

V-H Stereodynamics of Chemical Reactions and Photodissociation Dynamics

Ionization by metastable atoms (Penning ionization) consists of a spontaneous ionization of the intermediate collisional complex, therefore 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 of $\Gamma = \langle \phi_i | \Phi_{3p} \rangle$, but also on the collision dynamics *via* stereo-anisotropic intermolecular forces, where ϕ_i is the ionized molecular orbital and Φ_{3p} is the atomic orbital of a metastable rare gas. Therefore we study how such steric effect depends on collision energy, as well as on mutual orientation of reactants.

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

V-H-1 Direct Measurement of Oscillating Behavior in $Ar(^3P) + CH_3Cl \rightarrow Ar + CH_3Cl^+ + e^-$ Ionization Cross Section by Velocity and Orientational Angle Selected Collisions

OHOYAMA, Hiroshi¹; YAMATO, Masanori¹; OKADA, Seiki¹; KASAI, Toshio^{1,2}; BRUNETTI, Brunetto G.³; VECCHIOCATTIVI, Franco³
(¹Osaka Univ.; ²IMS; ³Univ. Perugia)

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Collision energy dependence of the ionization cross section for the $Ar(^3P) + CH_3Cl \rightarrow Ar + CH_3Cl^+ + e^-$ reaction was determined under specific relative orientation using an oriented CH_3Cl beam and time-of-flight measurements. A remarkable resonance-type structure is revealed in the energy dependence of orientation angle-resolved Penning ionization cross section. This novel resonance-type structure in Penning ionization cross section could be interpreted as a new-type "nuclear-excited Feshbach resonance" in the formation of vibrational excited Rydberg states leading to a competitive dissociative exit channel.

V-H-2 2D-Measurement of Penning Ionization Cross Section upon Molecular Orientation and Collision Energy in $Ar(^3P_{2,0}) + CHCl_3$ Crossed Beam Reaction

YAMATO, Masanori¹; OHOYAMA, Hiroshi¹; KASAI, Toshio^{1,2}
(¹Osaka Univ.; ²IMS)

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The Penning ionization cross section of $Ar^* + CHCl_3$ crossed beam reaction is determined as the function of both molecular orientation and relative collision energy using $CHCl_3$ oriented molecular beam. We find that, the steric opacity function at low collision energies is well correlated to the exterior electron density distribution of $CHCl_3$ molecular orbital which

plays a key role in the electron exchange. At high collision energies, however, the reactivity along the molecular axis is favorable while the sideways approach is found to be unfavorable. The result of our *ab initio* calculation reveals that the collision energy dependence if specified at the sideways shows clear discrepancy with the generally accepted propensity rule based on the type of interaction potential. We propose here that this discrepancy can be ascribed to the collision energy dependent competition of product branching between Penning ionization and neutral dissociation.

V-H-3 Velocity Dependence of the Ionization Cross Section of Methyl Chloride Molecules Ionized by Metastable Argon Atoms

BRUNETTI, Brunetto G.¹; CANDORI, P.¹; FALCINELLI, S.¹; KASAI, Toshio^{2,3}; OHOYAMA, Hiroshi²; VECCHIOCATTIVI, Franco¹
(¹Univ. Perugia; ²Osaka Univ.; ³IMS)

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The ionization of methyl chloride molecules by metastable argon atom collisions is studied in a crossed beam experiment. The relative cross sections exhibit a decreasing trend in the investigated collision energy range, 0.04–0.3 eV. The results have been analyzed in terms of the potential energy interaction between the two colliding partners, using the optical potential mode. The effect of potential energy anisotropy has also been investigated by the use of a simple sudden approximation within the semiclassical framework. The experimental cross-sections appear to be rather well reproduced by the theoretical calculation with a spherically average potential and very close to the calculation performed using the potential for a perpendicular orientation between the C–Cl axis and the approaching direction of the excited atom.

V-H-4 Photodissociation of DCI Dimer Selected by an Electrostatic Hexapole Field Combined with Doppler-Selected TOF Technique: Observation of [CIDCI] Transient Species

CHE, Dock-Chil; HASHINOKUCHI, Mitihiro¹; SHIMIZU, Yuichiro; KASAI, Toshio¹
(¹IMS and Osaka Univ.)

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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-H-5 A New Channel of Hydrogen Elimination in the 121.6-nm Photodissociation of Formic Acid Detected by a Doppler-Selected TOF Mass Spectrometry

HASHINOKUCHI, Mitihiro¹; KOUMURA, Ryouji; CHE, Dock-Chil; KASAI, Toshio¹
(¹IMS and Osaka Univ.)

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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-I Structure Determination of Neural Clusters

Over the past two decades, much attention has been paid to molecular clusters interfacing material between the gas phase and the condensed phase, from which network interactions could be analyzed at molecular level. Various spectroscopic techniques have been applied to newly synthesized clusters in order to obtain information about energetics, structures and dynamics. Bonding character and structure of clusters are usually reconstructed or modified from its constituent free molecules. Metal-ligand complexes could be treated as small sizes of clusters. Such small clusters serve as a model system for clarifying metal-ligand interaction.

we demonstrate a novel application of the electrostatic hexapole field to the supersonic beams of Al-CH₃CN and Al-NH₃ synthesized complexes for the determination of permanent dipole moments, which are relevant to the nature of dipole-induced dipole and dipole-dipole interactions between the metal atom and the ligand molecule. Second, in an attempt to clarify the weak interaction and the bonding nature between the Al atom and C₆H₆, we selected Al(C₆H₆) isomers and determined the dipole moments using the 2-meter electrostatic hexapole. We have also performed the density functional calculations (DFT) of the isomers at B3LYP/6-31G* level for obtaining geometries and electric features of the isomers.

V-I-1 Non-Destructive Selection of Geometrical Isomers of Al(C₆H₆) Cluster by a 2-Meter Electrostatic Hexapole Field

IMURA, Kohei¹; KAWASHIMA, Takahiro¹; OHYAMA, Hiroshi¹; KASAI, Toshio^{1,2}; NAKASHIMA, Atsushi³; KAYA, Koji
(¹Osaka Univ.; ²IMS; ³Keio Univ.)

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A supersonic cluster beam which contains isomers of Al(C₆H₆) complexes is generated by a laser evaporation, and the cluster is non-destructively selected using a 2-meter-long electrostatic hexapole. The focusing curve shows clear evidence that there are two kinds of Al(C₆H₆) isomers which are slightly different from each other in geometry; namely one is an asymmetric 1,2-complex and the other one is a nearly C_{6v} symmetric 1,4-complex. The electric dipole moments of the two isomers are found to be 1.5 ± 0.1 and 1.4 ± 0.1 D, respectively. We carried out

computation using the density functional theory in order to estimate their structures. We find that the 1,2-complex is more stable than the 1,4-complex. The present work confirms that the electrostatic hexapole technique is useful for non-destructive selection of the geometrical isomers in the beam.

V-I-2 Direct Determination of the Permanent Dipole Moments and Structures of Al-CH₃CN and Al-NH₃ by Using 2-Meter Electrostatic Hexapole Field

**IMURA, Kohei^{1,2}; KAWASHIMA, Takahiro¹;
OHOYAMA, Hiroshi¹; KASAI, Toshio^{1,2}**
(¹Osaka Univ.; ²IMS)

[*J. Am. Chem. Soc.* **123**, 6367 (2001)]

The supersonic beams of pure metal-ligand (1-1) complexes of Al-CH₃CN and Al-NH₃ were synthesized by a laser evaporation flow-tube-reactor method and non-destructively structure-selected by a 2-meter long electrostatic hexapole field. The permanent dipole moments of such selected complexes were determined. We find that the competing effects of "charge transfer" and "polarization" through the metal-ligand bond can be estimated by measuring the change in the magnitude of permanent dipole moments before and after the complex formation of Al-CH₃CN and Al-NH₃. The *ab initio* calculation at the MP2 level was performed in order to simulate the complex structures and to explain the experimental findings.