

Quenching of interconversion tunneling: The free HCl stretch first overtone of (HCl)₂

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Cavity ringdown laser absorption spectroscopy has been used to record spectra of (H³⁵Cl)₂ and its Cl-substituted mixed dimers at the first overtone of the free hydrogen stretch ($2\nu_1$). The dimers were produced in pulsed planar supersonic expansions. Significant quenching of interconversion tunneling (i.e., which exchanges the roles of H-bond donor and acceptor) has been observed. Thus, the H³⁵Cl–H³⁷Cl and H³⁷Cl–H³⁵Cl heterodimers are distinguished in the $2\nu_1$ eigenstates, which is not the case for the ground and HCl-stretch fundamental eigenstates because of facile tunneling mixing. © 1998 American Institute of Physics. [S0021-9606(98)02023-6]

Hydrogen halide dimers are important model systems for studying intermolecular forces and hydrogen bonding.¹ Notable among these are the L-shaped acid–base pairs (HF)₂ and (HCl)₂. In the case of (HF)₂, a 0.66 cm⁻¹ splitting—due to the geared tunneling motion that exchanges the roles of H-bond donor and acceptor—was first observed in the microwave region by Dyke *et al.*² Upon exciting the HF-stretch fundamental, Pine *et al.*^{3,4} found a smaller geared tunneling splitting (0.22 cm⁻¹), and for HF-stretch first-overtone excitation, Nesbitt and co-workers⁵ determined geared tunneling splittings of 0.09 and 0.21 cm⁻¹ for rotational quantum number $K_a=1$ and 0, respectively. A much smaller splitting (0.0024 cm⁻¹) was observed for second-overtone levels by Chang and Klemperer,⁶ indicating efficient quenching of the tunneling. This can be rationalized as due to the difficulty of transferring vibrational excitation between the two HF subunits in the tunneling process.⁷ Thus, the vibrational dependence of the tunneling splitting provides a test of the full six-dimensional potential energy surface.

The HCl dimer also displays a large decrease of the tunneling splitting (ν^T) in vibrationally excited states, relative to the ground state splitting.⁸ Furlan *et al.*⁹ used coherent anti-Stokes Raman spectroscopy to examine jet-cooled (HCl)₂, and by combining their results with the high-resolution infrared (IR) data of Ohashi and Pine,⁸ estimated ν^T values of 14.9 cm⁻¹ for the ground state and 3.4 cm⁻¹ for the HCl-stretch fundamentals of the free (ν_1) and H-bonded (ν_2) HCl moieties. Accurate ν^T values for (H³⁵Cl)₂, H³⁵Cl–H³⁷Cl, and (H³⁷Cl)₂ were determined by Schuder *et al.*^{10,11} in extensive IR measurements, and by Blake and Bumgarner,¹² who measured ground state tunneling transitions by using far-IR laser absorption spectroscopy. A least-squares fit of all ground state vibration-rotation-tunneling (VRT) data enabled Elrod and Saykally to establish the four-dimensional intermolecular potential surface (IPS).^{13,14}

Despite the large body of high resolution spectroscopic data on the ground state and HCl-stretch fundamentals of (HCl)₂, no data have been reported for interconversion tun-

neling in overtones. In this Communication, we report overtone spectra of jet-cooled (H³⁵Cl)₂ and its Cl isotope mixed dimers obtained by using IR cavity ringdown laser absorption spectroscopy (CRLAS). Specifically, findings related to the quenching of interchange tunneling are presented which indicate that the H³⁵Cl–H³⁷Cl and H³⁷Cl–H³⁵Cl heterodimers are distinguishable at the eigenstate level in the first overtone excited state ($2\nu_1$). This differs from the ground state and ν_1 fundamental levels.

The CRLAS method has advanced rapidly since the seminal work of O'Keefe and Deacon,¹⁵ as reviewed by Scherer *et al.*¹⁶ and Paul and Saykally.¹⁷ Paul *et al.*¹⁸ have recently demonstrated this technique in the 3 μm region by determining the absolute concentrations of jet-cooled small water clusters. Only a brief account of our key experimental features is given here. The 1.77 μm output of an OPO system (STI Mirage 3000) pumped by an injection seeded Nd:YAG laser (Continuum 9010) constitutes the tunable light source, with a spectral resolution of 0.015 cm⁻¹. The ringdown cavity consists of two highly reflective mirrors (99.992% at 5650 cm⁻¹) separated by 0.51 m. HCl dimers were prepared by supersonic expansion of 7% HCl in Ar with a pulsed slit nozzle (12.7 mm×0.1 mm). A unique feature of our approach is active background subtraction; namely, the signal is averaged on an alternate shot basis that corresponds to the nozzle being on and off. Sensitivity of 1 part-per-million (ppm) fractional absorption per roundtrip pass was accomplished.

Figure 1 shows some of the main results. For (H³⁵Cl)₂, the P and R branches of the $K_a=1\leftarrow 0$ (Fig. 1) and $0\leftarrow 1$ (not shown) subbands have been resolved. The $K_a=2\leftarrow 1$ subband (not shown) has also been recorded, but with unresolved asymmetry doubling. Prominent features (see Fig. 1) that are red-shifted relative to those of the $K_a=1\leftarrow 0$ and $2\leftarrow 1$ subbands of (H³⁵Cl)₂ by an amount close to the 4.0 cm⁻¹ Cl isotope shift of HCl monomer are attributed to the corresponding b -type transitions of H³⁷Cl–H³⁵Cl, as discussed below. We assign these bands to overtone excitation of the free hydrogen.

Central to this report is the excited state ν^T value ob-

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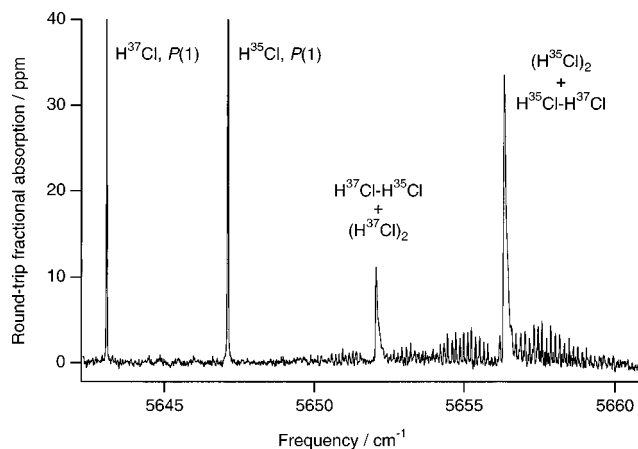


FIG. 1. The $2\nu_1$ overtone spectrum of the $K_a=1\leftarrow 0$ subbands of $(\text{H}^{35}\text{Cl})_2$, $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$ and $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$. Quenching of interchange tunneling in the upper state localizes the vibrational energy such that the isotope shifts in the band origins of the Cl substituted mixed dimers relative to that of $(\text{H}^{35}\text{Cl})_2$ depend only on the identity of the monomers being excited. Therefore, while the 4.0 cm^{-1} isotope shift between $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$ and $(\text{H}^{35}\text{Cl})_2$ is similar to that between H^{37}Cl and H^{35}Cl monomers [whose $P(1)$ transitions are also shown] there is nearly no shift between the corresponding transitions of $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$ and $(\text{H}^{35}\text{Cl})_2$. The $(\text{H}^{37}\text{Cl})_2$ line intensities should be approximately a factor of 3 weaker than those of $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$, and are obscured by the latter due to their similar isotope shifts.

tained from the overtone spectrum. The transitions $2\nu_1^+$ and $2\nu_1^-$ [plus and minus denote vibration-tunneling (VT) symmetry], which originate from the lower and upper tunneling components of the ground vibrational state, respectively, have been observed for $(\text{H}^{35}\text{Cl})_2$. The quantity $2\nu_1^+ - 2\nu_1^-$ is either the sum or difference of the tunneling splittings in the ground and excited states, depending on which of the upper VT symmetry species is higher in energy. Based on the $K_a''=0$ ground state splitting of $15.476\ 680\text{ cm}^{-1}$,¹² we estimate a tunneling splitting of 0.024 cm^{-1} for the $K_a'=1$ excited state, with a conservative uncertainty of $\pm 0.1\text{ cm}^{-1}$. Note that a positive splitting corresponds to $2\nu_1^+$ lying above $2\nu_1^-$. The large uncertainty is due to calibration [which is currently based on the $P(1)$ transitions of H^{35}Cl and H^{37}Cl monomers, see Fig. 1] as well as not fitting the $2\nu_1^-$ hot band because of low S/N. Simultaneously recording a water vapor photoacoustic spectrum will lessen markedly the uncertainty. Regardless, a quite pronounced quenching of interchange tunneling is seen with overtone excitation—much more than with $(\text{HF})_2$. This possibly reflects that vibrational exchange between the HCl subunits is modest relative to the equivalent exchange in $(\text{HF})_2$.

An interesting consequence of small excited state tunneling rates is localization of the heterodimers on the excited IPS. Consider first the ground vibrational level. Though $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$ and $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$ are nearly degenerate in the limit of no tunneling, it is known that tunneling is *facile* for the ground vibrational level, since no quanta are exchanged. Thus, there is a large tunneling splitting and both configurations are accessed with nearly equal probability.

Now consider the ν_1 fundamental. The energies of the nontunneling basis states differ by the 2.1 cm^{-1} isotope shift between H^{35}Cl and H^{37}Cl . Since this difference is comparable to the coupling matrix element (i.e., values of 1.54 and

1.66 cm^{-1} have been obtained for $K_a'=1$ and 0, respectively),¹¹ the nontunneling basis states are strongly mixed and to a first approximation the heterodimers are indistinguishable. In this sense, the situation with one quantum of ν_1 excitation is qualitatively similar to that of the ground vibrational level. The heterodimer spectrum is dominated by one line that lies between the corresponding $(\text{H}^{35}\text{Cl})_2$ and $(\text{H}^{37}\text{Cl})_2$ transitions. Intensity ratios are proportional to the relative concentrations of $(\text{H}^{35}\text{Cl})_2$, $(\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl} + \text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl})$, and $(\text{H}^{37}\text{Cl})_2$, namely, $9:3(3+3):1$.

For the $2\nu_1$ overtone level, the situation is different. The energy separation between $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$ and $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$ is at least an order of magnitude larger than the tunneling matrix element, resulting in wave functions that correspond to individual (localized) isomers in the excited state. This is manifest in (i) the observed $\sim 4.0\text{ cm}^{-1}$ red-shift (i.e., similar to the Cl isotope shift of the monomer) in both the $K_a=1\leftarrow 0$ and $2\leftarrow 1$ subband origins of $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$ relative to those of $(\text{H}^{35}\text{Cl})_2$; and (ii) the approximate 3:1 intensity ratio found between the unresolved Q branch clumps (Fig. 1) of $(\text{H}^{35}\text{Cl})_2$ and the $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$ heterodimer, i.e., with H^{37}Cl free. We have also found the $K_a=1\leftarrow 0$ subband of $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$; it has essentially no shift from that of $(\text{H}^{35}\text{Cl})_2$ and has line intensities comparable to those shown in Fig. 1 of $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$. Thus, the heterodimers are distinguishable in the $2\nu_1$ state. Schuder *et al.* have observed similar behavior for fundamentals of DCl heterodimers.¹⁹

Note that for the $\nu_1 + \nu_2$ level (i.e., simultaneous excitation of both the free and bonded HCl subunits), not only are the nontunneling basis states of the heterodimers nearly degenerate, as in the ground vibrational level, but also the barrier to exchange of (equal) vibrational quanta is likely to be lower than in the cases of $2\nu_1$ and $2\nu_2$. Thus, tunneling is expected to be significant and $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$ and $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$ may not be distinguishable at the eigenstate level. Clearly, obtaining tunneling rates for levels such as $\nu_1 + \nu_2$ and $2\nu_2$ can improve our understanding of vibrational coupling in weakly bound complexes.

Finally, we note that overtone states can be used in IR + UV double resonance experiments with HCl dimers, e.g., with H atom translational energies measured by using high- n Rydberg time-of-flight spectroscopy.²⁰ This enables photo-initiated reaction dynamics and long-range interactions in X-HY species to be examined with spectroscopically selected clusters.²¹ Initial success along this line has been reported by Nesbitt and co-workers.²²

In summary, the $(\text{HCl})_2$ first overtone corresponding to excitation of the free hydrogen has been investigated by using CRLAS. Evidence for strong quenching of interconversion tunneling upon vibrational excitation has been found. Thus, $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$ is distinguishable from $\text{H}^{37}\text{Cl}-\text{H}^{35}\text{Cl}$ in the vibrationally excited state. Measurements of interconversion tunneling rates for overtone levels should help quantify intermolecular forces in hydrogen-bonded systems. A search for the $\nu_1 + \nu_2$ and $2\nu_2$ vibrations is underway.

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