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Densities of Vibrational States of Given Symmetry Species and Their Use in Statistical Estimates Involving Coriolis and Anharmonic Effects

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A simple approximate statistical formula for densities of vibrational states of given symmetry is presented. The formula becomes increasingly exact at higher vibrational energies. Application to Coriolis and anharmonic effects is discussed.

1. Introduction

The symmetry of a vibrational quantum state affects its coupling to other vibrational states via anharmonic and Coriolis forces, and thereby can influence intramolecular relaxation. In recent experiments on vibronic excitation of molecules, specific vibrational modes of given symmetry have been excited in an electronically excited state and their spectroscopic behavior has been investigated. Coriolis coupling between degenerate or nearly degenerate states[1-4] and between nondegenerate states[5-8] has been invoked.

It is of interest to know the density of vibrational states of the desired symmetry for such coupling to a particular vibrational state. For example, a statistical theory of density of states of a given symmetry has been used as a possible explanation of the disappearance, via Coriolis coupling, of certain spectral lines.[2,3] This statistical approach involved direct counting of combination and overtone states having the specified symmetry. In the course of our study we noticed a striking regularity in this counting of states. We present here a simple statistical approximation for the density of states of any specified symmetry species, eq 2. We first illustrate it for several molecules of different symmetry types (section 2) and then give an approximate derivation in section 3. Equation 2 becomes increasingly exact with increasing vibrational energy. Applications are noted in section 4.

2. Results

All exact results were determined by precise computer counting of harmonic states. The number of states of a given symmetry species was determined by allowing any combination of overtones (and fundamentals). All quantum states were considered with equal a priori probability and standard rules were used to determine the symmetry species of the various resultant states.[9] Degeneracy was allowed for, but all energy splittings due to perturbations were ignored and energies were assigned their unperturbed values. The sum of the number of states of each symmetry species with this counting method represents the total number of states at any energy. A check of values was performed by comparing this total number of states to the semiclassical Whitten–Rabinovitch approximation.[10] At the energies investigated the total density of states (removing scatter and oscillations) was negligibly different from the Whitten–Rabinovitch estimate.

TABLE I: Numbers and Ratio of States of Benzene for Each Representation at Various Excess Energies[a]

	ϵ = 2004 cm^{-1}		ϵ = 4009 cm^{-1}		ϵ = 6013 cm^{-1}	
Γ	$N(\Gamma)$	$24\gamma(\Gamma)$	$N(\Gamma)$	$24\gamma(\Gamma)$	$N(\Gamma)$	$24\gamma(\Gamma)$
a_{1g}	99	1.39	10 759	1.03	508 350	1.00
a_{2g}	67	0.94	10 304	0.99	504 540	1.00
b_{1g}	47	0.66	10 122	0.97	503 872	1.00
b_{2g}	71	1.00	10 499	1.01	507 273	1.00
a_{1u}	73	1.03	10 387	1.00	506 161	1.00
a_{2u}	81	1.14	10 533	1.01	507 388	1.00
b_{1u}	71	1.00	10 425	1.00	506 267	1.00
b_{2u}	62	0.87	10 292	0.99	505 311	1.00
e_{1g}	236	3.32	41 210	3.96	2 022 314	4.00
e_{2g}	330	4.64	42 124	4.04	2 025 738	4.00
e_{1u}	262	3.69	41 440	3.98	2 023 098	4.00
e_{2u}	306	4.31	41 836	4.02	2 027 070	4.00

[a] The symbols are defined in the text: $\gamma(\Gamma)$ equals $N(\Gamma)/N$. The zero-point energy is 20 034 cm^{-1}. The number 24 is introduced to make clearer the relations among the γ's.

TABLE II: Numbers and Ratio of States of Methane for Each Representation at Various Excess Energies[a]

	ϵ = 9883 cm^{-1}		ϵ = 19 766 cm^{-1}		ϵ = 29 648 cm^{-1}	
Γ	$N(\Gamma)$	$24\gamma(\Gamma)$	$N(\Gamma)$	$24\gamma(\Gamma)$	$N(\Gamma)$	$24\gamma(\Gamma)$
a_1	83	1.52	3 131	1.12	41 114	1.05
a_2	38	0.70	2 545	0.91	37 687	0.96
e	236	4.33	11 326	4.06	157 536	4.02
t_1	408	7.49	24 063	8.64	346 749	8.85
t_2	543	9.96	25 812	9.26	356 985	9.11

[a] See footnote to Table I. Zero-point energy is 9882 cm^{-1}.

TABLE III: Numbers and Ratio of States of Formaldehyde at Various Excess Energies[a]

	ϵ = 11 293 cm^{-1}		ϵ = 22 586 cm^{-1}		ϵ = 45 157 cm^{-1}	
Γ	$N(\Gamma)$	$4\gamma(\Gamma)$	$N(\Gamma)$	$4\gamma(\Gamma)$	$N(\Gamma)$	$4\gamma(\Gamma)$
a_1	322	1.32	6508	1.16	210 880	1.08
a_2	172	0.70	4724	0.84	179 835	0.92
b_1	215	0.88	5073	0.90	183 701	0.94
b_2	268	1.10	6098	1.09	206 653	1.06

[a] See footnote to Table I. Zero-point energy = 5644 cm^{-1}. The number multiplying $\gamma(\Gamma)$ is now 4 instead of 24.

Tables I–III list the results for several representative molecules for various energies ϵ in excess of the zero-point energy. The values reported are the actual number $N(\Gamma)$ of harmonic states of each symmetry species Γ (equivalently, of each irreducible representation) with excess energy equal or less than ϵ. Also given is $\gamma(\Gamma)$, namely, the ratio $N(\Gamma)/N$, N being the total number of states with

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TABLE IV: Groups of Molecular Symmetries, Rules, and R Values

molecular symmetry	multiplication rules[a]	averaged overtone rules	R_A, R_E, R_T
	Group 1		
O, O_h, T, T_d, T_h	$A \times T = T$ $E \times E = 2A + E$ $E \times T = 2T$ $T \times T =$ $A + E + 2T$	$A^v \equiv A$ $E^v \equiv A + E$ $T^v \equiv$ $A + E + 3T$	1, 1, 3
	Group 2		
C_3, C_{3h}, C_{3v}, D_3, D_{3d}, D_{3h}, C_6, C_{6h}, C_{6v}, D_6, D_{6h}, S_6	$E \times E = 2A + E$	$A^v \equiv A$ $E^v \equiv A + E$	1, 1, 0
	Group 3		
C_4, C_{4v}, C_{4h}, D_{2d}, D_4, D_{4h}, S_4	$E \times E = 4A$	$A^v \equiv A$ $E^v \equiv 2A + E$	2, 1, 0

[a] There are also the rules, $A \times A = A$ and $A \times E = E$, which are the same for groups 1, 2, and 3.

energy equal or less than ϵ. Throughout, we suppress the ϵ in the notation for brevity. The sum of $\gamma(\Gamma)$ over all Γ equals unity.

The results in Table I are for benzene, an exmaple of the D_{6h} point group.[11] One sees that the populations of the nondengenerate symmetry species rapidly become equal as ϵ increases, as do those of the doubly degenerate symmetry species. One also sees that the ratio of the number of states for any nondegenerate symmetry species to that for any double degenerate one rapidly converges to 1:4.

The results in Table II are for methane,[12] an example of the T_d point group. As the energy increases, the ratio of the number of states for any nondegenerate to the doubly degenerate to any triply degenerate symmetry species approaches 1:4:9. Higher energies are needed to reach the limiting ratio than was needed in Table I, for reasons evident from the derivation in section 3.[13]

The results in Table III are for a C_{2v} molecule, formaldehyde, for which Coriolis coupling has been discussed, e.g., ref 4, 5, and 7. Only nondegenerate symmetry species occur and these populations become equal. We have also studied molecules in the point groups D_{4h}, D_{3h}, D_{3d}, C_{4v}, and O_h and in every case have found, as ϵ becomes large, that the numbers of states of each symmetry species with the same degeneracy become equal, and that the ratio of states of nondegenerate to doubly degenerate to triply degenerate symmetry species approaches a constant value.

These results for specific molecules can be generalized into three broad classes of molecular point groups listed in Table IV. We shall show that the ratio of the numbers of states of any nondegenerate to any doubly degenerate to any triply degenerate symmetry species $N(A)$:$N(E)$:$N(T)$, is given by eq 1, with increasing accuracy as ϵ increases

$$N(A):N(E):N(T) = R_A/n_A:2R_E/n_E:3R_T/n_T \qquad (1)$$

where R_A, R_E, and R_T are given in Table IV for the various types of molecular symmetry point groups. n_A is the total number of nondegenerate symmetry species from a character table of the relevant point group; n_E and n_T are the analogous quantities for the doubly and triply degenerate symmetry species, respectively. Equation 1 is derived in section 3, together with the values of the R's listed in Table IV. Using eq 1 we also show in section 3 that the density of states $\rho(\Gamma)$ for any particular symmetry species is given, with increasing accuracy as ϵ increases, by

$$\rho(\Gamma) = \rho g_\Gamma R_\Gamma/(R_A + 2R_E + 3R_T)n_\Gamma \qquad (2)$$

where ρ is the total density of states at the excess energy ϵ; g_Γ is 1, 2, or 3, R_Γ is R_A, R_E, or R_T, and n_Γ is n_A, n_E, or n_T, according as the Γ belongs to a nondegenerate, doubly degenerate, or triply degenerate symmetry species. Equations 1 and 2 are the principal results of this paper. Equations 1 and 2 assume that all n_Γ symmetry species are accessible. If some symmetry speecies are not accessible, n_Γ refers only to the accessible species. However, for all real molecules we have studied thus far, all symmetry species in a point group have been accessible. When the vibrations are anharmonic, the use of different symmetry types remains valid (ref 9, p 146).

In applications of eq 2 to molecules such as CH_2O, which have only nondengenerate representations, we have $R_A = 1$ and $R_E = R_T = 0$.

3. Derivation of Eq 1 and 2

To simplify the derivation of eq 1 and 2, two assumptions will be made:

The first assumption is that in building up various combinations of overtones of the various fundamentals there is randomization of the numbers of states between symmetry species having the same degeneracy (e.g., among the four E-symmetry species in Table I). The tendency to randomization is indeed evident in the exact multiplication rules given in ref 9.

The second assumption is that the energy is sufficently high that frequently some degenerate fundamental has several quanta in it. This causes representations of overtones of degenerate fundamentals to obey the averaged overtone rules given in the third column of Table IV.

The first assumption is seen to be true in Tables I–III within statistical deviations, for the three molecules given there. Consistent with this assumption, we adopt a notation such that all nondegenerate symmetry species are grouped together and each is called A (which now includes all A and B representations), each doubly degenerate symmetry species is called E (i.e., irrespective of whether it is e_{1g}, e_{2g}, e_{1u}, etc.), and each triply degenerate one is called T. Each E label contains two states and T contains three states. The first assumption simplifies the multiplication rules and, after examining Table X-12 of ref 9, led to the three sets of groups in Table IV. Within each set the now simplfied multiplication rules have become similar. The overtone rules of ref 9 also became simple

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[13] The exact recursion relation for the representation of triply degenerate overtones has a longer recursion cycle. Further, the approximation used in section 3 (Table IV) for the triply degenerate overtone rule is less accurate than the others at low energies, though it becomes increasingly exact at high energies.

after introducing the two assumptions, and represent averages, e.g, over the variable q in Table X-13, ref 9. (In the case of the overtone rule for a triply degenerate fundamental, the result in Table IV is an approximate average over q and over even and odd v in ref 9 and becomes increasingly exact as p in ref 9 becomes large.)

We illustrate the first assumption using a combination level in D_{6h}, such as $a_{1g} + a_{2g} + a_{1u} + a_{2u} + e_{1g} + e_{2g} + e_{1u} + e_{2u}$. Because of the first assumption this representation can be rewritten as $4A + 4E$. Because we are mainly interested in ratio of labels, we introduce an equivalency symbol $\equiv$:

$$4A + 4E \equiv A + E \tag{3}$$

Thus, the representation of the cited combination level in D_{6h} is, in this sense, equivalent to $A + E$. Its ratio of A labels to E labels is 1:1.

The following derivation of eq 1 and 2 is first given for group 1 type molecular point group symmetries in Table IV. We order the vibrational fundamentals of a molecule so that the first k of them are of the A type, the next m are of the E type, and the final n are of the T type, $k + 2m + 3n$ being therefore the total number of normal modes. We let A^{v_i} signify that the ith nondegenerate fundamental contains v_i quanta, and use an analogous notation for the other (E and T) fundamentals. The representation of any given vibrational excitation can be written as

$$\Gamma = A^{v_1} \ldots A^{v_k} E^{v_{k+1}} \ldots E^{v_{k+m}} T^{v_{k+m+1}} \ldots T^{v_{k+m+n}} = \Gamma_A \Gamma_E \Gamma_T \tag{4}$$

where Γ_A denotes the product of the A factors, etc. We evaluate Γ_A, Γ_E, and Γ_T separately. We shall assume in the following that at least one v_i in Γ_E and at least one in Γ_T exceeds unity.

We have

$$\Gamma_A = A^{v_1} \ldots A^{v_k} \tag{5}$$

From Table IV we know that $A^v \equiv A$ for any v, so that

$$\Gamma_A \equiv A \ldots A \equiv A \tag{6}$$

independently of k, using the multiplication rules for group 1 in Table IV.

Using the same method for combinations of overtones of E-type fundamentals, Γ_E is given by

$$\Gamma_E = E^{v_{k+1}} \ldots E^{v_{k+m}} \tag{7}$$

From Table IV one sees that

$$E^v \equiv A + E \ (v > 1) \qquad E^v = E \ (v = 1) \tag{8}$$

From the multiplication rules in Table IV

$$(A + E)(A + E) \equiv A + E \qquad E(A + E) \equiv A + E \tag{9}$$

Application of eq 8 and 9 to eq 7 yields[14]

$$\Gamma_E \equiv A + E \tag{10}$$

as long as at least one $v_i > 1$. For Γ_T we have

$$\Gamma_T = T^{v_{k+m+1}} \ldots T^{v_{k+m+n}} \tag{11}$$

From the overtone rules in Table IV we have $T^v \equiv A + E + 3T$ or T, according as $v > 1$ or $v = 1$. The multiplication rules in Table IV yield

$$\begin{gathered}(A + E + 3T)(A + E + 3T) \equiv A + E + 3T \\ T(A + E + 3T) \equiv A + E + 3T\end{gathered} \tag{12}$$

Application of eq 12 to 11 yields 13, as long as at least one $v_i > 1$.

$$\Gamma_T \equiv A + E + 3T \tag{13}$$

Equations 4, 6, 10, and 13 plus the multiplication rules in Table IV then yield

$$\Gamma \equiv A(A + E)(A + E + 3T) = 3A + 3E + 9T \equiv A + E + 3T \tag{14}$$

The ratio of labels given by eq 14 is seen to be independent of the specific vibrational excitation level. Therefore, the ratio of the total number of A labels to E labels to T labels is always 1:1:3. These numbers provide the R values listed as in the last column of Table IV.

To obtain eq 1 we now note that the ratio of labels is R_A:R_E:R_T, and so the ratio of states is R_A:$2R_E$:$3R_T$ when degeneracy is included. Since there are n_A symmetry species of the A type which share this R_A, n_E which share this $2R_E$, and n_T sharing the $3R_T$, eq 1 for ratios of numbers of states of specific symmetry species immediately follows.

We turn next to group 2 in Table IV, for which $R_A = 1$ and $R_E = 1$. Since the multiplication and overtone rules for group 2 are identical with those for group 1 except that there are no triply degenerate symmetry species, one finds that the representation of a combination of overtones is now given by

$$\Gamma = A^{v_1} \ldots A^{v_k} E^{v_{k+1}} \ldots E^{v_{k+m}} \equiv A(A + E) \equiv A + E \tag{15}$$

Once again, the ratio of A to E labels is independent of the vibrational excitation, namely, 1:1. One thus has $R_A = 1$ and $R_E = 1$, as reported in the last column of Table IV. Equation 1 again follows.

For group 3 one uses the same logic, except that now the rules for the E representations are different, as seen in Table IV. For the A overtones we have $\Gamma_A \equiv A$ as before. However, we have $E^v \equiv 2A + E$ or E, according as $v > 1$ or $v = 1$. Use of multiplication rules in Table IV yields

$$\begin{gathered}(2A + E)(2A + E) \equiv 2A + E \\ E(2A + E) \equiv 2A + E\end{gathered} \tag{16}$$

Application to eq 7 gives $2A + E$ for Γ_E. Hence

$$\Gamma \equiv A(2A + E) \equiv 2A + E \tag{17}$$

Thus, the ratio of A labels to E labels is 2:1 for group 3 symmetries, independently of the vibrational excitation. Hence, one obtains the $R_A = 2$, $R_E = 1$ in the last column of Table IV and eq 1 follows.

To obtain eq 2 we note that the total number of states N with excess energy equal to or less than ϵ is $n_A N(\Gamma_A) + n_E N(\Gamma_E) + n_T N(\Gamma_T)$, where Γ_A is a Γ of type A, etc. Equation 1 can be rewritten as $n_A N(\Gamma_A) = cR_A$, $n_E N(\Gamma_E) = 2cR_E$, and $n_T N(\Gamma_T) = 3cR_T$, where c is constant. Summing yields $N = c(R_A + 2R_E + 3R_T)$ and hence yields $N/(R_A + 2R_E + 3R_T)$ for c. One thus obtains (using the definition of g_Γ given earlier)

$$N(\Gamma) = N g_\Gamma R_\Gamma / (R_A + 2R_E + 3R_T) n_\Gamma \tag{18}$$

Differentiation of this equation with respect to ϵ yields eq

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[14] The associative law converts a multiplication such as $(E \times E \times E) \times (A + E)$ to $(E \times E) \times (E \times (A + E))$ and hence successive applications of eq 9 may be used to obtain eq 10.

2, since the R's, n_Γ's, and g_Γ's in eq 18 are independent of ϵ.

4. Discussion

Coriolis Coupling. To illustrate an application of eq 2 we consider benzene and parallel type Coriolis coupling. Riedle et al.[1,3] measured the Doppler-free rotationally resolved two-photon spectrum of the $14^1_0\,1^n_0$ bands of benzene (n = 1, 2). They excited an electronic state of B_{2u} symmetry and a vibrational state of b_{2u} symmetry, and examined the fluorescence excitation spectrum of the Q branch. Only the $K = 0$ levels remained when $n = 2$, plus some residual structure from the $K \neq 0$ states. One of the possible explanations involves Coriolis effects.[15]

The b_{2u} vibrational state couples by parallel Coriolis interactions to b_{1u} states,[1-3] giving new levels[16] $^1/_2(E_1 + E_2) \pm [(H_{12})^2 + (\Delta E/2)^2]^{1/2}$. H_{12} is the Coriolis interaction energy and ΔE ($= E_2 - E_1$) is the energy difference of the b_{1u} and b_{2u} states. When $\Delta E = 0$ there is extensive transfer of the oscillator strength from the b_{2u} level (50%), while when $|H_{12}/\Delta E| \ll 1$ there is little. There can be further splitting due to Coriolis effects, yielding a further reduction in intensity of $K \neq 0$ lines and still further irregularities in the spectrum. If the b_{1u} states to which the original b_{2u} state is coupled have large nonradiative rates, the total fluorescence intensity is also decreased,[3] in agreement with the experiment.[1,3]

The transfer of oscillator strength due to Coriolis coupling is significant for states within an energy ΔE of about, say, H_{12}. H_{12} equals $\pm 2C\zeta Kl$, where C ($= \hbar^2/2I_z$) is[17] 0.09 cm^{-1}, K and l are the z rotational and z vibrational angular momentum quantum numbers ($K > 0$), and ζ is a Coriolis interaction constant. If the maximum ζ is[18] about 0.8, H_{12} is about $\pm 0.15Kl$ cm^{-1} or less. (Any unfavorable vibrational overlap[19] decreases this ζ.) For comparison it may be noted that the separation of adjacent K states in the Q branch is about $0.008K$ cm^{-1}, according to available rotational constants.[17]

One sees that if there is sufficient parallel Coriolis coupling (sufficient proximity of *suitable* b_{1u} states to the original b_{2u} state) the fluorescence excitation spectrum will contain the $K = 0$ lines, which are unaffected by parallel Coriolis coupling, plus some residual irregular structure from the $K \neq 0$ lines. To create this Coriolis coupling the density of suitable vibrational states of the b_{1u} symmetry species would have to be about 6 per cm^{-1} ($\sim 1/H_{12}$) when $K = l = 1$. The total density of b_{1u} states (suitable and unsuitable) is given by eq 2 and by the R values in Table IV. It is approximately 1/24 the total density of states. In order for the total density of b_{1u} states to reach 6 per cm^{-1}, the total density of states would therefore have to be 144 per cm^{-1}. This density corresponds to an energy, determined from the Whitten–Rabinovitch approximation or from direct counting, of about 3370 cm^{-1}. This energy also corresponds roughly to the energy where disappearance of the $K \neq 0$ lines occurs in experimental measurements by Riedle et al.,[1] and so one has a *possible* statistical[2,3] explanation of the results. However, consistency of argument would require that one examine the effect of perpendicular Coriolis interactions[15] on the $K = 0$ state, using assumptions analogous to those used above, and vibrational overlap[19,20] aspects should also be explored.

Anhramonic Coupling. Other questions which can be addressed by use of eq 2 involve other types of coupling. For example, if a zeroth-order state (wavepacket) of some given symmetry species is excited, one can use eq 2 to calculate the density of vibrational states of the same symmetry species with which the wavepacket can be associated.

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(15) An alternative mechanism which still distinguishes $K = 0$ states is given by Callomon, J. H. *Faraday Discuss. Chem. Soc.*, in press (discussion comment).

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(18) We used the larger ones calcualted in ref 11.

(19) E.g., for harmonic states one requires[15] $\Delta v_i = -\Delta v_j = \pm 1$, $\Delta v_k = 0$. Sufficient anharmonicity would distribute the original vibrational parentage of the harmonic states more widely over the anharmonic states, and so the state-by-state requirement would then be less severe.

(20) E.g., if as a minimal requirement one added the supplementary conditions on the b_{1u} states that $v_{14} = 0$ and that $v_1 = 1$ or 2, the density of such b_{1u} states at $\epsilon = 3370$ cm^{-1} is found by using eq 2 and calculating ρ. One distributes among the remaining 28 modes an energy (3370–923) cm^{-1} when $v_1 = 1$, yielding $\rho(b_{1u}) = 0.65$ per cm^{-1}, and an energy (3370–1846) cm^{-1} when $v_1 = 2$, yielding $\rho(b_{1u}) = 0.05$ per cm^{-1}. The total density of such b_{1u} states is about 0.7 per cm^{-1} at 3370 cm^{-1} instead of 6 per cm^{-1}.