LETTERS TO THE EDITOR

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Direct measurement of the HCl dimer tunneling rate and Cl isotope dependence by far-infrared laser sideband spectroscopy of planar supersonic jets

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Large amplitude tunneling motions in hydrogen bonded clusters have become the subject of intense experimental and theoretical study since the pioneering work on the microwave rotation-tunneling spectrum of the HF dimer by Dyke et al.[1] in 1972. The interest in these modes stems from their intimate relationship to the intermolecular potential energy surface (PES) and the ubiquitous presence and central importance of hydrogen bonds in the chemical and physical properties of condensed media in general and biological systems in particular. The hydrogen halide homodimer series offers a particularly good set of test cases for examining the variation of tunneling rates with PES and structure, but while much is known about the HF dimer, only recently have other HX dimers been subjected to rigorous study. This is due primarily to the large tunneling splittings expected in these complexes which, in some cases, leave no microwave transitions observable. We report here the *direct* measurement of the far-infrared (FIR) tunneling splitting of three isotopic forms of the HCl dimer at sub-Doppler resolution.

High resolution spectroscopy of $(HCl)_2$ began with the near-infrared direct absorption experiment of Ohashi and Pine,[2] who obtained an estimated ground state tunneling splitting of 9–18 cm^{-1}. This range was narrowed down considerably to 14.9 ± 1.0 cm^{-1} by Furlan et al.[3] who performed a CARS analysis of the ν_2 vibration of the dimer. FIR laser sideband studies of the $K_a = 0 \to 1$ rotation-tunneling subband have been carried out by Blake et al.,[4] while Moazzen-Ahmadi et al.[5,6] have collected extensive Fourier transform measurements of the $K_a = 2 \to 3$ subband along with several intermolecular vibrational modes. In some very recent work, Schuder et al.[7] have determined accurately via combination differences the ground and excited state tunneling splittings of the $H^{35}Cl-H^{37}Cl$ dimer by detecting weakly allowed vibration-rotation lines in the two HCl stretching bands. Their best estimate of the mixed dimer tunneling splitting lies at 15.4561(4) cm^{-1} for $K_a = 0$ and 15.2525(4)

cm^{-1} for $K_a = 1$. A two-state model developed by these authors predicts that the ground state tunneling rates should vary by 0.01 cm^{-1} or less with chlorine isotopic substitution.

Guided in part by these predictions, we have successfully detected directly HCl dimer pure tunneling transitions for the three common isotopic forms [$(H^{35}Cl)_2$, $H^{35}Cl-H^{37}Cl$, and $(H^{37}Cl)_2$] at hyperfine resolution using a planar expansion source for the cluster and a tunable far-infrared laser. A complete description of the spectrometer system and a detailed analysis of the $K_a = 0$ and $K_a = 1$ tunneling splittings will be presented in a later paper. The Caltech tunable far-infrared cluster spectrometer is similar in construction to the Berkeley instrument described in Busarow et al.[8] and Blake et al.,[4] with some minor modifications in the cluster source, mixing electronics and sideband separation optics. Briefly, the fixed frequency output of an optically pumped far-infrared laser is mixed with a phase locked microwave synthesizer and its harmonics to give a total tuning range of over 5
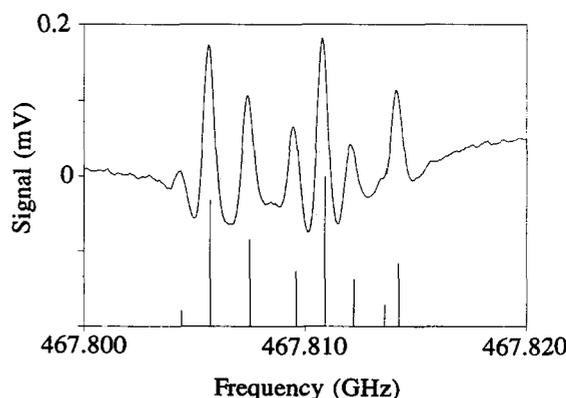

FIG. 1. Tracing of the $R(0_{00})$ line of the a-type $K = 0$ rotation-tunneling band of $(H^{35}Cl)_2$. Expected positions of the Cl hyperfine components are indicated by the vertical bars.

TABLE I. HCl dimer $K = 0(u)$ rotation-tunneling constants (2σ, MHz).[a]

	35–35	35–37	37–37
$(B + C)/2$	1915.0621(67)	1864.6220(61)	1814.3462(334)
D_J	0.007912(78)	0.006835(60)	0.01193(22)
H_J	− 1.47(59)E-06	− 0.71(5)E-05	− 0.40(9)E-04
eqQ_{aa}	− 12.646(430)	− 12.647(322)	− 10.154(245)
		− 10.155(325)	
ν_{tunn}	463979.197(109)	463357.743(78)	462733.686(315)

[a] Ground state constants fixed at values determined by Blake et al. (Ref. 4).

cm^{-1} per laser setting. In this case, all dimer transitions were recorded using the DCOOH laser line at 420.404 GHz. (HCl)$_2$ was produced by passing a 1–2% mixture of HCl in Ar through a 1.75″ × 0.001″ stainless steel slit nozzle.

As has been noted previously,[8] the planar jet produces quite intense far-infrared cluster absorption signals due to its long pathlength and sub-Doppler line widths. In the present study chlorine hyperfine structure is resolved for the lowest J transitions, as is shown for an $R(0)$ line in Figure 1. The linewidths of about 800 kHz are primarily due to time constant effects. With slower scans, linewidths of 300–400 kHz are easily obtained. J values up to 12 were measured for each of the dimer isotopic forms. Rotation-distortion constants through sixth-order in J were required to fit the data to an average rms of 450 kHz. Results of the fits are shown in Table I. The measured value for the mixed isotope tunneling splitting of 15.455951(3) cm^{-1} lies within the range of 15.4561(4) cm^{-1} determined indirectly by Schuder et al.,[7] but is two orders of magnitude more precise. Variations in tunneling frequency between the three isotopes are on the order of 0.04 cm^{-1}, with the lighter isotopes having the larger splitting. We note that the isotopic dependence of the tunneling frequency correlates well with the monomer moments of inertia, and that the change in homodimer tunneling frequencies is 4 times larger than the upper limit predicted by Schuder et al. Rotational constants for the $K_a = 0$ upper tunneling state are very similar to the upper $K_a = 1$ tunneling state constants determined by Blake et al.,[4] reflecting the small changes in the vibrationally averaged structure induced by both the tunneling motion and by rotational excitation about the a axis. The values of the quadrupole constants indicate that the vibrationally averaged projections on the a axis of both HCl subunits are nearly 47° in all of the rotation-tunneling states resolved to date, with remarkably little variation.

To summarize, we have directly detected the $K_a = 0$ tunneling splitting of the HCl dimer by tunable far-infrared laser spectroscopy at hyperfine resolution, and have determined the Cl isotope dependence of the tunneling rate and its effect on the vibrationally averaged structure. It is hoped that these results will be of use in determining a quantitatively accurate ground state PES for the HCl dimer, much as has been demonstrated recently for the direct inversion of high resolution far-infrared spectroscopic data of simpler atom–diatom systems such as Ar–HCl.[9,10]

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