

Raman investigation of 1,4-cyclohexadiene in the liquid and solid state

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Abstract—We have obtained the room temperature Raman spectra of liquid 1,4-cyclohexadiene and its isotopic analogs: C_6H_7D , *gem*- $C_6H_6D_2$, *trans*- $C_6H_6D_2$ and $C_6H_4D_4$. Additionally, we have measured the Raman spectra of 1,4-cyclohexadiene as a function of temperature from 5 to 300 K.

The conformation of 1,4-cyclohexadiene is found to be very likely planar in the solid state.

The solid–solid phase transition at 192 K reported by calorimetric measurements has been observed and is discussed qualitatively.

INTRODUCTION

The conformation of 1,4-cyclohexadiene has been the subject of a large number of theoretical and experimental investigations.

In the gaseous phase, the planar structure has been established by experimental i.r. [1, 2] and Raman [3] studies. The D_{2h} symmetry has been shown to be the most stable by theoretical *ab initio* [4, 5] and force field [6–8] calculations. A rotational Raman study [9] was interpreted in terms of planar or near planar conformation.

In the liquid phase, the conformation was questioned by early electron diffraction studies [10, 11]. The vibrational spectra in the liquid [1] confirmed the presence of a center of inversion in the molecule, but they did not allow one to distinguish clearly between C_{2h} and D_{2h} symmetry. More recent NMR investigations [12, 13] are discussed in terms of a planar ground state. The observed variations with temperature of the coupling constants between the homoallylic protons are explained by thermally excited vibrational states of the ring puckering mode. The fundamental transition of this mode has been observed at 108 cm^{-1} [2].

The conformation of 1,4-cyclohexadiene in the solid state has to the best of our knowledge not been studied to date.

In the course of our investigations on the stereospecificity and on the kinetics of reactions with 1,4-cyclohexadiene [14], we have prepared a series of deuterated analogs. In this work we present the room temperature Raman spectra of these compounds. Further, we have investigated the low temperature Raman spectra of 1,4-cyclohexadiene to obtain experimental information on the conformation in the solid state.

EXPERIMENTAL

Preparation and purity of the samples

3-Deutero- and 3,3-dideutero-1,4-cyclohexadiene were synthesized starting from 1-chlorobutadiene and 1,1-

dideuterobutadiene [14]. Reduction of the halogeno derivatives with a zinc-copper couple in the presence of D_2O [15] afforded the respective deuterobutadienes. Diels–Alder addition of the latter to fumaroyl chloride followed by hydrolysis and oxidative bis-decarboxylation [16] gave 3-monodeutero- and 3,3-dideutero-1,4-cyclohexadiene. *Trans*-3,6-dideutero-1,4-cyclohexadiene was synthesized following the procedure of FLEMING and WILDSMITH [17]. 3,3,6,6-Tetrautero-1,4-cyclohexadiene was prepared by the same sequence from 1,1,4,4-tetrautero-1,4-cyclohexadiene which in turn had been obtained by pyrolysis of deuterium-labelled sulfolene [18].

The samples were purified by preparative vpc. Their deuterium content was analysed by m.s., using chemical ionization with the following results (% composition).

	d_0	d_1	d_2	d_3	d_4	d_5
1,4-Cyclohexadiene	4	96	—	—	—	—
3-Deutero-	0	7	93	—	—	—
3,3-Dideutero-	—	15	85	—	—	—
<i>Trans</i> -3,6-dideutero-	—	—	—	4	95	1
3,3,6,6-Tetrautero-	—	—	—	—	—	—

The composition of *trans*-3,6-dideutero-1,4-cyclohexadiene was evaluated from Raman measurements.

Measurements

The Raman spectra have been obtained with the laboratory assembled Raman spectrometer consisting of the following parts: a Spectra Physics argon ion laser, a Spex 1403 double monochromator and a Brookdeal photon counting system. Most of the measurements were performed using the 488 nm line at a typical output power of 70 mW for the liquid samples at room temperature and up to 200 mW for the solid samples in low temperature experiments.

All the samples were sealed in melting point glass capillaries. Typically, the amount of deuterated samples ranged from 1 to $5\ \mu\text{l}$.

The low temperature experiments were performed using an Oxford Instruments helium flow cryostat in conjunction with a temperature controller. The precision of this device is about 0.1 K. All the temperatures quoted in this work are those read on this temperature controller.

The absolute temperature of the sample is found to be within 5 K of the reading of the electronically evaluated temperature. This somewhat large discrepancy is partially due to the fact that the sample is slightly insulated by the glass capillary.

The frequencies of the sharp lines are estimated to be correct within 2 cm^{-1} .

RESULTS AND DISCUSSION

Room temperature measurements

These spectra agree with those reported by STIDHAM [1] and the observed frequencies are col-

lected in Table 1. Typical spectra are shown in Fig. 1 ($C_6H_4D_4$ and C_6H_7D). The assignments proposed in the table are based on the results obtained by ERMER and LIFSON [19].

Inspection of Table 1 shows that the vibrations

Table 1. Room temperature Raman (in cm^{-1}) spectra of liquid 1,4-cyclohexadiene and its isotopic analogs. The assignments are based on ERMER and LIFSON [19]. Explanation of the abbreviations used: v = very, w = weak, sh = shoulder, m = medium, s = strong, ip = in-plane, oop = out-of-plane, p = polarized, dp = depolarized

C_6H_8	C_6H_7D	$C_6H_6D_2$ <i>trans</i>	$C_6H_6D_2$ <i>gem</i>	$C_6H_4D_4$	Assignment
3273 vw	3268 vvw				
3067 sh, dp	3069 w	3068 w	3068 w	3060 w, sh	=C-H stretching
3031 vs, p	3030 vvs, p	3030 vs, p	3030 vs, p	3030 s, p	
		2990 w, dp			
2974 mw, dp	2972 mw, dp	2971 w, dp	2976 w, dp	2976 w, dp	CH ₂ sym. stretching + Fermi res. DC-H stretching CH ₂ antisym. stretching 2 × CH ₂ scissors + Fermi res.
2884 vs, p	2884 vs, p	2860 s, p	2884 vs, p		
2866 sh, dp	2862 s, p		2863 mw, p		
2826 ms, p	2826 ms, p		2824 m, p		
		2828 w, p		2808 vw	
2751 vw	2745 vvw				
2690 vw	2678 vw		2676 vw, p		
2666 vw		2358 vvw	2384 vw, p	2361 w, p	
	2252 vvw		2254 vw		
	2178 w	2207 w, p			
	2166 w	2181 w, p	2168 w, dp	2175 m, p	
	2154 w, sh	2161 w, p			
		2138 mw, p			
	2107 m, p	2112 m, p	2139 m, p	2138 ms, p	CD ₂ stretching + Fermi res. CD ₂ antisym. stretching HC-D stretching CD ₂ stretching + Fermi res.
			2126 w, sh	2120 m, dp	
			2088 ms, p	2093 ms, p	
	2061 vw	2103 m, p			
	2043 vvw	2066 w, p		2065 m, p	
1774 vw	1773 vvw	1741 vw	2048 mw, p	2046 m, p	2 × ring breathing C=C stretching
1708 vw			1760 w, p	1725 w, p	
1680 vs, p	1684 ms, p	1678 vs, p	1659 w, p	1638 vw, p	
	1677 m, p		1682 vs, p	1681 m, p	
1670 w, sh	1673 sh		1673 sh, p	1670 m, p	
1428 s, p	1429 m, p		1428 ms, p		CH ₂ scissors ip HC=CH bending
1378 w, dp	1374 w, dp	1370 vw, dp	1372 vw		
		1300 w, dp			
	1279 mw, p	1280 m, p			CHD scissors ip HC=CH bending
1200 s, p	1199 vs, p	1198 vs, p	1200 s, p	1201 s, p	
	1178 w, sh		1178 vw		
		1103 vw, dp	1128 vvw		
	1082 vw, dp				
	1063 vvw		1064 w, dp	1062 m, dp	CD ₂ scissors
			1057 vw, dp		
1038 w, dp					Ring stretching oop HC=CH bending
986 w, dp	982 w, dp	978 w, dp	982 w, dp	977 w, dp	
				917 vw	
	895 w, p		880 w, p		
	876 mw, p	877 w, p		838 w, dp	
	852 mw, p				
856 vs, p	839 s, p		843 w, p		Ring breathing Ring breathing
		824 m, p	832 vs, p	822 vvs, p	
804 w, p	804 vvw		802 vvw	802 vw	
	768 vvw				
751 vvw			739 vvw, dp		
708 w, dp	697 w, dp	688 w, dp	686 w, dp	668 w, dp	oop HC=CH bending
571 w, dp	571 w, dp	570 w, dp	569 w, dp	569 w, dp	ip ring deformation
530 w, dp	527 w, dp	525 w, dp	523 w, dp	514 w, dp	ip ring deformation
	398 vw, sh		380 vw, dp		
403 w, dp	384 w, dp	367 w, dp	369 w, dp	341 mw, dp	Ring deformation

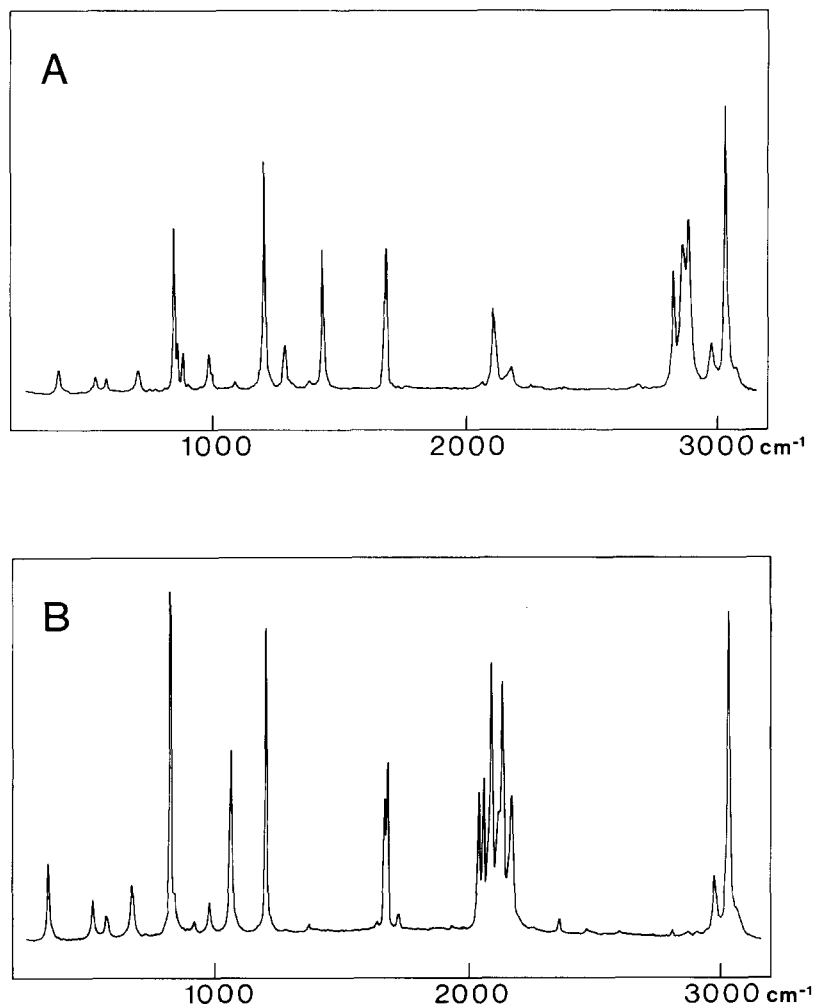


Fig. 1. Raman spectra of isotopically substituted liquid 1,4-cyclohexadiene at room temperature. A. 3-Deutero-1,4-cyclohexadiene. B. 3,3,6,6-Tetradeutero-1,4-cyclohexadiene.

related to the C=C double bonds are not affected very much by the isotopic substitutions on the methylene group. The C=C stretching mode (at 1680 cm^{-1}) is subject to small Fermi resonances with the first overtone of the ring breathing mode, but the observed frequency remains constant within 6 cm^{-1} for all the analogs investigated. The =C-H stretching mode at 3030 cm^{-1} appears to be the most localized mode in the spectra, as it is insensitive to the isotopic substitutions on the methylene group.

The CH₂ stretching vibrations have been reassigned by considering the Fermi resonance with the overtone of the scissoring mode at 1428 cm^{-1} . Then, the first overtone of the i.r. active scissoring mode at 1430 cm^{-1} can equally contribute to the Fermi resonance. The description proposed in Table 1 is supported by the fact that the lines at 2884 and 2826 cm^{-1} in C₆H₈ are polarized. The assignment of the transition at 2826 cm^{-1} to the scissoring overtone subject to Fermi resonance is justified by its lower intensity with respect to the 2884 cm^{-1} line. Additionally, the observed

energy is closer to the estimated value of the overtone without Fermi resonance by considering a normal anharmonicity of 15 cm^{-1} as proposed by SAUR *et al.* [20]. The unpolarized vibration at 2866 cm^{-1} corresponds thus to the antisymmetric stretching mode. The isotopic substitution in *trans*-C₆H₆D₂ shows that the unperturbed C-H stretching mode is located at 2860 cm^{-1} .

The Fermi resonances in the CD₂ stretching vibration region appear to be more complicated, as there are additional lines observed. For instance, one observes four lines at 2139 , 2126 , 2088 and 2048 cm^{-1} in *gem*-C₆H₆D₂. The lines at 2139 , 2088 and 2048 cm^{-1} are polarized and thus subject to Fermi resonance. The origin of the line at 2048 cm^{-1} is not very clear, while the lines at 2139 and 2088 cm^{-1} arise mainly from the fundamental CD₂ symmetric stretching mode and the first harmonic of the CD₂ scissoring mode (observed at 1064 cm^{-1}).

The depolarized line at 2126 cm^{-1} pertains to the antisymmetric CD₂ stretching mode.

An additional measurement of a 2:1 mixture of *cis:trans*- $C_6H_6D_2$ revealed a new polarized line at 835 cm^{-1} which is assigned to the ring breathing mode of the *cis* isomer. This observation illustrates the particular sensitivity of this mode upon isotopic substitution. The remaining parts of the spectra of the mixture are almost identical to the spectra of the *trans* isomer whose frequencies are collected in Table 1.

If one assumes D_{2h} symmetry for C_6H_8 and for $C_6H_4D_4$, one obtains C_{2v} and C_s symmetry for *gem*- $C_6H_6D_2$ and for C_6H_7D , respectively. Group theory predicts 18 Raman active modes for D_{2h} and 36 Raman active modes for C_{2v} and C_s . One expects thus to observe additional fundamental modes in the lower symmetry compounds. This is indeed observed (see Fig. 1) for the CH_2 resp. CHD bending mode in C_6H_7D which appear both in the Raman spectrum, while in the centrosymmetric analogs the CH_2 moiety has an i.r. and a Raman active component.

A comparison of the Raman spectra with i.r. measurements would, however, be more instructive, but a high resolution i.r. spectrometer was not available for this study. The limited amount of deuterated analogs (a few microliters) did not allow further measurements.

Low temperature spectra of liquid C_6H_8

If one considers that the excited vibrational states of the ring puckering mode (B_{2u}) at 108 cm^{-1} (observed in the gaseous phase [2]) are thermally populated at room temperature, one obtains additional understanding of the conformation of 1,4-cyclohexadiene in the liquid phase. Indeed, if the potential of this vibration were a double well involving the lowest vibrational states reasonably located within each of the minima, the Raman spectra should very clearly show the breakdown of the D_{2h} selection rules. This is not observed, as the Raman spectra of the liquid phase at low temperatures (240 K) and at 300 K are essentially the same. The potential of the ring puckering mode may thus have either two very weak minima with

respect to the vibrational groundstate (at 54 cm^{-1}) or a single minimum centered on the planar conformation.

Low temperature spectra of solid C_6H_8

A calorimetric investigation [21] of 1,4-cyclohexadiene yielded the following results. The melting point is observed at 224 K, preceded by some premelting behavior around 210 K. Additionally, a solid-solid phase transition is reported at 192 K.

At very low temperatures (from 5 to 190 K), the spectra exhibit a complex structure (see Fig. 2). The comparison of the spectra of liquid and solid 1,4-cyclohexadiene reveals that the numerous lines observed in the solid are found at very close frequencies to the lines observed in the liquid. Indeed, a careful inspection of the low temperature Raman spectra (at 10 K) revealed no coincidence with the i.r. spectra of liquid 1,4-cyclohexadiene reported in Ref. [1]. This observation leads us to conclude that 1,4-cyclohexadiene retains its planar conformation in the solid state. An additional argument in favor of the planar structure is the following. If the molecule had changed its conformation, one would expect to observe quite different fundamental frequencies for vibrations like the ring breathing or the ring deformation modes. We have shown the sensitivity of the ring breathing mode upon isotopic substitution in the liquid. In liquid 1,4-cyclohexadiene, the frequency of this mode is found to be 856 cm^{-1} . At 10 K, we observe in this part of the spectra two lines at 854 and 858 cm^{-1} .

We conclude thus that the spectra at low temperatures are subject to important factor group splittings.

The total number of external modes (10 at 27 K) observed indicates that there are more than two molecules in the unit cell. This is consistent with the observation of factor group splittings at higher frequencies.

Our measurements confirm the existence of a solid-solid phase transition observed by calorimetry.

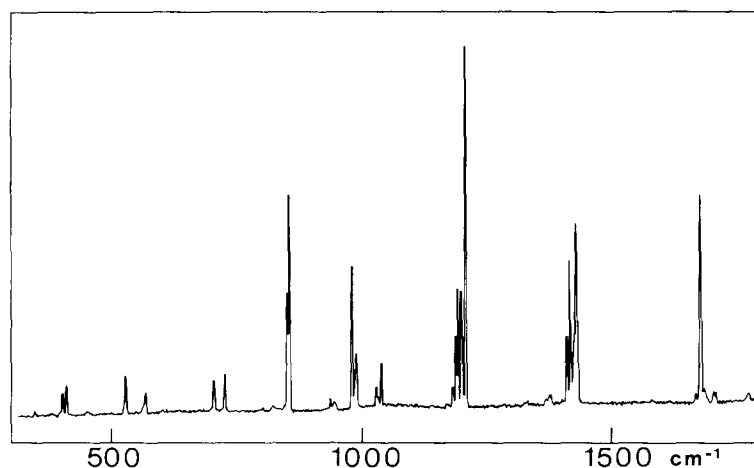


Fig. 2. Raman spectrum of solid 1,4-cyclohexadiene at 27 K from 300 to 1800 cm^{-1} .

metry [21]. With increasing temperature, one observes a simplification of the spectra and a considerable shift towards lower frequencies of the lattice modes (Fig. 3). The transition temperature as read on our instrument is found to be ca 196 K. The uncertainty of the value of the absolute temperature is about 5 K, as indicated in the experimental section. The transition temperature obtained in the calorimetric investigation is 192 K and agrees with our measurement within experimental error.

In the higher frequency region, the observed spectra exhibit less transitions than at 27 K (Fig. 2), but still in the same range of frequency. This solid-solid phase transition can thus be described by a reduction of the unit cell which very likely comes about due to the fact that the molecules begin to move locally.

The thermal anomaly observed at 210 K [21] has not been investigated in more detail. Figure 3 shows that the broad external mode is found at ca 40 cm^{-1} at 220 K, while it is observed at 48 cm^{-1} at 199 K. This shift towards lower frequencies with increasing temperature can be correlated to increased vibrational motion within the solid.

Further experiments are necessary (for instance on single crystals) to elucidate the low temperature crystal structures and melting behavior of 1,4-cyclohexadiene, as there are only very few data at low temperature available in the literature.

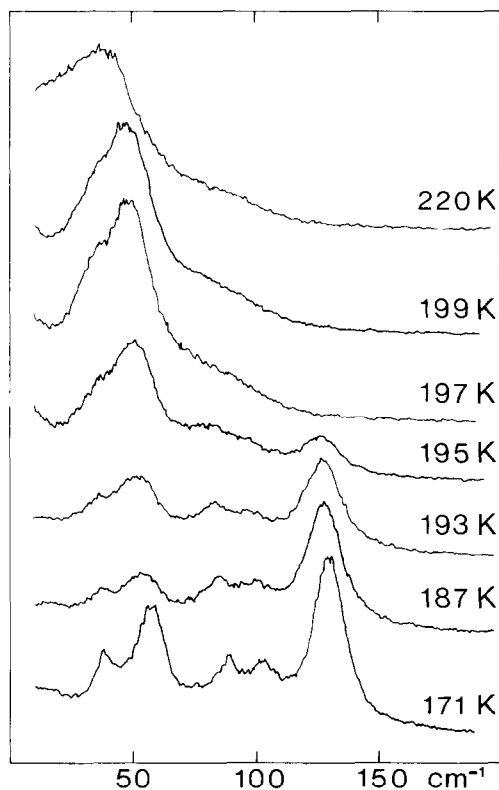


Fig. 3. Low frequency Raman spectra of solid 1,4-cyclohexadiene as a function of temperature from 171 to 220 K.

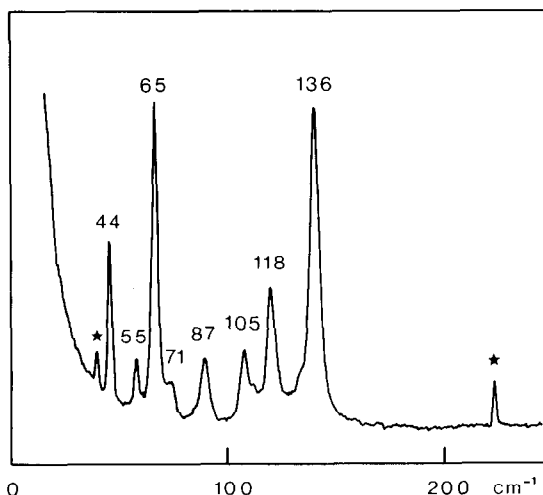


Fig. 4. Low frequency Raman spectrum of polycrystalline 1,4-cyclohexadiene at 7 K. The two peaks denoted by * are due to the argon plasma and do not belong to the spectrum. Experimental resolution: 1 cm^{-1} .

CONCLUSION

We have obtained the room temperature spectra of several isotopic analogs of 1,4-cyclohexadiene. The comparison of the spectra confirms the planar conformation in the liquid phase. Low temperature measurements suggest that this conformation is equally retained in the solid state. We have obtained finally the first spectroscopic evidence of the solid-solid phase transition observed previously by specific heat measurements.

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