

A Raman study of several isotopic derivatives of cyclopentene in condensed states

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 4205

(<http://iopscience.iop.org/0953-8984/4/16/020>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:11

Please note that [terms and conditions apply](#).

A Raman study of several isotopic derivatives of cyclopentene in condensed states

D Cavagnat†, R M Cavagnat, J C Cornut and S Banisaeid-Vahedie

Laboratoire de Spectroscopie Moléculaire et Cristalline (Unité de Recherche Associée au CNRS 124), Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence Cédex, France

Received 28 November 1991

Abstract. The Raman spectra of various isotopic derivatives of cyclopentene have been studied from 20 to 293 K as functions of temperature and isotopic substitution. In the solid phase I, two peaks between 130 and 180 cm^{-1} , assigned to the ring-puckering mode, allow the ring-puckering potential function to be determined in the one-dimensional approximation. Compared with the gas phase, it shows only a slight increase in the barrier height, smaller for monohydrogenated $-3h_1$ cyclopentene (C_5H_8) than for the perhydrogenated cyclopentene (C_5H_{10}), and a simultaneous decrease in the puckering angle value, more pronounced for C_5H_8 than for C_5H_{10} . These trends could explain the appearance of a new solid phase I', characterized by a planar conformation of the cyclopentene ring, in the multideuterated cyclopentene derivatives. In the solid I and plastic phases, the $\nu(\text{CH})$ stretching spectra of monohydrogenated $-3h_1$ (C_5H_8) and $-4h_1$ (C_5H_8) cyclopentenes show two distinct $\nu(\text{CH})$ bands assigned to the CH bond in the axial and equatorial positions. The coalescence of these two bands in the liquid state indicates an exchange rate between the two conformers of about $5 \times 10^{12} \text{ s}^{-1}$ at 295 K.

1. Introduction

Much spectroscopic work has been devoted to the study of cyclopentene in the gas phase and has led to the determination of a ring-puckering potential energy function $V_2x^2 + V_3x^3 + V_4x^4$, with x the ring-puckering coordinate and $V_3 \neq 0$ in the case of the isotopic derivatives monosubstituted in an allylic position [1-13]. The condensed phase has received less attention. Calorimetric studies show the existence of a plastic phase (phase II) between the melting point (138 K) and a solid-solid phase transition at 87 K [14]. In the same temperature range, NMR [15] and neutron scattering [16] studies show the presence of two plastic phases. These two plastic phases cannot be distinguished in the infrared and Raman spectra whereas considerable changes are observed in the entire spectral range on passing from the plastic phase (phase II) to the low-temperature ordered phase (phase I) [16, 17]. The structure of this phase I is not known, but spectroscopic results suggest that it is orthorhombic with either C_{2v} or D_2 symmetry and four molecules per unit cell [17].

Several spectroscopic arguments indicate that the molecule keeps a puckered equilibrium conformation in all the condensed phases [15-22]. However, a recent Raman study of perdeuterated (C_5D_8) and monohydrogenated cyclopentenes $-3h_1$

† To whom correspondence should be addressed.

(C₃H) and -4h₁ (C₄H) have evidenced a new solid phase I' [23]. This phase appears in the same temperature range as phase I and has not been obtained with the perhydrogenated (C₄H₈) and monodeuterated -3d₁ (C₃D) cyclopentenes. In this phase I', the cyclopentene ring takes a planar configuration.

Compared with the very detailed fine structure of the gas phase, the low-frequency ring-puckering spectrum in the condensed state presents only a few weak bands. Furthermore, it is situated in the same frequency range as the spectral densities arising from external motions of the molecule in the liquid state or lattice vibrations in the solid. Given these conditions, it is generally difficult to follow the evolution of the ring-puckering potential. As shown by several previous studies [12, 24–27], the isolated vibrator CH (or CD) can then be used as a spectroscopic probe to study indirectly the internal dynamics of these monosubstituted flexible molecules in the gaseous and solid states. Indeed, it gives rise to a simple diatomic stretching spectrum modulated by the internal motion and situated in a spectral range convenient for precise infrared and Raman measurements.

2. Experimental section

The two monohydrogenated cyclopentenes -3h₁ (C₃H) and -4h₁ (C₄H) have been synthesized by the organotin route according to the procedure described in an earlier paper [13]. As already pointed out, C₃H is obtained as a pure compound but C₄H can only be obtained mixed with C₃H in almost equal proportion. In both cases, the isotopic purity is higher than 96%.

The Raman spectra were recorded on a Z24 Dilor triple monochromator equipped with a Hamamatsu R943-02 Peltier effect refrigerated photomultiplier. A Spectra Physics 171 argon-ion laser 514.5 nm beam at 200 mW filtered by a Photo-Physics laser monochromator was used as the exciting radiation. The spectral resolution was 1.3 cm⁻¹.

The liquid and solid samples up to 80 K were contained in a sealed tube placed in a Dilor continuous liquid-N₂ convection cryostat. The temperature was determined to at least ±1 K accuracy by a platinum resistance detector and controlled by a Thermel temperature regulator. For the solid phase at a temperature lower than 80 K, the gas was trapped on a copper block sealed at the cold head of a Cryodine 20.

3. Results and discussion

3.1. Low-frequency study in the crystalline phase I

At a low temperature (20 K), in phase I, the Raman spectra of all the cyclopentene derivatives show several bands of varying intensity between 30 and 110 cm⁻¹ assigned to lattice vibrations [12, 16, 17]. The position of these bands is only slightly shifted when passing from perhydrogenated (C₄H₈) [16, 17] (see also this work) to monodeuterated (C₃D) [12] and to monohydrogenated (C₃H) derivatives (figure 1 and table 1) (in this region, the spectra of mixed C₄H/C₃H and pure C₃H are very similar).

In this spectral region, two very weak and broad bands centred at 156 and 180 cm⁻¹ for C₄H₈, at 153 and 175 cm⁻¹ for C₃D [12] and at 132 and 153 cm⁻¹ for C₃H are also detected (figure 1). As shown in table 1, these two bands exhibit almost

Table 1. Low-frequency Raman spectra of perhydrogenated C_5H_8 and monohydrogenated C_5D_7H cyclopentenes in the crystalline phase I at 20 K. The frequency ratio and the square root of the ratio of mass M , of the principal moments (I_a , I_b and I_c) of inertia and of ring-puckering reduced mass μ at $x = 0$ are also listed.

	C_5H_8	C_5D_7H	$\nu(C_5D_7H)/\nu(C_5H_8)$	$\sqrt{C_5H_8/C_5D_7H}$
ν	35.5	33.0	0.917	
	46.0	43.5	0.946	
		55.0		
	70.5	67.0	0.950	
	85.0	78.5	0.923	
		92.5		
		106.0	99.0	0.934
	156.0	132.0	0.846	
	180.0	153.0	0.850	
M (au)	68	75		0.952
I_a ($kg\ m^2$)	114.7×10^{-47}	144×10^{-47}		0.892
I_b ($kg\ m^2$)	115.8×10^{-47}	147.5×10^{-47}		0.886
I_c ($kg\ m^2$)	211.9×10^{-47}	259.5×10^{-47}		0.904
ν at $x = 0$ (au)	117.88	174.67		0.821

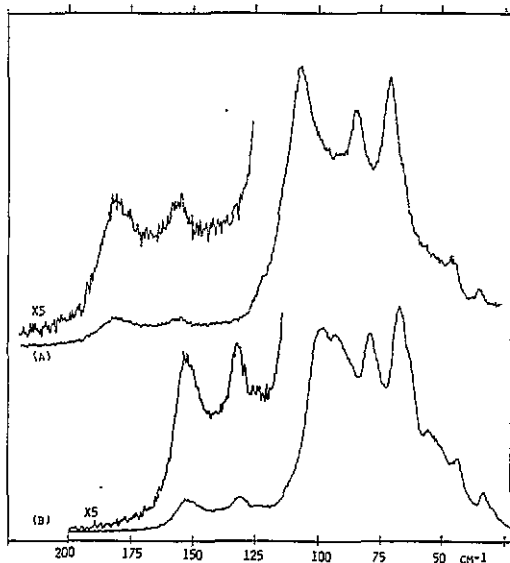


Figure 1. Low-frequency Raman spectra of crystallized I cyclopentenes at 20 K: spectrum (A) C_5H_8 ; spectrum (B) C_5D_7-3H .

the same isotopic effect. The observed isotopic frequency ratio (0.85) is lower than that of the other bands in this region (around 0.93) and close to the isotopic effect calculated for a ring-puckering mode in the harmonic approximation by using simply the ratio of the reduced masses of the ring-puckering motion (0.82 at $x = 0$ Å and 0.83 at $x = \pm 0.13$ Å the coordinates of the maximum and of the minima of the potential, respectively). Furthermore, a strong damping of these bands is observed as the temperature increases (figure 2). They can thus reasonably be assigned to ring-puckering vibrations. At this temperature (20 K), only the two lowest ring-puckering levels are populated and thus the only intense Raman transitions are $|0, 0\rangle \rightarrow |0, 2\rangle$

and $|0, 1\rangle \rightarrow |0, 3\rangle$. The corresponding transitions in the gas phase are situated at 128.4 and 151.8 cm^{-1} for C_5H_8 [1-10], 128.5 and 143.5 cm^{-1} for C_5D_8 [11] and 117.6 and 122.3 cm^{-1} for C_5H_7 [13].

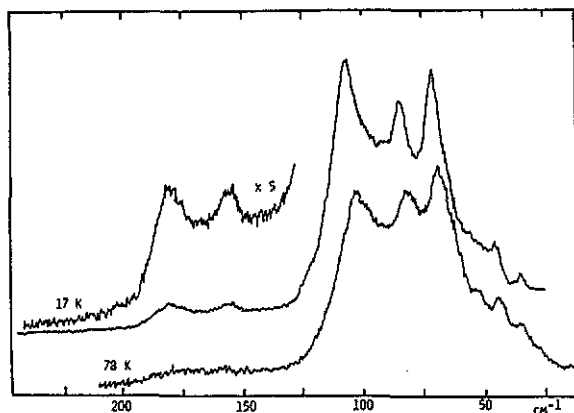


Figure 2. Low-frequency Raman spectra of crystallized I cyclopentene C_5H_8 at 17 and 78 K.

Owing to the poorness of the experimental data (only two puckering transition frequencies), the ring-puckering potential energy function in solid phase I cannot be precisely calculated. However, a rough determination of this potential can be made using the following assumptions.

(i) The same expansion of the reciprocal reduced masses of the ring-puckering (seven terms through $g_6 x^6$) as that calculated for the gas phase [10, 11, 13] is used for the solid state.

(ii) The ring-puckering potential is calculated with a one-dimensional treatment. This approximation supposes that the ring-puckering motion is uncoupled with other modes. As shown in the gas phase studies on the coupling with the ring-twisting mode [10, 13], this is actually not real and *a fortiori* in the solid state where the lattice modes could affect the potential. However, as previously discussed [13], a calculation including all these interactions is too complex and not possible at this time, as even the crystalline structure is not known. Then, the parameters of the potential function calculated in such an approximation are only 'effective' and their values reflect the effect of all the interactions with the other modes [13, 28].

(iii) As we have only two experimental data, we must fix the value of one of the three potential parameters V_2 , V_3 and V_4 . The parameters V_2 and V_4 principally determine the barrier and the shape of the potential and are thus highly affected by the change in physical state. On the contrary, the V_3 -term may be assumed to have almost the same value as in the gas phase. Indeed, as shown previously [11, 12] and confirmed by recent studies [13, 29], the value of this V_3 -term depends essentially on the CH and CD stretching vibrational energy difference between the two isomers. It can be reasonably assumed that this energy difference is not significantly changed when passing from the gas to the solid state. A variation in the value of the V_3 -term of up to 30% affects only slightly the values of the two parameters V_2 and V_4 ($\Delta V_2/V_2 \approx 0.9\%$; $\Delta V_4/V_4 \approx 2.7\%$). Knowledge of the crystal structure and of the puckered conformation of the molecule in this solid phase could markedly improve this calculation.

Table 2. Ring-puckering potential parameters, barrier height H and dihedral angle θ in the low-temperature crystalline phase I of CyH8, Cy3D and Cy3H. The gas phase data are also given for comparison. (The dihedral angle θ is calculated by averaging the extremes of the potential.) (The reciprocal reduced mass expansions $g(x)$ used in the calculation are as follows: CyH8 $8.34848 \times 10^{-3} - 2.1692 \times 10^{-2}x^2 - 0.2227x^4 + 1.0068x^6$; Cy3D $7.9121 \times 10^{-3} + 3.1638 \times 10^{-4}x - 1.4737 \times 10^{-2}x^2 + 1.7794 \times 10^{-3}x^3 - 2.4433 \times 10^{-1}x^4 - 5.0182 \times 10^{-2}x^5 + 9.1916 \times 10^{-1}x^6$; Cy3H $5.7251 \times 10^{-3} - 3.0529 \times 10^{-4}x - 8.8111 \times 10^{-3}x^2 + 3.2459 \times 10^{-3}x^3 - 1.8688 \times 10^{-1}x^4 - 9.4082 \times 10^{-3}x^5 + 6.5928 \times 10^{-1}x^6$.)

	CyH8		Cy3D		Cy3H	
	Solid I	Gas	Solid I	Gas	Solid I	Gas
V_2 (cm ⁻¹)	-38365	-27200	-39049	-26853	-40638	-26452
V_3 (cm ⁻¹)	0	0	910.7	910.7	952	952
V_4 (cm ⁻¹)	-1273114	793000	1362447	781449	1713639	745024
H (cm ⁻¹)	289	233	281.4	232.7	242.2	234.0
θ	24°3	25°8	23°6	25°9	21°4	25°9

The potential parameters calculated with these simplifying hypotheses show a strong increase in the quadratic and quartic terms ($\Delta V_2/V_2 \approx +50\%$ and $\Delta V_4/V_4 \approx +90\%$) compared with the gas phase potential [1-13,29] (table 2). This reflects the important contribution to the potential of the intermolecular forces. The so-determined barrier height value increases in the solid state but to a smaller extent for Cy3H than for CyH8. Simultaneously, the decrease in the puckering angle is more and more pronounced as the number of deuterium atoms increases (table 2). These trends could indicate that the formation of a new solid phase I', characterized by a planar conformation of the cyclopentene ring, is easier in the phase diagram of the multideuterated isotopic derivatives [23].

3.2. CH stretching vibration study in condensed phases

In the gas phase, the CH oscillator is modulated by both ring-puckering motion and overall rotation and the effects of these two motions on the $\nu(\text{CH})$ profile are easily separable and allow a simple analysis [29]. In the crystalline phase at low temperatures, the cyclopentene molecules oscillate about their bent conformation in a ring-puckering potential well and the intermolecular forces are expected to contribute significantly to the shape of this ring-puckering potential. As the temperature increases, the potential is submitted to stronger and stronger fluctuations of the phonon bath. At the transition to the liquid and plastic phases, the characteristic times of the ring puckering and of the whole molecule motions become of the same order of magnitude [15,18,20-22] and the low-frequency vibrational spectra become very broad and featureless.

3.2.1. Experimental results. The evolution of the Raman spectra in the $\nu(\text{CH})$ spectral region as a function of temperature is shown in figure 3 for pure Cy3H and mixed Cy3H-Cy4H.

In the case of pure Cy3H, the intense gas phase lines at 2885.5, 2909.5 and 2933 cm⁻¹ merge into a broad profile centred at 2895 cm⁻¹ in the liquid phase at room temperature. In the cold liquid, this profile splits into two broad bands,

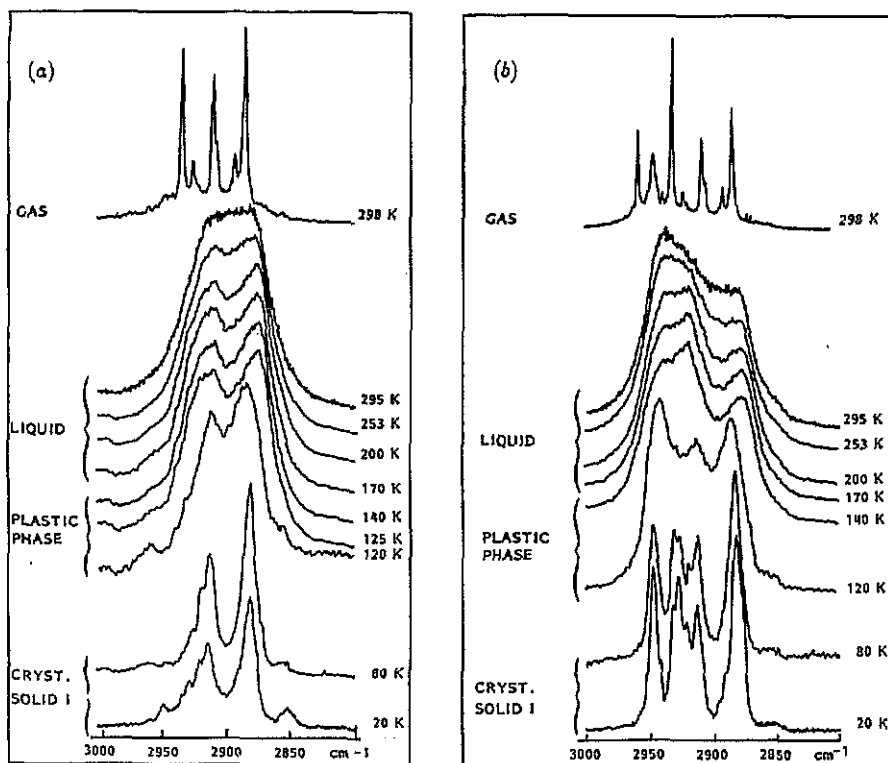


Figure 3. $\nu(\text{CH})$ Raman spectra (a) of mixed cyclopentenes C_3H and C_4H and (b) of pure cyclopentene C_3H in their different physical states.

which move apart from each other up to 2878 and 2912 cm^{-1} as the temperature decreases. These frequencies are changed very little in the plastic phase. In the crystalline phase I, the $\nu(\text{CH})$ profile exhibits an intense narrow and slightly asymmetric band at 2881.5 cm^{-1} and two less intense bands at 2913.5 and 2920 cm^{-1} . The weak bands at 2928 and 2948 cm^{-1} are due to C_4H isotopic impurity.

In the case of mixed C_3H – C_4H , the $\nu(\text{CH})$ profile corresponding to the pure C_4H compound is superimposed on that of C_3H described above and presents a similar evolution with temperature. The intense gas phase peaks at 2933, 2947.5 and 2958.5 cm^{-1} merge, in the liquid phase, into a broad profile centred at 2938.5 cm^{-1} which splits into two broad bands at 2923 and 2940 cm^{-1} in cold liquid. In the crystalline phase I, we observe a doublet at 2928 and 2932 cm^{-1} and a band at 2947.5 cm^{-1} with a weak shoulder at 2942.5 cm^{-1} .

3.2.2. Analysis of the crystalline phase I. In principle, the $\nu(\text{CH})$ spectra in the low-temperature solid phase are simple to analyse because the energy levels are still well defined and only the lowest levels are populated, which simplify the transition scheme. Indeed, only two principal $\nu(\text{CH})$ bands are observed (figure 3). As in the gas phase [29], the frequency splitting between the two $\nu(\text{CH})$ bands of C_3H (32 cm^{-1}) is almost twice that observed for C_4H (19 cm^{-1}). It can thus be supposed that the lower-frequency band is due to the transition $|0,0\rangle \rightarrow |1,0\rangle$ and corresponds to the axial $\nu(\text{CH})$ whereas the higher-frequency band is due to the transition $|0,1\rangle \rightarrow |1,1\rangle$ and corresponds to the equatorial $\nu(\text{CH})$. The transitions $|0,n\rangle \rightarrow |1,n\rangle$ with $n > 1$

have disappeared owing to depopulation of the levels $n > 1$. Because of the lack of experimental data, the ring-puckering potential in the first excited state of $\nu(\text{CH})$ can be determined only roughly. The value of the two parameters V_2 and V_4 cannot be precisely determined because of their very weak effect on the two observed transitions. Their variations between the ground and the first $\nu(\text{CH})$ excited state are assumed to be similar to those calculated for the gas phase. The calculated values of V_3' are then of the same order of magnitude as those determined in the gas phase [29] (table 3).

Table 3. Ring-puckering potential parameters in the first excited CH stretching state and calculated $\nu(\text{CH})$ transition frequencies and intensities in solid I C_3H and C_4H . (The same reciprocal reduced mass expansions as those of table 2 are used.)

	$V_2 \text{ cm}^{-1}$	$V_3 \text{ cm}^{-1}$	$V_4 \text{ cm}^{-1}$	$ 0, 0\rangle \rightarrow 1, 0\rangle$		$ 0, 1\rangle \rightarrow 1, 1\rangle$	
				$\nu \text{ (cm}^{-1}\text{)}$	I	$\nu \text{ (cm}^{-1}\text{)}$	I
C_3H	-40 687	14 337	1 725 635	2881.5	1.0	2913.0	0.86
C_4H	-39 262	8 511	1 636 478	2928.0	1.0	2947.5	0.89

3.2.3. *Analysis of the plastic and liquid phases.* The assignment of the doublet present in these phases up to 253 K follows that of the crystalline phase. Around 295 K, the spectrum exhibits only one broad band. A qualitative explanation of this behaviour can be given by analogy to the well known NMR phenomena of coalescence when fast exchange reactions occur.

In this case, the coalescence of the two $\nu(\text{CH})$ peaks of C_4H , split by 19 cm^{-1} at 20 K, is complete at 295 K, whereas that of the two $\nu(\text{CH})$ peaks of C_3H , split by 32 cm^{-1} at 20 K, begins. The exchange rate τ^{-1} between the two conformers can thus be evaluated to be between 4×10^{12} and $6 \times 10^{12} \text{ s}^{-1}$ at this temperature. This value is in good agreement with those previously determined by other methods on the perhydrogenated cyclopentene (around $5 \times 10^{12} \text{ s}^{-1}$ at 300 K and 10^{12} s^{-1} at 220 K from $^{13}\text{C } T_1$ NMR relaxation time measurements [18], and around $1.1 \times 10^{12} \text{ s}^{-1}$ at 180 K by analysis of the quasi-elastic neutron scattering profile [16]).

A better description of these results would require some more elaborate theoretical developments than the elementary jump model between two conformations. The latter is indeed insufficient to describe the conformational exchange at room temperature where numerous molecules are in excited ring-puckering states close to or above the top of the barrier. This work is in progress.

4. Conclusion

In the low-frequency spectral region of the solid phase I, two weak, broad and temperature-dependent Raman bands are assigned to the ring-puckering motion. They allow a rough but reasonable determination of the ring-puckering potential energy function in the one-dimensional approximation. The so-determined potential barrier is only slightly higher and the puckering angle slightly smaller than the gas phase values. The increase in the potential barrier becomes smaller, and the decrease in the bent angle larger, as the deuterium atom number increases. This could explain

why the solid phase I', characterized by a planar conformation of the cyclopentene ring, can be obtained easily in the multideuterated cyclopentenes [23].

The two $\nu(\text{CH})$ bands observed in the Raman spectra of the condensed phases of C_3H and C_4H are assigned to specific transitions $|0, 0\rangle \rightarrow |1, 0\rangle$ and $|0, 1\rangle \rightarrow |1, 1\rangle$ involving the excitation of the CH oscillator in its axial and equatorial configuration. With increasing temperature, a coalescence of these two lines occurs, implying an exchange rate between the two conformations of about $5 \times 10^{12} \text{ s}^{-1}$ at room temperature, in good agreement with other previous independent determinations.

Acknowledgment

The authors are grateful to J C Lassègues for a critical reading of this paper.

References

- [1] Laane J and Lord R C 1967 *J. Chem. Phys.* **47** 4941
- [2] Ueda T and Shimanouchi T 1967 *J. Chem. Phys.* **47** 5018
- [3] Durig J R and Carreira L A 1972 *J. Chem. Phys.* **56** 4966
- [4] Chao T H and Laane J 1972 *Chem. Phys. Lett.* **14** 595
- [5] Malloy T B 1972 *J. Mol. Spectrosc.* **44** 504
- [6] Harris W C and Longshore C T 1973 *J. Mol. Struct.* **16** 187
- [7] Villarreal J R, Bauman L E, Laane J, Harris W C and Bush S F 1975 *J. Chem. Phys.* **63** 3727
- [8] Villarreal J R, Bauman L E and Laane J 1976 *J. Chem. Phys.* **80** 1172
- [9] Villarreal J R, Laane J, Bush S F and Harris W C 1979 *Spectrochim. Acta A* **35** 331
- [10] Bauman L E, Killough P M, Cooke J M, Villarreal J R and Laane J 1982 *J. Phys. Chem.* **86** 2000
- [11] Rafilipomanana C, Cavagnat D, Cavagnat R, Lassègues J C and Biran C 1985 *J. Mol. Struct.* **127** 283
- [12] Rafilipomanana C, Cavagnat D and Lassègues J C 1985 *J. Mol. Struct.* **129** 215
- [13] Cavagnat D, Banisaeid-Vahedie S and Grignon-Dubois M 1991 *J. Phys. Chem.* **95** 5073
- [14] Huffman H M, Eaton M and Oliver G D 1948 *J. Am. Chem. Soc.* **70** 2911
- [15] Lawrenson I J and Rushworth F A 1968 *Proc. Phys. Soc.* **72** 791
- [16] Jobic H 1977 *Thesis* University of Bordeaux I, France
- [17] Haines J and Gilson D F R 1989 *J. Phys. Chem.* **93** 20
- [18] Besnard M, Lassègues J C, Lichanot A and Nery H 1984 *J. Physique* **45** 487
- [19] Villarreal J R, Laane J, Bush S F and Harris W C 1979 *Spectrochim. Acta A* **35** 331
- [20] Lassègues J C, Fouassier M, Besnard M, Jobic H and Dianoux A J 1984 *J. Physique* **45** 497
- [21] Besnard M, Lassègues J C, Guissani Y and Leicknam J C 1984 *Mol. Phys.* **53** 1145
- [22] Stephenson D S and Binsch G 1981 *Mol. Phys.* **43** 697
- [23] Cavagnat D, Roberts M P, Cavagnat R M and Banisaeid-Vahedie S 1991 *J. Phys. Chem.* **95** 134
- [24] Cavagnat D and Lascombe J 1982 *J. Mol. Spectrosc.* **92** 141
- [25] Cavagnat D and Lascombe J 1982 *J. Chem. Phys.* **76** 4336
- [26] Cavagnat D and Lascombe J 1983 *J. Physique* **44** 67
- [27] MacPhail R A and Variyar J E 1989 *Chem. Phys. Lett.* **161** 239
- [28] Malloy T B and Carreira L A 1979 *J. Chem. Phys.* **71** 2488
- [29] Cavagnat D, Banisaeid-Vahedie S 1991 *J. Phys. Chem.* **95** 8529