# Molecular Vibration Analysis of the Cage-Like Molecules $\beta$-$P_4S_5$, $As_4S_5$, $P_4S_7$, and $As_2P_2S_7$

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The cage-like molecules $\beta$-$P_4S_5$, $As_4S_5$, $P_4S_7$ and $As_2P_2S_7$ are all supposed to have $C_{2v}$-symmetry. A normal coordinate analysis was performed for those molecules, based on a very simple initial force field with three numerical parameters and valence coordinates including redundancies. A complete set of symmetry coordinates is given. The force field was refined by adjusting the symmetry force constants to fit exactly a set of observed frequencies. This was used to calculate the mean amplitudes of vibration and perpendicular amplitude correction coefficients. The standard thermodynamical values derived from spectroscopic data are also given. A set of frequencies was calculated for the so far unknown compound $P_4S_6$.

## Introduction

The cage-like structures of the binary phosphorous- and arsenic-sulfides are quite unusual. The substitution of As for P will yield a variety of new, sometimes isomeric compounds. Our studies of P–S-, As–S- and As–P–S-compounds [1–9] shall now be continued under the aspect of comparable structure elements. The available information on As–P–S-compounds is still very limited [4, 8, 10]. In special cases the replacement of P by As can be regarded as a quasi isotopic substitution which will become evident in the vibrational spectra. This assumption can be used during the assignment of frequencies. The recent spectroscopical investigations [6, 7, 9] are now supplemented by a normal coordinate analysis. The validity of a highly approximate force field is tested by an application to related molecules, viz. $\beta$-$P_4S_5$, $As_4S_5$, $P_4S_7$ and $As_2P_2S_7$. In all cases the vibrational frequencies are calculated with satisfactory results, sometimes leading to a slight reassignment of the reported frequencies [6, 9]. For $As_2P_2S_7$ these data were used as a set of reference for completing the assignment.

$\beta$-$P_4S_5$ has been characterized by x-ray diffraction [11] and vibrational spectroscopy [6, 8]. $As_4S_5$ is occasionally found after slow evaporation of $CS_2$ from $As_4S_4$–$CS_2$-solutions in form of yellow needles. Crystal data have been given [12] and recently also Raman frequencies were obtained [9]. $P_4S_7$ is one of the thermally stable phosphorous sulfides. Its crystal structure [13, 14] and vibrational spectra [6, 8, 15] are known. $As_2P_2S_7$ was recently investigated by us [7]. On the basis of vibrational spectra a model for its molecular structure was proposed. The crystal structure of this compound remains still unknown.

$P_4S_6$ has not been isolated until now, but some frequencies appearing in the $P_4S_7$ spectra after thermal treatment have been attributed to this compound by Bues et al. [6]. Therefore it seemed useful to include a set of calculated frequencies for this compound and to compare it with experimental data [6] as well as calculated frequencies of $P_4S_7$ and $\beta$-$P_4S_5$.

## Structure Parameters

The crystals of the title compounds consist of isolated cage-like $A_4S_5$- resp. $A_4S_7$-molecules (A=P, As) having $C_{2v}$-symmetry. The bonding distances and angles listed in Table 1 have been taken from published crystal data [11–14]. In the case of $As_2P_2S_7$, they were estimated from comparison with similar compounds.

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Table 1. Molecular parameters (mean values) of the title molecules.

| | $\beta$-$P_4S_5$ [11] | $As_4S_5$ [12] | $\alpha$-$P_4S_7$ [13, 14] | $As_2P_2S_7$* |
|---|---|---|---|---|
| $A_a{=}S$ | – | – | 1.92 | 1.92 |
| $A_a{-}S_a$ | 2.13 | 2.26 | 2.11 | 2.11 |
| $A_a{-}S$ | 2.12 | 2.24 | 2.08 | 2.10 |
| $A_b{-}S$ | 2.12 | 2.24 | 2.11 | 2.23 |
| $A_b{-}A_b$ | 2.29 | 2.54 | 2.33 | 2.54 |
| $<A_a{-}S_a{-}A_a$ | $115.5^0$ | $117.3^0$ | $110.1^0$ | $110.1^0$ |
| $<S{-}A_a{-}S$ | $97.6^0$ | $98.8^0$ | $102.8^0$ | $103.5^0$ |
| $<S_a{-}A_a{-}S$ | $107.4^0$ | $104.9^0$ | $109.1^0$ | – |
| $<A_a{-}S{-}A_b$ | $105.4^0$ | $108.4^0$ | $102.4^0$ | – |
| $<S{-}A_b{-}S$ | $104.6^0$ | $101.3^0$ | $103.9^0$ | $99.4^0$ |
| $<A_b{-}A_b{-}S$ | $102.6^0$ | $100.9^0$ | $102.7^0$ | $99.7^0$ |
| $<S{=}A_a{-}S_a$ | – | – | $107.7^0$ | $107.7^0$ |
| $<S{=}A_a{-}S$ | – | – | $114.0^0$ | – |

Atomic weights As: 74.9216
P: 30.9738
S: 32.0640

All distances in Å. * estimated values.

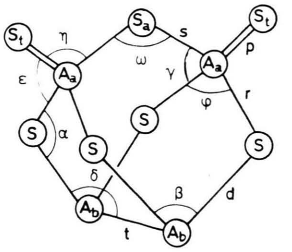

Fig. 1. Model for the $A_4S_5$- and $A_4S_7$-type molecules (A=As, P) with $C_{2v}$ symmetry. Only one of each set of valence coordinates is indicated.

## Symmetry Coordinates

For all of the studied cage-molecules models with $C_{2v}$-symmetry were used, cf. Figure 1. In case of the $A_4S_5$-type molecules the following distribution of the normal modes resulted:

$$\Gamma_{\mathrm{vib}} = 7\,A_1 + 4\,A_2 + 5\,B_1 + 5\,B_2\,.$$

All species but $A_2$, which is not active in the IR, can be observed in Raman and IR spectra. The models for the $A_4S_7$-type molecules were derived by adding two terminally bonded S-atoms $\mathrm{S}\diagdown\!\!\diagdown \mathrm{P_a}\diagup \mathrm{S}\diagdown \mathrm{P_a}\diagup\!\!\diagup \mathrm{S}$. The resulting distribution of normal modes is:

$$\Gamma_{\mathrm{vib}} = 9\,A_1 + 5\,A_2 + 7\,B_1 + 6\,B_2\,.$$

The above mentioned selection rules are valid.

A complete set of independent symmetry coordinates for the $A_4S_5$ model was constructed with the following result:

(i) $t$ stretching in $A_1$.
(ii) The appropriate combinations of $d$ and $r$ stretchings, $\alpha$ and $\beta$ bendings in all the species $A_1 + A_2 + B_1 + B_2$.
(iii) $\omega$ in species $A_1$.
(iv) $s$ stretching in species $A_1$ and $B_2$.
(v) One combination of the $\gamma$ bendings appropriate to the $B_2$ species.

The designations of the applied symbols are explained in Figure 1. For the $A_4S_7$ model the set of symmetry coordinates was augmented with the following members:

(vi) $p$ stretchings in species $A_1$ and $B_2$.
(vii) four combinations of the $\varepsilon$ bendings, belonging to $A_1 + A_2 + B_1 + B_2$.

All bending coordinates were scaled by factors of the dimension of length according to $(r_{ik}\,r_{jk})^{1/2}\,\Phi_{ikj}$.

## Initial Force Field

An extremely simple initial force field was assumed in the same way as it was done for $P_4S_3$ [2–4] and related molecules [4]. A diagonal force-constant matrix was constructed in terms of valence coordinates including redundancies. The inherent coordinates are: (a) All bond stretchings, viz. the four and five types in the cases of $A_4S_5$ and $A_4S_7$, respectively (cf. Fig. 1), (b) all interbond angle bendings of the types applied in the construction of symmetry coordinates, again four and five types in the cases of $A_4S_5$ and $A_4S_7$, respectively (cf. Fig. 1), and finally (c) the additional bendings not occurring among the symmetry coordinates, viz. the $S{-}A_b{-}S$ and $S{-}A_a{-}S$ types, and in the case of $A_4S_7$ also $S_t{=}A_a{-}S_a$.

Most of the numerical values of the initial force constants are transferred from $P_4S_3$ and related molecules [2–4]. For the stretchings it was adopted (in mdyne/Å): $f_t(A_b{-}A_b) = 1.1$; $f_d(A_b{-}S) = f_r(A_a{-}S) = f_s(A_a{-}S_a) = 1.3$; in the case of $A_4S_7$ the value of $f_p(A_a{=}S_t) = 3.4$ was adopted after a few trials. It appears to be substantially smaller than the corresponding value in $P_4S_{10}$ [16]. It should be noticed that the numerical values are the same whenever the A atom is P or As. The bending force constants were all assumed to have the same value, viz. 0.2 mdyne/Å.

## Vibrational Assignments

Tables 2, 3 include the calculated frequencies for the four title molecules from the initial force field (see above). They were used as an aid in the assignment of observed fundamentals. The final proposed assignments are shown in the columns labled b of each of the tables.

For $P_4S_5$ and $P_4S_7$ the observed frequencies of Bues et al. [6] were used. In the former case ($P_4S_5$) our assignment is identical with the one proposed by the mentioned authors [6] apart from some details in species $A_2$. The calculations strongly suggest the lowest frequency to appear below the range of observations in the experimental work [6]. Hence we have re-assigned the 227 $cm^{-1}$ Raman band from $\nu_{11}$ to $\nu_{10}$ and applied our calculated frequency (130 $cm^{-1}$) as $\nu_{11}$. Also in the $A_2$ species of $P_4S_7$ we have made a slight re-assignment, but not affecting the lowest frequency $\nu_{14}$ of 123 $cm^{-1}$. Guided by the calculated frequencies we found it plausible to assign the Raman 214 $cm^{-1}$ band as $\nu_{12}$ (instead of $\nu_{14}$). For $\nu_{14}$ we adopted the calculated value of 186 $cm^{-1}$. This band could very well be hidden together with the very strong 188 $cm^{-1}$ frequency observed in the Raman spectrum of the solid compound and assigned to $\nu_8(A_1)$; the corresponding value in the melt is actually 186 $cm^{-1}$. Finally, we have made a slight re-assignment for $P_4S_7$ within the $B_1$ species, whereas the 324 and 237 $cm^{-1}$ bands were assigned as $\nu_{18}$ and $\nu_{19}$ (instead of $\nu_{19}$ and $\nu_{20}$), respectively. As $\nu_{20}$ we adopted the calculated value of 200 $cm^{-1}$.

The approximately calculated frequencies from this initial force field are shown in Tables 2, 3 for the four molecules in question.

## Potential Energy Distribution

A critical examination has been made [3] for the PED in terms of independent symmetry coordinates of $P_4S_3$ as a representant of cage-like structures. The coordinate-dependance of the PED terms was pointed out in particular, and quite meaningless PED terms were shown for a certain choice of the symmetry coordinate set. Some of these difficulties

Table 2. Calculated and observed frequencies ($cm^{-1}$) and PED-terms for $\beta$-$P_4S_5$ and $As_4S_5$ (initial force field).

| Assignment | | $\beta$-$P_4S_5$ | | | $As_4S_5$ | | |
|---|---|---|---|---|---|---|---|
| | | [a] | [b] | PED-Terms[c] | [a] | [b] | PED-Terms[c] |
| $A_1$ | $\nu_1$ | 459 | 461 | $27d + 19t + 18r$ | 375 | 385 | $40d + 32r$ |
| | $\nu_2$ | 435 | 434 | $33r + 23t + 17s$ | 339 | 340 | $26r + 25\alpha$ |
| | $\nu_3$ | 346 | 391 | $43d$ | 303 | 327 | $36s + 27\omega$ |
| | $\nu_4$ | 337 | 350 | $37s + 31\gamma$ | 242 | 228 | $29\gamma + 20\beta + 20t$ |
| | $\nu_5$ | 280 | 285 | $37r + 18s$ | 224 | 211 | $37t + 21r + 16d$ |
| | $\nu_6$ | 216 | 254 | $46\Phi + 17\gamma$ | 183 | 191 | $42\Phi + 17d$ |
| | $\nu_7$ | 184 | 194 | $59\beta + 19\omega$ | 148 | 145 | $47\beta + 17\omega$ |
| $A_2$ | $\nu_8$ | 465 | 434 | $53d + 23r + 21\delta$ | 378 | (378) | $47r + 39d$ |
| | $\nu_9$ | 405 | 380 | $58r + 22d$ | 323 | (323) | $44d + 30r + 26\alpha$ |
| | $\nu_{10}$ | 211 | 227 | $52\delta + 22\alpha + 17\gamma$ | 169 | 166 | $63\delta + 16\gamma$ |
| | $\nu_{11}$ | 130 | (130) | $72\gamma$ | 119 | 120 | $78\gamma$ |
| $B_1$ | $\nu_{12}$ | 459 | 477 | $69s + 17r$ | 382 | (382) | $83s$ |
| | $\nu_{13}$ | 435 | 454 | $59d$ | 371 | 368 | $59d + 24r$ |
| | $\nu_{14}$ | 348 | 421 | $56r + 27d$ | 311 | 307 | $53r + 19\alpha$ |
| | $\nu_{15}$ | 249 | 337 | $40\alpha + 28\Phi$ | 184 | 180 | $40\Phi + 26d$ |
| | $\nu_{16}$ | 161 | 188 | $44\gamma + 29\Phi$ | 147 | 140 | $57\gamma + 16\Phi$ |
| $B_2$ | $\nu_{17}$ | 452 | 454 | $54r + 16d$ | 376 | (376) | $59r + 20d$ |
| | $\nu_{18}$ | 374 | 412 | $63d + 16r$ | 316 | 312 | $64d + 25\alpha$ |
| | $\nu_{19}$ | 303 | 313 | $37\delta + 26\alpha + 18\gamma$ | 236 | 220 | $56\gamma + 30\beta$ |
| | $\nu_{20}$ | 221 | 220 | $42\gamma + 25\beta + 19\delta$ | 186 | 188 | $53\delta + 25r$ |
| | $\nu_{21}$ | 143 | 184 | $54\beta + 32\gamma$ | 130 | 130 | $61\beta + 31\gamma$ |

[a] Frequencies calculated from the initial force field.

[b] Experimentally observed frequencies. Values in brackets were calculated (see also Vibrational Assignment).

[c] PED values under 15 are not included.

Table 3. Calculated and observed frequencies ($cm^{-1}$) and PED-terms for $P_4S_7$ and $As_2P_2S_7$ (initial force field).

| Assignment | | $P_4S_7$ | | | $As_2P_2S_7$ | | |
|---|---|---|---|---|---|---|---|
| | | a | b | PED-Terms[c] | a | b | PED-Terms[c] |
| $A_1$ | $\nu_1$ | 672 | 685 | 76p | 671 | 653 | 76p |
| | $\nu_2$ | 465 | 480 | 39s + 21r | 464 | 464 | 43s + 22r |
| | $\nu_3$ | 448 | 443 | 35t + 31d | 362 | 392 | 57d |
| | $\nu_4$ | 360 | 398 | 39d + 17t | 320 | 359 | 37r |
| | $\nu_5$ | 298 | 344 | $22\gamma$ | 272 | 269 | $33\gamma$ |
| | $\nu_6$ | 263 | 302 | 42r | 226 | 236 | 46t + 22r |
| | $\nu_7$ | 214 | 230 | $42\Phi + 20\alpha$ | 192 | 208 | $34\Phi$ + 17d |
| | $\nu_8$ | 173 | 188 | $51\beta + 19\omega$ | 164 | 184 | $62\beta + 20\omega$ |
| | $\nu_9$ | 126 | 136 | $53\eta + 20\varepsilon$ + 20s | 125 | 139 | $52\eta + 21\varepsilon$ + 20s |
| $A_2$ | $\nu_{10}$ | 471 | 448 | 56r + 15d | 467 | 520 | 68r |
| | $\nu_{11}$ | 446 | 434 | 58d | 360 | 339 | 77d |
| | $\nu_{12}$ | 210 | 214 | $52\delta + 20\alpha + 17\gamma$ | 196 | (196) | $28\gamma + 28\delta + 22\alpha + 19\varepsilon$ |
| | $\nu_{13}$ | 186 | (186) | $64\varepsilon$ + 21r | 161 | 144 | $42\varepsilon + 38\delta$ + 18r |
| | $\nu_{14}$ | 114 | 123 | $62\gamma + 17\varepsilon$ | 115 | 109 | $60\gamma + 16\varepsilon$ |
| $B_1$ | $\nu_{15}$ | 662 | 667 | 79p | 661 | 667 | 80p |
| | $\nu_{16}$ | 470 | 543 | 58s + 20r | 471 | 548 | 58s + 21r |
| | $\nu_{17}$ | 416 | 505 | 83d | 366 | (366) | 64d |
| | $\nu_{18}$ | 318 | 324 | 50r + 22s | 315 | 315 | 45r + 22s |
| | $\nu_{19}$ | 236 | 237 | $30\eta + 29\Phi + 18\alpha$ | 232 | 221 | $40\eta + 22\Phi$ |
| | $\nu_{20}$ | 200 | (200) | $37\varepsilon + 16\eta$ | 180 | (180) | $28\varepsilon$ + 24d |
| | $\nu_{21}$ | 142 | 130 | $36\gamma + 24\Phi + 19\eta$ | 141 | 139 | $31\gamma + 26\Phi + 21\eta$ |
| $B_2$ | $\nu_{22}$ | 477 | 467 | 61r | 472 | 434 | 65r |
| | $\nu_{23}$ | 401 | 413 | 72d | 344 | 330 | 78d |
| | $\nu_{24}$ | 304 | 317 | $38\delta + 29\alpha + 17\gamma$ | 261 | 232 | $47\gamma + 17\alpha + 17\beta + 17\delta$ |
| | $\nu_{25}$ | 227 | 245 | $40\gamma + 30\beta + 17\delta$ | 198 | 199 | $42\delta + 16\gamma$ |
| | $\nu_{26}$ | 188 | 218 | $49\varepsilon$ + 25r | 165 | 153 | $42\varepsilon$ + 25r + $17\beta$ |
| | $\nu_{27}$ | 120 | 149 | $38\beta + 26\varepsilon + 22\gamma$ | 119 | 120 | $46\beta + 21\varepsilon + 21\gamma$ |

[a–c] See footnotes in Table 2.

are removed by definition of PED in the presence of redundancy [17]. This theory was applied to the initial force fields of the molecules considered here. The calculated results of the PED terms are shown in Tables 2, 3. They are based on all the described valence coordinates including redundancies (cf. Figure 1).

The PED terms display an appreciable mixing between the different types of valence coordinates. This was expected because of the cage-like structure. A simple description of the normal modes as proposed for $P_4S_5$ and $P_4S_7$ by Bues et al. [6] is probably not adequate or at least highly approximate. Furthermore, we find several real discrepancies between the mentioned description [6] and the present one deduced from Table 2. In the light of the previous discussions [3, 17] it seems clear that the significance of the calculated PED terms is not so definite as to make us abandon the force field because of the mentioned discrepancies.

## Refined Force Field

The initial force field (see above) was transferred to the basis of the symmetry coordinates. Subsequently the force constants were, for each of the molecules individually, adjusted to fit exactly the final assignments as given in column b of Tables 2, 3. This step was achieved by the $L$-matrix method, i.e. the normal coordinate transformation matrix ($L$ of $S = LQ$) was maintained from the approximate calculation with the initial force field.

## Mean Amplitudes of Vibration

The final force field was used to calculate the mean amplitudes of vibration ($u$) [18] for all the interatomic distances of the title molecules at different temperatures. The results are given in Tables 7, 8. Also included are the calculated perpendicular amplitude correction coefficients ($K$-values [18, 19]), which are defined in the previous paper on $P_4S_3$ [2].

Table 4. The most important symmetry force constants (mdyne/Å) of the *F*-matrix blocks of the initial force field for the compounds β-$P_4S_5$ and $As_4S_5$.

| Species | Coordinate | Diagonal *F*-Matrix-Elements | | | |
|---|---|---|---|---|---|
| | | $P_4S_5$ | | $As_4S_5$ | |
| | | a | b | a | b |
| $A_1$ | $S_1$ | 2.64 | 3.36 | 2.73 | 2.76 |
| | $S_2$ | 1.58 | 1.81 | 1.57 | 1.60 |
| | $S_3$ | 2.14 | 2.33 | 2.19 | 2.29 |
| | $S_4$ | 0.68 | 0.78 | 0.74 | 0.71 |
| | $S_5$ | 2.95 | 3.60 | 3.10 | 3.02 |
| | $S_6$ | 0.42 | 0.48 | 0.42 | 0.43 |
| | $S_7$ | 1.69 | 1.86 | 1.69 | 1.73 |
| $A_2$ | $S_1$ | 5.52 | 5.45 | 5.70 | 5.72 |
| | $S_2$ | 4.21 | 4.07 | 4.29 | 4.28 |
| | $S_3$ | 3.54 | 3.69 | 3.49 | 3.49 |
| | $S_4$ | 0.78 | 0.77 | 0.83 | 0.84 |
| $B_1$ | $S_1$ | 1.42 | 1.81 | 1.42 | 1.37 |
| | $S_2$ | 1.81 | 2.36 | 1.82 | 1.76 |
| | $S_3$ | 0.47 | 0.69 | 0.49 | 0.46 |
| | $S_4$ | 1.58 | 2.22 | 1.61 | 1.49 |
| | $S_5$ | 1.36 | 1.56 | 1.36 | 1.35 |
| $B_2$ | $S_1$ | 4.94 | 6.29 | 5.32 | 5.07 |
| | $S_2$ | 2.34 | 3.14 | 2.52 | 2.42 |
| | $S_3$ | 3.04 | 4.19 | 3.24 | 3.08 |
| | $S_4$ | 1.58 | 2.17 | 1.69 | 1.65 |
| | $S_5$ | 0.20 | 0.25 | 0.20 | 0.18 |

[a] Initial force field. [b] Final force field.

Table 5. The most important symmetry force constants (mdyne/Å) of the *F*-matrix blocks of the initial force field for the compounds $P_4S_7$ and $As_2P_2S_7$.

| Species | Coordinate | Diagonal *F*-Matrix-Elements | | | |
|---|---|---|---|---|---|
| | | $P_4S_7$ | | $As_2P_2S_7$ | |
| | | a | b | a | b |
| $A_1$ | $S_1$ | 2.99 | 3.55 | 3.05 | 3.45 |
| | $S_2$ | 1.67 | 1.89 | 1.61 | 1.88 |
| | $S_3$ | 2.43 | 2.83 | 2.48 | 2.77 |
| | $S_4$ | 0.80 | 1.00 | 0.81 | 0.95 |
| | $S_5$ | 3.33 | 4.00 | 3.24 | 3.54 |
| | $S_6$ | 0.60 | 0.71 | 0.59 | 0.68 |
| | $S_7$ | 1.75 | 2.03 | 1.75 | 2.06 |
| | $S_8$ | 3.40 | 3.68 | 3.40 | 3.34 |
| | $S_9$ | 0.61 | 0.70 | 0.60 | 0.72 |
| $A_2$ | $S_1$ | 6.03 | 6.68 | 6.04 | 5.62 |
| | $S_2$ | 4.17 | 4.25 | 4.04 | 4.34 |
| | $S_3$ | 4.12 | 4.54 | 3.83 | 3.65 |
| | $S_4$ | 0.89 | 0.99 | 0.88 | 0.82 |
| | $S_5$ | 0.20 | 0.20 | 0.20 | 0.19 |
| $B_1$ | $S_1$ | 1.45 | 1.97 | 1.44 | 1.43 |
| | $S_2$ | 2.21 | 2.48 | 2.22 | 2.45 |
| | $S_3$ | 0.82 | 0.76 | 0.81 | 0.78 |
| | $S_4$ | 1.78 | 1.65 | 1.77 | 1.76 |
| | $S_5$ | 1.44 | 1.73 | 1.44 | 1.71 |
| | $S_6$ | 3.40 | 3.53 | 3.40 | 3.45 |
| | $S_7$ | 0.61 | 0.61 | 0.60 | 0.59 |
| $B_2$ | $S_1$ | 5.31 | 6.32 | 5.31 | 4.90 |
| | $S_2$ | 2.27 | 2.75 | 2.21 | 1.95 |
| | $S_3$ | 3.47 | 4.57 | 3.31 | 3.07 |
| | $S_4$ | 1.74 | 2.32 | 1.66 | 1.63 |
| | $S_5$ | 0.20 | 0.25 | 0.20 | 0.18 |
| | $S_6$ | 0.20 | 0.26 | 0.20 | 0.18 |

[a, b] see footnotes in Table 4.

Table 6. Calculated mean amplitudes of vibration (*u* in Å) and perpendicular amplitude correction coefficients (*K* in Å) for $P_4S_5$ and $As_4S_5$.

| Interatomic distances | Multiplicity | β-$P_4S_5$ | | | | | $As_4S_5$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *u* | | | *K* | | *u* | | | *K* | |
| | | *T*=0 K | 298 K | 773 K | 298 K | 773 K | *T*=0 K | 298 K | 773 K | 298 K | 773 K |
| $A_b$–S | 4 | 0.051 | 0.059 | 0.085 | 0.003 | 0.008 | 0.048 | 0.059 | 0.089 | 0.004 | 0.009 |
| $A_a$–$S_a$ | 2 | 0.051 | 0.059 | 0.085 | 0.003 | 0.007 | 0.047 | 0.060 | 0.089 | 0.004 | 0.009 |
| $A_a$–S | 4 | 0.051 | 0.060 | 0.087 | 0.003 | 0.007 | 0.047 | 0.059 | 0.089 | 0.004 | 0.009 |
| $A_b$–$A_b$ | 1 | 0.052 | 0.061 | 0.089 | 0.002 | 0.005 | 0.043 | 0.061 | 0.094 | 0.002 | 0.004 |
| S … S (via $A_a$) | 2 | 0.059 | 0.077 | 0.117 | 0.003 | 0.008 | 0.064 | 0.089 | 0.137 | 0.004 | 0.009 |
| S … S (via $A_b$) | 2 | 0.066 | 0.095 | 0.147 | 0.003 | 0.007 | 0.070 | 0.107 | 0.168 | 0.003 | 0.008 |
| $S_a$ … S | 4 | 0.064 | 0.092 | 0.142 | 0.002 | 0.005 | 0.067 | 0.100 | 0.156 | 0.003 | 0.007 |
| $A_a$ … $A_b$ | 4 | 0.056 | 0.068 | 0.102 | 0.001 | 0.003 | 0.048 | 0.073 | 0.114 | 0.001 | 0.002 |
| $A_a$ … $A_a$ | 1 | 0.059 | 0.076 | 0.114 | 0.001 | 0.003 | 0.049 | 0.077 | 0.121 | 0.001 | 0.002 |
| $A_b$ … S | 4 | 0.059 | 0.078 | 0.118 | 0.002 | 0.004 | 0.057 | 0.082 | 0.127 | 0.002 | 0.005 |
| $A_b$ … $S_a$ | 2 | 0.063 | 0.085 | 0.130 | 0.001 | 0.003 | 0.059 | 0.090 | 0.140 | 0.001 | 0.003 |
| $A_a$ … S | 4 | 0.065 | 0.093 | 0.143 | 0.001 | 0.003 | 0.063 | 0.102 | 0.160 | 0.001 | 0.003 |
| S … S (longest) | 2 | 0.063 | 0.086 | 0.132 | 0.001 | 0.003 | 0.065 | 0.093 | 0.143 | 0.002 | 0.004 |

Table 7. Calculated mean amplitudes of vibration ($u$ in Å) and perpendicular amplitude correction coefficients ($K$ in Å) for $P_4S_7$ and $As_2P_2S_7$.

| Interatomic distances | Multiplicity | $P_4S_7$ | | | | | $As_2P_2S_7$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $u$ | | | $K$ | | $u$ | | | $K$ | |
| | | $T = 0$ K | 298 K | 773 K | 298 K | 773 K | $T = 0$ K | 298 K | 773 K | 298 K | 773 K |
| $A_a{=}S_t$ | 2 | 0.041 | 0.044 | 0.057 | 0.005 | 0.013 | 0.041 | 0.044 | 0.059 | 0.006 | 0.015 |
| $A_b{-}S$ | 4 | 0.050 | 0.058 | 0.084 | 0.004 | 0.009 | 0.047 | 0.060 | 0.089 | 0.004 | 0.010 |
| $A_a{-}S_a$ | 2 | 0.049 | 0.058 | 0.084 | 0.003 | 0.007 | 0.049 | 0.058 | 0.085 | 0.004 | 0.009 |
| $A_a{-}S$ | 4 | 0.050 | 0.059 | 0.086 | 0.003 | 0.008 | 0.050 | 0.060 | 0.088 | 0.004 | 0.009 |
| $A_b{-}A_b$ | 1 | 0.052 | 0.060 | 0.087 | 0.002 | 0.005 | 0.042 | 0.057 | 0.087 | 0.002 | 0.005 |
| $S_a \ldots S_t$ | 2 | 0.064 | 0.094 | 0.145 | 0.004 | 0.010 | 0.064 | 0.094 | 0.145 | 0.005 | 0.013 |
| $S \ldots S_t$ (short) | 4 | 0.062 | 0.086 | 0.132 | 0.004 | 0.011 | 0.064 | 0.094 | 0.146 | 0.005 | 0.012 |
| $S \ldots S$ (via $A_a$) | 2 | 0.061 | 0.083 | 0.127 | 0.003 | 0.008 | 0.062 | 0.085 | 0.130 | 0.004 | 0.010 |
| $S \ldots S$ (via $A_b$) | 2 | 0.065 | 0.094 | 0.146 | 0.004 | 0.009 | 0.068 | 0.104 | 0.162 | 0.004 | 0.010 |
| $S_a \ldots S$ | 4 | 0.064 | 0.093 | 0.144 | 0.003 | 0.006 | 0.066 | 0.098 | 0.153 | 0.003 | 0.008 |
| $A_a \ldots A_b$ | 4 | 0.055 | 0.071 | 0.106 | 0.001 | 0.003 | 0.051 | 0.072 | 0.110 | 0.001 | 0.003 |
| $A_a \ldots A_a$ | 1 | 0.054 | 0.071 | 0.107 | 0.001 | 0.003 | 0.055 | 0.073 | 0.110 | 0.001 | 0.003 |
| $A_b \ldots S$ | 4 | 0.059 | 0.077 | 0.117 | 0.002 | 0.005 | 0.056 | 0.082 | 0.127 | 0.002 | 0.005 |
| $A_b \ldots S_a$ | 2 | 0.062 | 0.084 | 0.128 | 0.002 | 0.004 | 0.058 | 0.086 | 0.134 | 0.002 | 0.004 |
| $A_a \ldots S$ | 4 | 0.063 | 0.094 | 0.145 | 0.002 | 0.004 | 0.064 | 0.097 | 0.150 | 0.002 | 0.004 |
| $S \ldots S$ (longest) | 2 | 0.063 | 0.086 | 0.132 | 0.002 | 0.005 | 0.063 | 0.088 | 0.136 | 0.002 | 0.005 |
| $A_a \ldots S_t$ | 2 | 0.061 | 0.089 | 0.137 | 0.002 | 0.004 | 0.062 | 0.089 | 0.138 | 0.002 | 0.005 |
| $A_b \ldots S_t$ | 4 | 0.061 | 0.082 | 0.125 | 0.002 | 0.004 | 0.057 | 0.086 | 0.134 | 0.002 | 0.004 |
| $S \ldots S_t$ (long) | 4 | 0.070 | 0.111 | 0.173 | 0.001 | 0.003 | 0.071 | 0.116 | 0.182 | 0.002 | 0.004 |
| $S_t \ldots S_t$ | 1 | 0.073 | 0.122 | 0.191 | 0.001 | 0.004 | 0.073 | 0.119 | 0.187 | 0.002 | 0.005 |

Table 8. Calculated thermodynamical data for the $A_4S_5$ and $A_4S_7$ molecules in an ideal gas at 1 atm and temperatures up to 1000 K. Molar heat capacity $C_p^0$, reduced enthalpy $(H^0 - H_0^0)/T$, reduced Gibbs energy $-(G^0 - G_0^0)/T$ and entropy $S^0$. All values given in $JK^{-1}\ mol^{-1}$.

| $T\ (K)$ | $C_p^0$ | | $(H^0 - H_0^0)/T$ | | $(G^0 - G_0^0)/T$ | | $S^0$ | |
|---|---|---|---|---|---|---|---|---|
| | $\beta$-$P_4S_5$ | $As_4S_5$ | $\beta$-$P_4S_5$ | $As_4S_5$ | $\beta$-$P_4S_5$ | $As_4S_5$ | $\beta$-$P_4S_5$ | $As_4S_5$ |
| 100 | 77.96 | 103.16 | 46.63 | 57.56 | 241.76 | 259.78 | 288.39 | 317.35 |
| 200 | 143.38 | 163.64 | 80.37 | 98.00 | 284.46 | 312.88 | 364.83 | 410.88 |
| 300 | 173.31 | 185.44 | 107.05 | 124.08 | 322.41 | 357.96 | 429.46 | 482.04 |
| 400 | 186.96 | 194.61 | 125.52 | 140.71 | 355.90 | 396.10 | 481.42 | 536.81 |
| 500 | 194.00 | 199.17 | 138.59 | 152.00 | 385.39 | 428.79 | 523.98 | 580.78 |
| 600 | 198.05 | 201.75 | 148.19 | 160.09 | 411.55 | 457.25 | 559.74 | 617.34 |
| 700 | 200.56 | 203.33 | 155.50 | 166.16 | 434.97 | 482.41 | 590.47 | 648.57 |
| 800 | 202.23 | 204.38 | 161.25 | 170.88 | 456.12 | 504.92 | 617.37 | 675.80 |
| 900 | 203.39 | 205.10 | 165.87 | 174.64 | 475.39 | 525.27 | 641.26 | 699.91 |
| 1000 | 204.22 | 205.62 | 169.66 | 177.72 | 493.07 | 543.83 | 662.73 | 721.55 |
| | $P_4S_7$ | $As_2P_2S_7$ | $P_4S_7$ | $As_2P_2S_7$ | $P_4S_7$ | $As_2P_2S_7$ | $P_4S_7$ | $As_2P_2S_7$ |
| 100 | 101.69 | 116.47 | 56.46 | 63.23 | 254.42 | 263.35 | 310.88 | 326.59 |
| 200 | 176.02 | 187.42 | 99.70 | 110.02 | 307.27 | 322.41 | 406.97 | 432.43 |
| 300 | 211.76 | 218.61 | 131.84 | 141.69 | 354.16 | 373.54 | 486.00 | 515.14 |
| 400 | 229.18 | 233.52 | 154.24 | 162.99 | 395.34 | 417.32 | 549.58 | 580.31 |
| 500 | 238.53 | 241.48 | 170.25 | 177.97 | 431.57 | 455.39 | 601.82 | 633.36 |
| 600 | 244.02 | 246.13 | 182.12 | 188.98 | 463.71 | 488.86 | 645.84 | 677.84 |
| 700 | 247.48 | 249.07 | 191.23 | 197.37 | 492.50 | 518.65 | 683.73 | 716.01 |
| 800 | 249.80 | 251.03 | 198.42 | 203.96 | 518.52 | 545.45 | 716.94 | 749.41 |
| 900 | 251.41 | 252.40 | 204.22 | 209.27 | 542.24 | 569.79 | 746.46 | 779.06 |
| 1000 | 252.59 | 253.39 | 209.00 | 213.63 | 564.01 | 592.07 | 773.01 | 805.71 |

Both the quantities of *u* and *K* are useful in the interpretation of modern gas electron diffraction measurements [19].

Many characteristic values are found among the calculated mean amplitudes. For the bonded distances in particular we find firstly (in Å units at 25 °C) 0.044 for P=S in both $P_4S_7$ and $As_2P_2S_7$. For the P–S bond it was found 0.058 in $PAs_3S_3$ [4], 0.058–0.060 for $P_4S_7$ and $As_2P_2S_7$ (Table 8), 0.059–0.060 for $P_4S_5$ (Table 7), and 0.060 for $P_4S_3$ [2]. For the P–P bond the results are 0.060 for $P_4S_7$ (Table 8), 0.061 for $P_4S_3$ [2] and $P_4S_5$ (Table 7), and 0.062 for $P_4Se_3$ [4]. Similarly one has all As–S mean amplitudes in the range of 0.059–0.061 with a somewhat lower value (0.057) for $PAs_3S_3$. Finally the As–As values are found to be 0.061 for $As_4S_5$ and 0.057 for $As_2P_2S_7$ compared to 0.056 in $PAs_3S_3$ [4].

## Coriolis Coefficients

In the $P_4S_3$-type molecules of symmetry $C_{3v}$ there are first-order Coriolis coefficients of the type $E \times E$ [2, 4]. Because of the lack of degeneracy of normal modes of the present molecular models, which belong to the $C_{2v}$ symmetry, there are no such Coriolis coefficients in the present case. However, there are 163 and 269 second-order Coriolis coefficients in each of the $A_4S_5$ and $A_4S_7$ compounds, respectively. They were well all computed from the final force fields of the present work. The results which are too voluminous to be given here, are obtainable on request from S. J. Cyvin.

## Thermodynamical Data

By using the vibrational frequencies (Tables 2, 3) and the mentioned molecular parameters (Table 1) of the title molecules, the molar heat capacity ($C_p^0$), the reduced enthalpy ($(H^0-H_0^0)/T$), the reduced Gibbs energy ($(G^0-G_0^0)/T$) and the entropy ($S^0$) were calculated for an ideal gas at 1 atm and in the temperature range from 0–1000 K. The calculations were based on the usual models for a rigid rotator and harmonic oscillator [20]. The results are summarized in Tables 8 and 9.

Table 9. Comparison of the calculated frequencies for $P_4S_6$ with experimental data from Bues et al. [6] and the frequencies calculated for $P_4S_5$ and $P_4S_7$.

| $P_4S_7$ | $P_4S_6$ | | | $P_4S_5$ |
|---|---|---|---|---|
| a | Species | a | b | a |
| 672 ($A_1$) | A′ | – | – | – |
| 662 ($B_1$) | | 667 | 685 | – |
| 470 ($B_1$) | | 469 | 505 | 459 ($B_1$) |
| 465 ($A_1$) | | 453 | – | 459 ($A_1$) |
| 448 ($A_1$) | | 445 | – | 435 ($A_1$) |
| 416 ($B_1$) | | 418 | – | 435 ($B_1$) |
| 360 ($A_1$) | | 358 | 378 | 348 ($B_1$) |
| 318 ($B_1$) | | 340 | 370? | 346 ($A_1$) |
| 298 ($A_1$) | | 297 | 285 | 337 ($A_1$) |
| 263 ($A_1$) | | 280 | 268 | 280 ($A_1$) |
| 236 ($B_1$) | | 235 | – | 249 ($B_1$) |
| 214 ($A_1$) | | 216 | – | 216 ($A_1$) |
| 200 ($B_1$) | | 184 | – | 184 ($A_1$) |
| 173 ($A_1$) | | 175 | – | – |
| 142 ($B_1$) | | 138 | – | 161 ($B_1$) |
| 126 ($A_1$) | | – | – | – |
| 477 ($B_2$) | A″ | 474 | 529 | 465 ($A_2$) |
| 471 ($A_2$) | | 462 | – | 452 ($B_2$) |
| 446 ($A_2$) | | 431 | – | 405 ($A_2$) |
| 401 ($B_2$) | | 389 | 390? | 374 ($B_2$) |
| 304 ($B_2$) | | 304 | – | 303 ($B_2$) |
| 227 ($B_2$) | | 226 | – | 221 ($B_2$) |
| 210 ($A_2$) | | 210 | – | 211 ($A_2$) |
| 188 ($B_2$) | | 187 | 196 | – |
| 186 ($A_2$) | | – | – | – |
| 120 ($B_2$) | | 140 | 130? | 143 ($B_2$) |
| 114 ($A_2$) | | 116 | 115 | 130 ($A_2$) |

[a] Frequencies calculated from the initial force field.
[b] Experimental values taken from [6].

## The $P_4S_6$ Compound

Bues et al. [6] in their studies of $P_4S_5$ and $P_4S_7$ have tentatively assigned some of the observed frequencies to the intermediate compound of $P_4S_6$. We have therefore calculated approximate frequencies of this compound using the force constants of the initial force field. In Table 10 they are correlated with the corresponding calculations for $P_4S_7$ (Table 3) and $P_4S_5$ (Table 2), as well as experimental Raman frequencies from Bues et al. [6].

### *Acknowledgements*

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