Orientational dynamics and disorder of solid adamantane as studied by infrared spectroscopy

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The CH stretching and bending vibrations of isotopically dilute $C_{10}D_{15}H$ in a host crystal of perdeuterated adamantane have been monitored by infrared spectroscopy as a function of temperature from 7 to 300 K. The infrared bands depend upon both intramolecular and intermolecular interactions. The intramolecular splittings of the bands have been analyzed and compared with normal coordinate calculations. The intermolecular splittings of the CH stretches in the tetragonal phase are found to collapse and broaden with increasing temperature due to librational motion. A Redfield theory analysis of the temperature dependent line shifts and linewidths yields a correlation time of 2 ps for the adamantane libration. In the disordered plastic phase of adamantane, the intermolecular and intramolecular splittings of the CH stretches disappear and the rotational disorder yields a broad inhomogeneous band.

I. INTRODUCTION

Vibrational spectroscopy is uniquely sensitive to ultrafast nuclear motions that occur in a time scale faster than about 10 ps. In our previous work, we have shown that such motions in molecular solids can be analyzed using Redfield theory and thus that the spectra can reveal subtle structural and motional details. A given structure can be determined provided that it lasts for longer than the 10 ps. For example, we have analyzed both the relative position of the waters of hydration and the motion of these waters in solid $NaClO_4 \cdot H_2O$ and $LiI \cdot 3H_2O$.[1] Similarly, we have analyzed the rotation of the ammonium ion in NH_4ClO_4[2] and the torsional motion of methyl groups in alkane chains.[3]

In this paper, we investigate the solid-state structure and the motion of another prototypical molecule, adamantane. Adamantane is a rigid hydrocarbon $(C_{10}H_{16})$ which is nearly spherical (actually tetrahedral). It is a prototype of molecules that form plastic-crystal phases, and therefore an investigation of the rotational (orientational) correlation among adamantane molecules and of the rotational motion is particularly appropriate. Adamantane shows a rich variety of different structures and motions. First we consider the gas phase spectrum in order to assign the infrared lines, and then the solid phase spectrum to study the motional effects. The solid is examined over the temperature range from low temperature to room temperature, all at negligible pressure. A further paper[4] will consider solutions and also the room temperature solid at high pressures.

The rotational motion, the structure of the two solid phases, and the vibrational spectra have all been studied previously. Adamantane exhibits two solid phases, one orientationally ordered and one orientationally disordered.[5] Below 208 K solid adamantane exists in its ordered β phase where the crystal has a tetragonal space group symmetry, $P\bar{4}2_1c$.[6] The adamantane sits in a site of S_4 symmetry, oriented 9° off the tetragonal c crystal axis [Fig. 1(a)]. Above 208 K (in the α

phase) adamantane loses this orientational order, and the resulting crystal symmetry is cubic, space group $Fm3m$.[5] The adamantane molecules are disordered, being equally distributed between two possible orientations about the c
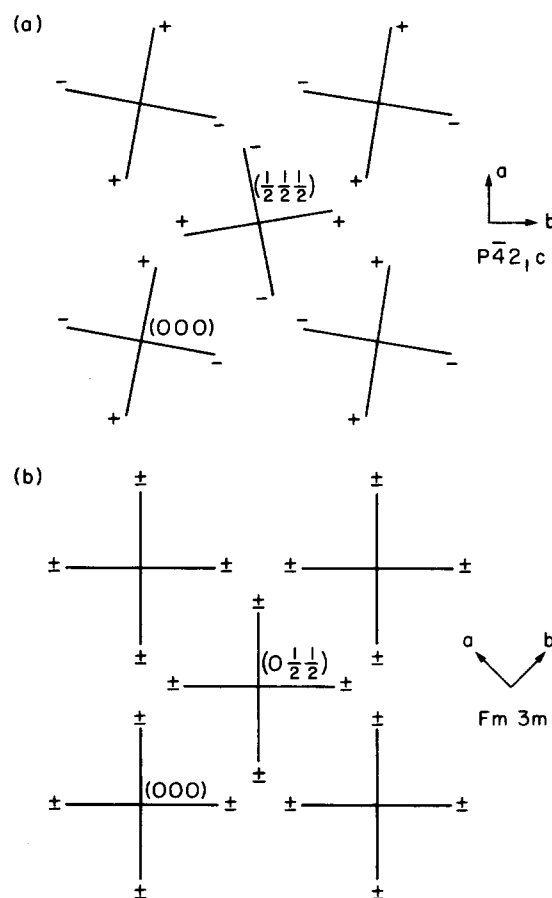

FIG. 1. Adamantane in the solid phase. The adamantane molecules are represented by tetrahedra. (a) Low temperature (β) phase, tetragonal space group $P\bar{4}2_1c$. In the diagram, we are looking down the tetragonal c axis; the adamantanes are oriented $\pm 9°$ off the b axis. (b) High temperature (α) phase, cubic space group $Fm3m$. The adamantane molecules are disordered; any particular molecule in a given site can exist in one of two possible orientations about the c axis. This figure is taken after Reynolds (Ref. 7). Note that the unit cell axes are rotated in (b) from their position in (a).

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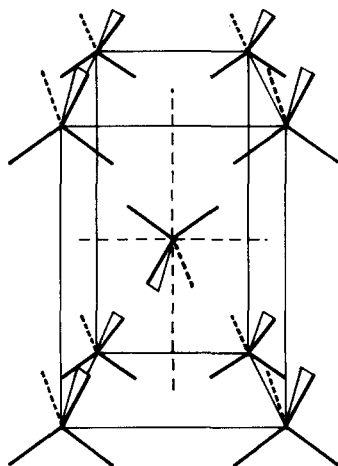
FIG. 2. A three-dimensional representation of the adamantane crystal in the β phase. The adamantane molecules are represented as tetrahedra. The tetrahedra approximately line up so that the methine CH bonds are parallel to the unit cell planes. They then rotate 9° off these positions to avoid the H–H intermolecular repulsions. The α form is qualitatively the same except that the crystal becomes cubic and the tetrahedra become disordered.

axis [see Fig. 1(b)]. A three dimensional view is found in Fig. 2. In both Figs. 1 and 2, the adamantane molecule is represented as tetrahedral. However, a space filling model of the molecule shows it to be nearly spherical. The molecules pack much like hard spheres, but we are concerned with the nonspherical interactions between the molecules, and it is this aspect of crystal structures that is emphasized in the figures.

The near spherical symmetry of adamantane allows it to rotate very quickly in both the disordered solid phase and in solution, despite its large size. NMR studies have measured rotational correlation times, at room temperature, of 20 ps for the solid[8] and 1–5 ps for solution.[9] However, despite the fast reorientation times, the rotation of adamantane is not hydrodynamic in nature; activation energies for the solid and in solution have been estimated from NMR measurements at 6.5 and 3.0 kcal/mol, respectively.[10]

The phase transition in adamantane has been previously studied by infrared[11] and Raman[12,13] spectroscopy. Hysteresis at the phase transition was observed in the infrared spectra. The infrared and Raman spectra of the lower temperature tetragonal phase show new factor-group splittings and several new bands. This same β phase has also been observed by Raman measurements above 5.3 kbar at room temperature.[13] From a careful study of the Raman bands of $C_{10}H_{16}$ as a function of both temperature and pressure, it was concluded[13] that the major part of the observed line shifts with temperature was not simply due to changes in the lattice parameters (i.e., lattice expansion), but arose from changes in the frequencies with temperature (at constant volume).

We present here the temperature dependence from 7 K to room temperature of the infrared bands of isotopically dilute $C_{10}D_{15}H$ in a host $C_{10}H_{16}$ crystal. The CH stretches and bends show a complex of bands that arise from a combination of site and intramolecular splittings. In the C–H stretching region we are able to detail the collapse of these splittings with increasing temperature in the ordered β phase. This collapse is primarily due to the motional orientational averaging of the adamantane molecule librating in its crystal site. The application of Redfield theory to the linewidths yields correlation times for librational level hopping of 1.5–2 ps. In the disordered phase, we find that the infrared bands are much broader, due to the inhomogeneous

broadening in the orientationally disordered adamantane crystal.

II. EXPERIMENTAL CONSIDERATIONS

Perdeuterated adamantane (98% D) was obtained from KOR Isotopes. The isotopic purity of the sample was checked by mass spectrometry and was found to be $98.8 \pm 0.5\%$ D. The distribution of the residual hydrogen between the methine and methylene sites was checked by measuring proton NMR intensities. The ratio of methylene protons to methine protons was determined to be three to one to within 4%, so that we can assume that the distribution

The assignments of vibrational bands of the randomly hydrogenated $C_{10}D_{15}H$ were ambiguous, and so we made and studied one specifically labeled isotope, 1-hydroperdeuteroadamantane, that is, adamantane with a hydrogen in one methine position. This compound was prepared via a two step synthesis. First, the commercially available perdeuteroadamantane (KOR Isotopes) was treated with an excess of bromine by the method of Stetter *et al.*[14] to yield 1-bromoperdeuteroadamantane. The product was purified by passing it through alumina. The Grignard reagent was then produced by adding the 1-bromoperdeuteroadamantane in anhydrous ethyl ether to clean, dry Mg turnings. The reaction vessel was placed in an ultrasonic bath to initiate the reaction. After the reaction was initiated, the vessel was then placed in an oil bath and the reaction mixture was allowed to reflux overnight. Quenching the Grignard reagent with H_2O displaced the 1-hydroperdeuteroadamantane, which was then removed from the mixture by successive extractions with CCl_4. The CCl_4 fractions were combined, washed with H_2O, dried over Na_2SO_4, and the solvent was then removed. Further purification was accomplished through sublimation. A mass spectrum showed 1-hydroperdeuteroadamantane as the only product, although a few percent of randomly substituted residual hydrogen in the original sample still remained.

Samples for the temperature dependence studies were prepared in KBr pellets. Studies in this laboratory[15] have shown that KBr pelleting may affect the kinetics of phase transitions of hydrocarbons (*n*-alkanes in particular); hence, we may expect to see an augumented hysteresis at the phase transition. To check the effects of KBr pelleting, a second experiment was run in which the adamantane was condensed onto a CsI window in the cryostat at 50 K, and the temperature dependence of the infrared spectra was subsequently examined. The initial spectra of the condensed adamantane showed considerably broadened lines; only after thorough annealing at 200 K did the spectra and their temperature dependence match those of the KBr pellet studies. We conclude that the pelleting did not cause spurious effects in the spectra.

The infrared spectra were taken on a model 8000 Nicolet Fourier transform infared spectrometer. The nominal resolution was 0.5 cm^{-1}. The temperature of the sample was held constant at 0.1 K and accurate to ± 1 K using the cryostat and controller of Ref. 1. The line shifts and linewidths for the CH stretches were obtained by fitting the spectra using the Nicolet-supplied curve analysis program.
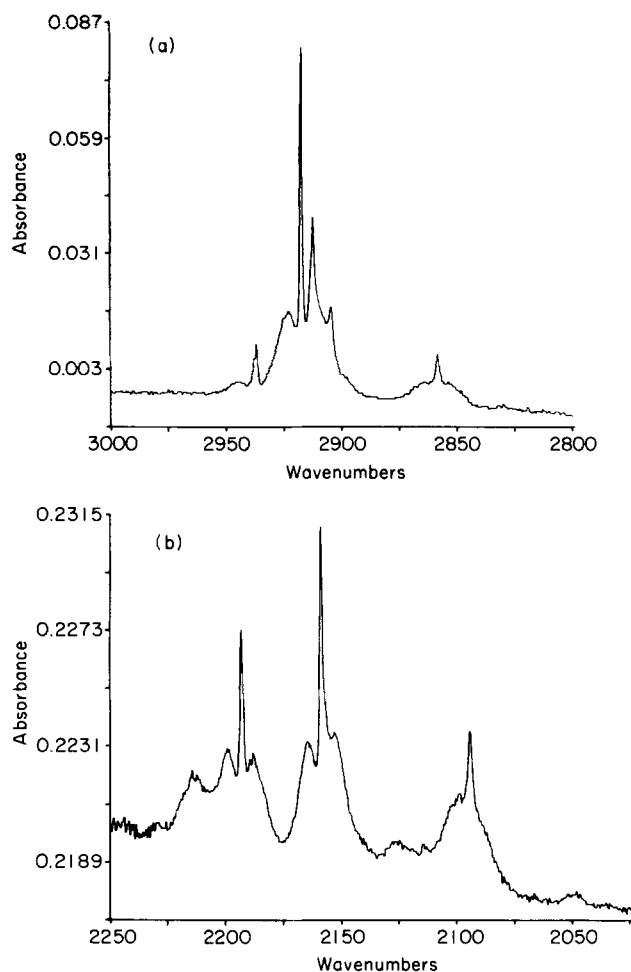
FIG. 3. Gas phase infrared spectra of (a) the CH stretching region of $C_{10}H_{16}$, and (b) the CD stretching region of $C_{10}D_{16}$. The spectra were taken at a pressure of 250 mTorr, with a pathlength of 10 cm and a nominal resolution of 0.5 cm^{-1}.
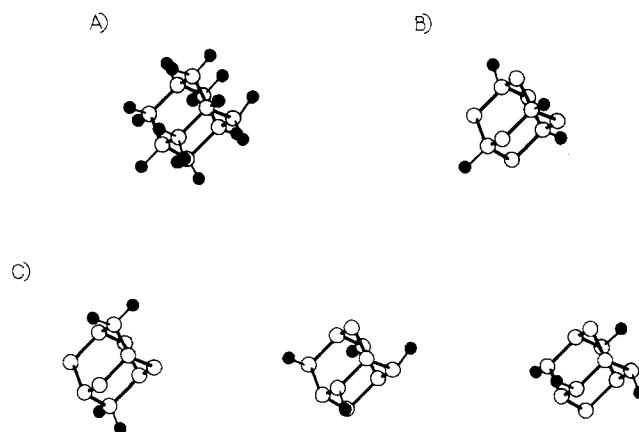

FIG. 4. The hydrogen atoms of adamantane in the solid phase. (a) Adamantane with all hydrogens depicted, (b) the four methine hydrogens of adamantane, (c) adamantane's three sets of equivalent methylene hydrogens in the low temperature (β) phase (molecular site symmetry S_4).

III. RESULTS AND DISCUSSION

A. Gas phase spectra and normal coordinate calculations

Adamantane ($C_{10}H_{16}$ or $C_{10}D_{16}$) has 72 normal modes of which 11 sets of three are of F_2 symmetry and therefore infrared active. Of these, three are CH (or CD) stretches [16,17]. Figure 3 shows the CH and CD stretching regions of $C_{10}H_{16}$ and $C_{10}D_{16}$, respectively, in the gas phase. A 10 cm cell of adamantane at 250 mTorr was used; the spectra were taken at 0.5 cm^{-1} resolution. Rotational structure is observable on the stretching fundamentals; $C_{10}H_{16}$ shows additional strong bands presumably due to Fermi resonance.[18] The analogous Fermi resonance interaction in the CD stretching region of $C_{10}D_{16}$ only became apparent when the adamantane was dissolved into CCl_4. The gas phase spectrum of the CH stretching region of the 1-$C_{10}D_{15}H$ exhibits a single band at 2904.8 cm^{-1} due to the methine hydrogen.

The adamantane molecule is depicted in Fig. 4(a). There are two types of hydrogen positions possible in the $C_{10}D_{15}H$ molecule: methine and methylene [Figs. 4(b) and (c)]. To determine the intramolecular differences in the stretching frequency, normal coordinate calculations were performed on a series of adamantanes: $C_{10}H_{16}$, $C_{10}D_{16}$, $C_{10}H_{15}D$ (two types), and $C_{10}D_{15}H$ (two types). The calculations employed the 36 parameter valence force field for saturated hydrocar-

bons developed by Snyder and Schachtschneider.[16] The calculated CH and CD stretching frequencies for the molecules are listed in Table I along with the experimental results. Astoundingly good agreement is achieved between the calculations and the measured frequencies. The normal coordinate calculations of the two types of $C_{10}D_{15}H$ state that the methine CH stretch should lie at a slightly higher frequency than the methylene CH stretch. This order is reversed in the low temperature solid phase (see below), an indication that the intermolecular interactions play an equal, if not dominant, role in defining the C–H stretching spectrum of the solid.

TABLE I. Adamantane room temperature vibrational frequencies.

Compound/vibration		ν_{calc} (cm^{-1})	ν_{obs} (cm^{-1})[a]
$C_{10}H_{16}$			
d^-	CH stretch (F_2)[b]	2931	2937 $\pm$ 0.5
s	CH stretch (F_2)	2903	2918, 2913, 2905[c]
d^+	CH stretch (F_2)	2856	2859
$C_{10}D_{16}$			
d^-	CH stretch (F_2)	2199	2194
s	CD stretch (F_2)	2150	2160
d^+	CD stretch (F_2)	2090	2095
$C_{10}H_{15}D$ (methine)			
CD stretch (A_1)		2154	2156[d]
$C_{10}H_{15}D$ (methylene)			
CD stretch		2140	2138[d]
$C_{10}D_{15}H$ (methine)			
CH stretch (A_1)		2905	2904.8[e]
CH bend (E)		1303	...
$C_{10}D_{15}H$ (methylene)			
CH stretch		2895	2893[f]
CH bend		1301, 1309	

[a] Unless otherwise stated, all observed frequencies are from the gas phase.
[b] s is methine stretch, $d^\pm$ are the symmetric and antisymmetric methylene stretches.
[c] Split by Fermi resonance.
[d] Solution spectra taken from Ref. 19.
[e] From the gas phase spectrum of specifically labeled adamantane.
[f] In solution of CCl_4. FHWM of the CH band was 25 cm^{-1}. (The gas phase spectrum of the randomly substituted adamantane was too weak to see with our small pathlength.)
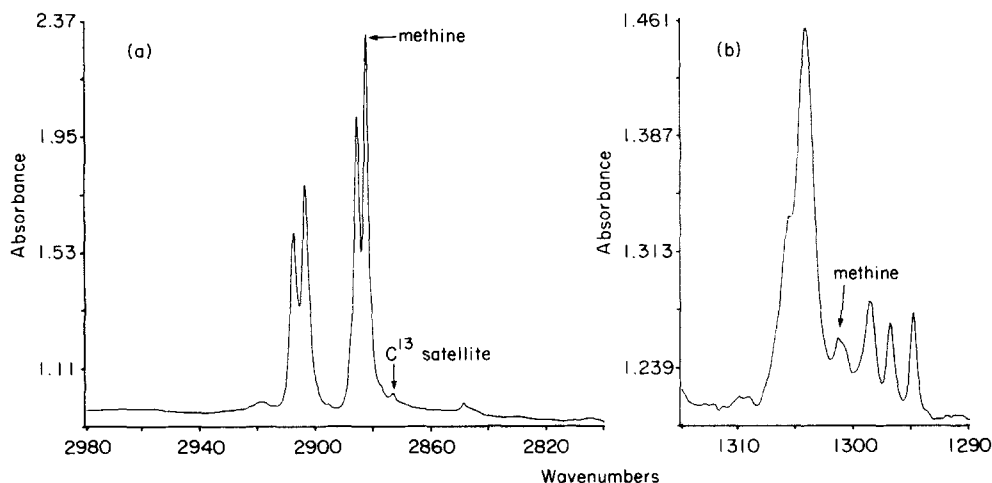
FIG. 5. Low temperature (7 K) infrared spectrum of isotopically dilute $C_{10}D_{15}H$ (in $C_{10}D_{16}$). (a) CH stretching region, (b) CH bending region. The arrows indicate the bands due to the methine C–H bond which were identified from the spectrum of the specifically labeled compound. There is what is probably a small C^{13} satellite band at about 2875 cm^{-1}.

In addition to the stretches, each of the two types of $C_{10}D_{15}H$ molecules has two identifiable CH bends whose calculated frequencies are also listed in Table I. For the molecule with a hydrogen in the methine position (molecular symmetry C_{3v}) the bends are degenerate. The calculated frequency for this doubly degenerate (E symmetry) vibration is 1303 cm^{-1}, whereas the pair of methylene bends are predicted to lie above and below this band at 1301 and 1309 cm^{-1}. No $C_{10}D_{16}$ fundamentals were calculated to be in this frequency region, so that the C–H bends will be observable in the isotopically dilute sample.

B. β phase spectra

1. Assignment

From 7 to 208 K, the adamantane exists in its low temperature tetragonal form. The 7 K spectra of the CH stretch and bend of a sample of randomly substituted $C_{10}D_{15}H$ dilute in $C_{10}D_{16}$ in a KBr pellet are shown in Fig. 5, and the frequencies are tabulated in Table II. At low temperature, the CH stretching band splits into a well defined quartet. This quartet is due to the separation of the 16 CH bonds of adamantane in its S_4 site into four sets of four. One set of equivalent CH bonds corresponds to the set of four methine hydrogens [Fig. 4(b)], and the other three sets consist of the various groups of the 12 methylene hydrogens [Fig. 4(c)]. The presence of the quartet pattern is a surprise—the methine C–H stretch is not easily distinguished from the methy-

lene C–H stretches. It was to solve this problem that the 1-hydro compound was made. Its spectrum shows that the lowest frequency band (at 2883 cm^{-1}) is due to the methine group, and so the other three are due by default to the three distinguishable methylene C–H stretches.

TABLE II. Low temperature CH vibrational frequencies and linewidths of $C_{10}D_{15}H$.

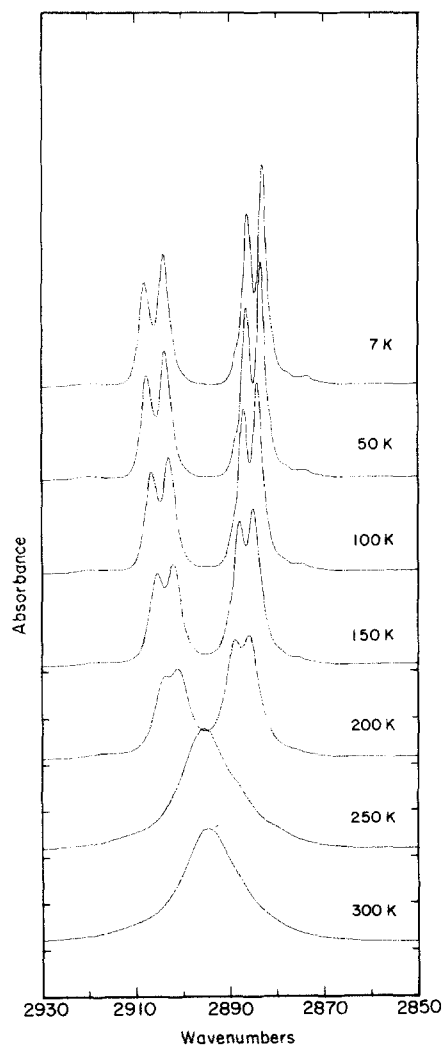| Vibration	$\nu(cm^{-1})$	FWHM (cm^{-1})
Methine stretch	2883.3 ± 0.1	1.9 ± 0.2
Methylene stretches	2908.4	2.6
	2904.3	2.4
	2886.5	2.1
Methine bend	1301	a,b
Methylene bends	1305.8	a,b
	1304	a
	1298.7	
	1297.0	
	1295.0	

a Strongly overlapped bands.
b Unresolved doublet.

FIG. 6. The temperature dependence of the infrared CH stretching bands of $C_{10}D_{15}H$ from 7 to 300 K. The $\beta \rightarrow \alpha$ phase transition occurs at 208 K.
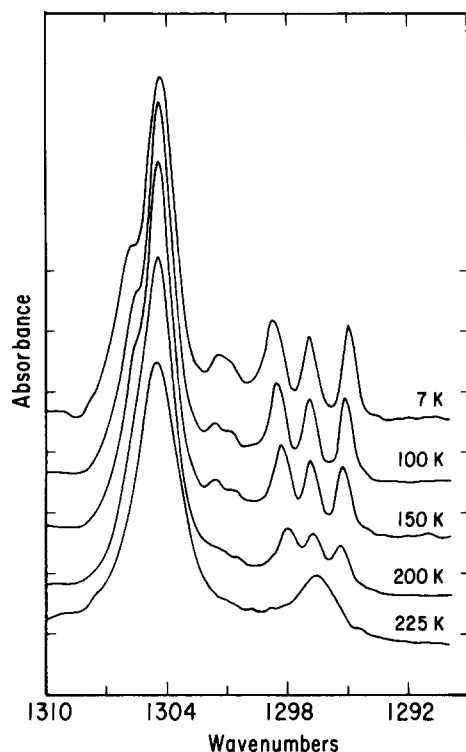
FIG. 7. The temperature dependence of the infrared CH bending bands of $C_{10}D_{15}H$ from 7 to 225 K. The highest temperature spectrum is of the α phase.
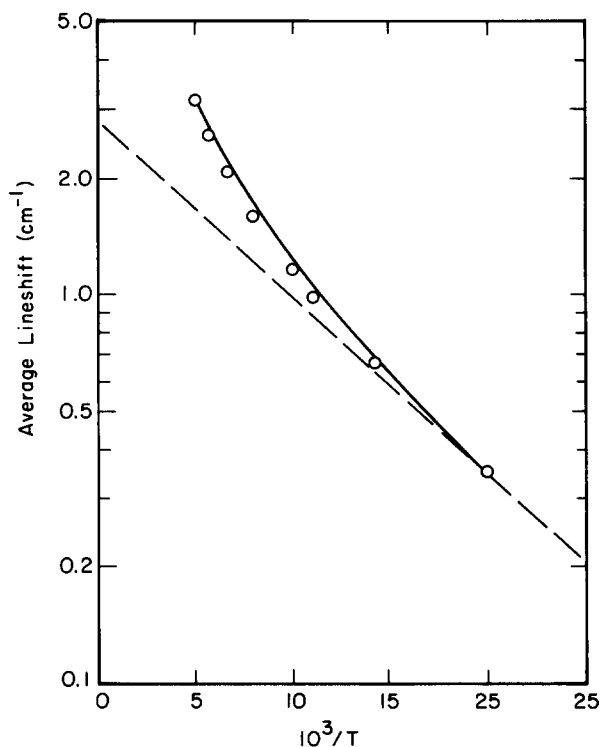

FIG. 8. The average absolute line shifts of the CH stretching bands in $C_{10}D_{15}H$ plotted semilogarithmically vs $1/T$. The solid line is a fit to Eq. (7) with values of A and ω_L of 0.95 and 65 cm^{-1}, respectively.

The C–H bends are similarly complicated and difficult to assign [Fig. 5(b)]. The spectrum of the 1-hydroperdeuteroadamantane shows that the single line at about 1301 cm^{-1} is the degenerate methine bend. Each of the methylene sets should give rise to two bends, leading to six bands in all. These are the triplet of lines centered at about 1297 cm^{-1} and the stronger set of unresolved lines at about 1304 cm^{-1}. The methine bands fall between the methylene bands as predicted from the normal coordinate calculations.

2. Temperature dependence

The temperature dependence of the CH stretches and bends of the $C_{10}D_{15}H$ dilute in crystalline $C_{10}D_{16}$ is shown in Figs. 6 and 7. In the β phase, the CH stretches smoothly collapse and broaden; the average line shifts are plotted in Fig. 8 and are listed along with the average line broadening in Table III. Unfortunately, the line shifts and changes in linewidth were too small to allow for a sufficiently accurate measurement which could distinguish any differences in the shifts between the methine and methylene bands (indeed the spectrum of the specifically labeled adamantane changes with temperature in the same way as does the spectrum of the randomly substituted compound and so we do not reproduce it here). The indistinguishability of the two types of shifts suggests that the different C–H bands are shifting under the same mechanism.

The temperature dependence of the CH bends in Fig. 7 shows changes similar to those of the CH stretches. In particular, the low frequency triplet of a site-split methylene bend smoothly collapses in the β phase, forming a single band after the phase transition. The methine band *splits* on in-

creasing the temperature; this split is clearer in the spectra of specifically labeled adamantane (not shown).

We found that the spectra of neat methine–H labeled adamantane had bands that were considerably broader than those shown in the figures. We diluted the H–labeled adamantane in perdeuterated adamantane in order to obtain the results we report. The broadening in the neat compound shows that there is coupling between C–H oscillators on *different* molecules, which we will consider in the future.[4] We confine our attention here to systems in which molecules are isotopically isolated so that coupling between C–H oscillators can be neglected.

The temperature dependent line shifts are due to interactions of the CH stretches with the rest of the motions of the crystal. Since adamantane is a rigid molecule, we can ignore

TABLE III. Average CH stretch line shift and line broadening in $C_{10}D_{15}H$ (β phase) vs temperature.

T(K)	Line shift (cm^{-1})[a]	Line broadening (cm^{-1})	τ_c(ps)
50	0.35 $\pm$ 0.05	b	...
70	0.66	b	...
90	0.98	b	...
100	1.16	b	...
125	1.58	0.62 $\pm$ 0.1	1.46
150	2.08	0.97	1.63
175	2.59	1.55	1.95
200	3.16	2.15	2.09

[a] Absolute value of the line shift.
[b] Too small to measure.

coupling to the other internal modes in discussing this temperature dependence and consider a simple model in which the C–H stretch of the $C_{10}D_{15}H$ is coupled to only *one* external mode. The obvious choice for the external mode is the rotation or libration, since a rotation of 9° about the *c* axis is what is responsible for the site splitting of the methylene hydrogens. Librational modes have been observed in the far infrared at 65 and 55 cm^{-1},[20] frequencies in fair agreement with calculations.[21]

To examine this coupling between the stretch and libration we use the same model Hamiltonian as used in the previous studies[1,2]:

$$H_{TOT} = H_V + H_L + H_{LV} \qquad (1)$$

with

$$H_V|\psi_n(q)\rangle = (T_V + \tfrac{1}{2}m\omega_0^2 q^2)|\psi_n\rangle = \hbar\omega_0(n + \tfrac{1}{2})|\psi_n\rangle, (2)$$

$$H_L|\phi_p(\theta)\rangle = (T_L + V_L)|\phi_p\rangle = \epsilon_p|\phi_p\rangle, \qquad (3)$$

$$H_{LV} = m\omega_0\delta\omega(\theta)q^2, \qquad (4)$$

where H_V is the Hamiltonian for the C–H stretching motion with coordinate q, harmonic frequency ω_0, effective mass m, and eigenfunctions ψ_n. H_L refers to the librational motion with eigenfunctions ϕ_p and eigenvalues ϵ_p. H_{LV} is the coupling term, which is proportional to a frequency shift $\delta\omega(\theta)$, where θ is the librational coordinate. T and V are kinetic and potential energies, respectively.

The coupling term between the two vibrations, $\delta\omega(\theta)$, can be linear, quadratic, or of higher order in the librational coordinate. For the two previously studied molecules[1,2] we have employed a linear coupling term of the form $K\theta q^2$, where θ is the librational coordinate and q is the vibrational coordinate. As shown in Ref. 1, if the coupling between the two modes is weak and the relaxation is fast, the high frequency line shift becomes a function of the average value of θ:

$$\Delta\omega(T) \propto \langle \bar{\theta} \rangle. \qquad (5)$$

This average must asymptotically reach its high temperature limit. To reproduce a line shift that becomes increasingly negative with increasing temperature (such as that in Fig. 8) requires contributions to the line shift from additional degrees of freedom at higher temperatures. Therefore, we turn to a second possibility, a quadratic dependence of the coupling constant on the librational angle

$$H_{LV} \propto m\omega_0 q^2 \theta^2. \qquad (6)$$

The quartic (i.e., quadratic in both θ and q) form of the coupling term in Eq. (6) is suggested by the Raman studies on adamantane[13] to be more important than a cubic (linear in θ) term (see discussion below). This coupling term has been considered by MacPhail *et al.*[3] Following our previous work, we can include higher energy levels in the line shift calculations, if we again assume that we are in the limit of motional narrowing and use a Redfield averaging theory.[1] As a first guess we approximate the level scheme of the adamantane libration by a harmonic oscillator (although it explicitly is not one). The temperature dependent line shift [Eq. (7)] now depends on $\langle \theta^2 \rangle$, which we know analytically for a simple harmonic oscillator[22] (see the Appendix),

$$\Delta\omega(T) = A\left[\coth(\hbar\omega_L/2kT) - 1\right], \qquad (7)$$

where ω_L is the frequency of the harmonic oscillator. A fit of Eq. (7) to the average line shifts for the stretches leads to a frequency ω_L of 65 cm^{-1}, which is approximately the frequency of the librational modes. This fits the data well (Fig. 8).

It is shown in the Appendix that the temperature dependent linewidths, $-2R_{1010}$, (which are obtained experimentally by subtracting off the linewidth at the lowest temperature) are given by Eq. (8):

$$-2R_{1010} = A^2\tau_c \; \text{csch}^2(\alpha/2)[1 + \cosh\alpha/(1 + \tau_c^2\omega_L^2)], \quad (8)$$

where $\alpha = \hbar\omega_L/kT$ and τ_c is a phenomenological correlation time for the libration. The correlation times calculated from the average line broadening are listed in Table III; they range from 1.5 to 2.1 ps. This puts the line shape into the limit of motional narrowing required by the Redfield theory.

The values of τ_c in Table III increase monotonically with temperature. This effect is the opposite of what one would expect. The anomalous temperature dependence is probably due to the omission of other line broadening mechanisms (e.g., site hopping) which contribute to the linewidth at higher temperatures and lead to a larger apparent correlation time.

3. Lattice expansion

As the temperature increases, the C–H stretching frequencies change due both to the temperature increases at constant volume and to density changes. The effect of the density changes or lattice expansion can be modeled most simply with a coupling term linear in the many lattice modes, $C_{kj}q_{kj}q^2$. This gives a line shift

$$\Delta\omega(T) = \sum_{kj} C_{kj}(\langle \overline{q_{kj}} \rangle - \langle q_{kj} \rangle_0), \qquad (9)$$

where C is a constant, k a reciprocal lattice vector, and j the polarization index for the mode. For $\langle q_{kj} \rangle$ to be nonzero, the lattice must be anharmonic, and the sum over the average displacements of the phonon modes is nothing more than a detailed representation of the change in the crystal structure, i.e., the lattice expansion. Thus the distinction between motional line shifts and lattice expansion is very subtle in these temperature dependence studies, since the lattice expansion at constant pressure is itself dynamical in nature. Note that a quadratic coupling term would allow temperature dependent line shifts without lattice expansion, since $\langle q_{kj}^2 \rangle$ is nonzero even for a harmonic lattice.

We can distinguish between the specific effects of libration and the more general effects of lattice expansion on the C–H line shifts by comparing our results to other data. The temperature dependence of the far-infrared bands of adamantane in the β phase has been measured[20] as has the pressure dependence of the C–H stretching Raman bands.[13] The line shifts for the 77 cm^{-1} lattice translation of adamantane[20] are plotted along with the average CH line shifts in Fig. 9 vs temperature. The plot indicates that the CH stretch is much less sensitive to temperature and to changes in the surrounding lattice than the lattice vibrations. This finding is in agreement with the general findings of pressure dependence studies of vibrations in molecular crystals.[23] Simply stated, the higher frequency molecular vibrations have
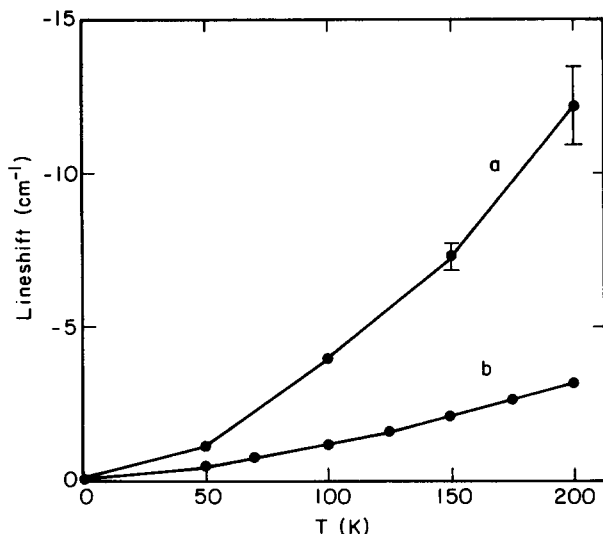
FIG. 9. Absolute lineshifts vs temperature of the 77 cm^{-1} translational phonon mode in $C_{10}H_{16}$ (labeled a) and the CH stretching modes to $C_{10}D_{15}H$ (labeled b). The line shifts for line a are taken from Ref. 19. The graph shows that the shift in the CH modes is not due to the lattice expansion in contrast to the translational phonon.

stiffer force constants than do the lower frequency vibrations, so that when the crystal relaxes the majority of the expansion occurs in the softer intermolecular modes rather than in the intramolecular ones. We therefore expect the high frequency molecular vibrations to depend strongly upon only specific intermolecular modes. For adamantane such a mode is the libration.

The pressure and temperature studies of intramolecular modes in crystals can yield different kinds of information. The difference is shown in the behavior of the vibrations of adamantane in the ordered β phase. Large absolute line shifts are observed with pressure in the Raman bands[13] (20 cm^{-1} at 30 kbar for the 1225 cm^{-1} band), whereas the temperature dependent line shifts of their experiments (and in our infrared studies) are very small (about a wave number for 30 K change for the same band). If one assumes that the stretching frequency is an intensive thermodynamic variable, $\omega(V,T)$, then the temperature dependent line shift at constant pressure is the sum of two terms:

$$(\partial \ln \omega/\partial T)_P = -(\alpha/\kappa)(\partial \ln \omega/\partial P)_T + (\partial \ln \omega/\partial T)_V, \quad (10)$$

where α is the thermal expansion coefficient $(\partial \ln V/\partial T)_P$, and κ is the volume compressibility coefficient $-(\partial \ln V/\partial P)_T$. The first term on the right-hand side of Eq. (10) arises from terms linear in the lattice modes such as those of Eq. (9) while the second term comes from quadratic terms such as those of Eq. (6). Thus the second term can be thought of as arising from the interaction of the CH stretch with a specific librational motion. For every Raman band examined in Ref. 13, the second term was larger than the first term in the temperature dependent line shifts by a least a factor of 2; so that as a first approximation, it is a fair approximation to ignore the effects of lattice expansion.

C. α phase spectra

At 208 K, the lines from the CH stretches merge into a single broad peak (the low frequency shoulder in the 250 K

spectrum in Fig. 6 is due to hysteresis introduced by the KBr pellet). The CH stretching band at 2895 cm^{-1} shifts less than two wave numbers from 210 K to room temperature, and the FWHM (14 cm^{-1}) remains relatively constant in the same temperature range. The lack of strongly temperature dependent line shifts is in strong contrast to the shifts with pressure of the Raman bands in the α phase[13] noted above.

Similarly, in the CH bending region at the phase transition the site splittings merge into broad peaks. However, the intramolecular splitting of the methylene bends and the methine bends persists, leaving three CH bending bands in the α phase.

As already mentioned, several studies have been undertaken to determine the nature of the molecular motions in the plastic phase of adamantane. A combination of incoherent quasielastic neutron scattering and NMR measurements indicates that the adamantane molecules undergo 90° jump reorientations in the crystal about the c axis with residence times at room temperature of 20 ps.[10]

The observation of broad bands immediately after the phase transition, the very small temperature dependence of the CH stretching linewidth from the phase transition to room temperature, and the long orientational residence times determined by NMR suggest that the effects in the infrared spectrum due to molecular reorientations at room temperature are not large enough to account for all of the linewidth. Instead we observe a primarily inhomogeneous line shape due to the several possible local configurations of the disordered adamantane molecules in the crystal. To verify the correlation times determined from NMR one needs to measure the linewidths at temperatures well above 300 K, where the correlation time for site hopping should become short enough to effect the infrared line shapes. Futher studies on the α phase of adamantane are planned.

IV. SUMMARY AND CONCLUSIONS

Our isotopic dilution studies on adamantane provide an assignment of the various CH stretching and bending vibrations and reveal a temperature dependence of the infrared spectra that is due to both motional effects and the presence of an order–disorder phase transition. In the low temperature β phase, the intermolecular and intramolecular splittings present at low temperature collapse and broaden as the temperature is increased. The CH stretching line shifts can be fit by a model coupling the internal mode to a single librational mode of adamantane. Correlation times for the libration calculated from Redfield theory with the assumption of motional narrowing range from 1.5 to 2 ps. There is some coupling to other lattice modes but a comparison to studies of the pressure dependence of the stretches and of temperature dependence of the far-infrared bands suggests that this coupling is small. In the disordered, high temperature α phase, the absence of strong temperature dependence in the CH stretching linewidths indicates that motional effects are not dominant at or below room temperature. Instead, the line shape is inhomogeneous, due to a sum of bands from the finite number of local configurations possible for the adamantane molecules in the disordered crystal.

The presence of motional effects such as those in adamantane is usually indicated by a strong temperature depen-

dence in the frequency and/or linewidth of the vibrational bands. A quantitative study of molecular motions through the vibrational line shape requires a careful separation of the motional contributions from everything else that can affect the infrared spectrum. The technique of isotopic dilution has proven to be very successful in eliminating long range interactions, (in addition to the convenience of decoupling the normal modes of the molecule.

Our series of papers have shown that once the motional contributions to the line shift and linewidth have been ascertained, the Redfield motional averaging theory can be readily applied if the following conditions are met: (i) the bands are motionally narrowed, i.e., the frequency separations are small compared to the inverse of the correlation time for the driving fluctuations as determined from the linewidth; and (ii) the number of degrees of freedom involved in the calculation is manageable. The latter condition is best fulfilled when most of the variation in the vibrational frequency is due to coupling to a single mode or motion, such as the libration of the adamantane molecule.

We expect the vibrational spectrum of a large class of molecules to be sensitive to molecular motions. Vibrational spectroscopy should be able to monitor processes much too quick to be observed by magnetic resonance methods. One such case could be the very fast chemical reactions in liquids which are now being observed by direct picosecond techniques.

$$\langle \overline{\theta^2} \rangle = (\hbar/2m_L\omega_L)\coth(\hbar\omega_L/2kT) \qquad (A5)$$

which leads to a temperature dependent line shift $\Delta\omega(T)$ given in Eq. A6,

$$\Delta\omega(T) = A\,[\coth(\alpha/2) - 1], \qquad (A6)$$

where $A = \hbar K/m_L\omega_L$ and $\alpha = \hbar\omega_L/kT$. To calculate the linewidth we are interested in the correlation $C(\tau)$ where

$$C(\tau) = K^2\big[\ \overline{\theta^2(0)} - \langle\overline{\theta^2}\rangle\,[\theta^2(\tau) - \langle\overline{\theta^2}\rangle\,]\,\big]. \qquad (A7)$$

This correlation function has been calculated for a quantum mechanical harmonic oscillator[3]:

$$C(\tau) = A^2\,\mathrm{csch}^2(\alpha/2)\cosh z \exp(-\tau/\tau_c), \qquad (A8)$$

where $z = \alpha/2 + i\omega\tau$ and τ_c is a phenomenological correlation time introduced to describe the coupling of the libration with the phonon bath.

The linewidth $-2R_{1010}$ is given by the integral of this correlation function[1]:

$$R_{1010} = -1/2\int_{-\infty}^{\infty} C(\tau)\,d\tau$$

$$= A^2\tau_c\,\mathrm{csch}^2(\alpha/2)[\,1 + \cosh\alpha/(1 + \tau_c^2\omega_L^2)\,]. \qquad (A9)$$

By knowing the line broadening, $-2R_{1010}$, and the temperature, Eq. (A9) can be inverted and solved iteratively for the correlation time τ_c. Table III lists the correlation times determined from the line broadening in adamantane.

ACKNOWLEDGMENTS

APPENDIX: LINEWIDTH CALCULATION FOR ADAMANTANE

The Hamiltonian for the CH stretching frequency ω can be broken up in a manner amenable to treatment by Redfield theory[1]:

$$H_0 = T_V + \tfrac{1}{2}m\omega_0^2 q^2 + \langle\overline{\delta\omega}\rangle q^2, \qquad (A1)$$

$$H_1 = m\omega_0[\delta\omega(\theta) - \langle\overline{\delta\omega}\rangle\,]q^2. \qquad (A2)$$

The symbols have the same meaning as in Eqs. (1)–(8). For our model of adamantane the coupling term is assumed to be quadratic, and the thermal bath is constructed from the librational coordinate which we approximate by a simple harmonic oscillator:

$$\delta\omega(\theta) = K\theta^2 \qquad (A3)$$

$$H_L = T_L + \tfrac{1}{2}m_L\omega_L^2\theta^2 \qquad (A4)$$

with T_L, the kinetic energy; m_L, effective mass; and ω_L, the frequency of the libration. The value of $\langle\overline{\theta^2}\rangle$ is known analytically for a simple harmonic oscillator in thermal equilibrium[22]:

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