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CH Stretching Vibrational Overtone Spectra of 1,3,5,7-Cyclooctatetraene and 1,1,1-Trichloroethane

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Local mode frequencies, $\tilde{\omega}$, and anharmonicities, $\tilde{\omega}x$, are obtained from the $\Delta v_{CH} = 2-7$ spectral regions of 1,3,5,7-cyclooctatetraene (COT) and 1,1,1-trichloroethane. In 1,1,1-trichloroethane $\tilde{\omega}$ and $\tilde{\omega}x$ are used in conjunction with ab initio potential energy surfaces to calculate local mode anharmonicity−torsion coupling terms, $\delta_{\tilde{\omega}x}$, and frequency−torsion coupling terms, $\delta_{\tilde{\omega}}$. Blue-shifting of sterically hindered CH oscillators in 1,1,1-trichloroethane indicates nonbonded, through-space intramolecular interactions with Cl. Multiple, complex Fermi resonances are observed in 1,1,1-trichloroethane and in COT between local mode states and local mode/normal mode combination states. Intensities of vibrational overtone transitions are calculated in the range $\Delta v_{CH} = 3-9$ using ab initio dipole moment functions and the harmonically coupled anharmonic oscillator (HCAO) model. HCAO intensities are compared to experimental intensities at $\Delta v_{CH} = 3$.

Introduction

Vibrational stretching energy becomes increasingly localized within one of a set of equivalent *X* H oscillators (where X = C, N, O, etc.) with increasing vibrational excitation.[1−5] Such localization of energy within local modes of vibration makes vibrational overtone spectroscopy a very sensitive probe for detecting energy flows in intramolecular vibrational energy redistribution (IVR),[6,7] and subtle changes in XH bond lengths[8−10] and molecular conformations.[11,12] Overtone spectroscopy can be used to probe how molecular geometry and the amplitudes of local XH stretching vibrational modes affect resonances, couplings, and the rate of IVR.

The molecular stretching Hamiltonian can be expressed in a local mode basis where (harmonic) off-diagonal coupling elements are small compared to (anharmonic) diagonal cubic and quartic terms.[13] The contributions of the diagonal terms in this Hamiltonian become increasingly dominant with increasing vibrational excitation. The stretching potential of a molecule may therefore be treated as a collection of isolated anharmonic oscillators in which interoscillator coupling is treated as a perturbation.[6] The resultant model is the harmonically coupled anharmonic oscillator (HCAO) model.[5,14−16] It is convenient to represent such anharmonic oscillators with the Morse oscillator expression as the energies and matrix elements of the Morse oscillator wave function have been solved analytically.[4,17]

The basis states for *n* XH Morse oscillators are expressed as a product of individual one-dimensional Morse wave functions $|v_1\rangle|v_2\rangle \ldots |v_i\rangle \ldots |v_n\rangle$ or simply $|v_1,v_2,...,v_i,...,v_n\rangle$, where v_i is the number of vibrational quanta of stretch in the i^{th} XH oscillator. Spectrally bright states are almost exclusively pure local mode states described by a linear combination of components where all of the vibrational energy is localized in a single oscillator (e.g., $|v,0,...,0\rangle$, $|0,v,...,0\rangle$, etc.). In the case of three coupled, identical XH oscillators of local C_{3v} symmetry, local mode wave functions arising from linear combinations of these basis states are denoted $|v,0,0\rangle_{A_1}$ and $|v,0,0\rangle_E$ (the pure local mode wave function of A_2 symmetry carries no intensity). Symmetrized wave functions become increasingly degenerate with increasing vibrational excitation such that symmetry effects are not generally observed where an XH oscillator has been excited by three or more vibrational quanta, v, i.e., where $\Delta v_{XH} \geq 3$. Nearly degenerate states of C_{3v} symmetry that cannot be resolved from one another can be collectively denoted as $|v,0,0\rangle_{A_1E}$.

In our earlier work, we have noted that CH stretching potentials can become more harmonic with increased steric crowding.[18,19,20] Recently, steric crowding in neopentane, $C(CH_3)_4$, was found to give rise to intramolecular coupling through space between proximal, nonbonded hydrogen atoms.[21] This coupling was found to enhance Fermi resonances and accelerate IVR, leading to complex spectral features. A recent study[22] of *tert*-butyl compounds has determined that through-space interactions, in which the van der Waals spheres of proximal, nonbonded atoms interact, causes increases in the local mode vibrational frequencies of the CH oscillators. Thus such through-space interaction would appear to be a general phenomenon and not restricted to $M(CH_3)_4$ homologues.

Another mechanism by which CH oscillators are perturbed is via halogen substitution. Studies on dihalomethanes indicate that the CH force constant increases with halogen substitution[23] and that the local mode frequency $\tilde{\omega}$ increases with increasing electronegativity.[24]

The purpose of this paper is to investigate the roles of steric crowding and halogen substitution on the local mode properties of CH oscillators in 1,1,1-trichloroethane and to compare these local mode properties with those in less crowded molecules and similarly crowded molecules which contain fewer halogens. We will present the CH stretching overtone spectra of cyclooctatetraene, an uncrowded, antiaromatic molecule. To the best of our knowledge, these are the first published CH stretching vibrational overtone spectra of an antiaromatic system.

Experimental Section

Sample Preparation. COT was obtained as a liquid (Aldrich, 98%, with 0.1 hydroquinone as an inhibitor), as was 1,1,1-

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trichloroethane (Aldrich, 99.5%, anhydrous). All samples were degassed by repeated freeze−pump−thaw cycles. The vacuum line and photoacoustic (PA) cell (vide infra) are evacuated to a pressure of 10^{-4} to 10^{-5} Torr for at least 4 h prior to sample introduction to ensure dryness.

Owing to the low vapor pressure of COT, argon (Cannox, 99%) was used to (1) carry the COT/Ar mixture through the vacuum line into the evacuated PA cell, and (2) act as a "buffer" gas, aiding in the propagation of the acoustic signal. Prior to use the argon was slowly passed through Drierite (which had been heated under vacuum and allowed to cool) and introduced into the vacuum vial containing COT. The COT/Ar mixture was allowed to equilibrate for at least 2 h before the mixture was allowed to expand into an evacuated PA cell (vide infra). The final pressure of the mixture ranged from 100 Torr to 700 Torr.

The purity of 1,1,1-trichloroethane was investigated via nuclear magnetic resonance and was estimated to contain less than 1% impurity.

Intracavity Laser Photoacoustic Spectroscopy. Our ICL-PAS setup has been previously described.[25,26] A 20 W Coherent Innova 200 argon ion laser is used to pump a broadband Coherent 890 Ti:sapphire (Ti:sapph) laser or a Coherent 599 tunable dye laser. In this work we scan a region from 9300 to 19 000 cm^{-1} ($\Delta v_{\mathrm{CH}} = 4-7$) using short wave and mid wave Ti:sapph optics, and the laser dyes DCM and Coumarin 6. Birefringent filters with resolutions of approximately 0.4 cm^{-1} are used to tune across the range of a given laser configuration. Referencing to known water lines[27] results in an estimated peak position error of less than 2 cm^{-1}.

Our standard PA cell was modified in order to allow us to study 1,1,1-trichloroethane. 1,1,1-Trichloroethane is an excellent solvent—it dissolves the adhesive which we routinely use in the construction of PA cells, as well as the microphones (Knowles EK-3132) which detect the PA signal. A new PA cell was constructed using Varian UltraTorr epoxy glue as this adhesive resists attack by 1,1,1-trichloroethane vapor for tens of hours. The microphones were destroyed by 1,1,1-trichloroethane vapor in a matter of hours, therefore the PA cells were designed in such a way as to allow easy microphone replacement. The microphones were glued into one end of a glass tube which was affixed to the PA cell, perpendicular to the axis of the cell, via a high vacuum Swage-Loc.

Theory and Calculations

Local Modes of Vibration and the HCAO Model. Vibrational stretching overtone spectra of XH bonds can be interpreted within the local mode model of molecular vibration.[2,3] The anharmonic XH stretching potential can be approximated by a Morse potential.[6] The Morse oscillator energy eigenvalues, $\tilde{E}_v$, are[6,28]

$$\tilde{E}_v = \tilde{\omega}\left(v + \frac{1}{2}\right) - \tilde{\omega}x\left(v + \frac{1}{2}\right)^2 \tag{1}$$

which is rearranged[6] to yield the frequency, $\tilde{\nu}_{v\leftarrow 0}$, of an overtone transition (from the ground state) $v' = v \leftarrow v'' = 0$ given by

$$\tilde{\nu}_{v\leftarrow 0} = v\tilde{\omega} - (v^2 + v)\tilde{\omega}x \tag{2}$$

The values of the Morse parameters $\tilde{\omega}$ and $\tilde{\omega}x$ are obtained from a Birge−Sponer plot of $\tilde{\nu}_{v\leftarrow 0}/v$ vs v or from a quadratic fit of $\tilde{\nu}_{v\leftarrow 0}$ vs v. Eigenstates are obtained within the HCAO model[5,14−16] in terms of Morse oscillator wave functions[6] with the assumption of harmonic interoscillator coupling.

Three Coupled Methyl Oscillators. The (unsymmetrized) wave function of three coupled local mode CH oscillators excited by v vibrational quanta can be expressed as $|0,0,v\rangle$. The frequency of a transition out of the ground $|0,0,0\rangle$ state to the state $|0,0,v\rangle$ is[5]

$$\frac{H - E_{|0,0,0\rangle}}{hc} = \sum_{i}^{3} v_i\tilde{\omega}_i - \sum_{i}^{3}(v_i^{\,2} + v_i)\tilde{\omega}x_i - \sum_{i\neq j}^{3}\gamma'_{ij}(a_i a_j^{+} + a_i^{+} a_j) \tag{3}$$

where $E_{|0,0,0\rangle}$ is the energy of the vibrational ground state and γ'_{ij} is the intramanifold coupling parameter[5]

$$\gamma'_{ij} = (\gamma_{ij} - \phi_{ij})\sqrt{\tilde{\omega}_i\tilde{\omega}_j} \tag{4}$$

where γ_{ij} and ϕ_{ij} are, respectively, the kinetic and potential energy coupling terms.

Spectral Manifestations of Fermi Resonances. An initially prepared pure local mode state $|v, 0, 0\rangle$ can couple with a near-resonant local mode-normal mode combination state $|v - 1, 0, 0\rangle|n\nu_{\mathrm{b}}\rangle$ (where $|\nu_{\mathrm{b}}\rangle$ is typically a bending mode excited by n vibrational quanta). The resultant energy flow between these vibrational modes is observed as a splitting in the frequency domain (i.e., a Fermi resonance[29]) caused by a mixing between the wave functions,[7] with the magnitude of the splitting reflecting the rate of vibrational energy flow.[30] The frequency of the state $|v, 0, 0\rangle$ in the absence of this perturbing interaction, $\tilde{\nu}_{\mathrm{iso}}$, is approximated by the average of the perturbed energies of the observed combination and local mode peaks, $\tilde{\nu}_{\mathrm{comb}}$ and $\tilde{\nu}_{\mathrm{lm}}$, weighted by their relative intensities[31]

$$\tilde{\nu}_{\mathrm{iso}} = \frac{\tilde{\nu}_{\mathrm{lm}}f_{\mathrm{lm}} + \tilde{\nu}_{\mathrm{comb}}f_{\mathrm{comb}}}{f_{\mathrm{lm}} + f_{\mathrm{comb}}} \tag{5}$$

where f_{comb} and f_{lm} denote the intensities of the observed combination and local mode peaks, respectively.

Oscillator Strength. The experimental intensity of a vibrational overtone transition can be expressed in terms of the dimensionless oscillator strength, f.[32] Applying the ideal gas law and using the appropriate physical constants[33] f can be expressed as

$$f = 2.6935 \times 10^{-9}\frac{T}{pl}\int A(\tilde{\nu}_{eg})\,\mathrm{d}(\tilde{\nu}_{eg}) \tag{6}$$

where T is the temperature (in Kelvin), p is the gas pressure (in Torr), l is the path length (in meters), and $A(\tilde{\nu}_{eg})$ is the absorbance as a function of frequency (in wavenumbers).

The oscillator strength of an overtone transition can be calculated[32] from the transition dipole moment function, μ_{eg}, the transition frequency, $\tilde{\nu}_{eg}$, and appropriate physical constants[33]

$$f = 4.70175 \times 10^{-7}(\mathrm{cm\ D^{-2}})\tilde{\nu}_{eg}|\mu_{eg}|^2 \tag{7}$$

The Dipole Moment Function. The continuous DMF of two coupled XH oscillators is approximated with a Taylor series expansion, taken up to fourth order, along the two internal stretch coordinates q_1 and q_2 obtained by fitting a polynomial to ab initio values of the dipole moment, $\vec{\mu}$.[34−38] Values of $\vec{\mu}$ were calculated for displacements of q_1 and q_2 up to ± 0.30 Å from the equilibrium XH bond length, r_{e}, in steps of 0.05 Å with all other molecular coordinates held constant at their equilibrium values. Diagonal terms were retained up to fourth

TABLE 1: Ab Initio Calculated Bond Lengths of the D_{2d} Stationary Point Structure of 1,3,5,7-Cyclooctatetraene

	bond length (Å)		
theory/basis set	CH	CC$_s$[a]	CC$_l$[a]
HF/6-31G(d,p)	1.0795	1.3234	1.4778
HF/6-311++G(2d,2p)	1.0762	1.3202	1.4758
B3LYP/6-31G(d,p)	1.0909	1.3419	1.4734
B3LYP/6-311++G(2d,2p)	1.0860	1.3363	1.4704
B3LYP/cc-pVDZ	1.0976	1.3449	1.4746
B3LYP/cc-pVTZ	1.0866	1.3351	1.4699
B3LYP/cc-pVQZ	1.0859	1.3349	1.4696

[a] The subscript "s" denotes the shorter C−C bond length of the conformer while "l" denotes the longer C−C bond length.

order while pairwise mixed derivatives $\partial^2\vec{\mu}/\partial q_1{}^1\partial q_2{}^1$, $\partial^3\vec{\mu}/\partial q_1{}^1\partial q_2{}^2$, and $\partial^3\vec{\mu}/\partial q_1{}^2\partial q_2{}^1$ were retained up to third order. It is important to include terms beyond linear as second-order derivatives $\partial^2\vec{\mu}/\partial q_1{}^2$ and $\partial^2\vec{\mu}/\partial q_2{}^2$ contribute significantly more intensity to overtone transitions than do linear terms.

Computational Details. Ab initio calculations were carried out with Gaussian 98 revision A.5[39] on an SGI Octane with a MIPS R10000 processor, Gaussian 98 revision A.11[40] on a cluster with Compaq Alpha ES40 processors, and Gaussian 03W revision B.03[41] on a personal computer with a Pentium 4, 2.8 GHz processor. Unless noted otherwise, calculations used all Gaussian defaults except that the Gaussian overlay option IOP-(3/32=2) was used with all calculations to prevent the reduction of expansion sets. All calculations were carried out using SCF=Tight since many of the basis sets used in this paper contained diffuse functions.

Results and Discussion

General Characteristics of Vibrational Overtone Spectra and Spectral Fitting. Experimental spectra are deconvoluted in SpectraCalc[42] with the least number of peaks needed to reproduce the spectrum. All spectral deconvolutions use Lorentzian profiles as constituent peaks. The maximum standard deviations introduced by the deconvolution procedure are 3 cm^{-1}, 3%, and 6% for the peak centers, heights, and full-widths at half-maximum (fwhm), respectively.

In the absence of coupling, one overtone transition peak is observed for each nonequivalent XH oscillator with the frequency of that transition given by eq 2. In cases where more than one Lorentzian is required to deconvolute a spectral region, the dominant Lorentzian is chosen to represent the pure local mode transition. In cases where two or more Lorentzians are of comparable intensity, that Lorentzian is chosen to represent the pure local mode transition which gives the most linear Birge−Sponer plot. The transition frequencies of pure local mode transitions in the absence of perturbations by Fermi resonances are approximated with eq 5.

The frequencies of the observed overtone transitions, ν, are much greater than the inverse of the excited-state lifetime, $1/\tau$, thus justifying the use centrosymmetric Lorentzians as fitting functions rather than more general, noncentrosymmetric Lorentzian expressions.[22,43,44] Owing to the very short lifetimes of the prepared vibrational overtone states, collisional deactivation, dephasing, and the influence of inhomogeneity in the various local environments[45] have a negligible influence on lifetimes and peak shapes under the experimental conditions employed.[21]

1,3,5,7-Cyclooctatetraene. COT contains $(4n)\pi$ electrons and is *antiaromatic*.[46] In Table 1 we note that COT exhibits alternations in C−C bond lengths characteristic of single bond/double bond alternations.[47]

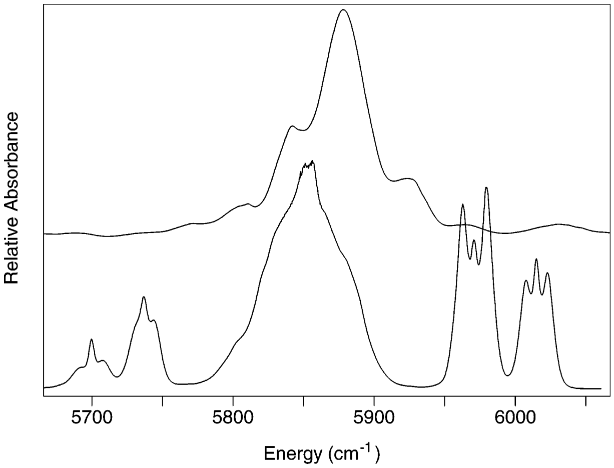

Figure 1. $\Delta\upsilon_{CH} = 2$ region of the Cary/5e vapor phase spectrum of 1,3,5,7-cyclooctatetraene (top) and 1,1,1-trichloroethane obtained at a path length of 20.25 m and a temperature of 22.1 °C. The sample pressures were 5.9 Torr and 62.1 ± 0.2 Torr, respectively.

Previous[48] calculations carried out at CASSCF/6-31G(d) predicted the forbidden $S_1(^1A_{1g}) \leftarrow S_0(^1A_1)$ transition to occur at 17200 cm^{-1}. This transition requires skeletal change from ground-state D_{2d} symmetry to excited-state D_{8h} symmetry. Forbidden electronic transitions are likely to have an oscillator strength much stronger than the (forbidden) $\Delta\upsilon_{CH} = 7$ transition. The assignment of the transition observed at $\Delta\upsilon_{CH} = 7$ as a vibrational overtone transition is verified by the excellent fit of these data point in a Birge−Sponer plot (vide infra). No electronic transitions were observed during our experiments over the energy range studied ($\Delta\upsilon_{CH} = 2-7$, 5600 to 18 700 cm^{-1}). This fact, coupled with the large uncertainty in the $S_1(^1A_{1g}) \leftarrow S_0(^1A_1)$ transition energy, indicates that the lowest-lying excited electronic state most probably lies higher in energy than our experiments had accessed.

This study of COT can be viewed as an investigation of the photochemical relevance of CH stretching vibrational overtones in COT. The presence of simple overtone spectra indicates that we are not promoting reactions in COT as the reaction products should have nonequivalent CH oscillators and would give rise to more complex spectra. Since the $\Delta\upsilon_{CH} = 2-7$ overtone states are photochemically unreactive (vide infra), a lower energy limit to photochemical reactivity in COT is approximately 18700 cm^{-1}.

Structurally there is fast interconversion between the four D_{2d} stable conformations of COT mediated by the ring inversion and bond shifting processes.[49] All eight CH oscillators are identical. Therefore in the absence of coupling, the vibrational overtone spectra of (ground state, D_{2d} symmetry) COT are expected to be simple, with only one Lorentzian profile at each overtone.

The $\Delta\upsilon_{CH} = 2$ spectrum of COT is shown in Figure 1. There are several normal mode-local mode combination bands in this region which make the spectrum appear complex.

At $\Delta\upsilon_{CH} = 3$ the spectrum of COT, presented in Figure 2, appears much simpler. The high energy shoulder at 8650 cm^{-1} indicates a Fermi resonance between the states $|3, 0, 0\rangle$ and $|2, 0, 0\rangle|n\upsilon_b\rangle$ (where n is the number of quanta in a bending mode υ_b).

In Figure 3 we note that the high energy shoulder which had indicated a Fermi resonance at $\Delta\upsilon_{CH} = 3$ has disappeared at $\Delta\upsilon_{CH} = 4$, and a low energy shoulder has appeared. Normally Fermi resonances are "tuned" in to and out of resonance[50,51] more slowly, requiring several contiguous overtone spectral

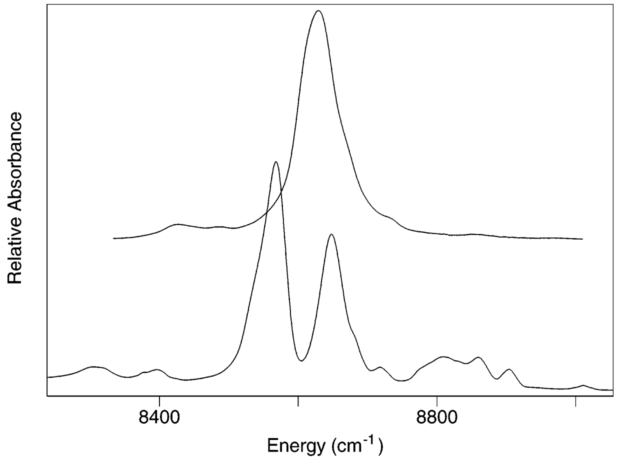

Figure 2. $\Delta v_{\mathrm{CH}} = 3$ region of the Cary/5e vapor phase spectrum of 1,3,5,7-cyclooctatetraene (top) and 1,1,1-trichloroethane obtained at a path length of 20.25 m. The sample pressures were 5.9 Torr at a temperature of 23.0 °C and 62.1 ± 0.2 Torr at a temperature of 22.1 °C, respectively.

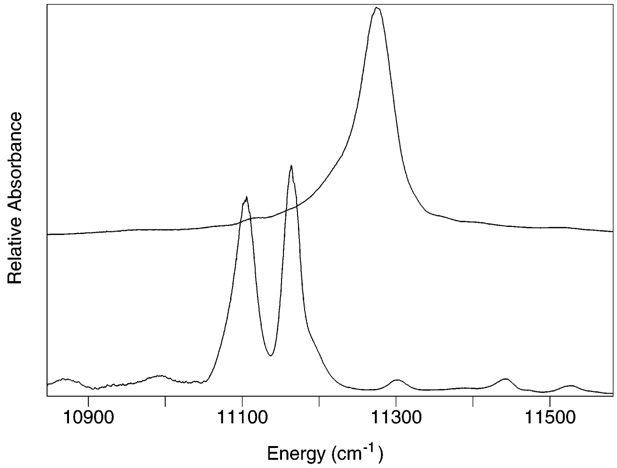

Figure 3. The ICL-PAS (Ti:sapph (mw)) $\Delta v_{\mathrm{CH}} = 4$ region of the vapor phase overtone spectrum of 1,3,5,7-cyclooctatetraene (top) and 1,1,1-trichloroethane. The COT spectrum was obtained with an ICL-PAS cell containing approximately 200 Torr of dried Ar buffer gas and sample present at its vapor pressure at 23.7 °C. The 1,1,1-trichloroethane spectrum was obtained at a pressure of 91.2 ± 0.2 Torr at room temperature.

regions to disappear entirely. Intense resonance bands and rapid oscillations in to and out of resonance at successive overtones in COT indicate that there are several different near resonant states $|v - 1, 0, 0\rangle|nv_b\rangle$ with which the pure local mode states $|v, 0, 0\rangle$ couple strongly.

At $\Delta v_{\mathrm{CH}} = 5$ we observe a strong Fermi resonance in Figure 4. This resonance disappears abruptly in Figure 5 at $\Delta v_{\mathrm{CH}} = 6$ and does not reappear in Figure 6 at $\Delta v_{\mathrm{CH}} = 7$. There is a slight asymmetry to the observed profile at $\Delta v_{\mathrm{CH}} = 7$. A two Lorentzian deconvolution better approximates the true band center, and as such the pure local mode position is taken to be that at 18460 cm^{-1}.

A summary of the pure local mode overtone peak positions and fwhm values are given in Table 2. Italicized values indicate the combination state $|v - 1, 0, 0\rangle + |nv_b\rangle$. The regression is seen to be excellent in Table 3 and Figure 7. The local mode parameters $\tilde{\omega}$ and $\tilde{\omega}x$ obtained via quadratic fits and Birge–Sponer regressions are identical.

1,1,1-Trichloroethane. In its equilibrium geometry there is a unique CH oscillator in 1,1,1-trichloroethane. In Table 4 we note that the ab initio geometries indicate that the hydrogen and chlorine atoms are in close proximity to one another, such that their van der Waals spheres (120 pm and 180 pm, respectively[52]) are in contact. In light of what we have observed in other molecules[21,22] we expect through-space interactions will be strong in 1,1,1-trichloroethane.

The equivalence of the three CH oscillators leads us to expect one Lorentzian profile at each vibrational overtone, especially at the higher overtones (i.e., $\Delta v_{\mathrm{CH}} = 4-7$). Instead, we observe rich structure which is indicative of resonances.

Figure 1 reveals combination states at $\Delta v_{\mathrm{CH}} = 2$. At $\Delta v_{\mathrm{CH}} = 3$ the spectrum appears simpler, with two primary transition peaks appearing in Figure 2. This situation remains largely unchanged in Figure 3 at $\Delta v_{\mathrm{CH}} = 4$, Figure 4 at $\Delta v_{\mathrm{CH}} = 5$, and Figure 5 at $\Delta v_{\mathrm{CH}} = 6$. At $\Delta v_{\mathrm{CH}} = 7$ the spectrum in Figure 6 was deconvoluted as a single extremely broad (380 cm^{-1}) peak, despite the fact that there appear to be two overlapping peaks. These overlapping peaks are too complex for successful deconvolution. There is an increase in fwhm values in going

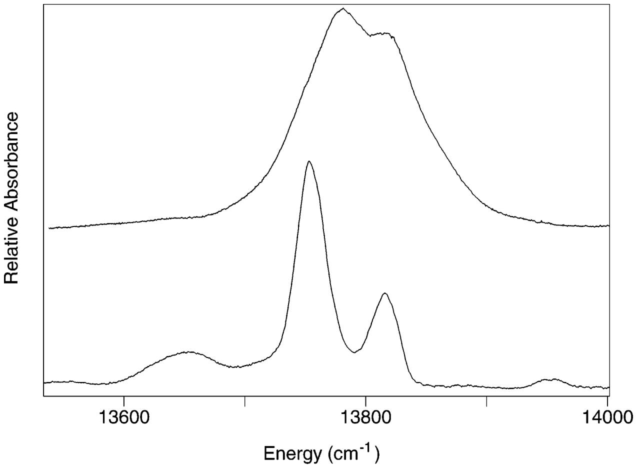

Figure 4. The ICL-PAS (Ti:sapph (sw)) $\Delta v_{\mathrm{CH}} = 5$ region of the vapor phase overtone spectrum of 1,3,5,7-cyclooctatetraene(top) and 1,1,1-trichloroethane. The COT spectrum was obtained with an ICL-PAS cell containing approximately 200 Torr of dried Ar buffer gas and sample present at its vapor pressure at 24.7 °C. The 1,1,1-trichloroethane spectrum was obtained at a pressure of 84.4 ± 0.4 Torr at room temperature.

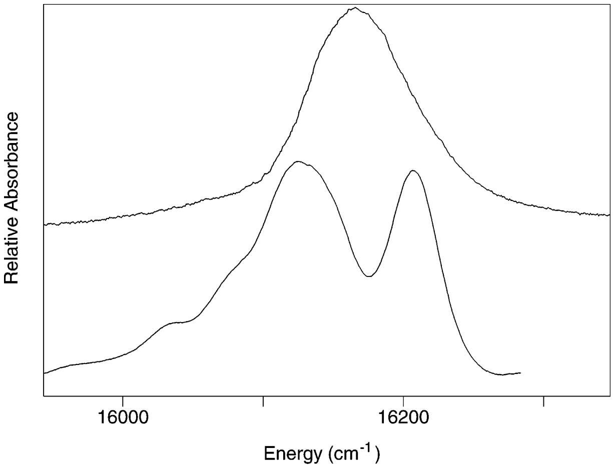

Figure 5. The ICL-PAS (DCM dye) $\Delta v_{\mathrm{CH}} = 6$ region of the vapor phase overtone spectrum of 1,3,5,7-cyclooctatetraene (top) and 1,1,1-trichloroethane. The COT spectrum was obtained with an ICL-PAS cell containing approximately 200 Torr of dried Ar buffer gas and sample present at its vapor pressure at 24.5 °C. The 1,1,1-trichloroethane spectrum was obtained at a pressure of 93.1 ± 0.3 Torr at room temperature.

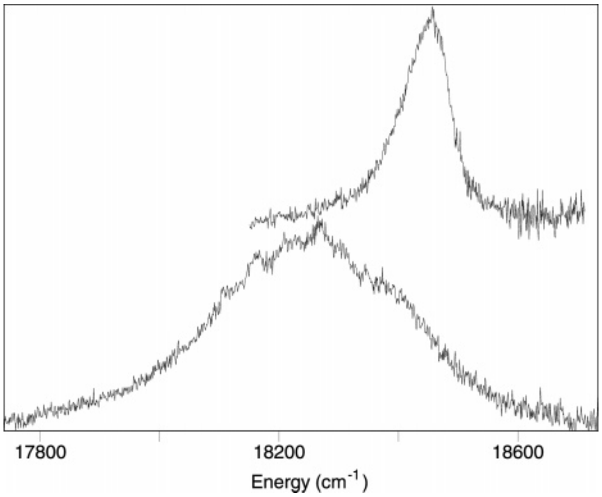

Figure 6. The ICL-PAS (C6 dye) $\Delta\upsilon_{\rm CH} = 7$ region of the vapor phase overtone spectrum of 1,3,5,7-cyclooctatetraene (top) and 1,1,1-trichloroethane. Both spectra were obtained with an ICL-PAS cell containing approximately 200 Torr of dried Ar buffer gas. COT was present at its vapor pressure at 25.3 °C, and the sloping baseline was leveled with a polynomial function. 1,1,1-trichloroethane was present at its vapor pressure at 25.0 °C.

TABLE 2: Pure Local Mode Transition Peak Properties of Vapor Phase 1,3,5,7-Cyclooctatetraene As Observed via ICL-PAS ($\Delta\upsilon_{\rm CH} = 4-7$) and Conventional Absorption Spectroscopy ($\Delta\upsilon_{\rm CH} = 2, 3$)

$\Delta\upsilon_{\rm CH}$	spectrometer	pressure (Torr)	energy (cm^{-1})[a]	fwhm (cm^{-1})[a,b]
2	Cary 5e	5.9 ± 0.1	5878	38
3	Cary 5e	5.9 ± 0.1	8623, *8650*	53, *65*
4	Ti:sapph (mw)	≈206[c]	*11224*, 11276	*99*, 46
5	Ti:sapph (sw)	≈206[c]	*13774*, 13824	*75*, 71
6	DCM dye	≈206[c]	16168	87
7	Coumarin 6 dye	≈206[c]	18462	53

[a] Italicized values are for $|\upsilon - 1, 0, 0\rangle + |n\upsilon_{\rm b}\rangle$. [b] Full width at half-maximum. [c] ICL-PAS cell contained approximately 200 Torr of dried Ar buffer gas and sample present at its vapor pressure of 5.9 Torr.

TABLE 3: Experimental[a] Local Mode Parameters and Their Standard Deviations (in cm^{-1}) As Obtained from Birge−Sponer Plots and Quadratic Fits

	Birge−Sponer		quadratic	
molecule	$\tilde{\omega}$	$\tilde{\omega}x$	$\tilde{\omega}$	$\tilde{\omega}x$
1,3,5,7-cyclooctatetraene	3121 ± 2	60.7 ± 0.4	3121 ± 3	60.7 ± 0.6
1,1,1-trichloroethane	3102 ± 7	58.4 ± 1.4	3106 ± 4	59.0 ± 1.8

[a] Calculated from experimental data in the energy regime $\Delta\upsilon_{\rm CH} = 3-7$ for COT and at $\Delta\upsilon_{\rm CH} = 3, 5, 6$ for 1,1,1-trichloroethane.

from $\Delta\upsilon_{\rm CH} = 5$ to $\Delta\upsilon_{\rm CH} = 6$ and again in going from $\Delta\upsilon_{\rm CH} = 6$ to $\Delta\upsilon_{\rm CH} = 7$, indicating that higher vibrational overtone states are shorter lived than lower overtone states. The vibrational amplitude of the CH oscillators increases with increasing vibrational excitation, making CH···Cl interactions through space increasingly more important.[21,44] A summary of peak centers and fwhm values are presented in Table 5.

In his recent study of HCN, Sage[53] has cautioned that vibrational overtones may give contaminated potential energy surfaces. This is the case with 1,1,1-trichloroethane. The presence of two pronounced peaks at $\Delta\upsilon_{\rm CH} = 4-7$ appears, at first glance, to be indicative of a simple two-tier Fermi resonance from which the CH potential energy surface can be deduced. Further analysis reveals instead that we are likely observing numerous, complicated resonances at $\Delta\upsilon_{\rm CH} = 4-7$ which obfuscate the true potential surface.

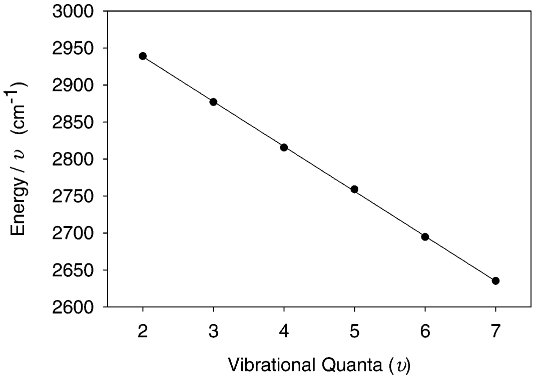

Figure 7. Birge−Sponer plot of the vibrational overtone transitions in 1,3,5,7-cyclooctatetraene in the range $\Delta\upsilon_{\rm CH} = 2-7$. Regression results for the local mode parameters are $\tilde{\omega} = 3121 \pm 2$ cm^{-1} and $\tilde{\omega}x = 60.7 \pm 0.4$ cm^{-1}.

TABLE 4: Ab Initio Calculated Bond Lengths and through Space Nuclear Separations in 1,1,1-Trichloroethane, C_{3v} Symmetry

	bond length (Å)			
theory/basis set	CCl	CC	CH	$\delta_{\rm ClH}$ (Å)[a,b]
HF/6-31G	1.839	1.509	1.080	2.929
HF/6-31G(d,p)	1.778	1.520	1.082	2.882
HF/6-31++G(d,p)	1.778	1.521	1.082	2.883
HF/6-311G(d,p)	1.780	1.517	1.082	2.881
HF/6-311+G(d,p)	1.780	1.518	1.082	2.882
HF/6-311++G(d,p)	1.780	1.518	1.082	2.882
HF/6-311++G(2d,2p)	1.780	1.513	1.080	2.881
B3LYP/6-31G(d,p)	1.806	1.520	1.092	2.907
B3LYP/6-311++G(d,p)	1.805	1.516	1.090	2.905
B3LYP/6-311++G(2d,2p)	1.804	1.512	1.088	2.903
B3LYP/cc-pVDZ	1.809	1.518	1.099	2.913
B3LYP/cc-pVTZ	1.800	1.512	1.088	2.900
B3LYP/cc-pVQZ	1.797	1.513	1.087	2.898

[a] Distance (through space) between the nuclear centers of the chlorine atom and the proximal hydrogen atom. [b] The van der Waals radii for hydrogen and chlorine are 120 pm and 180 pm, respectively (from ref 52).

TABLE 5: Pure Local Mode Transition Peak Properties of Vapor Phase 1,1,1-Trichloroethane As Observed via ICL-PAS ($\Delta\upsilon_{\rm CH} = 4-7$) and Conventional Absorption Spectroscopy ($\Delta\upsilon_{\rm CH} = 3$)

$\Delta\upsilon_{\rm CH}$	spectrometer/laser	gas pressure (Torr)	energy (cm^{-1}) [a]	fwhm (cm^{-1}) [a,b]
3	Cary 5e	62.1 ± 0.2	8567, *8648*	29, *33*
4	Ti:sapph (mw)	91.2 ± 0.2	11103, *11165*	30, *22*
5	Ti:sapph (sw)	84.4 ± 0.4	13754, *13816*	28, *24*
6	DCM dye	93.1 ± 0.3	16127, *16209*	77, *33*
7	Coumarin 6 dye	≃100	18250	381[c]

[a] Italicized values are for $|\upsilon - 1,0,0\rangle + |n\upsilon_{\rm b}\rangle$. [b] The full width at half-maximum of the dominant peaks from the deconvolution. [c] Likely consists of multiple peaks, see text.

In the case of a simple, two-tier Fermi resonance we expect the pure local mode state $|\upsilon, 0, 0\rangle$ to tune in to and out of resonance[50,51] with the normal mode-local mode combination state $|\upsilon - 1, 0, 0\rangle + |n\upsilon_{\rm b}\rangle$ as we proceed through the progression of overtone states from $\Delta\upsilon_{\rm CH} = 4$ to $\Delta\upsilon_{\rm CH} = 7$. This trend arises from the anharmonicity of the CH local mode oscillator which results in a smaller spacing between successive pure local mode states than between successive resonant combination states. In proceeding from $\Delta\upsilon_{\rm CH} = 4$ through $\Delta\upsilon_{\rm CH} = 7$ we expect to observe an overtone at which resonance is strongest, corresponding to the smallest energy mismatch between local mode and combination states. As the energy mismatch between

TABLE 6: Comparison of Tentative Experimental[a] and Calculated[b] Pure Local Mode Transition Frequencies of Vapor Phase 1,1,1-Trichloroethane

	energy (cm^{-1})	
$\Delta\upsilon_{CH}$	experimental	calculated
3	8603	8614 ± 17
4	11132	11252 ± 22
5	13770	13772 ± 27
6	16150	16174 ± 33
7	18250	18460 ± 38

[a] Pure local mode transition frequencies estimated using data from Table 5 and eq 5. [b] Transition frequencies calculated from scaled ab initio local mode parameters $\tilde{\omega}(60°) = 3106 \pm 5$ cm^{-1}, $\tilde{\omega}x(60°) = 58.6 \pm 1.0$ cm^{-1}, and eq 2.

the states becomes smaller, the separation between the pure local mode and the combination transitions decreases.[50,51]

The decrease in the separation between the pure local mode and combination transitions is one spectral manifestation of "tuning into" resonance. Another is that the intensity of the transition to the higher energy $|\upsilon - 1, 0, 0\rangle + |n\upsilon_b\rangle$ state (which does not have any intrinsic intensity) increases because this combination state is able to steal intensity from the pure local mode state with increasing efficiency.[50,51]

Neither of the two above-mentioned Fermi resonance characteristics were observed in the overtone spectral regions of 1,1,1-trichloroethane. First, the intensities of the combination states are always high and do not change in an orderly manner in proceeding from $\Delta\upsilon_{CH} = 4$ through $\Delta\upsilon_{CH} = 7$. Second, the spacing between the pure local mode and combination states does not lessen, rather, it is nearly invariant. Finally, in the $\Delta\upsilon_{CH} = 5$ spectral region there are three (not two) pronounced peaks. We are likely observing resonances between the state $|\upsilon, 0, 0\rangle$ and one (or more) states $|\upsilon - 1, 0, 0\rangle + |n\upsilon_b\rangle$ where the identity of $|\upsilon_b\rangle$ changes from overtone to overtone.

In the case of a simple, two-tier Fermi resonance (where the state $|\upsilon_b\rangle$ is identical at successive overtones) it is straightforward to assign the transitions to the states $|\upsilon, 0, 0\rangle$ and $|\upsilon - 1, 0, 0\rangle + |n\upsilon_b\rangle$. Once the transitions are assigned, eq 5 is used to obtain the *true* vibrational overtone transition frequencies from the (resonance) contaminated vibrational overtones. It is therefore possible to obtain the *true* CH stretching potential energy surface from the *effective* stretching potential.

In the case of 1,1,1-trichloroethane the *effective* local mode potential energy surface is contaminated by numerous, complex Fermi resonances. Without any corroborating information (such as from ab initio calculations, vide infra) it is not possible to assign the transitions to the states $|\upsilon, 0, 0\rangle$ and $|\upsilon - 1, 0, 0\rangle + |n\upsilon_b\rangle$.

Tentative spectral assignments were made for the states $|\upsilon, 0, 0\rangle$ and $|\upsilon - 1, 0, 0\rangle + |n\upsilon_b\rangle$. The energies of transitions to these states were used along with eq 5 to arrive at energies of transitions to the "isolated" states $|\upsilon, 0, 0\rangle$, which are presented in Table 6. These energies of transition to "isolated" states were used to make the Birge−Sponer plot in Figure 8. The Birge−Sponer plot was insufficient to resolve which (if any) of the overtone spectra reflect the true molecular CH stretching potential energy surface.

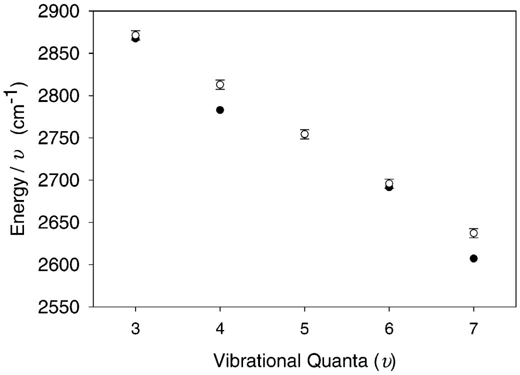

Figure 8. Tentative experimental (solid) and ab initio (hollow) Birge−Sponer data points of the CH vibrational overtone transitions in 1,1,1-trichloroethane in the range $\Delta\upsilon_{CH} = 3-7$. Experimental and ab initio data points overlap at $\Delta\upsilon_{CH} = 3, 5, 6$.

We obtain an a priori knowledge of the approximate values of the local mode parameters in 1,1,1-trichloroethane by first calculating their unscaled values ab initio. These values are obtained from a fit of an ab initio PES (as a function of CH displacement q), in the range $q \in [-0.20, 0.20]$ Å in steps of 0.05 Å, to eq 2. Calculations were carried out at HF/6-311+G(d,p). The ab initio local mode parameters are then scaled by applying published[44,22] averaged local mode scaling factors for sterically hindered CH oscillators. In the case of the staggered conformer of 1,1,1-trichloroethane this leads to *scaled* ab initio values of $\tilde{\omega}(60°) = 3106 \pm 5$ cm^{-1} and $\tilde{\omega}x(60°) = 58.6 \pm 1.0$ cm^{-1}. The notation (60°) denotes that the calculated values are for the staggered conformer where the H−C−C−Cl dihedral angle ϕ is 60°. These predicted values are used along with eq 2 to estimate the overtone transition frequencies, which are presented in Table 6.

Ab initio predicted overtone transition frequencies are added to the Birge−Sponer plot in Figure 8 to determine which states $|\upsilon, 0, 0\rangle$ and $|\upsilon - 1, 0, 0\rangle + |n\upsilon_b\rangle$ were correctly assigned in the tentative assignment (vide supra). The experimental Birge−Sponer data points $\Delta\upsilon_{CH} = 3, 5, 6$ were found to agree with ab initio predicted values. In fact, the point at $\Delta\upsilon_{CH} = 5$ overlaps exactly. These data points are believed to represent the true CH potential energy surface. Local mode parameters were calculated for 1,1,1-trichloroethane from the $\Delta\upsilon_{CH} = 3, 5, 6$ experimental data points and are presented in Table 3. The values of $\tilde{\omega}$ and $\tilde{\omega}x$ obtained via Birge−Sponer plots and via quadratic fit to eq 2 are identical to within experimental error. Refinement of the tentative experimental assignments was not possible owing to the participation of several near-resonant states. Owing to the success of this approach it is recommended that ab initio local mode parameters be used routinely to verify that experimental local mode transition frequencies correspond to true (and not effective) potentials.

Typical $\tilde{\omega}$ values in hindered CH oscillators range from 3049 ± 3 cm^{-1} (in neopentane) to 3085 ± 7 cm^{-1} (in *tert*-butyl chloride).[22] Based upon ab initio calculated geometries and van der Waals atomic radii, the steric crowdings of CH oscillators in 1,1,1-trichloroethane are comparable to those in *tert*- butyl chloride and greater than those in neopentane. The $\tilde{\omega}$ value for 1,1,1-trichloroethane obtained via quadratic fit is 3106 ± 4 cm^{-1} while that obtained via a Birge−Sponer fit is 3102 ± 7 cm^{-1}. The very high local mode frequency is ascribed to both through-space interactions (which make the CH stretching potential more harmonic) and to the effect of halogen substitution[23] in which the local mode frequency $\tilde{\omega}$ increases with increasing electronegativity in the substituents.[24] Despite the fact that 1,1,1-trichloroethane and *tert*-butyl chloride have similar steric crowding of their CH oscillators, the much higher $\tilde{\omega}$ value in 1,1,1-trichloroethane indicates that the presence of three halogen atoms in that molecule has a cumulative effect on the local mode frequency.

Coupling Between Stretching and Torsional Motions. The scaled local mode parameters $\tilde{\omega}(0°)$ and $\tilde{\omega}x(0°)$ were calculated

TABLE 7: HCAO Calculated[a] CH Vibrational Overtone Intensities in COT and 1,1,1-Trichloroethane

COT			1,1,1-trichloroethane		
state	$\tilde{\nu}_{v\leftarrow 0}$ (cm^{-1})[b]	f_{osc}	state	$\tilde{\nu}_{v\leftarrow 0}$ (cm^{-1})[b]	f_{osc}
$\|3\rangle$	8633	6.6×10^{-8}[c]	$\|3, 0, 0\rangle_{A_1}$	8567	4.6×10^{-9}[d]
			$\|3, 0, 0\rangle_{E}$	8584	7.2×10^{-9}[d]
$\|4\rangle$	11268	1.1×10^{-8}	$\|4, 0, 0\rangle_{A_1}$	11215	3.9×10^{-10}
			$\|4, 0, 0\rangle_{E}$	11217	7.7×10^{-10}
$\|5\rangle$	13782	2.3×10^{-9}	$\|5, 0, 0\rangle_{A_1}$	13734	2.6×10^{-11}
			$\|5, 0, 0\rangle_{E}$	13735	8.9×10^{-11}
$\|6\rangle$	16174	4.2×10^{-10}	$\|6, 0, 0\rangle_{A_1E}$	16133	1.3×10^{-11}
$\|7\rangle$	18445	7.9×10^{-11}	$\|7, 0, 0\rangle_{A_1E}$	18414	1.8×10^{-12}
$\|8\rangle$	20595	1.6×10^{-11}	$\|8, 0, 0\rangle_{A_1E}$	20575	2.9×10^{-13}
$\|9\rangle$	22623	3.7×10^{-12}	$\|9, 0, 0\rangle_{A_1E}$	22619	5.5×10^{-14}

[a] Calculated with a DMF at HF/6-311++G(2d,2p) and Morse wave functions from $\tilde{\omega}$ and $\tilde{\omega}x$ values in Table 3. [b] Calculated with the HCAO model. [c] Experimental oscillator strength at $\Delta\upsilon_{CH} = 3$ is 8.7×10^{-8}. [d] Total experimental oscillator strength of states $|3, 0, 0\rangle_{A1}$ and $|3, 0, 0\rangle_{E}$ is 2.0×10^{-8}. The individual states could not be resolved experimentally.

for the eclipsed conformer of 1,1,1-trichloroethane (where $\phi = 0°$) in a manner identical to that used for the staggered conformer (vide supra). The local mode-torsion coupling terms, $\delta_{\tilde{\omega}}$ and $\delta_{\tilde{\omega}x}$, were obtained from the scaled ab initio local mode parameters $\tilde{\omega}(60°)$, $\tilde{\omega}(0°)$, $\tilde{\omega}x(60°)$, and $\tilde{\omega}x(0°)$ in a manner identical to that used by Low and Kjaergaard.[54] The modulation of $\tilde{\omega}$ and $\tilde{\omega}x$ with internal rotation about the methyl dihedral angle coordinate ϕ has a 3-fold barrier in 1,1,1-trichloroethane. The dependence of $\tilde{\omega}$ and $\tilde{\omega}x$ on ϕ is approximated as a cosine squared function.[21] Calculations were carried out at HF/6-311+G(d,p) and HF/LanL2DZ in the range $q \in [-0.20, 0.20]$ Å in steps of 0.05 Å. Local mode-torsion coupling terms are $\delta_{\tilde{\omega}} = 15.4$ cm^{-1} and $\delta_{\tilde{\omega}x} = 0.215$ cm^{-1} at HF/6-311+G(d,p), while at HF/LanL2DZ we obtained $\delta_{\tilde{\omega}} = 13.8$ cm^{-1} and $\delta_{\tilde{\omega}x} = 0.550$ cm^{-1}. As 1,1,1-trichloroethane rotates from the (equilibrium) staggered conformer to the more sterically hindered eclipsed conformer, the $\delta_{\tilde{\omega}}$ term leads to an increase in the local mode frequency and the $\delta_{\tilde{\omega}x}$ term leads to an increase in the local mode anharmonicity. The dominant effect on the energy eigenvalues in eq 1 is through the $\delta_{\tilde{\omega}}$ term, leading to a blue-shifting of the CH oscillators with increasing steric hindrance.

HCAO Intensities. Dipole moment values were calculated in the range $q \in [-0.30, 0.30]$ Å, with a step size of 0.05 Å. The HF wave functions are stable provided that $|q| \leq 0.50$ Å.[44]

The experimental and HCAO calculated intensities for vibrational overtone transitions in COT are given in Table 7. The HCAO intensities were calculated from eq 7 using Morse wave functions[6] obtained from the experimental local mode parameters presented in Table 3, $\tilde{\omega} = 3121$ cm^{-1} and $\tilde{\omega}x = 60.7$ cm^{-1}, and a fourth order polynomial approximation to the dipole moment function calculated from ab initio data points at HF/6-311++G(2d,2p).

HCAO calculated intensity for COT underestimates the experimental data point at $\Delta\upsilon_{CH} = 3$ by 25% at the HF/6-311++G(2d,2p) level. HCAO calculated intensity for COT carried out at the B3LYP level of theory using the 6-311++G-(2d,2p) and cc-pVTZ basis sets were found to overestimate the experimental data point at $\Delta\upsilon_{CH} = 3$ by almost 300%. B3LYP calculated DMFs were found to lead to poor HCAO overtone intensities for both COT and 1,1,1-trichloroethane.

The infrared spectrum of 1,1,1-trichloroethane shows the symmetric (ν_1) and asymmetric (ν_7) fundamentals occur at 2938 and 3003 cm^{-1}, respectively.[55,56] Taking the coupling constant γ' to be twice the splitting between the symmetric and asymmetric CH stretching states we arrive at $\gamma' = 32.5$ cm^{-1}.

The experimental and HCAO calculated intensities for vibrational overtone transitions in 1,1,1-trichloroethane are given in Table 7. The HCAO intensities were calculated from eq 7 using Morse wave functions[6] obtained from the (Birge−Sponer) local mode parameters $\tilde{\omega} = 3102$ cm^{-1} and $\tilde{\omega}x = 58.4$ cm^{-1} and a fourth order polynomial approximation to the dipole moment function calculated from ab initio data points at HF/6-311++G(2d,2p).

The $|3, 0, 0\rangle_{A1}$ and $|3, 0, 0\rangle_{E}$ states of 1,1,1-trichloroethane could not be resolved experimentally. The total HCAO calculated intensity for these states underestimates the experimental $\Delta\upsilon_{CH} = 3$ data point by 42% at the HF/6-311++G(2d,2p) level. The local mode states of A_1 and E symmetry of 1,1,1-trichloroethane are effectively degenerate above $\Delta\upsilon_{CH} = 5$. These two nearly degenerate states are collectively expressed as $|\upsilon, 0, 0\rangle_{A_1E}$.

Conclusion

The first CH stretching vibrational overtone spectrum of an antiaromatic system (COT) was presented in the $\Delta\upsilon_{CH} = 2-7$ regions. The spectrum of COT was complicated by numerous Fermi resonances between pure local mode states and local mode/normal mode combination states. No electronic transitions were detected in the range $\Delta\upsilon_{CH} = 2-7$, or 5600 to 18 700 cm^{-1}, setting an experimentally determined low energy limit of approximately 18700 cm^{-1} below which COT is photochemically unreactive.

An analysis of the vibrational overtone spectrum enabled the experimental determination of the local mode parameters of COT, which were found to be $\tilde{\omega} = 3121 \pm 2$ cm^{-1} and $\tilde{\omega}x = 60.7 \pm 0.4$ cm^{-1}. These parameters were used along with the HCAO model and a DMF calculated at HF/6-311++G(d,p) to obtain calculated vibrational overtone transition intensities in the range $\Delta\upsilon_{CH} = 3-9$. The application of uncorrelated calculations to this antiaromatic system seem justified based upon the agreement between the HCAO intensity (calculated using HF theory) and experimental results. Intensity calculations carried out with a B3LYP quality DMF gave very poor agreement with experiment.

The molecule 1,1,1-trichloroethane has sterically hindered CH oscillators. Its CH stretching vibrational overtone spectrum shows evidence of through-space interactions between CH oscillators and the proximal Cl atoms to which the oscillator was not bound. Specifically, the fwhm values of the overtone transitions increase markedly with increasing vibrational excitation in going from $\Delta\upsilon_{CH} = 5$ to $\Delta\upsilon_{CH} = 6$ and again in going from $\Delta\upsilon_{CH} = 6$ to $\Delta\upsilon_{CH} = 7$. This indicates that higher vibrational overtone states are shorter lived than lower overtone states. The vibrational amplitude of the CH oscillators increase with increasing vibrational excitation, making CH···Cl interactions through space increasingly more pronounced. Further indications of through-space interactions were found in the blue-shifting of the vibrational overtone transition frequencies.

The vibrational overtone spectrum of 1,1,1-trichloroethane in the energy regime $\Delta\upsilon_{CH} = 2-7$ was complicated by resonances. Individual spectral regions were obfuscated by a dense bath of near resonant states, resulting in numerous complex Fermi resonances between pure local mode states and local mode/normal mode combination states. Ab initio calculations and general scaling factors were used to distinguish between pure local mode transitions in 1,1,1-trichloroethane and resonances. This approach allowed us to distinguish between those local mode transition frequencies which correspond to the true stretching potential and those which correspond to an effective potential.

The experimental local mode parameters of 1,1,1-trichloroethane were determined to be $\tilde{\omega} = 3102 \pm 7$ cm^{-1} and $\tilde{\omega}x = 58.4 \pm 1.4$ cm^{-1}. The local mode frequency was much higher than that in a similarly crowded molecule, *tert*-butyl chloride. The presence of multiple chlorine atoms in 1,1,1-trichloroethane (as compared to *tert*-butyl chloride) was determined to have a cumulative effect on the local mode frequency.

The interoscillator coupling term was calculated to be $\gamma' = 32.5$ cm^{-1}. This value was used along with the local mode parameters and the HCAO model and a DMF calculated at HF/6-311++G(d,p) to obtain calculated vibrational overtone transition intensities in the range $\Delta v_{\mathrm{CH}} = 3-9$.

Local mode-torsion coupling terms were calculated for 1,1,1-trichloroethane. As the methyl group rotates from the (equilibrium) staggered conformer to the more sterically hindered eclipsed conformer, the $\delta_{\tilde{\omega}}$ term leads to an increase in the local mode frequency and the $\delta_{\tilde{\omega}x}$ term leads to an increase in the local mode anharmonicity. The dominant effect is through the $\delta_{\tilde{\omega}}$ term, leading to a blue-shifting of the CH oscillators with increasing steric hindrance.

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