V-P Millimeter-Wave Spectroscopy Combined with Pulsed-Jet Expansion Technique for the Detection of the Novel Unstable Species and the van der Waals Mode Transitions of Molecular Clusters

Molecular clusters have inherently low-frequency vibrations, so called van der Waals (vdW) vibrational modes, which are characteristic of the weakly bound complexes. The frequency of the vdW mode usually falls in the far-infrared region (30–300 cm^{-1}). However, if a cluster is extremely floppy, it sometimes falls in the submillimeter-wave (SMMW) region below 30 cm^{-1}.

The ArHCN cluster is a typical example which has extremely low-frequency vdW bending vibrations. Although the frequency of the vdW stretching is estimated to be 23.8 cm^{-1}, those for the bending vibrations are calculated to be as low as 4–7 cm^{-1}. Following the observation of the pure rotational spectra in the microwave region below 20 GHz, the vdW bending transitions of ArHCN have been measured in the millimeter-wave region near 180 GHz by molecular beam electric resonance optothermal spectroscopy (EROS).

In this project, a millimeter-wave absorption spectrometer combined with pulsed-jet expansion technique has been devised and applied to the direct observation of the rovibrational transitions of the vdW bending band of molecular clusters. We have applied this technique to observe the vdW bending bands of the ArHCN ($j = 1$–0 and 2–1) and ArDCN ($j = 1$–0) clusters as well as the ArHBr (Σ_1–Σ_0) and OCO·HF (1^1–0^0 (v_b)) clusters.

In the supersonic jet expansions short lived species can survive thanks to the collision-less environment and ultra low rotational as well as vibrational temperature. The millimeter-wave spectrometer combined with supersonic jet nozzle and glow discharge electrodes, as well as the UV excimer laser photolysis devices, also have been set up for the detection of novel unstable species, such as radicals, molecular ions, and ionic and radical clusters.

V-P-1 Millimeter-Wave Spectroscopy of the van der Waals Bending Band of the ArDCN Cluster

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Millimeter-wave absorption spectroscopy combined with pulsed-jet expansion technique was applied to the measurement of the rovibrational transitions in the van der Waals bending band of the ArDCN cluster in the frequency region of 182–294 GHz. Sixteen and thirty-seven rovibrational lines were observed for the Σ_1–Σ_0 and Π_1–Σ_0 bands, respectively, split into hyperfine structure due to the nitrogen nucleus. The spectrum of the $R(1)$ line of the Σ_1–Σ_0 band observed at 196 GHz is shown in Figure 1.

An accurate set of molecular constants, including the band origins, rotational constants, quadrupole coupling constants, and the Coriolis coupling constant between the Σ_1 and Π_1 bending substates, was determined. The rotational and quadrupole coupling constants for the excited states are much different from those of the ground state indicating the change in average molecular structure, from the linear form in the ground state to the T-shaped form in the first excited ($j = 1$) state. The band origins for the Σ_1–Σ_0 and Π_1–Σ_0 bands, 189.017 391 (7) GHz and 195.550 737 (12) GHz, are larger by 24.126 596 (9) and 13.566 315(16) GHz than the corresponding values of ArHCN.[1] The abnormal isotopic effect on the vibrational frequencies is attributed to the characteristic potential energy surface of ArH(D)CN, which have two minima corresponding to linear and T-shaped configurations with similar well depth and connected with a shallow channel. The determined molecular constants were compared with those calculated with potential energy surface given by CCSD(T) level *ab initio* calculation.[2]

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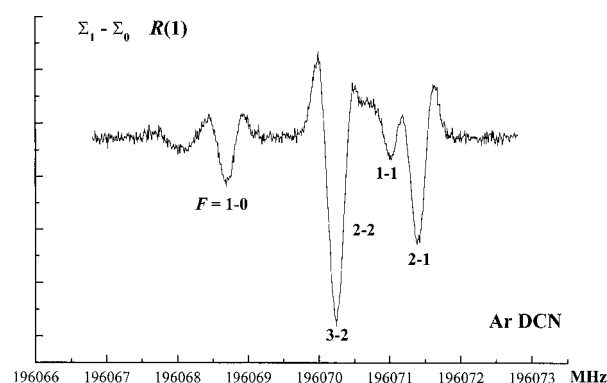
Figure 1. Hyperfine structure of the $R(1)$ line of the Σ_1–Σ_0 subband of the $j = 1$–0 vdW bending band of ArDCN.

V-P-2 Direct Observation of the van der Waals Bending Hot Bands of the Ar-HCN Cluster by Millimeter-Wave Spectroscopy

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The previous spectroscopic studies of the "ball and ball"-type cluster such as the Ar-HCl and Ar-H_2O clusters gave the computational techniques for evaluating the experimental potential energy surface (PES). As a next target, many experimentalists and theoreticians have investigated the Ar-HCN cluster because it is one of the simplest "ball and rod"-type cluster.

Since the first observation of the rotational spectrum of Ar-HCN was carried out by Leopold *et al.*,[1] many

studies have been reported. The observation of the vdW vibration is important to determine the intermolecular PES. The vdW bending fundamental bands were observed by Drucker *et al.*[2] These experimental results showed that this cluster has abnormally large centrifugal distortion constants and isotopic effect on the molecular constants of the normal and deuterated species. *Ab initio* calculation by Tao *et al.*[3] and Cybulski *et al.*[4] showed that this abnormality is due to the characteristic PES of Ar-HCN (Figure 1), which has large angular-radial coupling and anisotropy in the vdW vibration.

In the present work, the vdW bending hot bands of Ar-HCN have been observed by using the millimeter-wave absorption spectroscopy combined with the pulsed supersonic jet expansion technique. In the frequency region of 150–290 GHz, the six bands correlated to the $j = 2$–1 transition in the free rotor limit were assigned and least-squares fitted simultaneously to the effective Hamiltonian including the Coriolis interaction (Figure 2). The order of the sublevels in the $j = 2$ state is reversed to that of $j = 1$ state, which is consistent with the vibrational analysis with the PES by Cybulski *et al.* Since the observed rotational constants in the $j = 2$ state have almost the same values as those of the $j = 1$ state, the average distance between Ar and center of mass of HCN in the $j = 2$ state is not changed so much. The signs of nuclear quadrupole coupling constants in the $j = 2$ state are the same as those of the coupling constants predicted in the free rotor limit.

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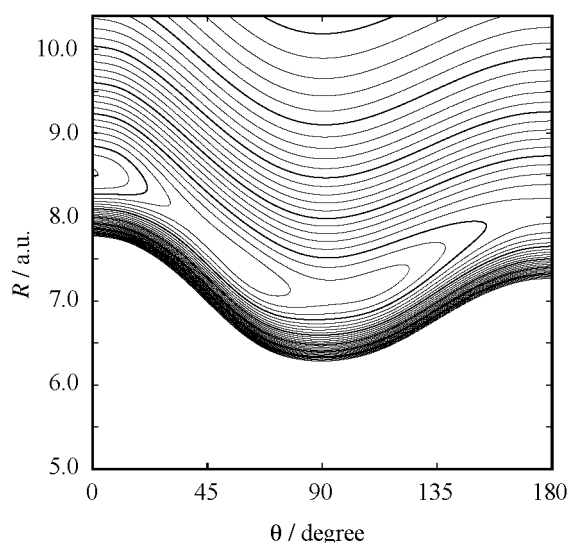
Figure 1. The PES of Ar-HCN. This PES was obtained by the high-level *ab initio* calculation with CCSD(T)/aug-cc-pVTZ+bf method.[4]
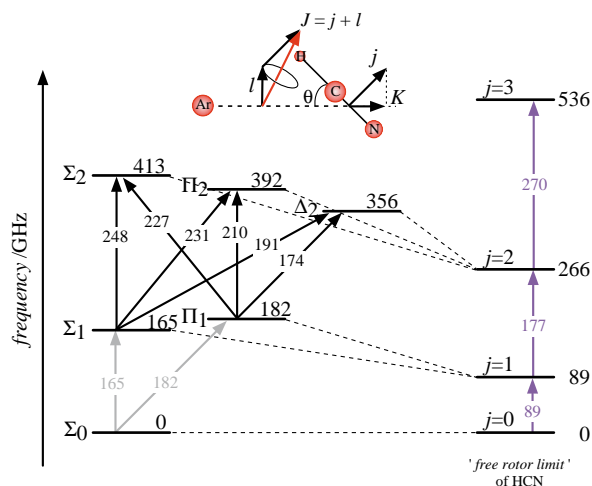
Figure 2. Energy level diagram of Ar-HCN. Since each vibrational energy level correlates to the free rotor energy levels of HCN, the vdW vibrational levels are labeled with $|K|_j$.

V-P-3 Submillimeter-Wave Spectroscopy of the van der Waals Bending Band of Ar-HBr

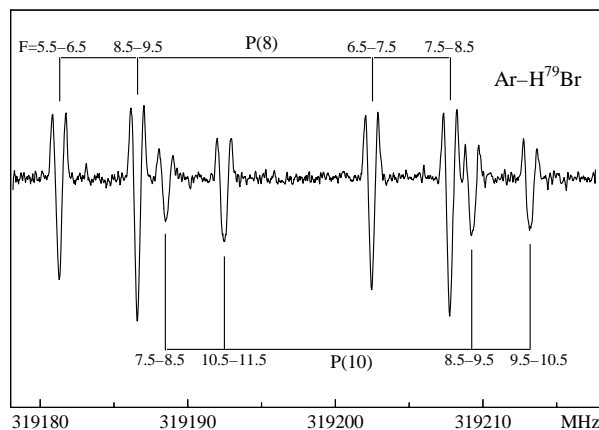**HARADA, Kensuke; MIZOGUCHI, Asao; TANAKA, Keiichi[1]**
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The Ar-HBr cluster has a large amplitude intermolecular bending motion. It has nearly a "linear" structure of Ar-HBr in the ground state (Σ_0 state), while nearly an "anti-linear" structure of Ar-BrH in the first excited state (Σ_1 state) by the calculation of Hutson.[1] Recently, the excited states of the van der Waals vibrations were observed by infrared[2] and far infrared[3] laser spectroscopy. The energy difference between the Σ_1 and Σ_0 state was determined to be 10.995 cm^{-1} from the combination difference of the infrared data.[2] In the present study, we have observed direct submillimeter-wave transitions of the Σ_1–Σ_0 band of Ar-HBr generated in a pulsed supersonic jet expansion.

The millimeter-wave jet spectrometer have been used for the experiment. The 8 atm mixed gas of 1% HBr, 49% Ar, and 50% Ne was injected to the vacuum chamber from a pulsed nozzle. In the frequency region of 318–335 GHz, the 14 rovibrational transition of P(12)-P(1), R(0), and R(1) have been observed for both Ar-H^{79}Br and Ar-H^{81}Br isotopic species. Since the van der Waals bond length in the Σ_1 states is 0.2 Å shorter than that in the ground state, the spectrum has a band head at P branch side. Figure 1 shows the P(8) and P(10) lines near the band head at 319 GHz, split due to the nuclear quadrupole interaction of the bromine nucleus.

The eQq constants in the the Σ_1 state were determined to be 260.90(12) and 217.854(98) MHz for Ar-H^{79}Br and Ar-H^{81}Br, respectively, which are 51% larger than the values in the ground state. The rotational dependence of the eQq constant, eQq_J in the the Σ_1 state has reverse sign to that in the ground state. The big change of the eQq constant and the reverse sign of the eQq_J indicate that the cluster is in the different minima of the potential surface at the "linear" and "anti-linear" structures, in the Σ_0 and Σ_1 state, respectively.

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Figure 1. The observed spectrum of the Σ_1–Σ_0 vdW bending band of Ar-HBr.

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Figure 1. The stick diagram of the observed spectrum of the vdW bending band of OCO-HF.

V-P-4 Millimeter-Wave Spectroscopy of the van der Waals Bending Band of OCO-HF with a Supersonic Jet Expansion Technique

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The OCO-HF is a hydrogen-bonded quasi-linear cluster with a dissociation energy of 672 cm^{-1}. The intermolecular potential is double minimum at a bend structure of the COH angle of 22° and a potential barrier of about 1 cm^{-1} is expected in the linear configuration.[1] The rotational spectrum[2] and infrared spectrum[3] have been already reported. In the present study, we have measured the van der Waals (vdW) bending 1^1–0^0 ($v_b I$) band by the millimeter wave jet spectroscopy.

The 8 atm mixed gas of 1% HF, 5% CO_2, 31% Ar, and 63% Ne was injected into the vacuum chamber by a pulsed nozzle. In the 250–325 GHz region, 30 rovibrational transitions, P(2)-P(5),Q(1)-Q(15), and R(0)-R(10), were assigned to the 1^1–0^0 (v_b^1) fundamental band. Figure 1 shows the stick diagram of the observed spectrum. The band has intense Q and R branch lines, while the P branch lines are rather weak.
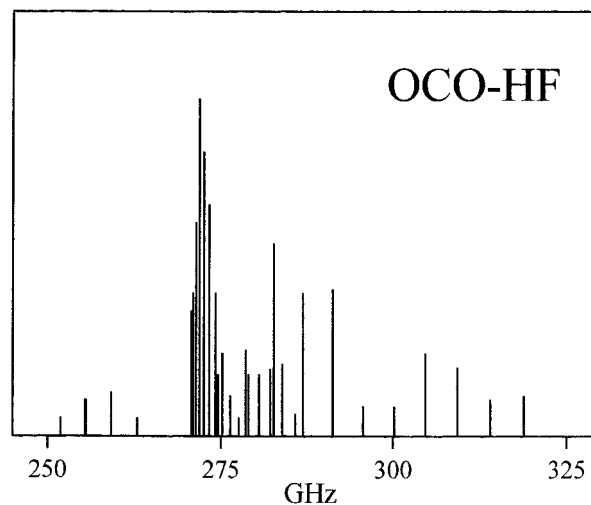
An usual linear molecule Hamiltonian with the (2,2) interaction was used for the analysis. The band origin of the 1^1–0^0 band was determined to be 272548.8017 (49) MHz. The rotational constant, centrifugal distortion constant, l-type doubling constant, and its higher order term were determined precisely. In order to determine the two dimensional intermolecular bending potential surface, the measurement of the vdW hot band and vdW band of the deuterated species will be important.

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