V-Q 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 $(30-300 \text{ cm}^{-1})$. However, if a cluster is extremely floppy, it sometimes falls in the submillimeter-wave (SMMW) region below 30 cm⁻¹.

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 Ar–HCN (j = 1-0 and 2–1) and Ar–DCN (j = 1-0) clusters as well as the Ar–HBr ($\Sigma_1-\Sigma_0$) and OCO–HF (1^1-0^0 (v_b^1)) clusters. In this year, we have extended our measurements to the clusters as He–HCN, Ne–HCN, H₂–HCN, and H₂–H₂O. To increase the detection sensitivity, we employed a White-type multi-reflection optical system in the millimeter-wave region. The radiation was focused 20 times on the jet beam, and the improved sensitivity (of about one order of magnitude) was attained than the previous single path measurement.

The He–HCN cluster, for example, is a very weakly bound cluster with a binding energy of only 9 cm⁻¹. We have observed a number of j = 1-0 vdW transitions in 95–125 GHz and several observed levels are very close to the dissociation limit. The HCN part behave almost like a free rotor and dissociate with the excitation of vdW bending mode. The anisotropic intermolecular potential was determined by the least square fitting of the observed transitions.

The H₂–HCN, and H₂–H₂O clusters have rather complicated energy levels, because they have two internal rotors in the cluster, although the H₂ part behaves as a free rotor. Due to the spin statistics, the clusters have different internal rotation states between *para* and *ortho*-H₂ species, thus different dissociation energies, structures and vdW bending frequencies. The observed vdW transitions were analyzed to discuss the potential energy surface around HCN and H₂O.

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-Q-1 Millimeter-Wave Spectroscopy of the van der Waals Bending Band of He–HCN

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The He–HCN cluster is a quite weakly bound cluster with the binding energy D_0 of 9 cm⁻¹.^{1,2}) The HCN part is almost freely rotating in the cluster. Recently two vdW bending transitions have been reported by molecular beam electric resonance technique.¹) The observation of the vdW transitions up to the dissociation limit is quite important for the determination of the potential energy surface and the theoretical analysis of the potential energy surface and intermolecular dynamics. In the present work, we observed the vdW bending transitions of the He–HCN cluster up to the dissociation limit and determined the empirical intermolecular potential function.

The multi-reflection millimeter wave jet cell was used for the experiment. The 14 atm mixed gas of 0.3% HCN and 99.7% He was injected to the vacuum chamber from a pulsed nozzle with a repetition rate of 60 Hz. The vacuum chamber was evacuated by a 10 inch diffusion pump. The millimeter wave radiation from a backward wave oscillator was passed twenty times through the jet expansion using a White type optical path and detected by InSb detector.

The energy level of He–HCN is labeled by the quantum numbers of j, l, and J where j is the internal

rotation quantum number of HCN part, l is the rotational quantum number of the pseudo-diatomic complex and J is the total rotational quantum number. The stick diagram of the observed vdW transitions of He–HCN is shown in Figure 1. The 13 vdW bending transitions with $\Delta l = 0$ and l = 0~4 have been assigned in the frequency region of 95–125 GHz. The Q branch transitions and part of the R branch transitions are split to the hyperfine components due to the nuclear quadrupole interaction of the nitrogen nucleus. The highest observed energy level is the j = 1, l = 4, J = 5 level which is predicted to locate 0.5 cm⁻¹ below the dissociation limit from the semi-empirical potential analysis.²)

We used the one dimensional internal rotation Hamiltonian with the anisotropic intermolecular potential for the analysis. The potential function determined is shown in Figure 2. The angle between the HCN axis and the cluster axis is denoted by θ . The intermolecular potential $V(\theta)$ has a global minimum at θ = 0° (the linear structure of He–HCN) and the energy difference between θ = 0° and θ = 180° (the linear structure of He–NCH) is 6 cm⁻¹. The center of mass distance *R* of He and HCN is 4.3 Å at θ = 0°, while it is 0.8 Å shorter at θ = 70° than that at θ = 0°.

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Figure 1. The stick diagram of the observed vdW bending transitions of He–HCN.



Figure 2. The *R*- θ and *V*- θ dependence curve of He–HCN.

V-Q-2 Millimeter Wave Spectroscopy of the $HCN-H_2$ Cluster

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Hydrogen H₂ containing molecular clusters are very weakly bound having large amplitude motion of both H₂ and its partner and they could have different configurations of between *para* (j = 0) and *ortho* (j = 1)hydrogen species. Recently, vibrational spectrum in the superfluid He droplets and ro-vibrational spectrum in the gas phase for the HCN-H₂ clusters have been observed. Vibrational spectrum in the He droplets suggests that o-H₂ binds to the N site of HCN molecule. Contrastedly, p-H₂ binds to the H site of HCN.¹⁾ In the gas phase, only HCN-(o-H₂) was detected.²⁾ In this work, millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique was applied to the measurement of the pure rotational and rovibrational transitions of the van der Waals (vdW) bending band of the HCN-H₂ cluster in the 75-150 GHz region.

So far, four rotational lines (J = 3-2 to 6–5) for the ground Σ_0 state of the HCN–(o-H₂) cluster split into hyperfine structure due to the nitrogen nucleus were observed. Rotational constant $B_0 = 12899.718(20)$ MHz and centrifugal distortion constant $D_0 = 12.2470(16)$ MHz were derived together with its higher order constants. The hyperfine constants determined eqQ = -2.830(33) MHz which is smaller than that of HCN molecule means a large amplitude motion of HCN < θ > = 31.1° in the ground linear form. The bond length between HCN and H₂ parts is derived to be 3.90 Å. This value strongly suggests that o-H₂ is bonding to the N site of the HCN molecule in the gas phase.

Some lines belonging to the $\Sigma_1 - \Sigma_0$ vdW bending band of HCN–(*o*-H₂) were also observed. The $\Sigma_1 - \Sigma_0$ vdW bending frequency 136.831 GHz of HCN–(*o*-H₂) is larger than that of He–HCN 96.8 GHz, but much smaller than that of Ar–HCN 164.89 GHz. The hyperfine constant in the Σ_1 state indicate the cluster has T-shape in the excited state of the vdW bending mode.

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Figure 1. The J = 3-4 rotational line of the HCN–(*o*-H₂) in the ground Σ_0 state.

V-Q-3 Millimeter Wave Spectra of the H_2 - H_2O van der Waals Complex

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The hydrogen-water system is of interest due to the lightness (ie large rotational constants) of both parts which means that quantum dynamics effects are very important. High resolution spectra of such systems is helpful in developing models of the dynamics which include internal rotations of both partners.¹⁾ In addition, hydrogen–water collisions are believed to be important in the astronomical observations of intense water maser radiation.²⁾ A recent infrared study of H₂–H₂O provided the motivation for this study.³⁾

We have observed pure rotational transitions of the weakly bound H_2 – H_2O and H_2 – D_2O complexes using a direct absorption millimeter wave spectrometer in the

range 70–300 GHz. Internal rotation states involving ortho:H₂ (j = 1) Σ , ortho:H₂O $\Pi(1_{01})$ and para:H₂O $\Sigma(0_{00})$ were observed. The *e/f* parity splitting in the Π state provides important information on the intermolecular bending potential. Further work includes observation of the more weakly bound para:H₂–H₂O complex and direct excitation of the H₂O $\Sigma(1_{01})$ – $\Pi(1_{01})$ transition which is predicted to lie in the 350 GHz region.

References

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Table 1. Table of observed rotational transitions (MHz).

		H_2-H_2O	
J _{upper} -J _{low}	ver $\Pi_{e}(1_{01})$	$\Pi_{\rm f}(1_{01})$	$\Sigma(0_{00})$
2-1	71683.66	84983.56	85793.39
3–2	108760.57	126875.70	128002.72
4–3	146471.39	168017.75	169333.54
5–4	184341.19	208103.49	209391.38
		H_2-D_2O	
2-1	70684.54	82151.76	84412.97
3–2	106026.81	122766.98	126060.49
4–3	143955.50	162801.07	167009.37
5–4		202008.61	206976.05

V-Q-4 Millimeter Wave Spectroscopy of the van der Waals Bending Band of OCO-DF Generated in a Supersonic Jet Expansion

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The OCO-HF is a hydrogen-bonded quasi-linear cluster with a dissociation energy of 672 cm^{-1} .¹⁾ The inter molecular potential has minima at a bend structure of the COH angle of 22° and $\sim 10 \text{ cm}^{-1}$ potential barrier is expected at the linear structure of OCO-HF.²⁾ In the preceding work, we have measured the van der Waals (vdW) bending band of OCO-HF directly by the millimeter wave jet spectroscopy. As a result, the vibrational frequency of vdW bending mode of OCO-HF has been determined precisely to be 272548.8017(49) MHz. To determine the complicated two dimensional inter molecular potential function with the COH bending and the OHF bending vibrations, it is important to observe vdW bending mode of OCO-DF as well as OCO-HF. In the present work, we have measured the vdW bending band of OCO-DF by the millimeter wave jet spectroscopy.

The 10 atm mixed gas of 1% DF, 5% CO₂, 31% Ar, and 63% Ne was injected to the vacuum chamber by the pulsed nozzle. We have measured 235-315 GHz region.

The 31 rovibrational transitions of P(2)-P(4), Q(1)-Q(15), and R(0)-R(12) were assigned to the 1^1-0^0 (v_b^1) fundamental band of the lowest vdW bending mode. The spectral pattern for OCO–DF was almost same as OCO–HF. The band has intense Q and R branch lines, while the P branch lines were rather weak. Figure 1 shows the fast scan spectrum of the band head of Q branch.

The usual linear molecule Hamiltonian with the rotational energy and the (2,2) interaction energy was used for the analysis. The band origin of the $1^{1}-0^{0}$ (v_{b}^{1}) band has been determined to be 255815.6639(31) MHz, which is 6.1% smaller than that of OCO–HF. Furthermore, the rotational constant, centrifugal distortion constant, *l*-type doubling constant, and its higher order term were determined precisely. The analysis of the intermolecular potential function is now underway. In order to determine the precise two dimensional intermolecular bending potential surface, the measurement of the van der Waals hot band will be important.

References

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Figure 1. Fast scan spectrum of the head of Q branch for the OCO–DF.