Spectrochimica Acta, Vol. 45A, No. 10, pp. 1015-1024, 1989.
Printed in Great Britain.

0584-8539/89 \$3.00+0.00

Vibrational spectra and possible conformers of dimethylmethylphosphonate by normal mode analysis

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(*Received* 1 *November* 1988; *in final form* 31 *March* 1989; *accepted* 5 *April* 1989)

Abstract—A careful assignment of the i.r. and Raman spectra of $CH_3P(O)(OCH_3)_2$, $CD_3P(O)(OCH_3)_2$, $CH_3P(O)(OCD_3)_2$ and $CD_3P(O)(OCD_3)_2$ and a comparison with those of the parent molecules $CH_3OP(O)Cl_2$ and $CD_3OP(O)Cl_2$ suggest that only one conformer exists in the liquid state. This conformer is probably close to the most stable one calculated by CNDO/2 and *ab initio* STO-3G methods, with one CH_3O group *trans* and the other *cis* to the P=O group. The characteristic modes of the $CP(O)(OC)_2$ skeleton are analysed through a force field calculation. It is shown that the stretching vibrations of the single bonds PC and PO are strongly coupled. As already observed for carboxylic esters, it is shown that only mixed skeletal modes and mostly the bending modes are sensitive to the conformation of the methoxy groups around the P–O single bond. On the other hand the ν(P=O) mode does not vary for the different conformers, and the extra components appearing in its vicinity, as well as in that of the ν(P–C) main vibrational mode, are best understood as being due to Fermi resonances with harmonic or combination tones coupling with these modes.

INTRODUCTION

It is well known that for the esters of carboxylic acids, the *s-cis* conformation of the R–O group is usually the more stable one [1]. Nevertheless, when the R group is bulky, an equilibrium between the *s-cis* and *s-trans* conformers may be observed, as for tertiobutyl formate [2, 3]. Existence of conformers for phosphonic esters is still questioned, and splittings of the i.r. and Raman bands, ν(P=O) for tributylphosphate [4] or ν(P=O) and ν(P–C) for dimethylmethylphosphonate [5–7] are often assumed to reflect the presence of such conformers. As we have done for the carboxylic esters [2], a careful assignment of the spectra and a normal mode analysis allows us the possibility of detecting such conformers through vibrational spectroscopy.

As we are interested in obtaining a good understanding of the vibrational spectra of the substituted phosphonates $(RO)_2P(O)CH_2Y$, which are used both as extractants—mainly when Y = -CONR$'_2$ [8]—and as Wittig–Horner reagents [9], we have undertaken a normal mode analysis of the model compound dimethylmethylphosphonate $(CH_3O)_2P(O)CH_3$. In the course of this study we shall discuss the possibility of observing conformers for this compound through vibrational spectroscopy.

EXPERIMENTAL

Dimethylmethylphosphonate (D_0) and its deuterated homologues, $CD_3P(O)$ $(OCH_3)_2$ (D_3), $CH_3P(O)$ $(OCD_3)_2$ (D_6) and $CD_3P(O)$ $(OCD_3)_2$ (D_9), were carefully distilled before use. The (D_9) compound has been prepared by an Arbusov reaction of the trimethylphosphite $(CD_3O)_3P$ in the presence of CD_3I [10] The trimethylphosphite is obtained from the reaction of CD_3OD over PCl_3. The (D_6) compound is obtained from the action of $SOCl_2$ over the (D_0) compound to give $CH_3P(O)Cl_2$ [11] which reacts with CD_3ONa in CD_3OH [12]. The (D_3) compound is obtained in a similar way from the (D_9) compound.

Raman spectra were obtained using a PHO Coderg or T800 Coderg modified Raman spectrometer. The 514.5 nm exciting radiation was provided by an argon ion laser (Spectra-Physics 164) with 200 mW power measured at the sample position. The slit width was 3 cm^{-1}. The calibration of the spectrometers has been checked with reference to emission lines.

RESULTS AND DISCUSSION

Structure of dimethylmethylphosphonate

The structure of dimethylmethylphosphonate has not been measured by X-ray or electron diffraction. It may show different conformations by a rotation of the two methoxy groups around the P–O(C) bond, and in order to get an insight into this conformational behaviour, VAN DER VEKEN and HERMAN have undertaken a theoretical calculation at the CNDO/2 level of approximation [13] which has further been confirmed by an *ab initio* calculation using a STO-3G basis [14]. The *cis* positions of the two methoxy groups (the methyl eclipsing the phosphoryl oxygen) define the origin of the dihedral angles ϕ_1 and ϕ_2 of the (O)PO and POC planes, describing their orientation.* Six energetically different minima have been determined on the conformation map, and only four of them (**I**, **II**, **IV** and **V**) have ϕ_1 and ϕ_2 values which are close to the ideal positions $\phi_1 = 60n_1$, $\phi_2 = 60n_2$, the most stable conformation (**I**), being that where one of the methoxy group is *trans* and the other *gauche* ($\phi_1 = 189.0°$, $\phi_2 = 50.5°$) [13]. In what follows we shall assume that the dimethylmethylphosphonate has this structure and consequently has no symmetry element except for the

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*The rotation is counted positive when starting from the origin to the direction of the methyl substituant.

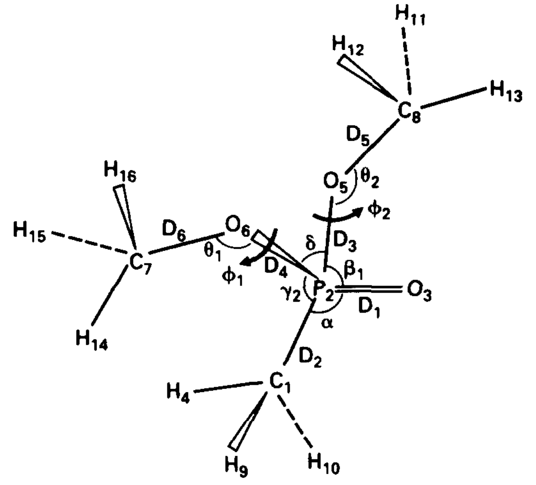

Fig. 1. The geometry of dimethylmethylphosphonate.

identity. We will further consider what changes may be expected for the vibrational spectra of the **II**, **IV** and **V** conformers close to the ideal positions.

Assignment of spectra

Dimethylmethylphosphonate has 16 atoms, and no symmetry. Its 42 fundamental vibrations may be expected to be both i.r. and Raman active. The vibrational spectra of the compound D_0 and of its deuterated homologues D_3, D_6, D_9 have already been reported and analysed [5] but the Raman data were obtained with a slit width of only 8 cm^{-1} which is too large for a precise measure of close vibrational modes. Our Raman frequencies are in rather good agreement with i.r. ones (Table 1), as expected, but they sometimes show differences of some cm^{-1} from those of the previous authors [5]. These small differences may be due both to the calibration of the spectrometer and to the low resolution used by these authors [5].

The synthesis procedure that we have used allows a slight exchange of the hydrogen or deuterium atoms of the CX_3P group (X = H or D) with the solvent (methanol): small amounts (< 10%) of CH_2DP and CD_2HP were observed in compound D_6 and a very small amount of CD_2HP is observed in compound D_3. These isotopic impurities were easily identified through ^1H NMR spectra, the CH_3P, CH_2DP and CD_2HP groups having been characterized by a doublet, a triplet and a quintuplet, respectively, with chemical shifts relative to TMS of 1.447, 1.432 and 1.417 ppm. The coupling constants are $J = 17.38$ Hz and $J = 2.20$ Hz. Their corresponding i.r. and Raman bands are not seen in the spectra of VAN DER VEKEN *et al.* and are thus easily identified (Table 1). On the other hand, our D_9 compound does not show visible CH bands due to incomplete deuteration. These extra bands are easily assigned, mainly to the stretching or rocking vibrations of the CH_2DP or CD_2HP groups, by comparison with the observed frequencies for such groups in partially deuterated ethane [15]. Only the most intense symmetric stretching and parallel rocking modes are observed in the spectra of VAN DER VEKEN and HERMAN [5] for D_9 and in our spectra for D_3 and D_6.

Our assignments for different isotopic compounds are supported by comparison with the assignment of the CH_3P group in $CH_3P(O)Cl_2$ [16] or in CH_3PO_3 [17], and with those of the CH_3OP or CD_3OP groups in $CH_3OP(O)Cl_2$ and $CD_3OP(O)Cl_2$ [14]. All the bands observed for these groups in $(CH_3O)_2P(O)CH_3$ and its isotopic homologue are, indeed, very close to those observed in the previous molecules where these group vibrations are well separated from the low frequency vibrations of the PCl_2 group. The $O_2P(O)C$ skeleton vibrations are assigned by comparison with the spectra of the $(CH_3O)_3P(O)$ molecule [18].

Our assignments are in general agreement with those of VAN DER VEKEN and HERMAN [5], except for the $\delta_s(OCH_3)$ or $\delta_s(OCD_3)$ vibrations and for the deformation vibration of the POC angles. We assign the band at 500 cm^{-1} in D_0 to a rocking PO_2 mode rather than to a POC mode, in agreement with the absence of isotopic $^{13}C/^{12}C$ shift when the substitution is on the (OCH_3) groups [5].

Normal mode frequency calculation

The spectra of the four compounds show two ν(C–O) stretching vibrations with frequencies very close to those found for the *trans* and *gauche* conformers of $CH_3OP(O)Cl_2$ and $CD_3OP(O)Cl_2$ respectively [14], this seems in agreement with the existence of only one conformer for this molecule with probably one methoxy group *trans* and the other *gauche*. It is for this reason that the normal mode calculation has been done for the ideal conformation $\phi_1 = 180°$ and $\phi_2 = 60°$ which is very close to the most stable conformer **I** as calculated by the CNDO/2 method [13].

The exact geometry of dimethylmethylphosphonate is unknown, and so to establish the G matrix, we have used the bond lengths and angles already selected by VAN DER VEKEN [13] and summarized in Table 2. Valence angle and bond coordinates have been used, except for the $CP(O)O_2$ skeleton where group coordinates individualizing the PO_2 group have been introduced (Table 3). For the methyl group, usual group coordinates have been employed (see for instance [19] and [20] for the torsional frequencies).

The initial set of force constants has been transferred from molecules having similar groups, viz. $CH_3P(O)(OCH_3)_2$ [21], $CH_3PO_3^{2-}$ [17], $HCOOCH_3$ [22] and the calculations were performed using the GMAT and VBN programs [23]. The calculated frequencies for the four isotopic molecules and potential energy distributions are summarized in Table 4. Most of the 93 observed frequencies are reproduced very accurately, using only 38 interaction force constants, supplemented by 29 diagonal force constants. The diagonal force constants have been assumed to be the same for the two OCH_3 groups and are given in Table 5 with the initial force field. The

Table 1. Observed band frequencies and assignments for dimethylmethylphosphonate

Compound Assignment	D_0 R	 i.r.	D_3 R	 i.r.	D_6 R	 i.r.	D_9 R	 i.r.
$\nu_a(CH_2)(PCH_2D)$			3002 vw					
$\nu_a(CH_3)(PCH_3)$	2992 S	2992 w			2998 m	2996 m		
$\nu_a(CH_3)(OCH_3)$	2955 S	2957 m	2955 vS	2958 m				
$\nu_s(CH_2)(PCH_2D)$					2949 wp*	2949 vw*		
$\nu(CH)(PCD_2H)$			2930 wp*					
$\nu_s(CH_3)(PCH_3)$	2926 vSp	2926 w			2926 Sp	2927 m		
$2\delta_s(CH_3)(OCH_3)$		2914 e		2912 sh				
$\nu_s(CH_3)(OCH_3)$	2851 Sp	2852 m	2851 vSp	2851 m				
$\delta_s(CH_3)+\delta_a(CH_3)(PCH_3)$	2819 vw				2820 vwp			
$\nu(CD_2)(PCD_2H)$					2265 vwdp*		2265 shdp	
$\nu_a(CD_3)(PCD_3$ and $OCD_3)$			2246 mdp	2244 w	2244 vwdp	2248 mw	2245 mdp	2247 mS
$\nu(OC)+\rho(CH_3)(OCH_3)$		2232 vw						
		2212 vw						
$\nu(CD_2)(PCD_2H)$			2205 vwp*	2199 vw*				
$\nu(CD)(PCH_2D)$			2165 shp*	2164 sh*	2165 mp*			
$\nu(CD_2)(PCD_2H)$					2147 shp*	2141 m*		
$\nu_s(CD_3)(PCD_3)$			2149 vSp	2150 w			2147 mp	2146 w
$\nu(P{=}O)+\rho(CD_3)(OCD_3)$					2132 mp		2137 sh	
$\nu(P{=}O)+\rho(CH_3)(PCH_3)$		2132 vw						
$\nu_s(CD_3)(OCD_3)$					2079 vS	2080 S	2079 vS	2079 mS
$2\nu(OC)$		2076 vwp	2071 vwp	2078 vw				
$\nu(P{=}O)+\nu(PO)$		2025 vw	2042 w	2043 vw	2037 vw		2036 vw	
$\nu(OC)+\rho(PO_2)$	1550 vw							
$\delta_a(CH_3)(PCH_3)$						1497 vw		
$\delta_a(CH_3)(OCH_3)$	1467 mSdp	1465 w	1467 mw	1464 mS				
$\delta'_s(CH_3)(OCH_3)$	1452 e	1450 sh	1450 sh	1449 sh				
			1422vw					
$\delta'_s(CH_3)(PCH_3)$	1422 mwdp	1419 vw			1421 wdp	1420 m		
$2\omega(PO_2)+\delta(PO_2)$ or				1397 vw		1397 vw		
$\omega(PO_2)+2\rho(PO_2)$								
$\omega(PO_2)+\rho(PO_2)+\delta(CPO)$			1347 vw					
$\delta_s(CH_3)(PCH_3)$	1313 vwp	1317 S			1320 vwp	1320 S		
$\nu(P{-}O)+\rho(PO_2)$	1260 shdp		1261 shdp				1248 wp	1253 sh
$\nu(P{=}O)$	1240 Sp	1242 vs	1244 mw	1246 vS	1250 mwp	1249 vS		1263 S
$\nu(P{-}O)+\delta(CPO)$				1215 sh	1215 vw	1219 sh		
$\rho_{\parallel}(CH_3)(OCH_3)$	1187 wp	1186 m	1187 wp	1186 mS				
$\rho_{\perp}(CH_3)(OCH_3)$	1162 vwdp		1164 vw					
$\rho_{\parallel}(CD_3+\delta(POC)$					1098.5 wp		1096 w	1100 w
$\nu(OC)$						1072 vS	1074 sh	1083 S
$\delta_a(CD_3)(OCD_3)$					1066 mwdp		1064 wdp	
$\nu(PO)+\delta(POC)$			1065 mwp					
$\nu(OC)$	1058 mwp	1058 vS	1058 sh	1051 vS		1049 vS		1053 S

Table 1. (*continued*)

Compound Assignment	D_0 R	i.r.	D_3 R	i.r.	D_6 R	i.r.	D_9 R	i.r.
$\nu(PO)+\delta(POC)$			1043 sh					
$\delta_s'(CD_3)(OCD_3)$					1042 vw		1036 mwdp	
$\nu(PC)\delta(POC)+t(CD_3)$							1027 sh	1028 sh
$\nu(OC)$	1033 mwdp	1034 vS	1033 mwdp	1030 vS				
$2\omega(PO_2)$				965 vw				
$\omega(PO_2)+\delta(CPO)$	916 sh	916 vS						
$\rho_{\parallel}(CH_3)(PCH_3)$	897 mwp	896 sh			900 vw	897 S		
$\rho(CD_2H)(PCD_2H)$				915 w*				
$\rho_{\parallel}(CD_3)(OCD_3)$					924.5 mp	928 S	921 mp	926 m
$\rho_{\perp}(CD_3)(OCD_3)$					900 vwdp		899 vw	902 vw
$\omega(PO_2)+\delta(CPO)$			894 vwp	892 w				
$\nu(PO)$	820 mwdp	822 vS	843 wdp	844 S	806 Sdp	804 vS	803 wdp	805 mS
$2\delta(CPO)$				823 m				
$\nu(P\text{–}O)$	789 mwdp	789 vS	800 mp	802 m				
$\rho(CH_2D)(PCH_2D)$					778 wp*	781 w*		
$\nu(P\text{–}O)$					754 vwdp	756 mS	776 mp	779 mS
$\rho(CD_2H)(PCD_2H)$			738 wp*	748 vw*	720 sh*	725 vw*		
$\rho_{\parallel}(CD_3)(PCD_3)$			713 vSp	714 m			708 mSp	711 S
$\omega(PO_2)+\delta(POC)$	705 mp		703 sh		710 mw	713 mw	672 vwdp	676 vw
$\nu(P\text{–}C)$	714 vSp	714 mS	671 vSp	671 m	687 vSp	689 m	643vSp	655 mS
$\omega(PO_2)+\delta(POC)$					679 vSp			
$\rho(CH_2D)(PCH_2D)$					656 Sp*	659 w*		
$t(CH_3)+\delta(POC)$				501 sh				
$\omega(PO_2)$	500 w	500 S	484 Sdp	484 m	489 mSdp	491 S	471 S	475 m
$\rho(PO_2)$	467 mwdp	467 m	460 wdp	459 mw	475 sh	478 sh	445 wdp	450 w
$\delta(PO_2)$	455 sh	448 sh		436 vw	454 dp	455 w		424 vw
$\delta(CPO)$	415 mw	413 mw	410 wdp	409 m	404 Sdp	405 S	399 wdp	401 mw
$2\delta(POC)$	399 wdp	402	391 w	395 w				
$\delta(POC)+t(CD_3)$					386 vw	393	379 vw	384 w
$t(CH_3)(PCH_3)$	306 mdp	310 m			295 wdp	297 w		
$t(CH_3)(OCH_3)$			287 mwdp	291 mS				
$\delta(POC)+\gamma(POC)(OCD_3)$					280 sh	278 vw	274 mdp	279 vw
$2\gamma(POC)(OCD_3)$							260 shdp	
$\delta(POC)(OCH_3)$	233 shdp		222 sh					
$\delta(POC)OCD_3)$					{ 210 shdp		{ 206 shdp	
$t(CD_3)(OCD_3)$								
$\delta(POC)(OCH_3)$	204 mwdp		197 wdp					
$\delta(POC)(OCD_3)$					186 mwdp		174 vwdp	

Intensity of the bands is given: S, strong; vS, very strong; m, mean; w, weak; mw, medium weak or vw, very weak.
Polarization state is given: p, polarized; dp, depolarized.
sh indicates a shoulder.
*Bands due to traces of CD_2HP and CDH_2P (see text).

Table 2. Angle and bond distances used for $CH_3P(O)(OCH_3)_2$

Bonds	d (Å or 10^2 pm)	Angles (°)	
P=O	1.488	POC	116
P–O	1.560	ϕ_1	180
P–C	1.788	ϕ_2	60
O–C	1.450		
C–H	1.110		

For the selection of values see Ref. [13]. The other valence angles around P or C atoms have been taken to be tetrahedral. For the definition of the torsional ϕ_1 and ϕ_2 angle between the COP and OPC planes, see the text.

different conformations of the two OCH_3 groups ($\phi_1 = 180°$, $\phi_2 = 60°$) are reproduced using only three different interaction force constants: $\nu(OC)-\delta(PO_2)$, $\delta(PO_2)-\delta(POC)$ and $t(PO_2)-t(OCH_3)$, two of them having opposite signs. These opposite signs may be partly compared with the behaviour observed for the interaction force constant $\nu(C{=}O)-\delta(COC)$ found in tertiobutylformate [2] in which a change of sign is seen when going from the *cis* to the *trans* conformation relative to the C–O single bond. This fact has been interpreted as a change of sign of the dipole–dipole interaction due to the angle variations [3].

It may be noticed (Table 5) that the most relevant diagonal and off-diagonal force constants remain close to those initially proposed for similar groups in other molecules. The diagonal force constants of the methoxy groups, which were those of carboxylic esters in set I, are all lowered in the phosphonic ester (set II) in agreement with the electron withdrawing effect of the phosphorus atom. Low intensity bands, both in i.r. and Raman, appearing between 402 and 379 cm^{-1} for compounds D_0, D_3, D_6 and D_9 could not be calculated as a $t(PO_2)$ mode (which is strongly mixed with the $\delta(CPO)$ and $\rho(PO_2)$ modes); we suggest that these bands are overtones or combinations involving mainly the $\delta(POC)$ mode which can be in resonance with the $\delta(CPO)$ mode located between 400 and 410 cm^{-1} (Tables 1 and 4).

Calculated and observed frequencies for different conformations

The possible conformers for the dimethylmethylphosphonate are related to the rotation of the OCH_3 group around the P–O(C) bonds. As for the esters [2] we expected that only the skeleton vibration modes and mainly those involving the angle deformation be sensitive to the conformation. We have calculated the frequencies for the three other conformations which have been shown to be close to the ideal positions: **II** ($\phi_1 = -60°$, $\phi_2 = 180°$), **IV** ($\phi_1 = -60°$, $\phi_2 = 60°$), **V** ($\phi_1 = 60°$, $\phi_2 = 60°$). As expected the normal modes involving the CH_3 and OCH_3 groups (as well as the $\nu(P{=}O)$) vary very little with the conformation. We have summarized in Table 6 the calculated frequencies for the four different conformations of the D_0 isotopic species using the same force field as for conformer I. The calculated frequencies for the D_0 species are shown in Table 6 and similar results have been obtained for the species D_3, D_6 and D_9. While the conformations **I** and **II** differ only by their bending skeleton vibrations, the conformations **IV** and **V** may be distinguished from the others by a change in the skeleton stretching mode frequencies, related to the changes in the PO and OC mixing.

Splittings of bands in the $\nu(P{=}O)$ *and* $\nu(P–C)$ *region*

Solvent or temperature changes may both lead to a variation in the relative intensities of the two components of a vibrational mode, related to changes in the position of the equilibrium between two conformers of the same product. Temperature [24] or solvent [25] effects may also induce small variations of the relative positions of the levels involved in a Fermi resonance, producing a similar intensity evolution. Isotopic substitution, which changes the form of some normal modes, may lead to the disappearance of certain resonances, as well as to the appearance of others, while the existence of two conformers must preserve the existence of two components for the vibrational modes at least when the nature of the normal coordinate does not change.

The calculation of the $\nu(P{=}O)$ frequencies for the four different conformations (Table 6) shows that this

Table 3. Group coordinates of the skeleton modes used for the force field calculation

$\nu(P{=}O)$	$= D_1$	$\delta(CPO)$	$= 1/\sqrt{30}(5\alpha - \beta_1 - \beta_2 - \delta - \gamma_1 - \gamma_2)$
$\nu(P–C)$	$= D_2$	$\delta(PO_2)$	$= 1/\sqrt{20}(4\delta - \gamma_1 - \gamma_2 - \beta_1 - \beta_2)$
$\nu(P–O_5)$	$= D_3$	$\omega(PO_2)$	$= 1/2(\beta_1 + \beta_2 - \gamma_1 - \gamma_2)$
$\nu(P–O_6)$	$= D_4$	$\rho(PO_2)$	$= 1/2(\beta_1 - \beta_2 + \gamma_1 - \gamma_2)$
$\nu(O_5–C)$	$= D_5$	$t(PO_2)$	$= 1/2(\beta_1 - \beta_2 - \gamma_1 + \gamma_2)$
$\nu(O_6–C)$	$= D_6$	$\delta(PO_5C)$	$= \vartheta_2$
		$\delta(PO_6C)$	$= \vartheta_1$
		$\gamma(PO_5C)$	$= \phi_2$
		$\gamma(PO_6C)$	$= \phi_1$

For simplicity D, α, β, γ, δ, ϑ, ϕ have been written for their variation. For their definitions see Fig. 1. The symbols for the group vibrations ν, δ, . . . have been used to indicate in this table the corresponding coordinates.

Table 4. Observed and calculated frequencies and potential energy distribution* for dimethylmethylphosphonate. (conformer I)

	D$_0$ obs. cm^{-1}	calc. cm^{-1}	PED (%)	D$_3$ obs.	calc.	PED (%)	D$_6$ obs.	calc.	PED (%)	D$_9$ obs.	Calc.	PED (%)
$\nu_a(OCH_3)$		3005	93	3002	3005	96	2244	2242	98	2245	2242	95
$\nu_a(OCH_3)$		3005	93		3005	96		2242	98		2242	98
$\nu_a(CH_3)$	2992	3001	99	2246	2239	98		3001	99		2239	95
$\nu'_s(OCH_3)$	2955	2957	96	2955	2957	99		2209	93		2209	98
$\nu'_s(OCH_3)$		2957	96		2957	99		2209	93		2209	98
$\nu'_s(CH_3)$		2948	99	2205	2200	98	2949	2948	99		2200	98
$\nu_s(CH_3)$	2926	2924	100	2149	2103	99	2926	2924	100	2147	2103	99
$\nu_s(OCH_3)$	2914$^{i.r.}$	2883	99	2912$^{i.r.}$	2883	95	2079	2080	97	2079	2080	97
$\nu_s(OCH_3)$		2883	99		2883	95		2080	97		2080	97
$\delta_a(CH_3)$		1491	100		1088	97	1497	1491	100		1089	95
$\delta_a(OCH_3)$	1467	1471	$76+22\rho_{\perp}(OCH_3)$	1467	1471	$67+22\rho_{\perp}(OCH_3)$	1066	1049	$62+28\rho_{\perp}(OCD_3)$	1064	1049	$52+28\rho_{\perp}(OCD_3)$
$\delta_a(OCH_3)$												
$\delta_a(OCH_3)$		1472	$76+22\rho_{\perp}(OCH_3)$		1472	$67+23\rho_{\perp}(OCH_3)$		1050	$60+28\rho_{\perp}(OCD_3)$		1050	$51+29\rho_{\perp}(OCD_3)$
$\delta'_s(OCH_3)$	1452	1451	90	1450	1451	$90+10\tilde{\rho}_{\parallel}(OCH_3)$	1042	1042	94	1036	1042	95
$\delta'_s(OCH_3)$		1451	90		1451	$90+10\rho_{\parallel}(OCH_3)$		1042	95		1043	92
$\delta'_s(CH_3)$	1422	1422	100		1037	93	1421	1422	100		1037	92
$\delta_s(OCH_3)$		1349	100	1347	1349	100		1003	$73+9\nu(PO)$		1002	75
$\delta_s(OCH_3)$		1348	100		1348	100		987	$52+11\nu(PO)$		984	$53+10\nu(PO)$
$\delta_s(CH_3)$	1313	1315	$87+10\nu(P=O)$		1031	$53+37\nu(OC)$ $+11\nu(PC)$	1320	1315	$87+10\nu(P=O)$	1027	1028	$84+16\nu(PC)$
$\nu(P=O)$	1240	1242	$73+13\delta_s(CH_3)$	1244	1253	85	1250	1239	$80+13\delta_s(Ch_3)$	1248	1250	90
$\rho_{\parallel}(OCH_3)$	1187	1185	72	1187	1186	73		956	$40+26\nu(PO)$ $+10\delta_s(OCD_3)$		951	$51+29\nu(PO)$
$\rho_{\parallel}(OCH_3)$		1193	70		1193	70		947	$55+18\nu(PO)$ $+11\rho_{\parallel}(CH_3)$		942	$63+16\nu(PO)$
$\rho_{\perp}(OCH_3)$	1162	1164	$64+32\delta_a(OCH_3)$	1164	1164	$64+32\delta_a(OCH_3)$	928$^{i.r.}$	926	$48+34\delta_a(OCD_3)$	926$^{i.r.}$	921	$53+34\delta_a(OCD_3)$
$\rho_{\perp}(OCH_3)$		1165	$63+32\delta_a(OCH_3)$		1166	$63+32\delta_a(OCH_3)$		922	$48+32\delta_a(OCD_3)$		924	$51+35\delta_a(OCD_3)$
$\nu(OC)$	1034$^{i.r.}$	1029	$83+11\nu(PO)$	1030$^{i.r.}$	1023	$50+33\delta_s(CD_3)$ $+12\nu(PC)$	1049$^{i.r.}$	1056	$70+30\,\delta_s(OCD_3)$	1053$^{i.r.}$	1055	$68+32\delta_s(OCD_3)$

ν(OC)	$1058^{i.r.}$	1059	71 + 14ν(PO)	$1057^{i.r.}$	1058	71 + 13ν(PO)	$1072^{i.r.}$	1081	74 + 25δ_s(OCD$_3$)	$1083^{i.r.}$	1081	73 + 24δ_s(OCD$_3$)
$\rho_\parallel$(CH$_3$)	$916^{i.r.}$ 897	917	90	713	701	61 + 9ω(PO$_2$)	$897^{i.r.}$	909	73	708	697	78
$\rho_\perp$(CH$_3$)		919	77		659	83		900	76 + 12$\rho_\parallel$(OCD$_3$)		655	83
ν(PO) ν_{III}	820	824	41 + 22ν(PC)	843	848	60 + 13ρ(PO$_2$) + 11ν(OC)	687	681	30 + 23ν(PC)	803	799	29 + 28$\rho_\parallel$(OCD$_3$) + 11ν(OC) + 11ρ(PO$_2$)
ν(PO) ν_{II}	789	797	4 + 18ν(PC) + 11ν(OC)	800	796	42 + 18ν(PC + 13ν(OC)	754	765	31 + 15$\rho_\parallel$(OCD$_3$) + 9ν(OC)	776	765	15 + 25ν(PC) + 13ν(OC) + 9δ(CPO)
ν(PC) ν_I	714	709	35 + 20ν(PO)	671	668	22 + 32$\rho_\parallel$(CD$_3$)	806	795	44 + 17ν(PO) + 13$\rho_\parallel$(OCD$_3$)	643	650	28 + 16ρ(CD$_3$) + 13ν(PO)
ω(PO$_2$)	500	501	28 + 16ρ(PO$_2$) + 13ν(PC) + 12δ(POC)	460	469	26 + 22δ(PO$_2$) + 10δ(CPO)	489	487	33 + 15δ(CPO) + 13ν(PC) + 12ρ(PO$_2$)	445	456	21 + 17t(PO$_2$) + 14ρ(PO$_2$) + 11δ(PO$_2$) + 14δ(CPO)
ρ(PO$_2$)	467	473	18 + 16ω(PO$_2$) + 15t(PO$_2$) + 15δ(PO$_2$) + 13δ(CPO) + 10δ(POC)	484	487	28 + 14t(PO$_2$) + 13ω(PO$_2$) + 11ν(PC) + 19δ(POC)	454	460	29 + 21t(PO$_2$) + 14δ(CPO) + 9δ(POC)	471	473	24 + 19ω(PO$_2$) + 12ν(PC) + 11t(PO$_2$)
δ(PO$_2$)	455	450	37 + 14ν(PO) + 10δ(CPO) + 10ρ(PO$_2$)	$436^{i.r.}$	442	32 + 12ν(PC) + 11ν(PO) + 10t(PO$_2$)		431	42 + 14ν(PC) + 9δ(CPO)	$424^{i.r.}$	426	44 + 12ν(PO)
δ(CPO)	415	421	40 + 30t(PO$_2$) + 14ω(PO$_2$)	410	396	40 + 25t(PO$_2$) + 10ω(PO$_2$)	404	414	37 + 28t(PO$_2$) + 17ω(PO$_2$) + 10δ(PO$_2$)	399	388	43 + 21t(PO$_2$) + 15ω(PO$_2$)
t(PO$_2$)		378	29 + 15ρ(PO$_2$) + 13δ(CPO)		358	20 + 17δ(CPO) + 12ρ(PO$_2$)		362	37 + 18ρ(PO$_2$) + 9δ(CPO)		341	30 + 16ρ(PO$_2$) + 10δ(CPO)
t(CH$_3$)	306	305	84		201	42 + 31δ(POC) + 9δ(PO$_2$)	295	302	97		204	43 + 42t(OCD$_3$)
t(OCH$_3$)		290	79	287	292	89 + 11δ(POC)	210	203	81	206	201	54 + 13δ(POC) + 10t(CD$_3$)
t(OCH$_3$)		281	83		280	83		221	41 37δ(POC) + 14ρ(PO$_2$)		233	36 + 36t(CD$_3$) + 13δ(POC)
δ(POC)	233	240	62 + 15ρ(PO$_2$)	222	236	40 + 19t(CD$_3$) + 17ρ(PO$_2$)	186	181	34 + 35t(OCD$_3$) + 12δ(PO$_2$) + 9t(PO$_7$)	174	179	36 + 28t(OCD$_3$) + 12δ(PO$_2$)
δ(POC)	204	211	51 + 13δ(PO$_2$) + 9t(PO$_2$)	197	218	28 + 37t(CD$_3$) + 13t(PO$_2$)	210	226	48 + 30t(OCD$_3$)	206	219	44 + 27t(OCD$_3$)
γ(POC)		141	100		132	97		117	94		116	95
γ(POC)		133	100		132	97		125	100		124	100

*Only contributions larger than 8% have been given.

Table 5A. Diagonal force constants

Vibrational mode	Coordinate	Set I	Set II	Fundamental	Coordinate	Set I	Set II
ν(P=O)	S_1	9.27*	9.150	$\delta_s(OCH_3)$	S_{21},S_{23}	0.62‖–0.648**	0.585
ν(P–C)	S_2	3.50*†	3.290	$\delta'_s(OCH_3)$	S_{22},S_{24}	0.548**	0.535
ν(P–O)	S_3,S_4	3.92*	4.240	$\rho_{\parallel}(OCH_3)$	S_{25},S_{26}	0.769**–0.871‖	0.870
ν(O–C)	S_5,S_6	4.82*–4.85**	4.519	$\nu_a(CH_3)$	S_{27}	4.71¶–4.788§	4.750
$\nu_s(CH_3)$	S_7	4.80†–4.788§	4.890	$\nu_a(OCH_3)$	S_{28},S_{29}	4.82‖–4.903*	4.765
$\nu'_s(CH_3)$	S_8	4.78*§	4.585	$\rho(PO_2)$	S_{30}	0.50	1.420
$\nu_s(OCH_3)$	S_9,S_{11}	5.033**–5.091‖	4.730	t(PO_2)	S_{31}	0.50	1.540
$\nu'_s(OCH_3)$	S_{10},S_{12}	4.78–4.919‖	4.610	$\delta_a(CH_3)$	S_{32}	0.50†–0.54¶	0.599
δ(CPO)	S_{13}	0.50	1.600	$\rho_{\perp}(CH_3)$	S_{33}	0.63†	0.536
$\delta(PO_2)$	S_{14}	0.50‡	1.920	$\delta_a(OCH_3)$	S_{34},S_{35}	0.517‖–0.554**	0.499
$\omega(PO_2)$	S_{15}	0.50	1.478	$\rho_{\perp}(OCH_3)$	S_{36},S_{37}	0.842**–0.871‖	0.923
δ(POC)	S_{16},S_{17}	0.50	0.895	t(CH_3)	S_{38}	0.13¶	0.168
$\delta_s(CH_3)$	S_{18}	0.483†–0.519§	0.510	t(OCH_3)	S_{39},S_{40}	0.03‖–0.035**	0.158
$\delta'_s(CH_3)$	S_{19}	0.50†–0.58¶	0.541	γ(POC)	S_{41},S_{42}	0.03	0.230
$\rho_{\parallel}(CH_3)$	S_{20}	0.63†	0.555				

Stretching force constants: mdyn $Å^{-1}$ (or $10^{-2} N m^{-1}$). Bending force constants: mdyn Å rad^{-2} (or 10^{18} J rad^{-2})
*[21], †[17], ‡[27], §[28], ‖[22], ¶[2],** [29].
The initial force constants are those of Set I.

Table 5B. Off diagonal force constants

Coordinates	Set I	Set II	Coordinates	Set I	Set II	Coordinates	Set I	Set II
$S_1 \times S_2$		0.010	$S_3 \times S_{20}$		−0.100	$S_{22} \times S_{25}$		−0.030
$S_1 \times S_3$		0.120	$S_4 \times S_{20}$			$S_{24} \times S_{26}$		
$S_1 \times S_4$			$S_3 \times S_{25}$		0.080	$S_{30} \times S_{31}$		−0.200
$S_1 \times S_{15}$		0.150	$S_4 \times S_{26}$			$S_{30} \times S_{32}$		−0.020
$S_1 \times S_{18}$		0.105	$S_5 \times S_{14}$		0.030	$S_{30} \times S_{33}$		−0.050
$S_1 \times S_{20}$		0.120	$S_6 \times S_{14}$		0.120	$S_{31} \times S_{39}$		−0.100
$S_2 \times S_3$		0.290	$S_5 \times S_{21}$	−0.539†	−0.500	$S_{31} \times S_{40}$		0.030
$S_2 \times S_4$			$S_6 \times S_{23}$			$S_{31} \times S_{41}$		0.050
$S_2 \times S_{15}$		−0.180	$S_5 \times {}_{25}$	−0.022†	−0.150	$S_{31} \times S_{42}$		
$S_2 \times S_{18}$	−0.13*	−0.200	$S_6 \times S_{26}$			$S_{32} \times S_{33}$		0.080
$S_2 \times S_{20}$		0.100	$S_9 \times S_{21}$		−0.080	$S_{34} \times S_{36}$		−0.030
$S_3 \times S_4$		0.310	$S_{11} \times S_{23}$			$S_{35} \times S_{37}$		
$S_3 \times S_5$		0.150	$S_{13} \times S_{14}$		0.250	$S_{34} \times S_{41}$		0.020
$S_4 \times S_6$			$S_{13} \times S_{20}$		−0.050	$S_{35} \times S_{42}$		
$S_3 \times S_{15}$		0.110	$S_{14} \times S_{16}$		−0.040	$S_{36} \times S_{41}$		0.115
$S_4 \times S_{15}$			$S_{14} \times S_{17}$		0.030	$S_{37} \times S_{42}$		
$S_3 \times S_{16}$		0.220	$S_{16} \times S_{22}$		−0.040	$S_{39} \times S_{41}$		0.040
$S_4 \times S_{17}$			$S_{17} \times S_{24}$			$S_{40} \times S_{42}$		
			$S_{19} \times S_{20}$		−0.070			

Stretch–bend interactions force constants: mdyn rad^{-1} (or 10^8N rad^{-1}).
*[17], †[29].

mode varies only slightly with the conformation. The very close position observed for the i.r. and Raman components in the pure liquid indicates small aggregation effects due to a centrosymmetric dipolar coupling, as is usually observed in other polar solvents [26]. The ν(P=O) main band frequency increases by 8–10 cm^{-1} when comparing the polar pure liquid spectra to those of the same compounds diluted in an apolar solvent like CS_2 [5]. This upward shift due to the local field effect of the surroundings is only observed for the D_0, D_3 and D_6 compounds. For the D_9 compound the main component is observed at the same frequency (1263 cm^{-1}) in the i.r. spectra of the pure liquid and of the dilute CS_2 solution. The other component appears at different frequencies in the pure liquid (1248 cm^{-1} in Raman and 1253 sh in i.r.) and in the CS_2 solution (1280 sh in i.r.). This particular behaviour in the D_9 compound is explained by a Fermi resonance with different combination tones having a small anharmonic coupling with the ν(P=O) mode for the pure liquid and the CS_2 solution. In the pure liquid the ν(P–O)+$\rho(PO_2)$ combination is expected at $471 + 776 = 1247$ cm^{-1} in the Raman and at $475 + 779 = 1254$ cm^{-1} in the i.r. spectra. The unperturbed ν(P=O) level may be estimated from the solution frequency at $1263 - 8 = 1255$ cm^{-1}, which explains the repulsion of the observed levels at 1248 and 1263 cm^{-1}. The combination is expected at $473 + 778 = 1251$ cm^{-1} in CS_2 solution, and the energy exchange and repulsion between levels is very small

Table 6. Calculated frequencies for the skeleton modes of four $CH_3P(O)(OCH_3)_2$ conformers

Vibrations modes	obs.	I($\phi_1 = 180°, \phi_2 = 60°$) calc.	II($\phi_1 = -60°$, $\phi_2 = 180°$) calc.	IV(ϕ_1) = $-60°$, $\phi_2 = 60°$) calc.	V($\phi_1 = 60°, \phi_2 = 60°$) calc.
ν(P=O)	1240	1242	1242	1243	1247
ν(OC)	1058	1059	1052	1047	1055
ν(OC)	1034	1029	1028	1036	1027
ν(PO)	820	824	830	841	823
ν(PO)	789	797	798	786	814
ν(PC)	714	709	709	704	690
$\omega(PO_2)$	500	501	508	505	494
$\rho(PO_2)$	467	473	494	489	463
$\delta(PO_2)$	455	450	471	441	443
δ(CPO)	415	421	433	419	427
$t(PO_2)$		378	378	388	403
δ(POC)	233	240	236	243	246
δ(POC)	204	211	209	194	202
γ(POC)		141	140	169	140
γ(POC)		133	131	116	132

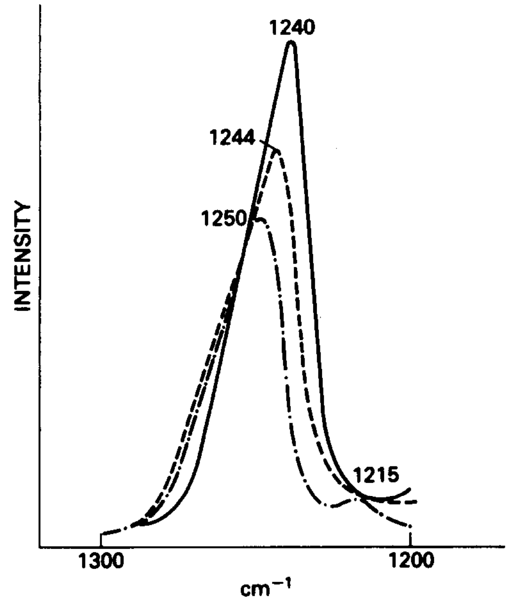

Fig. 2. Raman spectra in the ν(P=O) region of compounds D_0, D_3, D_6. (——)D_0, (---)D_3, (-.-.-)D_6.

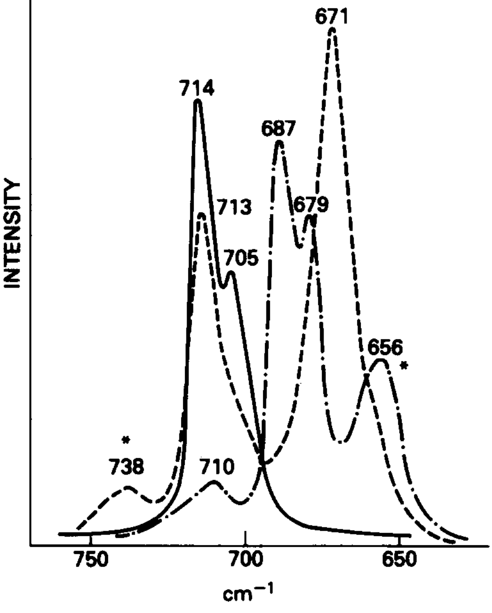

Fig. 3. Raman spectra in the ν(PC) region of compounds D_0, D_3, D_6. (——)D_0, (---)D_3, (-.-.-)D_6.

due to a small anharmonic coupling term. The shoulder seen at 1280 cm^{-1} in the D_9 compound and at 1295 cm^{-1} in the D_6 compound is assigned to another combination $\nu(PO) + \omega(PO_2)$, expected at $806 + 473 = 1279$ cm^{-1} and $806 + 491 = 1297$ cm^{-1} in the D_9 and D_6 compounds respectively. The shoulders observed at 1260 and 1261 cm^{-1} in the Raman spectra of the pure liquid D_0 and D_3 compounds corresponds to the $\nu(P\text{–}O) + \rho(PO_2)$ combination expected at $789 + 467 = 1256$ cm^{-1} and $800 + 460 = 1260$ cm^{-1} respectively.

For the bands observed in the ν(P–C) region, the solvent effects observed on the frequencies [5] are negligible, and the lowering of the temperature from room temperature to liquid nitrogen temperature for the D_0 and D_9 compounds gives only a slight band frequency increase of 3–4 cm^{-1}. The calculation shows that the PO and PC vibration coordinates are strongly mixed. These normal modes also involve the $\rho(CD_3)$ coordinate in the D_3 and D_9 compounds and the $\rho_{\parallel}$ (OCD_3) coordinate in the D_6 and D_9 compounds (Table 4). This mixing satisfactorily explains the frequency variations of the intense Raman ν(PC) band. On the other hand, changes of the conformation (Table 6) give only small frequency variations of this normal mode which is calculated at 709, 668, 681 and 650 cm^{-1} for the D_0, D_3, D_6 and D_9 compounds respectively. We note (Table 4) that the $\omega(PO_2)$ mode partly involves the ν(PC) and δ(POC) coordinates. Non-negligible anharmonic coupling terms between the ν(PC) fundamental modes and the combination mode $\omega(PO_2)+\delta(POC)$ may be assumed [25]. This combination is calculated from the fundamentals at $500+204=704\ cm^{-1}$, $484+222=706\ cm^{-1}$, $489+210=699\ cm^{-1}$ and $489+186=675\ cm^{-1}$, $445+219=664\ cm^{-1}$ for the D_0, D_3, D_6 and D_9 compounds respectively. They fit very well the two components observed mainly in Raman spectra (Fig. 3) for the D_0, D_3 and D_9 compounds and for the three components observed from the D_6 compound, taking into account the slight repulsion and energy exchange of the levels due to the resonance. Although other combinations may be found, this one, taking into account all the components or shoulders for the four isotopic compounds in agreement with the calculation, seems the more convincing.

Acknowledgements—The authors thank M. F. LAUTIÉ and N. RATOVELOMANANA for the synthesis of the labelled compounds and C. COUPRY for their NMR analysis.

REFERENCES

[1] N. L. OWEN, *J. molec. Struct.* **18**, 1 (1973).
[2] Y. OMURA, J. CORSET and R. M. MORAVIE, *J. molec. Struct.* **52**, 175 (1979).
[3] Y. OMURA, J. CORSET and P. BONNET, *J. molec. Struct.* **66**, 83 (1980).
[4] F. S. MORTIMER, *Spectrochim. Acta* **9**, 270 (1957).
[5] B. J. VAN DER VEKEN and M. A. HERMAN, *Phosphorus Sulfur* **10**, 357 (1981).
[6] A. J. BARNES, S. LOMAX and B. J. VAN DER VEKEN, *J. molec. Struct.* **99**, 137 (1983).
[7] B. J. VAN DER VEKEN and A. J. BARNES, *J. molec. Struct.* **99**, 187 (1983).
[8] S. M. BOWEN, E. N. DUESLER and R. T. PAINE, *Inorg. Chim. Acta* **61**, 165 (1982); *ibid.*, **24**, 4441 (1985); *ibid.*, **24**, 4626 (1985); J. P. BRUNETTE, L. JURDY, M. J. F. LEROY and B. ALLARD, *Spectrochim. Acta* **37A**, 991 (1981).
[9] W. S. WODSWORTH, *Org. React.* **25**, 73 (1978); T. BOTTIN-STRZALKO, J. CORSET, F. FROMENT, M. J. POUET, J. SEYDEN-PENNE and M. P. SIMONNIN, *J. org. Chem.* **45**, 1270 (1980).
[10] S. R. LANDAUER and H. N. RYDON, *J. chem. Soc.* 2224 (1953).
[11] K. MOEDRITZER and R. E. MILLER, *Synth. React. inorg. Met. org. Chem.* **4**, 417 (1974).
[12] E. GRYSZKIEWIEZ-TROCHINOWSKI, M. BOUSQUET and J. QUINCHON, *Bull. Soc. chim. Fr.* 1222 (1961).
[13] B. J. VAN DER VEKEN and M. A. HERMAN, *J. molec. Struct.* **42**, 161 (1977).
[14] G. H. PIETERS, B. J. VAN DER VEKEN and M. A. HERMAN, *J. molec. Struct.* **102**, 27 (1983).
[15] L. M. SVERDLOV, M. A. KOVNER and E. P. KRAINOV, *Vibrational Spectra of Polyatomic Molecules*, p. 184. Halsted Press, John Wiley & Sons (1974).
[16] J. R. DURIG, F. BLOCK and I. W. LEVIN, *Spectrochim. Acta* **21**, 1105 (1965).
[17] M. T. FOREL, C. DESTRADE and C. GARRIGOU-LAGRANGE, *J. Chim. phys.* **66**, 1991 (1969).
[18] V. VON HORNUNG, O. ABOUL WAFA, A. LENTZ and J. GOUBEAU, *Z. Anorg. allg. Chem.* **380**, 137 (1971).
[19] M. T. FOREL and M. FOUASSIER, *J. Chim. phys.* **67**, 1132 (1970).
[20] G. CHASSAING, J. CORSET and J. LIMOUZI, *Spectrochim. Acta* **37A**, 721 (1981).
[21] W. D. VON BURKHARDT, E. G. HOHN and J. GOUBEAU, *Z. anorg. allg. Chem.* **442**, 19 (1978).
[22] H. SUSI and J. R. SCHERER, *Spectrochim. Acta* **25**, 1243 (1969).
[23] J. H. SCHACHTSCHNEIDER and R. D. SNYDER, *Spectrochim. Acta* **19**, 117 (1963).
[24] J. CORSET and F. FROMENT, C. r. *hebd. Séanc. Acad. Sci., Paris B* **280**, 125 (1975).
[25] R. M. MORAVIE, J. CORSET and A. BURNEAU, *J. Chim. phys.* **79**, 119 (1982).
[26] P. BONNET, A. BURNEAU, J. CORSET and M. L. JOSIEN, C. r. *hebd. Séanc. Acad. Sci., Paris C* **281**, 797 (1975), and references therein.
[27] J. HILBRAND and G. KAUFMANN, *Spectrochim. Acta* **26**, 1407 (1970).
[28] J. R. DURIG, H. G. HUDSON, M. R. JALILIAN and Y. S. LI, *J. chem. Phys.* **74**, 772 (1981).
[29] P. CAILLET and M. T. FOREL, *J. Chim. phys.* **72**, 522 (1975).