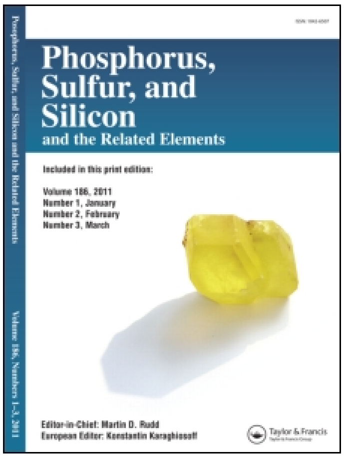

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

VIBRATIONAL SPECTRA OF $CH_3PO(OCH_3)_2$ AND ISOTOPICALLY SUBSTITUTED DERIVATIVES

B. J. Van Der Veken[a]; M. A. Herman[a]
[a] Laboratorium Anorganische Scheikunde, Rijksuniversitair Centrum Antwerpen, Antwerpen, Belgium

To cite this Article Van Der Veken, B. J. and Herman, M. A.(1981) 'VIBRATIONAL SPECTRA OF $CH_3PO(OCH_3)_2$ AND ISOTOPICALLY SUBSTITUTED DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 10: 3, 357 — 367

To link to this Article: DOI: 10.1080/03086648108077388

URL: http://dx.doi.org/10.1080/03086648108077388

Phosphorus and Sulfur, 1981, Vol. 10, pp. 357–368
0308-664X/81/1003-0357$06.50/0

VIBRATIONAL SPECTRA OF $CH_3PO(OCH_3)_2$ AND ISOTOPICALLY SUBSTITUTED DERIVATIVES

B. J. VAN DER VEKEN and M. A. HERMAN

Laboratorium Anorganische Scheikunde, Rijksuniversitair Centrum Antwerpen,
Groenenborgerlaan 171, B2020 Antwerpen, Belgium.

(*Received September 17, 1980, in final form December 1, 1980*)

Infrared, far-infrared and Raman spectra of liquid $CH_3PO(OCH_3)_2$, $CD_3PO(OCH_3)_2$, $CH_3PO(OCD_3)_2$, $CD_3PO(OCD_3)_2$ and $CH_3PO(O^{13}CH_3)_2$ are reported and the assignments proposed. Possible conformational splittings are discussed.

INTRODUCTION

The NaCl region of the infrared spectrum of pure $CH_3PO(OCH_3)_2$ was reported many years ago by Meyrick *et al.*[1] In the published spectrum, not only fine structure, but also an intense band is missing. These earlier investigators made no attempt to interpret the observed bands in detail. This same study[1] reports Raman data in which several fairly strong bands are missing. In a later infrared study by Guilbault *et al*,[2] only the most intense bands of the region down to only 700 cm^{-1} have been assigned. Results on the CH_3-P and CH_3-OP vibrations in i.r. have been reported by F. Hérail,[3,4] while the same author has given some attention to the ν(P=O).[5] Although some earlier work is recorded, it is clear that insufficient data have been published to allow the complete assignment of the fundamentals. Therefore it was thought necessary to reinvestigate the i.r. and Raman spectra of the normal compound $CH_3PO(OCH_3)_2$ (H9), using isotope substitution as a tool to confirm assignments. Species studied were: $CD_3PO(OCH_3)_2$(D3), $CH_3PO(OCD_3)_2$ (D6), $CD_3PO(OCD_3)_2$ (D9) and $CH_3PO(O^{13}CH_3)_2$ (13C), which makes the assignments more reliable. The symbols between brackets will be used in the following to indicate the correct species.

EXPERIMENTAL

The Raman spectra were recorded with a Coderg PHO instrument, equipped with an OIP 181E He Ne laser and a Spectra-Physics Model 164 Ar$^+$-laser. Spectra were recorded with 8 cm^{-1} slit width, unless otherwise specified, in standard 0.3 ml cells, except 13C which was recorded in a capillary. Frequency calibration of the instrument was done with benzene and CCl_4.

The infrared spectra were recorded on a Perkin-Elmer 580 instrument, using a slit program with a maximum resolution of 3.7 cm^{-1}. Pure liquids were investigated in a 0.1 mm CsI cell and as a film between AgCl windows. Solutions of approximately 5% by volume were run in a 0.1 mm CsI cell. In these cases solvent absorptions were matched with a variable path CsI cell in the reference beam.

The far infrared spectra were run on a Beckman IR 720 Fourier transform spectrometer using Mylar beam splitters of 6.25 μm and 12.5 μm, in polyethylene cells of 1 mm thickness, as solutions of approximately 15% by volume in benzene and CCl_4.

Intensity indications for the i.r. spectra in the tables apply to the mid-infrared spectra of the solutions, and to the 0.1 mm recordings of the pure liquids.

DISCUSSION

Dimethylmethylphosphonate has 16 atoms and thus 42 normal vibrations. As has been shown by a theoretical treatment of this compound,[6] for the most favourable conformers no symmetry elements other than the unit operation are present, which means the molecular point group is C_1. As a consequence, all fundamentals, over- and combination bands are allowed both in i.r. and Raman, while in the latter all bands can be polarized.

The characteristic vibrations that have to be assigned are gathered in Table I. Most of these need no comment. The P-O stretches are described as coupled to a symmetric and an asymmetric component: this is justified by the identity of the two chemical bonds and the common central atom. The absence of the latter is the reason for

TABLE I

Characteristic vibrations of $CH_3PO(OCH_3)_2$

Type	Symbol	Number
CH_3(O) stretches	ν_a, ν'_a, ν_s	6
CH_3(O) deformations	$\delta_a, \delta_a, \delta_s$	6
CH_3(O) rockings	ρ, ρ'	4
CH_3(O) torsion	τ	2
CH_3(P) stretches	ν_a, ν'_a, ν_s	3
CH_3(P) deformations	$\delta_a, \delta_a, \delta_s$	3
CH_3(P) rockings	ρ, ρ'	2
CH_3(P) torsion	τ	1
P=O stretch	ν	1
P—O stretches	ν_a, ν_s	2
C—O stretches	ν	2
P—C stretch	ν	1
CPO_3 deformations	$\delta_u, \delta'_a, \delta_s$	3
CPO_3 rockings	ρ, ρ'	2
POC in plane deformations	δ	2
POC out-of-plane deformations	δ	2
	total	42

treating the C-O stretches separately. For $CH_3PO_3^{2-}$, a clear description as $\delta(CPO_3)$ $(a_1 + e)$ and $\rho(CPO_3)$ (e) of the skeletal deformations is possible; for $CH_3PO_3H_2$ the same nomenclature was used for these modes, owing to the similarity of the vibrational spectra in the concerned region.[7] Because of the structural resemblance of the $CH_3PO_3H_2$ skeleton with the skeleton of the present compounds, we will use the notations of $CH_3PO_3H_2$, and thus of $CH_3PO_3^{2-}$, to describe the skeletal deformational modes in the compounds presently under investigation.

In order to be able to distinguish between out-of-plane deformations of the P-O-C parts, for which only secondary isotope effects are expected, and methyl torsions, it is necessary to know the effects on the latter. It has been shown by J. Laane that the ν_H/ν_D ratio for this type of vibrations depends on the barrier height.[8] Assuming identical barriers in CH_3 and CD_3 compounds, and using the barriers determined by inelastic neutron scattering,[9] with the inertial constants of model geometries described before,[6] these ratios were determined as 1.39 for CH_3-P and 1.37 for CH_3-O groups, independent of the conformation (whose influence comes from the reduced moment of inertia in the rotational constant). This means that for the methyl torsions isotopic shifts are expected that are very similar to those of harmonic oscillator H/D substitution (1.36 for CH/CD).

As an example, in Figures 1 and 2 the mid-infrared and Raman spectrum of H9 are shown;[10] the frequencies together with the proposed assignments are gathered in Tables II to VI.

The CH_3 stretching region of H9 appears rather complex. Comparison with D3 and D6 however allows assignment of the observed bands to modes localised in CH_3(O) and CH_3(P) groups. This region in D6 appears as could be anticipated for a methyl group. The situation is different however for D3, where one depolarized and two polarized bands are found. The latter two are, in agreement with observations on other O-CH_3 compounds, assigned to $\nu_s(CH_3O)$ and $2\delta_s(CH_3O)$, of which the

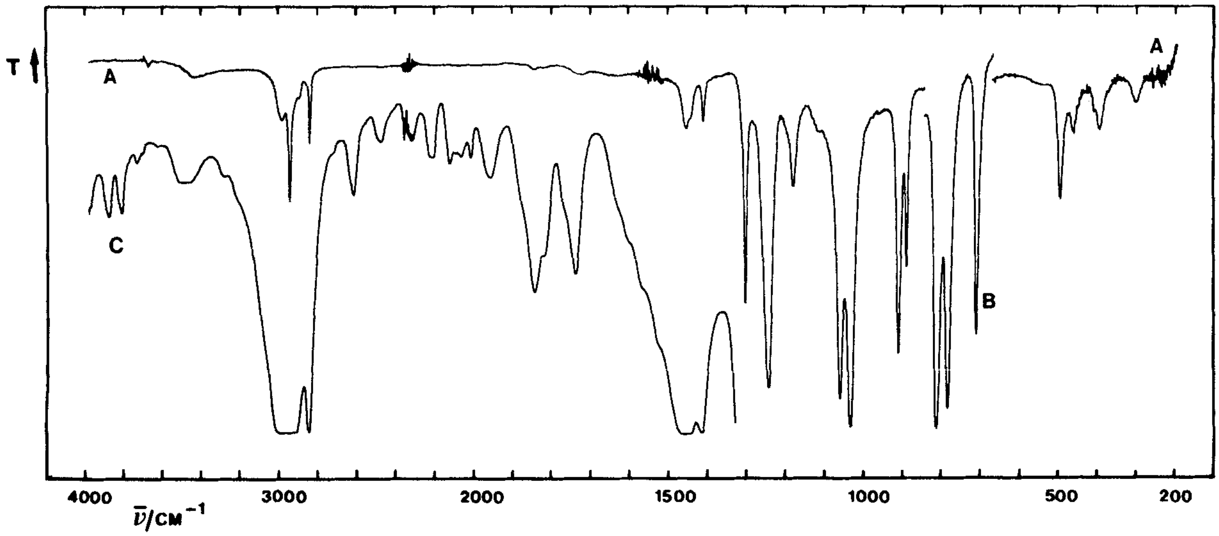

FIGURE 1 Infrared spectrum of liquid $CH_3PO(OCH_3)_2$. A: 5%-solution in CCl_4; B: 5%-solution in CS_2; C: pure liquid.

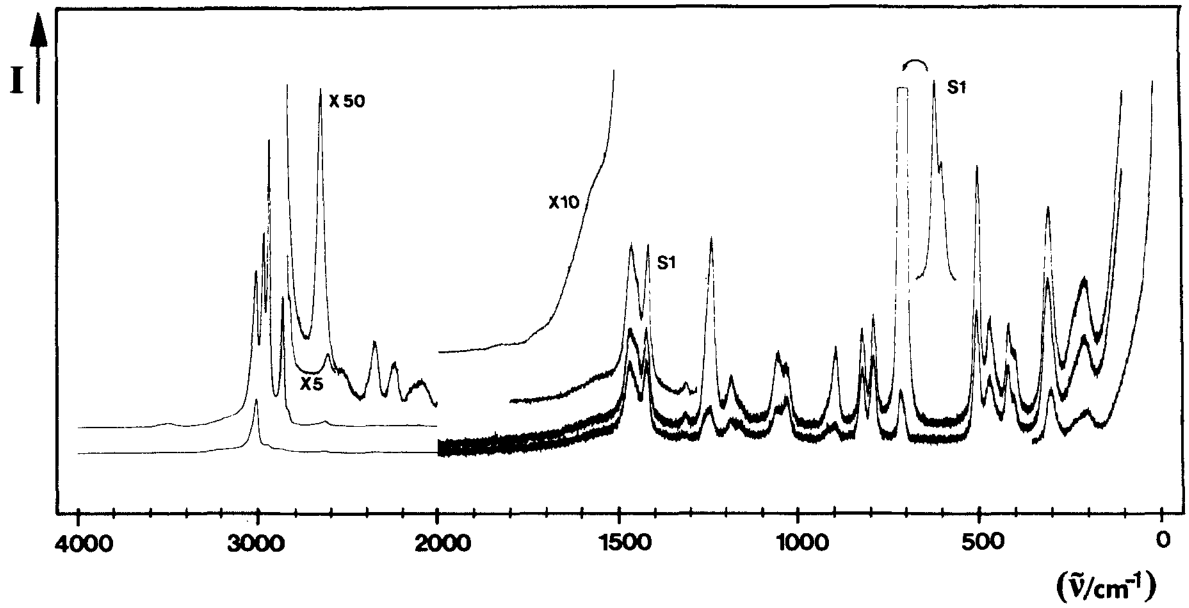

FIGURE 2 Raman spectrum of liquid $CH_3PO(OCH_3)_2$. (SI: details recorded with 1 cm^{-1} slit).

latter is in strong Fermi resonance with the former. Analogously, the region of CD_3 stretches is analyzed. Here also some unusual bands are observed, which we interpret to be due to Fermi resonances and wherefor possible interpretations are presented in the tables.

The assignments of F. Hérail of the $CH_3(P)$ and $CH_3(O)$ deformation and rocking vibrations[3,5] are substantiated by the present deuteration experiments. No special problems are encountered in detecting and assigning the CD_3 deformations and rockings.

The ν(P=O) in H9 has been observed to be split in two components[11] which was taken as evidence for the presence of two conformers in the liquid. We observe the same splitting in all the isotopic derivatives; this appears to lend support to the above proposal. If we look at the frequency of the most intense component (the other one appears as a shoulder, preventing accurate reading of the band maximum), we observe an upward shift, both in the pure liquid as in apolar solvents, when passing from H9 to D9. This behaviour can be explained by coupling of ν(P=O) with methyl deformations. In H9 they all lie on the high frequency side of ν(P=O), giving rise to a lowering of the latter. With increasing deuteration, more methyl deformations fall below ν(P=O), which in the case of coupling would tend to shift ν(P=O) in the opposite direction. Anyway, although the observations show that coupling exists, the magnitude of the shifts indicates the coupling is small.

L. C. Thomas[12] has specified the region from 680 to 785 cm^{-1} for the P-C stretch. It was assigned for H9 in i.r. to the 714 cm^{-1} band by G. G. Guilbault,[2] and to the band at 785 cm^{-1} by F. Hérail.[3] For $CH_3PO_3H_2$ and its anions this stretch has been assigned to the highly polarized, most intense band in the Raman spectrum near 760 cm^{-1}.[13] In the appropriate region of the Raman spectrum of H9, two bands are found at 786 and 712 cm^{-1} respectively. As is clear from Figure 2, the latter is the most intense band of the spectrum and is highly polarized, while the former is of medium intensity and depolarized. The analogy with $CH_3PO_3H_2$ then requires that the P-C stretch must be assigned to the 712 cm^{-1} band as suggested by Guilbault.[2] The same arguments were used to locate this vibration in the isotopically substituted derivatives. A high resolution scan of this band of H9 in Raman shows that it is actually a doublet, a weaker component appearing on the low frequency side. This, as for ν(P=O) could indicate the presence of two conformers in the liquid. Remarkable is the disappearance of the splitting in D3 and D9, accompanied by drastic intensity changes of other bands in the same region of the Raman spectra. A full understanding

TABLE II

Vibrational spectra of $CH_3PO(OCH_3)_2$

i.r. pure $\bar{\nu}$ I	i.r. CCl_4 $\bar{\nu}$ I	i.r. CS_2 $\bar{\nu}$ I	Raman pure $\bar{\nu}$ I	Assignments
3890 *w*				894 + 2992 = 3886
3825 *w*				894 + 2922 = 3816
3745 *vw*				786 + 2951 = 3737
	3688 *vw*			712 + 2951 = 3663
3630 *vw*				H_2O
3520 *w*				
3460 *w*	3450 *vw*	3450 *vw*		
3295 *vw*				303 + 2992 = 3295
	3015 *sh*		3015 *sh*	$\nu_a(CH_3O)$, $\nu'_a(CH_3O)$
2995	2995 *m*	2990 *m*	2992 *m*	$\nu_a(CH_3P)$, $\nu'_a(CH_3P)$
2955	2952 *m*	2950 *m*	2951 *m*, *p*	$\nu_s(CH_3O)$
2930	2908 *vw*	2905 *vw*	2922 *s*, *p*	$\nu_s(CH_3P)$
2852 *s*	2851 *m*	2848 *m*	2848 *m*, *p*	$2\delta_s(CH_3O)$ (see text)
			2820 *vw*, *sh*	1418 × 2 = 2836
2625 *w*			2609 *vw*	1185 + 1450 = 2635
2490 *w*			2480 *w*	1236 × 2 = 2476
2320 *w*			2320 *vw*	1418 + 849 = 2312
2220 *w*			2211 *vw*	786 + 1418 = 2204
2135 *w*			2116 *vw*, *sh*	1065 × 2 = 2130
2075 *w*			2052 *vw*	818 + 1238 = 2056
2025 *w*				786 + 1238 = 2024
1962 *w*				786 + 1183 = 1969 818 + 1152 = 1970
1875 *sh*				1065 + 818 = 1883
1848 *m*	1855 *vw*	1847 *vw*		1037 + 818 = 1855
1822 *sh*	1825 *vw*	1823 *vw*		1037 + 786 = 1823
1775 *sh*				1065 + 712 = 1777
1740 *m*	1750 *vw*	1747 *vw*		1240 + 499 = 1739
1605 *sh*				818 + 786 = 1604
1565 *sh*				1065 + 499 = 1564
1535 *sh*				1048 + 499 = 1538
1465	1462 *w*		1463 *m*	$\delta_a(CH_3O)$, $\delta'_a(CH_3O)$
1450	1450 *sh*		1450 *sh*	$\delta_s(CH_3O)$
1418 *s*	1418 *w*		1418 *m*	$\delta_a(CH_3P)$, $\delta'_a(CH_3P)$
1312	1309 *m*	1308 *s*	1310 *vw*, *p*	$\delta_s(CH_3P)$
1260(~)	1270 *sh*	1270 *sh*	1257 *sh*	$\nu(P{=}O)$ (see text)
1240	1250 *vs*	1250 *vs*	1238 *s*, *p*	$\nu(P{=}O)$
1185	1185 *m*	1185 *m*	1183 *w*, *p*	$\rho(CH_3O)$
			1152 *vw*, *sh*	$\rho(CH_3O)$
1058	1064 *vs*	1063 *vs*	1065 *m*, *p*	$\nu(CO)$
1032	1037 *vs*	1037 *vs*	1048 *w*	$\nu(CO)$
912	914 *s*	911 *s*	917 *sh*	$\rho'(CH_3P)$
895(~)	896 *m*	892 *m*	894 *m*, *p*	$\rho(CH_3P)$
818		814 *s*	818 *m*	$\nu(PO_2)$
787		788 *m*	786 *m*	$\nu(PO_2)$
712 *s*		713 *m*	712 *vs*, *p*	$\nu(PC)$ (see text)
			701 *sh*, *p*	$\nu(PC)$
		654 *vw*		231 + 412 = 643
499	501 *m*	500 *m*	499 *s*, *p*	$\delta(POC)$
467	468 *w*	468 *w*	464 *m*	$\delta_s(CPO_3)$
411	415 *sh*		412 *m*	$\delta_a(CPO_3)$, $\delta'_a(CPO_3)$
398	398 *w*		394 *w*, *sh*, *p*	
	307 *w*		303 *s*	$\rho(CPO_3)$, $\rho'(CPO_3)$
	232 *sh*		231 *w*, *sh*	$\gamma(POC)$
	205		201 *m*	$\gamma(POC)$
	98			libration

vs: very strong; *s*: strong; *m*: medium; *w*: weak; *vw*: very weak; *sh*: shoulder; *p*: polarized.

TABLE III

Vibrational spectra of $CH_3PO(O^{13}CH_3)_2$

i.r. CCl_4 $\tilde{\nu}$ I	i.r. CS_2 $\tilde{\nu}$ I	Raman pure $\tilde{\nu}$ I	Assignments
3675 ***vw***	3680 *vw*		710 + 2947 = 3657
3450 ***vw***	3445 *vw*		H_2O
		3060 *vw*	220 + 2843 = 3063
3000 ***w***	2995 *w*	2992 *s*	$\nu_a(CH_3O)$, $\nu'_a(CH_3O)$
2980 ***w***	2977 *w*		$\nu_a(CH_3P)$, $\nu'_a(CH_3P)$
2947 ***m***	2943 *m*	2945 *s*	$\nu_s(CH_3O)$
2903 ***vw***	2899 *vw*	2921 *vs*	$\nu_s(CH_3P)$
2846 ***w***	2843 *w*	2843 *s*	$2\delta_3(CH_3O)$ (see text)
	1965 *vw*		816 + 1150 = 1966 782 + 1175 = 1957
1835 *vw*	1835 *vw*		784 + 1052 = 1836 1025 + 814 = 1839
1805 *vw*	1808 *vw*		1025 + 784 = 1809
	1765 *vw*		1025 + 705 = 1757
1735 *vw*	1730 *vw*		1252 + 499 = 1751
1625 *vw*			H_2O
		1573 *vw*	1055 + 499 = 1554
1523 *m*			impurity
1517 *sh*			
1460 ***w***		1460 *m*	$\delta_a(CH_3O)$, $\delta'_a(CH_3O)$
1442 ***sh***		1442 *sh*	$\delta_s(CH_3O)$
1418 ***w***		1417 *m*	$\delta_a(CH_3P)$, $\delta'_a(CH_3P)$
1309 ***s***	1309 *s*	1309 *vw*	$\delta_s(CH_3P)$
1270(~) ***sh***	1270(~) *sh*		$\nu(P{=}O)$ (see text)
1252 ***vs***	1253 *vs*	1239 *m*	$\nu(P{=}O)$
1177 ***m***	1178 *m*	1175 *w*	$\rho(CH_3O)$
		1150(~) *sh*	$\rho'(CH_3O)$
1052 ***vs***	1052 *vs*	1055(~) *sh*	$\nu(CO)$
1025 ***vs***	1025 *vs*	1035 *w*	$\nu(CO)$
1003 ***w***	1002 *w*		impurity
		987 *w*	impurity
913 ***s***	912 *s*	911 *sh*	$\rho(CH_3P)$
894 ***m***	893 *m*	895 *vw*	$\rho'(CH_3P)$
869 ***w***			impurity
	814 *s*	816 *w*	$\nu_a(PO_2)$
	784 *m*	782 *w*	$\nu_s(PO_2)$
710 ***m***	711 *m*	705 *vs*	$\nu(PC)$ (see text)
700(~) ***sh***	700(~) *sh*	696 *m*	$\nu(PC)$
499 ***m***	500 *m*	499 *m*	$\delta(POC)$
467 ***w***	468 *w*	464 *w*	$\delta_s(CPO_3)$
408 ***w***		408 *sh*	$\delta_a(CPO_3)$, $\delta'_a(CPO_3)$
395 ***w***		389 *sh*	
305 ***w***	304 *w*	301 *m*	$\rho(CPO_3)$, $\rho'(CPO_3)$
		220 *sh*	$\gamma(POC)$
		201 *w*	$\gamma(POC)$

vs: very strong; *s*: strong; *m*: medium; *w*: weak; *vw*: very weak; *sh*: shoulder; *p*: polarized.

TABLE IV

Vibrational spectra of $CD_3PO(OCH_3)_2$

i.r. pure $\bar{\nu}$ I	i.r. CCl_4 $\bar{\nu}$ I	i.r. CS_2 $\bar{\nu}$ I	Raman pure $\bar{\nu}$ I	Assignments
3785 *vw*				802 + 2985 = 3787
3520 *w*				H_2O
3470 *w*			3472 *vw*	
	3450 *vw*	3450 *vw*		
3275 *w*	3275 *vw*	3270 *vw*	3014 *m*	1034 + 2247 = 3281
	3015 *sh*	3010 *sh*		
2995	2992 *w*	2985 *w*		$\nu_a(CH_3O)$, $\nu'_a(CH_3O)$
	2958 *m*	2950 *m*	2956 *s*, *p*	$\nu_s(CH_3O)$
2910 *sh*	2909 *vw*	2903 *vw*	2908 *vw*	673 + 2247 = 2920
2855 *vs*	2857 *m*	2851 *m*	2852 *s*, *p*	$2\delta_s(CH_3O)$ (see text)
2635 *w*			2620 *vw*	1185 + 1450 = 2635
			2522 *vw*	1067 + 1452 = 2519
2490 *w*				1246 × 2 = 2492
			2377 *vw*	1188 × 2 = 2376
2243 *s*	2250 *vw*		2247 *s*	$\nu_a(CD_3P)$, $\nu'_a(CD_3P)$
2148 *s*	2150 *vw*		2152 *s*, *p*	$\nu_s(CD_3P)$
2080 *w*	2080 *vw*		2077 *w*, *p*	1067 × 2 = 2134
2040 *w*			2042 *m*, *p*	1034 × 2 = 2068
			1967 *vw*	716 + 1246 = 1962
1905 *w*	1915 *vw*	1910 *vw*		840 + 1069 = 1909
1870 *m*	1880 *vw*	1875 *vw*		840 + 1034 = 1874
1835 *m*	1840 *vw*	1840 *vw*	1847 *vw*	802 + 1034 = 1836
1735 *m*	1745 *vw*	1747 *vw*		1248 + 487 = 1735
1705 *m*	1710 *vw*	1705 *vw*	1705 *vw*	673 + 1027 = 1700
	1660 *vw*	1665 *vw*		840 × 2 = 1680
1638 *vw*	1620 *vw*	1635 *vw*		H_2O
			1572 *w*	716 + 846 = 1562
1465	1461 *m*		1468 *s*	$\delta_a(CH_3O)$, $\delta'_a(CH_3O)$
1450(~)	1448 *sh*		1452 *m*, *sh*, *p*	$\delta_s(CH_3O)$
1270(~)	1275 *sh*	1274 *sh*	1265 *m*, *sh*, *p*	$\nu(P{=}O)$ (see text)
1248	1253 *vs*	1253 *vs*	1246 *s*, *p*	$\nu(P{=}O)$
1186	1184 *m*	1185 *m*	1188 *w*, *p*	$\rho(CH_3O)$
			1163 *w*	$\rho'(CH_3O)$
1067	1069 *vs*	1069 *vs*	1067 *m*, *p*	$\nu(CO)$
1035(~)	1038 *vs*	1038 *vs*	1034 *s*	$\nu(CO)$
1028	1028 *sh*	1027 *sh*		$\delta_a(CD_3P)$, $\delta'_a(CD_3P)$
965 *vw*	960 *vw*	961 *vw*		488 × 2 = 976
			926 *vw*	$\delta_s(CD_3P)$
842	847 *s*	840 *s*	846 *m*	$\nu_a(PO_2)$
802		799 *s*	802 *s*, *p*	$\nu_s(PO_2)$
716	704 *m*	711 *m*	716 *s*, *p*	$\rho(CD_3P)$
671	661 *m*	667 *m*	673 *vs*, *p*	$\nu(PC)$, $\rho'(CD_3P)$
487	482 *m*	481 *m*	488 *s*, *p*	$\delta(POC)$
458	461 *w*	461 *sh*		$\delta_s(CPO_3)$
410	409 *vw*		412 *m*	$\delta_a(CPO_3)$, $\delta'_a(CPO_3)$
392	392 *w*		396 *sh*, *p*	
	286 *w*		286 *s*	$\rho(CPO_3)$, $\rho'(CPO_3)$
	224 *sh*		229 *w*, *sh*	$\gamma(POC)$
	195		198 *m*	$\gamma(POC)$
	94			libration

vs: very strong; *s*: strong; *m*: medium; *w*: weak; *vw*: very weak; *sh*: shoulder; *p*: polarized.

TABLE V

Vibrational spectra of $CH_3PO(OCD_3)_2$

i.r. pure $\bar{\nu}$ *I*	i.r. CCl_4 $\bar{\nu}$ *I*	i.r. CS_2 $\bar{\nu}$ *I*	Raman pure $\bar{\nu}$ *I*	Assignments
3884 *w*				896 + 2996 = 3892
3817 *w*				896 + 2925 = 3821
2735 *vw*				806 + 2925 = 3731
	3683 *vw*			688 + 3000 = 3688
3520 *w*				H_2O
3460 *w*	3450 *vw*	3450 *vw*		
3360 *sh*				1068 + 2265 = 3333
3312 *w*				1068 + 2250 = 3318
3140 *vw*				1068 + 2080 = 3148
2996 *s*	3000 *vw*	2995 *vw*	2998 *m*	$\nu_a(CH_3P)$, $\nu'_a(CH_3P)$
2925 *s*	2933 *vw*	2930 *vw*	2927 *s*, *p*	$\nu_s(CH_3P)$
2860 *vw*	2860 *vw*		2850 *vw*, *sh*	1423 × 2 = 2846
2830 *sh*			2825 *vw*, *p*	
2740 *vw*				494 + 2250 = 2744
2625 *w*			2622 *vw*	494 + 2140 = 2634
2495 *w*				1251 × 2 = 2502
	2265 *w*, *sh*		2267 *m*	$\nu_a(CD_3O)$
2250 *vw*	2257 *w*			$\nu'_a(CD_3O)$
2210 *s*	2215 *w*		2214 *m*, *p*	1101 × 2 = 2202
	2157 *vw*			901 + 1251 = 2152
2140 *s*	2138 *vw*		2136 *m*, *p*	1069 × 2 = 2138
2080 *vs*	2083 *m*	2078 *m*	2083 *s*, *p*	$\nu_s(CD_3O)$
2000 *sh*			1995 *vw*	758 + 1251 = 2009
1975 *m*				901 + 1068 = 1969
1855 *sh*				809 + 1052 = 1861
1820 *m*	1825 *vw*			758 + 1068 = 1826
1800 *sh*			1800 *vw*	758 + 1052 = 1810
1734 *m*	1740 *w*	1738 *w*		1249 + 491 = 1740
1614 *w*			1625 *vw*	690 + 932 = 1622
1562 *vw*				758 + 809 = 1567
1496 *w*				688 + 809 = 1497
1483 *sh*				407 + 1072 = 1482
1418 *s*	1418 *w*		1423 *m*	$\delta_a(CH_3P)$, $\delta'_a(CH_3P)$
1355 *sh*				300 + 1045 = 1345
1314	1313 *m*	1310 *m*	1318 *vw*	$\delta_s(CH_3P)$
	1295 *vw*	1295 *vw*		491 + 806 = 1297
1249	1257 *s*	1257 *s*	1251 *s*, *p*	$\nu(P{=}O)$
1099	1101 *m*	1099 *m*	1101 *w*, *p*	$\delta_a(CD_3O)$, $\delta'_a(CD_3O)$, $\delta_s(CD_3O)$
1060(~)	1072 *vs*	1071 *vs*	1068 *m*	$\nu(CO)$
1043	1056 *vs*	1052 *vs*	1045 *w*, *sh*	$\nu(CO)$
930	932 *w*	932 *w*	932 *m*, *p*	$\rho(CH_3O)$, $\rho'(CH_3O)$
895	896 *m*	896 *m*	901 *m*	$\rho(CH_3P)$, $\rho'(CH_3P)$
808		806 *m*	809 *m*	$\nu_a(PO_2)$
755		754 *m*	758 *m*	$\nu_s(PO_2)$
688 *vs*	688 *m*	687 *m*	690 *vs*, *p*	$\nu(PC)$ (see text)
			682 *vs*, *p*	$\nu(PC)$
		605 *vw*		302 × 2 = 604
491	491 *m*	491 *m*	494 *s*, *p*	$\delta(POC)$
456 *vs*	457 *w*	458 *w*	458 *w*	$\delta_s(CPO_3)$
435 *sh*			435 *vw*	190 + 225 = 415
407 *vs*	404 *vw*, *sh*		408 *m*	$\delta_a(CPO_3)$, $\delta'_a(CPO_3)$
392 *sh*	389 *w*		394 *w*	
			375 *sh*, *p*	190 × 2 = 380
300 *s*	298 *w*		302 *s*	$\rho(CPO_3)$, $\rho'(CPO_3)$
	207 *sh*		225 *w*, *sh*	$\gamma(POC)$
	192		190 *w*	$\gamma(POC)$
	85			libration

vs: very strong; *s*: strong; *m*: medium; *w*: weak, *vw*: very weak; *sh*: shoulder; *p*: polarized.

TABLE VI

Vibrational spectra of $CD_3PO(OCD_3)_2$

i.r. pure $\bar{\nu}$ *I*	i.r. CCl_4 $\bar{\nu}$ *I*	i.r. CS_2 $\bar{\nu}$ *I*	Raman pure $\bar{\nu}$ *I*	Assignments
3515 *w*				H_2O
3450 *w*, *sh*	3450 *vw*	3450 *vw*		
3315 *w*				1080 +′ 2247 = 3327
3275 *w*				1030 + 2247 = 3277
3150 *w*				1080 + 2081 = 3161
2983 *m*	2983 *vw*	2980 *w*	2978 *vw*	CH stretches of incompletely deuterated molecules
	2965 *vw*			
2940 *vw*	2930 *vw*	2930 *vw*	2936 *vw*	
2915 *w*	2908 *vw*	2905 *vw*	2903 *vw*	
2875 *vw*			2876 *vw*	
2830 *vw*				
2745 *vw*				476 + 2247 = 2723
2505 *w*				1254 × 2 = 2508
2270(~)	2262 *sh*	2265 *sh*	2268 *w*, *sh*	$\nu_a(CD_3O)$, $\nu'_a(CD_3O)$
2250	2247 *w*	2245 *w*	2247 *m*	$\nu_a(CD_3P)$, $\nu'_a(CD_3P)$
2213 *s*	2209 *w*		2213 *w*, *p*	1099 × 2 = 2198
2144 *s*	2153 *vw*		2150 *m*, *p*	$\nu_s(CD_3P)$
	2133 *w*			1052 × 2 = 2104
2080 *s*	2079 *m*	2079 *m*	2081 *s*, *p*	$\nu_s(CD_3O)$
2040 *vw*			2039 *w*, *p*	1040 × 2 = 2080
			1987 *vw*, *sh*	712 + 1254 = 1966
1966 *w*				1068 + 900 = 1966
1885 *vw*				806 + 1080 = 1886
1847 *w*			1848 *vw*	806 + 1054 = 1860
1828 *w*				781 + 1054 = 1835
			1803 *vw*	712 + 1080 = 1792
1738 *w*		1730 *vw*	1740 *vw*	1080 + 655 = 1735
1705 *m*		1705 *vw*	1710 *vw*	1040 + 655 = 1695
1647 *vw*		1655 *vw*		H_2O
1481 *w*			1484 *vw*, *sh*	CH deformations of incompletely deuterated molecules
1459 *vw*			1458 *w*	
1446 *w*				
1393 *w*			1398 *vw*	
1369 *vw*		1367 *vw*	1371 *vw*	
		1280 *sh*		$\nu(P{=}O)$ (see text)
1252	1261 *s*	1263 *vs*	1254 *m*, *p*	$\nu(P{=}O)$
1163 *vw*	1165 *vw*	1165 *vw*		$\delta_a(CD_3O)$, $\delta'_a(CD_3O)$, $\delta_s(CD_3O)$
1100	1100 *m*	1099 *m*	1099 *m*, *p*	
1080	1080 *vs*	1080 *vs*	1068 *m*	$\nu(CO)$
1052	1055 *vs*	1054 *vs*		$\nu(CO)$
1030	1029 *w*	1037 *w*	1040 *m*, *p*	$\delta_a(CD_3P)$, $\delta'_a(CD_3P)$
965	955 *w*	955 *w*		$\delta_s(CD_3P)$
925	928 *w*	928 *m*	925 *m*, *p*	$\rho(CD_3O)$
900	895 *w*	900 *w*	900 *w*, *sh*	$\rho'(CD_3O)$
807		806 *s*	808 *w*	$\nu_a(PO_2)$
781		778 *s*	781 *m*, *p*	$\nu_s(PO_2)$
712	710 *m*	709 *m*	712 *s*, *p*	$\rho(CD_3P)$
674 *w*			677 *w*, *sh*	$\rho'(CD_3P)$
655 *s*	654 *m*	655 *m*	655 *vs*, *p*	$\nu(PC)$
	473 *m*	473 *m*	476 *s*, *p*	$\delta(POC)$
447 *s*	449 *w*	446 *w*	451 *w*	$\delta_s(CPO_3)$
401 *s*	402 *vw*		403 *w*	$\delta_a(CPO_3)$, $\delta'_a(CPO_3)$
382 *s*	381 *w*		384 *w*, *p*	
279 *s*	275 *w*		278 *m*	$\rho(CPO_3)$, $\rho'(CPO_3)$
	203 *sh*		211 *w*, *sh*	$\gamma(POC)$
	183		185 *m*	$\gamma(POC)$
	82			libration

vs: very strong; *s*: strong; *m*: medium; *w*: weak; *vw*: very weak; *sh*: shoulder; *p*: polarized.

of these phenomena appears to require more detailed (low temperature investigation, etc. ...) study of this region.

Some ambiguity in assignment of the intense i.r. band near 1000 cm^{-1}, characteristic for P-O-C groups exists.[12] As there are two P-O and two C-O stretches in the molecule, a total of 4 stretching bands will be anticipated. It can be expected that the P-O stretches will couple to a symmetric and an asymmetric component, while this would be much less so for the C-O stretches. This then implies that the P-O frequencies would be more separated than the C-O frequencies, while for the former, one polarized and one depolarized component can be expected. For H9 two intense i.r. doublet come into consideration for these vibrations. Due to their intensity, they are easily recognized in the other derivatives. As can be seen from the tables, in general the 800 cm^{-1} doublet separation is higher than for the 1060 cm^{-1} doublet, which would allow assignment based on the above separation consideration. For H9, the 1050 cm^{-1} doublet consists in Raman of one depolarized and one weakly polarized component, while the 850 cm^{-1} doublet consists of two depolarized bands. For D3 for instance the polarization situation is the same for the 1050 cm^{-1} doublet, while near 820 cm^{-1} one depolarized and one strongly polarized component are present. It is clear that depolarization ratios are an inadequate criterion to assign the present vibrations. Also, inspection of the tables shows that the band shifts upon deuteration are contradictory with anticipations from mass effects upon $\nu(CO)$ and $\nu(PO_2)$ vibrations. The reason for this probably is mechanical coupling of these stretches with CH_3 deformational modes, which undergo strong shifts with deuteration. Much "softer" however is the $^{12}C/^{13}C$ substitution: all methyl deformation and rocking frequencies remain almost unaltered, showing that the coupling does not change. Shifts then must be due to mass effects. A harmonic oscillator approximation suggests that the frequency ratio for CO stretches should be 1.023, while PO_2 stretches should remain unaltered. From the tables it is seen that the 1050 cm^{-1} doublet is lowered by some 11.5 cm^{-1} by the substitution, while the 800 cm^{-1} doublet lowers 2 cm^{-1}. It is thus clear that for dimethylmethylphosphonate the 1050 cm^{-1} doublet is due to CO stretches, leaving the PO_2 stretches to be assigned near 820 cm^{-1}. This is in agreement with the separation result stated above. Another, indirect, indication for this assignment can be found in the magnitude of the frequencies. It has been shown by D. W. J. Cruickshank[14,15] that in a P-O(H) bond there is more $(d_\pi - p_\pi)$ overlap than in a P-O(C) bond, due to hydrogen bonding effects. Thus the total P-O bond order in $CH_3PO_3H_2$ will be higher than for the ester. In the absence of force constants we have to use the sum of all P-O stretching frequencies as a measure for the total bond order. In this way we obtain 3135 cm^{-1} for the acid,[13] 3357 cm^{-1} if we assign the 1050 cm^{-1} doublet to the PO_2 stretches, and 2859 cm^{-1} if the 850 cm^{-1} doublet is identified with these vibrations. From what has been stated above, it is clear that the assignment of the 850 cm^{-1} doublet to the PO_2 stretches is to be preferred over the other possibility.

The methyl torsions $\tau(CH_3O)$ and $\tau(CH_3P)$ can be expected in the region 100–300 cm^{-1}. As has been stated above, for these vibrations the isotopic ratios are practically the same as for C–H stretches. In this region of the spectra some shifts are observed upon deuteration. They however are all much smaller than those calculated from the $\tau(CH_3)/\tau(CD_3)$ ratio. We therefore conclude that neither in Raman nor in infrared are the methyl torsions observed. A theoretical argument for the absence of the torsions in i.e. can be suggested on the basis of CNDO/2 calculations on the compound:[6,16] using dipole moment data obtained with this method, and employing a single symmetry coordinate to represent the torsions and a P-O-C out-of-plane deformation, an intensity ratio of 10^5 in favour of the out-of-plane deformation is calculated.[16] Even allowing for the simplicity of the vibration model and for inadequacies of the CNDO/2 method, the observation of only weak i.r. bands in the POC deformation region suggests strongly that the torsions are too weak to be detected in the i.r.

In Table VII we have indicated the observed CPO_3 deformation and rocking frequencies, together with the total π-bond order, of some phosphonic acids. These data were taken from Refs. 7, 15 and 17. It is clear that with increasing total π-bond order the deformations shift upward while the

TABLE VII

CPO_3-Deformation frequencies

Compound	$\Sigma n\pi$	$\delta s(CPO_3)$	$\delta a(CPO_3)$	$\rho(CPO_3)$
$CH_3PO_3H_2$	1.62	493	446	305
$CH_2ClPO_3H_2$	1.66	518	456	302

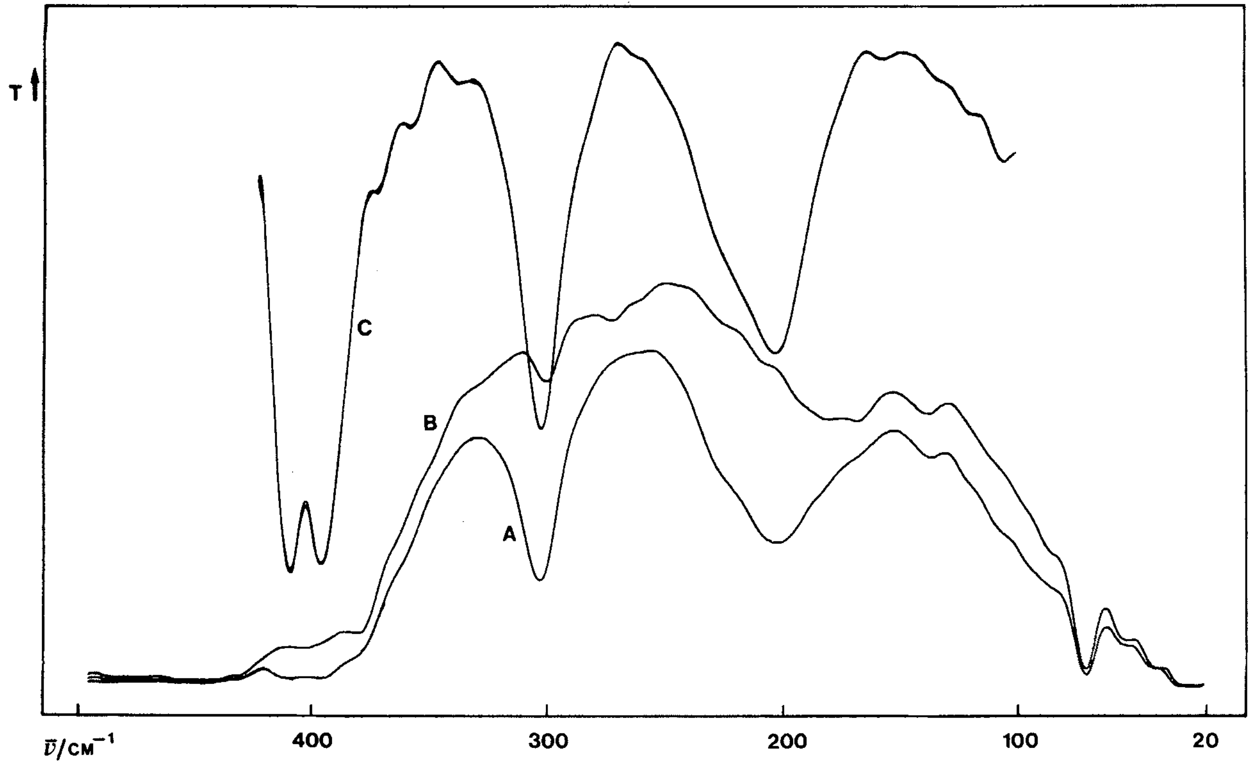

FIGURE 3 Far-infrared spectrum of $CH_3PO(OCH_3)_2$ in benzene (10%) with 6.25 μm beam splitter. A: sample, B: background; C: ratio.

rocking frequencies are less influenced. In the Raman spectrum of H9 bands are observed at 499, 464 and a doublet at 412–394 cm^{-1}. Due to the lower total π-bond order in the ester compared to $CH_3PO_3H_2$, it is logical, in view of the frequencies in Table VII, to assign the CPO_3 deformations in H9 to the bands at 464, 412 and 394 cm.$^{-1}$ In the region around 300 cm^{-1}, where from the results in Table VII the rockings are predicted, only a single band is observed. This is assigned to the CPO_3 rocking.

In the low frequency region of the spectra, the P-O-C in-plane and out-of-plane deformations remain to be assigned. The former are to be expected at higher frequencies because of the rehybridisation during this motion. In the spectra of H9 bands at 499, 231 and 201 cm^{-1} have not been identified yet. Consequently we assign both in-plane deformations accidentally degenerate at 499 cm^{-1} and the out-of-plane deformations at 231 and 201 cm^{-1}. The frequency ratio of the out-of-plane deformations is 1.15. This appears rather large for vibrations localised in analogous groupings. This number can however be rationalized from the truncated Fourier series analysis we performed on the conformational curves of CH_3-$PO(OCH_3)_2$: this analysis allows an analytical representation of the curves that give the energy of the molecule as a function of the dihedral angle defining the orientation of a methoxy grouping.[6] Near the minima, such a curve describes the out-of-plane vibrational coordinate for that particular equilibrium position. It consequently is possible to calculate $(\partial^2 V/\partial\rho^2)_{\rho=\min}$, the force constant governing the out-of-plane movement. This has been performed for the curve $\rho_2 = 60°$ (using the nomenclature of Ref. 18) for each of the three minima that occur in it. These minima correspond to the three staggered conformations that are possible for the methoxy grouping. The force constants that are obtained show the ratio 1 : 1.79 : 0.86 for the minima at 59, 188 and 290° respectively. For the (±ap; +sc) conformer, which is the most stable according to CNDO/2[6] the methoxy groupings appear with dihedral angles of 51 and 189 degrees. The above model calculation then shows that the ratio of the out-of-plane force constants must be near 1.79, which gives a frequency ratio of $(1.79)^{1/2} = 1.34$. This result clearly shows that, as observed, the out-of-plane frequencies can differ substantially from one another.

Below 100 cm^{-1} an intense, wide band is observed. Although the maximum is obscured by phenomena due to the polyethylene window absorption, the maxima can be determined reproducibly by extrapolation from band centres at transmissions below the band maximum. As is clear from the tables, a downward shift of the band maximum is observed with increasing deuteration. This band is assigned to the librational motions of the molecules. Its high intensity and relatively high frequency can be understood from the high polarity of the molecule, while the frequency shift must be due to the increasing moments of inertia.

REFERENCES

1. C. I. Meyrick and H. W. Thompson, *J. Chem. Soc.*, **1950**, 225.
2. G. G. Guilbault, E. Scheide, and J. Das, *Spectrosc. Lett.*, **1**, 167 (1968).
3. F. Hérail, *C.R. Acad. Sci. Paris, Sér. C.*, **262**, 1493 (1966).
4. F. Hérail, *C.R. Acad. Sci. Paris, Sér. C.*, **262**, 1624 (1966).
5. F. Marsault-Hérail, *J. Chim. Phys.*, **68**, 274 (1971).
6. B. J. Van der Veken and M. A. Herman, *J. Mol. Struct.*, **42**, 161 (1978).
7. B. J. Van der Veken and M. A. Herman, *J. Mol. Struct.*, **15**, 225 (1973).
8. J. Laane, *J. Chem. Phys.*, **55**, 2514 (1971).
9. B. J. von der Veken, D. H. C. Harris and G. Haines, *J. Chem. Soc. Farad. II*, **76**, 7485 (1980).
10. Upon request to the authors, copies of the spectra of the other species will be supplied.
11. F. Hérail and V. Viossat, *C.R. Acad. Sci. Paris*, **259**, 4629 (1964).
12. L. C. Thomas, Interpretation of the infrared spectra of organophosphorus compounds, Heyden, London, 1974, p. 90.
13. B. J. Van der Veken and M. A. Herman, *J. Mol. Struct.*, **15**, 225 (1973).
14. D. W. J. Cruickshank *J. Chem. Soc.*, **1961**, 5486.
15. B. J. Van der Veken and M. A. Herman, *J. Mol. Struct.*, **34**, 229 (1976).
16. B. J. Van der Veken, *Aggregaathesis*, Antwerpen, 1979.
17. B. J. Van der Veken, *J. Mol. Struct.*, **25**, 75 (1975).
18. B. J. Van der Veken and M. A. Herman, *J. Mol. Struct.*, **44**, 245 (1978).