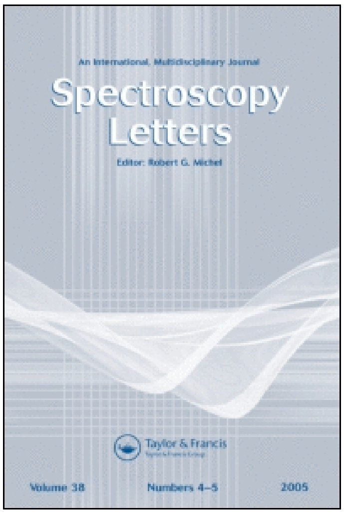

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Molecular Vibrational Energy Distributions: A New Sum Rule for PED, KED, and TED

Alain J. P. Alix[a]
[a] (Laboratoire de Recherches Optiques, Faculté des Sciences, REIMS Cedex, FRANCE

To cite this Article Alix, Alain J. P.(1981) 'Molecular Vibrational Energy Distributions: A New Sum Rule for PED, KED, and TED', Spectroscopy Letters, 14: 6, 441 — 454

To link to this Article: DOI: 10.1080/00387018108062604

URL: http://dx.doi.org/10.1080/00387018108062604

SPECTROSCOPY LETTERS, 14(6), 441-454 (1981)

MOLECULAR VIBRATIONAL ENERGY DISTRIBUTIONS : A NEW SUM RULE FOR PED, KED AND TED.

Keywords : Molecular vibrations; PED, KED, TED; normal modes; sum rules.

ALAIN J.P. ALIX
(Laboratoire de Recherches Optiques, Faculté des Sciences
B.P. 347, 51062 REIMS Cedex, FRANCE)

ABSTRACT

The summations over all vibrations (index k) of the different kinds of energy distributions (potential: PED, kinetic : KED and total : TED) lead to a set of very simple sum rules, expressed in terms of fundamental parameters such as F, $\mathsf{C} = \mathsf{F}^{-1}$, G and G^{-1} constants.

For instance one gets $\sum_k \text{PED} = \sum_k V_{ij}^{(k)} = F_{ij} \cdot (\mathsf{F}^{-1})_{ij} \ldots$

Theoretical implications of that results in the problem of characterization of normal modes of vibration are investigated and practical examples are given too.

RESUME

Les sommes sur l'ensemble des vibrations (indice k) des différentes distributions énergétiques (potentielle DEP, cinétique DEC et totale DET) conduisent à l'obtention de "règles de sommes" très simples, exprimées en termes de paramètres moléculaires fondamentaux tels que les constantes de force, de compliances, cinétiques...

On obtient par exemple $\sum_k$ DEP $= \sum_k V_{ij}^{(k)} = F_{ij}\ (\mathbf{F}^{-1})_{ij}$

Les applications théoriques de ces résultats dans le domaine des modes normaux caractéristiques de vibration sont développées en détail et des exemples concrets sont présentés à titre d'illustration.

INTRODUCTION

The definitions, properties and the applications of the molecular vibrational energy distributions, say

potential energy distribution : PED → $V_{ij}^{(k)}$,

kinetic energy distribution : KED → $T_{ij}^{(k)}$,

total energy distribution : TED → $E_{ij}^{(k)}$,

vibrational energy distribution : PKTED→ $M_i^{(k)}$,

in terms of symmetry coordinates ($\mathbf{S}$), generalized conjugate momenta ($\mathbf{P}$) and generalized symmetry forces ($\mathbf{f}$), have been subject of numerous fundamental works during many years (see the references classified in chronological order).

The principal aim of the use of such distributions was to answer to the question : "How a characteristic mode of vibration should be recognized?" This special type of interrogation explains us why all the defined methods worked in terms of one vibration, i.e., the distributions are determined for each mode of vibration, taken one by one separately. The derived sum rules are then in fact usual conditions of normalization.

In the present communication, will be developped a point which does not appear to have been emphasized, that is the result which may be obtained by considering all the modes of vibration taken simultaneously. Then, the summations over all modes of the different kinds of energy distributions lead to a set of very simple sum rules expressed in terms of fundamental molecular parameters such as force constants F_{ij}, compliants $C_{ij} = (\mathbf{F}^{-1})_{ij}$, kinetic constants G_{ij} and/or $(\mathbf{G}^{-1})_{ij}$.

POTENTIAL ENERGY DISTRIBUTIONS : PED

The basic formulae of the potential energy distributions in terms of symmetry coordinates (3), generalized conjugate momenta (28) and generalized forces (12,16,18) read

$$V_{ij}^{(k)}\ (\mathbf{S}) = F_{ij}\ L_{ik}\ L_{jk}/\lambda_k \qquad (1)$$

$$V_{ij}^{(k)}\ (\dot{\mathbf{P}}) = C_{ij}\ (\tilde{\mathbf{L}}^{-1})_{ik}\ (\tilde{\mathbf{L}}^{-1})_{jk}/\sigma_k \qquad (2)$$

$$V_{ij}^{(k)}\ (\mathbf{f}) = C_{ij}\ (\tilde{\mathbf{L}}^{-1})_{ik}\ (\tilde{\mathbf{L}}^{-1})_{jk}/\sigma_k \qquad (3)$$

where F_{ij} are the symmetrical force constants, C_{ij} the compliants $(\mathbf{C} = \mathbf{F}^{-1})$, $\mathbf{L}$ is the matrix of eigenvectors of the secular equation, λ_k is the k-th eigenvalue of the secular equation, related to the k-th mode of vibration and $\sigma_k = \lambda_k^{-1}$.

The vibrational energy distribution (PKTED) is linked to the PED by

$$V_i^{(k)} = \sum_j V_{ij}^{(k)} = L_{ik}\ (\tilde{\mathbf{L}}^{-1})_{ik} \equiv M_i^{(k)} \qquad (4)$$

and takes the same expression, whatever the PED is defined.

The normalization conditions are summarized as follows :

$$\sum_i \sum_j (ij) = \sum_j \sum_i (ij) = 1 ; \sum_i (i) = 1 \qquad (5)$$

and give the usual sum-rules.

Let us now consider the summations over k, it is over all modes of vibration, of the PED.

One gets, by using the following general relations

$$F = \tilde{L}^{-1} . \Lambda . L^{-1} , \quad C = L . \sigma . \tilde{L} \qquad (6a)$$

$$G = L . \tilde{L} \quad , G^{-1} = \tilde{L}^{-1} . L^{-1} \qquad (6b)$$

a <u>unique</u> result which reads

$$\boxed{\sum_k \mathrm{PED} = \sum_k V_{ij}^{(k)} = F_{ij} . C_{ij} \quad \begin{cases} i = 1,2 \ldots n \\ j = 1,2 \ldots n \end{cases}} \qquad (7)$$

Equation (7) may also be developped for $i = j$ and $i \neq j$ and gives

$$\sum_k V_{ii}^{(k)} = F_{ii} . C_{ii} , \quad i = 1,2 \ldots n \qquad (8a)$$

$$\sum_k V_{ij}^{(k)} = 2F_{ij} . C_{ij} , \quad i = 1,2 \ldots (n-1) ; j > i \qquad (8b)$$

In cases of use of equations (8) no distinction have been made between the ij-term and the ji-term appearing in equation (7), this explaining the introduction of the coefficient 2 in eqs (8b).

KINETIC ENERGY DISTRIBUTIONS : KED

The unusual formulae of the kinetic energy distributions in terms of symmetry coordinates (4), generalized conjugate momenta (28) and generalized forces (27-29) read

$$T_{ij}^{(k)} (\dot{S}) = (G^{-1})_{ij} L_{ik} L_{jk} \qquad (9)$$

$$T_{ij}^{(k)}\ (P) = G_{ij}\ (\tilde{L}^{-1})_{ik}\ (\tilde{L}^{-1})_{jk} \qquad (10)$$

$$T_{ij}^{(k)}\ (\dot{f}) = (C\,G^{-1}C)_{ij}\ (\tilde{L}^{-1})_{ik}\ (\tilde{L}^{-1})_{jk}.\lambda_k^2 \qquad (11)$$

where the symbols have the same meanings as in eqns (1,2, 6).

The vibrational energy distribution (PKTED) is linked to the KED by :

$$T_i^{(k)} = \sum_j T_{ij}^{(k)} = L_{ik}\ (\tilde{L}^{-1})_{ik} \equiv M_i^{(k)} \qquad (12)$$

The normalization conditions are the same as the ones given in eqn (5).

Now, considering the summations over k of the different KED leads to :

$$\boxed{\begin{array}{l} \sum_k T_{ij}^{(k)}\ (\dot{S}) = \sum_k T_{ij}^{(k)}\ (P) = G_{ij}.\ (G^{-1})_{ij} \\ \sum_k T_{ij}^{(k)}\ (f) = (C\,G^{-1}C)_{ij}.\ (FGF)_{ij} \end{array}} \qquad \begin{array}{r} (13a) \\ (13b) \end{array}$$

In this case, one sees that the sum rules are different depending on the definition of the KED.

Equation (13a) may also be developped for i = j and i ≠ j and gives

$$\sum_k T_{ij}^{(k)}\ (\dot{S}) = G_{ii}.\ (G^{-1})_{ii},\ i = 1,2...n \qquad (14a)$$

$$\sum_k T_{ij}^{(k)}\ (\dot{S}) = 2G_{ij}.\ (G^{-1})_{ij},\ i = 1,2..(n-1);j>i \qquad (14b)$$

when only one term is associated to ij-and ji-interactions.

TOTAL ENERGY DISTRIBUTIONS : TED

The corresponding formulae and results may be obtained directly from above, by using the fundamental following properties :

$$E_{ij}^{(k)} = \left[V_{ij}^{(k)} + T_{ij}^{(k)} \right] /2, \qquad (15a)$$

$$E_{i}^{(k)} = \sum_{j} E_{ij}^{(k)} = \left[V_{i}^{(k)} + T_{i}^{(k)} \right] /2 \equiv M_{i}^{(k)} \qquad (15b)$$

but are not given for the sake of brevity. (For details on definitions see Refs (22-29)).

DISCUSSION

The present discussion will be first focused on the energy distributions defined in terms of symmetry coordinates which are the most usual ones.

The new sum rules are summarized below as :

$$\sum_{k} PED = \sum_{k} V_{ij}^{(k)} = F_{ij} \cdot C_{ij}, \qquad (16)$$

$$\sum_{k} KED = \sum_{k} T_{ij}^{(k)} = G_{ij} \cdot (G^{-1})_{ij}, \qquad (16b)$$

$$\sum_{k} TED = \sum_{k} E_{ij}^{(k)} = \left[F_{ij} \cdot C_{ij} + G_{ij} \cdot (G^{-1})_{ij} \right] /2. \qquad (16c)$$

(a) computational purposes :

First of all it can be recall that the mapping of the energy distributions related to one mode of vibration is identical to build up three matrices : e.g.,

$$PED \rightarrow \| V_{ij}^{(k)} \|, \quad KED \rightarrow \| T_{ij}^{(k)} \|, \quad TED \rightarrow \| E_{ij}^{(k)} \|.$$

The usual sum rules work on each matrix such as :

$$\sum_i = \sum (\text{columm } j) = \sum_j = \sum (\text{row } i) = \text{PKTED}_i^{(k)},$$

$$\sum_{ij} = \sum (\text{all elements}) = 1$$

The sum rules defined over k permits one :

- to serve as a check of the calculations,
- to simplify some calculations.

The sum over k of the principal distributions ($\sum_k (ii)$) are always strictly positive as the diagonal elements of the matrices **F**, **C**, **G** and $\mathbf{G}^{-1}$ are positive.

The sum over k of the coupling distributions ($\sum_k (ij)$) may be positive, negative or null, depending on the interactions elements. When the sum is null, two cases haves to be considered : for instance :

(i) $(\mathbf{G}^{-1})_{ij} = 0$: all the $T_{ij}^{(k)}$ are null and their sum is zero.

(ii) $G_{ij} = 0$; $(\mathbf{G}^{-1})_{ij} \neq 0$ then the $T_{ij}^{(k)}$ are not null but their sum is zero (see the case of G_{68} and G_{69} being zero but $(\mathbf{G}^{-1})_{68}$ and $(\mathbf{G}^{-1})_{69}$ being non null in Table1b).

In second order problems one gets :

$$\sum_k V_{11}^{(k)} = \sum_k V_{22}^{(k)} = F_{11} \; F_{22}/|\mathbf{F}| = 1 + \frac{F_{12}^2}{|\mathbf{F}|} \geqslant 1, \quad (17a)$$

$$\sum_k V_{12}^{(k)} = \sum_k V_{21}^{(k)} = -F_{12}^2/\ |\mathbf{F}| \leqslant 0. \quad (17b)$$

TABLE 1 A

Molecular Vibrational Energy Distributions and Sum Rules For The Molecule: Mo $\left[{}^{12}C\ {}^{16}O\right]_6$ (Oh); Species A1g, F_{1u}.

A_{1g}			Potential Energy Distribution[d]		
ij	F_{ij}^{b}	C_{ij}^{c}	Σ_k PED	$V_{ij}^{(1)}$	$V_{ij}^{(2)}$
11	17.8456	0.0560	100.11	96.27	3.83
22	2.7690	0.3615	100.11	5.19	94.92
12[h]	0.2322	-0.0047	-0.11	-0.74	0.63
Σ_{ij}			200.00	100.00	100.00

A_{1g}			Kinetic Energy Distribution[g]		
ij	G_{ij}^{e}		Σ_k KED	$T_{ij}^{(1)}$	$T_{ij}^{(2)}$
11	0.1458	16.0000	233.29	232.96	0.33
22	0.0833	16.0000	233.29	141.80	91.49
12h	-0.0833	28.0037	-133.29	-137.42	4.13
Σ_{ij}			200.00	100.00	100.00

(a) all calculations have been done with at least six figures by number (only some of them are reported here)

(b) force constants in units of mdyn/Å (see i)

(c) compliants in units of Å/mdyn.

(d) potential energy distributions in %

(e) inverse kinetic constants in units of $am.u^{-1}$

(f) kinetic constants in units of a.m.u.

(g) kinetic energy distributions in %

(h) corresponding terms "ji" have the same values

(i) Ref.L.H.JONES,R.S.Mc DOWELL and M.GOLDBLATT,Inorg.Chem. 8 2349 (1969).

(see Table 1a for application).

(b) dynamical and/or kinematical couplings :

Equations (16)**permits** one to detect directly the presence of dynamical couplings (eqn.16a)and/or kinematical couplings (equ.16b) between the different vibrations

(i) Due to the invariance of the force constants F_{ij} (and/or compliants) with respect to isotopic substitution (within the Born-Oppenheimer approximation), it is seen that the $\sum_k$ PED is invariant too (see eqn 16a).

(ii) This is not the case for the KED and/or the TED which are mass dependant through the $(G^{-1})_{ij}$ elements

(iii) A remarkable property of the KED, is that the sum over k is independant of the force field and can be computed as soon as the molecular configuration is known. Then, the eventual couplings between the different symmetry coordinates can be detected directly from eqn.16b (see table 1b for application).

It must be pointed out that, by a special choice of the set of symmetry coordinates, it is possible to diagonalize the kinetic energy matrix. In this case G and G^{-1} are diagonal and equation (16b) reduces to :

$$\sum_k T_{ij}^{(k)} = 1, \ \sum_k T_{ij}^{(k)} = 0, \quad i = 1,2\ldots n; \ j \neq i.$$

(c) characteristic normal modes of vibration :

A characteristic normal mode of vibration implies for instance that $V_{ii}^{(k)} = 1$ and all others $V_{ij}^{(k)} = 0$ for the PED (same relations are valid for KED and TED).

TABLE 1 B

F_{1u}	Potential Energy Distribution^d					
ij	F^b_{ij}	Σ_k	$V^{(6)}_{ij}$	$V^{(7)}_{ij}$	$V^{(8)}_{ij}$	$V^{(9)}_{ij}$
66	17.141	104.5	103.3	0.0	0.0	1.2
77	1.357	124.7	2.6	5.8	79.5	36.7
88	0.554	121.3	0.0	49.7	12.5	59.0
99	0.813	134.2	0.0	19.9	0.0	114.2
67k	0.873	-4.2	-3.0	-0.0	-0.0	-1.2
68k	0.082	-0.2	0.0	-0.0	0.0	-0.2
69k	0.013	-0.0	-0.0	0.0	0.0	-0.0
78k	-0.097	-3.6	0.0	-1.9	3.5	-5.2
79k	-0.342	-16.8	-0.0	3.5	0.7	-21.0
89k	-0.227	-17.4	0.0	10.6	-0.3	-27.7
Σ_{ij}		400.0	100.0	100.0	100.0	100.0

F_{1u}		Kinetic Energy Distribution^g				
ij	G^{-1}_{ij}	Σ_k	$T^{(6)}_{ij}$	$T^{(7)}_{ij}$	$T^{(8)}_{ij}$	$T^{(9)}_{ij}$
66	14.060	205.0	205.0	0.0	0.0	0.0
77	22.062	229.7	104.4	19.8	102.5	2.9
88	16.030	334.7	0.0	297.5	28.7	8.3
99	64.920	375.1	0.0	330.2	0.4	44.4
67k	12.605	-105.0	-104.7	-0.1	-0.0	-0.0
68k	3.154	0.0	0.2	-0.1	0.0	-0.0
69k	9.292	0.0	-0.1	0.3	0.0	-0.1
78k	5.521	7.8	-0.2	22.5	-15.9	1.4
79k	16.264	-32.6	0.1	-34.7	-2.8	4.8
89k	26.914	-242.5	-0.0	-261.5	2.9	16.0
Σ_{ij}		400.0	100.0	100.0	100.0	100.0

* see Footnotes in Table 1a.

A situation in which all normal modes of vibration would be characteristic would imply that $\sum_k$ PED = $\sum_k$ KED = $\sum_k$ TED = δ_{ij} (1 for i = j, 0 for i ≠ j).

Such a case can not occur, except if the **G** and **F** matrices are diagonal (see (b) and eqn (16b)).

It may this be concluded (by study of the reciprocal) that if the sum over k of the principal distributions ($\sum_k$ (ii)) are nearly equal to unity and the sum over k of the coupling distributions ($\sum_k$ (ij)) are close to zero, this <u>simultaneously</u> for the PED and the KED, then the different modes of vibration of the molecule are rather characteristic.

This is the case of numerous molecules exhibiting small dynamical and kinematical couplings.

All the preceeding discussion may be extended without difficulties to the cases of energy distributions defined in terms of generalized symmetry conjugate momenta (**P**) and/or generalized symmetry forces (**f**).

Finally the Mo $\left[{}^{12}C\ {}^{12}O\right]_6$ molecule has been choosen as illustration. In table 1a are only reported the results for the species A1g (2x2 problem). The Eg, F2g and F2u species have results following the same pattern and are not reported here.

The choice of such example is characteristic as that molecule present strong kinematical couplings between vibrations, and this in all species.

The calculations of the new sum rules permit ones to detect (before and without solving the inverse eigenvalue problem) directly the kinematic couplings and in cases of transfer of forces constants from similar molecules, the dynamical couplings.

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Received: March 14, 1981
Accepted: April 28, 1981