT, uncovering numerous low-energy isomers. These isomers are pivotal in explaining the transition from linear to cyclic structures and further demonstrate that NNP-based structure searches, with DFT-level accuracy, are reliable and efficient.

References

[1] A. Fujii, N. Sugawara, P.-J. Hsu, et al., Phys. Chem. Chem. Phys. 20, 14971 (2018).

[2] S. Jindal, P.-J. Hsu, H. T. Phan, et al., *Phys. Chem. Chem. Phys.* 24, 27263 (2022).

Unravelling the low-energy conformers of disaccharides with first-principles accuracy assisted by neural network potentials

H. T. Phan^{1,2,3}, P.-K. Tsou¹, P.-J. Hsu¹, J.-L. Kuo¹



¹Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan
²Molecular Science and Technology Program, TIGP, Academia Sinica, Taipei, Taiwan
³Chemistry Department, National Tsing Hua University, Hsinchu, Taiwan

Email: phanhuutrong93@gmail.com

We introduce an efficient algorithm for exploring the conformational space of protonated disaccharides using neural network potentials (NNP) combined with local minima structure sampling. Our NNP models achieve decent accuracy with mean absolute errors of energy (E-MAE) of 3.02 kJ/mol and mean absolute errors of atomic forces (F-MAE) of 2.14 kJ/mol/Å, enabling reliable identification of low-energy conformers. The sampling approach leverages neutral di-saccharides local minima as template structure [1], substantially reducing computational costs while preserving structural relenvance. Validation through simulated vibrational spectra of the identified low-energy conformers shows decent qualitative agreement with experimental infrared multiple photon dissociation (IRMPD) spectra [2], demonstrating the effectiveness of combining NNP with strategic conformational sampling for advancing our understanding of protonated di-saccharide structures and their molecular spectroscopy.

- H. T. Phan, P.-K. Tsou, P.-J. Hsu, J.-L. Kuo, *Phys. Chem. Chem. Phys.* 26, 9556 (2024).
- [2] B. Schindler, L. Barnes, G. Renois, et al., Nat. Commun. 8, 973 (2017).

Radical-molecular reaction dynamics probed using ab initio/RRKM calculations: $CH_2(^1A_1)$ + acetylene

C.-H. Chin¹, Y.-J. Wu^{1,2}

¹National Synchrotron Radiation Research Center, Hsinchu, Taiwan
²Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan e-mail: <u>chin.ch@nsrrc.org.tw</u>

Ab initio CCSD(T)/CBS//B3LYP/6-311G(d,p) calculations of the singlet C_3H_4 potential energy surface were performed to investigate the reaction mechanism underlying the reaction of singlet methylene with acetylene. Rice-Ramsperger-Kassel-Marcus (RRKM) calculations^{1,2} of reaction rate constants and product branching ratios were performed under single-collision conditions. The results show that at the initial step of the $CH_2(^1A_1) + C_2H_2$ reaction carbon site attacks the π -orbital of the C₂H₂ molecule yielding cyclopropene (*c*C₃H₄, i1) without entrance barrier. The $CH_2(^1A_1) + C_2H_2$ reaction in the case of statistical behaviour is expected to produce a propargyl radical (CH₂CCH) plus an hydrogen atom (94.7%–89.2%), a propynylidene (HCCCH) plus a hydrogen molecule (4.7%–9.7%), and propynl radical (CH₂CC) plus a hydrogen molecule (0.6%-1.1%), with the most favourable pathways as follows: (1) initial adduct i1 by hydrogen migration to the formation of propyne (CH_3CCH , i4) then via an hydrogen elimination; and (2) a multistep route featuring an intramolecular ring-opening process involving hydrogen migration to yield allene (CH₂CCH₂, i3), followed by hydrogen elimination, thus forming a propargyl radical. This study completes a comprehensive investigation of the $CH_2(^1A_1) + C_2H_2$ reaction; its rate constants have been calculated from the collision energies at 0 to 8 kcal mol^{-1} , the reaction dynamics has been unraveled by crossed molecular beam experiments,³ and the reaction potential energy surface has been explored by ab initio calculations.



- [1] C.-H. Chin, T. Zhu, J. Z. H. Zhang, Phys. Chem. Chem. Phys. 21, 23044 (2019).
- [2] C.-H. Chin, T. Zhu, J. Z. H. Zhang, Phys. Chem. Chem. Phys. 23, 12408 (2021).
- [3] H. F. Davis, J. Shu, D. S. Peterka, J. Chem. Phys. 121, 6254 (2004).



VUV photolysis of silane with nitric oxide in solid neon

S.-L. Chou¹, C.-H. Chin¹, J. F. Ogilvie², Y.-J. Wu^{1,3}

¹National Synchrotron Radiation Research Center, Hsinchu, Taiwan
²Centre for Experimental and Constructive Mathematics, Department of Mathematics, Simon Fraser University, Burnaby, BC V5A1S6, Canada
³Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan e-mail: chou.sl@nsrrc.org.tw



We report the results of vacuum-ultraviolet (VUV) photolysis of SiH₄ and NO in solid neon at 3 K. Photolysis at 130 nm produced a complex range of products, including SiH₂, Si₂H₆, and various silicon oxides. Additionally, with the support of quantum-chemical calculations and D-isotopic substituted experiments, we tentatively identified a new species, H₂SiN(H)O, as an intermediate in the reaction of SiH₃ with NO. These findings provide new insights into the VUV photochemistry of SiH₄ and NO in a solid matrix and offer valuable information for understanding silicon-based combustion chemistry and astrochemistry.

Participants

Name	Institution/University	E-mail
Chen-An Chung	NYCU	bruce84723@gmail.com
Cheng-Han Tsai	NYCU	hank112211@gmail.com
Che-Wei Chang	IAMS	victorchang12323@gmail.com
Chien-Heng Chen	NYCU	pvnrt123@gmail.com
Chih-Hao Chin	NSRRC	chin.ch@nsrrc.org.tw
Ching-Hua Chang	NYCU	edward890615@nycu.edu.tw
Chun-Yi Lee	NCU	kailee@phy.ncu.edu.tw
Daniel Harsono	NTHU	dharsono@gapp.nthu.edu.tw
Dong Cao Hieu	IAMS	dongcaohieu@gmail.com
Han-Tang Chen	NYCU	thomaschen0405@gmail.com
Hsin-Yu Tang	NYCU	angelatang1224@gmail.com
Huu Trong Phan	IAMS	phanhuutrong93@gmail.com
I-Yun Chen	IAMS	yiyunchen21@gmail.com
Jer-Lai Kuo	IAMS	jlkuogm@gmail.com
Jim Jr-Min Lin	IAMS	jimlin@gate.sinica.edu.tw
Jun-Hao Yu	IAMS	opp40111@gmail.com
Jun-Ying Feng	NYCU	jyfeng.sc08@nycu.edu.tw
Ju-Yin Hsu	NYCU	hsudiana910210@gmail.com
Kai-His Hung	NYCU	explosioncena@gmail.com
Kai-ju Yu	NYCU	kambion5582@gmail.com
Kai-Yan Chen	NYCU	kaiyanchen.sc13@nycu.edu.tw
Kamal K Mishra	NYCU	mishra.kamal56@gmail.com
LIN Meng Yeh	NSRRC	lin.my@nsrrc.org.tw
Manish Kumar Tripathi	NYCU	manishkrtripathi.rs.chy17@itbhu.ac.in
Mao-Chang Liang	IAMS	mcl@gate.sinica.edu.tw
Pei-Ling Luo	IAMS	plluo@gate.sinica.edu.tw
Po-Jen Hsu	IAMS	clusterga@gmail.com
Prasad Ramesh Joshi	NYCU	prasad.nctu@gmail.com
Qian-Rui Huang	IAMS	Append@gmail.com
Sheng-Lung Chou	NSRRC	chou.sl@nsrrc.org.tw
Shun-Lin Tseng	NCU	ninomiyarin0309@gmail.com
Shu-Yu Lin	NYCU	lin.shuyu.nsrrc@gmail.com
Ssu-Ju Huang	NYCU	ssuju1119.sc12@nycu.edu.tw
Tang-Yu, Kao	NYCU	yrr687@gmail.com
Wen-Jian Huang	NSRRC	huang.wj@nsrrc.org.tw
Yasuki Endo	NYCU	endo@nycu.edu.tw
Yen-Hsiu Lin	IAMS	thereistoomuchtrouble@gmail.com

Yi-Hsuan Chiu	NCU	gina.yhchiu@gmail.com
Yi-Tang Chen	NYCU	ytchenisaac1007.sc11@nycu.edu.tw
Yuan-Pern Lee	NYCU	yplee@nycu.edu.tw
Yuan-Pin Chang	NSYSU	ypchang@mail.nsysu.edu.tw
Yueh-Kuei Cheng	NYCU	yuegui@nycu.edu.tw
Yu-Hsuan Chang	NYCU	mowmoww14@gmail.com
Yu-Jong Wu	NSRRC	yjwu@nsrrc.org.tw
Yu-Xuan Wu	IAMS	iamwustw@gamil.com
Yu-Yi Hong	NYCU	hongyuyi0302.sc11@nycu.edu.tw