Potential Energy Distribution in the Presence of Redundancies

J. Brunvoll, B. N. Cyvin, and S. J. Cyvin
Institutt for teoretisk kjemi, Universitet i Trondheim

Z. Naturforsch. **37a**, 342—345 (1982); received March 8, 1982

A theory is outlined for the potential energy distribution in the presence of redundancies. Numerical examples are given for the cage-like molecules P_4S_3, P_4Se_3, As_4S_3, As_4Se_3 and PAs_3S_3, for which the molecular vibrations have been analysed previously.

Introduction

Let S denote a complete set of *independent* internal coordinates in the theory of molecular vibrations [1, 2]. They may, for instance, be symmetry coordinates. The matrices F (force-constant matrix) and L ($S = LQ$, where Q designates the normal coordinates) are supposed to be based on the S coordinates. For the frequency parameter λ_k one has

$$\lambda_k = \sum_i \sum_j L_{ik} L_{jk} F_{ij} . \qquad (1)$$

This parameter is the coefficient in the part of $2V$ (V is the potential energy) belonging to the normal coordinate Q_k. The potential energy distribution (PED) terms are defined by [3—5]

$$x_{ik} = L_{ik}^2 F_{ii} / \lambda_k . \qquad (2)$$

Cyvin et al. [5] have discussed the influence on PED terms when redundancies from the internal coordinates are removed in different ways. The PED for the cage-like molecule P_4S_3 was analysed using two different sets of symmetry coordinates (A and B), both without redundancies. The PED terms were found to be critically dependent on this choice of coordinates and hardly meaningful at all in one of the cases (A).

In the present work it is shown how the PED terms may be derived uniquely even in the presence of redundancies. Hence the dilemma of choosing an adequate set of independent internal coordinates (such as the A and B symmetry coordinates in the cited example [5]) is eliminated in one sense. But it is true that the PED terms depend on the particular choice of coordinates [5, 6]. However, they may be chosen as a set of linearly *dependent* coordinates. Let such a set of internal coordinates be identified by the symbol $\hat{R}$. The PED terms of course also depend on the force field; it may be defined by $\hat{F}$ in terms of the $\hat{R}$ coordinates.

The present theory is applied to P_4S_3 [5, 7, 8], P_4Se_3, As_4S_3, As_4Se_3 [7, 9] and PAs_3S_3 [9].

Theory

Definition of $\hat{x}_{ik}$

The PED terms based on a set of $\hat{R}$ coordinates are defined in analogy with (2):

$$\hat{x}_{ik} = \hat{L}_{ik}{}^2 \hat{F}_{ii} / \lambda_k . \qquad (3)$$

Here the $\hat{L}_{ik}$ elements belong to the transformation matrix of

$$\hat{R} = \hat{L} Q . \qquad (4)$$

The $\hat{x}_{ik}$ terms are not uniquely defined in as much as the force field does not uniquely determine an $\hat{F}$ matrix when redundancies are involved. When a linear dependence exists among the $\hat{R}$ coordinates, there is namely an infinite number of $\hat{F}$ matrices compatible with the same physical force field. On the other hand, when a definite $\hat{F}$ matrix is chosen to define a force field, the corresponding $\hat{x}_{ik}$ terms may be derived uniquely. The $\hat{L}_{ik}$ elements are completely determined when the force field is given.

Derivation of $\hat{L}$

Let the $\hat{R}$ coordinates be given in terms of the cartesian displacement coordinates by

$$\hat{R} = \hat{B} x . \qquad (5)$$

In terms of a set of *independent* internal coordinates, S, one has $x = AS$, where $A = m^{-1} B' G^{-1}$ by virtue of the Crawford-Fletcher formula [1, 2, 10].

Reprint requests to Prof. S. J. Cyvin, Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norwegen.

Hence

$$\hat{R} = \hat{B} m^{-1} B' G^{-1} S\,. \tag{6}$$

This equation is consistent with the T-matrix formulation of Cyvin [11],

$$\hat{R} = TS\,, \quad T = \hat{B} m^{-1} B' G^{-1}\,. \tag{7}$$

By inserting $S = LQ$ into (6) and simultaneously making use of $G^{-1} = (L^{-1})' L^{-1}$, one arrives at

$$\hat{R} = \hat{B} m^{-1} B' (L^{-1})' Q\,. \tag{8}$$

On comparing (8) with (4) one finally obtains

$$\hat{L} = \hat{B} m^{-1} B' (L^{-1})'\,. \tag{9}$$

It should be noted that the matrix $\hat{L}$ does not depend on the particular choice of the S coordinates.

Alternative Derivation of $\hat{L}$

The T matrix [11] is defined in a general sense. It may be adapted to the $\hat{L}$ matrix when the independent coordinates are taken as the normal coordinates (Q):

$$\hat{R} = T_Q Q\,, \quad T_Q = \hat{B} m^{-1} B'_Q G_Q^{-1}\,, \tag{10}$$

cf. (7). Here $T_Q = \hat{L}$, $G_Q = G_Q^{-1} = E$, and the B'_Q matrix is obtained from

$$S = LQ = Bx\,, \quad Q = L^{-1} Bx\,;$$
$$B_Q = L^{-1} B\,. \tag{11}$$

Insertion into (10) gives the above formulas (8) and (9).

Practical Application

In practical computations it is often useful to define a force field by means of an $\hat{F}$ matrix in the presence of redundancies. The corresponding PED terms, $\hat{x}_{ik}$, may hence be given according to the theory outlined above. These terms are particularly meaningful if $\hat{F}$ is a diagonal matrix. In that case one has [5]

$$\sum_i \hat{x}_{ik} = 1\,. \tag{12}$$

A diagonal $\hat{F}$ matrix in terms of valence coordinates including redundancies has frequently been assumed to define an initial force field of cage-like [5, 8, 9, 12—15], planar cyclic [16] and planar polycyclic [17—19] molecules.

Numerical Examples

The present theory has been applied to some cage-like molecules with the structure of P_4S_3 [5, 7, 8]. This molecule has one apical P atom (P_a) and three basal P atoms (P_b). The other molecules of this investigation are P_4Se_3, As_4S_3, As_4Se_3 and PAs_3S_3 [7, 9]. A simple force field approximation represented by a diagonal $\hat{F}$ matrix in terms of valence coordinates including redundancies was assumed. In fact the same numerical form of the $\hat{F}$ matrix [5, 8, 9] was assumed for all the five molecules in question. All stretchings and bendings were employed as the valence coordinates. They are listed in Table 1.

Table 2 shows the calculated frequencies and the PED terms $\hat{x}_{ik}$ of (3) multiplied by 100. Contributions from symmetrically equivalent coordinates are added in accord with their multiplicity (cf. Table 1). The condition (12) or

$$\sum_i \hat{X}_{ik} = 100\,; \quad \hat{X}_{ik} = 100\,\hat{x}_{ik} \tag{13}$$

is fulfilled in the present case.

It is interesting to observe the great shifts of PED terms from one molecule to the other; in many cases the whole pattern of dominating terms is altered. These effects are entirely due to the large mass shifts, in addition to smaller shifts in structural parameters [8, 9]. The present results show many similarities with those of the computations [5, 8, 9] based on the independent symmetry coordinates designated S_4 [5] (where the α and δ coordinates are omitted). The computations confirm many of the empirical descriptions of normal modes in the experimental assignments of P_4S_3 [7, 8], P_4Se_3, As_4S_3 and As_4Se_3 [7]. Thus, for instance, the $\nu_1(A_1)$ frequency is assigned to the s, s, t and s types, respectively, through this series of molecules. For As_4S_3 the agreement is excellent throughout, but otherwise there are several controversies.

Multiplicity	Symbol	Definition referred to the $P_aS_3(P_b)_3$ molecule (P_4S_3)
3	r	P_a-S stretching
3	t	P_b-S stretching
3	s	P_b-P_b stretching
6	γ	P_bP_bS bending
3	α	P_aSP_b bending
3	β	SP_aS bending
3	δ	$P_bP_bP_b$ bending

Table 1. The employed valence coordinates.

Table 2. Calculated frequencies (in cm^{-1}) and PED terms ($\hat{X}_{ik} = 100\hat{x}_{ik}$) for five molecules. Dominating terms are marked with asterisks. In the one-dimensional block for $\nu_5(A_2)$ one has 100γ throughout.

	Species A_1				Species E				
	1	2	3	4	6	7	8	9	10
P_4S_3	485	415	329	276	465	422	372	263	175
r	0.83	39.31 *	36.80	9.45	37.34 *	11.25	33.64 *	3.38	6.40
t	18.08	19.62	53.30 *	7.79	28.14	28.06 *	13.39	13.01	5.42
s	57.83 *	15.84	8.34	11.07	0.11	28.58 *	24.30	8.11	0.18
γ	6.06	7.27	0.09	9.26	27.60	4.63	12.16	37.77 *	27.92
α	12.92	1.17	0.35	38.97 *	3.17	11.88	0.46	17.06	0.54
β	4.29	16.79	1.12	23.46	3.58	0.01	2.79	16.25	59.43 *
δ	—	—	—	—	0.06	15.59	13.25	4.42	0.10
P_4Se_3	470	356	297	187	415	402	353	201	117
r	0.43	45.08 *	3.78	37.30 *	6.89	10.62	64.96 *	0.54	9.17
t	8.19	4.17	85.92 *	0.13	44.63 *	0.11	6.70	33.08 *	3.69
s	75.65 *	6.48	2.76	8.35	5.47	44.15 *	6.11	5.29	0.33
γ	6.23	2.01	2.36	11.40	38.57	11.57	7.87	28.23	23.76
α	8.38	10.79	4.21	30.75	0.23	8.46	1.44	21.85	0.00
β	1.11	31.46	0.98	12.07	1.24	1.00	9.60	8.12	62.86 *
δ	—	—	—	—	2.98	24.08	3.33	2.89	0.18
As_4S_3	375	341	263	199	382	332	247	199	163
r	13.09	48.88 *	18.91	5.72	53.30 *	10.69	10.74	12.20	4.78
t	55.22 *	0.13	10.43	33.29 *	22.22	55.78 *	5.04	0.06	4.62
s	4.73	17.35	67.08 *	3.83	0.07	3.87	48.17 *	9.08	0.08
γ	0.05	20.37	0.08	2.51	18.20	2.91	9.03	44.59 *	35.46
α	10.67	13.24	0.98	27.44	3.85	22.45	0.04	6.31	1.90
β	16.23	0.02	2.52	27.20	2.32	2.19	0.72	22.81	53.11 *
δ	—	—	—	—	0.04	2.11	26.27	4.95	0.04
As_4Se_3	312	258	211	176	298	271	238	168	110
r	1.28	41.48 *	33.11	11.00	34.23 *	12.43	35.77 *	3.61	5.83
t	18.57	16.23	57.19 *	6.73	30.93	24.48	13.01	14.09	5.36
s	57.07 *	16.95	8.17	10.99	0.02	29.91 *	23.33	7.89	0.19
γ	5.56	7.07	0.01	9.61	28.77	4.53	11.87	36.60 *	27.33
α	12.82	1.09	0.50	38.60 *	2.82	12.31	0.64	17.17	0.46
β	4.70	17.18	1.02	23.07	3.22	0.03	2.66	15.33	60.72 *
δ	—	—	—	—	0.01	16.31	12.73	4.30	0.10
PAs_3S_3	418	343	270	246	438	338	260	216	167
r	32.91 *	38.67 *	12.04	2.51	75.26 *	2.75	4.37	0.44	9.25
t	25.01	8.34	40.29 *	25.59 *	4.44	75.15 *	3.71	0.07	4.08
s	1.20	20.18	44.69 *	27.03 *	0.06	2.07	34.90 *	24.26	0.00
γ	0.14	18.15	1.72	2.76	7.74	2.89	27.21	29.04 *	42.26 *
α	15.25	14.26	1.24	23.52	5.92	14.50	3.53	7.19	3.00
β	25.49	0.40	0.02	18.59	6.55	1.53	7.24	25.76	41.40 *
δ	—	—	—	—	0.03	1.13	19.04	13.23	0.00

In particular the computations suggest the empirical descriptions of $\nu_2(A_1)$ and $\nu_3(A_1)$ to be interchanged for P_4S_3, P_4Se_3 and As_4Se_3. This is also the case for $\nu_6(E)$ and $\nu_8(E)$ in P_4Se_3. In species E the results of the computations (Table 2) display a somewhat confusing pattern. In general it is concluded that the normal modes are highly mixed; a description of them in terms of simple motions is hardly possible.

Acknowledgement

Financial support to BNC from the Norwegian Council for Science and the Humanities is gratefully acknowledged.

[1] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York 1955.
[2] S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo and Elsevier, Amsterdam 1968.
[3] Y. Morino and K. Kuchitsu, J. Chem. Phys. **20**, 1809 (1952).
[4] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2. Edition, John Wiley Intersci., New York 1970.
[5] S. J. Cyvin, B. N. Cyvin, M. Somer, and W. Brockner, Z. Naturforsch. **36a**, 774 (1981).
[6] J. C. Whitmer, J. Mol. Spectry. **68**, 326 (1977).
[7] W. Bues, M. Somer, and W. Brockner, Z. Naturforsch. **35b**, 1063 (1980).
[8] S. J. Cyvin, J. Brunvoll, B. N. Cyvin, M. Somer, and W. Brockner, Z. Naturforsch. **35a**, 1062 (1980).
[9] W. Brockner, M. Somer, B. N. Cyvin, and S. J. Cyvin, Z. Naturforsch. **36a**, 846 (1981).
[10] B. L. Crawford, Jr. and W. H. Fletcher, J. Chem. Phys. **19**, 141 (1951).
[11] S. J. Cyvin (Edit.), Molecular Structures and Vibrations, Chapter 6, Elsevier, Amsterdam 1972.
[12] S. J. Cyvin and B. N. Cyvin, Z. Naturforsch. **26a**, 901 (1971).
[13] L. Lyhamn, S. J. Cyvin, B. N. Cyvin, and J. Brunvoll, Z. Naturforsch. **31a**, 1589 (1976).
[14] S. J. Cyvin, B. N. Cyvin, W. Brockner, and A. F. Demiray, Z. Naturforsch. **33a**, 714 (1978).
[15] L. E. Lyhamn and S. J. Cyvin, Z. Naturforsch. **34a**, 867 (1979).
[16] B. N. Cyvin and S. J. Cyvin, Acta Chem. Scand. **23**, 3139 (1969).
[17] J. C. Whitmer, S. J. Cyvin, and B. N. Cyvin, Z. Naturforsch. **33a**, 45 (1978).
[18] A. Bakke, B. N. Cyvin, J. C. Whitmer, S. J. Cyvin, J. E. Gustavsen, and P. Klaeboe, Z. Naturforsch. **34a**, 579 (1979).
[19] S. J. Cyvin, B. N. Cyvin, J. Brunvoll, J. C. Whitmer, P. Klaeboe, and J. E. Gustavsen, Z. Naturforsch. **34a**, 876 (1979).