Study of the P_4O_7, P_4O_6S, and P_4O_6Se Vibrational Spectra

A. R. S. Valentim, B. Engels,* and S. Peyerimhoff

Institute of Physical and Theoretical Chemistry, Bonn University, Wegelerstrasse 12,
D-53115 Bonn, Germany

J. Clade and M. Jansen

Institute of Inorganic Chemistry, Bonn University, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

Received October 2, 1996⊗

The theoretical vibrational spectra of P_4O_6X (X = O, S, and Se) molecules are determined by employing the Hartree−Fock method in combination with a basis set of double-ζ quality plus polarization functions. A comparison of the three spectra is undertaken, and the shifts of the vibrational frequencies found in the spectra are analyzed. Two effects are considered to explain the changes in the band positions: the mass effect due to the replacement of oxygen by sulfur and selenium, respectively, and the bond strength effect. The mass effect of the substituent is as important as the different bond strengths of the $P^V{=}X$ bonds. Previous assignments of the bands in the P_4O_7 spectrum are also corrected by the theoretical research, and a new correlation among the experimental vibrational spectra of the three compounds is put forth. Newly performed Raman polarization measurements confirm our theoretical findings.

I. Introduction

Phosphorus heptoxide, P_4O_7, possesses the adamantane-like cage of P_4O_6 and one additional oxygen atom, which is localized in a peripheral position and linked to the cage by a pentavalent phosphorus atom. It is also known that the symmetry of the P_4O_6 cage is lowered in P_4O_7.[1−3]

When the peripheral oxygen atom is replaced by a sulfur or selenium atom, P_4O_6S or P_4O_6Se is obtained. Both molecules have basically the same structure as P_4O_7. Figure 1 shows the molecular structure of P_4O_6X and a summary of abbreviations used in the text. In comparison with P_4O_6, the monosubstituted compounds P_4O_6X show characteristic distortions in their structures: the bonds between P(V) and the neighboring oxygen atoms (O_b) are shorter than the P−O bonds in P_4O_6,[4,5] while the bonds between these oxygen atoms (O_b) and P(III) are slightly longer. Surprisingly, the distortion effects in P_4O_7, P_4O_6S, and P_4O_6Se are of the same magnitude.[6,7]

In recent work,[8,9] theoretical calculations have been performed for P_4O_6X for several different substituents X, ranging from the very electronegative F^+ to the electropositive N^-. The results showed that the changes in the bond lengths can be described in terms of the amount of charge being transferred from P(V) to the substituent, as indicated by the 1s orbital energy at P(V). A direct correlation between the 1s orbital energy of P(V) and the shortening of the P(V)−O_b bonds has been established. These studies showed no essential differences between the P_4O_6 cage geometries of P_4O_7 and P_4O_6S.

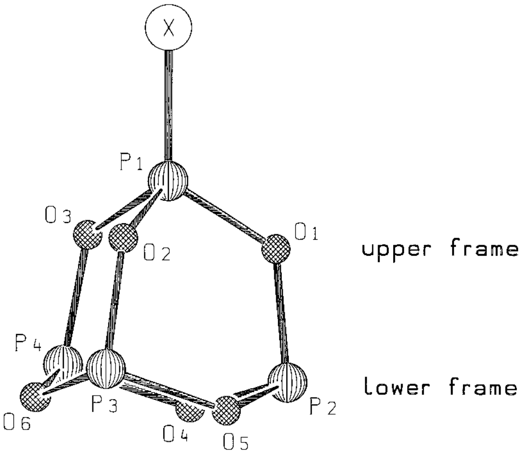

Figure 1. Molecular structure of P_4O_6X (X = O, S, and Se). The *xz* plane contains the nuclear centers X, P_1, O_1, P_2, and O_6. In the text P_1 will be called P(V). The centers O_1, O_2, and O_3, which possess the same chemical surroundings, will be abbreviated as O_b, while the name O_a is used for the centers O_4, O_5, and O_6. The remaining phosphorus atoms are called P(III) centers. The upper frame of the P_4O_6 cage consists of the centers P_1, O_1, O_2, and O_3, while the "lower frame" represents the ring built up from the centers P_2, P_3, P_4, O_5, O_6, and O_7.

In the present study, differences in the bonding situation in P_4O_7, P_4O_6S, and P_4O_6Se will be investigated by analyzing the frequency shifts in the vibrational spectra of these molecules. New experimental investigations are also performed to complete the data available in the literature.[1,7,10−15]

---

* E-mail: bernd@thch.uni-bonn.de.

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.

(1) Jansen, M.; Moebs, M. *Z. Anorg. Allg. Chem.* **1984**, *514,* 39.
(2) Jansen, M.; Voss, M. *Angew. Chem.* **1981**, *93*, 120.
(3) Jost, K.-H.; Schneider, M. *Acta Crystallogr. B* **1981**, *37*, 222.
(4) Jansen, M.; Voss, M.; Deiseroth, H.-J. *Angew. Chem.* **1981**, *93,* 1023.
(5) Jansen, M.; Moebs, M. *Inorg. Chem.* **1984**, *23*, 4486.
(6) Frick, F.; Jansen, M.; Bruna, P. J.; Peyerimhoff, S. D. *Chem. Ber.* **1991**, *124*, 1711.
(7) Clade, J.; Jansen, M.; Engels, B.; Marian, C. M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 2065.
(8) Mülhäuser, M.; Engels, B.; Marian, C. M.; Peyerimhoff, S. D.; Bruna, P. J.; Jansen, M. *Angew. Chem.* **1994**, *106*, 578.
(9) Mülhäuser, M. Quantenmechanische Rechnungen an Phosphoroxiden. Diplomarbeit, Bonn University, Bonn, 1991.
(10) Mielke, Z.; Andrews, L. *J. Phys. Chem.* **1989**, *93*, 2971.
(11) Slivko, S. A.; Krivovyazov, E. L. *Zh. Neorg. Khim.* **1993**, *38*, 1755; *Russ. J. Inorg. Chem.* **1993**, *38*, 1735.
(12) Walker, M. L.; Peckenpaugh, D. E.; Mills, J. L. *Inorg. Chem.* **1979**, *18*, 2792.
(13) Frick, F. Dissertation, Bonn, 1993.
(14) Frick, F. Diplomarbeit, Bonn University, Bonn. 1990.
(15) Clade, J.; Frick, F.; Jansen, M. *Adv. Inorg. Chem.* **1994**, *41*, 327.

S0020-1669(96)01202-5 CCC: $14.00

Table 1. Description of the Vibrational Modes Calculated for P_4O_7, P_4O_6S, and P_4O_6Se

mode no.	sym	description
1	A_2	bulk, upper frame; deformation of P(V)−O_b
2	A_2	bulk, lower frame deformation; P(III)−O_a stretching motion
3, 4	E	P(V)═O bending (X = O, S, and Se) (Figure 4)
5, 6	E	bulk (Figure 5)
7, 8	E	bulk; for P_4O_7 some contribution of P(V)═O bending
9, 10	E	bulk
11, 12	E	bulk, bending lower and upper frame due to O movement
13, 14	E	bulk, lower frame deformation; POP symmetric stretching
15, 16	E	bulk, connecting upper−lower frame motion; antisymmetric stretching of P(III)−O_b
17, 18	E	bulk, upper frame; antisymmetric stretching of P(V)−O_b (Figure 6)
19, 20	E	bulk; antisymmetric stretching in upper and lower frame (Figure 7)
21	A_1	P(V)═X moves as a unit for X = O, S, out of phase with lower frame oxygen atoms; for X = Se, only Se moves but not P(V) (Figure 8)
22	A_1	similar to mode 21
23	A_1	bulk, cage breathing; small contributions from P(V)═X stretching; for X = O, P(V)═X moves in phase; for X = S, Se, out of phase
24	A_1	bulk, lower frame primarily stretching
25	A_1	bulk, upper frame symmetric bending and lower frame symmetric stretching; small contribution of P(V)═X stretching; P(V)═X moves in phase for X = O, but out of phase for X = S, Se
26	A_1	bulk, upper frame symmetric stretching; small contribution of, P(V)−O_b stretching; P(V)═X moves in phase for X = O, but out of phase for X = S, Se (Figure 9)
27	A_1	P(V)═X stretching for P_4O_7, P_4O_6S; for P_4O_6Se, Se does not move significantly (Figure 10)

In order to explain the frequency shifts, three effects will be considered in this work. Two obvious effects are the different masses of the substituents X and the varied bond strengths of P(V)═X. In addition, differences in the bonding situation of the P_4O_6 cage will be addressed. A short description of the vibrational modes will also be provided, and selected modes will be plotted for an easier understanding of the nuclear motion. Our results will be compared to previous experimental studies reported in the literature.[1,10] Recently Slivko and Krivovyazov performed a theoretical study of the vibrational frequencies of the P_4O_7 molecule based upon MNDO/H calculations.[11] However, their results do not show the right molecular geometry, i.e., they do not yield the trend of alternate shortening and lengthening of the cage bonds. Furthermore, their assignment does not agree with previously reported Raman polarization data.[1]

II. Methods

The molecular geometries of P_4O_7, P_4O_6S, and P_4O_6Se were optimized using the SCF procedures employing a DZP basis set given by Schäfer.[16] For the phosphorus atom the AO basis set consists of a (11s7p1d) Gaussian set contracted to [6s4p1d], using $\alpha_d = 0.45$ as the exponent for the d-function. The oxygen basis set consists of the (8s4p1d) set contracted to [4s2p1d] with a d-function exponent of $\alpha_d = 1.20$. For the sulfur atom the (11s7p1d)/[6s4p1d] set with $\alpha_d = 0.55$ was used, while the basis set for selenium consists of (14s11p6d)/[8s5p3d] with $\alpha_d = 0.338$. Hence the total numbers of contracted Gaussians are 197, 205, and 223 for P_4O_7, P_4O_6S, and P_4O_6Se, respectively.

In order to check the accuracy of the method as a function of various technical parameters, a larger AO basis set and improved methods of calculation were employed. Calculations for P_4O_7 using the same DZP basis set but the DFT (B3-LYP) method overestimate the P(V)−O_b bond by 4.6 pm relative to the corresponding HF result, which in turn yields a bond length which is already longer than that obtained from crystal structure analysis.[1−3] If the larger TZ2P (527 AOs) set is used, the error in the calculated bond length is reduced to 1.8 pm (B3-LYP) and −1.5 pm (Hartree−Fock) relative to the experimental value. It was concluded that even more expensive calculations would be necessary for perfect agreement and that, due to error cancellation, the Hartree−Fock method in combination with the DZP basis set represents an adequate tool for the present investigation.

The vibrational frequencies including the IR and Raman intensities were calculated at the optimized geometry for each of the molecules considered. The calculated intensities, which are in qualitative agreement with those determined experimentally, were used for the assignment of the normal modes. All calculations were performed with the GAUSSIAN92 code.[17] In order to correct errors of the Hartree−Fock force field,[18] the frequencies were scaled uniformly by factors of 0.92, 0.90, and 0.91 for P_4O_7, P_4O_6S, and P_4O_6Se, respectively. The scaling factor was obtained by adjusting the calculated value for the most intense Raman band to its experimental counterpart.

The experimental vibrational spectra of P_4O_7 were discussed earlier,[1] and the experimental vibrational frequencies of P_4O_6S[12,14,15] and P_4O_6Se[7] have been briefly reported. To check the new assignments suggested by the computations of the present work, new Raman polarization measurements were performed for P_4O_6S and P_4O_6Se. Measurements of P_4O_6S and P_4O_6Se were examined in CS_2 solutions using a Bruker RFS 100 Raman interferometer. It should be kept in mind that with the help of Raman polarization measurements an unambiguous assignment of the symmetry classes of the modes is possible for C_{3v} molecules because only a_1 modes show strongly polarized Raman bands and a_2 modes are inactive in both Raman and IR spectra.

III. Results and Discussion

As shown in previous studies,[8,9] the geometries optimized with the HF/DZP method are in good agreement with the structures obtained by X-ray diffraction methods,[1−3,6,7] the deviations between the theoretical and experimental bond lengths being approximately 2 pm.

In Table 1 a short description is given for each calculated P_4O_6X vibrational mode, while the computed frequencies and the calculated IR and Raman intensities of P_4O_7, P_4O_6S, and P_4O_6Se are shown in Tables 2, 3, and 4, respectively. The tables also contain the experimental results. In addition, the newly obtained experimental Raman spectra of P_4O_6S and P_4O_6Se are depicted in Figures 2 and 3, respectively. The symmetry of the P_4O_6X frame is C_{3v}. The various vibrational modes will be discussed in terms of symmetry classes A_2, E, and A_1.

As already mentioned above, the geometrical distortions of all three compounds P_4O_7, P_4O_6S, and P_4O_6Se relative to P_4O_6

---

(16) Schäfer, A. *J. Chem. Phys.* **1992**, *97*, 2571.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Gordon, M. H.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN92*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1992.

(18) Pulay, P. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; Part II.

Table 2. Correlation between Experimental and Theoretical Uniformly Scaled Infrared Bands of P_4O_7

		expt[a]			theory		
		intensities[b]				rel intensities	
mode no.	sym	IR	Raman	freq (cm^{-1})	freq (cm^{-1})	IR	Raman
1	A_2				292	0	0
2	A_2				670	0	0
3, 4	E	m	m	269	255	0	5
5, 6	E	vw	m	306	302	0	7
7, 8	E	vw	w	333	338	0	1
9, 10	E	m	m	392	429	5	17
11, 12	E				578	0	0
13, 14	E	w	m, p[c]	657	653	5	19
15, 16	E	m	vw	708	731	9	0
17, 18	E				763	0	0
19, 20	E	s, br	vw	960	1008	100	4
21	A_1	m	m, p	429	389	1	17
22	A_1	m	m, p	534	557	2	11
23	A_1	m	vs, p	625	624	1	100
24	A_1	w	m, p[c]	657	645	15	31
25	A_1				738	0	13
26	A_1	sh	vw, p (?)	935	993	70	4
27	A_1	s	m, p	1333	1373	46	46

[a] Reference 1. [b] p = polarized, vs = very strong, s = strong, m = medium, w = weak, vw = very weak. [c] These bands of A_1 and E symmetries appearing nearly at the same frequency could not be separated.

Table 3. Correlation between Experimental and Theoretical Uniformly Scaled Infrared Bands of P_4O_6S

		expt			theory		
		intensities				rel intensities	
mode no.	sym	IR	Raman	freq (cm^{-1})	freq (cm^{-1})	IR	Raman
1	A_2				284	0	0
2	A_2				666	0	0
3, 4	E		s	178	171	0	35
5, 6	E		m	296	295	0	1
7, 8	E		w	313	311	0	4
9, 10	E	m	m	415	412	3	27
11, 12	E				574	0	1
13, 14	E	w	w[a]	653	640	3	28
15, 16	E	m	w, p[b]	690	680	2	1
17, 18	E				726	0	0
19, 20	E	sh		1010[c]	979	59	5
21	A_1		m, p	344	335	0	64
22	A_1	w	s, p	505	507	5	56
23	A_1	m	s, p[d]	≈592	590	3	100
24	A_1	w	s, p[d]	≈632	626	6	88
25	A_1		w, p[b]	690	697	0	53
26	A_1	s, br	w, p	945	968	100	12
27	A_1	m	w[a]	814	795	0	6

[a] Only visible in the spectrum of crystalline P_4O_6S. [b] These bands of A_1 and E symmetries appearing nearly at the same frequency could not be separated. [c] Appears as a shoulder in the IR spectrum; not visible in the Raman spectrum. [d] The splitting of these bands is probably due to Fermi resonances with 2×(5,6) and 2×(7,8), respectively (see Figure 2).

are of the same order of magnitude. Therefore it is expected that the modes which involve primarily the cage atoms are very little affected if the substituent is varied from O to S and Se. Because we are interested in the influences of the various substituents X on the bonds in the P_4O_6 cage, the most interesting modes in this context are those in which the P(V)−O_b distances change. Clearly, the modes in which the motion of the X atom is involved are expected to show large frequency shifts when X changes from O to S and Se. To distinguish between mass and bond strength effects, as mentioned above, additional calculations are carried out in the following manner: the molecular geometry and the bond strengths of P_4O_7 being maintained, but the mass of the terminally bound atom being replaced by the mass of sulfur (32 amu) and selenium (79 amu), respectively, the frequencies were calculated again.

Due to the molecular symmetry, the internal coordinate P(V)═X does not change in a_2 modes, i.e., only cage atoms are involved in vibrational motion belonging to this symmetry class. The first a_2 mode shows predominantly a deformation of the "upper frame", while the second involves primarily the "lower frame" atoms. For the reasons given above, the frequencies for these modes are expected to be essentially the same in P_4O_7, P_4O_6S, and P_4O_6Se. Indeed, Tables 2−4 show very small shifts for the calculated bands: 8 cm^{-1} for the first located at 292 cm^{-1}, and 7 cm^{-1} for the second around 670 cm^{-1}. Unfortunately, we cannot support this fact by the experimental spectra, because the modes of this symmetry are inactive in both IR and Raman spectra.

The first e mode (numbers 3 and 4) is plotted in Figure 4 and consists of a bending motion of the P(V)═X bond. For this reason a strong dependence on the substituent is expected for this band, causing a large frequency shift in the spectra going from P_4O_7 to P_4O_6Se, as is seen from Table 2 to 4. For P_4O_7, the frequency of this band is 255 cm^{-1} in our calculations and changes to 171 cm^{-1} and 130 cm^{-1} for P_4O_6S and P_4O_6Se, respectively, i.e., a lowering of almost 50%. The calculated frequency shift of 125 cm^{-1} (P_4O_7 to P_4O_6Se) is in perfect agreement with the measured shift of 128 cm^{-1} (in the present

Table 4. Correlation between Experimental and Theoretical Uniformly Scaled Infrared Bands of P_4O_6Se

		expt			theory		
		intensities				rel intensities	
mode no.	sym	IR	Raman	freq (cm^{-1})	freq (cm^{-1})	IR	Raman
1	A_2				288	0	0
2	A_2				663	0	0
3, 4	E		vs	141	130	0	16
5, 6	E		w	297	298	0	5
7, 8	E		vw	310	310	0	2
9, 10	E	s	w	413	415	2	18
11, 12	E		vw[a]	555	565	0	1
13, 14	E	s	m[a]	648	642	5	36
15, 16	E	sh	m[a]	663	665	1	2
17, 18	E	sh		768[b]	719	0	0
19, 20	E	vs, br	w[a]	955	983	53	3
21	A_1		vs, p	259	250	0	38
22	A_1	s	s, p	466	417	7	18
23	A_1	m	s, p	579	585	1	32
24	A_1	s	s, p	628	629	4	76
25	A_1	m	m, p	752	672	1	100
26	A_1	vs	w, br, p	920	953	100	4
27	A_1	s		817[c]	760	0	3

[a] Only visible in the spectrum of crystalline P_4O_6Se. [b] Appears as a shoulder in the IR spectrum; not visible in the Raman spectrum. [c] IR frequency; band does not appear in the Raman specturm.

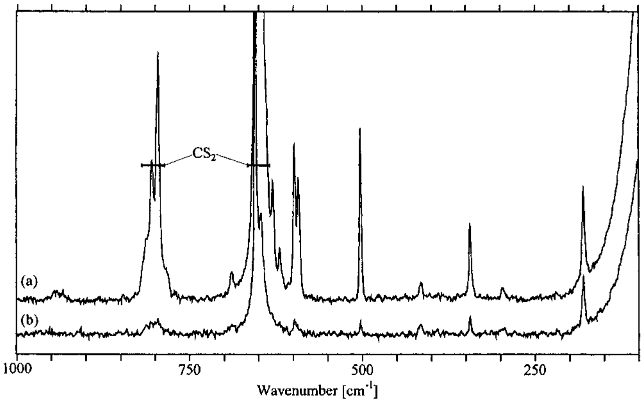

Figure 2. Raman spectrum of P_4O_6S in CS_2 solution: (a) parallel and (b) crossed polarization.

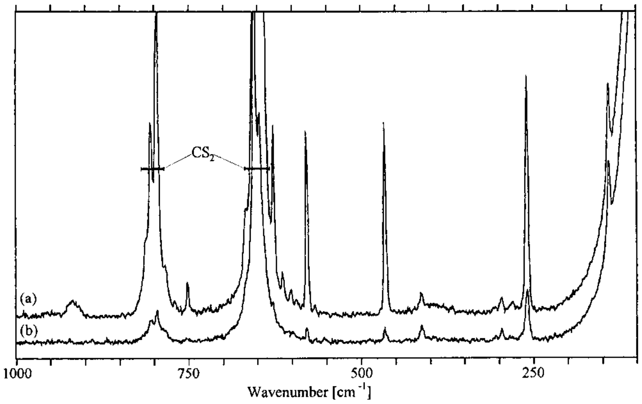

Figure 3. Raman spectrum of P_4O_6Se in CS_2 solution: (a) parallel and (b) crossed polarization.

assignment) also given in Tables 2−4. The E symmetry of this band is confirmed by the lack of polarization effects in the experimental spectra of P_4O_6S and P_4O_6Se (Figures 2 and 3). Our assignment differs from that of Mielke and Andrews,[10] who assigned the terminal bending motion of P_4O_7 to a band appearing at 537.7 cm^{-1} (see below).

If we now consider only the effect of the increased mass of the terminal substituent on the vibrational frequency, by replacing the mass of the peripheral oxygen in P_4O_7 by the mass of sulfur, the frequency changes from 255 cm^{-1} to 215 cm^{-1}. By comparing this shift (40 cm^{-1}) to the total shift discussed above (85 cm^{-1}), we can see clearly that mass and bond strength effects are of the same order of magnitude.

Modes 5 and 6 around 300 cm^{-1} consist mostly of cage vibrations (Figure 5); hence there is very little shift in the spectra of the three compounds when going from P_4O_7 to P_4O_6Se. Considering the experimental assignment,[1] this band in P_4O_7 is assumed to be a mode of A_1 symmetry. However, this experimental assignment was uncertain because the polarization effect could not be clearly observed (as indicated by a question mark in the work of Jansen and Moebs[1]). Since the corresponding lines in the Raman spectra of P_4O_6S and P_4O_6Se do not exhibit polarization effects (i.e., are assigned to e modes), we conclude that our new assignment is correct.

In the next five vibrational modes of E symmetry, mainly motions of the bulk (cage) atoms are involved; the shifts in the frequencies when going from P_4O_7 to P_4O_6S and P_4O_6Se are therefore, as expected, quite small. In the first modes (7, 8) the motion of the P(V)=O (but not P=S or P=Se) unit contributes somewhat to the normal mode, and hence there is a shift of 27 cm^{-1} (20 cm^{-1} experimental) when going from P_4O_7 to P_4O_6S, but only 1 cm^{-1} (3 cm^{-1} experimental) when going from P_4O_6S to P_4O_6Se. A similar observation can be made for the next e mode (9, 10), while the shifts in the three spectra are indeed very small for the remaining modes (11, 12) and (13, 14). If attention is given to modes 17 and 18, the theoretical study shows a shift from 763 cm^{-1} to 726 cm^{-1} and 719 cm^{-1} for P_4O_7, P_4O_6S, and P_4O_6Se, respectively. Considering Figure 6, in which this mode is depicted, we can see that this motion is concentrated in the cage and is dominated by the P(V)−O_b stretching motion. Since it is a cage motion, no shifts in the frequencies are expected when going from P_4O_7 to P_4O_6S and P_4O_6Se. On the other hand, if the X atom retains its position in space during this motion, the mode gets a slight participation of a P(V)=X stretching vibration caused by the movement of the P(V) atom. This contribution is responsible for the observed shift of the frequency in this series. Because the X atom does not move, no mass effect is expected. Indeed, the frequency stays at 763 cm^{-1} if the bond strength of P(V)=O is retained in the calculations and only the mass of the substituent X is changed from oxygen to sulfur and selenium.

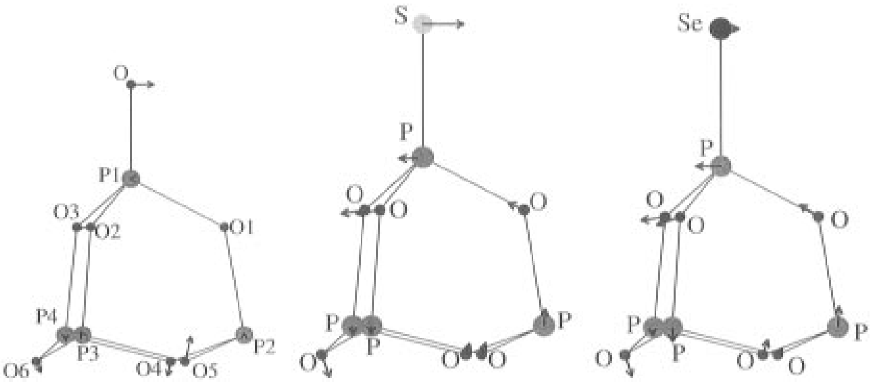

Figure 4. Indication of the nuclear motions connected with mode 3. The numbering of the centers of P_4O_6S and P_4O_6Se follows that specified for P_4O_7. The sizes of the arrows indicate the relative magnitudes of the displacements for the various centers from equilibrium.

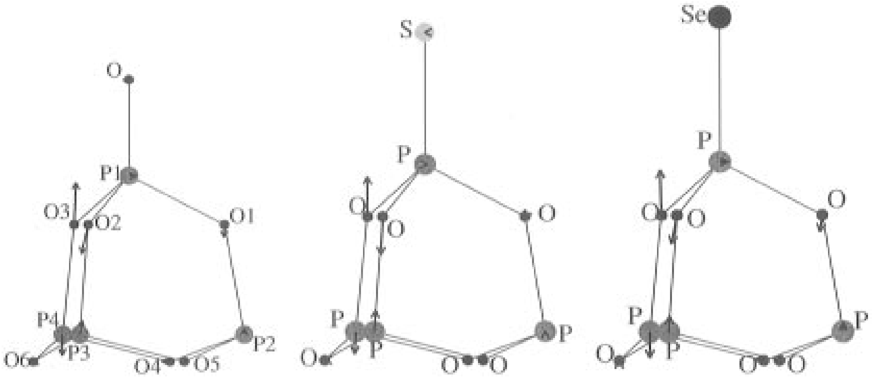

Figure 5. Indication of the nuclear motions connected with mode 5. For more details, see Figure 4.

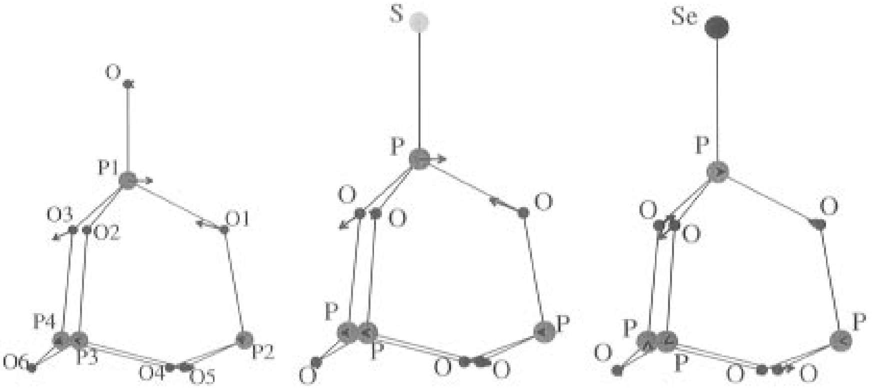

Figure 6. Indication of the nuclear motions connected with mode 17. For more details, see Figure 4.

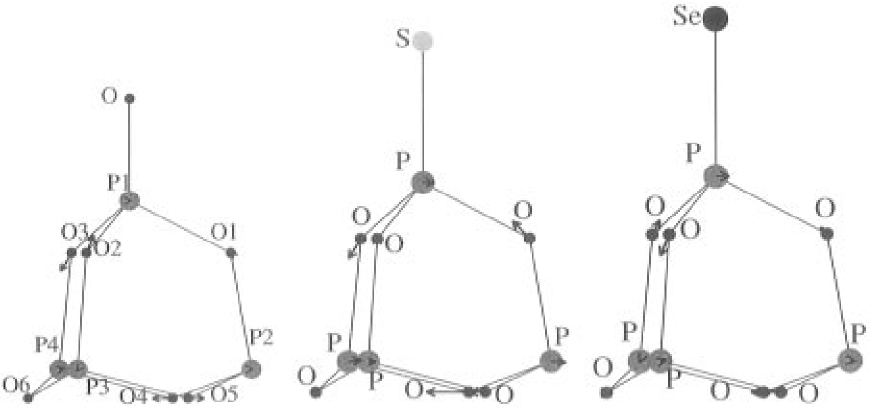

Figure 7. Indication of the nuclear motions connected with mode 19. For more details, see Figure 4.

The strongest IR absorption band in the entire P_4O_7 spectrum[1] is assigned to the e mode (19, 20), shown in Figure 7. It is a pure bulk motion. The calculated frequencies for the three molecules differ very little from each other (2%). Likewise the experimental shifts of this band when going from P_4O_7 to P_4O_6S and P_4O_6Se are very small; the apparent larger shift from P_4O_7 to P_4O_6S in the experimental spectra might be somewhat uncertain because the line for this e mode (19, 20) in the IR

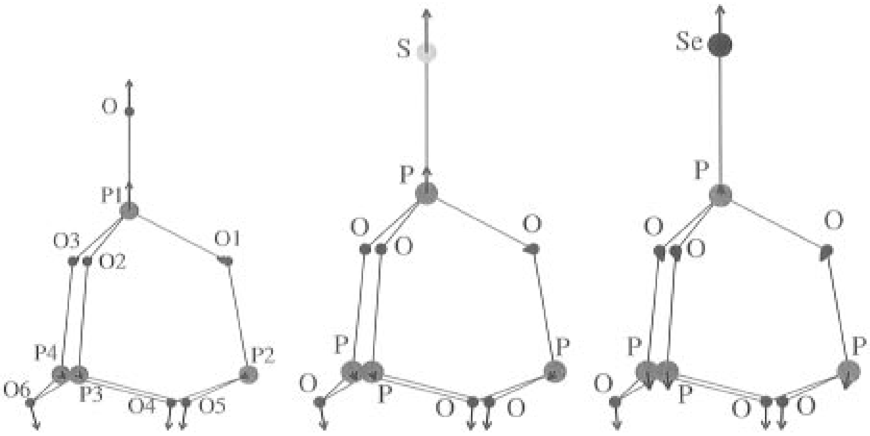

Figure 8. Indication of the nuclear motions connected with mode 21. For more details, see Figure 4.

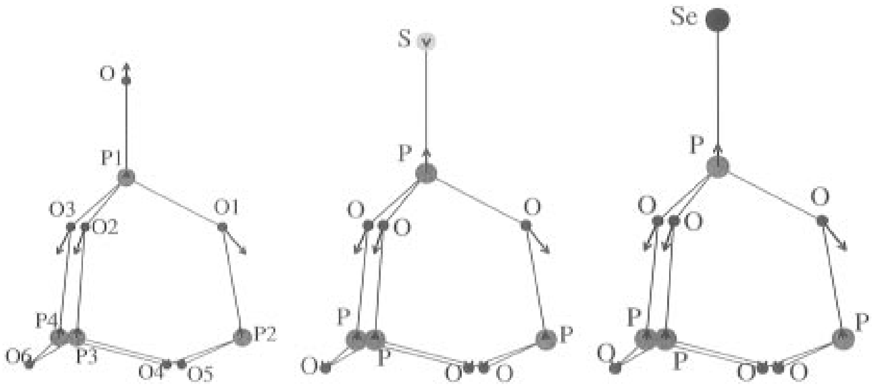

Figure 9. Indication of the nuclear motions connected with mode 26. For more details, see Figure 4.

spectrum of P_4O_6S is characterized as a shoulder next to the strong a_1 line at 945 cm^{-1} and hence its position might actually be lower than the experimental value[14,15] of 1010 cm^{-1}.

Let us now turn to the modes of A_1 symmetry. Since the internal P(V)═X coordinate transforms as the A_1 irreducible representations, a stretching vibration (A_1 symmetry) of this bond can participate in all normal modes of A_1 symmetry with the consequence that all a_1 modes will show larger shifts in the series of P_4O_7 to P_4O_6Se than the modes of the A_2 and E symmetries.

Mode 21 (Figure 8) is basically described as a stretching motion of the P(V)═S and P(V)═O units with respect to the lower frame oxygens atoms. Since the P(V)═X bond strength decreases from $X = O$ to $X = Se$, in P_4O_6Se mainly the Se atom moves, but not the entire P(V)═Se unit. An indication of this “decoupling” of the motion of the substituent from that of P(V) can already be seen in P_4O_6S (Figure 8), in which the sulfur atom shows somewhat greater displacements from its equilibrium position than the P(V) atom. The total shift from P_4O_7 to P_4O_6Se is large (139 cm^{-1} calculated, 170 cm^{-1} experimental), as expected. The effect of the different masses in this case amounts to about 70% of the total frequency shift; as expected, the “decoupling” of the Se motion from that of P(V) is not quite as marked as if both mass and bond strength are changed in the calculations. Mode 22 closely resembles mode 21. In P_4O_7, the P(V)═O bond is seen to move as a unit; in P_4O_6S, the motion of the peripheral sulfur atom is entirely “decoupled” from that of P(V), which does not move. In P_4O_6Se, P(V) and Se move in opposite directions so that a P(V)═Se bond stretching motion results. The calculated frequency shifts are quite similar to those calculated for mode 21; the effect of the different masses amounts to about 50%. We correlate this motion in P_4O_7 to the experimentally observed band at 534 cm^{-1} in contrast to the analysis of Mielke and Andrews,[10] who have assigned this band to a P(V)═X bending motion (E symmetry). However, the assignment of this band to an e mode is inconsistent with the findings of Jansen and Moebs, who have reported this band to exhibit a strong polarization effect.[1] This finding is supported by our newly performed Raman polarization measurements on P_4O_6S and P_4O_6Se, which show strong polarization effects for the corresponding bands at 505 cm^{-1} and 466 cm^{-1}, respectively (Figures 2 and 3).

Modes 23−25 are all predominantly bulk motions. As expected, the frequency shifts in the series P_4O_7 to P_4O_6Se are small and in general the shifts determined theoretically and experimentally are in good agreement. Mode 26 (Figure 9) possesses the strongest IR intensity. It can be described as a symmetric stretching motion of the upper frame with some contribution of the P(V)═X unit (P(V)═Se bond stretching for P_4O_6Se but movement of the P(V)═O unit for P_4O_7). As this motion is dominated by the bulk, the frequency shift within the series of these compounds is small.

The last mode of A_1 symmetry, depicted in Figure 10, is mainly a P(V)═X stretching mode. There is a very large shift of this mode when going from P_4O_7 to P_4O_6S (578 cm^{-1} calculated, 519 cm^{-1} experimental), as expected from the different character of the PO and PS bonds. At the same time it is seen that the intensity also changes drastically, showing the different changes of the dipole moments arising from the stretching of this bond. The situation is somewhat different in P_4O_6Se, because the P(V)═Se stretching motion is not concentrated in this mode alone, but has been distributed over a series of a_1 modes as discussed above. The frequency shift of this mode is therefore smaller from P_4O_6S to P_4O_6Se than from P_4O_7 to P_4O_6S. If only the oxygen mass were replaced by the sulfur

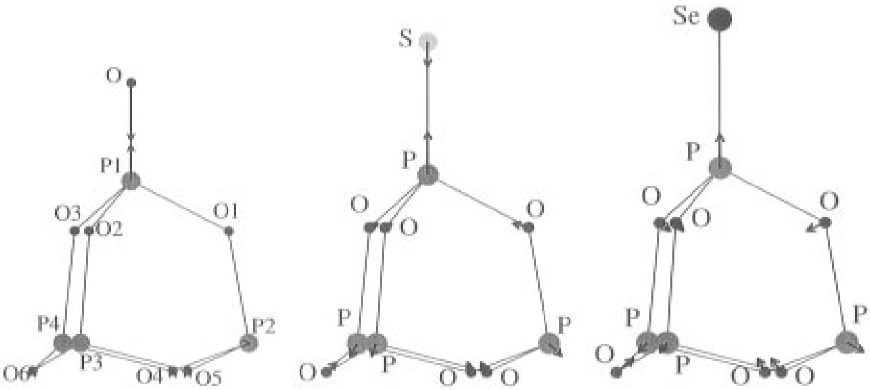

Figure 10. Indication of the nuclear motions connected with mode 27. For more details, see Figure 4.

or selenium mass, the frequency shift would be only about 50% of the value actually observed.

IV. Conclusion

The present analysis of the normal modes of the molecules P_4O_6X ($X = O$, S, and Se) shows that a correlation of bands based only on frequencies and intensities can be quite misleading. In particular, the P(V)═O stretching mode of A_1 symmetry has the highest frequency in P_4O_7, whereas the next one on the energy scale is the (19, 20) e mode, characterizing the “stretching” motion of the lower frame with respect to the upper frame, i.e., representing a bulk mode. In P_4O_6S, the a_1 mode corresponding to the P(V)═S stretching motion is only the third highest in frequency, and both the bulk e mode (19, 20) and the bulk a_1 mode (26) (corresponding to the symmetric stretching of the upper frame) are found at higher frequencies and possess stronger intensities. They are seen as peak and shoulder in the IR spectrum.[14,15] In P_4O_6Se, the two bulk motions of A_1 and E symmetries possess the highest frequencies and have, as in P_4O_6S, the highest IR intensity. The P(V)═Se stretching motion is not localized in one particular mode but contributes to various a_1 modes of lower frequencies. The largest motion of the selenium atom is observed in the lowest normal mode of A_1 symmetry.

The fact that the normal modes of the P_4O_6 bulk remain essentially unchanged from P_4O_7 to P_4O_6S and P_4O_6Se supports the earlier conclusions[8,9] that the cage bonds are not altered in the P_4O_7 to P_4O_6S and P_4O_6Se series. In particular, the P(V)−O_b bond strengths are shown to be of the same order of magnitude in all three compounds, which is consistent with X-ray crystallographic data published earlier.[1−3,6,7]

The large frequency shifts found for the modes in which the P(V)═X normal coordinate is involved are seen to arise about equally from the effects of the different masses of the substituents and the differences in the P(V)═X bond strengths.

Acknowledgment. We thank gratefully the Deutsche Forschungsgemeinschaft (SFB 334) for supporting this work. The computer time provided by the Computing Center of the RWTH Aachen has been essential to the present study.

IC961202S