V-O Determination of Structures of Neutral Clusters

The relationship between the structure and dynamics in floppy systems is a subject that has focused much attention recently. Specifically the “geared interconversion” of hydrogen bonded dimers such as $(HCl)_2$, $(DCl)_2$, and $(HF)_2$ have been studied extensively both experimentally and theoretically. Most of the experimental studies focused on the spectroscopy of these species, from which the tunneling splitting could be extracted. We applied a hexapole field to extract the dipole moment of $(HCl)_2$ and we find that interconversion’’ of hydrogen bonded dimers can be directly observed by the hexapole field method. Secondly, the metal-ligand cluster beam serves as a model system for studying metal-ligand interaction, however little is known about interaction between Al and simple molecule as isolated system in the gas phase. We demonstrate again how successfully the hexapole method can be applied to newly synthesized complexes of Al–CH_3CN and Al–NH_3.

V-O-1 Focusing of DCl and HCl Dimers by an Electrostatic Hexapole Field—The Role of the Tunneling Motion

IMURA, Kohei[1]; KASAI, Toshio[2]; OHOYAMA, Hiroshi[1]; NAAMAN, Ron[3]
([1]Osaka Univ.; [2]IMS and Osaka Univ.; [3]Weizmann Inst. Sci.)

[*J. Chem. Phys.* **110**, 355 (1999)]

The focusing of HCl and DCl dimers was observed using a 2-m-long electrostatic hexapole field. The results indicate the existence of two types of species. The first is the homodimers, either the $H^{35}Cl\cdot H^{35}Cl$ or the $D^{35}Cl\cdot D^{35}Cl$, for which the data indicate a fast tunneling motion. The second is the heterodimers, $H^{35}Cl\cdot H^{37}Cl$ or $D^{35}Cl\cdot D^{37}Cl$, that do not show evidence for significant tunneling motion on the time scale of the experiment. In the case of HCl dimers, even at relatively high fields, only one species could be focused, the heterodimer. The electric dipole moments for both $(DCl)_2$ isotopomers were determined to be 1.5 ± 0.2 D, which is the same value as observed for $(HCl)_2$.

V-O-2 Tunneling Motion in $(HCl)_2$ Hydrogen-Bonded Dimer Probed by Electrostatic Hexapole and Doppler-Selected TOF Measurement for the Internal Energy Distribution of [ClHCl]

IMURA, Kohei[1]; OHOYAMA, Hiroshi[1]; NAAMAN, Ron[2]; CHE D.-C.[3]; HASHINOKUCHI, Masahiro[3]; KASAI, Toshio[3]
([1]Osaka Univ.; [2]Weizmann Inst. Sci.; [3]IMS and Osaka Univ.)

[*J. Mol. Struct.* **552**, 137 (2000)]

The tunneling motion in $(HCl)_2$ hydrogen bonded dimer and its deuterate was probed by a 2-m long electrostatic hexapole field. The focusing curves of the dimers confirmed existence of homo and hetero dimers in the cluster beam. The homodimer, either $H^{35}Cl\cdot H^{35}Cl$ or $H^{37}Cl\cdot H^{37}Cl$, undergoes fast tunneling motion for the two hydrogen atoms in the dimer. The heterodimer, namely $H^{35}Cl\cdot H^{37}Cl$ on the other hand, does not show such fast tunneling motion on the time scale of experiment. The observed ratio of homo to hetero dimer was estimated to be 20 ± 10, and this value differs largely from the natural abundance for chlorine isotope. An experimental scheme to discern homo and hetero dimers is proposed here. By looking at fragments in $(HCl)_2$ dimer photodissociaiton using a Doppler-selected time-of-flight (TOF) technique, internal energy distribution of [ClHCl] fragment was measured in 121.6-nm photodissociation. The TOF spectrum consists of fast and slow velocity components for dissociated H atoms. It is found that the slow H component arises from the hydrogen escapes after many collisions. The fast H component arises from direct H escape without any collision, thus this component reflects internal and/or electronic state of counter part fragment, *i.e.* [ClHCl]. Vibrational structure of [ClHCl] was observed for the fast H component of the TOF spectrum.

V-P Reaction Dynamics in the Gas Phase and on Surface

The reactions of metastable rare gas atoms with small molecules have provided a long-standing interest, because of the variety of possible involved reaction channels. These include electronic energy transfer, molecular dissociation, excimer formation, Penning ionization, etc. Among them, Penning ionization has been widely studied in recent years. It has been suggested that anisotropy effects influence Penning ionization. We explore the stereodynamical aspect of this reaction using the oriented molecular beam of CH_3Cl.

Surface reactions of hydrogen with atomic and molecular adsorbates on metal and semiconductor surfaces have been paid much attention because of the fundamental interest in the mechanism and dynamics of these reactions. Especially, abstraction of chemisorbed H(D) atoms by the gas-phase H(D) atoms have been extensively studied theoretically and experimentally because of its simplicity and its important roles in the catalytic reactions. We directly identify the desorbed molecules during the reaction and discuss a possible model of H-D exchange reaction.

V-P-1 Evidence for Steric Effect in Methyl Chloride Ionization by Metastable Argon Atoms

OHOYAMA, Hiroshi[1]; KAWAGUCHI, Hiroshi[1]; YAMATO, Masanori[1]; KASAI, Toshio[2]; BRUNETTI, Brunetto G.[3]; VECCHIOCATTIVI, Franco[3]
([1]Osaka Univ.; [2]IMS and Osaka Univ.; [3]Univ. Perugia)

[*Chem. Phys. Lett.* **313**, 484 (1999)]

The orientation dependence of methyl chloride ionization by collision with metastable argon atoms at an average collision energy of 0.09 eV has been investigated, using an electric hexapole field selector followed by an orienting field. The steric opacity function of the process has been determined. The highest reactivity has been found for approaches of the metastable atom towards the Cl-end of the molecule, while the lowest corresponds to the opposite approaches close to the CH_3-end. The stereo-selectivity is discussed in terms of spatial distribution of the highest occupied molecular orbital of CH_3Cl, mainly localized on the chlorine atom.

V-P-2 Direct Observation of Steric Effect in Penning Ionization Reaction of Ar* + $CHCl_3 \rightarrow CHCl_2^+ + Cl + e^- + Ar$

YAMATO, Masanori[1]; OKADA, Seiki[1]; WU, Victor Wei-Keh[1]; OHOYAMA, Hiroshi[1]; KASAI, Toshio[2]
([1]Osaka Univ.; [2]IMS and Osaka Univ.)

[*J. Chem. Phys.* **113**, 6673 (2000)]

Steric effect in the Penning ionization reaction of Ar* ($^3P_{2,0}$) + $CHCl_3 \rightarrow Ar + CHCl_2^+ + Cl + e^-$ was directly observed at an average collision energy of 0.13 eV using the oriented $CHCl_3$ molecular beam. The product $CHCl_2^+$ ions are measured for the H-end, the CCl_3-end, and sideways orientations. The obtained steric opacity function reveals that the CCl_3-end orientation is more favorable than the H-end orientation, and the sideways approach is found to be more favorable than the collinear approaches from both ends of the molecule. Furthermore, we confirm the good correlation between Penning ionization anisotropy and the electron density distribution of $2a_2$ HOMO orbital of $CHCl_3$ molecule, whose electron cloud is mostly localized around the sideways. These results substantiate the electron exchange mechanism which is commonly accepted for Penning ionization reaction, where the overlap of projectile atomic and target molecular orbital plays a key role in Penning ionization efficiency.

V-P-3 Hydrogen Adsorption and Reaction on the Ir{100}-(1×5) Surface

MORITANI, Kousuke[1]; OKADA, Michio[1]; KASAI, Toshio[2]; MURATA, Yoshitada[3]
([1]Osaka Univ.; [2]IMS and Osaka Univ.; [3]Univ. Electro-Commun.)

[*Surf. Sci.* **445**, 315 (2000)]

Adsorption of hydrogen (deuterium) on the Ir{100} surface has been studied with low-energy electron diffraction (LEED) and temperature-programmed desorption (TPD). At least three well-defined peaks can be identified with peak temperatures (T_p) of 125, 240, and 375 K in the TPD spectrum for the surface saturated with H at ~100 K. From the LEED observations, it can be concluded that these three peaks in the TPD spectrum correspond to H_2 desorption from the (1×5), (1×3), and (1×1) restructured phases, respectively. Furthermore, the result suggests that a metastable state of (1×3) exists on the Ir{100} surface in addition to the (1×1) phase. The series of TPD spectra for coadsorption of H_2 and D_2 on the Ir{100} surface show that an energetic D(H) atom produced in the dissociation process of incident $D_2(H_2)$ replaces a preadsorbed H(D) atom via energy transfer and the expelled H(D) atom moves to another adsorption site.

V-P-4 Hot Atom Mechanism in Hydrogen Exchange Reaction on the Ir{100} Surface

OKADA, Michio[1]; MORITANI, Kousuke[1]; NAKAMURA, Mamiko[1]; KASAI, Toshio[2]; MURATA, Yoshitada[3]
([1]Osaka Univ.; [2]IMS and Osaka Univ.; [3]Univ. Electro-Commun.)

[*Chem. Phys. Lett.* **323**, 586 (2000)]

H_2 exposure was found to induce the desorption of HD and D_2 molecules from the D-precovered Ir{100} surface. This result suggests that energetic H atoms (hot H atoms) produced in the dissociation process of incident H_s molecules react with preadsorbed D atoms and desorb as HD molecules or produce secondary energetic D atoms via energy transfer. Secondary energetic D atoms (secondary hot D atoms) also induce the associative reactions with preadsorbed D atoms and desorb as D_2 molecules.