Vibrations of a Cage-like Molecule, P_4S_3 : Some Theoretical Aspects

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Two independent symmetry coordinate sets for P_4S_3 are developed, starting from the "method of fragments". A simple, approximate force field is expressed in terms of the two sets of symmetry coordinates, and the corresponding compliance matrices are given. The invariance of compliants is demonstrated. The potential energy distribution (PED) is discussed. An example is shown where the PED terms are clearly inadequate for the description of normal modes. A general warning against the interpretation of the PED in terms of such descriptions for cage-like structures seems to be warranted.

Introduction

Recent spectroscopical investigations of P_4S_3 [1] have been supplemented by a normal coordinate analysis [2]. The molecular model was assumed to be of a cage-like structure with the C_{3v} symmetry. The validity of a highly approximate force field [2] was tested by an application to related molecules corresponding to the same model, viz. P_4Se_3, As_4S_3, As_4Se_3 and PAs_3S_3 [3]. In all cases the vibrational frequencies were calculated with satisfactory results. The potential energy distribution (PED), however, showed some seemingly anomalous behaviour. The present work is supposed to contribute to a better understanding of these features. We wish to point out the coordinate-dependence of the PED and give some illustrating examples. Furthermore, we wish to demonstrate the behaviour of force constants depending on two choices of symmetry coordinate sets. At the same time we demonstrate the invariance properties [4] of compliance constants [4, 5]. These properties are important in presence of redundancies, which can not be avoided in cage-like structures. In the present case of P_4S_3 the seven atoms of the molecule are interconnected to a high extent: an equilateral P_3 triangle at the base and three P–S–P–P–S rings are distinguished.

Symmetry Coordinates

In a cage-like structure it may be a problem to develop a complete set of *independent* internal coordinates. The removal of redundancies in one way or the other can not be avoided since a complete set of symmetrically equivalent valence coordinates must be included for every type. The "method of fragments" has been described for the out-of-plane [6] and in-plane [7] vibrations of polycenes in the course of an extensive study of condensed aromatics; see [8] and references cited therein. The method is a useful aid in constructing independent symmetry coordinates; in many cases we are assured with complete confidence that all redundancies have been removed. Two characteristics of the method are formulated below. (i) "Opening" of the structure as far as possible by omitting interatomic bondings. Complete sets of symmetrically equivalent bonds must be omitted every time. (ii) Stepwise construction of symmetry coordinates by considering "fragments" of the molecule. A new fragment is obtained from the foregoing one by adding one set of symmetrically equivalent atoms.

In the case of P_4S_3 the cage structure (see Fig. 1) is opened by omitting the P_b–P_b bonds at the molecule base. When starting with the ammonia-like P_aS_3 fragment, say (I), we obtain the whole molecule (II) already at the next step. Table 1 summarizes the symmetrical structures of the models (I) and (II). In model (I) the three r- and three β-type coordinates are known to be independent, and the symmetry coordinates may easily be constructed on the basis of the symmetrical structures

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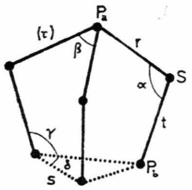

Fig. 1. The P_4S_3 model; symmetry C_{3v}. P_a and P_b denote the apical and basal P atoms, respectively. Types of valence coordinates are indicated.

Table 1. Symmetrical structures for models (I) and (II) in the "method of fragments".

Model	Γ_{vib}
P_aS_3 (I)	$2A_1 + 2E$
$P_aS_3(P_b)_3$ (II)	$4A_1 + A_2 + 5E$

$r(A_1 + E)$ and $\beta(A_1 + E)$. The same symmetry coordinates must also apply to model (II). In addition we obtain the corresponding symmetry coordinates on the basis of $t(A_1 + E)$ and $\alpha(A_1 + E)$. The remaining three coordinates belong to $A_2 + E$. For the open structure of Fig. 1 we have no other choice than the P_a–S torsions (τ) among the standard types of valence coordinates [9] for the construction of the symmetry coordinates. There are six symmetrically equivalent torsions of this type, and their symmetrical structure is $A_1 + A_2 + 2E$. Only three of the symmetry-adapted combinations of τ coordinates are independent together with the other coordinates described above.

In the present work we have not taken the full consequences of the open structure without P_b–P_b bonds. The τ torsions were not used in the construction of the symmetry coordinates. Instead we have employed the S–P_b–P_b bendings, γ (cf. Figure 1), which have the same symmetrical structure as the τ torsions, viz. $A_1 + A_2 + 2E$. In conclusion we arrive at a complete set of independent symmetry coordinates, say (A), built up from the following types of valence coordinates:

(A_1) r, t, α, β,
(A_2) γ,
((E) $r, t, \gamma, \alpha, \beta$.

An alternative set has been derived by interchanging the α bendings with $s(P_b$–$P_b)$ stretchings. Thus the symmetry coordinate set designated (B) contains the types:

(A_1) r, t, s, β,
(A_2) γ,
(E) r, t, γ, s, β.

This set (B) has been employed in the previously reported normal coordinate analysis of P_4S_3 [2], where the appropriate symmetry-adapted linear combinations of the valence coordinates are given.

A linear dependence (redundancy) between internal coordinates may be revealed through the fact that the corresponding G matrix becomes singular in that case. In the present case it was checked that both G matrices based on the coordinates (A) and (B) are non-singular and may hence be inverted (into G^{-1}) in the usual way.

Approximate Force Field

The extremely simple approximation used previously as the initial force field [2] is the only one to be considered in the present work. It is defined by the force constant parameters (in mdyne/Å):

$$f_r(P_a\text{–}S) = 1.3\,, \quad f_t(S\text{–}P_b) = 1.3\,,$$
$$f_s(P_b\text{–}P_b) = 1.1\,, \quad f_\alpha = f_\beta = f_\gamma = f_\delta = 0.2\,.$$

Thus the corresponding force-constant matrix, say $\hat{F}$, is based on 24 valence coordinates, say $\hat{R}$, which are not independent. Since the number of independent internal coordinates is 15, the number of redundancies in $\hat{R}$ amounts to 9.

The force field may be converted into the two systems of independent symmetry coordinates, viz. (A) and (B). For this purpose the T matrix method [10] is convenient, especially in computer techniques.

Table 2. Symmetry force constants (mdyne/Å).

Symmetry coordinates (A)									
A_1	(r)	3.86							
	(t)	−0.77	1.53						
	(α)	2.80	−0.84	3.59					
	(β)	3.30	−0.98	3.86	4.64		A_2	(γ)	0.20
E	(r)	66.9							
	(t)	135.1	279.7						
	(γ)	69.3	143.0	73.7					
	(α)	123.1	253.8	130.3	231.5				
	(β)	0.5	1.2	0.7	1.1	0.26			
Symmetry coordinates (B)									
A_1	(r)	1.73							
	(t)	−0.13	1.34						
	(s)	−0.28	0.08	1.28					
	(β)	0.33	−0.10	−0.21	0.52		A_2	(γ)	0.20
E	(r)	1.45							
	(t)	0.09	1.55						
	(γ)	−0.02	0.15	0.33					
	(s)	0.12	−0.01	−0.09	1.85				
	(β)	−0.07	0.02	0.06	−0.10	0.26			

The resulting symmetry force-constant matrices (say F_A based on S_A and F_B based on S_B) are given in Table 2. Although the two matrices F_A and F_B express exactly the same force field they look very different. Especially the E species in F_A displays force-constant values which may seem abnormally high. However, the same orders of magnitude have been encountered in analyses of other cage-like structures [11, 12]. It is seen that corresponding force constants have different values in the two sets F_A and F_B. Thus, for instance, $F_r(A_1)$ as well as $F_r(E)$ are different in the two cases, and it is so because the force constants compensate for the removal of redundancies in different ways. It is apparently not possible to deduce an f_r ("P_a–S stretching force constant") with physical significance from the symmetry coordinates.

It is emphasized that both treatments based on the S_A and S_B coordinates are mathematically correct. The calculated vibrational frequencies using the F_A and F_B matrices were verified to be exactly equal to those of the column *a* in Table 2 of [2].

Compliance Constants

When based on independent coordinates the compliance matrix is equal to the inverse force-constant matrix, $N = F^{-1}$ [4], but not otherwise! Here we have an opportunity to demonstrate the invariance of compliants [4]. Since both S_A and S_B are independent coordinate sets, the F_A and F_B matrices (see Table 2) may be inverted in the usual way to give the corresponding N_A and N_B. The results are shown in Table 3. As expected the corresponding compliants in the two systems have identical values. For instance is (in Å/mdyne) $N_r(A_1) = 0.664$ and $N_r(E) = 0.708$ unambiguously. It is also possible to derive the invariant values of valence compliants, e.g.

$$n_r = (1/3)[N_r(A_1) + 2N_r(E)] = 0.693$$

and the interaction term

$$n_{rr} = (1/3)[N_r(A_1) - N_r(E)] = -0.014.$$

It should be noticed that the n_r constant derived above is *not* the inverse of $f_r = 1.3$ mdyne/Å. In fact we might develop every valence compliant corresponding to the terms of the $\hat{F}$ matrix. The resulting $\hat{N}$ would no longer be a diagonal matrix and hence *not* the inverse of $\hat{F}$. In fact the $\hat{N}$ matrix, being based on the dependent coordinates $\hat{R}$, must be singular.

Table 3. Symmetry compliants (Å/mdyne).

Symmetry coordinates (A)									
A_1	(r)	0.66							
	(t)	0.03	0.76						
	(α)	−0.11	0.03	2.67					
	(β)	−0.37	0.11	−2.14	2.28		A_2	(γ)	5.00
E	(r)	0.71							
	(t)	−0.05	0.68						
	(γ)	0.01	−0.30	3.35					
	(α)	−0.33	−0.55	−1.56	1.66				
	(β)	0.19	0.00	−0.75	0.30	4.10			
Symmetry coordinates (B)									
A_1	(r)	0.66							
	(t)	0.03	0.76						
	(s)	0.08	−0.02	0.85					
	(β)	−0.37	0.11	0.29	2.28		A_2	(γ)	5.00
E	(r)	0.71							
	(t)	−0.05	0.68						
	(γ)	0.01	−0.30	3.35					
	(s)	−0.04	−0.01	0.12	0.56				
	(β)	0.19	0.00	−0.75	0.17	4.10			

Potential Energy Distribution

The potential energy (V) in terms of normal (Q) and symmetry (S) coordinates is given by [9]

$$2V = \sum_k \lambda_k Q_k^2 = \sum_i \sum_j F_{ij} S_i S_j . \tag{1}$$

The part of $2V$ belonging to one normal coordinate (Q_k) is:

$$\lambda_k Q_k^2 = Q_k^2 \sum_i \sum_j L_{ik} L_{jk} F_{ij} . \tag{2}$$

In order to deduce the PED [13, 14] in the usual way it is necessary to introduce the approximation

$$\lambda_k Q_k^2 \approx Q_k^2 \sum_i L_{ik}^2 F_{ii} \tag{3}$$

by omitting the terms with $i \neq j$ in (2). Consequently it becomes possible to associate a given normal mode with a sum of PED terms (x_{ik}) defined by

$$x_{ik} = L_{ik}^2 F_{ii} / \lambda_k . \tag{4}$$

One obtains

$$\sum_i x_{ik} = \sum_i L_{ik}^2 F_{ii} / \lambda_k \approx 1 . \tag{5}$$

The validity of this approximation (5) follows from (3). On the other hand, if (5) is approximately fulfilled it does not imply the validity of (3). Another conventional definition is

$$X_{ik} = 100\, x_{ik} = 100\, L_{ik}^2 F_{ii} / \lambda_k . \tag{6}$$

Although the definition (6) was used in Ref. [2] it will not be applied here.

For the sake of illustration the PED terms were computed in the cases (A) and (B) for the choices of symmetry coordinates (see above). The results are shown in Table 4. As expected the great differences in symmetry force constants (cf. Table 2) are reflected in great differences between corresponding PED terms. Especially the x_{ik} values of species E in the case (A) are extremely large. It seems quite clear that the approximation (3) has broken down completely in this case, and the PED terms are quite inadequate for a description of the normal modes. Also in the case (B), however, where the orders of magnitude of the x_{ik} values seem to be reasonable, one should be very careful in the interpretation of the PED in terms of normal mode descriptions. The coordinate-dependence of PED terms [15] must be kept in mind. These features become especially critical for cage-like structures, where the problem of redundancies must be faced.

Table 4. Potential energy distribution (x_{ik} terms).

Symmetry coordinates (A)

		ω_1	ω_2	ω_3	ω_4			ω_5
A_1	(r)	0.02	1.17	1.09*	0.28	A_2	(γ)	1.00*
	(t)	0.21	0.23	0.63	0.09			
	(α)	2.32*	0.21	0.06	6.99*			
	(β)	0.99	3.89*	0.26	5.44			

		ω_6	ω_7	ω_8	ω_9	ω_{10}
E	(r)	19.2	5.8	17.3	1.7	3.3
	(t)	60.6	60.4	28.8	28.0	11.7*
	(γ)	89.9*	0.8	44.1*	111.8	0.8
	(α)	36.7	137.5*	5.3	197.5*	6.3
	(β)	0.0	0.0	0.0	0.2	0.8

Symmetry coordinates (B)

		ω_1	ω_2	ω_3	ω_4			ω_5
A_1	(r)	0.01	0.52*	0.49*	0.13	A_2	(γ)	1.00*
	(t)	0.19	0.20	0.55*	0.08			
	(s)	0.68*	0.18	0.10	0.13			
	(β)	0.11	0.44*	0.03	0.61*			

		ω_6	ω_7	ω_8	ω_9	ω_{10}
E	(r)	0.42*	0.13	0.37*	0.04	0.07
	(t)	0.34*	0.33*	0.16	0.15	0.06
	(γ)	0.40*	0.00	0.20	0.50*	0.00
	(s)	0.00	0.48*	0.41*	0.14	0.00
	(β)	0.05	0.00	0.04	0.21	0.78*

* Main terms are marked with asterisks.

From empirical knowledge it is found possible to describe the normal modes approximately as "stretchings", "bendings", etc., to a large extent even for cage-like systems of the P_4S_3 type [1, 2]. These descriptions should not be exaggerated, both because of mixtures in the different types of modes, which may be expected to be pronounced in cage-like molecules, and because of ambiguous descriptions.

Nevertheless we feel that there is a break-down of the theory when the PED is tentatively applied to cage-like structures. It seems to be yet an unsolved problem to deduce quantities which could reflect justly the experimental descriptions of normal modes. We believe that this is the case in spite of a considerable amount of recent studies of PED and proposals of other approaches, e.g. those based on TED (total energy distribution) [15—21].

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