The 3rd Workshop on Frontier Investigations of Key Species in Atmospheric Chemistry and Astrochemistry

PROGRAM BOOK

Aug. 10, 2023
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". The project focus on two major research directions:

(A) Spectroscopy and reactions of key atmospheric free radicals.

(B) Spectral identification and reactions of key astrochemical species.

The participants mainly come from the research groups of Prof. Yuan-Pern Lee (NYCU), Dr. Jim Jr-Min Lin (IAMS), Dr. Kaito Takahashi (IAMS), Dr. Pei-Ling Luo (IAMS), Prof. Chao-Yu Chung (NSYSU), Dr. Yu-Jong Wu (NSRRC), and Dr. Jer-Lai Kuo (IAMS). 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 group.

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

Session B: each presenter has 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 in which the poster presenter has the chance to promote their poster.

Speakers

A-1	Pei-Ling Luo	Institute of Atomic and Molecular Sciences, Academia Sinica
A-2	Kaito Takahashi	Institute of Atomic and Molecular Sciences, Academia Sinica
A-3	Yen-Ru Wu	Institute of Atomic and Molecular Sciences, Academia Sinica
A-4	Takayuki Ebata	Department of Applied Chemistry, National Yang Ming Chiao Tung University
B-1	Qian-Rui Huang	Institute of Atomic and Molecular Sciences, Academia Sinica
B-2	Shu-Yu Lin	National Synchrotron Radiation Research Center
B-3	Jun-Ying Feng	Department of Applied Chemistry, National Yang Ming Chiao Tung University
B-4	Isabelle Weber	Department of Applied Chemistry, National Yang Ming Chiao Tung University

Sponsored by National Science and Technology Council
(NSTC112-2639-M-A49-002-ASP)

Program

09:00~	Registration
09:30-10:00	**A-1 Pei-Ling Luo (IAMS)** *Reaction between Criegee intermediate* CH_2OO *and formaldehyde: Kinetics and atmospheric implications*
10:00-10:30	**A-2 Kaito Takahashi (IAMS)** *Looking back at failed transition state theory predictions for Criegee intermediate reactions*
10:30-11:00	Coffee break & photo
11:00-11:20	**A-3 Yen-Ru Wu (IAMS)** *Kinetic isotope effect of the simplest Criegee intermediate reaction with water vapor reaction*
11:20-11:50	**A-4 Takayuki Ebata (NYCU)** *Magic number observed in the mass spectra of* $H^+(\text{pyrazine})_m(H_2O)_n$ *and* $H^+(\text{pyridine})_m(H_2O)_n$ *clusters*
11:50-13:30	Lunch (PI discussion in R323)
13:30-14:00	**B-1 Qian-Rui Huang (IAMS)** *A perturb-then-diagonalize algorithm for high-dimensional anharmonic vibrational analysis*
14:00-14:20	**B-2 Shu-Yu Lin (NSRRC)** *Vacuum UV photolysis of benzene in solid nitrogen*
14:20-14:40	**B-3 Jun-Ying Feng (NYCU)** *Infrared spectra of isomers of protonated and hydrogenated phenanthrene isolated in solid para-hydrogen*
14:40-15:00	**B-4 Isabelle Weber (NYCU)** *Electronic spectroscopy of ovalene isolated in solid para-hydrogen: Finding the missing* S_1 *state*
15:00-15:30	Coffee break
15:30-16:30	Flash talks for poster presenters
16:30-18:00	Poster section
18:00~	Dinner

Poster Presentations

#	Presenter	Title
P01	Kai-Yan Chen	The temperature effect of the Criegee intermediate reaction with water vapor
P02	I-Yun Chen	High-resolution infrared spectra and band strength of gaseous methanediol
P03	Che-Wei Chang	Absolute line strength of ν_1 transitions of OH radical near 3 μm
P04	Chen-An Chung	Rate coefficient of *syn*-CH_3CHOO with HCl and the rate coefficient of $CH_3CHI + O_2$ investigated with a quantum cascade laser system
P05	Yi-Ting Liu	Pure rotational spectrum of the CH_2CHCO radical
P06	Ching-Hua Chang	Pure rotational spectra of ClSO
P07	Chia-I Huang	Structures and anharmonic analyses of the O-H stretching vibrations of Jet-Cooled (benzoic acid)$_{m=1,2}$(H_2O)$_{n=0\text{-}2}$ and (benzoic acid-d_5)$_{m=1,2}$(H_2O)$_{n=0\text{-}2}$ – unraveling the complex anharmonic couplings in the cyclic clusters
P08	Dong Cao Hieu	Exploring energy landscape of neutral and protonated di-, tri- and tetra-glycine with assistance of neural network potentials
P09	Jer-Lai Kuo	Understanding the role of multi-quanta states in FR for aromatic molecules: A case study for pyridine and deuterated pyridine
P10	Rona F. Barbarona	Fermi resonance in protonated cyano-containing complexes $RCNH^+X$ ($R = H, CH_3, C_6H_5$; $X = Ne, Ar, N_2, CO, W$)
P11	Po-Jen Hsu	Structure search on the pyrazine/pyridine-water clusters: Competition among π-π, CH... π, and hydrogen bond interactions
P12	Jun-Hao Yu	A theoretical investigation on the 2DIR signatures of fermi resonance in solvated hydronium and methylammonium systems
P13	Man-Lin Yang	Infrared spectra of various isomers of hydrogenated phenanthridine ($HC_{13}H_9N$) isolated in solid *para*-hydrogen
P14	Chun-Kai Chen	Electronic spectra of quinoline and isoquinoline isolated in solid *para*-hydrogen
P15	Sheng-Lung Chou	Far-UV absorption spectra of SiH_2 and dibridged Si_2H_2 isolated in solid argon
P16	Wen-Jian Huang	Commissioning of the newly-built mass-selective matrix isolation system
P17	Chih-Hao Chin	Theoretical study of the $N(^2D)$ + benzene reaction and implications for planetary atmospheres

A-1

Reaction between Criegee intermediate CH_2OO and formaldehyde: Kinetics and atmospheric implications

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ABSTRACT

In this work, we have investigated the kinetics and product branching ratios of the reaction between the simplest Criegee intermediate (CH_2OO) and formaldehyde (HCHO),[1] both of which are the important molecules in atmospheric chemistry. In addition to measuring the rate coefficients of the reaction CH_2OO + HCHO under varied experimental conditions, the branching ratios of the formic acid (HCOOH) and CO product channels were also determined with synchronized two-color time-resolved dual-comb spectroscopy.[1,2] Furthermore, the atmospheric implications of the title reaction were also evaluated and discussed.

References

1. P.-L. Luo, I-Y. Chen, M. Anwar, H. Khan, and D. E. Shallcross, **Commun. Chem.** *6*, 130 (2023).
2. P.-L. Luo and I-Y. Chen, **Anal. Chem.** *94*, 5752 (2022).

A-2

Looking back at failed transition state theory predictions for Criegee intermediate reactions

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ABSTRACT

Due to its importance in atmospheric chemistry, the reactions involving Criegee intermediates and trace gases have attracted significant attention. This has led to a great number of experimental and computational studies on this topic in the past decade. For most computational studies, transition state theory (TST) has been utilized for predicting rate coefficients. In its most basic form, TST assumes thermal equilibrium, and due to its numerical stability and ease, most studies are based on harmonic approximation with rigid rotor approximations. For the reaction between the simplest Criegee intermediate and water vapor, this approach has given room temperature rate coefficients that are consistent with experimental ones for the CH_2OO+H_2O and CH_2OO+2H_2O reactions.[1] However, TST calculation for the CH_2OO+3H_2O reaction underestimates the rate coefficient compared to a very recent experimental study.[2]

In this talk, we will discuss some issues in utilizing TST for the calculation of reaction rate coefficients. Detailed evaluation of possible errors and computational limitations will be presented in this talk.

References

1. L.-C. Lin, W. Chao, M. Smith, J. J.-M. Lin, amd K. Takahashi, **Phys. Chem. Chem. Phys.** *18*, 4557 (2016).
2. Y.-J. Wu, K. Takahashi, and J. J.-M. Lin, **J. Phys. Chemi. A** (submitted).

A-3

Kinetic isotope effect of the simplest Criegee intermediate reaction with water vapor reaction

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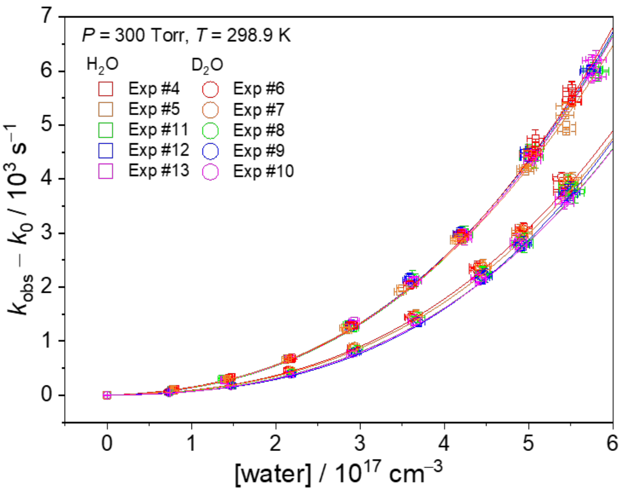
ABSTRACT

In this work, we measured the kinetic isotope effect (KIE = k_H/k_D) of the reaction between the simplest Criegee intermediate (CH_2OO) and water vapor using UV absorption spectroscopy at pressures of 300 Torr and 600 Torr and temperatures of 298.9 K. Additionally, we observed a distinct reaction pathway of $CH_2OO + 3H_2O$. The results yield a reaction-order-unresolved KIE of 1.6 ± 0.2. When analyzing KIEs separately for different reaction pathways, we obtained KIE(k_1) = 1.47 ± 0.68, KIE(k_2) = 2.23 ± 0.57, and KIE(k_3) = 1.01 ± 0.16 for (CH_2OO + n(H_2O), k_n). The KIE(k_1) and KIE(k_2) results are consistent with those reported in a theoretical paper,[1] primarily attributed to the higher zero point corrected barrier energy upon deuteration, with a minimal contribution from hydrogen atom tunneling. However, KIE(k_3) was not calculated in that paper. By improving the precision of water vapor concentration in our experiment, we observed a minor pressure effect in the reaction between CH_2OO and water vapor, with the ratio of reaction rate constants $k_{600torr}/k_{300torr}$ being approximately 1.06 ± 0.04.



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A-4

Magic number observed in the mass spectra of $H^+(\text{pyrazine})_m (H_2O)_n$ and $H^+(\text{pyridine})_m (H_2O)_n$ clusters

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ABSTRACT

The mass distributions of ($H^+[(\text{Pyra})_m w_n]$) ($m = 1 - 6$, $n = 1 - 8$) and ($H^+[(\text{Pyd})_m w_n]$) ($m = 1 - 7$, $n = 1 - 5$), generated by the VUV ionization of their neutral clusters at 9. 3 eV, respectively, have been investigated by mass spectrometry and quantum chemical calculation. Fig. 1(a) shows the TOF-mass spectrum after the VUV ionization of $(\text{Pyra})_m(H_2O)_n$ clusters. The mass spectrum of $H^+[(\text{Pyra})_m w_n]$ showed strong peaks at (m, n) = (3,1), (4,2), (5,3) and (6,4), showing the magic number satisfying the relationship $m = n + 2$. This magic number indicates the formation of the closed-shell structure in thes clusters. On the other hand, the mass pattern of $H^+[(\text{Pyd})_m w_n]$, Fig. 1(b), is quite different from $H^+[(\text{Pyra})_m w_n]$. We will discuss how the difference of the proton affinity between (Pyra) and (Pyd) affects the observed mass distribution.

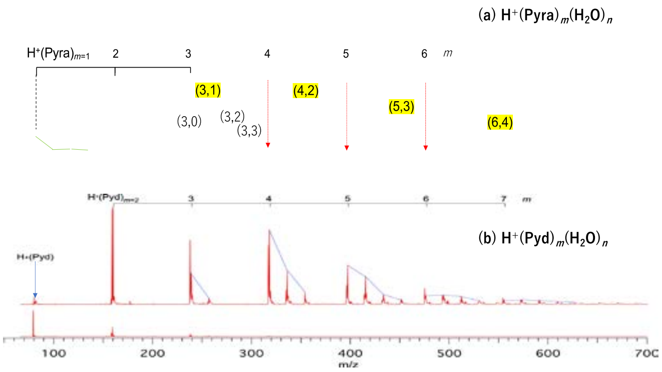

Fig. 1 TOF-mass spectrum after the VUV ionization of (a) $(\text{Pyra})_m(H_2O)_n$ clusters and (b) $(\text{Pyd})_m(H_2O)_n$ clusters at 9. 3 eV.

A perturb-then-diagonalize algorithm for high-dimensional anharmonic vibrational analysis

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ABSTRACT

Recent developments in infrared action spectroscopy, such as IRMPD and IRPD spectroscopy, have unlocked the potential to measure high-resolution vibrational spectra of molecule species. These advanced techniques have unveiled anharmonic phenomena, including Fermi Resonance and Combination bands, which were previously forbidden in harmonic approximations. To interpret these experimental spectra accurately, explicit treatments of anharmonic vibrational analysis have become essential.

Currently, two primary methods are employed for anharmonic vibrational analysis. The perturbative approach, such as vibrational second-order perturbation theory (VPT2), is typically faster but can suffer from accuracy issues, especially when encountering resonance conditions. In contrast, the variational approach, such as vibrational configuration interaction (VCI), offers improved accuracy in such cases but lacks scalability. To address this challenge, a potential solution lies in the reduced-dimensional approach, where specific vibrational modes are chosen for explicit anharmonic analysis, assuming they are uncoupled from the remaining modes.

In our research group, we have implemented a VCI-based method on a quartic potential energy surface (PES) capable of analyzing ~40 high-frequency vibration modes previously. However, this capability falls short when dealing with larger molecules. Moreover, incorporating low-frequency modes significantly increases the number of required eigenstates, worsen the situation even when considering only ~25 modes. To overcome this limitation, we have devised a novel approach that combines the strengths of both perturbative and variational methods, resulting in a perturb-than-diagonalize technique. Through this approach, we have performed efficient vibrational analyses on some azine systems, completing a ~30-modes analysis in just a few minutes.

References

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2. J.-Y. Feng, Q.-R. Huang, H.-Q. Nguyen, J.-L. Kuo, and T. Ebata, **J. Chinese Chem. Soc.** *69*, 160 (2022).

B-2

Vacuum UV photolysis of benzene in solid nitrogen

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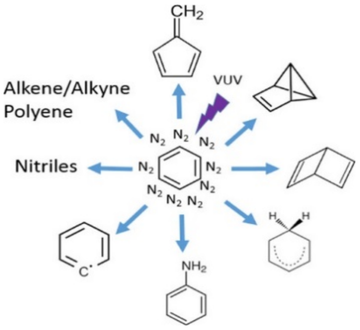
ABSTRACT

The photolysis of C_6H_6/N_2 matrix samples at 10 K under 121.6 and 175 nm was investigated, and the observed IR lines were identified by comparison with literature results, expected photochemical trends, and isotopic substitution experiments. Under 175 nm photolysis, photoproducts were identified, including isomers of benzene, phenyl (Ph) radicals, alkenes and/or alkynes, and pure linear carbon clusters (C_3 and C_5); however, N-bearing hydrocarbons were not detected. In contrast, several new IR signatures were observed upon 121.6 nm photolysis; some of these signatures were readily identified as absorptions of CN, HCNC, NC_6N, and phenylnitrene (PhN), while the other unknown lines observed in the typical C≡N stretching region were expected to correspond to linear nitriles. By further warming the sample to 30 K, the line intensities of PhN decreased, and the IR lines of aniline radicals (PhNH) and aniline ($PhNH_2$) were observed, indicative of the recombination of H atoms with primary photofragments via diffusion. This study provides possible synthetic routes of nitriles and aromatic amines in planetary atmospheres and icy surfaces dominated by N_2.



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Infrared spectra of isomers of protonated and hydrogenated phenanthrene isolated in solid *para*-hydrogen

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) and their derivatives, including protonated, hydrogenated, and cationic species, were proposed to be carriers of the unidentified infrared (UIR) emission bands observed in the outer space. Because protons are abundant in the outer space and PAH have a high proton affinity, protonated PAH (H^+PAH) might be produced in significant proportions. H^+PAH has a stable closed-shell structure so that it is relatively stable and can be the carrier of UIR bands. Although past studies have pointed out that small PAH (with the number of carbon atoms less than 40) are difficult to preserve in space for an extended period, these small PAH can be the building blocks of large PAH. Identification of these smaller PAH and their derivatives are important in astrochemistry.

In this work, we focused on the vibrational absorption spectra of protonated and hydrogenated phenanthrene ($C_{14}H_{10}$) isolated in solid *para*-hydrogen (*p*-H_2). *p*-H_2 flowed through and mixed with phenanthrene vapor before deposition onto the nickel-plated Cu substrate at 3.2 K. During deposition, we used an electron gun to bombard the mixture of *p*-H_2 and $C_{14}H_{10}$ to generate $H^+C_{14}H_{10}$ and $HC_{14}H_{10}$. Electron bombardment of H_2 produced H_3^+ and H; the former can readily transfer its proton to $C_{14}H_{10}$ to form $H^+C_{14}H_{10}$, whereas the reaction of the latter with $C_{14}H_{10}$ and neutralization of $H^+C_{14}H_{10}$ generated $HC_{14}H_{10}$. Protonated species are expected to decrease in darkness over time through the neutralization process with trapped electrons to produce hydrogenated species. By observing the decay and the increase of infrared absorption lines, we could unambiguously classify features associated with protonated or hydrogenated species after the matrix was maintained in darkness for an extended period. $C_{14}H_{10}$ has a total of seven protonation or hydrogenation sites, including two for the carbons on the fused ring. Among isomers of $H^+C_{14}H_{10}$ or $HC_{14}H_{10}$, spectral assignments were achieved according to the behavior upon secondary irradiation and a comparison of experimental results with vibrational wavenumbers and IR intensities predicted with the B3LYP/6-311++G(d,p) method. For $H^+C_{14}H_{10}$, secondary irradiation was performed at 619, 544, 524, and 463 nm. The absorption lines of $H^+C_{14}H_{10}$ could be divided into 4 groups and assigned to 10-, 1-, 3-, and 4-$H^+C_{14}H_{10}$, respectively. In the case of $HC_{14}H_{10}$, secondary irradiation at 423, 380, 315, and 223 nm helped to identify 1-, 4-, 3-, 10-, and 2-$HC_{14}H_{10}$; only hydrogenation at the carbon on the fused ring was not observed. Nearly all feasible protonated and hydrogenated PAH were produced and identified in one experiment; all spectra are new.

B-4

Electronic spectroscopy of ovalene isolated in solid *para*-hydrogen: Finding the missing S_1 state

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ABSTRACT

The identification of carriers of the Diffuse Interstellar Bands (DIB) remains one of the great challenges in astronomy and astrochemistry today. Whilst well over 500 DIB have been confirmed, only two have so far been assigned to a specific carrier molecule, the buckminsterfullerene cation C_{60}^+. Ovalene ($C_{32}J_{14}$) has been considered as a potential DIB carrier and its absorption spectrum has been studied by jet-expansion[1] and matrix isolation methods;[2] the observed bands with an origin near 21450 cm^{-1} have been assigned to the weakly allowed S_1–S_0 transition predicted near 20125 cm^{-1} with a large deviation.

Over the past years, we have recorded fluorescence excitation and emission spectra of PAH isolated in solid *para*-H_2 to assess the properties of *para*-H_2 as a matrix host for electronic spectroscopy. Fluorescence excitation and emission spectra of $C_{32}H_{14}$ in solid *p*-H_2 are consistent with data from the literature and suggest a matrix shift of ~90 cm^{-1} due to the *p*-H_2 environment. However, a comparison to simulated electronic absorption and emission spectra obtained from Franck-Condon Herzberg-Teller calculations indicates that the observed spectra with an origin near 21050 cm^{-1} are associated with the S_2–S_0 transition of $C_{32}J_{14}$ rather than the previously reported S_1–S_0 transition.

In our contribution, we present the fluorescence excitation and emission spectrum of $C_{32}H_{14}$ in solid *para*-H_2 including the previously unobserved S_1–S_0 transition. Assignments for the observed bands are provided. We found the electronic origin of the S_1–S_0 transition at 19429 cm^{-1}, 1620 cm^{-1} below the origin of the S_2–S_1 transition at 21049 cm^{-1}.

References

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P01

The Temperature Effect of the Criegee Intermediate Reaction with Water Vapor

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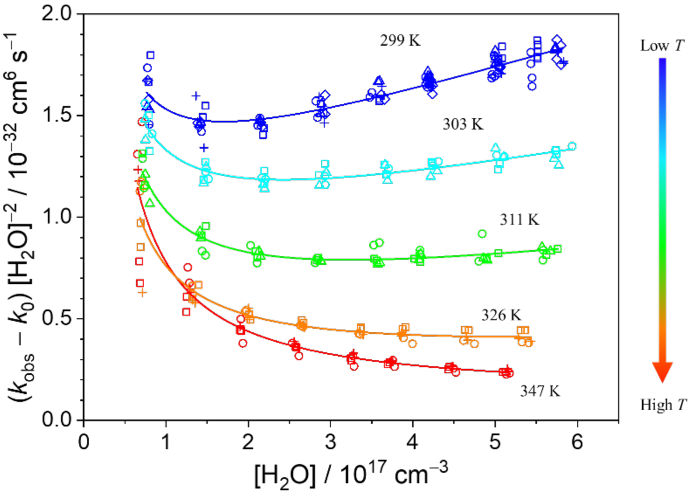
ABSTRACT

This experiment investigates the temperature effect on the simplest Criegee intermediate (CH_2OO) reaction with water. Unlike the previous study[1] which modeled the relation only with two water molecules, our previous research has shown that this reaction has a significant contribution at room temperature (298K) when the Criegee intermediate reacts with three water molecules. To further investigate, we conducted experiments at temperatures between 299 K and 347 K. **Figure 1** shows the relationship between water concentration and the rate constant $k_{obs}-k_0$ / $[H_2O]^2$, where k_{obs} represent the observed rate constant and k_0 represents the rate constant of other reactions (such as wall loss, unimolecular dissociation, etc). At lower temperatures, the reaction with three water molecules has a greater impact, while at higher temperatures, the reaction with one water molecule becomes dominant. The activation energies for the reactions with one, two, and three water molecules were determined using the Arrhenius plot and are represented as 2.27 ± 0.14, −9.14 ± 0.40, −18.27 ± 0.58 kcal/mol, respectively.

Figure 1. The relationship between water concentration and the rate constant $k_{obs}-k_0$ / $[H_2O]^2$ at temperatures between 298.9K and 346.6K.



References

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P02

High-resolution infrared spectra and band strength of gaseous methanediol

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ABSTRACT

Methanediol ($CH_2(OH)_2$), generated from the hydration of formaldehyde (HCHO) in cloud droplets, has been proposed to be a potential precursor in the formation of formic acid (HCOOH) in the atmosphere.[1] In recent studies, a rapid preparation method of the gaseous methanediol has been reported by employing the aqueous solution of formaldehyde and the FTIR spectrum of gaseous methanediol at 980–1100 cm^{-1} has been identified and assigned to be the antisymmetric and symmetric O–C–O stretching modes of the *trans*-$CH_2(OH)_2$ with the band origins at 1058 and 1027 cm^{-1}, respectively.[2] Herein, we report the rotationally resolved infrared absorption spectrum of gaseous methanediol in the range of 1016–1084 cm^{-1} and its integral infrared (IR) cross-section. The spectra of gaseous methanediol were recorded with a spectral resolution of 0.0013 cm^{-1} by using a tunable difference frequency generation (DFG) laser system coupled with a multipass absorption cell. Furthermore, the concentrations of $CH_2(OH)_2$ in the flowing gaseous mixture were determined by simultaneously recording the infrared spectra of $CH_2(OH)_2$ near 1058 cm^{-1} and the real-time dual-comb spectra of H_2O and HCHO near 3078 cm^{-1}. The integral IR cross-section of the recorded spectrum in range 1056.9–1058.6 cm^{-1} was determined to be $(1.72 \pm 0.67) \times 10^{-18}$ cm $molecule^{-1}$ and the overall IR intensity of the antisymmetric and symmetric O–C–O stretching modes was also estimated and compared with the theoretical calculations.[3,4]

References

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2. Y.-F. Chen and L.-K. Chu **Chem. Commun.** *58*, 4208 (2022).
3. M. C. Davis, N. R. Garretta, and R. C. Fortenberry, **Phys. Chem. Chem. Phys.** *24*, 18552 (2022).
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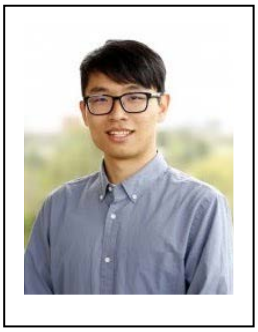
P03

Absolute line strength of ν_1 transitions of OH radical near 3 μm



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ABSTRACT

In this work, we have measured the line strengths of several transitions of the ν_1 fundamental band of OH radical by simultaneous determination of the precursor H_2O_2 and OH radicals. OH radical is generated by photolysis of H_2O_2 with an excimer laser at 248 nm and it can undergo the secondary reaction with H_2O_2. By employing the synchronized two-color time-resolved dual-comb spectroscopy [1], the high-resolution spectra of H_2O_2 and OH were respectively recorded near 7.9 and 2.9 μm before and after laser photolysis. In addition to analyzing the high-resolution spectra of H_2O_2 and measuring the rate coefficient of the reaction between OH and H_2O_2, we further determine the line strength of OH radical by using the formula $S_{OH}=S_{H_2O_2}\frac{\Delta A_{OH}(t=0)}{-2\Delta A_{H_2O_2}(t=0)}$, where S_{OH} and $S_{H_2O_2}$ are the line strengths of OH radical and H_2O_2, respectively. $\Delta A_{OH}(t=0)$ and $\Delta A_{H_2O_2}(t=0)$ represent the integral areas of difference absorbance of OH and H_2O_2 transitions obtained at t=0 right after laser photolysis. Considering the errors of $S_{H_2O_2}$ (8%), $\Delta A_{OH}(t=0)$ (3%), and $\Delta A_{H_2O_2}(t=0)$ (10%), the overall uncertainty of ~13% for determination of OH line strengths was estimated. Over ten transitions of the OH radical were evaluated and compared with values tabulated in the HITRAN database [2].

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P04

Rate coefficient of *syn*-CH_3CHOO with HCl and the rate coefficient of $CH_3CHI + O_2$ investigated with a quantum cascade laser system

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ABSTRACT

The reactions between Criegee intermediates and hydrogen chloride (HCl) might play a significant role in the atmosphere, particularly in the polluted urban areas, because of their large rate coefficients. We employed a tunable cw external-cavity quantum-cascade laser coupled with a Herriott cell to record the high-resolution spectra of CH_3OO by photolyzing a gas mixture of 1,1-diiodoethane/O_2/HCl with laser light at 248 nm. By monitoring the bands in region 883.13−883.15 cm^{-1}, we recorded the temporal evolution of the *syn*-CH_3CHOO conformer and measured the rate coefficient of *syn*-CH_3CHOO + HCl at 298 K under total pressure of 4–8 Torr. The measured rate coefficient was determined to be $(4.8\pm1.3)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is similar to the value $(4.8\pm1.0)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} reported by Liu et al. by employing the laser-induced fluorescence detection of OH.[1] We also measured the rate coefficient of the $CH_3CHI + O_2$. The rate coefficient of $CH_3CHI + O_2$ was determined to be $(3.4\pm0.7)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, which is ~2.5 times smaller than that reported by Howes et al. and Sheps et al. by employing mass spectroscopy and UV absorption spectroscopy, respectively.[2,3]

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Pure rotational spectrum of the CH_2CHCO radical

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ABSTRACT

The CH_2CHCO radical serves as an important intermediate in combustion and atmospheric chemistry,[1] and its infrared spectrum in solid para-H_2 was reported.[2] In order to further investigate this radical in gas phase, we produced it in the discharge plasma of acryloyl chloride, $CH_2CHC(O)Cl$, and characterized it by Fourier transform microwave spectroscopy in a pulsed supersonic jet. High-level *ab initio* calculations at the levels of RCCSD(T)-F12a/cc-pCVTZ-F12 and B3LYP/aug-cc-pVTZ were used to compare the experimental results. Two low lying isomers, *s-trans*-3-propenalyl (*s-trans*-$CH_2CH\dot{C}O$) and 3-propenonyl ($\cdot CH_2CHCO$), were observed by rotational spectra with the sample gas diluted in argon and neon respectively. The geometrical structures of the CH_2CHCO radical were obtained by the experimental molecular parameters. Furthermore, their complicated fine and hyperfine structures were well resolved in this work, providing important information on their unpaired electron distributions.

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P06

Pure rotational spectra of ClSO

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ABSTRACT

ClSO radical was investigated widely since its importance in the organic syntheses and battery science. [1, 2] Also, it is a common resource for the Cl atom. In the present study, the rotational spectra of both isotopologues (^{35}Cl and ^{37}Cl) are measured by Fourier-transform microwave spectroscopy (FTMW) and FTMW-microwave double-resonance spectroscopy. The electric discharge of the precursor, Cl_2SO diluted in Ne, was used to generate the radical. Due to the low rotational temperature of 2-3 K, the radicals were cooled down to very stable state. The rotational transitions with $J > 6$ or $K_a = 2$ were too weak to be reproduced. The fine and hyperfine components of ^{35}ClSO and ^{37}ClSO were observed and fully assigned. 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 chlorine nucleus, have been determined precisely for the two isotopologues. The radicals have X^2A'' electronic ground state, and the unpaired election occupies the p_z orbital perpendicular to the ClSO plane.

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P07

Structures and Anharmonic Analyses of the O−H Stretching Vibrations of Jet-Cooled (Benzoic acid)$_{m=1,2}$(H_2O)$_{n=0\text{-}2}$ and (Benzoic acid-d_5)$_{m=1,2}$(H_2O)$_{n=0\text{-}2}$ – Unraveling the Complex Anharmonic Couplings in the Cyclic Clusters

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ABSTRACT

The IR spectra of series of (Benzoic acid)$_m$(H_2O)$_n$ (m = 1, 2; n = 0-2) and (Benzoic acid-d_5)$_m$(H_2O)$_n$ (m = 1, 2; n = 0-2) clusters in the 2800−3750 cm^{-1} region were measured by IR excitation -VUV ionization with a reflectron time-of-flight mass spectrometer (RF-TOF-MS). The IR spectra of (Benzoic acid)$_m$(H_2O)$_n$ and (Benzoic acid-d_5)$_m$(H_2O)$_n$ have very similar features, which indicates the structure of non-deuterated cluster is the same as that of the deuterated one and the IR intensities of C−H stretching vibrations are negligible. The anharmonic analyses based on the second-order vibrational perturbation theory indicates the complexity of the IR spectra is due to the strong coupling between the hydrogen-bonded O−H stretching band and (i) the combination and overtone bands involving the in-plane O−H bending vibrations of Benzoic acid and H_2O, and C=O stretching vibration, or (ii) the combination bands involving the H-bonded O−H stretch and low-frequency intermolecular vibrations.

P08

Exploring energy landscape of neutral and protonated di-, tri- and tetra-glycine with assistance of neural network potentials

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ABSTRACT

Understanding the structure-activity relationship of short peptides is crucial for applications in drug discovery, ranging from screening potential drug candidates to optimizing their properties [1,2]. Computational methods with high accuracy are employed to study key structural features that aid in interpreting this relationship.[3] Our study demonstrates the utility of deep-learning neural network potential (DL-NNP) [4] in exploring the energy landscape of neutral and protonated di-, tri-, and tetra-glycine peptides. The best NNP models provide energy and gradient predictions for n-glycine that are lower by 2 kJ/mol. By re-optimizing the DFT method, we establish the differences in structural features resulting from changes in the peptide bond. These findings contribute to a deeper understanding of the structure-activity relationship in short peptides.

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P09

Understanding the role of multi-quanta states in FR for aromatic molecules: A case study for pyridine and deuterated pyridine

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ABSTRACT

As a result of the extensive stretch-bend Fermi resonance (FR), the CH-stretching region of aromatic compounds are highly complex.

From the studies done in past, it is well-established that the stretch fundamentals undergo FR with the two-quanta states of in-plane bending modes in the C-H stretch region.[1] There is, however, an unresolved ambiguity concerning the role of multi-quanta states in this region. Using algorithms based on quartic-potentials[2], we conduct anharmonic simulations to investigate the role of multi-quanta states in FR with the C-H/C-D stretching fundamental modes. The molecular systems of investigation are pyridine, mono-deuterated pyridine, and fully-deuterated pyridine. In this presentation, however, we take the example of mono-deuterated Pyridine to explain the role of multi-quanta states. Here, we present a comprehensive treatment of mode couplings and Fermi resonances in both C-H (2900-3200 cm-1) and C-D (2200-2400 cm-1) stretching regions. Based on Yagi et al.'s theoretical scheme,[3] we employ a hierarchical approach to understand the mechanism of coupling among stretching fundamentals, two-quanta states and multi-quanta states. According to our analysis, FR is generated by coupling between stretching fundamentals and two quanta states of the in-plane bending modes. Nonetheless, this FR is significantly affected by the presence of multi-quanta bands, i.e., three and four quanta states comprising combination bands of in-plane and out-of-plane bending modes. Multi-quanta states are therefore important in determining the spectral characteristics of these materials in the C-H/C-D stretching region.

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P10

Fermi resonance in protonated cyano-containing complexes $RCNH^+X$ ($R = H, CH_3, C_6H_5$; $X = Ne, Ar, N_2, CO, W$)

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ABSTRACT

The presence of cyano-containing (–CN) molecules has garnered growing attention in astrochemical environments due to their abundance in interstellar and circumstellar media. In this work we explore the vibrational signature of molecular systems with the protonated cyano group as a moiety. Employing *ab initio* anharmonic calculations, we determine the relevant modes of vibration with significant coupling strengths and found that the additional features in the calculated spectra of these complexes are primarily due to the Fermi resonance interactions of the NH stretching fundamental and the NH bending overtone. The modes associated with the functional group *R* and the tagging molecules *X* do not give rise to new bands.

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Structure search on the pyrazine/pyridine-water clusters: Competition among π-π, CH… π, and hydrogen bond interactions.

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ABSTRACT

π-π interaction is known to play a crucial role in stabilizing proteins, DNA, and complexes involving aromatic rings. The pyrazine/pyridine clusters and their mixtures with water molecules are the ideal systems for investigating the essential roles of the π-π, CH…π and hydrogen bond interactions in stabilizing a molecular cluster [1, 2]. In this work, we performed a systematic structure search and the frequency calculations at B3LYP+D3/6-311+G(d,p) level of theory on the protonated (pyrazine/pyridine)$_m$(water)$_n$ clusters for m = 2 – 4 and n = 0 – 4. Our preliminary results show that the pyrazine/pyridine clusters can be π-π stacked or T-shape structures. With the presence of the water molecules, the subtle difference in the proton affinity of Pyrazine and Pyridine can lead to a different preference between protonated water clusters and protonated pyridine clusters. The searched isomer structures can provide a fundamental analysis for the IR-VUV experiments and help us to understand the vibrational modes in the IR spectra.

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P12

A theoretical investigation on the 2DIR Signatures of fermi resonance in solvated hydronium and methylammonium systems

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ABSTRACT

The theoretical method combining high-level *ab initio* anharmonic algorithms with a quantum Langevin equation approach was developed to simulate two-dimensional infrared (2DIR) spectra of anharmonic vibrational systems. Our focus lies on solvated hydronium and methylammonium systems to investigate the spectral signatures of Fermi resonance. We construct highly accurate effective Hamiltonians for these solvated systems with Fermi resonance, and the theoretical simulations of infrared spectra based on this effective model exhibit excellent agreement with experimental data. Our simulated 2DIR spectra reveal coherent vibrational couplings and quantum dissipative dynamics. Notably, square patterns and quantum beating of peaks in the simulated spectra provide clear distinctions between systems with and without Fermi resonance. Furthermore, we explore the systems with complicated anharmonic couplings using our theoretical scheme, and we expect this tool to have wide application in providing convincing assignments for chemical species.

P13

Infrared Spectra of Various Isomers of Hydrogenated Phenanthridine ($HC_{13}H_9N$) Isolated in Solid *para*-Hydrogen

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ABSTRACT

Large polycyclic aromatic hydrocarbons (PAH) and their derivatives have been proposed to be possible carriers of the unidentified infrared emission (UIR) bands observed in the interstellar media. The feature of UIR bands near 6.2 μm does not match the experimental spectra of neutral PAH that show bands near 6.3 μm. However, corresponding bands of polycyclic aromatic nitrogen heterocycles (PANH), produced on substitution of a CH moiety with a nitrogen atom, agree better with the UIR band near 6.2 μm because the nitrogen induces a blue shift of the CC-stretching bands of PAHs near 6.3 μm. This blue shift has been observed between several protonated polycyclic aromatic hydrocarbons (H^+PAH) and their corresponding nitrogen heterocycles (H^+PANH).[1,2] Therefore, H^+PANH could be potential candidates that contribute to the UIR bands; its neutral species, the hydrogenated nitrogen heterocycles are also worth investigating.

In this work, we report the IR spectrum of six isomers of mono-hydrogenated phenanthridine ($C_{13}H_9N$) produced from the $C_{13}H_9N/Cl_2/p\text{-}H_2$ matrices at 3.2 K after irradiation at 365 nm to generate Cl atoms, followed by IR irradiation to generate H atoms via $Cl + H_2 (v = 1) \rightarrow HCl + H$; the H atoms reacted with $C_{13}H_9N$ through quantum tunneling. In addition to the hydrogenation on the N atom ($C_{13}H_9NH$), hydrogenation at five carbon sites (1-$HC_{13}H_9N$, 2-$HC_{13}H_9N$, 7-$HC_{13}H_9N$, 9-$HC_{13}H_9N$, and 10-$HC_{13}H_9N$) were also observed. Spectral assignments were achieved according to the behaviors of the lines upon secondary photolysis at various wavelengths, and the comparison of experimental results with vibrational wavenumbers and IR intensities of possible isomers predicted with the B3LYP/6-311++G(d,p) method. The photolytic behaviors of the isomers are discussed and compared with predicted TD-B3LYP/6-311++G(d,p) calculations. A majority of intense lines of the hydrogenated species were observed near 13—14 μm, with the out-of-plane CH-bending modes at 13.43, 13.16, and 13.55 μm for $C_{13}H_9NH$, 9-$HC_{13}H_9N$, and 2-$HC_{13}H_9N$, respectively; these hydrogenated species are hence unlikely to be the carriers of the UIR bands which show emission bands near 11.2 and 12.8 μm.

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P14

Electronic spectra of quinoline and isoquinoline isolated in solid *para*-hydrogen

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ABSTRACT

Polycyclic aromatic nitrogen heterocycles (PANH) and their cationic, protonated, and hydrogenated derivatives have been proposed to contribute to the 6.2 μm unidentified infrared band. Therefore, they might also be considered as promising candidates for the carriers of the diffuse interstellar bands (DIB), which are electronic absorption bands in the visible to near IR. However, laboratory spectra of these species for the comparison to astronomical observations are scarce.

Using the unique properties of solid *para*-hydrogen (p-H_2) as a matrix host, we acquired the excitation and dispersed phosphorescence spectra of quinoline (C_9H_7N) and isoquinoline (*iso*-C_9H_7N), the two smallest PANH. The dispersed phosphorescence spectra were recorded over the range 450–550 nm after excitation of C_9H_7N and *iso*-C_9H_7N at 311.4 nm and 314.0 nm, respectively. Phosphorescence lifetimes of 0.85 s and 0.64 s for C_9H_7N and *iso*-C_9H_7N, respectively, were observed, in satisfactory agreement with earlier studies reported in the literature.[1] We monitored phosphorescence emission as a function of excitation wavelength in region 290–320 nm to record the excitation spectra. To further analyse our experimental results, we performed quantum-chemical calculations at the (TD-)B3LYP/6-311++G(2d,2p) level of theory for the electronic ground and the lowest excited states, and simulated the corresponding electronic absorption and emission spectra using a Franck–Condon Herzberg–Teller approach. We provide the first tentative assignments of the observed bands and discuss the effect of nitrogen substitution at different positions on the electronic spectra.

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P15

Far-UV absorption spectra of SiH_2 and dibridged Si_2H_2 isolated in solid argon

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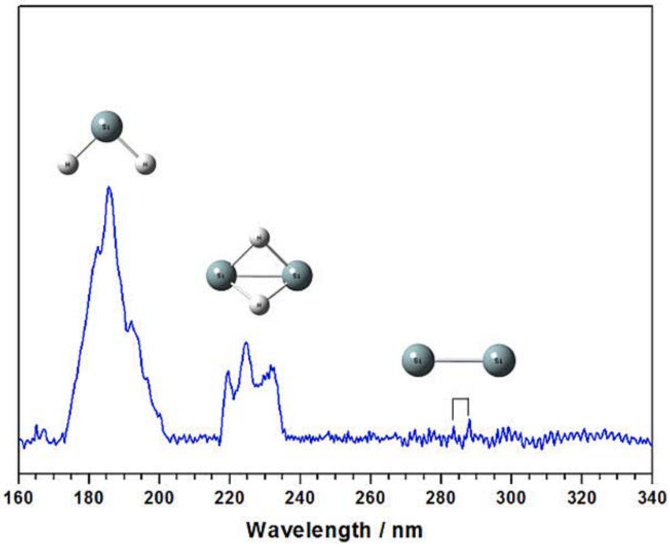
ABSTRACT

We employ electron bombardment during the deposition of an Ar matrix containing a small proportion of SiH_4 to generate various silicon hydrides. Subsequently, the irradiation of a matrix sample at 365 nm decomposes SiH_2 and dibridged Si_2H_2 in solid Ar, which we identify through infrared spectroscopy. We further recorded the corresponding ultraviolet absorption spectra at each experimental stage. An intense band observed in the range of 170 – 203 nm is largely destroyed upon 365 nm photolysis, which is assigned to the C $^1B_2 \leftarrow X\ ^1A_1$ transition of SiH_2. Moreover, a moderate band observed in the region of 217 – 236 nm is reduced slightly, which is assigned to the 3 $^1B_2 \leftarrow X$ $^1A_1$ transition of dibridged Si_2H_2. These assignments are made based on the observed photolytic behavior, and the prediction of the vertical excitation energies with the corresponding oscillator strengths by using time-dependent density functional theory and equation-of-motion coupled cluster theory.



P16

Commissioning of the newly-built mass-selective matrix isolation system

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ABSTRACT

The newly-built mass-selective matrix isolation system has been successfully used to obtain IR spectrum of CO_2^+ cations isolated in solid Ne. Through optimizing the parameters of the mass-selective system, CO_2^+ cations can be produced as a major product and other species were suppressed in a very tiny proportion of production. After codeposition of mass-selective CO_2^+ with excess neon over 4 hours, the IR features of CO_2^+ have been detected with an observable intensity. Only absorptions of CO_2± and CO_2 (precursor) were observed and no detection of other fragments. Later, the UV absorption measurement of the matrix sample was performed and recorded the electronic transitions of CO_2^+ from the ground state to its *A* and *B* state in the spectral region 280-350 nm, as shown in Fig. 1.

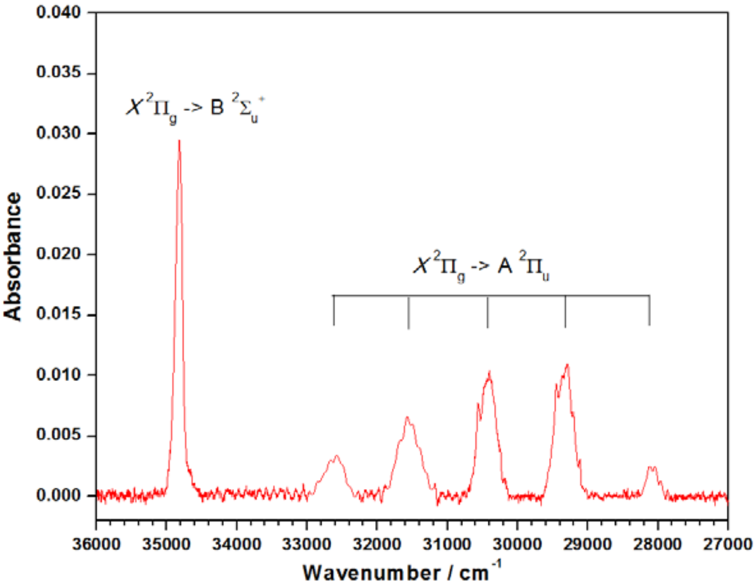

Figure 1 Absorption spectrum of CO_2^+ in solid Ne at 3 K.

P17

Theoretical study of the N(^{2}D) + benzene reaction and implications for planetary atmospheres

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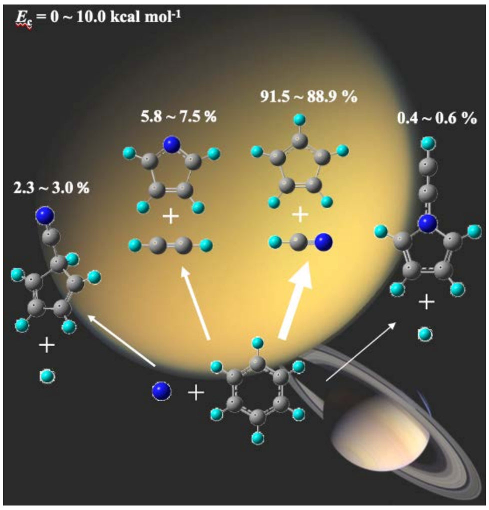
ABSTRACT

Scientists are interested in simulating the gas phase reactions of radical and hydrocarbon species in non-terrestrial environments and planetary atmospheres. These reaction mechanisms have been previously studied by experiments and theoretical calculations, but there is still great uncertainty about the product distribution. The geometry optimizations of reactants, products, intermediates, and transition states were calculated using the hybrid DFT functionals and the potential energy surface was established on the basis of the relevant chemistry, physics, and astrophysics literature [1–3]. These reactions underwent multiple internal isomerizations by adding radical to the hydrocarbon species, forming an initial dual-state adduct, resulting in many possible product pathways. RRKM theory and microscopic transition state theory were used to calculate the rate constants of each reaction step, and steady-state methods were used to calculate the relative product branching ratio of dissociation products. For RRKM calculations at low collision energies (representing planetary atmospheric conditions), HCN and cyclopentadiene form the main product cleavage channels of N(^{2}D) with benzene reaction. This reaction is a process of ring expansion and ring contraction, which may be of key significance for the formation of PAH degradation in the upper atmosphere of Titan and can also explain the mass growth process of nitrogenous polycyclic aromatic hydrocarbons (NPAH).



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