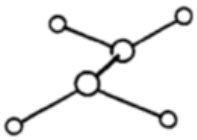
EXERCÍCIO 16

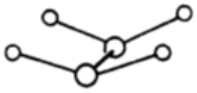
Segue anexo o artigo do Prof. Hans Stammreich sobre os espectros IR e Raman de P_2I_4 (S. G. Frankiss, F. A. Miller, H. Stammreich, Th. T. Sans, *Spectrochim. Acta* **23A**, 543 (1967)).

O artigo demonstra a estrutura *trans* do P_2I_4 

de acordo com o número de vibrações de cada espécie de simetria:

I_2PPI_2 structure with C_{2h} symmetry in the solid state and in solution. The fundamental frequencies suggested for the solution are: a_g — 316, 303, 114, 78; a_u — 327, 90, 51; b_g — 330, 95; b_u — 313, 109 and 65 cm^{-1}.

Mostre que esses números de vibrações de cada espécie de simetria para a estrutura *trans* do P_2I_4 estão corretos.

Por outro lado, se a estrutura do P_2I_4 fosse *cis*, grupo de ponto C_{2v}, 

como seria a representação de cada espécie de simetria?

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Infrared and Raman spectra and structure of P_2I_4

S. G. FRANKISS* and FOIL A. MILLER
Mellon Institute, Pittsburgh, Pa. 15213, U.S.A.

H. STAMMREICH and TH. TEIXEIRA SANS
Department of Physics, University of São Paulo, São Paulo, Brazil

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Abstract—The infrared spectrum from 33 to 550 cm^{-1}, and the Raman spectrum with some polarisation measurements, are reported for P_2I_4. The data indicate that P_2I_4 has the *trans* I_2PPI_2 structure with C_{2h} symmetry in the solid state and in solution. The fundamental frequencies suggested for the solution are: a_g – 316, 303, 114, 78; a_u – 327, 90, 51; b_g – 330, 95; b_u – 313, 109 and 65 cm^{-1}.

The infrared spectrum of PI_3 is also reported.

INTRODUCTION

MOLECULES of the type X_2Y_4 present interesting structural problems because they may have one or more of several conformations which may vary with the molecular state. The Group III subhalides B_2F_4 and B_2Cl_4, for example, are planar (D_{2h} symmetry) in the crystalline state [1, 2], but they are staggered (D_{2d} symmetry) in the vapor phase [3–6]. The vibrational spectra of the Group V hydrides N_2H_4[7] and P_2H_4[8, 9] in their various states have been interpreted on the basis of a *gauche* structure (C_2 symmetry). The subhalide N_2F_4 has also been reported to have a *gauche* structure in the vapor and solid states [10–12], but a recent fluorine resonance study has shown that the liquid probably consists of a mixture of *gauche* (C_2 symmetry) and *trans* (C_{2h} symmetry) conformers [13]. P_2Cl_4 has a *trans* structure in the vapor, liquid and solid states [14]. In contrast, P_2I_4 has been reported to have a *trans*

* Work carried out in part by this author at William Ramsay and Ralph Forster Laboratories, University College London, England.

[1] L. TREFONAS and W. N. LIPSCOMB, *J. Chem. Phys.* **28,** 54 (1958).
[2] M. AJOTI, P. J. WHEATLEY and W. N. LIPSCOMB, *J. Chem. Phys.* **27,** 196 (1957).
[3] J. N. GAYLES and J. SELF, *J. Chem. Phys.* **40,** 3530 (1964).
[4] A. FINCH, J. HYAMS and D. STEELE, *Spectrochim. Acta* **21,** 1423 (1965).
[5] D. E. MANN and L. FANO, *J. Chem. Phys.* **26,** 1665 (1957).
[6] K. HEDBERG and R. RYAN, *J. Chem. Phys.* **41,** 2214 (1964).
[7] A. YAMAGUCHI, I. ICHISHIMA, T. SHIMANOUCHI and S–I. MIZUSHIMA, *Spectrochim. Acta* **16,** 1471 (1960).
[8] M. BAUDLER and L. SCHMIDT, *Z. Anorg. Allgem. Chem.* **289,** 219 (1957) and *Naturwiss.* **44,** 488 (1957).
[9] E. R. NIXON, *J. Phys. Chem.* **60,** 1054 (1956).
[10] D. R. LIDE, JR., and D. E. MANN, *J. Chem. Phys.* **31,** 1129 (1959).
[11] J. R. DURIG and R. C. LORD, *Spectrochim. Acta* **19,** 1877 (1963).
[12] E. N. MOSKVITINA, Y. Y. KUZYAKOV, N. A. KNYAZEVA and V. M. TATEVSKII, *Opt. Spektroskopiya* **16,** 768 (1964); *Opt. Spectry.* **16,** 418 (1964).
[13] C. B. COLBURN, F. A. JOHNSON and C. HANEY, *J. Chem. Phys.* **43,** 4526 (1965).
[14] S. G. FRANKISS and F. A. MILLER, *Spectrochim. Acta* **21,** 1235 (1965).

structure in the solid state [15] and a *gauche* structure when dissolved in CS_2 [16, 17]. From this it has been concluded that an isolated P_2I_4 molecule probably has a *gauche* structure, but that the effects of crystal packing give rise to the *trans* structure in the solid [18]. The study of the Raman and infrared spectra of P_2I_4 reported here, however, is consistent with P_2I_4 having the *trans* structure both in CS_2 solution and in the crystalline state.

EXPERIMENTAL

Diphosphorous tetraiodide is an orange–red solid which melts (with decomposition) at about 124° [19]. It was prepared by a standard procedure from the constituent elements [19, 20]. In the solid state it was found to be stable indefinitely, but in solution it decomposes gradually: solutions of P_2I_4 in CS_2 or CH_3I become turbid and yellow decomposition products are formed, while solutions in CCl_4 or C_6H_6 darken rapidly.

The Raman spectrum of P_2I_4 was obtained at the University of São Paulo by excitation with the helium radiation 6678·15 Å using techniques outlined in previous communications by one of us [21]. The spectrum was photographically recorded on 103a F plates using a high speed spectrograph with an 1800 lines/mm plane grating having a ruled area of 128 × 102 sq mm and the first-order blaze at 5000 Å. The focal length of the camera is 76 mm, and its aperture is f/0·87. The reciprocal dispersion near 6750 Å, which corresponds to the position of the P_2I_4 spectrum, is approximately 87 cm^{-1}/mm, and the resolution here is better than 2 cm^{-1}. The frequency of sharp Raman bands could be determined with an error of $\pm 0{\cdot}5$ cm^{-1}.

The Raman spectrum of the solid was obtained from samples of the crystalline compound held in a space 1 mm thick between two glass cones. The intense radiation of the exciting line was adsorbed by a sharp cut-off secondary filter consisting of a 20 mm–50 mm layer of a nearly saturated aqueous solution of erbium perchlorate containing 325 g/l of erbium oxide. A 50 mm thickness of this solution transmits 0·003 per cent of the existing radiation 6678 Å and 50 per cent at 6738 Å, which corresponds to a Raman shift of 133 cm^{-1}. For the present work this filter is far superior to an arrangement of interference filters used in reflection. A nearly background-free spectrum showing the Raman active fundamental bands could be obtained with 2–5 minute exposures. Even with exposures of the order of an hour the background was sufficiently weak to allow the observation of very weak overtone and combination tones. Further details of this technique for the study of the Raman spectra of powdered or finely crystalline samples will be described separately.

The Raman spectra of solutions of P_2I_4 in CS_2, CH_3I, CCl_4 and C_6H_6 were

[15] Y. C. LEUNG and J. WASER, *J. Phys. Chem.* **60,** 539 (1956).
[16] M. BAUDLER and G. FRICKE, *Z. Anorg. Allgem. Chem.* **320,** 11 (1963).
[17] A. H. COWLEY and S. T. COHEN, *Inorg. Chem.* **4,** 1200 (1965).
[18] A. H. COWLEY, *Chem. Rev.* **65,** 617 (1965).
[19] F. E. E. GERMANN and R. N. TRAXLER, *J. Am. Chem. Soc.* **49,** 307 (1927).
[20] M. BAUDLER, *Z. Naturforsch.* **13b,** 266 (1958).
[21] H. STAMMREICH, *Spectrochim. Acta* **8,** 41 (1956), *Pure Appl. Chem.* **4,** 97 (1962) and elsewhere.

recorded; the spectrum of each of the solutions was overlaid by a strong fluorescence particularly in the region where the low-frequency fundamentals are located. Due to the background of the fluorescence spectrum only six strong bands, assigned to fundamental modes, were observed. The state of polarisation of three bands near 300 cm^{-1} was determined, but the background prevented polarisation measurements of the remaining three bands near 100 cm^{-1}.

The infrared spectrum of P_2I_4 was measured at Mellon Institute from 33 to 550 cm^{-1} with a Beckman IR-11 spectrophotometer. The compound was studied as a Nujol mull and as solutions in CS_2, C_6H_6 or CH_2Cl_2 in polyethylene or polypropylene cells. The infrared spectrum of PI_3 was also recorded in order to complement an earlier Raman study by one of us [22]. It too was studied as a Nujol mull and as solutions in CS_2, C_6H_6 or CH_2Cl_2.

Results

The Raman and infrared spectra of P_2I_4 and PI_3 are given in Tables 1 and 2, respectively. The frequencies of the bands for the various solutions are coincident to within experimental error, and the mean values are listed in Tables 1 and 2.

Four bands 313(m), 328(s), 332(s) and 355(w) cm^{-1} have been reported in the infrared spectrum of P_2I_4 dissolved in CS_2 [17]. We have examined this region under a resolution of less than 1 cm^{-1} but have not observed a strong band at 332 cm^{-1}. A weak–medium intensity shoulder at 332 cm^{-1} was observed in some of the CS_2 (but not C_6H_6) solutions. It cannot therefore be confidently assigned to the spectrum of P_2I_4, and it may be due to a decomposition product. We are, however, able to confirm the other three bands and the previously reported spectrum of solid P_2I_4 in this region [17].

The infrared spectrum of PI_3 as a Nujol mull has been reported to have a broad, featureless band between 290 and 330 cm^{-1} [17]. We observed this band in samples of PI_3 which had been recently recrystallised from CS_2. If the compound were left in a desiccator for an extended period, however, or were recrystallised from C_6H_6, then the well-defined bands reported in Table 2 were observed. The broad featureless band appears to be a superposition of the bands observed for the solid and the solution. It may occur only in samples of PI_3 which have a disordered structure.

Discussion of the Results

1. *The structure of solid* P_2I_4

An X-ray diffraction study of crystalline P_2I_4 has shown that it has a *trans* I_2PPI_2 structure with C_{2h} symmetry [15]. The vibrational spectrum of P_2I_4 can be satisfactorily assigned using this model (Table 1), and it therefore provides confirmatory evidence that this is indeed the correct structure. The absence of correlation field splitting is also consistent with the X-ray structure, which has shown that there is only one P_2I_4 molecule per unit cell [15].

[22] H. Stammreich, R. Forneris and Y. Tavares, *J. Chem. Phys.* **25**, 580 (1956).

Table 1. Raman and infrared spectra of P_2I_4

Solid		Solution		
Raman (cm^{-1}) I	Infrared (cm^{-1}) I	Raman (cm^{-1}) I ρ	Infrared (cm^{-1}) I	Assignment
	52 w		(51)	ν_7
	62(?) vw		(65)	Real? ν_{12}?
78·1* s		78† s, br		ν_4
	89 w		90 vw	ν_6
92·0 * s		95s		ν_9
106 w, br				$2 \times 52 = 104$
	112 m		109 m	ν_{11}
116·8* vs		114 vs		ν_3
139† vw, br				$52 + 89 = 141$
154† vw, br				$2 \times 78 = 156$: $(62) + 90 = 152$
166† vw, br				$78 + 92 = 170$: $52 + 112 = 164$
176† vw, br				$2 \times 89 = 178$: $62 + 112 = 174$
			179 w	$(65) + 114 = 179$
			190 vw	$78 + 109 = 187$
208† vw				$92 + 117 = 209$
				$109 + 114 = 223$: $313 - 95 = 218$
			216 vw	$303 - 90 = 213$: $327 - 114 = 213$ impurity?
	301 s		313 m	ν_{10}
306.9* vs		303 vs, p		ν_2
319 vw		316 s, p		ν_1: $92 + 2 \times 117 = 326$: $\nu_i + 328 - \nu_i$
327.8* s		330 s, dp		ν_8
	330 s		327 vs	ν_5
			354 w	$(51) + 303 = 354$
383† vw, br				$52 + 330 = 382$: $78 + 307 = 385$
406† vw				$78 + 328 = 406$
419† vw, br				$89 + 330 = 419$: $92 + 328 = 420$
442 w				$112 + 330 = 442$: $117 + 328 = 445$

w, m, s = weak, medium, strong
v = very
br = broad
p = strongly polarised band
dp = apparently depolarised band
( ) = assumed fundamental
ν_i = low-frequency bending fundamental

Estimated error: ± 1 cm^{-1}, except *: ± 0.5 cm^{-1} and †: ± 2 cm^{-1}.

Table 2. Raman and infrared spectra of PI_3

Solid		Solution					
Infrared		Raman [22]			Infrared		Assignment
(cm^{-1})	I	(cm^{-1})	I	ρ	(cm^{-1})	I	
84	w	79	10	dp	80	vw, br	ν_4, degen. PI_3 deformation
112	vw	111	7	p	112	vw	ν_2, sym. PI_3 deformation
					214	vw	impurity? $328 - 112 = 216$?
297	m	303	3	p	306	m	ν_1, sym. PI stretch
310	vs	325	1, br	dp	328	vs	ν_3, degen. PI stretch
					386	vw	$80 + 306 = 386$

w, m, s = weak, medium, strong
v = very
br = broad
p = strongly polarised band
dp = apparently depolarised band

2. *Previous structural determinations of* P_2I_4 *in solution*

There have been two previous structural determinations of P_2I_4 in solution, and both of them reported a *gauche* structure [16, 17]. The first was based on a calculation by BAUDLER and FRICKE [16] of the dipole moment of P_2I_4 in CS_2 from dielectric constant data. They obtained a dipole moment of 0·45 D, which was considered to be due to a *gauche* conformation with θ, the azimuthal angle of rotation of one PI_2 group relative to the other, equal to 85°. However, apart from possible experimental errors, there are two reasons why this conclusion is unreliable. The first reason is that the calculation of the 0·45 D dipole moment contains rather arbitrary estimates of the electron (P_e) and atom (P_a) polarisation terms in P_2I_4. We could expect that a molecule like P_2I_4 would have an abnormally high atom polarisation due to the large number of low-lying bending fundamentals and due to the presence of opposed dipoles [23]. An increase of only 5 per cent in the value of $P_e + P_a$ above that estimated by BAUDLER and FRICKE would account for the reported 0·45 D dipole moment. The second possible source of error comes from the decomposition of P_2I_4 in CS_2, since the decomposition products rather than P_2I_4 may have given the reported dipole moment. Because of these two reasons we feel that little weight should be attached to the *gauche* structure reported by BAUDLER and FRICKE [16].

The second previous structural determination was based on the observation of four bands between 300 cm^{-1} and 400 cm^{-1} in the infrared spectrum of P_2I_4 in CS_2 solution [17]. These bands were assigned to three or possibly four infrared active PI stretching fundamentals. Since the *trans* structure has only two infrared-active PI stretches it was concluded that P_2I_4 in solution has a *gauche* or possibly a *cis* structure. The present study shows, however, that one of these bands (355 cm^{-1}) is probably a combination tone, and that another (332 cm^{-1}) is not consistently observed. Thus only two (313 and 328 cm^{-1}) of the reported four bands can be confidently assigned to infrared-active PI stretches in P_2I_4. The infrared spectrum of P_2I_4 in this region is therefore consistent with the *trans* structure.

We conclude that the previously reported *gauche* or *cis* structures for P_2I_4 in solution are based on little if any substantial evidence.

3. *Determination of the structure of* P_2I_4 *in solution from its vibrational spectrum*

The vibrational spectrum of P_2I_4 provides no evidence that P_2I_4 in solution consists of two or more forms in equilibrium since the entire spectrum can be satisfactorily assigned to just one form. There is a considerable degree of similarity between the spectrum of the solid and the solution, particularly for the deformation fundamentals which do not differ by more than 3 cm^{-1} between the two states. Since P_2I_4 has a *trans* I_2PPI_2 structure in the solid state this similarity suggests that P_2I_4 in solution has a similar structure. It certainly precludes the possibility of a gross change of structure between the two states, and so P_2I_4 in solution does not have a structure with a bridged grouping or a planar PPI_2 group, similar to the structures that were discussed for P_2Cl_4[14]. We therefore conclude with confidence that P_2I_4 in solution has an I_2PPI_2 structure with a non-planer PPI_2

[23] J. W. SMITH, *Electric Dipole Moments*, pp. 264–276, Butterworth (1955).

group. The symmetry will be C_{2h}, C_2 or C_{2v} depending on whether the two I_2 groups are *trans*, *gauche* or *cis* to each other, respectively. The spectroscopic activity of these three models are described in Table 3.

An important criterion for deciding between these three models is whether or not the molecule contains a center of symmetry. This can be determined, for the point groups considered, from whether or not the rule of mutual exclusion is operating. There are some near coincidences between infrared and Raman bands, which are believed to be due to weak coupling between the vibrations in the two PI_2 groups, but there are no coincidences to within the reported experimental errors. This strongly suggests that the rule of mutual exclusion is operating and that P_2I_4 in solution

Table 3. Some possible conformations of P_2I_4; point groups; numbers and activity of normal P_2I_4; vibrations and stretching modes

Conformation	Point group	No. of fundamentals which are: Raman active	Infrared active	Both R and IR-allowed	No. of Raman-active stretches which are: polarised	depolarised
Trans ($\theta = 180°$)	C_{2h}	6	6	0	2	1
Gauche ($0 < \theta < 180°$)	C_2	12	12	12	3	2
Cis ($\theta = 0$)	C_{2v}	12	9	9	2	3

has the *trans* structure. Additional evidence favoring the *trans* structure comes from the direct observation of only six Raman-active and four infrared-active fundamentals. For the *gauche* and *cis* structures one would expect at least twelve Raman-active and nine infrared-active fundamentals (see Table 3). Finally, two of the Raman-active stretching fundamentals are polarised and one of them is depolarised, which is fully consistent with the *trans* structure. Thus the vibrational spectrum of P_2I_4 in solution clearly indicates that it has the *trans* structure, and this is confirmed by the satisfactory assignments that can be made on the basis of this structure (Table 1).

4. *Possible steric crowding in* P_2I_4

It is interesting to consider briefly some of the stereochemical implications of the *gauche* conformation that has been previously proposed for P_2I_4 in solution [16, 17]. We have calculated some of the non-bonded interatomatic distances in P_2I_4 assuming that P_2I_4 in solution has the same bond lengths and angles as in the crystalline state except that the azimuthal angle θ may differ from the value (180°) that it has in the solid. BAUDLER and FRICKE have suggested that θ decreases from 180° in the solid to 85° in CS_2 solution [16], but in order to reach this conformation the molecule would have to pass through a semi-eclipsed form where $\theta = 102°$ and the distance between the centers of the two eclipsed iodine atoms is only 2·55 Å. This distance is considerably less than the sum of the van der Waals radii of two iodine atoms (4·3 Å), and it is even less than twice the iodine covalent radius (2·7 Å). Very severe crowding is therefore expected for this semi-eclipsed conformation, so it is unlikely that the molecule could cross this potential barrier. Even if it could cross this barrier we find that when $\theta = 85°$ the shortest (I—I) distance is only 2·66 Å, and when $\theta = 51°$ (the *gauche* structure with one iodine atom staggered

between two at the opposite end of the molecule) there are three (I—I) distances of only 3·33 Å. We therefore expect that there would be severe crowding in these *gauche* conformations as well as in the semi-eclipsed conformation and it would be surprising from these considerations alone if P_2I_4 could be stable in any conformation except the *trans* one.

5. *Assignment of the fundamentals*

The normal vibrations and assignments for the *trans* non-planar I_2PPI_2 model are summarised in Table 4.

Table 4. Fundamental vibrations of *trans*-I_2PPI_2

C_{2h} Species	Activity	No.	Schematic description	Frequency (cm^{-1}) Solid	Solution
a_g	R(p), —	1	PP stretch	319 or 307	316
		2	PI stretch	307	303
		3	PI_2 wag	117	114
		4	PI_2 scissors	78	78
a_u	—, IR	5	PI stretch	330	327
		6	PI_2 twist	89	90
		7	PI_2 rock (torsion)	52	(51)
b_g	R(dp), —	8	PI stretch	328	330
		9	PI_2 twist	92	95
b_u	—, IR	10	PI stretch	301	313
		11	PI_2 wag	112	109
		12	PI_2 scissors	62(?)	(65)(?)

( ) From combination tone.

The fundamentals in P_2I_4 can be divided into a group above 300 cm^{-1} which are essentially stretching modes, and a group below 150 cm^{-1} which are largely deformation modes. We shall consider these two groups separately.

The fundamentals above 300 cm^{-1} in P_2I_4 solution can be assigned with some confidence since Raman polarisation data have been obtained. The apparently depolarised Raman band 330 cm^{-1} must be the b_g PI stretch ν_8, while the polarised Raman lines 316 and 303 cm^{-1} are clearly ν_1 and ν_2. These two fundamentals can be described as the symmetric PI stretch and the PP stretch, but we are unable to say which is which. It is possible that these descriptions are purely formal since the potential energy of two nearby fundamentals in the same species is expected to be distributed between the two corresponding symmetry coordinates. On the other hand, the fact that these two fundamentals are so close together may indicate that there is relatively little mixing.

The two infrared bands 327 and 313 cm^{-1} in the solution are assigned by analogy with the nearby Raman-active fundamentals. We take 327 cm^{-1} as the a_uPI stretch ν_5 and 313 cm^{-1} as the b_uPI stretch ν_{10}, thus making the frequency of the mode where the two geminal iodine atoms move out-of-phase higher than where they move in-phase in both the Raman and infrared spectra.

The infrared bands 330 and 301 cm^{-1} and the Raman bands 328 and 307 cm^{-1}

in the solid are assigned by analogy with the solution to ν_5, ν_{10}, ν_8 and ν_2 respectively. The assignment of ν_1 in the solid presents a difficulty as there is no band in the solid which corresponds clearly to the strong Raman band 316 cm^{-1} in the solution. Possible candidates for ν_1 in the solid are the very weak 319 cm^{-1} and the very strong 307 cm^{-1} (which has also been assigned to ν_2). The difficulty with taking 319 cm^{-1} as ν_1 is that it is very weak while 316 cm^{-1} in the solution is strong, though this could be partly explained if there were a first-order interaction between ν_1 and ν_2 in the solution but not in the solid. Alternatively, 319 cm^{-1} could be the ternary combination $92 + 2 \times 117 = 326$ cm^{-1} in Fermi Resonance with 328 cm^{-1}, or it may be a hot band of the type $\nu_i + 328 - \nu_i$, where ν_i is one of the low-lying bending modes, though this would require a rather high anharmonicity. If either of these two alternative assignments for 319 cm^{-1} is accepted then 307 cm^{-1} would have to be assigned to ν_1 as well as ν_2. This must be considered unlikely because two fundamentals belonging to the same species are expected to split apart. Nevertheless, since the magnitude of perturbation of two vibrational levels depends on interaction terms whose magnitude is unpredictable, one cannot rule out the possibility that the repulsion is negligible. Thus the assignment of 307 cm^{-1} to two a_g fundamentals, though unlikely, is by no means impossible. We feel that there is little to choose between these two sets of assignments, neither of which is wholly satisfactory, and we therefore prefer to assign ν_1 in the solid to 307 cm^{-1} or 319 cm^{-1}.

The remaining bands in the solid that can be assigned to the fundamental deformation modes are the three strong Raman lines 117, 92 and 78 cm^{-1} and the infrared bands 112, 89, 62 and 52 cm^{-1}. Although 89, 62 and 52 cm^{-1} are weak they are taken as fundamentals because they cannot be assigned to plausible difference tones, and because there is a shortage of any other bands that can be assigned to infrared-active deformations. The assignment of these bands cannot be made with certainty as Raman polarisation data are lacking. Nevertheless, it appears likely that each 'internal' vibrational motion in each of the two PI_2 groups gives rise to two normal modes of the whole molecule, one of species g and the other belonging to species u. The coupling between the two PI_2 groups is rather weak, and so there are near coincidences between corresponding g and u modes. Consequently, if we take the lowest infrared fundamental 52 cm^{-1} as the torsion ν_7, we are left with three pairs of fundamentals (62, 78 cm^{-1}), (89, 92 cm^{-1}) and (112, 117 cm^{-1}) which may be assigned to pairs of PI_2 scissoring, PI_2 twisting and PI_2 wagging fundamentals. We assign these three pairs of fundamentals by analogy with the similar modes in P_2Cl_4 [14] so that their frequencies decrease along the series PI_2 wag > PI_2 twist > PI_2 scissors.* A possible alternative assignment with the PI_2 scissors > PI_2 twist is less satisfactory as it places the neighboring bands 52 cm^{-1} and 62 cm^{-1} in the same species (a_u).

The deformation fundamentals in the solution are assigned by analogy with the solid. Infrared bands corresponding to the weak bands 52 cm^{-1} and 62 cm^{-1} in

* We have changed slightly the schematic descriptions of three of the fundamentals of P_2Cl_4 given in reference [14]. The description "PCl_2 rock" has been changed to "PCl_2 twist", while "PCl_2 twist (torsion)" has been changed to "PCl_2 rock (torsion)". These changes do not affect the assignments of P_2Cl_4 in reference [14].

the solid were not observed in the solution. The presence of infrared-active fundamentals near 51 cm^{-1} and 65 cm^{-1}, however, is inferred from the weak infrared bands 354 cm^{-1} and 179 cm^{-1} which are assigned to the combination tones (51) + 303 = 354 cm^{-1} and (65) + 114 = 179 cm^{-1}, respectively.

6. *Assignment of combination tones and overtones*

Plausible assignments for all the remaining bands in the solid can be made using the above fundamentals, and they are given in Table 1. For the solution, only the very weak infrared band 216 cm^{-1} is not satisfactorily assigned. The combination tone 109 + 114 = 223 cm^{-1} is probably too high. Alternative possible assignments are the difference tones 303 − 90 = 213 cm^{-1}, 313 − 95 = 218 cm^{-1} or 327 − 114 = 213 cm^{-1}, since the corresponding sum tones, if present, would not have been observed for the CS_2 or C_6H_6 solution because of nearby solvent bands, nor would they have been observed in the CH_2Cl_2 solution which was too dilute.

Conclusion

We have confirmed that crystalline P_2I_4 has a *trans* I_2PPI_2 structure with C_{2h} symmetry. In addition, we have shown that P_2I_4 also has the *trans* structure in solution. Thus P_2I_4 in the solid and liquid states has a geometry that is similar to P_2Cl_4 in its various states [14] but different from N_2H_4 [7], P_2H_4 [8, 9] and N_2F_4 [10–13].

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