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报告摘要集

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===========专题二：离子、自由基和团簇化学动力学===========

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Steric Control of Polyatomic Chemical Reactions

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The long-range anisotropic interaction in the entry valley of a chemical reaction has a tremendous influence on the types of steric control that can be performed. For the reactions of $CHD_3(v_1=1)$ with the F atoms [1-3] and $O(^3P)$ atoms [4], where such anisotropic interactions are relatively strong, the chemical reactivity is best controlled in a *passive* manner. On the other hand, the anisotropic interactions in the Cl + $CHD_3(v_1=1)$ reaction appears to be sufficiently weak so that an *active* control can be effectually exerted by exploiting the IR laser polarization (when preparing the vibrationally excited reactants) to prealign the $CHD_3(v_1=1)$ reactants in the collision frame [5]. I shall also demonstrate a robust experimental scheme to disentangle the polarization-dependent differential cross sections (PDDCS) encoded in the acquired images, and show how such PDDCSs can reveal the stereodynamics in a three-dimensional portrait [6]. Lastly, some intriguing results on the differential reactivity of the rotationally state-selected reagents, in the lowest few quantum numbers, will be presented [7].

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The translational, rotational, and vibrational energy effects on the chemical reactivity of the cations: $N_2^+(X^2\Sigma_g^+; v^+, N^+)$ and $H_2O^+(X^2B_1; v_1^+v_2^+v_3^+; N^+_{Ka+Kc+})$

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The vacuum ultraviolet laser pulsed field ionization-photoion (PFI-PI) technique is employed to prepare reactant $N_2^+(X^2\Sigma_g^+)$ and $H_2O^+(X^2B_1)$ ions in single rovibronic states. By using a novel electric field pulsing PFI-PI scheme, we have achieved high internal energy selection and high kinetic energy resolution, which allow absolute total cross section measurements of the rovibrationally selected ion-molecule reactions, N_2^+ $(X^2\Sigma_g^+; v^+=0\text{-}2, N^+=0\text{-}8)$ + CH_4 (Ar, D_2, H_2O, C_2H_2, and C_2H_4) and $H_2O^+(X^2B_1; v_1^+v_2^+v_3^+ = 000; N^+_{Ka+Kc+})$ + H_2 (HD, D_2, and CO) at the collision energy range of 0.01-10.00 eV. The absolute total cross sections for these reactions have been determined as a function of the ion rotational and vibrational energies. While the cross sections of the reaction involving N_2^+ $(X^2\Sigma_g^+; v^+=0\text{-}2, N^+=0\text{-}9)$ are found to exhibit negligible rotational effects, a strong rotational enhancement effect is observed for the cross sections of the $H_2O^+(X^2B_1; v_1^+v_2^+v_3^+ = 000, 100, \text{and } 020; N^+_{Ka+Kc+})$ reactions.

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Vibrationally mediated photodissociation of CH_3I [$v_1 = 1$]

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The photodissociation dynamics of C—H symmetric stretch excited CH_3I [$v_1 = 1$, $v_2 = 0$] has been studied by our mini-TOF photofragment translational spectrometer (Figure 1) at 277.5 and 304.2 nm. Three lasers are used, one IR laser tuned at 2969.3 cm^{-1} for the excitation of parent molecules CH_3I to $v_1 = 1$ state, one UV laser for the photodissociation, and the other UV laser for the REMPI detection of CH_3 fragments.

At 277.5 nm, the photodissociation processes are via $^3Q_0$ or $^1Q_1 \leftarrow {}^3Q_0$. The total photodissociation cross section of CH_3I [$v_1 = 1$] is nearly the same to that of CH_3I [$v_1 = 0$]. In the I* channel, the vibrational populations of photofragments CH_3 ($v_1 = 0$, $v_2 = 0$), (0, 1), (1, 0), (1, 1) are measured to be 0.02, 0.02, 0.47, 0.25, and in the I channel the populations of CH_3 (1, 0), (1, 1) are 0.04, 0.05, respectively. This shows that during the photodissociation most of the CH_3I [1, 0] retain the C—H symmetric stretch vibration $v_1 = 1$ in the photofragments CH_3 and the vibrational distribution in the umbrella mode is not seriously affected by the initial C—H symmetric stretch excitation. The photodissociation of CH_3I [1, 0] mainly follows the vibrationally adiabatic process (Figure 2). The initial vibrational excitation [$v_1 = 1$] of CH_3I is quite like a spectator, and the internal vibrational redistribution (IVR) does not play obvious part during photodissociation.

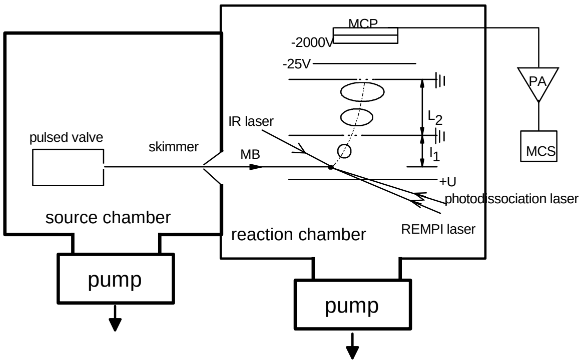

Fig.1. Schematic diagram of the experimental apparatus

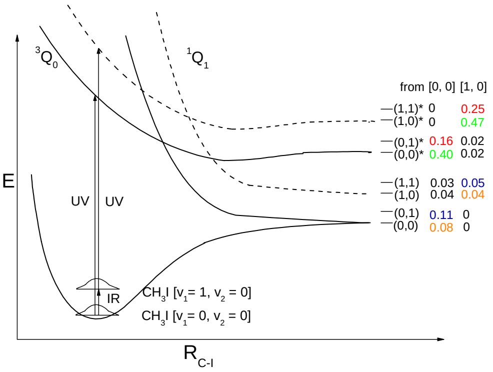

Fig2. The schematic diagram of CH_3I photodissociation at 277.5 nm and a summary of the experimental results. The dash lines are v_1 = 1 vibrationally adiabatic potential energy curves.

But at 304.2 nm, the photodissociation of CH_3I [$v_1 = 1$] is affected intensely by the initial vibrational excitation. The photodissociation cross section ratio is determined to be $\sigma_{[1,0]} / \sigma_{[0,0]}$ = 2.67. The branching fractions from the photodissociation of CH_3I [1, 0] are measured to be 0.24 for I* channel via $^3Q_0$, 0.62 for I channel via $^1Q_1 \leftarrow {}^3Q_0$, and 0.14 for I channel via $^3Q_1$. This shows that Φ(I*) is much higher than that from CH_3I [0, 0], related to the lower curve-crossing probability. From the measured photofragment translational spectra from iodine and CH_3 fragments, it is found that the initial $v_1 = 1$ vibrational excitation of parent molecule is less retained than at 277.5 nm.

The photodissociation dynamics of CH_3I [1, 0] are more complex than that of ground state CH_3I [0, 0]. The initial $v_1 = 1$ vibrational excitation plays different role in the photodissociation process at different wavelength.

Infrared photodissociation spectroscopy of mass-selected cluster ions in the gas phase

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Infrared photodissociation spectroscopy is used to investigate the infrared spectra of cluster ions in the gas phase. The cluster ions are produced via a laser vaporization supersonic cluster source. The ions of interest are each mass-selected and their infrared spectra are measured via infrared photodissociation spectroscopy using a collinear tandem time-of-flight mass spectrometer. The structures of the ions are established by comparison of the experimental spectra with simulated spectra derived from density functional theory calculations. Recent results on transition metal carbonyl cluster cations and anions as well as transition metal oxide/dioxygen complexes will be presented. The results provide new insight into the structure and bonding of transition metal-containing cluster ions.

Study of ultrafast non-adiabatic dynamics in molecules and ultrafast control of chemical reaction

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Using femtosecond time-resolved mass spectrometry (fs-MS), photofragment imaging (fs-PFI), and photoelectron imaging (fs-PEI), we have studied the non-adiabatic dynamics of some polyatomic molecules. Work focus on fs-PEI with the aim to track the temporal populations of relevant optically bright and dark states populated and depopulated by ultrafast non-radiative transitions via conical intersections. The followings are some examples of research works.

The laser induced predissociation dynamics of the *B* Rydberg state of CH_3I following two-photon absorption of a pump pulse was studied. The predissociation lifetime was measured to be 1.55 ps induced by the crossing between the *B* state and the repulsive *A*-band. Two possible predissociation channels were observed originating from (a) direct coupling between the *B* state and the repulsive $^3Q_0$ state and (b) a second crossing between the $^3Q_0$ and $^1Q_1$ states after the coupling between the *B* and $^3Q_0$ states, respectively.

The ultrafast internal conversion in o-xylene molecules from the S_2 state to the vibrationally hot S_1 state on timescale of 60 fs is observed on real time. The secondarily populated high vibronic S_1 state deactivates further to the S_0 state on timescale of 9.85 ps. Interestingly, the lifetime of the low vibronic S_1 state is much longer, extrapolated to ~12.7 ns. The great differences of lifetime of different vibronic S_1 state are due to their different radiationless dynamics.

The electron dephasing mechanism of S_1 (B_2) state of *p*-bromofluorobenzene is determined to be the intersystem crossing (ISC) from the S_1 (B_2) to the T_1 (B_2) state and predissociation S_1 (B_2) *via* T_1 (B_1) state. The lifetime of S_1 (B_2) and T_1 (B_2) is determined to be 40ps and 33ps from the decay of the photoelectron signal.

The intramolecular vibrational energy redistribution (IVR) induced by a Fermi resonance in the S_1 low energy regime of *p*-difluorobenzene has been experimentally observed for the first time. The corresponding photoelectron angular distributions (PADs) clearly reflect each Fermi component character of the resonance $5^1 \cdots 6^2$. The oscillation period for the IVR is estimated to be less than 20 ps.

Non-adiabatic alignment of the asymmetric molecule on excited state by femtosecond laser pulse was observed on real time via time-resolved photoelectron angular distributions (TRPAD). Surprisingly, the molecular-axis alignment revival at as long as 296 ps of S_1 o-dichlorobenzene was observed.

The pump-control-probe scheme is used to control chemicak reaction process. Combining the merits of the femtosecond and nanosecond lasers, we use the femtosecond lasers as the pump and control pulses, and nanosecond laser as the probe beam to detect the products with resonant enhanced multiphoton ionization scheme. Now, by introducing AC Stark shift with an IR fs laser as the control beam, we try to control the photodissociation of iodobenzene.

Studies of UVA-Induced DNA oxidative damage reactions

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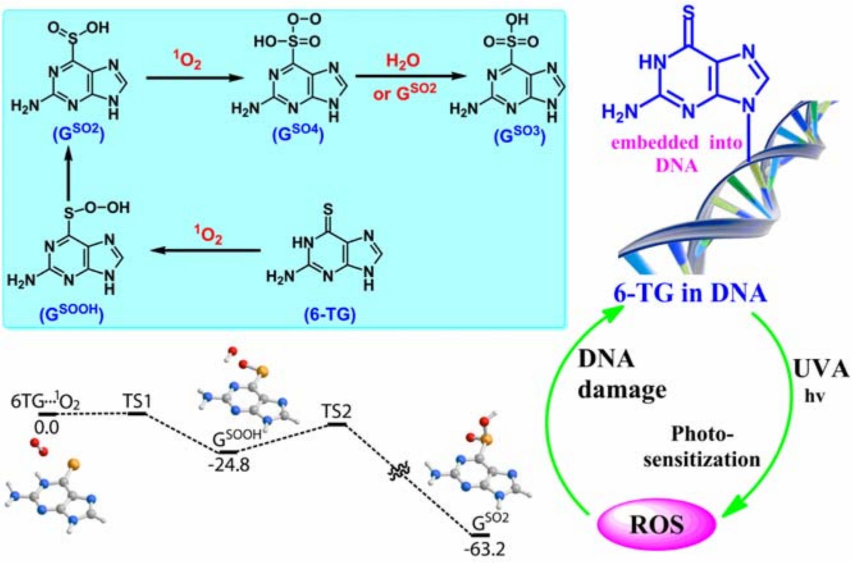
Ultraviolet solar radiation reaching the Earth's surface comprises wavelengths ranging from 290 to 320 nm (UVB) and 320 to 400 nm (UVA). Both UVB and UVA radiations have been demonstrated to induce DNA photodamage. UVA comprises >90% of incident ultraviolet radiation at the earth's surface and the UVA-induced DNA damage is detrimental but has been subject to lesser molecular dynamics studies compared to the reactions at shorter wavelength range of UVB. By absorbing UVA light through some endogenous or exogenous chromophores, the hazardous Reactive Oxygen Species (ROS) such as singlet oxygen and hydroxyl radical may be generated and cause successive DNA oxidative damage. The UVA-photocarcinogenesis has been mostly related to oxidative stress. In this context, we have studied a series of elementary reactions of ROS with nucleobases by means of transient IR, UV-Vis spectroscopy together with theoretical calculations. As two examples, we will report our most recent results on the OH reacting with guanine and $^1O_2$ reacting with 6-thioguanine (6-TG).



The revealed reaction mechanisms that 6-TG absorbs UVA generating $^1O_2$ and the oxidation of 6-TG itself by $^1O_2$ to the promutagenic product guanine-6-sulfonate (G^{SO3})

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Ultrafast mapping of population dynamics in the dark Triplet space via optical blockade enhanced emission

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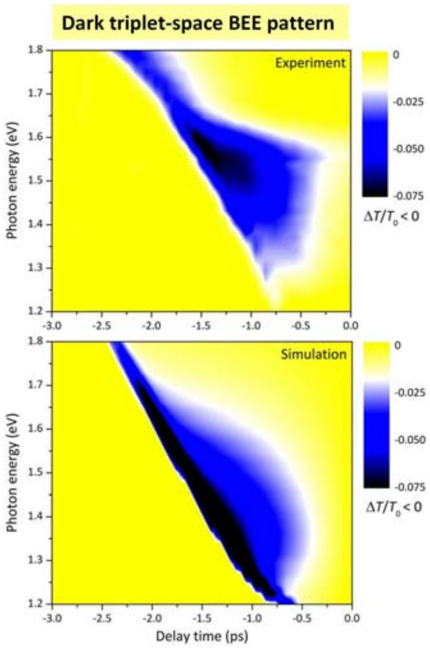
Effective manipulation between molecular singlet and triplet spaces holds the key to many new applications such as solar cells, photocatalysis, and organic light-emitting diodes, in which enhanced spin–orbit coupling or intersystem crossing (ISC) usually leads to greatly improved performance. In this context, insights into dynamics involved in singlet–triplet coupled molecular systems are highly desirable. The singlet dynamics can be routinely examined by conventional femtosecond (fs) pump–probe spectroscopy.

However, owing to the involvement of intrinsic, fast decay channels such as intramolecular vibrational redistribution (IVR) and internal conversion (IC), it is very difficult to single out the triplet dynamics. Here we develop a novel approach that uses an ultrafast white-light continuum to optically blockade decay channels within the singlet space, and hence to force the singlet-space populations to flow into the triplet space. With a set of well-designed fs time-reversed pump–probe (fs-TRPP) experiments assisted with modeling and simulations, we demonstrate on a proof-of-concept molecular system that the triplet dynamics can be mapped out through monitoring the blockade enhanced emission (BEE) solely in the triplet space. This new approach provides a general vehicle for exploring photonics and optoelectronics based on singlet–triplet coupled molecular systems.



Keywords: Singlet–Triplet Coupled Molecular Systems, Optical Blockade, Femtosecond Time-Reversed Pump–Probe

Ultrafast spectroscopy in nanosystems and biomedical application

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Nanopmaterials are found significant potential in health care application, including drug carrier, therapy, imaging and labeling. Photonic nanomaterials are one of the most studied species. In this presentation I will introduce some of our recent work on ultrafast spectroscopy of quantum dots, as well as our effort of using rare earth ions doped luminescence upconversionnanomaterials for biomedical application.

Our study reveals that the ultrafast emission in Si nanoparticles comes from hot electrons, and the long decay part is related with self-trapped excitons. NaYF4:Yb,Er upconversion nanoparticles demonstrate visible luminescence around 540nm and 650nm, upon 980nm cw excitation. We introduce covalent bonding to conjugate photosensitizing molecules to the nanoparticles, which significantly improves the drug loading capacity and photoexcited energy transfer efficiency from the nanoparticle to the photosensitizers. Results of *In vitro* test of cancer cells will be demonstrated.

Acknowledgement

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Conjugation Mediated Electronic Energy Transfer in Branched Chromophores Studied by Single Molecule Spectroscopy

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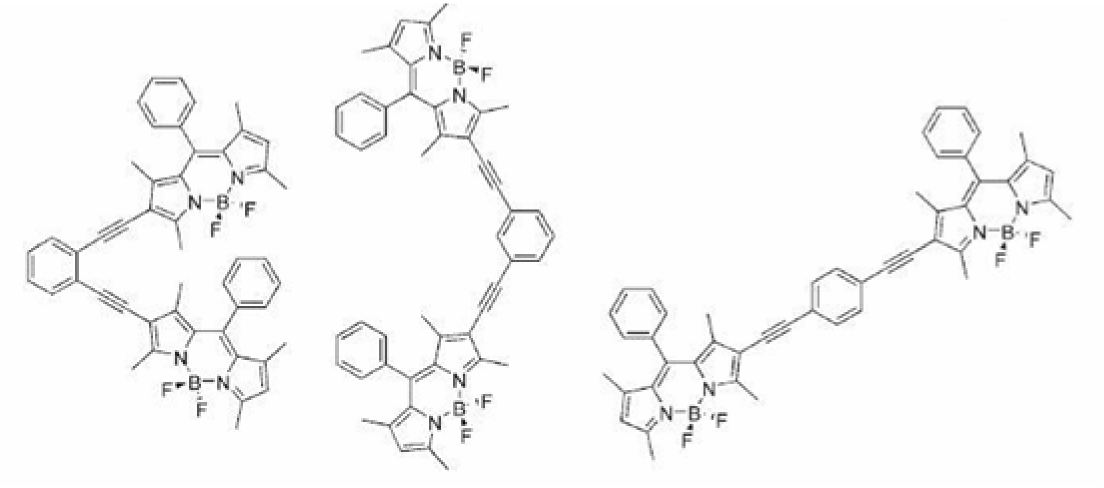
In this report, we will introduce a single molecule analysis of superexchange mediated-electronic energy transfer in branched chromophores. The purpose of the present work is to explore the role played by through-space (TS) and through-bond (TB) couplings on exciton interactions by examining electronic absorption spectra and single molecule spectra of three different BODIPY-dimers, in which the pair of BODIPY chromophores are held at well-defined distances and orientations by three typical rigid bridges (para-, meta- and ortho-linkers) of variable length and orientations. The strong-coupling and stepwise photobleaching of the two branches, depending on different pi-bridges have been observed at SM level. The TS and TB interactions are identified according quantum chemical calculation and single molecule analysis.



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Femtosecond X-ray Spectroscopy Studies of Electronic Excited States in Coordination Chemistry

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Transition metal complexes have many advantageous properties for solar energy applications, including strong visible absorption and photocatalytic activity. However finding earth abundant transition metal complexes with the optical excited state lifetimes necessary for maintaining an electrical or chemical potential has been proven challenging. Isoelectronic iron and ruthenium based complexes represent a clear example. The ruthenium-polypyridal based molecules have been the workhorse of solar energy related research and dye sensitized solar cells for decades, but the replacement of low abundance ruthenium with iron leads to million-fold reductions in optical excited state lifetimes.

Understanding the origin of this million-fold reduction in lifetime and how to control excited state relaxation in 3d-metal coordination complexes motivates our work using the x-ray free electron laser at the LCLS. We studied the impact of ligand field strength and solvent environment on the spin dynamics of a series of electronically excited $[\mathrm{Fe(CN)}_{6\text{-}2N}(2,2'\text{-bipyridine})_N]^{2N-4}$ complexes, with N = 1-3. These measurements verify the role of triplet ligand field excited states in the spin crossover dynamics from singlet to quintet spin configurations and demonstrate that modification of the ligand and solvent environment can lengthen the charge transfer lifetime by more than two orders of magnitude.

Microsolvation of monovalent salts in water: Anion photoelectron spectroscopy and ab initio calculations

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In order to understand the microsolvation of monovalent salt in water and provide information about the dependence of solvation processes on different ions, we investigated a series of salt-water clusters, such as $LiI(H_2O)_n^-$, $CsI(H_2O)_n^-$, and $NaCl(H_2O)_n^-$, using photoelectron spectroscopy. The structures of these clusters and their corresponding neutrals were investigated with *ab initio* calculations and confirmed by comparing with the photoelectron spectroscopy experiments. Our studies show that the SSIP type of structures start to appear at n=3 in $LiI(H_2O)_n^-$ cluster anions and at n=5 in neutral $LiI(H_2O)_n$. However, the separation of the Cs^+-I^- ion pair by water is insignificant in $CsI(H_2O)_n$ clusters. In $NaCl^-(H_2O)_n$ clusters, the Na-Cl distance increases abruptly at n=2, then decreases slightly and remains at about 4.0Å for n=3-6; while the Na-Cl distance in $NaCl(H_2O)_n$ neutral increases slightly from n=0 to n=3, reaches a maximum at n = 3 and then stays at about 2.75 Å for n=4-6. The neutral $NaCl(H_2O)_n$ clusters have CIP type of structures for cluster size up to n=6. The M-X distance in $MX(H_2O)_n^-$ is longer than that in neutral $MX(H_2O)_n$ and it is easier to separate the M and X atoms in $MX(H_2O)_n^-$ than those in neutral $MX(H_2O)_n$, because the excess electron weakens the Coulomb attraction of the M^+-X^- ion pair. The effect of water-water interactions starts to show up when the number of water molecules increases to five. These results indicate that the structural variation and microsolvation in $MX(H_2O)_n$ clusters are determined by the delicate balance between ion-ion, ion-water, and water-water interactions, which may have significant implications for the general understanding of salt effects in water solutions.

$\mathrm{CH_3F^+}$中的 Jahn-Teller 效应及隧道能级分裂

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The energy levels of $\mathrm{CH_3F^+}\left(\tilde{X}\,^2\mathrm{E}\right)$, which show strong vibronic coupling effect (Jahn-Teller effect), have been measured up to 3600 $\mathrm{cm^{-1}}$ above the ground vibrational state using one-photon zero-kinetic energy photoelectron (ZEKE) spectroscopic method. Theoretical calculations have also been performed to calculate the spin-vibronic energy levels using a diabatic model and *ab initio* adiabatic potential energy surfaces (APESs) including the energy gradients and derivative couplings between the APESs. The calculations showed that the tunneling splittings of the vibrational energy levels occur due to the deep potential energy wells formed by the Jahn-Teller deformation. The calculated spin-vibronic energy levels are in good agreement with the experimental data. For example, the energy splitting for the first excited vibrational energy level is calculated as 111 $\mathrm{cm^{-1}}$ that is confirmed by the experimental value. The experimental spectrum was assigned based on the fundamental vibrational modes calculated at the energy minimum. The fundamental vibrational modes related to the H-C-F bending, H-C-H bending, C-F stretching and C-H stretching vibrations have been observed.

State-to-state photodissociation dynamics of H_2O

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While photodissociation has been extensively studied in the past, new experiments have revealed more details of the dynamics. For example, Yang and coworkers have recently employed the high resolution H-Rydberg tagging technique to measure product state-resolved differential cross sections for the photodissociation of H_2O. While providing the most detailed information about dynamics, state-to-state DCSs in polyatomic photodissociation have seldom been calculated quantum mechanically, despite the existence of the photodissociation theory for more than 30 years. Recently, we developed a new set of non-adiabatically coupled potential energy surfaces for the lowest two $^1A'$ states of H_2O at the internally contracted multi-reference configuration interaction level with the aug-cc-pVQZ basis set. Quantum dynamical calculations carried out using the Chebyshev propagator yield absorption spectra, product state distributions, branching ratios, and differential cross sections, which are in reasonably good agreement with the latest experimental results.

Besides the non-adiabatic pathway by conical intersections between the $\tilde{B}$ and $\tilde{X}$ states of H_2O, there is another non-adiabatic pathway by the Renner-Teller coupling between the $\tilde{B}/\tilde{X}$ and $\tilde{A}$ states near linearity. To investigate the dissociation dynamics involving all three electronic states, a set of coupled diabatic PESs has been determined . We performed state-to-state quantum dynamics for the photodissociation of H_2O in its B band involving both non-adiabatic pathways in addition to the adiabatic pathway leading to the excited OH($\tilde{A}$) fragment. Our dynamical results indicate that, although the Renner-Teller non-adiabatic pathway plays a relatively minor role in the dissociation, the inclusion of all three electronic states is necessary to resolve the fine-structure population of the OH($\tilde{X}$) fragment.

Dissociation dynamics of state-selected molecular ions:application of threshold photoelectron-photoion coincidence velocity imaging

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Dissociation dynamics of state-selected (or energy-selected) molecular ions have been explored for a long history. Many significant parameters, e.g. bond energy (BE), appearance potential (AP) and branching ratio, can be obtained from them. In the past decades,threshold photoelectron-photoion coincidence (TPEPICO) measurement has been extensively applied as a powerful approach to investigate energy-selected molecular ions[1,2]. However, accuracy of BE and AP parameters is limited by the low coincidence efficiency and simulation of breakdown curves[1]. Recently, we have developed an upgraded experimental technique, named as TPEPICO velocity imaging[3],which combined synchrotron radiation and the high-resolution ion velocity imaging.Using this new technique, dissociations of several state-selected (or energy-selected)molecular ions have been investigated, especially for the high-symmetry halogenatedhydrocarbon, e.g. CH_3Cl^+, $C_2H_3Cl^+$, CF_4^+.More details of dissociation mechanisms and potential energy surfaces have been revealed. Moreover, dependence of vibrational modes on fragmentation branching ratios of molecular ions has been discussed as well.

Keywords: phtodissociation, photoionization, coincidence, halogenatedhydrocarbon

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Steric parameters in a chemical reaction from the aligned reagent experiment

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Effect of reagent approach geometry on reactivity has been investigated in alignment or orientation experiments for almost half a century. Until recently the complete 3-dimensional view of the steric effects of CH stretch excited CHD_3 molecules with Cl atoms have been successfully revealed by employing the crossed-beam technology in conjunction with an aligned reagent and a time-sliced, velocity-map-imaging method for probing the products. The angular distributions and speed distributions of products in these alignment experiments are fully resolved in a scattering plane, which provide all necessary ingredients to clearly delineate the very detailed aspects of stereodynamics in bimolecular reactions. For a more conventional and chemically intuitive quantity, the so-called "steric parameter" is used to describes the differential reactivity preference between the two limiting approach geometries: in the case of $Cl + CHD_3 \rightarrow HCl + CD_3$, the broken C-H bond pointing to the direction of the attacking Cl atoms versus the C-H bond lying in a plane perpendicular to the Cl atoms. Clearly, the steric parameter is a quantity exhibiting cylindrical symmetry with respect to the collision axis. However, the product images acquired in a typical alignment (orientation) experiment are in general azimuthal-asymmetric. This is because the three-vector (j, k, k') correlation information are intrinsically encoded in the images, which not only enables us to unfold the impact parameters (the "unfoldables") but also breaks the axial symmetry of the product images in the collision frame. We will show here how one can recover such steric parameters from a set of sliced images by proper symmetry considerations followed by the integration of the product fluxes over the entire scattering space.

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Spectral lineshape and Coherent Vibrational Dynamics of Molecules at Interfaces and in condensed phases: what sub-wavenumber resolution broadband sum frequency generation and stimulated Raman spectroscopy can offer?

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Spectroscopy and dynamics are the two faces of the same coin in understand the structure and interactions in the molecular and other physical systems. In principle, the molecular responses to the optical field in the frequency domain (spectroscopy) and in the time domain (dynamics) are connected by Fourier transformation of the respective induced polarizations. In this talk, I will discuss recent experimental development in sub-wavenumber high resolution spectral lineshape measurement with broadband surface sum frequency generation vibrational spectroscopy (SFG-VS) and femtosecond stimulated Raman spectroscopy (FSRS) in our laboratory, and the theoretical framework on understanding the lineshape in the complex SFG and SRS vibrational spectra and the coherent vibrational dynamics. Examples on how to resolve fine split in the vibrational spectra, on how to determine homogeneous and inhomogeneous interaction in the confined molecules, etc., are to be discussed. The perspective on how these new tools and concepts will impact our understanding and characterization of the details and inhomogeneity in the molecular world is also to be discussed.

Structures and Reactions of Methanol and Water on TiO2 surfaces Studied by Sum Frequency Generation VibrationalSpectroscopy

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TiO_2 material has attracted more and more attention in both scientific fields and industries due to its wide application in photosplitting of water and photodegradation of organic contaminants, which are strongly relating to the energy crisis and the environmental pollution in our world. We have concluded that methanol molecules on TiO_2 surface can be photoinduced dissociation, photooxidized to formaldehyde, and even further oxidized to methylformate in cross-coupling mechanism studied by two-photon photoemission spectroscopy(2PPE) and temperature programmed desorption(TPD) with laser in the last three years. In this talk, we will show our latest results of the structures and reactions of methanol and water molecules on TiO_2 film studied by sum frequency generation vibrational spectroscopy(SFG-VS), which was newly set up in Peking University.

Key word: Surface Photocatalysis, Surface Reaction, TiO2, SFG-VS

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Reactivity of Atomic Oxygen Radical Anions over Metal Oxide Nano-Particles in the Gas Phase: C−H Bond Activation and CO Oxidation

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Atomic oxygen radical anions (O^-) are important reactive intermediates involved in oxidation reactions over widely used transition metal oxide catalysts.[1,2] Due to short life-times and low concentrations, the chemistry of O^- radicals is often poorly characterized in condensed phase systems. We have prepared a few series of O^- containing transition metal oxide cluster ions with dimensions up to nano-sizes and studied their reactivity toward C-H bond activation and CO oxidation by mass spectrometry and quantum chemistry computations.[3-5] We will introduce interesting cluster-size and metal-type dependent reactivity for nano-particle bounded O^- anions in the gas phase.

Keywords: Oxygen-centred radical; Atomic cluster; Nano size; Mass spectrometry; Density functional theory

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Neat Liquid Structural Dynamics Probed with Femtosecond Overtone Two-dimensional Infrared Spectroscopy

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Understanding the structure and dynamics of neat liquid at the chemical-bond level is of great importance. Here, an overtone two-dimensional infrared (2D IR) method is reported, allowing correlated molecular motions of neat liquid at the frequencies of overtone transitions to be examined. Waiting time-resolved overtone 2D IR spectra of the C-O stretching in neat liquid methanol reveal that the auto-correlation of the $v = 0 \rightarrow 2$ transition and the cross-correlation of the $v = 0 \rightarrow 2$ / $v = 2 \rightarrow 4$ transitions differ considerably in relaxation times, suggesting different spectral diffusion dynamics. Quantum-chemical computations in combination with *ab initio* molecular dynamics simulations suggest that the overtone transition frequency of the C-O stretching mode in liquid methanol is of more structural sensitivity than its fundamental counterpart. This work demonstrates a new 2D IR approach to examining the structural sensitivities of the anharmonic potential parameters of higher vibrational states, which can be used to gain new insights into the ultrafast structural dynamics particularly for neat liquids. Systems containing coupled vibrators are currently under investigation.

Keywords: 2D IR spectroscopy; FFCF; anharmonicity; neat liquid; ultrafast structural dynamics

Spectroscopic observationof Photo-Induced Metastable Linkage Isomers of Coinagemetal (Cu, Ag, Au) Sulfur DioxideComplexes

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Coinage metal atom (Cu, Ag, Au) reactions with SO_2 were investigated by matrix isolation infrared absorptionspectroscopy. Both the mononuclear complexes $M(\eta^1\text{-}SO_2)$ (M=Ag, Au) and $M(\eta^2\text{-}O_2S)$ (M=Ag, Cu),and the binuclear SO_2-bridged species $M_2(\mu_2\text{-}SO_2)$(M=Ag, Au) were observed during condensation in solid argon or neon. Interestingly, the silver participated mononuclear complexes are interconvertible; that is, visible light induces theconversion of the S-coordinated complex$Ag(\eta^1\text{-}SO_2)$ to theη^2-O,O′ coordinated one $Ag(\eta^2\text{-}O_2S)$and vice versa on annealing. However, there is no evidence for $Au(\eta^2\text{-}O_2S)$ molecule. These different behaviors are discussed within the bonding considerations for all the obtained products.

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Coherent energy transfer in light-harvesting: symmetry, disorder, and aggregation

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Quantum coherence plays a central role in natural and artificial light-harvesting complexes and is explored by my group in terms of symmetry, static disorder, and the size and alignment of these complexes.

(1) An intriguing observation of photosynthetic light---harvesting systems is the N-fold Symmetry of light-harvesting complex 2 (LH2) of purple bacteria. We have calculated the optimal rotational configuration of N fold rings on a hexagonal lattice, and established the symmetry principles for the promotion of maximum excitation energy transfer (EET). For certain fold numbers, there exist optimal basis cells with rotational symmetry, extendable to the entire hexagonal lattice for the global optimization of the EET network, such that these basis cells can reduce or remove the frustration of EET rates across the photosynthetic network. [1] Remarkably, one consecutive group of such symmetry numbers consists of the naturally occurring 8-,9-&10-fold rings, suggesting the design principle of matching the internal symmetry with the lattice order.

(2) We have studied coherent quantum transport in disordered 1-D and 2-D systems and clearly showed an optimal diffusion constant at an intermediate level of noise. [2] Scaling Analysis similar to the mean first passage time analysis [3] indicates the crucial role oflocalization length. Further detailed studies reveal that optimal diffusion depends ritically on dimensionality and range of interactions, and may not be observed in certain systems due to different scaling laws. We are also developing methods to calculate transport in a thermal environment and predict its temperature-- ‐ dependence.

(3) We have developed a novel numerical method [4] to predict the quantum dynamics of extended systems. Based on the concept of dynamical maps, our method extracts all available information encapsulated in short-time non-Markovian quantum trajectories and compresses it into tensors of reduced size. Efficient propagation of these tensors generates dissipative quantum dynamics of large systems with arbitrary spectral densities, e.g., molecular chains of hundreds of sites with strong quantum dissipation. Further, it can be applied to experimental settings in the same spirit as processing tomography and permits direct reconstruction of dynamical operators, i.e., the Hamitonian and memory kernel.

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有机太阳能电池中的相干电荷和能量转移

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电荷和能量转移广泛存在于物理、化学、生物、材料等体系中，尤其是最近发展起来的有机太阳能电池中，电荷和能量转移过程对电池效率起到决定性作用[1]。理论上理解其过程不仅要考虑电荷和能量在电子态之间的转移过程，同时要考虑电声耦合作用，使得传统电荷转移理论如发展较成熟的相干能带机制和局域蛙跳模型无法直接应用，导致对载流子迁移是蛙跳或相干机制的确定还存在争议。本文工作中，我们提出了将蛙跳和能带模型统一起来的含时波包扩散动力学方法来克服传统动力学方法的局限性，同时结合电子结构计算，找出控制载流子和能量传输机制的关键因素。具体内容包括：从含有动态涨落的微绕理论出发提出的有别于著名 Marcus 公式的电荷转移解析表示[2]；相干电荷转移的含时波包扩散方法[3]；电子结构计算和发展的速率模型结合起来研究有机体系中的电荷转移过程和理论上设计高效有机太阳能电池的途径等[4,5]。

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Small-Number Effects: Novel Stability Induced by Fluctuation and Discreteness in a Genetic Toggle Switch System

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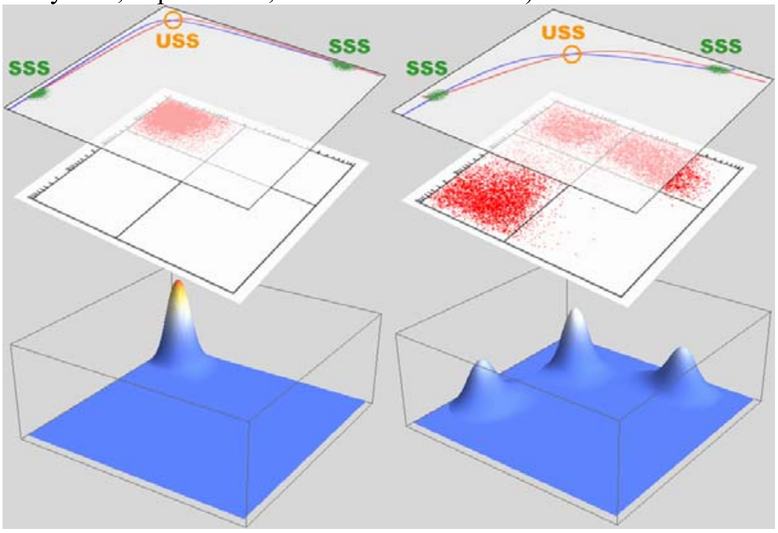
A third stable state has been found in a genetic toggle switch system that was supposed to be bistable. Our study[1] identified, for the first time in experiment, discrete and fluctuate nature can bring on additional kinetic stability of chemical reaction system, especially nearby the unstable steady state (USS) predicted by differential dynamical systems theory. Stochastic simulation via kinetic Monte Carlo (KMC) method agrees with the experimental results. (Results are briefly drawn below, from top to bottom: differential dynamical system, experiments, and KMC simulation.)



It is a dramatic phenomenon to present additional stability just nearby traditionally regarded unstable point. We have theoretically revealed that this is because of molecular numbers' fluctuation and discreteness in small chemical reaction systems, which have pivotal molecules fluctuating on the verge of extinction. Similar effects have general significance in kinds of small systems, and have been called attention to in several theoretical works [2,3]. Furthermore, the additional stable state makes order-of-magnitude change on sensitivity of our practical system; hence it becomes supersensitive to some certain external signals, and this can be used for biosensors.

Keywords: Discreteness, Fluctuation, Stochastic Stable State, Genetic toggle switch

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State-to-state Reactive Scattering by MCTDH method

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In this report, new development on state-to-state (SS) triatomic reactive scattering using quantum wavepaket method in our group will be introduced, using MCTDH method, basing upon our recently developed reactant coordinate based method [1,2,3,4]. Using MCTDH method, now we can extract state-to-state DCS of triatomic reactive scattering and further development is ongoing [5]. The merits and disadvantages of this method will be discussed.

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Development of New Density Functionals: Towards Accurate Descriptions of Potential Energy Surfaces

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A potential energy surface (PES)is a mathematical function thatgives the energy of a molecule as a function of its geometry.It is a central concept in computational chemistry that plays an important role in understandingthe chemical reaction dynamics.

Quantum Mechanics provides an energy function whichcan be exact in principle and works for any molecule. Inpractice,however, approximate quantum methods have to be used except for some trivial systems.This talk will be devoted to the development of new density functionals. Emphasis will be laid on the XYG3-type doubly hybrid functionals(xDHs) in predicting the reaction energies and reaction barrier heights.

The most interesting points on PES' are the stationary points (minima and transition states),where the gradients with respect to all internal coordinates arezero.We will introduce a theoretical development of the equations required to perform an analytic geometry optimization of a complex molecular system using xDHs.

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Theoretical study of photoionization dynamics of alkyl peroxy radicals

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The ionization energies (IEs), electron affinities (EAs), and heats of formation ($\Delta_f H$) for the methyl peroxy (CH_3OO), ethyl peroxy (CH_3CH_2OO) and benzyl peroxy radicals ($C_6H_5CH_2OO$) have been calculated by the wave-function-based *ab initio* CCSD(T)/CBS approach included with energy corrections such as zero-point vibrational energy (ZPVE), core-valence (CV), scalar relativistic (SR) and spin-orbit (SO) corrections. Ionization of methyl peroxy radical gives a stable CH_3OO^+ cation in triplet state whereas the methyl peroxy radical dissociatively photoionizes into $CH_3CH_2{}^+$ and O_2. The benzylperoxy cation unexpectedly is found to be stable and non-dissociative. This finding is inconsistent with the general trend that the stability of alkyl peroxy cation (ROO^+) decreases with the size of R. The stability of benzylperoxy cation is rationalized with the considerations of potential energy surface, molecular orbitals and structures. The comparison between the theoretical predictions and the highly precise experiment EA values for the peroxyl radicals show that the CCSD(T)/CBS method is capable of providing an accurate EA prediction for the peroxyl radicals with an uncertainty of ±10 meV. The present calculations gives prediction to IE(CH_3OO) = 10.27 eV, which is 0.06 eV lower than the experimental value of 10.33 ± 0.05 eV. For the CH_3CH_2OO and $C_6H_5CH_2OO$ radicals, our computed IE values are IE(CH_3CH_2OO) = 9.60 eV and IE($C_6H_5CH_2OO$) > 9 eV, respectively.

Keywords: ionization energy, peroxy radical, photoionization

Probing hydrated anion and neutral clusters using size-selected, low temperature photoelectron spectroscopy and ab initio calculations

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In this talk, I will present our recent development in using size-selected, low-temperature photoelectron spectroscopy and ab initio calculations to study a variety of complex anions solvation. We found significant solute anisotropy effects in preferably selecting solvent network to align solute permanent dipole with the solvent electric field in hydrated neutral clusters. Thermodynamic advantage of organic acids in facilitating formation of bisulfate ion clusters, an important issue related to atmospheric chemistry will also be discussed in my talk.

理论化学在燃烧化学动力学中的应用

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燃烧是非常复杂的化学和物理过程，除了热传导、扩散等物理过程，还伴随着燃料分子的解离、氧化以及小分子的复合等多种类型的化学反应的发生。研究燃料燃烧过程中的化学反应机理及其动力学机制是认识燃烧现象的本质的基础，同时对实现数值模拟宏观燃烧现象如火焰温度、点火延迟时间以及污染物的排放等至关重要。如何利用实验或计算的手段得到准确的基元反应热力学和动力学数据从而提高数值模拟的精度是目前燃烧研究的热点和难点问题之一。

随着量子化学方法和计算机水平的发展，理论计算在燃烧化学动力学基础研究领域逐渐发挥越来越重要的作用[1,2]。由于燃烧体系中涉及到的化学反应网络复杂、计算量较大，需探索适合燃烧体系研究的精度高、计算量适中的量子化学方法尤其需在热力学计算方面具有良好的表现；在燃烧条件下发生的许多反应如单分子反应、复合反应具有较强的压力效应，目前考虑温度和压力效应的统计动力学理论如 RRKM/主方程方法在对压力效应的模拟方面主要采用的是经典的能量传递模型，其中参数的选择带有较强的经验性；理论计算化学反应的热力学(如熵和焓)和动力学数据(即反应速率常数)的准确性同时依赖于量子化学计算和统计动力学计算的精确性，预测燃烧化学动力学模型的不确定性要求从量子化学计算和统计动力学模型的不确定性出发分析热力学和动力学数据的不确定性[3]。因此，如何从量子化学计算和统计动力学理论两个方面提高考虑温度和压力效应的基元反应速率常数的计算精度并对其进行精确的不确定性分析是化学动力学理论研究面临的极大挑战，而近年来燃烧化学的飞速发展为此提供了良好的契机。

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Mode and Bond Selectivity in Bimolecular Reactions: Extension of Polanyi's Rules

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It is well established that different forms of energy have different efficacies in promoting an activated bimolecular reaction in the gas phase. Based on both experimental and theoretical evidence of the time, Polanyi's proposed a set of rules to determine the relative efficacies of vibrational vs. translational energy in atom-diatom reactions. These rules were based on the location of the barrier: translational energy is more effective in promoting an early barrier reaction than vibrational energy, while vibrational energy is more effective in promoting a late barrier reaction than translational energy. However, an increasing body of evidence suggests a straightforward extension of Polanyi's rules to polyatomic molecules is difficulty. We reexamine the Polanyi's rules for several prototypical atom-diatom reactions and propose a sudden vector projection (SVP) model based on the alignment of reactant translational/vibrational normal mode vectors with the transition state vector representing the reaction coordinate. It is shown that SVP is consistent with Polanyi's rules for atom-diatom systems and is capable of explaining the mode and bond selectivities in polyatomic reactions as well.

The Effect of Ion Pairing on the Dynamics and Spectroscopy of the Strong Electrolyte Solutions

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We carried out series of spectral modeling based on the molecular dynamics simulation to help understanding the dynamic events in the ionic solution systems. By calculating different ionic solution spectra based on the same simulation trajectory ensemble, they achieved a better understanding of the underlying physics. Simulation suggests that ion pairing is the reason of various spectroscopic features. Spectroscopy provides vivid microscopic evidences for the existence of ion pairing.

Ab initio based non-adiabatic dynamics simulation on photophysics and photoisomerization of acrolein in the gas phase and aqueous solution

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Acrolein (CH_2CHCHO) is the simplest member of the unsaturated aldehyde family. The photophysics and photochemistry of this class of compounds are extremely varied and are of unique interest, which has been the subject of numerous experimental and computational studies.[1-3] In this presentation, the combined CASPT2/CASSCF electronic structure method has been used to determine stationary and intersection structures of CH_2CHCHO on the lowest five electronic states (S_0, $^{1,3}n\pi^*$, $^{1,3}\pi\pi^*$), which is followed by non-adiabatic dynamics simulation. These provide new insight into photophysics and photoisomerization of CH_2CHCHO and the related compounds.

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Effect of intermolecular hydrogen bonding on molecular fluorescence

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Because of its fundamental importance in many branches of science, hydrogen bonding is a subject of intense contemporary research interest. The physical and chemical properties of hydrogen bonds in the ground state have been widely studied both experimentally and theoretically by chemists, physicists, and biologists. However, hydrogen bonding in the electronic excited state, which plays an important role in many photophysical processes and photochemical reactions, has scarcely been investigated.

Upon electronic excitation of hydrogen-bonded systems by light, the hydrogen donor and acceptor molecules must reorganize in the electronic excited state because of the significant charge distribution difference between the different electronic states. The electronic excited-state hydrogen-bonding dynamics, which are predominantly determined by the vibrational motions of the hydrogen donor and acceptor groups, generally occur on ultrafast timescales of hundreds of femtoseconds. As a result, state-of-the-art femtosecond time-resolved vibrational spectroscopy is used to directly monitor the ultrafast dynamical behavior of hydrogen bonds in the electronic excited state. It is important to note that the excited-state hydrogen-bonding dynamics are coupled to the electronic excitation. Fortunately, the combination of femtosecond time-resolved spectroscopy and accurate quantum chemistry calculations of excited states resolves this issue in laser experiments. Through a comparison of the hydrogen-bonded complex to the separated hydrogen donor or acceptor in ground and electronic excited states, the excited-state hydrogen-bonding structure and dynamics have been obtained. Moreover, we have also demonstrated the importance of hydrogen bonding in many photophysical processes and photochemical reactions.

In this Talk, I will present our recent advances in electronic excited-state hydrogen-bonding dynamics and the significant role of electronic excited-state hydrogen bonding on internal conversion (IC), electronic spectral shifts (ESS), photoinduced electron transfer (PET), fluorescence quenching (FQ), intramolecular charge transfer (ICT), and metal-to-ligand charge transfer (MLCT). The combination of various spectroscopic experiments with theoretical calculations has led to tremendous progress in excited-state hydrogen-bonding research. We first demonstrated that the intermolecular hydrogen bond in the electronic excited state is greatly strengthened for coumarin chromophores and weakened for thiocarbonyl chromophores. We have also clarified that the intermolecular hydrogen-bond strengthening and weakening correspond to red-shifts and blue-shifts, respectively, in the electronic spectra. Moreover, radiationless deactivations (via IC, PET, ICT, MLCT, and so on) can be dramatically influenced through the regulation of electronic states by hydrogen-bonding interactions. Consequently, the fluorescence of chromophores in hydrogen-bonded surroundings is quenched or enhanced by hydrogen bonds.

Keywords: Hydrogen bonding; Electronic excited state; Structures and dynamics; Internal conversion; Radiationless deactivations; Fluorescence quenching and enhancement

Direct Dynamics Simulations of the Nucleophilic Substitution Reactions. Unanticipated Atomistic Mechanisms

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Anion-molecule nucleophilic substitution (S_N2) reactions are known for their rich reaction dynamics, caused by a complex potential energy surface with a submerged barrier and by weak coupling between the intermolecular and intramolecular modes of collision complexes. Recently, Mikosch *et al.* reported kinematically complete reactive scattering experiments of the S_N2 reactions $X^- + CH_3I \rightarrow XCH_3 + I^-$ (X = F and Cl) using crossed molecular beam imaging.[1] For the work reported here direct dynamics simulations were performed to obtain an atomistic understanding of the experiments. The simulations well reproduce the product energy partitionings and the velocity scattering angle distributions measured in the experiments and show nontatistical dynamics. For $Cl^- + CH_3I$ reaction, a previously unknown roundabout reaction mechanism involving CH_3 rotation has been identified.[1,2] The principal mode for this mechanism is depicted in Figure 1. The simulations reveal that the $F^- + CH_3I$ reaction occurs by three atomic-level mechanisms, an indirect reaction proceeding via an $F^-{-}HCH_2I$ hydrogen-bonded complex, a direct rebound, and a direct stripping reaction.[3,4] The indirect mechanism is found to contribute about one-half of the overall substitution reaction rate. These mechanisms may play an important role for more complex ion-molecule reactions.

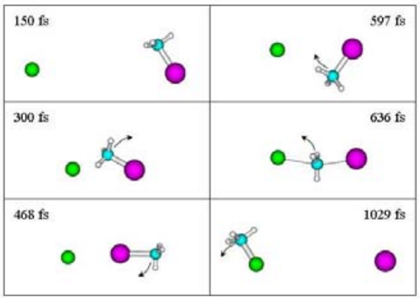

Figure 1. View of a typical trajectory for the roundabout reaction mechanism that proceeds via CH_3 rotation.

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Ab Initio Kinetics for the Decomposition of Hydroxybutyl and Butoxy Radicals of n-Butanol

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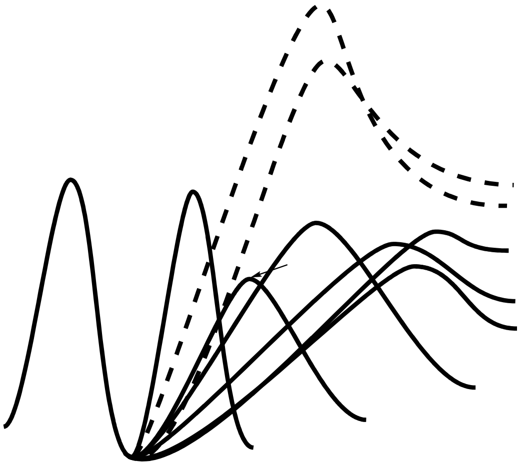
The decomposition kinetics of the hydroxybutyl and butoxy radicals (C_4H_9O) arising via H abstraction from n-butanol were studied theoretically with *ab initio* transition-state-theory-based master equation analyses. Stationary points on the C_4H_9O potential energy surface were calculated at either the RQCISD(T)/CBS//B3LYP/6-311++G(d,p) level or the RQCISD(T)/CBS//CASPT2/aug-cc-pVDZ level. Unimolecular pressure- and temperature- dependent rate coefficients were calculated over broad ranges of temperature (300-2500 K) and pressure (1.3×10^{-3}-10^2 atm) by solving the time-dependent multiple-well master equation. The "well merging" phenomenon was observed and analyzed for its influence on the branching ratios and rate coefficients. The theoretical predictions were compared with the available experimental and theoretical data and any discrepancies were analyzed. The predicted rate coefficients are represented with forms that may readily be used in combustion modeling of n-butanol.

Keywords: *Ab initio* Kinetics, n-butanol, decomposition reaction, transition-state theory, multiple-well master equation



Accurate Determination of Interfacial Protein Structure Probed by Combining Amide I and Amide III signals

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Accurate determination of protein structures and dynamics at interface is essential to understand the nature of interfacial protein interaction and thus control bio-interface in a desired manner. To this end, sum frequency generation vibrational spectroscopy (SFG-VS) has been successfully applied to characterize the structure and orientation of various biomolecules (including peptides and proteins) in different chemical environments by detecting SFG amide I signals from surfaces or interfaces. However, amide I signals overlap with the water bending modes at ~1645 cm^{-1}. Besides this, the characteristic amide I bands of various secondary structures are clustered in the spectral region of 1600-1700 cm^{-1}, and it is extremely difficult to distinguish α-helical and random-coil structures because of their serious overlapping in the frequency at ~1650 cm^{-1}. In contrast, amide III bands comprise the spectral range between about 1200 and 1400 cm^{-1}. There is no water interference in the amide III spectral region. In this report, we demonstrate it is feasible to collect amide III SFG spectra of protein and peptide molecules at solid/air and solid/liquid. We successfully determined interfacial protein secondary structure accurately by employing the combination of amide I and amide III signals. To our knowledge, this work is the first to report amide III SFG vibrational spectra from the interfacial proteins and peptides experimentally. We believe the application of combination of multiple amide bands will provide an effective probe to characterize cooperative action of interfacial protein molecules as well as their localized structure changes.

Ultraviolet Photochemistry of Alkyl Radicals

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The H-atom elimination channels in the ultraviolet (UV) photodissociation of a series of prototypical alkyl radicals (methyl, ethyl, propyl, butyl, and cyclo-hexyl) are investigated using the high-n Rydberg atom time-of-flight (HRTOF) technique. In the photodissociation of methyl radical at 216.3 nm, the H + CH_2 product translational energy distribution shows that CH_2 is produced exclusively in the ground vibrational level of the $\tilde{a}^1A_1$ state with modest rotational excitation. A negative anisotropy parameter is observed, consistent with the perpendicular B^2A_1' <- X^2A_2'' transition and a fast dissociation by tunneling. The rotational structure of the CH_2 ($\tilde{a}^1A_1$, $v = 0$) product is well resolved, providing detailed information of the tunneling dissociation dynamics.

Upon excitation to the $\tilde{A}^2A_1(3s)$ state at 245-nm, ethyl dissociates into H atom and ethylene. Bimodal profile in the product translational energy distribution and energy-dependent product angular distribution suggest two different dissociation pathways. A slow and isotropic component corresponds to unimolecular dissociation of the hot radical after internal conversion from the Ã state to the ground state. A fast and anisotropic component corresponds to a direct, rapid H-atom scission via a nonclassical H-bridged transition state from the 3*s* state to yield H + C_2H_4. The dissociate rate of the H-atom elimination channel of ethyl is reinvestigated.

Upon excitation to the 3*p* state in the region of 237 nm, *n*-propyl radical and *iso*-propyl radical dissociate into the H atom and propene products. The product translational energy release of both *n*-propyl and *iso*-propyl radicals also have bimodal distributions. The H-atom product angular distribution in *n*-propyl is anisotropic (with ~ 0.5), while that in *iso*-propyl is isotropic. The bimodal translational energy distributions also indicate two dissociation pathways, a unimolecular dissociation pathway from the ground-state propyl after internal conversion from the 3*p* state and a repulsive pathway directly connected with the excited state of the propyl radical. Isotope labeling experiments are also carried out.

掺杂和缺陷对碳纳米管吸收及发射光谱的影响

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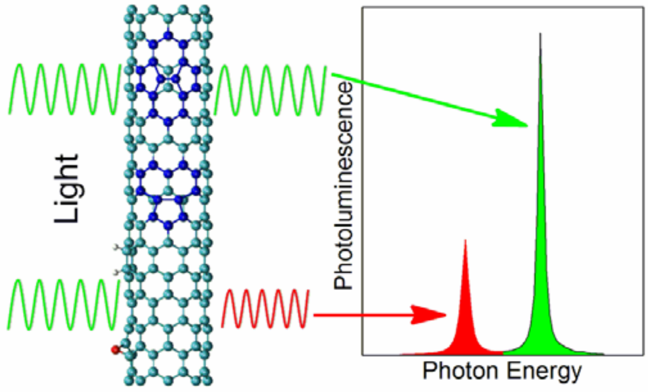
碳纳米管作为一种新型的准一维材料，自 1991 年被 Iijima 发现以来，由于其独特的光学性能，在纳米光学器件方面有着良好的应用前景，成为国际新材料领域的一个热门课题。然而，碳纳米管本身的荧光产率很低，不易检测，这一定程度上限制了其应用。近年来，实验上发现，在单壁碳纳米管的表面用 O、H 进行修饰，或者引入空位、Stone-wales 缺陷，可以在碳纳米管的荧光谱中产生强度很高的红移峰[1]。以前的理论工作大多认为，这些新的红移峰是由碳纳米管自身的暗激子产生的，比如三重态激子，或者偶宇称激子。由于完美单壁碳纳米管本身的吸收和发射峰位置基本重合(Stokes 位移只有约 4 meV)，这些理论工作忽略了掺杂和缺陷存在下，碳纳米管激发态动力学的影响。另外，在引入掺杂剂和缺陷之后，碳纳米管本身的能带结构和跃迁选律也会变化。为了更好的解释这些新的红移峰产生的原因，本文应用基于多体格林函数理论的 GW 方法和 Bethe-Salpete 方程[2,3]，详细研究了掺杂和缺陷对单壁碳纳米管吸收及发射光谱的影响。结果表明，吸附 H 和引入缺陷后，碳纳米管自身的能带结构会发生变化，且在费米能级附近产生新的态，进而影响了碳纳米管的跃迁选律。激发态动力学在掺杂碳纳米管的发射光谱中起非常重要的作用，其 Sokes 位移可达 170 meV。

关键词：单壁碳纳米管、缺陷、激发态动力学、吸收和发射光谱、Stokes 位移



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The AC frequency driven collision-induced dissociation (CID) of gas phase ions in digital ion trap mass spectrometer

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Introduction

In mass spectrometry, the collision-induced dissociation (CID) of mass selected ions in the ion trap by resonance excitation has become the most popular method for the tandem mass analysis of chemical and biological molecules[1-10]. The CID results could be used for several purposes, such as to obtain the information about molecular structure and conformation, to achieve more sensitive and specific detection of molecule by looking for a unique fragment ion in the presence of other molecules of the same nominal molecular weight, essentially reducing the background and increasing the limit of detection. The conventional CID process was realized by applying a small supplementary AC potential which with the same frequency as the secular frequency of mass selected parent ion to the end-cap electrodes of an ion trap. And then the parent ions could be resonance excited to a higher kinetic energy level, when these high energy ions collided with bath gas molecule, they would dissociate to fragment ions.

In this work, a new method for CID experiments was further developed and studied in a digital ion trap mass spectrometer. A well-defined dipolar DC potentials were applied to one pair of x-electrodes for ion excitation and collision induced dissociation by change the period or the frequency of the excitation waveform. Since the dipolar DC could be simply produced by computer software, any additional power supply and experimental setup modification is unnecessary.

Method

A homemade three-stage differential pumping vacuum system as previously described was used in this studied as shown in Figure 1. Briefly, the sample ions from an electrospray (ESI) source were transferred by a RF-only quadrupole ion guide, and then into the ion trap.

基于变温红外光解离光谱的团簇结构及反应动力学研究

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光学光谱和质谱对研究分子反应动力学做出了巨大的贡献。其中，红外光谱由于能很好的鉴别同分异构体的功能，因而在表征分子结构方面比其他光谱学方法有着明显的优越性。在气相中，直接测量红外吸收光谱(即傅里叶变换红外)至少需要 10^{13} 分子/立方厘米的数量密度；然而，在通常的气相实验中，离子的数量密度是 10^{6-8} 分子/立方厘米，低得不足以用传统的红外吸收光谱仪来测量。因此，需要用替代的技术(如红外光解离光谱学，Infrared Photodissociation Spectroscopy，以下简称IRPD)[1]来测量。IRPD 的基本原理是离子吸收特征波长的光子发生共振解离，通过测量碎片离子的产率随红外光解离光源波长的变化关系获得振动光谱。该方法被认为是研究选质量团簇结构的最有效方法之一。虽然 IRPD 实验方法早在 1985 年就出现了，但只有在过去 10 年里 OPO/OPA 和自由电子激光等红外激光光源出现以后，IRPD 光谱才得到很大的发展。在本报告中，我们将首先介绍变温红外光解离光谱的实验方法，然后介绍其在团簇结构及反应动力学研究中的几个应用实例(例如，硝酸镁离子对水合作用机理，二羧酸双负离子折叠机理，以及参杂金属团簇活化 C-H 机理等)[2-7]。

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多原子反应动力学的理论研究

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四原子反应全维态-态微分截面的成功计算表明了四原子反应量子散射问题最终得到了彻底的解决，而多原子反应的精确动力学研究也就成了我们目前最大的挑战。在这个报告中，我将介绍我们最近在 H/F/Cl+CH_4 及其同位素取代物这类六原子反应的理论研究方面所做的一些工作。我们利用神经网络成功构造了这些六原子反应的势能面，比较发现新拟合的势能面比已有的通过交换不变多项式拟合的势能面在精度上有明显的提高。我们也发展了一个新的七维模型，实现了这类六原子反应的态-态动力学研究。理论与实验的比较显示我们已经能比较精确地研究这类多原子反应，并在一定程度具有了检验实验的能力。

全微分符合测量技术在强激光场原子分子物理实验研究中的应用

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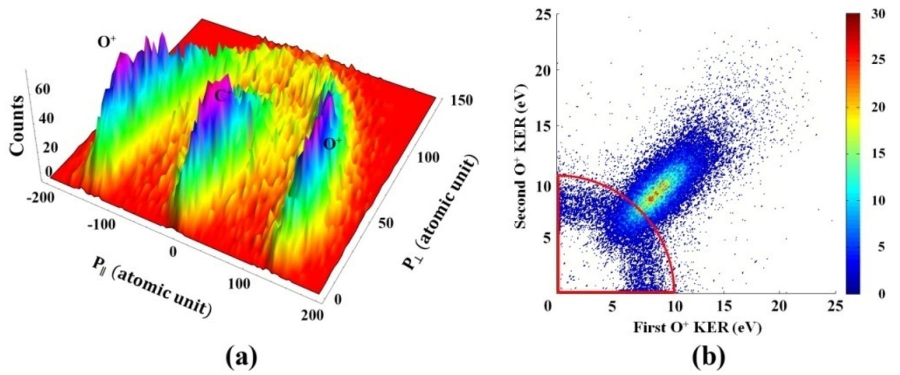
飞秒激光具有超短的脉冲宽度和超强的峰值功率，已经成为测量和操控原子分子超快动力学行为的重要工具。但是飞秒强激光场下，原子分子有多个反应通道，如单电离、双电离、电离后的解离以及库仑爆炸等。特定反应通道精确的动力学数据是建立和验证强场原子分子理论模型，揭示强激光场与原子分子相互作用物理本质的重要基础。冷靶反冲离子动量谱仪能够对所有反应产物的三维动量进行全微分符合的高精度测量，提供特定反应通道的精确实验数据，重构光物理化学反应进程，是研究强场原子分子物理的重要工具。经过多年努力，北京大学物理学院新建成了一台冷靶反冲离子动量谱仪，各项性能指标均达到国际同类装置的先进水平。利用其强大的全微分符合测量性能，我们在强激光场原子分子物理实验研究方面取得了一些突破[1-6]，研究成果入选“2012 年度中国高等学校十大科技进展”。本报告将介绍我们自建的这台冷靶反冲离子动量谱仪的全微分符合测量性能以及我们在强激光场原子分子超快成像研究中的所取得的重要进展。



(a) (b)

图 1：飞秒激光场驱动的 CO_2^{3+}三体解离生成的(a)关联离子动量分布和(b)关联 O^+的能量关联。

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低能量电子贴附分子解离动力学

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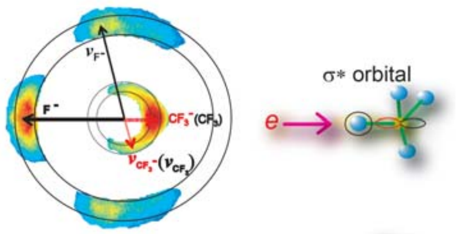
低能量电子贴附到分子上可以形成处于电子－分子共振态(electron-molecule resonance)的瞬态负离子分子，其衰退中比较重要的一个过程是解离为中性和带负电的碎片，此过程被称为电子贴附解离(dissociative electron attachment，DEA)。DEA 过程多见于高能粒子的辐射损伤和等离子体中。



图(一) CF$_4$ 分子的电子取向贴附与负离子碎片 F$^-$和 CF$_3^-$动量角度分布[6]。

FIG.1 Orientation effect on the electron attachment to CF$_4$ and the momentum angular distributions of F$^-$ and CF$_3^-$ fragments[6].

我们将脉冲低能电子束和离子速度成像技术相结合，研制了一台用于 DEA 动力学研究的谱仪装置[1]。我们最近开展了一系列相关实验研究，揭示了 CO$_2$ 分子 DEA 中的 Renner-Teller 效应[2]、N$_2$O 分子 DEA 中的通道竞争机制[3]、CFCl$_3$ 分子 DEA 中的 Jahn-Teller 效应等[4]、NF$_3$ 分子 DEA 中的三体解离过程[5]、CF$_4$ 分子的电子贴附空间取向效应[6]、CO 和 BrCN 分子 DEA 中的量子相干和物质波干涉效应、ICl 分子 DEA 中的非绝热效应等[7]。

以上研究表明 DEA 过程包含了丰富的动力学信息，并具有明显的量子散射特征。这是一个全新的研究领域，我们将进一步深入开展相关研究工作。

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Photoionization of atoms and small molecules in the laser field

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ABSTRACT:

(1) Photoionization of many-electron atoms: Using the saturation method, we measured the absolute photoionization cross-sections of several excited states of titanium, vanadium, Chromium, iron, and cobalt. The measured values range from 0.4±0.1 Mb to 6.9±2.0 Mb. The results show that the photoionization cross-section depends on the atomic state and not just on the electronic configuration. (Figure 1)

(2) Photoionization of small molecules in the laser field: In the experiment, we combined pulsed molecular beam, broadband femtosecond laser, and high time-resolution time of flight spectrometer to investigate ionization of molecules. By studying high-precision ion yield measurement in small molecules N_2, O_2, and CO_2 with 35-fs linearly and circularly polarized light, we extend to molecules the study of ellipticity effects on both single and double ionization in the 10^{14}-2×10^{15} W/cm2 laser intensity range. Typical results are shown in figure 2.

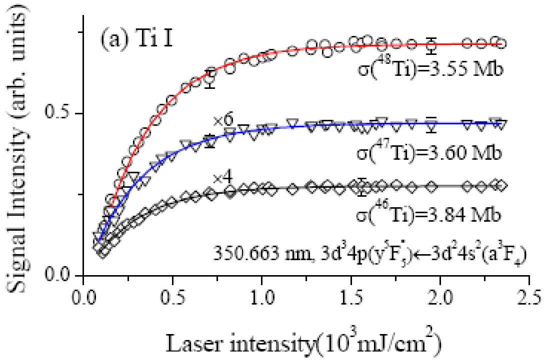

Figure 1. Photoionization data for Ti ($3d^34p\ y^5F^\circ_5$).

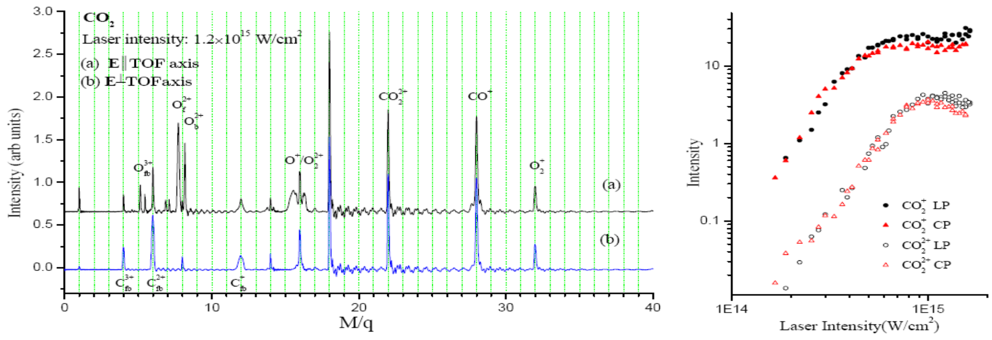

Figure 2. TOF mass spectra of CO2 with the linear polarization light and Ionization yields of CO_2^+ and CO_2^{2+} with LP and CP.

Mass-selected IR-VUV (118 nm) spectroscopy and its applications on the detection of jet cooled species

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Mass-selected IR plus UV/VUV spectroscopy coupled with mass spectroscopy has been married to be a powerful technique to investigate chemical, physical, structural, and electronic properties of radicals, molecules and clusters. Advantages of the use of vacuum ultraviolet (VUV) radiation are its application to all compounds with ionization potentials below the energy of single VUV photon, its circumventing the requirement of UV chromophore group, its inability to ionize background gases and minimal ion fragmentation.

As a promising spectroscopic technique, mass-selected IR-VUV (118 nm) spectroscopy is mainly employed for vibrational spectroscopic investigations of isolated molecules, its neutral clusters and cluster cations based on the VUV one-photon ionization. Thus it can reveal the weak interactions of inter- and intra-molecules, cluster structures and nature of unstable species. Furthermore, as a new method to detect and analyze peroxyl radicals, IR-VUV photoionization spectroscopy also has its unique advantages to investigate the nature of radicals. In recent years, we systematically studied of structural, electronic, and chemical properties of radicals, organic and biological molecules and their clusters in the gas phase by combining mass-selected IR/VUV (118 nm) spectroscopy and theoretical calculations.

In present report, we introduced a powerful technique called as mass-selected infrared (IR) plus vacuum ultraviolet (VUV 118 nm) spectroscopy firstly. Thereafter, selective application examples of this spectroscopy are described, which include the detections and analysis of jet cooled radicals, isolated molecules and molecular clusters.

Key words: Clusters; VUV; Photoionziation; IR spectroscopy; TOF-MS

用单纵模 OPO 系统高效制备振动激发的氢气分子

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氢气分子参与的基元反应，例如 $H+H_2$, $F+H_2$, $OH+H_2$ 及其同位素反应，一直以来是化学动力学研究的基准体系。因此，将其高效抽运至特定的振动激发态，是进一步研究振动激发对化学反应的影响的前提条件，也是当前实验研究面临的主要挑战之一。氢气分子不具有偶极矩，无法用红外激光直接将其振动激发，而以往的受激拉曼的技术也难以达到较高的激发效率。我们认为，氢气分子的谱线漂移(line shifting)和谱线展宽(line broadening)是限制分子束条件下的激发效率进一步提高的主要因素。因此，我们搭建了一套单纵模、高脉冲能量的光参量振荡器(Optical Parametric Oscillator, OPO)，它能够产生 630-680nm 的激光，作为受激拉曼过程中的斯托克斯光。带种子注入的 Nd:YAG 激光器的二倍频输出作为受激拉曼的泵浦光。这两束单纵模激光通过程序控制，精确地锁定于分子的跃迁谱线上。在这两束光的共同作用下，分子束中的氢气分子从 v=0 态高效的抽运至 v=1 振动激发态。这为交叉分子束实验研究氢气分子的振动激发对化学反应的影响提供了坚实的基础。

大气气溶胶成核机理研究

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摘要：

我们主要围绕气溶胶核化，形成，生长，老化，成云的物理和化学过程，发展相关的在线检测方法和技术，开展气溶胶对气候和环境的直接和间接影响的实验和理论研究。特别是对于成核的第一阶段即临界核的形成阶段，通过相关的实验和理论研究获得比较清晰和深刻的认识。