SPECTROSCOPY OF THE CH_3-HCL COMPLEX IN HELIUM NANODROPLETS

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The CH_3-HCl van der Waals complex has been isolated in superfluid helium nanodroplets, and the infrared-active hydrogen stretching vibrations have been identified. A 153 cm^{-1}redshift of the HCl stretch is observed (relative to the HCl monomer peak at 2905 cm^{-1}), consistent with the predicted hydrogen bonding interaction between the two molecules. The perpendicular CH stretching transitions originating from (N,K) = (0,0) and (1,1) are also observed, and simulations indicate that the band origin is shifted by roughly 6 cm^{-1}relative to the band origin of methyl radical in helium droplets[a] (3160.9(1) cm^{-1}). The barrier height to formation of CH_4 + Cl from CH_3 + HCl is only 1.5 kcal mol^{-1} with a 0 K reaction exothermicity of about 1.2 kcal mol^{-1}.[b] The broad linewidth of the parallel transition, relative to the perpendicular transition, indicates that excitation of the HCl stretch may be lifetime broadened due to optical pumping of the weakly bound complex over the barrier to form CH_4 + Cl. Additionally, one of the HCl stretches due to CH_3-$(HCl)_2$ has been identified and lies approximately 27 $\mathrm{cm}^{-1}$to the red of the "bound" stretch of the HCl dimer at 2852 cm^{-1}. The feasibility of an IR-IR double resonance experiment to probe for the photo-induced formation of CH_4-Cl will be discussed.

[a] A. M. Morrison, P. L. Raston, G. E. Douberly. *J. Phys. Chem. A.* **2013**, in press.
[b] A. J. Orr-Ewing, C. Murray. *Int. Rev. Phys. Chem.* **2004**, *4*, 435-482.