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# Overtone band shapes and IVR: C–H stretch overtones in $\text{CHCl}_3$

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The intracavity photoacoustic dye laser spectrum of  $\text{CHCl}_3$  in the gas phase at  $16\,350\text{ cm}^{-1}$  is reported. The  $\nu = 6-0$  overtone of the CH stretch is observed, and found to exhibit a rotational band contour closely analogous to the  $\nu = 1-0$  fundamental. The implication of this result for intramolecular vibrational energy redistribution is discussed.

The relationship between the shapes (widths) of C–H stretch overtone absorption features in the visible spectral region and intramolecular vibrational energy redistribution (IVR) has been the subject of considerable interest and some controversy in the recent literature.<sup>1–4</sup> Two views have been advanced; (i) that the often near-Lorentzian band shapes characteristic of overtone absorption bands in many C–H containing polyatomic molecules have their origin in ultrafast IVR involving decay of the initially prepared state into a significant fraction of the available density of other excited vibrational states of a similar energy, and (ii) that such absorption profiles are misleadingly simple and disguise the fact that there are many contributions, from spectral congestion and hot bands, etc., in addition to any homogeneous broadening due to dynamical processes. The latter argument has been nicely illustrated in a recent low temperature study of the  $\nu = 6$  C–H stretching overtone in  $\text{CH}_4$ .<sup>5</sup>

In a recent paper, Kato<sup>6</sup> has discussed the dynamics of IVR in  $\text{CHCl}_3$ , modeled using classical trajectory methods on an *ab initio* potential energy surface. C–H stretch overtone absorption band shapes were also calculated and compared with the spectroscopic measurements of Fang and Swofford.<sup>7</sup> The IVR dynamics were found to be characterized by processes occurring on two different time scales; rapid energy transfer from the C–H stretch  $\nu_1$  to the C–H bending vibration  $\nu_4$  facilitated by Fermi resonance between  $\nu_1$  and  $2\nu_4$ , and a subsequent slow redistribution into the remaining C–Cl vibrations. Energy transfer into the C–Cl modes was found to be negligible for the  $\nu = 1$  and  $\nu = 3$  C–H stretching states, which exhibited relatively narrow absorption profiles. In contrast, for the  $\nu = 5$  and  $\nu = 7$  overtones energy transfer to the C–Cl modes was found to be much more efficient, presumably aided by the stronger stretch/bend Fermi resonance interactions present at these higher vibrational levels. These overtones exhibited very broad absorption profiles suggested to be characteristic of rapid, global redistribution of the energy. The theoretical spectra (Fig. 9 of Ref. 6) compared favorably with experimental spectra reported by Fang and Swofford,<sup>7</sup> although the theoretical bandwidths of the  $\nu = 5$  and  $\nu = 7$  overtones appeared somewhat broader ( $300\text{ cm}^{-1}$  FWHM for  $\nu = 7$  compared to the experimental value of  $180\text{ cm}^{-1}$ ).

In this letter we present evidence that the bandwidths

observed in the thermal lensing study of Fang and Swofford<sup>7</sup> have their origin largely in interactions characteristic of the liquid phase, such as hydrogen bonding. Overtone band shapes determined in the vapor phase show no such broadening and, indeed, the  $\nu = 6$  overtone absorption profile reported here is comparable to the C–H stretch *fundamental* measured using FTIR spectroscopy. The difficulties of extracting band shape information from studies in the liquid phase were recognized by Fang and Swofford, and some attempt was made to determine the dependence of the overtone bandwidths on the concentration of  $\text{CHCl}_3$  in  $\text{CCl}_4$ , (see Fig. 5 of Ref. 7). Even when specific hydrogen-bonding interactions are absent, overtone bandwidths determined in the liquid phase are generally much larger than their counterpart in the dilute gas phase.

As part of a systematic study of interbond coupling and Fermi resonances in C–H overtones of polyatomic molecules, we have determined FTIR and laser photoacoustic spectra of gas phase  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{Cl}$ . A full discussion of these spectra and their modeling in terms of suitable local mode descriptions is reserved for a later publication.<sup>8</sup> However, because of the great disparity observed in overtone band shapes of gas phase and liquid phase  $\text{CHCl}_3$ , and the conclusions reached by Kato,<sup>6</sup> we feel it is pertinent to present some preliminary results on the C–H stretch fundamental and the  $\nu = 6$  overtone.

Figure 1 shows part of a FTIR spectrum of  $\text{CHCl}_3$  in the region  $2990\text{--}3070\text{ cm}^{-1}$  recorded at a pressure of 2.2 Torr with a total path length of 3.9 m. This spectrum shows the anticipated  $A_1$  C–H stretch fundamental,  $\nu_1$ , centered at  $3033.0\text{ cm}^{-1}$ . Under the experimental resolution of  $0.12\text{ cm}^{-1}$ , rotational structure can be seen. The bands at  $3029.4$  and  $3023.4\text{ cm}^{-1}$  have been assigned as hot bands. According to the analysis of Kato,<sup>6</sup> such well-defined structure is characteristic of relatively slow redistribution with little energy transfer to the C–Cl modes.

We also believe that the Fermi resonance between  $\nu_1$  and  $2\nu_4^0$  (where the superscript denotes the quantum number  $l_4$ ) is weak, and is unlikely to be affecting the band centers by more than a few  $\text{cm}^{-1}$ . We have two reasons for this view. First, the  $2\nu_4$  band is observed as a well characterized band at  $2409\text{ cm}^{-1}$ , more than  $600\text{ cm}^{-1}$  below  $\nu_1$ ; the band origins are simply too far apart for significant resonance. Second, if the resonance were important it would make a large positive contribution, with a resonant denominator ( $\nu_1 - 2\nu_4$ ), to the anharmonicity constant  $x_{14}$  (see the general formulas for  $x_{rs}$  in Mills' review<sup>9</sup>). However, the

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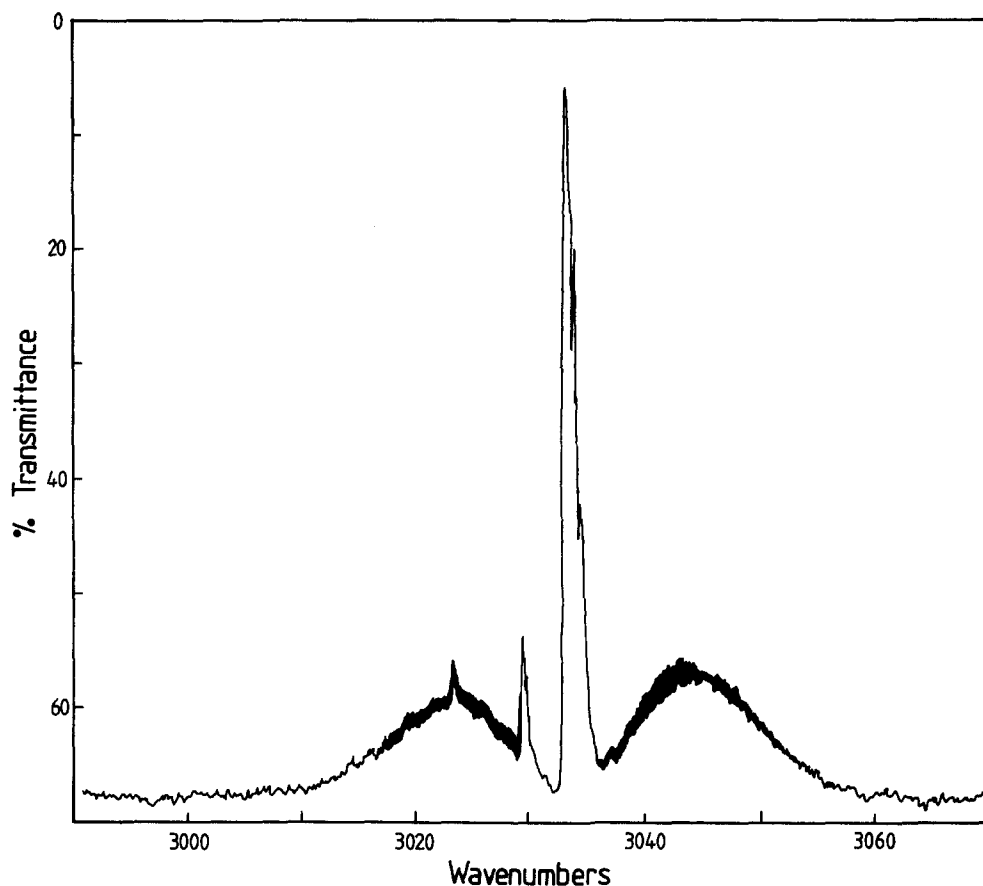


FIG. 1. Part of a FTIR spectrum of gas phase  $\text{CHCl}_3$  showing the C-H stretch fundamental  $\nu_1$ . The spectrum was recorded with a sample pressure of 2.2 Torr and a total path length of 3.9 m.

$(\nu_1 + \nu_4) \pm 1$  combination band is well characterized at  $4235 \text{ cm}^{-1}$ , and with  $\nu_1$  at  $3033 \text{ cm}^{-1}$  and  $\nu_4$  at  $1220 \text{ cm}^{-1}$  this determines  $x_{14}$  to be  $-18 \text{ cm}^{-1}$ . This negative value can hardly be consistent with any significant  $\nu_1$ ,  $2\nu_4$  resonance.

Figure 2 shows part of the photoacoustic spectrum of  $\text{CHCl}_3$  obtained using mechanically modulated intracavity cw dye laser excitation in the region of the  $\nu = 6$  overtone. A sample pressure of 100.7 Torr was used. The spectrum has

been calibrated for wavelength and normalized to the variation in dye laser power over the wavelength range of the laser dye according to the procedures described previously.<sup>10</sup> In complete contrast to the observations of Fang and Swofford<sup>7</sup> and the theoretical calculations of Kato,<sup>6</sup> the  $\nu = 6$  C-H stretch overtone shows a *well defined rotational band contour even at the limited ( $\sim 1 \text{ cm}^{-1}$ ) resolution of the photoacoustic spectrometer*. It is possible that individual ro-

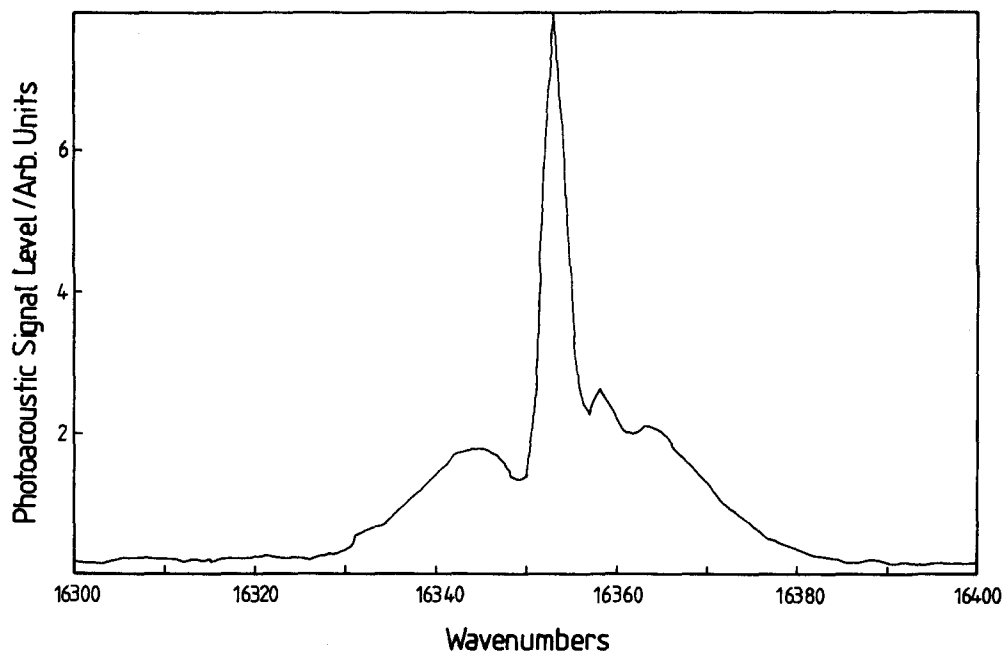


FIG. 2. Part of a laser photoacoustic spectrum of gas phase  $\text{CHCl}_3$  showing the  $\nu = 6$  C-H stretching overtone. A sample pressure of 100.7 Torr was used.

tational lines might be resolved with a narrower bandwidth excitation source. The small feature at  $16\,354\text{ cm}^{-1}$ , i.e., to high energy of the band center has yet to be assigned. We note that this spectrum has been reported previously by Wong and Moore.<sup>11</sup>

Lewerenz and Quack<sup>12</sup> have modeled the stretch/bend Fermi resonance in  $\text{CHCl}_3$  using an effective vibrational Hamiltonian described in detail in previous publications.<sup>13,14</sup> Using their<sup>12</sup> best-fit parameters for the frequencies, anharmonicities, etc., we are able to reproduce quantitatively features in the photoacoustic spectra for both the  $\nu = 5$  and  $\nu = 6$  overtone band systems, leading us to the conclusion that some mixing with the bending mode is present in the spectrum shown in Fig. 2. However, unlike the case of  $(\text{CF}_3)_3\text{CH}$ ,<sup>14</sup> which also shows stretch/bend Fermi resonance in its overtone band systems in the visible region, the overtones of  $\text{CHCl}_3$  show very little additional broadening when compared with the C-H stretch fundamental. We feel that this indicates that the extent of coupling between the mixed stretch/bend states and the remaining C-Cl vibrations is almost nonexistent at these high levels of stretch excitation or, at least, is insufficient to produce observable spectroscopic consequences. It is worth recalling that the highest energy C-Cl fundamental vibration is the C-Cl<sub>3</sub> stretch ( $\nu_5$ ,  $774\text{ cm}^{-1}$ ), sufficiently far removed from the C-H bend fundamental to lead us to expect that any coupling between these modes should be weak.

In summary, we have shown that the C-H stretching overtone band shapes determined by Fang and Swofford<sup>7</sup> for  $\text{CHCl}_3$  are dominated by contributions from liquid phase interactions. The conclusions of Kato's recent theoretical study of IVR in  $\text{CHCl}_3$ ,<sup>6</sup> which predicts very broad, featureless overtone band shapes at high vibrational levels, must therefore be reassessed.

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