Ab initio calculations on the structure and vibrational properties of some phosphorus-selenium molecules: applications to zero-dimensional glasses

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Abstract. We use local density functional theory to calculate the structure and vibrational properties of small molecules containing phosphorus and selenium atoms in varying concentrations in an attempt to shed light on the composition of zero-dimensional P–Se glasses. We examine the structure and modes of P_4Se_n, $n = 0, 1, 2, 3, 4, 5, 6, 10$, P_8Se_8 and $P_{10}Se_6$. Our results enable us to exclude some molecules from being present. For the Se-rich glasses we find that the singly bonded molecules P_4Se_n, $n = 3, 4, 5, 6$ are stable and are likely to be present. For the P-rich glasses P_4Se_3, P_4Se_2 and possibly $P_{10}Se_6$ are present.

1. Introduction

The structure of P–Se alloys has recently excited interest because of suggestions by Price *et al* (1984), Verrall and Elliott (1988) and Phillips *et al* (1989) that they are representative of what are called zero-dimensional glasses. That is, for some compositions, they consist of discrete molecules bonded together by van der Waals forces in contrast to a continuous random network of Se–Se, P–P and Se–P bonds. Such glasses possess very sharp Raman lines, as found by Phillips *et al*, which are closely correlated with vibrations of the individual molecules. Glass formation in P_xSe_{1-x} occurs for $x < 0.52$ (the Se-rich glasses) and for $0.63 < x < 0.85$ (the P-rich glasses). For $0.52 < x < 0.63$ P_4Se_3 readily crystallises preventing glass formation. There are two crystalline forms of P_4Se_3: alpha and beta; the latter is a plastic crystal and is stable above 355 K. Both consist of the cage molecule illustrated in figure 1. Most workers consider that P_4Se_3 plays a central role in P–Se glasses.

The Se-rich glasses were studied extensively by Price *et al* using neutron diffraction, Raman spectroscopy and EXAFS. They conclude that P_4Se_n cage molecules with $n = 3$, 4 and 5 dominate the structure for $x = 0.5$, 0.4 and 0.25. The Raman data for $P_{0.5}Se_{0.5}$ has many modes close to those of P_4Se_3. Lines due to the stretching of Se–Se bonds, which are expected to occur at about 254 cm^{-1}, are weak for this glass but become the dominant feature for $x = 0.4$ and $x = 0.25$. It is not clear, for small x, whether Se–Se chains coexist with the discrete molecular units or bond these units together as in $(P_4Se_3)_2Se_2$. The molecules P_4Se_4 and P_4Se_5 have many isomers; however, P_4Se_5 has been prepared in crystalline form (Penney and Sheldrick 1971) and possesses a P atom attached to Se by a double bond. The stretch frequency of this bond is about 500 cm^{-1}.
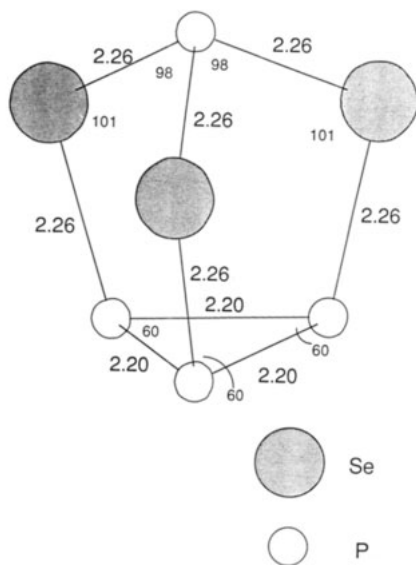
Figure 1. The calculated structure of P_4Se_3.

Now, although modes with this frequency are seen by Price *et al* for $x < 0.4$ they are attributed to overtones of the Se–Se stretch frequency mentioned above. Thus it may be that the P_4Se_n molecules are made up entirely of single bonds. However, Monteil and Vincent (1977) claim to have prepared an amorphous compound corresponding to P_4Se_{10} which they suggest is a cage structure with five double-bonded Se atoms. They analysed the vapour by mass spectrometry and found an infra-red absorption around $500\,cm^{-1}$. There is then considerable uncertainty about which cage molecules are present in these glasses.

For the P-rich glasses, Verrall and Elliott carried out inelastic neutron scattering experiments and concluded that $P_{0.67}Se_{0.33}$ has six modes close to those of P_4Se_3 whereas Phillips *et al*, using Raman spectroscopy, resolved nine modes for the same glass. Verrall and Elliott also found a mode around $278\,cm^{-1}$ and, as this mode is not found in P_4Se_3, attributed it to phosphous clusters either arising from phase separation or comprising bridging units between P_4Se_3 units as for example $(P_4Se_3)_2P_2$. This mode was not reported by Phillips *et al*. For concentrations of P greater than 0.67 the correspondence between the Raman lines with those of P_4Se_3 becomes more tenuous. Thus there is a clear need to learn about the modes of cage molecules having a great range of P and Se content. We report here results of calculations on the structure and vibrational modes of P_4Se_n for $n = 0, 1, 2, 3, 4, 5, 6, 10$ as well as P_8Se_8 and $P_{10}Se_6$. We use *ab initio* local density pseudo-potential theory whose only input parameters are atomic numbers and atomic masses. Where comparison can be made with experiment, namely for P_4, P_4Se_3, P_4Se_5 we find bond lengths and angles to within 1 or 2%. These inaccuracies give an error in the vibrational modes of about $30\,cm^{-1}$. Nevertheless the calculations reveal significant trends with molecular Se content. The method used successfully describes the structure and vibrational properties of small molecules (Jones and Sayyash 1986) as well as bond lengths and bulk modes in silicon and diamond (Jones 1988). We have also shown that the method describes well the structure and dynamic properties of Hittorf's P. (Briddon and Jones 1989).

2. Method

We use self-consistent local density functional theory with normconserving pseudo-potential to calculate the total energy of the molecule as a function of the nuclear coordinates. Details of our method have been published elsewhere (Jones 1988). We allow structural relaxation of the whole molecule and converge the energy to 10^{-5} au. The dynamical matrix is then evaluated and diagonalised to obtain the vibrational frequencies and modes.

Our wavefunction basis set for the calculation consists of s and p Gaussian orbitals centred on the atomic sites and on the bond centres. We have tested two basis sets, the first has 16 orbitals per P atom, 20 per Se atom and 4 per bond centre. This amounts to a total of $d = 160$ basis functions for P_4Se_3. The smaller basis simply has 4 orbitals per atom and per bond centre. In order to avoid the problem of evaluating $O(d^4)$ integrals per self-consistency loop we introduce a charge-density-fitting basis comprising s Gaussians centred on atoms and bond centres. For this basis we use 4, 5 and 1 s Gaussians for P atoms, Se atoms and bond centres respectively. The different basis sets yield structural results which differ by about 2%.

The force acting on each atom was evaluated by a semi-analytic expression and the structures relaxed using a conjugate gradient method. The dynamical matrix was formed by numerical differentiation of the forces acting on each atom in the relaxed state. Numerical derivatives were evaluated using a double-sided formula with a displacement of 0.35 au and, although taking numerical derivatives is notoriously difficult, we believe that the error introduced in the vibrational frequencies in doing so is only about 10 cm^{-1}. More serious is the sensitivity of the results to the length of the P–P bond. We find that the high-frequency modes—those associated with the P–P vibrations—may vary by as much as 30 cm^{-1} for a 1% change in the P–P bond length, and we consistently over-estimate the high-frequency modes by about this much.

3. Results and discussion

Rather than give every bond length and bond angle for every molecule considered, we shall present the structural results in detail for P_4, P_4S_3, the three forms of P_4Se_4, and the P_4Se_5 molecule as synthesised by Penney and Sheldrick, then merely mention some relevant details for the other molecules. Our rationale for so doing is that these six molecules are sufficient to expose the strengths and weaknesses of our method and that what is important for the remaining molecules, in terms of identifying them in a glass, is not so much their structure but their vibrational modes. The results from these six molecules are a good illustration of the effect on the vibrational spectra of the charac-teristic types of bonding present, especially the presence of the P_3 ring and the P$=$Se double bond.

3.1. P_4Se_3

We start with P_4Se_3 (figure 1) since it is thought to be the main component of many of the P–Se glasses. The experimentally observed average P–P and P–Se bond lengths are 2.25 Å and 2.24 Å respectively (Keulen and Vos 1959). We obtain the values 2.20 Å and 2.26 Å. The experimentally observed average Se–P–Se, P–Se–P, Se–P–P and P–P–P bond angles are 99.9°, 100.1°, 105.3° and 60.1° respectively. We obtain the values 98.3°,

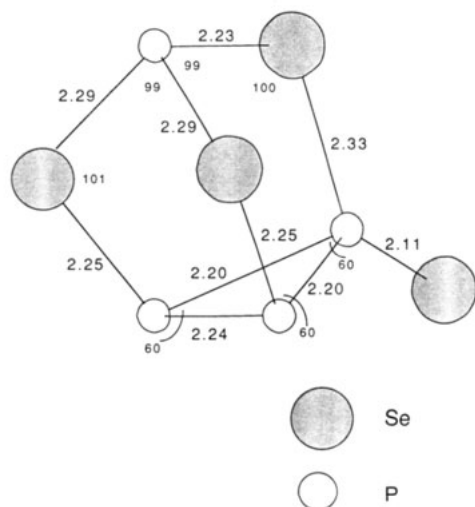**Figure 2.** The calculated structure of P_4Se_4I.

101.2°, 105.5° and 60°. Our results differ most in the length of the P–P bond, which we predict to be 2% shorter than that observed. In all other respects the agreement is very good. The calculated vibrational frequencies are given in figure 7 below, where we have indicated the E modes as broken lines, along with those measured for α-P_4Se_3 (Bues *et al* 1980). Bues *et al* give Raman spectra for various forms of P_4Se_3, namely α, β and the melt, and although most of the lines are coincident there is some variability for those seen at about 320 cm^{-1} and the weak mode at 160 cm^{-1} is seen only in the β-form and the melt, and was not reported at all by Price *et al*. This mode is assigned as an E mode by Bues *et al*. We believe that this assignment is in error and consistently find that the calculated mode at about 160 cm^{-1} is an A_2 mode and is therefore Raman inactive in the vapour, but it could lead to weak lines in the melt. Instead we would place the E mode at about 210 cm^{-1}, very close to an A_1 mode. Our calculated highest-frequency mode corresponds to the breathing mode of the basal P_3 ring and is overestimated by 8% due to the 2% underestimate in the P–P bond length.

3.2. P_4Se_4

We have considered three possible structures for P_4Se_4. They are shown in figures 2, 3 and 4, where the calculated bond lengths and angles are indicated. The first structure (referred to as P_4Se_4 1 in figure 7) is that proposed by Monteil and Vincent (1975) in order to account for their infra-red data. It is obtained by adding an extra Se atom to P_4S_3 by means of a double bond to a basal P atom. The length of the P═Se double bond is in very good agreement with that obtained experimentally by Penney and Sheldrick for P_4Se_5. They find a value of 2.12 Å and we get 2.08 Å. It is of interest to see how attaching this extra Se atom to the basal P_3 ring affects the vibrational modes. These are shown in figure 7. There is still a high-frequency mode in this molecule, but now instead of being associated with the P_3 ring it is due to the P═Se vibration. It is not easy to follow any of the modes in particular as we increase the Se content, but overall they do not differ substantially from those of P_4Se_3.
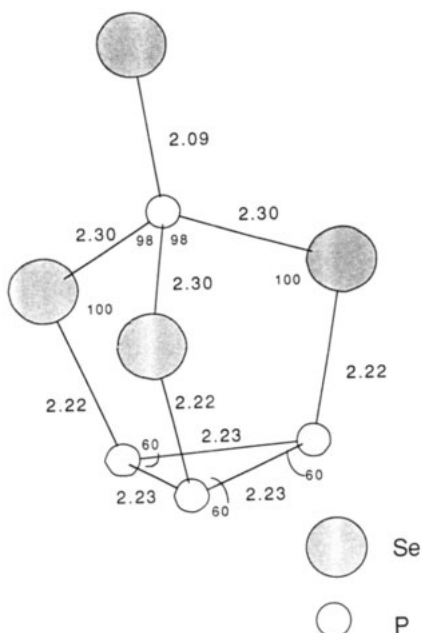
Figure 3. The calculated structure of P_4Se_4II.

Our second choice of P_4Se_4 is obtained by attaching the additional Se atom by a double bond to the apicial P atom of P_4Se_3. The resulting structure is given in figure 3 and we refer to it as P_4Se_4II in figure 7. As expected, the vibrational modes are similar to those of the previous P_4Se_4 molecule, except that now there are two high-frequency modes—one associated with the P_3 ring and the other associated with the P=Se double bond. This molecule retains the C_{3v} symmetry of P_4Se_3, which accounts for the grouping of nearly degenerate lines in the spectrum (our calculated spectra do not exhibit exact degeneracy due to the numerical errors incurred when taking the second derivatives).

The final P_4Se_4 molecule was obtained by breaking the P_3 ring and inserting the extra Se atom to form a P–Se–P linkage. It is illustrated in figure 4 and referred to as P_4Se_4III in figure 7. The most striking feature in its vibrational spectrum is the absence of high-frequency modes, a feature which is obviously due to the removal of the P_3 ring. It was suggested by Price *et al*, based on the result that infrared bands observed by Monteil and Vincent agree to some extent with those in $P_{0.4}Se_{0.6}$, that a dominant molecular unit in $P_{0.5}Se_{0.5}$ is P_4Se_4: presumably in that form suggested by Monteil and Vincent. However, the failure to observe a mode at 500 cm^{-1} strongly suggests that if indeed P_4Se_4 is a major component of $P_{0.5}Se_{0.5}$ then it is the singly bonded molecule which is present and not those with double bonds. Our total-energy calculations show that the three molecules have almost identical energies.

3.3. P_4Se_5

One form of this molecule has been synthesised by Penney and Sheldrick. They determined the structure as that arising from our P_4Se_4III by adding an additional Se atom to one of the basal P atoms with a double bond (see figure 6 below). This molecule was obtained at room temperature by reacting P_4Se_3 and Br. We have considered another
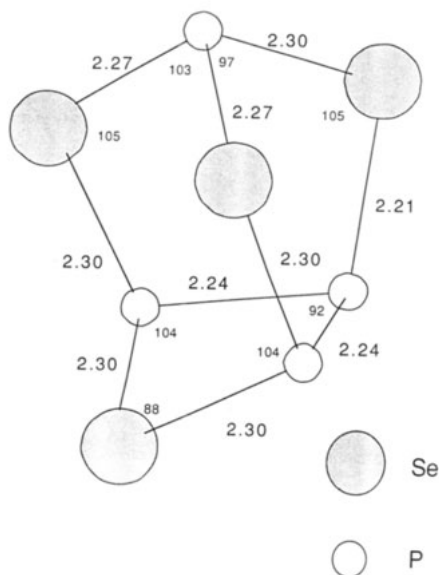
Figure 4. The calculated structure of P_4Se_4III.

possibility whereby a basal P–P bond is broken and the Se inserted. This second molecule has no double bonds and therefore has a rather different vibrational structure. The spectra of both molecules are shown in figure 7, where the original is labelled P_4Se_5I and the other P_4Se_5II. The highest-frequency mode of P_4Se_5I is associated with the stretching vibration of the P=Se double bond. Price *et al* proposed that P_4Se_5I is a major component of $P_{0.25}Se_{0.75}$; we would argue that if a molecule with this stoichiometry is a major component and the mode observed at 505 cm^{-1} is a Se–Se overtone, then it is not the double-bonded species which is present. Our total-energy calculations again indicate that both molecules have almost identical energies.

3.4. P_4Se_6 and P_4Se_{10}

P_4Se_6 has a highly symmetrical (symmetry group T_d); it is obtained by removing the three P–P bonds in P_4Se_3 by inserting Se atoms. The P–Se bond length is 2.31 Å, and the P–Se–P and Se–P–Se bond angles are 105° and 115° respectively. P_4Se_{10} has T_d symmetry and is obtained from P_4Se_6 by adding doubly bonded Se atoms to each P; the P–Se single and double bonds are 2.31 Å and 2.13 Å respectively and all bond angles are 109°.

Monteil and Vincent found, for P_4Se_{10} in the vapour phase, a very strong infrared absorption at about 500 cm^{-1}, which they attribute to the P=Se double bond; we calculate modes in the range 460–490 cm^{-1} (see figure 7).

It is rather surprising, considering its high symmetry, that P_4Se_6 has not been synthesised. We have calculated its vibrational spectrum (figure 7) and find that it has modes only at <380 cm^{-1}. It cannot be the only component of the $P_{0.4}Se_{0.6}$ glass since Price *et al* report modes at 440 cm^{-1}.

3.5. P_8Se_8

We have calculated the vibrational spectrum of P_8Se_8 in an attempt to verify an idea put forward by Verrall *et al*. They suggest that, in order to retain the vibrational character of P_4Se_3, Se-rich glasses may form by polymerisation. This molecule is the simplest in a series of polymers with increasing Se content. It is formed by attaching two P_4Se_3 molecules via a pair of Se atoms bonded to the basal P atoms. The resulting form is stable, but the P_3 ring is no longer intact. The modes of this molecule are given in figure 7. The wide range of modes suggests that the Raman spectrum should consist of broad bands rather than discrete lines associated with the smaller cages.

3.6. $P_{10}Se_6$

The phosphorus-rich glasses have only recently been studied in any depth. Verrall *et al* used neutron diffraction to obtain a vibrational density of states for $P_{0.67}Se_{0.33}$ and argue that the material comprises P_4Se_3 molecular units embedded in some kind of P network. They propose further, based on the appearance of a mode at $278\ cm^{-1}$ on increasing P content, that the P network may comprise Hittorf's P_8 and P_9 cages. The simplest molecule to exhibit a P_8-like cage and retain some P_4Se_3 character is $P_{10}Se_6$. Figure 7 shows that $P_{10}Se_6$ does have vibrational modes at about $280\ cm^{-1}$ and like Hittorf's phosphorus at about $480\ cm^{-1}$. Phillips *et al* have performed Raman spectroscopy on samples of P_4Se_n for $n = 2, 3, 4$ and on $P_{0.84}Se_{0.16}$. They too argue that these glasses comprise P_4Se_3 molecules embedded in a P matrix, but they do not see any evidence for P_8 or P_9 cages.

3.7. P_4, P_4Se and P_4Se_2

It may be that the P-rich glasses contain the molecules P_4Se_n with $n = 0, 1, 2$, and 3. We have evaluated the vibrational spectra of P_4, P_4Se, P_4Se_2, (we consider only those molecules obtained from P_4 with single P–Se bonds). The P_4 molecule assumes tetrahedral symmetry and is shown in figure 5. Its vibrational frequencies are given in figure 7. The experimentally observed bond length is 2.21 Å and the frequencies are 363, 456 and $606\ cm^{-1}$ (Gutowsky and Hoffman 1950). Our results are in reasonable agreement with those experimentally observed although they are somewhat overestimated, due to the underestimation of the P–P bond length.

We see from figure 6 that the P_4Se molecule retains some of the characteristic high frequencies of P_4 and argue therefore that this species is probably not present in the P-rich glasses. P_4Se_2 on the other hand has a spectrum which does not differ appreciably from that of P_4Se_3 and may well be present.

4. Conclusions

The *ab initio* calculations have given excellent results for the structures of known P_4Se_n molecules with $n = 0, 3$ and 5. The vibrational modes of these molecules are also in reasonable agreement with experiment. We believe, however, that the assignment of the $160\ cm^{-1}$ line to an E mode in P_4Se_3 is in error. We think that it is an A_2 mode and that the E mode lies close to an A_1 mode at $200–210\ cm^{-1}$. The energies of isomers of P_4Se_4 containing respectively double P=Se bonds and single P–Se–P bonds are
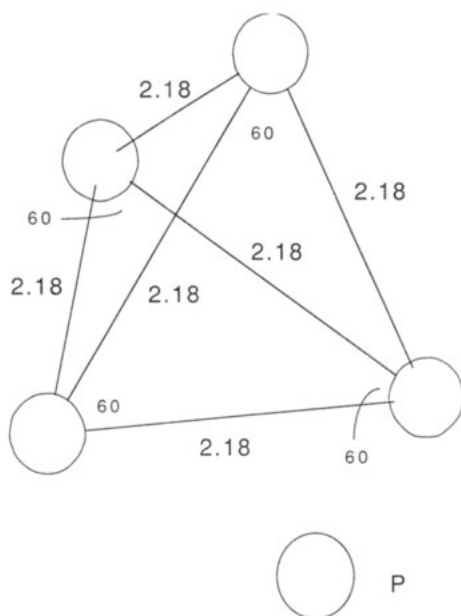
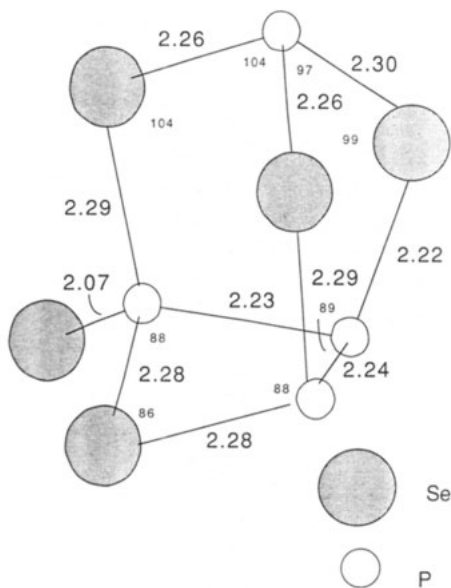**Figure 5.** The calculated structure of P_4.

Figure 6. The calculated structure of P_4Se_5I.

extremely close. We cannot conclude then that the glasses favour one or other. However, their frequencies differ enormously, especially around 500–550 cm^{-1}. If Price *et al* are correct in that these modes are due to Se–Se overtones in the Se-rich glass ($x < 0.4$) then the double-bonded units cannot be present which leaves the possibility that the single-bonded molecules P_4Se_n, $n = 3$, 4, 5 and 6, are present. The polymerised units like
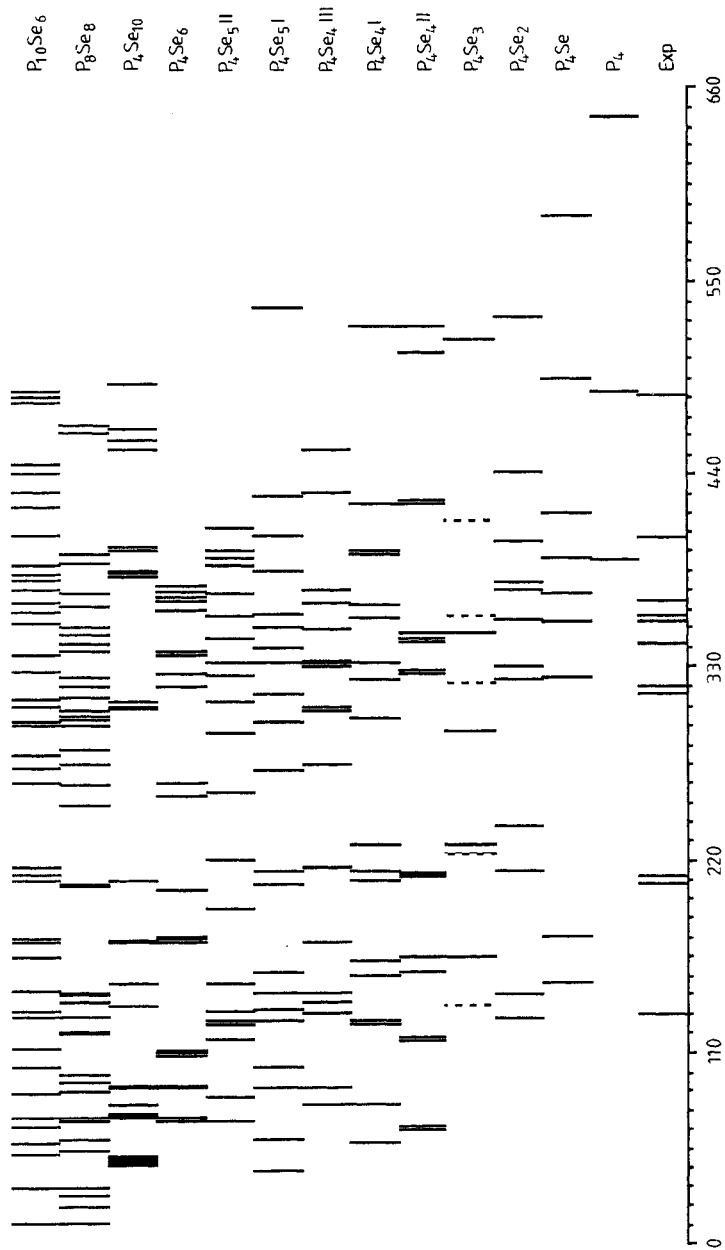
Figure 7. The vibrational spectra of the P–Se molecules considered in the text. Experimental values are for α-P_4Se_3, taken from Bues *et al* (1980). The E modes of P_4Se_3 are indicated with broken lines. Frequencies are in cm^{-1}.

$(P_4Se_3)_2Se_2$ and $(P_4Se_3)_2P_2$ have a broad band of modes which is inconsistent with the observation of sharp Raman lines. In the P-rich glasses the modes of P_4Se_2 are very close to those of P_4Se_3. We consider then it is not easy to exclude either molecule from being present.

P_4 and P_4Se are also stable and have very high frequencies >530 cm^{-1} and as there is no evidence of these lines, we conclude that these molecules are not present in the P-rich glasses.

Acknowledgments

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