

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

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Chlorine atoms, generated through the thermal decomposition of Cl $_2$ , are solvated in superfluid helium nanodroplets and clustered with HCl molecules. The H–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 Cl $\cdots$ HCl complex. The band center is red shifted by only  $7.4\text{ cm}^{-1}$  from the “free” HCl stretch ( $\nu_1$ ) of (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 H–Cl stretch; the band is lifetime broadened to a similar extent as the predominantly *b*-type  $\nu_1$  stretch of (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 ( $\approx 700$  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 Cl $\cdots$ HCl complex. Additionally, we located two bands at  $2764.0$  and  $2798.5\text{ cm}^{-1}$  that are consistent with the pick-up of two HCl molecules and are therefore assigned to vibrations of the Cl $\cdots$ (HCl) $_2$  complex.