

MILLIMETER WAVE SPECTROSCOPY OF WEAKLY BOUND MOLECULAR COMPLEXES.

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The millimeterwave absorption spectroscopy combined with a pulsed supersonic jet expansion technique has been applied to the observation of the vdW bands of weakly bound molecular complexes. The molecular structures, intermolecular potentials, and dynamic properties of the floppy molecular complexes is discussed with the result of the analysis. The He-HCN complex is a weakly bound complex with binding energy of about 9 cm^{-1} . We have measured the internal rotation and intermolecular stretching bands of the He-HCN complex by millimeter-wave absorption spectroscopy.^a The PES obtained from the analysis has a global minimum in the linear configuration with a depth of 29.6 cm^{-1} and has a saddle point at the anti-linear configuration with a depth of 20.5 cm^{-1} . The first excited state of the intermolecular stretching and the second excited ($j = 2$) state of the internal rotation are determined to be located 9.14 and 9.05 cm^{-1} above the ground state, very close to the calculated dissociation limit (D_0) of 9.33 cm^{-1} . We have extended the measurement to the transitions to the bound states above the "dissociation limit" (D_0) and assigned several such transitions in the ground vibrational state by millimeter wave-millimeter wave double resonance technique. The rovibrational levels of He-HCN with e label dissociate to the HCN molecule with $J = 0$ and the He atom (D_0), while those with f label, due to the total J and parity conservation, to the HCN molecule with $J = 1$ and the He atom which is higher in energy by about $2B_{\text{HCN}} \sim 2.96\text{ cm}^{-1}$ than D_0 , as discussed in the infrared study of He-HF.^b The PES obtained in the present analysis indicates that four f levels in the $j = 1$ and 2 excited states are bound above the "dissociation limit" (D_0). In addition several levels (both of e and f labels) are calculated to be bound by centrifugal barrier with finite lifetimes.

The H_2 -HCN complex is a weakly bound molecular complex including molecular hydrogen. The hydrogen molecule attaches to the nitrogen end of HCN for (ortho) H_2 -NCH, while to the hydrogen end for (para) H_2 -HCN in the ground state according to the observation of the pure rotational transitions.^c The Σ symmetry of the internal rotation ground state has been confirmed for both ortho and para H_2 -HCN. We have also observed the $\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$ bands of the $j=1-0$ internal rotation band of (ortho) H_2 -HCN, where j denotes the quantum number for the HCN internal rotation. The assignments of the internal rotation transitions have been confirmed by the millimeter wave-millimeter wave double resonance technique. The band origins of the $\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$ bands of (ortho) H_2 -HCN have been determined to be 187 and 165 GHz .

^aK. Harada, K. Tanaka, T. Tanaka, S. Nanbu, and M. Aoyagi, *J. Chem. Phys.* **117**, 7041 (2002).

^bC. M. Lovejoy and D. J. Nesbitt, *J. Chem. Phys.* **93**, 5387 (1990).

^cM. Ishiguro, T. Tanaka, K. Harada, C. J. Whitham and K. Tanaka, *J. Chem. Phys.* **115**, 5155 (2001).

RAMAN SPECTROSCOPY IN SUPERSONIC JETS: COLD MOLECULES AND CLUSTERS

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The vibrational spectra of molecules and molecular complexes are considerably simplified by supersonic jet cooling, even in the absence of rotational resolution. The combination of Raman detection with jet expansions is feasible, even in the case of spontaneous scattering. Raman and infrared spectra can provide nicely complementary information, even in the absence of an inversion center. Hydrogen bonds can give rise to blue-shifted hydride stretching bands, even if they are red-shifted at room temperature.

This will be exemplified by a few model systems which we have recently studied using Raman jet spectroscopy, including alkanes [1] (elastic modulus of polyethylene from gas phase spectroscopy), carboxylic acid dimers [2] (anharmonicity of low frequency modes), malonaldehyde [3] (sub-picosecond proton tunneling), pyrrolidine (vibrational temperature and adaptive aggregation) and halothane-benzene (C-H hydrogen bonding, cooperation with the Antwerp group).

1. T. N. Wassermann, J. Thelemann, P. Zielke, and M. A. Suhm, *J. Chem. Phys.* 131 (2009) 161108
2. Z. Xue and M. A. Suhm, *J. Chem. Phys.*, 131 (2009) 054301
3. N. O. B. Lüttschwager, T. N. Wassermann, S. Coussan and M. A. Suhm *Phys. Chem. Chem. Phys.* (2010) DOI: 10.1039/c002345k

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