MILLIMETER WAVE SPECTROSCOPY OF THE INTERMOLECULAR STRETCHING BAND OF He-HCN.

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Millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique was applied to the observation of the intermolecular stretching excited state (ν_s) and internal rotation second excited state ($j = 2$) of the He-HCN complex. Two supersonic jet nozzles and 10 round trip multi-reflection optical path were used for the measurement. Transitions belonging to the ν_s, $\nu_s \leftarrow j = 1$, $j = 2 \leftarrow 1$, and $j = 2 \leftarrow 0$ bands were observed in the frequency region of 150–280 GHz, where ν_s refers to the intermolecular stretching excited state, and $j = 1$ and 2 to internal rotation excited states. These transitions were definitely assigned using combination differences. The observed transition frequencies as well as the transition frequencies of the internal rotation fundamental band[a] ($j = 1 \leftarrow 0$) were analyzed to improve an empirical intermolecular potential energy surface. The intermolecular stretching frequency obtained is 9.1618 cm^{-1}, while the dissociation energy (D_0) is 9.4411 cm^{-1}. The average distance $< R >$ from the He atom to the center of mass of HCN and the root mean square amplitude of the intermolecular stretching vibration is 5.572 Å and 2.182 Å for the ν_s, $J = 1$ state, which is far longer and larger than those for the ground state (4.306 Å and 0.576 Å). The wavefunction of the intermolecular stretching excited state has a node along the radial coordinate and the probability density extends up to more than 12 Å .

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