MILLIMETER WAVE SPECTROSCOPY OF THE INTERNAL ROTATION BANDS OF He-HCN AND He-DCN.

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Millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique was applied to the measurement of the internal-rotation band of the He-HCN complex in the frequency region of 95–125 GHz. In total 13 rovibrational lines, split into nitrogen nuclear hyperfine structure, were observed for the fundamental internal-rotation band, $j = 1 - 0$. The observed transition frequencies and the previous MBER data[a] were analyzed to yield an empirical intermolecular potential energy surface, which was obtained by improving the recent *ab initio* potential surface.[b] The surface obtained has a global minimum in the linear configuration (He$\cdots$H–C–N) with a well depth of 30.2 cm^{-1}, and the saddle point located in the anti-linear configuration (H–C–N$\cdots$He) is higher in energy than the global minimum by 8.92 cm^{-1}. The distance R_{m} from the He atom to the center of mass of HCN along the minimum energy path shows a large angular dependence; R_{m} is 4.169 Å and 4.039 Å in the linear and anti-linear forms, respectively, and has a minimum value of 3.528 Å in a T-shaped configuration. The He-DCN was also measured and analyzed. The empirical potential energy surfaces are compaired with the *ab initio* potential energy surface[b] for both isotopic species.

[a] S. Drucker, F. Tao, and W. Klemperer, J. Phys. Chem. 99, 2646(1995).

[b] R. R. Toczylowski, F. Doloresco, and S. M. Cybulski, J. Chem. Phys. 114, 851(2001).