

INFRARED LASER STARK SPECTROSCOPY OF THE PRE-REACTIVE $\text{Cl}\cdots\text{HCl}$ COMPLEX FORMED IN SUPERFLUID ^4He DROPLETS

CHRISTOPHER P. MORADI, GARY E. DOUBERLY, *Department of Chemistry, University of Georgia, Athens, GA, USA.*

Chlorine atoms, generated through the thermal decomposition of Cl_2 , are solvated in superfluid helium nanodroplets and clustered with HCl molecules. The $\text{H}-\text{Cl}$ stretching modes of these clusters are probed via infrared laser spectroscopy. A broad band centered at $\approx 2880.9\text{ cm}^{-1}$ is assigned to the binary $\text{Cl}\cdots\text{HCl}$ complex. The band center is red shifted by only 7.4 cm^{-1} from the “free” HCl stretch (ν_1) of $(\text{HCl})_2$ and, as such, is consistent with an assignment to a similarly “free” HCl stretch. Also, the breadth of the band ($\approx 2\text{ cm}^{-1}$ FWHM) is consistent with assignment to a mostly b -type component of the $\text{H}-\text{Cl}$ stretch; the band is lifetime broadened to a similar extent as the predominantly b -type ν_1 stretch of $(\text{HCl})_2$, due to fast rotational relaxation facilitated by the helium droplet environment. Despite the lack of rotational structure, which would verify our assignment, the spectrum is consistent with stabilization of a weakly-bound complex having an L-shaped geometry. Computations reveal that the projection of the transition dipole moment onto the a -axis results in a dramatic decrease (≈ 700 times) in the intensity of the a -type band relative to the b -type band intensity; indeed, the signal-to-noise ratio in our experiment precluded observation of an a -type band for this complex. No bands were observed that could derive from a strongly H-bonded $\text{Cl}\cdots\text{HCl}$ complex. Additionally, we located two bands at 2764.0 and 2798.5 cm^{-1} that are consistent with the pick-up of two HCl molecules and are therefore assigned to vibrations of the $\text{Cl}\cdots(\text{HCl})_2$ complex.