

V-J Stereodynamics of Crossed Beam Reactions

Reactions of metastable noble gas atoms with small molecules have provided a long-standing interest because of the diversity of reaction channels. Penning ionization consists of a spontaneous ionization of intermediate collisional complex, therefore it is a process of fundamental interest behind its importance in plasma and astrochemistry. It has been demonstrated that Penning ionization probes the electron density distribution of the orbital from where the electron is removed, and the collision energy dependence of the ionization cross section has been suggested to be a good measure to clarify anisotropy of intermolecular forces. The reactivity depends not only on the anisotropy of the coupling matrix but also on stereo-anisotropic intermolecular forces. Therefore we study how such steric effect depends on collision energy, as well as on mutual orientation of reactants.

V-J-1 Stereo-Selectivity in the Penning Ionization Reaction of CH_3X ($X = \text{Cl}, \text{Br}, \text{I}$) + $\text{Ar}({}^3\text{P}) \rightarrow \text{CH}_3\text{X}^+ + \text{Ar} + \text{e}^-$

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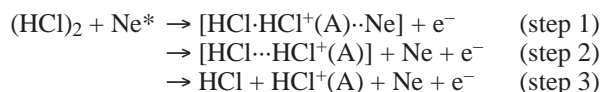
Recently, we have performed the direct observation of steric effect in CH_3Cl Penning ionization with the metastable argon atom using the hexapole state-selector, and we verified a good correlation between stereo-selectivity in the Penning ionization cross section and the spatial distribution of the electron density of HOMO orbital of the CH_3Cl molecule. In order to substantiate the above-mentioned relationship, we extended the study by replacing halogen atom of the molecule. In the present study, we determined the steric opacity functions for the two similar Penning ionization reactions of CH_3X ($X = \text{Br}, \text{I}$) + $\text{Ar}({}^3\text{P}) \rightarrow \text{CH}_3\text{X}^+ + \text{Ar} + \text{e}^-$ at an average collision energy of 0.1 eV. We find that the most reactive site shifts from the collinear X-end toward sideways as the mass number of X increases (i.e. from Br to I). Taking into account the previously obtained result for the CH_3Cl reaction, a good correlation can be seen again between the steric opacity function and the electron density distributions of the lone-pair HOMO orbital of CH_3X molecule.

V-J-2 Evidence for the $\text{HCl}^+(\text{A})$ Formation in the Reaction of $\text{Ne}({}^3\text{P})$ with the Size-Selected HCl Dimer Using an Electrostatic Hexapole Field

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There has been no evidence so far that reaction of $\text{Ne}({}^3\text{P})$, with the HCl dimer produces $\text{HCl}^+(\text{A})$, though the corresponding HCl monomer reaction produces $\text{HCl}^+(\text{A})$ in the vibrational states $v' = 0, 1$, and 2. Naaman and co-workers pointed out that chemical reactivity of monomers and clusters strongly depends on species of the reactant atom. For the $\text{Ne}^+(\text{HCl})_2$ reaction, there are many exit channels open such as electronic excitation, ionization, and dissociation from energetic point of view. In this work, Penning ionization of $\text{Ne}({}^3\text{P})$ metastable atom with size-selected HCl dimer was studied by using an electrostatic hexapole state-selector and chemiluminescence detection. We find that the HCl dimer can also produce $\text{HCl}^+(\text{A})$ ions in the reaction with $\text{Ne}({}^3\text{P})$ just like its corresponding monomer reaction. The internal energy distribution of $\text{HCl}^+(\text{A})$ in the dimer reaction is found to be cooler than that in the monomer reaction, reflecting the third-body effect in the dimer. The suggested reaction scheme is shown as follows.



V-K Photodissociation Dynamics

Photo-initiated reaction of weakly hydrogen bonded halide dimer, $(\text{HX})_2$, has a basic potentiality to produce $[\text{XHX}]$ transient specie by means of the hydrogen atom elimination from $(\text{HX})_2$ dimer. By measuring translational energy distribution of the eliminated hydrogen atom, one can extract information about van der Waals interaction of reactants in the $X + \text{HX}$ reaction system. We study the 243-nm photo-dissociation of the DCI clusters by using a Doppler-selected TOF (DS-TOF) technique in order to detect $[\text{CIDCI}]$ transient species. We employed the hexapole method to select only the DCI dimer in cluster beam and to exclude any ambiguity about precursor cluster size.

V-K-1 Photodissociation of DCI Dimer Selected by an Electrostatic Hexapole Field Combined with Doppler-Selected TOF Technique: Observation of [CIDCI] Transient Species

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The photodissociation of DCI dimer, which is preferentially selected from the cluster beam using a hexapole electrostatic field prior to the photolysis, has been studied by a Doppler-selected time-of-flight (DS-TOF) technique at 243 nm. We observed the [CIDCI] transient species through the hydrogen atom elimination from (DCI)₂. By measuring the dependence of the enhancement for the photodissociated D-atom signal upon the hexapole voltage, we find that the DS-TOF spectrum exhibits two kinds of velocity components; one is fast velocity component which originates from only dimer photodissociation, and the other is slow velocity component which originates from not only dimer but also higher sizes of the DCI clusters. For the fast velocity component, the observed spectrum shows an oscillating structure, which could reflect a footprint of nascent internal states (mainly vibration) of the [CIDCI] transient species. The spacing of the observed peaks is about 1000 cm⁻¹, which is much smaller than

that of the normal stretching frequency (2091 cm⁻¹) of the DCI monomer. This result suggests that the observed spectrum reflects the strong perturbation from the Cl atom in [CIDCI].

V-K-2 A New Channel of Hydrogen Elimination in the 121.6-nm Photodissociation of Formic Acid Detected by a Doppler-Selected TOF Mass Spectrometry

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The 121.6-nm photodissociation of formic acid was investigated by a Doppler-Selected TOF mass spectrometry (DS-TOF-MS) that enables us to map out 3D velocity distributions of photodissociated products through REMPI for the H atoms. The main channel is found to be the HCOO* formation. A new channel of H + CO + OH(X) hydrogen elimination reaction is observed. We estimate that the branching ratio to [H + HCOO*] with respect to [H + CO + OH(X)] is ~ 5 and those to HCOO(X), HOCO(X) and [2H + CO₂] formation channels are very small. These results show that the DS-TOF-MS method is useful to determine branching ratios and internal energy distributions of photodissociated products in both excited and ground states.

V-L Non-Destructive Structure Determination of Neural Clusters

Van der Waals clusters give a great interest as interfaces on chemical and physical properties between the gas phase and the condensed phase. Especially, the relationship between structure and dynamics is often called stereodynamics. From this sense, it is important to determine structure of cluster and to select special size and/or geometric isomers of cluster. In general, relative population of geometric isomers has been discussed in terms of stability of the isomers at equilibrium structure, but such a common sense is not necessarily appropriate in the case if dynamics of the cooling process induces special selectivity on isomer formation. It is plausible that different conditions for cluster beam preparation produced different clusters. Along this context, we investigate cooling process of geometric isomers during cluster formation.

V-L-1 Focusing and Selecting the Linear Type HBr-N₂O by Using a 2 m Long Electrostatic Hexapole Field

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Although N₂O-HCl and N₂O-HBr are expected to have similar two types of geometric isomers from the analogs of ONN-HF, it has been reported that extensive searches revealed only bent N₂O-HCl and N₂O-HBr and that there was no trace of linear ONN-HCl or

ONN-HBr. We performed focusing and selecting the HBr-N₂O cluster beam by using a 2m-long electrostatic hexapole field. The observed focusing curve shows a clear evidence that the linear type HBr-N₂O isomer which has symmetry of symmetric top molecule was preferentially produced in the cluster beam nevertheless our previous *ab initio* calculation predicts the bent type isomer. The best fit simulation for the experimental focusing curve was achieved only if we assume vibrational excitation in the van der Waals mode of the linear type HBr-N₂O. The permanent dipole moment is determined to be 0.70 ± 0.05 D. The potential energy of the O-end bent type is more stable than the N-end linear type. From the potential energy surface made by transferring HBr-N₂O geometry, the formation of the

two isomers is selected at a fairly long bond length between HBr and N₂O.

V-M Reaction Dynamics at Surfaces

The interaction of hydrogen with surfaces has been a subject of intense interest in surface science because it is the simplest paradigm relevant to single valence electron. The reaction of hydrogen on a surface can be an ideal candidate for testing validity of various concepts in surface chemical reaction. Also, it is known that adsorbed hydrogen can provide a significant effect on kinematical and electronic properties in the surface region of materials, inducing embrittlement and fracture. To understand how hydrogen interacts with surface atoms and reacts with other atoms on the surface and its possible diffusion into and from the bulk is important in various fields; heterogeneous catalysis, material science, metallurgy, hydrogen storage, etc. These phenomena embodied in hydrogen interaction with metal surfaces encompass most of basic physical and chemical concepts in material science.

V-M-1 Hydrogen-Exchange Reactions *via* Hot Hydrogen Atoms Produced in the Dissociation Process of Molecular Hydrogen on Ir{100}

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Adsorption of hydrogen(deuterium) on Ir{100} surface has been studied with temperature-programmed desorption and direct measurements of describing molecules using quadrupole mass spectrometry at ~ 100 K. H₂ exposure of the D-pre-covered Ir{100} surface was found to induce the desorption of HD and D₂ molecules. This result can not to be explained by conventional simple adsorption/desorption kinetics and it suggests that energetic H atoms (hot H atoms) produced in the dissociation process of incident H₂ molecules react with pre-adsorbed D atoms and then desorb as HD molecules or produces secondary energetic D atoms via energy transfer. Secondary energetic D atoms also induce associative reactions with pre-adsorbed D atoms and desorb as D₂ molecules. We propose the hot-H-atom-mediated reaction based on both empirical and steady-state approximation models for interpreting the present experimental results.