Spectroscopic Analysis with Calculated Mean Amplitudes for P_4O_6 and P_4O_{10}

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Normal coordinate analyses are reported for P_4O_6 and P_4O_{10}. Harmonic force constants are given in terms of precisely defined symmetry coordinates. The force fields are used to calculate mean amplitudes of vibration, which are compared with electron diffraction data, and some discrepancies are discussed. Calculated atomic vibration mean-square amplitudes, which are of interest in crystallographic studies, are also given.

Different molecules of phosphorus oxides have been studied by several investigators. For some of the molecules the structures are known with great accuracy. Modern gas electron diffraction data exist for [1] P_4O_6 and for [2–5] P_4O_{10} in addition to previous works [6, 7]. Crystallographic studies have been performed for [1, 8] P_4O_8, for [2, 9] P_4O_9 and for [2, 10, 11] P_4O_{10}. Recently a spectroscopic inevstigation of the two most symmetrical ones of these molecules, viz. P_4O_6 and P_4O_{10}, has been communicated [12] as a part of an article series [12–14] dealing with phosphorus compounds. Previous investigations of the spectra for [15–17] P_4O_6 and for [17–20] P_4O_{10} have been reported, and also a very recent investigation of Raman spectra [21].

In the present work a complete normal coordinate analysis of harmonic vibrations for P_4O_6 and P_4O_{10} has been performed. Mean amplitudes of vibration [22] and related quantities have been calculated from the spectroscopic data. It is interesting to compare the calculated values with observed mean amplitudes [1, 2] from electron diffraction.

Molecular Models

The molecules of P_4O_6 and P_4O_{10} are both known to have structures of the symmetry T_d. Figures 1 and 2 explain the orientation of Cartesian axes and numbering of atoms adopted here. The applied structure parameters are [1]

$$S(\mathrm{P-O}) = 1.638\ \text{Å}, \qquad 2\,A(\mathrm{OPO}) = 99.8^\circ$$

for P_4O_6, and [2]

$$\begin{aligned} S(\mathrm{P-O_{br}}) &= 1.604\ \text{Å},\\ T(\mathrm{P=O}) &= 1.429\ \text{Å},\\ 2\,A(\mathrm{O_{br}PO_{br}}) &= 101.6^\circ \end{aligned}$$

for P_4O_{10}. Here O_{br} denotes a bridged oxygen atom.

Valence Coordinates

Fig. 1 shows the twelve P – O stretching coordinates, s_i. The twelve OPO bendings are represented by α_1, α_3 and α_5. In general each α_i is chosen as opposite to s_i. These two types of valence coordinates

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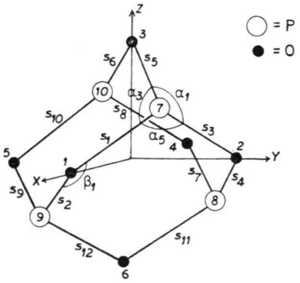

Fig. 1. The tetrahedral P_4O_6 type model.

are sufficient for a complete description of the molecular vibrations of the P_4O_6 model. Two additional types were introduced in order to analyse the P_4O_{10} model (see Fig. 2), viz. four $P=O$ stretchings, t_j, and twelve $O-P=O$ bendings, δ_i. The latter type is represented by δ_1 in Fig. 2. In gneeral each δ_i involves the two atoms of the s_i stretching in addition to a terminal oxygen atom. Six auxiliary bending coordinates were introduced, viz. the POP bendings β_k represented by β_1 in Fig. 1, and in general having atom number k as the apex. These coordinates have not been employed in the construction of symmetry coordinates, but they represent important bending motions of interbond angles.

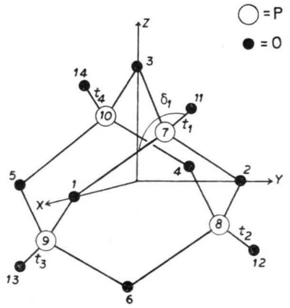

Fig. 2. The tetrahedral P_4O_{10} type model.

Symmetry Coordinates

The normal modes of vibration for P_4O_6 and P_4O_{10} are distributed among the symmetry species according to

$$\Gamma_{\text{vib}}(P_4O_6) = 2\,A_1 + 2\,E + 2\,F_1 + 4\,F_2$$

and

$$\Gamma_{\text{vib}}(P_4O_{10}) = 3\,A_1 + 3\,E + 3\,F_1 + 6\,F_2$$

respectively. A complete set of independent symmetry coordinates for the P_4O_{10} type model is specified in the following. A selection from the coordinates, namely the combinations of s_i and α_i, are applicable to the P_4O_6 type model.

$$S_1(A_1) = 12^{-\frac{1}{2}} \sum_{i=1}^{12} s_i\,,$$

$$S_2(A_1) = 12^{-\frac{1}{2}} S \sum_{i=1}^{12} \alpha_i\,,$$

$$S_3(A_1) = \sum_{j=1}^{4} t_j\,,$$

$$S_{1a}(E) = 24^{-\frac{1}{2}}(-s_1 - s_2 - s_3 - s_4 + 2\,s_5 + 2\,s_6 - s_7 - s_8 - s_9 - s_{10} + 2\,s_{11} + 2\,s_{12})\,,$$

$$S_{2a}(E) = 2^{-\frac{1}{2}} S(-\alpha_1 - \alpha_2 - \alpha_3 - \alpha_4 + 2\,\alpha_5 + 2\,\alpha_6 - \alpha_7 - \alpha_8 - \alpha_9 - \alpha_{10} + 2\,\alpha_{11} + 2\,\alpha_{12})\,,$$

$$S_{3a}(E) = (S\,T/24)^{\frac{1}{2}}(-\delta_1 - \delta_2 - \delta_3 - \delta_4 + 2\,\delta_5 + 2\,\delta_6 - \delta_7 - \delta_8 - \delta_9 - \delta_{10} + 2\,\delta_{11} + 2\,\delta_{12})\,,$$

$$S_{1b}(E) = 8^{-\frac{1}{2}}(s_1 + s_2 - s_3 - s_4 + s_7 + s_8 - s_9 - s_{10})\,,$$

$$S_{2b}(E) = 8^{-\frac{1}{2}} S(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 + \alpha_7 + \alpha_8 - \alpha_9 - \alpha_{10})\,,$$

$$S_{3b}(E) = (S\,T/8)^{\frac{1}{2}}\,(\delta_1 + \delta_2 - \delta_3 - \delta_4 + \delta_7 + \delta_8 - \delta_9 - \delta_{10})\,,$$

$$S_{1a}(F_1) = 8^{-\frac{1}{2}}(s_3 - s_4 - s_5 + s_6 + s_9 - s_{10} + s_{11} - s_{12})\,,$$

$$S_{2a}(F_1) = 8^{-\frac{1}{2}} S(\alpha_3 - \alpha_4 - \alpha_5 + \alpha_6 + \alpha_9 - \alpha_{10} + \alpha_{11} - \alpha_{12})\,,$$

$$S_{3a}(F_1) = (S\,T/8)^{\frac{1}{2}}\,(\delta_3 - \delta_4 - \delta_5 + \delta_6 + \delta_9 - \delta_{10} + \delta_{11} - \delta_{12})\,,$$

$$S_{1b}(F_1) = 8^{-\frac{1}{2}}(s_1 - s_2 - s_5 + s_6 + s_7 - s_8 - s_{11} + s_{12})\,,$$

$$S_{2b}(F_1) = 8^{-\frac{1}{2}} S(\alpha_1 - \alpha_2 - \alpha_5 + \alpha_6 + \alpha_7 - \alpha_8 - \alpha_{11} + \alpha_{12})\,,$$

$$S_{3b}(F_1) = (S\,T/8)^{\frac{1}{2}}\,(\delta_1 - \delta_2 - \delta_5 + \delta_6 + \delta_7 - \delta_8 - \delta_{11} + \delta_{12})\,,$$

$$S_{1c}(F_1) = 8^{-\frac{1}{2}}(s_1 - s_2 - s_3 + s_4 - s_7 + s_8 + s_9 - s_{10})\,,$$

$$S_{2c}(F_1) = 8^{-\frac{1}{2}} S(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 - \alpha_7 + \alpha_8 + \alpha_9 - \alpha_{10})\,,$$

$$S_{3c}(F_1) = (S\,T/8)^{\frac{1}{2}}\,(\delta_1 - \delta_2 - \delta_3 + \delta_4 - \delta_7 + \delta_8 + \delta_9 - \delta_{10})\,,$$

$$S_{1a}(F_2) = \tfrac{1}{2}(s_1 + s_2 - s_7 - s_8)\,,$$

$$S_{2a}(F_2) = 8^{-\frac{1}{2}}(s_3 - s_4 + s_5 - s_6 + s_9 - s_{10} - s_{11} + s_{12})\,,$$

$$\begin{aligned}
S_{3a}(F_2) &= \tfrac{1}{2} S(\alpha_1+\alpha_2-\alpha_7-\alpha_8),\\
S_{4a}(F_2) &= 8^{-\frac{1}{2}} S(\alpha_3-\alpha_4+\alpha_5-\alpha_6+\alpha_9-\alpha_{10}-\alpha_{11}+\alpha_{12}),\\
S_{5a}(F_2) &= \tfrac{1}{2}(t_1-t_2+t_3-t_4),\\
S_{6a}(F_2) &= \tfrac{1}{2}(ST)^{\frac{1}{2}}(\delta_1+\delta_2-\delta_7-\delta_8),\\
S_{1b}(F_2) &= \tfrac{1}{2}(s_3+s_4-s_9-s_{10}),\\
S_{2b}(F_2) &= 8^{-\frac{1}{2}}(s_1-s_2+s_5-s_6+s_7-s_8+s_{11}-s_{12}),\\
S_{3b}(F_2) &= \tfrac{1}{2} S(\alpha_3+\alpha_4-\alpha_9-\alpha_{10}),\\
S_{4b}(F_2) &= 8^{-\frac{1}{2}} S(\alpha_1-\alpha_2+\alpha_5-\alpha_6+\alpha_7-\alpha_8+\alpha_{11}-\alpha_{12}),\\
S_{5b}(F_2) &= \tfrac{1}{2}(t_1+t_2-t_3-t_4),\\
S_{6b}(F_2) &= \tfrac{1}{2}(ST)^{\frac{1}{2}}(\delta_3+\delta_4-\delta_9-\delta_{10}),\\
S_{1c}(F_2) &= \tfrac{1}{2}(s_5+s_6-s_{11}-s_{12}),\\
S_{2c}(F_2) &= 8^{-\frac{1}{2}}(s_1-s_2+s_3-s_4-s_7+s_8-s_9+s_{10}),\\
S_{3c}(F_2) &= \tfrac{1}{2} S(\alpha_5+\alpha_6-\alpha_{11}-\alpha_{12}),\\
S_{4c}(F_2) &= 8^{-\frac{1}{2}} S(\alpha_1-\alpha_2+\alpha_3-\alpha_4-\alpha_7+\alpha_8-\alpha_9+\alpha_{10}),\\
S_{5c}(F_2) &= \tfrac{1}{2}(t_1-t_2-t_3+t_4),\\
S_{6c}(F_2) &= \tfrac{1}{2}(ST)^{\frac{1}{2}}(\delta_5+\delta_6-\delta_{11}-\delta_{12}).
\end{aligned}$$

In the above set of symmetry coordinates some redundant combinations of δ_i are omitted, viz.

$$\begin{aligned}
S_{r1}(A_1) &= (ST/12)^{\frac{1}{2}} \sum_{i=1}^{12} \delta_i,\\
S_{r1a}(F_2) &= (ST/8)^{\frac{1}{2}}(\delta_3-\delta_4+\delta_5-\delta_6+\delta_9-\delta_{10}-\delta_{11}+\delta_{12}),\\
S_{r1b}(F_2) &= (ST/8)^{\frac{1}{2}}(\delta_1-\delta_2+\delta_5-\delta_6+\delta_7-\delta_8+\delta_{11}-\delta_{12}),\\
S_{r1c}(F_2) &= (ST/8)^{\frac{1}{2}}(\delta_1-\delta_2+\delta_3-\delta_4-\delta_7+\delta_8-\delta_9+\delta_{10}).
\end{aligned}$$

Also the inclusion of the β type bendings would lead to redundancies. The redundant symmetry coordinates are:

$$\begin{aligned}
S_{r2}(A_1) &= 6^{-\frac{1}{2}} S \sum_{k=1}^{6} \beta_k,\\
S_{ra}(E) &= 12^{-\frac{1}{2}} S(-\beta_1-\beta_2+2\beta_3-\beta_4-\beta_5+2\beta_6),\\
S_{rb}(E) &= \tfrac{1}{2} S(\beta_1-\beta_2+\beta_4-\beta_5),\\
S_{r2a}(F_2) &= 2^{-\frac{1}{2}} S(\beta_1-\beta_4), \quad S_{r2b}(F_2) = 2^{-\frac{1}{2}} S(\beta_2-\beta_5), \quad S_{r2c}(F_2) = 2^{-\frac{1}{2}} S(\beta_3-\beta_6).
\end{aligned}$$

Phosphorus Trioxide

Spectral Data

Phosphorus trioxide, P_4O_6, was investigated by Raman spectroscopy as early as 1942 by GERDING et al.[15]. It is interesting that modern investigations of both SIDOROV and SOBOLEV[16] and CHAPMAN[12] exactly confirm the F_2 frequencies of the old observation[15]. For frequencies of species E, however, there are serious discrepancies between GERDING et al.[15] and CHAPMAN[12]. In view of the more elaborate techniques and modern equipment of CHAPMAN, and his combined observations in infrared and Raman, it is reasonable to adopt his final assignment of frequencies with good confidence.

Force Field

It was attempted to produce a very simple force field according to

$$2V = f_s \sum_{i=1}^{12} s_i^2 + S^2 f_\alpha \sum_{i=1}^{12} \alpha_i^2 + S^2 f_\beta \sum_{k=1}^{6} \beta_k^2$$

with $f_\alpha = f_\beta$. The P – O stretching force constant was assumed to be $f_s = 3.4$ mdyne/Å according to CHAPMAN[12], and series of alternatives were tested for the bending constants. With $f_\alpha = f_\beta = 0.35$

mdyne/Å the calculated frequencies (see Table 1) were judged to be satisfactorily close to the observed values that the simple force field could be used as the initial set before the last refinement. Also the derived force constant values may be useful for tentative transferring to related molecules.

Table 1. Vibrational frequencies (cm^{-1}) for P_4O_6: wave numbers calculated from the initial approximate force field and observed values [12]. The parenthesized value is calculated by CHAPMAN [12].

Species	Approx. calc.	Obs.
A_1	620	613
	508	569
E	683	691
	291	285
F_1	906	832
	235	(282.6)
F_2	899	919
	624	643
	466	407
	326	302

The initial approximate force field was expressed in terms of the symmetry $\boldsymbol{F}$ matrix with the result as shown in Table 2. Let $\boldsymbol{f}$ be the diagonal matrix with elements f_s, f_α and f_β, which corresponds to the potential function (V) given above. Since the symmetry coordinates are independent and form a complete set, all the s_i, α_i and β_k coordinates may be expressed in terms of the symmetry coordinates.

Table 2. Initial and final symmetry force constants (mdyne/Å) for P_4O_6.

		Initial			Final	
A_1		3.40	0.00		4.180	− 0.128
			0.79			0.791
E		4.47	−0.52		4.584	− 0.527
			0.60			0.576
F_1		3.40	0.00		2.942	− 0.123
			0.35			0.500
F_2	initial	3.88	0.24	0.27	0.38	
			3.52	0.13	0.19	
				0.50	0.21	
					0.65	
F_2	final	4.066	0.316	0.305	0.477	
			3.599	0.072	0.132	
				0.442	0.205	
					0.542	

If the transformation is given as

$$\boldsymbol{R} = \boldsymbol{T}\,\boldsymbol{S}$$

in matrix notation it means that the $\boldsymbol{T}$ matrix may be determined uniquely. Consequently the $\boldsymbol{f}$ matrix may be converted to the symmetry $\boldsymbol{F}$ matrix by means of $\boldsymbol{T}$ according to

$$\boldsymbol{F} = \boldsymbol{T}'\,\boldsymbol{f}\,\boldsymbol{T}\,.$$

It is interesting to notice the existence of interaction force constants in $\boldsymbol{F}$ of the initial force field for species E and F_2, to which some of the β combinations belong. These terms are introduced merely through the mathematical conversion of the diagonal $\boldsymbol{f}$ matrix to $\boldsymbol{F}$. In species A_1 the relatively high value for the bending constant F_{22} obviously compensates for the omission of $S_{r2}(A_1)$ from the chosen symmetry coordinate set. These examples may be used as a warning against uncritical use of symmetry coordinates as the basis of an initial force field. In the present case, for instance, it seems unrealistic to assume a diagonal $\boldsymbol{F}$ matrix to be a good approximation.

A final harmonic force field was adjusted to fit exactly the observed frequencies [12] (see Table 1) with 283 cm^{-1} taken as the lowest F_1 frequency according to the cited Ref. [12]. The corresponding $\boldsymbol{F}$ matrix is shown in Table 2.

Mean Amplitudes of Vibration

The final force field was used to calculate the mean amplitudes of vibration [22]. Table 3 shows the results at absolute zero, 25 °C and 70 °C. The latter temperature is reported to be the nozzle and sample temperature of the electron diffraction experiment [1]. The electron diffraction results [1] for mean amplitudes are included in the table for comparison.

Atomic Vibration Mean-Square Amplitudes

Atomic mean-square amplitudes of vibration are important in modern interpretations of crystallographic data. Crystallographic analyses including these quantities are reported for [1] P_4O_8 and for [2] P_4O_9. The main contribution to the atomic mean-square amplitudes is supposed to be due to lattice vibration, but contributions from internal vibrations may be of importance. Internal atomic vibration mean-square amplitudes were calculated in the present work, and the results for P_4O_6 are shown in Table 4.

Table 3. Mean amplitudes of vibration (Å units) for P_4O_6. Electron diffraction values (with parenthesized standard deviations) are from Ref. [1].

Distance	(Equil.)	Spectroscopic 0 °K	Spectroscopic 25 °C	Spectroscopic 70 °C	Electron diffraction 70 °C	
P–O	(1.638)	0.0455	0.0472	0.0480	0.060	(0.002)
P···P	(2.925)	0.0497	0.0580	0.0605	0.053	(0.003)
O···O short	(2.506)	0.0669	0.0779	0.0812	0.086	(0.004)
O···O long	(3.544)	0.0674	0.0795	0.0829	0.09	(0.02)
P···P	(3.164)	0.0628	0.0760	0.0796	0.086	(0.003)

Hexagonal Phosphorus Pentoxide

In the calculations for hexagonal phosphorus pentoxide, P_4O_{10}, the same procedure was used as outlined above. The approximate form of the initial potential function was augmented to include f_t and f_δ for P=O stretchings and O–P=O bendings, respectively. After several trials the following values were determined as an acceptable starting point. $f_s = 5.3$ and $f_t = 10.9$ mdyne/Å for the P–O and P=O stretchings, respectively, in accordance with Chapman[12]; $f_\alpha = f_\beta = 0.35$ mdyne/Å transferred from P_4O_6 of the present work; $f_\delta = 0.60$ mdyne/Å.

The calculated frequencies from the initial approximate force field are shown in Table 5 along with different assignments. The observed frequencies from Chapman[12] are considered as the best experimental data. The assignment from his work (column 'b' of Table 5) displays several significant discrepancies on comparison with previous assignments (cf. column 'a' from a recent compilation by Krasnov et al.[23]). As the final assignment of the present calculations the observed frequencies from Chapman[12] were adopted and supplemented with calculated values from the approximate force field.

Table 4. Tensors of atomic vibration mean-square amplitudes (Å² units) for P_4O_6.

	Atom O (no. 1) x	Atom O (no. 1) y	Atom O (no. 1) z	Atom P (no. 7) x	Atom P (no. 7) y	Atom P (no. 7) z
0°K	0.0019	0.0000	0.0000	0.0009	0.0001	0.0001
		0.0020	–0.0008		0.0009	0.0001
			0.0020			0.0009
25°C	0.0025	0.0000	0.0000	0.0012	0.0002	0.0002
		0.0029	–0.0015		0.0012	0.0002
			0.0029			0.0012
70°C	0.0027	0.0000	0.0000	0.0013	0.0002	0.0002
		0.0032	–0.0017		0.0013	0.0002
			0.0032			0.0013

Table 5. Vibrational frequencies (cm^{-1}) for P_4O_{10}: wave numbers calculated from the initial approximate force field and different assignments. a: From Ref. [23], where a misprint for ν_2 (A_1) is corrected. This compilation includes Raman frequencies (A_1+F_2) from Ref. [19] of the year 1945. b: Chapman[12] with his calculated values in parentheses. c: Present final assignment with observed frequencies from Chapman[12] and calculated values from the approximate force field.

Species	Approx. calc.	Assignments a	Assignments b	Assignments c
A_1	1372	1417	1413	1413
	674	721	720	720
	451	424	556	556
E	959	952	(781)	(959)
	299	650	(370)	(299)
	280	278	257	(280)
F_1	1120	600	(954)	(1120)
	497	450	(389)	(497)
	222	300	(317)	(222)
F_2	1390	1386	1390	1390
	1064	1033	1010	1010
	822	764	760	760
	456	559	573	573
	339	329	424	424
	229	257	278	278

Table 6. Initial and final symmetry force constants (mdyne/Å) for P_4O_{10}.

	Initial			Final		
A_1	5.30	0.00	0.00	6.74	–0.35	0.59
		0.82	0.00		1.11	–0.28
			10.90			11.93
E	6.32	–0.49	0.00	6.32	–0.49	0.00
		0.58	0.00		0.58	0.00
			0.60			0.60
F_1	5.30	0.00	0.00	5.30	0.00	0.00
		0.35	0.00		0.35	0.00
			0.60			0.60
F_2 initial						
	5.75	0.24	0.26	0.37	0.00	0.00
		5.43	0.14	0.20	0.00	0.00
			0.50	0.21	0.00	0.00
				0.65	0.00	0.00
					10.90	0.00
						0.60
F_2 final						
	5.94	–0.04	0.15	0.20	0.29	0.50
		5.09	0.34	0.31	–0.42	0.00
			0.74	0.28	–0.09	0.02
				0.96	–0.19	0.05
					10.95	0.11
						0.81

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Table 7. Mean amplitudes of vibration (Å units) for P_4O_{10}. Electron diffraction values (with parenthesized reproducibilities) are from Ref. [2]. O_b and O_t designate bridged and terminal oxygen atoms, respectively.

Distance	(Equil.)	Spectroscopic			Electron diffraction	
		0 °K	25 °C	70 °C		
$P-O_b$	(1.604)	0.0405	0.0414	0.0418	0.057	(0.002)
$P=O_t$	(1.429)	0.0344	0.0345	0.0346	0.040	(0.003)
$P\cdots P$	(2.827)	0.0424	0.0477	0.0494	0.052	(0.003)
$O_b\cdots O_b$ short	(2.486)	0.0615	0.0711	0.0738	0.093	(0.006)
$O_b\cdots O_b$ long	(3.516)	0.0647	0.0765	0.0798	0.10	(0.03)
$O_b\cdots O_t$ short	(2.581)	0.0551	0.0610	0.0628	0.090	(0.006)
$O_b\cdots O_t$ long	(4.415)	0.0649	0.0792	0.0828	0.10	(0.01)
$P\cdots O_b$	(3.098)	0.0578	0.0698	0.0730	0.089	(0.004)
$P\cdots O_t$	(4.078)	0.0501	0.0560	0.0579	0.082	(0.005)
$O_t\cdots O_t$	(5.160)	0.0631	0.0746	0.0778	0.11	(0.02)

Table 8. Tensors of atomic vibration mean-square amplitudes (Å² units) for P_4O_{10}.

	O_{bridged} (no. 1)	P (no. 7)	O_{terminal} (no. 11)
	$x \quad y \quad z$	$x \quad y \quad z$	$x \quad y \quad z$
0 °K	$\begin{bmatrix} 0.0018 & 0.0000 & 0.0000 \\ & 0.0021 & -0.0010 \\ & & 0.0021 \end{bmatrix}$	$\begin{bmatrix} 0.0007 & -0.0000_2 & -0.0000_2 \\ & 0.0007 & -0.0000_2 \\ & & 0.0007 \end{bmatrix}$	$\begin{bmatrix} 0.0021 & -0.0004 & -0.0004 \\ & 0.0021 & -0.0004 \\ & & 0.0021 \end{bmatrix}$
25 °C	$\begin{bmatrix} 0.0024 & 0.0000 & 0.0000 \\ & 0.0034 & -0.0022 \\ & & 0.0034 \end{bmatrix}$	$\begin{bmatrix} 0.0009 & -0.0001 & -0.0001 \\ & 0.0009 & -0.0001 \\ & & 0.0009 \end{bmatrix}$	$\begin{bmatrix} 0.0032 & -0.0009 & -0.0009 \\ & 0.0032 & -0.0009 \\ & & 0.0032 \end{bmatrix}$
70 °C	$\begin{bmatrix} 0.0026 & 0.0000 & 0.0000 \\ & 0.0038 & -0.0025 \\ & & 0.0038 \end{bmatrix}$	$\begin{bmatrix} 0.0010 & -0.0001 & -0.0001 \\ & 0.0010 & -0.0001 \\ & & 0.0010 \end{bmatrix}$	$\begin{bmatrix} 0.0035 & -0.0010 & -0.0010 \\ & 0.0035 & -0.0010 \\ & & 0.0035 \end{bmatrix}$

Table 9. Alternative values of mean amplitudes (Å units) for P_4O_{10} at 70 °C consistent with assignments "a", "b" and "c" of Table 5. See also Table 7.

Distance	a	b	c	Electr. diff.[2]
$P-O_b$	0.049	0.044	0.042	0.057
$P=O_t$	0.035	0.035	0.035	0.040
$P\cdots P$	0.052	0.049	0.049	0.052
$O_b\cdots O_b$ short	0.070	0.068	0.074	0.093
$O_b\cdots O_b$ long	0.060	0.074	0.080	0.10
$O_b\cdots O_t$ short	0.069	0.066	0.063	0.090
$O_b\cdots O_t$ long	0.081	0.076	0.083	0.10
$P\cdots O_b$	0.068	0.067	0.073	0.089
$P\cdots O_t$	0.064	0.060	0.058	0.082
$O_t\cdots O_t$	0.083	0.079	0.078	0.11

The initial approximate force field was expressed in terms of the symmetry ***F*** matrix with the result as shown in Table 6. The table also gives the final ***F*** matrix, which is consistent with the frequency assignment of column 'c' in Table 5.

The final force field was used to calculate the mean amplitudes of vibration with the results shown in Table 7. Electron diffraction results[2] are included for comparison. Table 8 gives the calculated results for the internal atomic vibration mean-square amplitudes.

Discussion of Mean Amplitudes of Vibration

The comparison of mean amplitudes from spectroscopic calculations and from electron diffraction (see Tables 3 and 7) reveals several discrepancies which deserve a closer inspection. The most serious discrepancy occurs for the bonded P – O (bridged) distance in both molecules. The electron diffraction values for the $O_b \ldots O_t$ (short) and $P \ldots O_t$ distances in P_4O_{10} (see Table 7) are much larger than the values calculated here, but are of the same orders of magnitude as the corresponding values adopted by RAMBIDI et al.[4, 5] for characterization of P_4O_{10}, viz. $l_4 = 0.08$ and $l_7 = 0.10$ Å.

Additional calculations of mean amplitudes for P_4O_{10} were performed in the present work in order to judge the influence of different assignments of vibrational frequencies. Table 9 shows the results at 70 °C which are consistent with the assignments 'a' – 'c' of Table 5. It is clearly seen that these alternative assignments do not resolve the discrepancies. On the contrary the tendency of too large mean amplitudes from electron diffraction is accentuated for two additional distances, viz. $O_b \ldots O_b$ (short) and $P \ldots O_b$. In conclusion it seems inevitable to admit that some of the observed mean amplitudes for P_4O_6 and especially for P_4O_{10} are incompatible with the available spectroscopic data.