Densities of vibrational states of given symmetry species. Linear molecules and rovibrational states of nonlinear molecules

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A simple statistical expression is given for the density of states of any symmetry species for linear molecules. Molecules with one and two pairs of doubly degenerate bending modes are considered. The results of our previous paper for vibrational states of nonlinear molecules are also extended to include density of rotational-vibrational states by symmetry species. The various expressions are tested by comparing with exact counts of states.

I. INTRODUCTION

In a recent paper,[1] we derived a simple statistical expression for the density $\rho(\Gamma)$ of vibrational states with symmetry species Γ for nonlinear molecules, or for the number $N(\Gamma)$ of states of symmetry Γ with energy less than or equal to E in terms of the total number of states N with energy less than or equal to E:

$$\rho(\Gamma) = \rho f_\Gamma, \quad N(\Gamma) = N f_\Gamma, \tag{1a}$$

where the fraction of states of symmetry Γ is

$$f_\Gamma = g_\Gamma R_\Gamma/(R_A + 2R_E + 3R_T)n_\Gamma. \tag{1b}$$

Here, ρ is the total density of states, determined by exact count or by use of an approximate formula such as that of Whitten–Rabinovitch. [In using a formula such as Eq. (1a) one is often interested in the case of high energies, where Whitten–Rabinovitch is applicable.] g_Γ is 1, 2, or 3 accordingly as Γ is of an A, E, or T (non, doubly, or triply degenerate) species, the R's are small integers whose values for the various types of molecular point groups are given in Ref. 1 and n_Γ is the number of symmetry species of type A, E, or T. An equivalent equation appears in the general work by Quack[2] on group representations in scattering theory and most recently by Pechukas[3] in his nice treatment of molecular symmetry point groups. For any given symmetry species the number of scattering channels (Quack) or fraction of vibrational states (Pechukas) is written in their notation as $[\Gamma_m] W(E,J)/g$ or n_μ^2/g, respectively. In each case the result excluded the symmetry associated with rotation about the C_∞ symmetry axis of linear molecules.

Exact counts were given to test the accuracy of the formula in Ref. 1. Sinha and Kinsey[4] have recently presented a fast computational method for an exact count.

In Sec. II of the present paper we develop statistical formulas for the density of vibrational states by symmetry species for *linear* molecules. In the process we first consider the purely classical density of states, using the vibrational angular momentum component as a representation of symmetry species. The formulas are then converted to a "semiclassical" form (to agree better with the exact quantum count) by introducing an expression analogous to that of

Whitten and Rabinovitch[5] for unrestricted counts of states. Comparisons with exact quantum counts are given in Sec. III.

The density of rovibrational states by symmetry species is treated for nonlinear molecules in Sec IV. Such systems are of interest because coupled rovibrational states have been invoked to explain the onset of intramolecular vibrational relaxation at energies where the density of vibrational states alone is too small to explain the data.[6] A simple formula, analogous to that which we derived in Ref. 1, is obtained for these rovibrational states. The formula is compared with an exact quantum count of rovibrational states. The results are discussed in Sec. V.

II. DENSITY OF VIBRATIONAL STATES OF LINEAR MOLECULES BY SYMMETRY SPECIES

In the case of nonlinear molecules there are a finite number of symmetry species. With increasing energy, the partitioning of states among symmetry species became energy independent and was given by a simple formula [Eq. (1)]. In the case of linear molecules, however, there are an infinite number of symmetry species, each characterized by the projection of the angular momentum along the internuclear axis.[7] The partitioning of states by symmetry species no longer approaches a constant value with increasing energy, and so the formula derived in the present paper is no longer quite as simple.

Two cases are considered below: (A) linear molecules with one degenerate pair of bending modes (e.g., CO_2); and (B) linear molecules with two degenerate pairs of bending modes (e.g., C_2H_2). The case of more than two degenerate modes can be treated similarly, but is rarer and is omitted here.

A. One degenerate pair of modes

We use the symbol l to denote quantum number for the (signed) component of angular momentum along the internuclear axis of the molecule. We first show that the classical number of vibrational states with energy less than or equal to E for a molecule with s vibrations and with a given value of l is $N_s^l(E)$:

$$N_s^l(E) = (E - |l|h\nu)^{s-1}/2(s-1)!h\nu\Pi_i h\nu_i, \tag{2}$$

where v is the vibration frequency of the degenerate bending mode $(i = 1,2)$ and in the present section the v_i $(i = 3$ to $s)$ are vibration frequencies of the remaining s-2 modes.

The derivation of Eq. (2) is given in Appendix A. It involves consideration of the partitioning of the energy E among all vibrational modes subject to the constraint that the (signed) component of the vibrational angular momentum along the internulcear axis is specified. Incidentally, integration of Eq. (2) over the limits of l, namely from $-E/hv$ to E/hv (Appendix A), for a given E yields $E^s/s!(hv)^2\Pi_i hv_i$, the conventional expression for the classical number of states of s oscillators with energy less than or equal to E.

The accuracy of Eq. (2) can be improved by converting to an expression which parallels that used by Whitten and Rabinovitch[5] for the unrestricted number of states (cf. Appendix A)

$$N_s^l(\epsilon) = (\epsilon + aE_{z,s} - |l|hv)^{s-1}/2(s-1)!hv\Pi_i hv_i, \quad (3a)$$

where

$$\epsilon = E - E_{z,s} \quad (3b)$$

and $E_{z,s}$ is the zero-point energy of the set of s oscillators; a is a factor given by Whitten and Rabinovitch, which we calcu-late at a reduced[5] energy $(E - |l|hv)/E_{z,s}$ and for the given s frequencies.

The density of states by angular momentum is found by differentiating Eq. (3):

$$\rho_s^l(\epsilon) = \frac{(\epsilon + aE_{z,s} - |l|hv)^{s-2}}{2(s-2)!hv\Pi_i hv_i}\left[1 + \frac{da}{d\epsilon}E_{z,s}\right]. \quad (4)$$

When $+l$ and $-l$ states are grouped together, to form the $\Pi, \Delta, ...$ states,[7] we have as their number

$$\begin{aligned} N_s^{|l|} &= 2N_s^l \quad (l \neq 0) \\ &= N_s^l \quad (l = 0), \end{aligned} \quad (5)$$

where N_s^l is given by Eq. (3). Similar remarks are applicable in obtaining $\rho_s^{|l|}(\epsilon)$ from the $\rho_s^l(\epsilon)$ in Eq. (4).

B. Two degenerate pairs of modes

The derivation for this case parallels the previous one, but involves more complicated limits. If v_1 and v_2 are the vibration frequencies of the two degenerate pairs of modes $(i = 1$–$4)$, the classical expression for the number of states with a specified (signed) l and with an energy less than or equal to E is shown in Appendix B to be

$$N_s^l(E) = \frac{hv_2(E - |l|hv_1)^{s-1} - hv_1(E - |l|hv_2)^{s-1}\theta(E/hv_2 - |l|)}{(s-1)!2hv_1 hv_2[(hv_2)^2 - (hv_1)^2]\Pi_i hv_i} \quad (6)$$

when $v_2 > v_1$. Here, the product Π_i is from $i = 5$ to s throughout this section and $\theta(x)$ is 0 if $x < 0$ and 1 if $x > 0$. Integration of Eq. (6) over all l from $-E/hv_1$ to E/hv_1 yields the conventional classical expression for the number of states, namely, $E^s/s!(hv_1)^2(hv_2)^2\Pi_i hv_i$.

Once again, a Whitten–Rabinovitch[5] type of modification is introduced to convert the expression in Eq. (6) to one which better approximates the quantum results, namely,

$$N_s^l(\epsilon) = \frac{hv_2(\epsilon + a_1 E_{z,s} - |l|hv_1)^{s-1} - hv_1(\epsilon + a_2 E_{z,s} - |l|hv_2)^{s-1}\theta(E/hv_2) - |l|)}{2(s-1)!hv_1 hv_2[(hv_2)^2 - (hv_1)^2]\Pi_i hv_i}, \quad (7)$$

where ϵ is again given by Eq. (3b), a_1 is computed at a reduced energy $(\epsilon - |l|hv_1)/E_{z,s}$, and a_2 at a reduced energy of $(\epsilon - |l|hv_2)/E_{z,s}$ and in each case for s oscillators.

The density of states, obtained by differentiating Eq. (7) is

$$\rho_s^l(\epsilon) = \frac{hv_2(\epsilon - a_1 E_{z,s} - |l|hv_1)^{s-2}(1 + \zeta_1) - hv_1(\epsilon - a_2 E_{z,s} - |l|hv_2)^{s-2}(1 + \zeta_2)\theta(E/hv_2 - |l|)}{2(s-2)!hv_1 hv_2[(hv_2)^2 - (hv_1)^2]\Pi_i hv_i}, \quad (8)$$

where $\zeta_i = (da_i/d\epsilon)E_{z,s}$.

Once again, when $+l$ and $-l$ states are grouped together to represent the symmetry species we have

$$N_s^{|l|} = 2N_s^l(l \neq 0) \quad (9a)$$

$$= N_s^l(l = 0), \quad (9b)$$

where N_s^l is given by Eq. (7) and with analogous remarks for $\rho_s^{|l|}(\epsilon)$.

III. RESULTS FOR LINEAR MOLECULES

In this section we give the quantum count $N(\Gamma)$ of harmonic vibrational states by symmetry species Γ with energy less than or equal to ϵ. Standard tables were used for computing the symmetry of overtone and combination states.[8]

The Σ states are those for which $|l| = 0$, the E_2 states (or Π states) are those for which $|l| = 1$, etc.[7] When two degenerate pairs of modes are present both Σ^+ and Σ^- states occur. In applying Eqs. (7) and (9) we assume a randomness

among these states and so to count each of the symmetry species Σ^+ and Σ^- we divide Eq. (7) for $l = 0$ by a factor of 2. In examples of molecules with an inversion center, g and u states occur, but Eqs. (3), (5), (7), and (9) refer to the sum of the (g,u) pairs. We assume a randomness among this type of pair and so also divide these equations by a factor of 2. Thus, when one has Σ_g^-, Σ_u^+, Σ_g^-, and Σ_u^- states, the equations for $l = 0$ are divided by a factor of 4.

Results for four representative linear molecules are given in Tables I to IV. Results for HCN,[9] a $C_{\infty v}$ molecule with one degenerate pair of normal modes, are given in Table I. R is the ratio of the exact $N(\Gamma)$ to the approximate number given by Eq. (3) and (5). In the last row ("total") the item labeled $N(\Gamma)$ is really the total number of states [i.e., $\Sigma N(\Gamma)$, summed over all Γ, even those that are not listed]. The "R" in this row is the ratio of this $\Sigma N(\Gamma)$ to the standard Whitten–Rabinovitch expression[5] for the total number of states. We also note that Σ^- states are not allowed for a molecule with

TABLE I. Number of vibrational states of HCN by Symmetry type at various excess energies and ratio R of exact number to approximate formulas.[a]

Γ	$\epsilon = 10\,250\ \text{cm}^{-1}$		$\epsilon = 20\,250\ \text{cm}^{-1}$		$\epsilon = 40\,250\ \text{cm}^{-1}$	
	$N(\Gamma)$	R	$N(\Gamma)$	R	$N(\Gamma)$	R
Σ^+	41	0.98	221	1.00	1 404	1.00[c]
E_1^b	70	0.99	404	1.00	2 672	1.00
E_2	60	1.01	368	1.00	2 544	1.00
E_3	50	1.01	332	1.00	2 416	1.00
E_4	40	0.99	300	1.00	2 294	1.00
E_5	34	1.04	270	1.00	2 176	1.00
E_6	26	1.00	242	1.00	2 062	1.00
E_7	20	0.98	216	1.00	1 952	1.00
E_8	16	1.04	192	1.00	1 846	1.00
E_9	12	1.05	170	1.00	1 744	1.00
E_{10}	8	0.99	150	1.00	1 646	1.00
E_{11}	6	1.10	130	1.00	1 550	1.00
E_{12}	4	1.16	114	1.00	1 460	1.00
E_{13}	2	0.94	98	1.00	1 372	1.00
E_{14}	2	2.35	84	1.00	1 288	1.00
E_{15}			70	0.98	1 208	1.00
E_{16}			60	1.00	1 132	1.00
E_{17}			50	1.00	1 058	1.00
E_{18}			40	0.98	988	1.00
E_{19}			34	1.03	922	1.00
E_{20}			26	0.99	856	1.00
E_{21}			20	0.97	796	1.00
E_{22}			16	1.02	738	1.00
Total	391	0.99	3 641	0.99	42 952	1.00

[a] Zero-point energy is 3412.5 cm^{-1}.

[b] As in Ref. 7, E_1 is a Π state, E_2 is a Δ state, etc.

[c] In this and other tables the formulas in Ref. 4 were used in some cases outside the suggested range of accuracy, but we still, as the results show, found the formula of Ref. 4 to be quite accurate.

TABLE II. Number of vibrational states for CO_2 by symmetry type at (A) $\epsilon = 20\,250\ \text{cm}^{-1}$ and (B) $\epsilon = 40\,250\ \text{cm}^{-1}$ and ratio of exact number to approximate formula.[a]

Γ	$N_g(\Gamma)$	R_g	$N_u(\Gamma)$	R_u	R
(A)					
Σ^+	276	1.18	194	0.83	1.01
E_1	346	0.81	500	1.17	0.99
E_2	466	1.20	320	0.82	1.01
E_3	282	0.80	418	1.18	0.99
E_4	388	1.21	260	0.81	1.01
E_5	226	0.78	346	1.20	0.99
E_6	320	1.23	208	0.80	1.01
E_7	178	0.76	282	1.21	0.99
E_8	260	1.25	164	0.79	1.02
E_9	138	0.75	226	1.22	0.98
E_{10}	208	1.27	126	0.77	1.02
E_{11}	104	0.72	178	1.23	0.98
E_{12}	164	1.30	94	0.75	1.02
E_{13}	76	0.69	138	1.26	0.98
E_{14}	126	1.33	68	0.72	1.03
E_{15}	54	0.67	104	1.28	0.97
E_{16}	94	1.37	48	0.70	1.03
E_{17}	36	0.62	76	1.31	0.97
E_{18}	68	1.41	32	0.66	1.04
E_{19}	22	0.56	54	1.36	0.96
E_{20}	48	1.49	20	0.62	1.06
E_{21}	12	0.47	36	1.41	0.94
E_{22}	32	1.60	12	0.60	1.10
Total	7926				1.00
(B)					
Σ^+	1 706	1.10	1417	0.91	1.01
E_1	2 684	0.91	3250	1.10	1.00
E_2	3 114	1.10	2568	0.91	1.01
E_3	2 428	0.90	2958	1.10	1.00
E_4	2 832	1.11	2320	0.91	1.01
E_5	2 188	0.90	2684	1.10	1.00
E_6	2 568	1.11	2088	0.90	1.01
E_7	1 964	0.89	2428	1.11	1.00
E_8	2 320	1.11	1872	0.90	1.01
E_9	1 756	0.89	2188	1.11	1.00
E_{10}	2 088	1.12	1672	0.90	1.01
E_{11}	1 564	0.89	1964	1.11	1.00
E_{12}	1 872	1.12	1486	0.89	1.01
E_{13}	1 386	0.88	1756	1.12	1.00
E_{14}	1 672	1.13	1314	0.89	1.01
E_{15}	1 222	0.88	1564	1.12	1.00
E_{16}	1 486	1.13	1156	0.88	1.01
E_{17}	1 072	0.87	1386	1.13	1.00
E_{18}	1 314	1.14	1012	0.88	1.01
E_{19}	934	0.86	1222	1.13	1.00
E_{20}	1 156	1.14	880	0.87	1.01
E_{21}	808	0.86	1072	1.14	1.00
E_{22}	1 012	1.15	760	0.87	1.01
Total	99 757				1.00

[a] Zero-point energy is 2510 cm^{-1}.

only one pair of degenerate modes[10] and hence we did not divide Eq. (7) for $l = 0$ by the factor of 2 mentioned in the preceding paragraph.

Results for CO_2,[11] a $D_{\infty h}$ molecule with one degenerate pair of modes, are given in Table II. Here, there are g and u states due to the inversion center and $N_g(\Gamma)$ and $N_u(\Gamma)$ represent the exact quantum number of states with g and u symmetry, respectively, with the cited value of $|l|$. Thus, R_g and R_u denote the ratios of exact counts to those based on the right-hand side of Eq. (5) divided by 2, as discussed above. R in the last column represents the ratio of $N_g(\Gamma) + N_u(\Gamma)$ to the number of states given by Eqs. (3) and (5).

Table III contains results for C_2BrCl,[12] a $C_{\infty v}$ molecule with two degenerate pairs of modes. R is the ratio of exact count $N(\Gamma)$ to the number given by Eq. (9a) when $l \neq 0$. When $l = 0$ (i.e., $\Gamma \equiv \Sigma$), R is the ratio of the sum of $N(\Gamma)$'s for Σ^+ and Σ^- to the number given by Eq. (9b).

Table IV contains results for C_2H_2,[13] a $D_{\infty h}$ molecule with two degenerate modes. Here, there are both g and u states and Σ^+ and Σ^- states occur. Thus, for $l \neq 0$, one divides the right-hand side of Eq. (9a) by a factor of 2 to calculate R_g and R_u. When computing R_g and R_u for the four Σ states one divides the right-hand side of Eq. (9b) by a factor of 4, as already noted. When $l = 0$, R is the ratio of the sum of $N(\Gamma)$ for Σ_g^+, Σ_g^-, Σ_u^+, and Σ_u^-, to the number given by Eq. (9b).

IV. DENSITY OF ROVIBRATIONAL STATES FOR NONLINEAR MOLECULES

Just as the vibrational states in Ref. 1 were characterized by symmetry species, the rotational and the rovibrational states are similarly characterized. It is shown in Appendix C that the fraction of rovibrational states of a given symmetry species is the same as that of vibrational states alone and is therefore equal to the f_Γ given by Eq. (1b).

TABLE III. Number of vibrational states for C_2BrCl by symmetry type at various excess energies and ratio of exact number to approximate formula.[a]

Γ	$\epsilon = 3050$ cm^{-1}		$\epsilon = 6050$ cm^{-1}		$\epsilon = 9050$ cm^{-1}	
	$N(\Gamma)$	R	$N(\Gamma)$	R	$N(\Gamma)$	R
Σ^+	393 }	1.07	6317 }	1.03	40594 }	1.01
Σ^-	216	1.06	4405	1.02	31313	1.01
E_1	1170		21110		142760	
E_2	1096	1.07	20564	1.03	140632	1.01
E_3	962	1.06	19562	1.02	136936	1.01
E_4	848	1.08	18512	1.03	132642	1.01
E_5	702	1.07	17156	1.02	127216	1.01
E_6	586	1.09	15886	1.03	121580	1.01
E_7	460	1.08	14414	1.02	115148	1.01
E_8	368	1.11	13100	1.03	108804	1.01
E_9	274	1.09	11668	1.02	101928	1.01
E_{10}	210	1.13	10436	1.03	95364	1.01
E_{11}	148	1.10	9132	1.03	88464	1.01
E_{12}	108	1.14	8054	1.04	82040	1.01
E_{13}	72	1.12	6932	1.03	75416	1.01
E_{14}	50	1.17	6034	1.04	69374	1.01
E_{15}	30	1.12	5110	1.03	63236	1.01
E_{16}	20	1.26	4396	1.05	57734	1.02
E_{17}	10	1.15	3662	1.04	52202	1.01
E_{18}	6	1.43	3118	1.06	47322	1.02
E_{19}	2	1.24	2554	1.04	42458	1.02
E_{20}	2	4.19	2152	1.06	38232	1.02
E_{21}			1734	1.05	34038	1.02
E_{22}			1446	1.08	30464	1.02
Total	7733	0.99	232508	1.00	2177519	1.00

[a] Zero-point energy is 2245.5 cm^{-1}.

TABLE IV. Number of vibrational states for C_2H_2 by symmetry type at (A) $\epsilon = 9900$ cm^{-1} and (B) $\epsilon = 19\,900$ cm^{-1} and ratio of exact number to approximate formulas.[a]

Γ	$N_g(\Gamma)$	R	$N_u(\Gamma)$	R_u	R
(A)					
Σ^+	223	1.49	171	1.14 }	1.04
Σ^-	97	0.65	131	0.88 }	1.05
E_1	608	1.05	608	1.05	
E_2	578	1.07	544	1.01	1.04
E_3	508	1.05	506	1.04	1.05
E_4	448	1.07	424	1.01	1.04
E_5	372	1.05	368	1.04	1.05
E_6	308	1.07	294	1.02	1.05
E_7	244	1.07	242	1.07	1.07
E_8	188	1.08	178	1.02	1.05
E_9	144	1.12	138	1.07	1.10
E_{10}	98	1.07	92	1.01	1.04
E_{11}	70	1.14	64	1.04	1.09
E_{12}	44	1.13	40	1.03	1.08
E_{13}	28	1.12	26	1.04	1.08
E_{14}	14	1.17	12	1.00	1.09
E_{15}	8	1.68	6	1.26	1.48
E_{16}	2	1.70	0	0.00	0.85
Total	7 826				1.00
(B)					
Σ^+	3 979	1.23	3 600	1.12 }	1.02
Σ^-	2 612	0.90	2 895	0.90 }	1.01
E_1	12 922	1.01	12 964	1.02	
E_2	12 678	1.02	12 510	1.01	1.01
E_3	12 042	1.01	12 078	1.01	1.01
E_4	11 488	1.02	11 342	1.00	1.01
E_5	10 644	1.01	10 678	1.01	1.01
E_6	9 928	1.02	9 798	1.01	1.01
E_7	9 006	101	9 034	1.02	1.01
E_8	8 228	1.02	8 120	1.01	1.01
E_9	7 314	1.01	7 340	1.02	1.01
E_{10}	6 562	1.02	6 468	1.01	1.01
E_{11}	5 710	1.01	5 736	1.02	1.02
E_{12}	5 032	1.02	4 952	1.01	1.01
E_{13}	4 282	1.01	4 310	1.02	1.02
E_{14}	3 700	1.03	3 636	1.01	1.02
E_{15}	3 078	1.01	3 098	1.02	1.02
E_{16}	2 602	1.03	2 556	1.01	1.02
E_{17}	2 112	1.02	2 124	1.02	1.02
E_{18}	1 740	1.04	1 706	1.02	1.03
E_{19}	1 370	1.02	1 376	1.03	1.02
E_{20}	1 092	1.04	1 074	10.2	1.03
E_{21}	830	1.03	832	1.03	1.03
E_{22}	638	1.05	628	1.03	1.04
Total	281 302				1.00

[a] Zero-point energy is 5860.5 cm^{-1}.

In the exact counts of rovibrational states listed in Tables V to VIII each harmonic vibrational state was coupled to each of the $2J + 1$ rotational states, where J was assigned various values. The coupling was assumed weak and the new states were assumed to have the sum of the energies of the separated states. The symmetry of the rotational states was found within the full molecular point group using the method given by Hougen.[14] The tables of the symmetry of rotational states for the molecular groups D_{nd}, D_{nh}, C_{nv}, and C_{nh} by Weber[15] were useful, as were the symmetries for methane.[16]

Results for benzene,[17] a symmetric top, are given in Table V. $N_{VR}(\Gamma)$ denotes the exact quantum number of rovibrational states of energy less than or equal to ϵ for symmetry species Γ, ϵ being the total rovibrational energy above the zero-point energy and $\gamma(\Gamma)$ is the ratio $N_{VR}(\Gamma)/f_\Gamma \Sigma_\Gamma N_v(\Gamma)$, where $N_v(\Gamma)$ is the exact number of vibrational states of symmetry Γ. The results are given for several values of J, where $J = 30$ is close to the room temperature value. One sees that for the rovibrational states the ratio of any nondegenerate symmetry species to any double degenerate symmetry species is 1:4, just as it was for the vibrational states.

We explore three approximations for the number of rovibrational states from a knowledge of the number of vibrational states:

(i) In this first approximation the rotational energy is neglected in the approximate formula for the number of states, i.e., we assume in this approximation that

$$N_{VR}(\Gamma;\epsilon) = (2J + 1)f_\Gamma N_v(\epsilon), \tag{10}$$

where $N_{VR}(\Gamma;\epsilon)$ denotes the number of rovibrational states of symmetry Γ with total energy less than or equal to ϵ and $N_v(\epsilon)$ is the number of vibrational states for this ϵ, regardless of symmetry. ϵ is the *total* energy in excess of the zero-point energy, as before. To test the approximation given by Eq. (10) we calculate a quantity $\alpha(\Gamma)$ defined by

$$\alpha(\Gamma) = N_{VR}(\Gamma;\epsilon)/(2J + 1)f_\Gamma N_v(\epsilon). \tag{11}$$

(ii) In this second approximation the rotational energy E_{rot} of the molecule (as a symmetric top) is averaged over the K quantum number assuming a uniform distribution in K. Instead of Eq. (10) we now use

$$N_{VR}(\Gamma;\epsilon) = (2J + 1)f_\Gamma N_v(\epsilon - \langle E_{rot} \rangle). \tag{12}$$

TABLE V. Number and ratio of rotational-vibrational states $N_{VR}(\Gamma)$ for benzene at $\epsilon = 3004.8$ cm^{-1} for various J's.[a]

Γ	$J = 1$		$J = 20$		$J = 30$	
	$N_{VR}(\Gamma)$	$\gamma(\Gamma)$	$N_{VR}(\Gamma)$	$\gamma(\Gamma)$	$N_{VR}(\Gamma)$	$\gamma(\Gamma)$
a_{1g}	3 100	1.00	36 545	1.00	44 682	1.00
a_{2g}	3 024	0.97	36 430	1.00	44 582	1.00
b_{1g}	3 100	1.00	36 334	1.00	44 562	1.00
b_{2g}	3 200	1.03	36 431	1.00	44 648	1.00
a_{1u}	3 066	0.99	36 464	1.00	44 544	1.00
a_{2u}	3 108	1.00	36 506	1.00	44 584	1.00
b_{1u}	3 150	1.01	36 424	1.00	44 557	1.00
b_{2u}	3 118	1.00	36 387	1.00	44 531	1.00
e_{1g}	12 586	1.01	145 538	1.00	178 402	1.00
e_{2g}	12 262	0.98	145 958	1.00	178 544	1.00
e_{1u}	12 528	1.01	145 654	1.00	178 148	1.00
e_{2u}	12 356	1.00	145,918	1.00	178 278	1.00

[a] Zero-point energy is 20034 cm^{-1}. Note that $\gamma(\Gamma)$ is defined differently than in paper I to include the degeneracy.

The rotational energy E_{rot} of a symmetric top having moments of inertia I_B and $I_A = I_C$ is

$$E_{rot}(K) = BJ(J+1) + K^2(C - B), \tag{13}$$

where the rotational constant $C > B$ for an oblate and $C < B$ for a prolate, symmetric top. Thus, $\langle E_{rot} \rangle$ depends on the $\langle K^2 \rangle$. For a given J, we have

$$\langle K^2 \rangle = \sum_{K=-J}^{J} K^2/(2J+1) = \tfrac{1}{3}J(J+1). \tag{14}$$

Thereby,

$$\langle E_{rot} \rangle = BJ(J+1) + \tfrac{1}{3}J(J+1)(C-B). \tag{15}$$

The expression for a spherical top is obtained by setting $C = B$ in Eqs. (13) and (15). To test Eq. (12) we define a ratio $\beta(\Gamma)$:

$$\beta(\Gamma) = N_{VR}(\Gamma;\epsilon)/(2J+1)f_\Gamma N_v(\epsilon - \langle E_{rot} \rangle). \tag{16}$$

(iii) In this third approximation we calculate an $N_v(\Gamma)$ at $\epsilon - E_{rot}(J,K)$ and then average this over K. Thus, now

$$K_{VR}(\Gamma;\epsilon) = (2J+1)f_\Gamma N_v', \tag{17}$$

TABLE VI. Ratio of exact to three approximate results for benzene at various J's[a] and $\epsilon = 3004.8$ cm^{-1}.

Γ	$J = 1$			$J = 20$			$J = 30$		
	$\alpha(\Gamma)$	$\beta(\Gamma)$	$\Delta(\Gamma)$	$\alpha(\Gamma)$	$\beta(\Gamma)$	$\Delta(\Gamma)$	$\alpha(\Gamma)$	$\beta(\Gamma)$	$\Delta(\Gamma)$
a_{1g}	1.00	1.00	1.00	0.86	1.00	1.00	0.71	1.01	1.00
a_{2g}	0.97	0.98	0.98	0.86	1.00	1.00	0.71	1.00	1.00
b_{1g}	1.00	1.00	1.00	0.86	1.00	1.00	0.71	1.00	1.00
b_{2g}	1.03	1.03	1.03	0.86	1.00	1.00	0.71	1.00	1.00
a_{1u}	0.99	0.99	0.99	0.86	1.00	1.00	0.71	1.00	1.00
a_{2u}	1.00	1.00	1.00	0.86	1.00	1.00	0.71	1.00	1.00
b_{1u}	1.01	1.02	1.02	0.86	1.00	1.00	0.71	1.00	1.00
b_{2u}	1.00	1.01	1.01	0.86	1.00	1.00	0.71	1.00	1.00
e_{1g}	1.02	1.01	1.01	0.86	1.00	1.00	0.71	1.00	1.00
e_{2g}	0.99	0.99	0.99	0.86	1.00	1.00	0.71	1.00	1.00
e_{1u}	1.01	1.01	1.01	0.86	1.00	1.00	0.71	1.00	1.00
e_{2u}	0.99	1.00	1.00	0.86	1.00	1.00	0.71	1.00	1.00

[a] The total number of all vibrational states is 24 866. When $J = 1$, $\langle E_{rot} \rangle = 0.3$ cm^{-1}; when $J = 20$, $\langle E_{rot} \rangle = 63.5$ cm^{-1}; when $J = 30$, $\langle E_{rot} \rangle = 140.6$ cm^{-1}.

TABLE VII. Ratio of exact to two approximate results for formaldehyde at various excess energies.[a]

Γ	$\epsilon = 5640$ cm^{-1}		$\epsilon = 11\,280$ cm^{-1}		$\epsilon = 22\,572$ cm^{-1}	
	$\beta(\Gamma)$	$\Delta(\Gamma)$	$\beta(\Gamma)$	$\Delta(\Gamma)$	$\beta(\Gamma)$	$\Delta(\Gamma)$
a_1	1.03	1.00	1.02	1.01	1.01	1.01
a_2	1.05	1.01	1.00	0.99	1.00	1.00
b_1	1.03	1.00	1.01	1.00	1.00	1.00
b_2	1.04	1.00	1.02	1.01	1.01	1.00
	$\sum_\Gamma N_v(\Gamma) = 73$		$\sum_\Gamma N_v(\Gamma) = 976$		$\sum_\Gamma N_v(\Gamma) = 22\,392$	

[a] $J = 15$, $\langle E_{rot} \rangle = 946.72$ cm^{-1}, zero-point energy is 5644 cm^{-1}.

where

$$N_v' = \sum_{K=-J}^{J} N_v[\epsilon - E_{rot}(J,K)]/(2J+1). \tag{18}$$

To test this approximation we define a ratio $\Delta(\Gamma)$:

$$\Delta(\Gamma) = N_{VR}(\Gamma)/(2J+1)f_\Gamma N_v'. \tag{19}$$

Equations (10), (12), and (17) are tested for benzene, by calculating the $\alpha(\Gamma)$, $\beta(\Gamma)$, and $\Delta(\Gamma)$ using Eqs. (11), (16), and (19), respectively. The results are given in Table VI for several J's. Equations (12) and (16) are tested for formaldehyde,[18] a near symmetric top, in Table VII and for methane,[19] a spherical top, in Table VIII. The closer the values of α, β, or Δ to unity the better, of course, the approximation.

V. DISCUSSION

Examination of Table I for linear molecules shows that the approximate formula [Eqs. (3) and (5)] for linear molecules agrees well with the exact results at the given energies. The deviations at very high $|l|$ at the lowest energy are due to poor statistics. Comparison of the R 's calculated at each l with the R in the last line shows that our Whitten–Rabinovitch type expression by angular momentum [Eq. (3)] is virtually as accurate as the standard total Whitten–Rabinovitch expression (except at large enough $|l|$'s). Similar remarks apply to its use for the sum of g and u states in Table II, but even for the counting of g states or u states alone it is seen to agree quite well. The remarks about Table I apply also to Table III, though there is less randomization between the Σ^+ and Σ^- than between g and u states. Equations (7) and (9) are seen to agree well with the exact count. A similar remark applies to Table IV.

TABLE VIII. Ratio of exact to two approximate results for methane.[a]

Γ	$\epsilon = 4940$ cm^{-1} $\beta(\Gamma), \Delta(\Gamma)$	$\epsilon = 9880$ cm^{-1} $\beta(\Gamma), \Delta(\Gamma)$	$\epsilon = 19\,760$ cm^{-1} $\beta(\Gamma), \Delta(\Gamma)$
a_1	0.88	0.95	0.99
a_2	1.05	1.03	1.01
e	0.98	0.99	1.00
t_1	1.03	1.02	1.00
t_2	0.99	0.99	1.00
	$\sum_\Gamma N_v(\Gamma) = 79$	$\sum_\Gamma N_v(\Gamma) = 1308$	$\sum_\Gamma N_v(\Gamma) = 66\,877$

[a] $J = 5$, $\langle E_{rot} \rangle = 157.56$ cm^{-1}, zero-point energy is 9883 cm^{-1}.

In Table V for rovibrational states, $\gamma(\Gamma)$ for benzene is even closer to unity than it was in Ref. 1 at the same number of states, perhaps due to the extra number of degrees of freedom. The three approximations for counting rovibrational states of nonlinear molecules of any symmetry species are embodied in Eqs. (10), (12), and (17). The results in Table VI for benzene show that even Eq. (10) is a good approximation except at high J. Equation (12) is seen to be even better than Eq. (10) and it agrees so closely with the exact results as not to make the use of Eq. (17) worthwhile for the present results. The tests in Table VII of Eqs. (12) and (17) for formaldehyde shows them to be satisfactory for the energy and J tested. Once again Eq. (17) contributes a negligible improvement over Eq. (12). Since methane is a spherical top, $E_{\rm rot}$ is independent of K and Eqs. (12) and (17) give identical results in Table VIII.

ACKNOWLEDGMENT

APPENDIX A: DERIVATION OF EQS. (2) AND (3)

We let ν be the vibration frequency of each member of the degenerate pair and let $n^a h\nu$ and $n^b h\nu$ be the amounts of energy present in each member of the degenerate pair. Thereby $n^a h$ and $n^b h$ are the values of the classical action. Classically, n^a and n^b are continuous variables with a minimum value of zero. Quantum mechanically, n^a and n^b are half-integers, $1/2, 3/2, \ldots$. For any pair of values (n^a, n^b) the component of angular momentum $|l|$ along the molecular axis is $|n^a - n^b|$.

We define a variable l' equal to $n^a - n^b$ and note that it can be positive or negative. We also define a principal vibrational "quantum number" n (the corresponding classical action being nh) for the degenerate pair

$$l' = n_1 - n_2, \quad n = n_1 + n_2. \tag{A1}$$

l' is the quantum number for a signed angular momentum component along the internuclear axis. The classical number of states $N_s^l(E)$ with a particular value of l of l', and with energy less than or equal to E, is

$$N_s^l(E) = \int_{n_2 = 0}^{E/h\nu} dn_2 \int_{n_1 = 0}^{E/h\nu - n_2} dn_1$$
$$\times N_{s-2}(E - n_1 h\nu - n_2 h\nu)\delta(n_1 - n_2 - l), \tag{A2}$$

where s is the total number of vibrations and $N_{s-2}(x)$ is the number of vibrational states of $s - 2$ oscillators with energy equal or less than x:

$$N_{s-2}(x) = \frac{x^{s-2}}{(s-2)!\Pi_i h\nu_i}. \tag{A3}$$

Here, the product over i is from $i = 3$ to s, oscillators 1 and 2 being the pair of degenerate bending vibrations. Using the transformation in Eq. (A1), the area element $dn_1\, dn_2$ in Eq. (A2) becomes $\frac{1}{2} dn\, dl'$ and the delta function becomes $\delta(l' - l)$. We consider first the case of $l > 0$. Here, because of the delta function, only the domain of $l' > 0$ need be considered. Equation (A2) then becomes

$$N_s^l(E) = \frac{1}{2} \int_0^{E/h\nu} dl' \int_{l'}^{E/h\nu} dn\, N_{s-2}(E - nh\nu)\delta(l' - l). \tag{A4}$$

[The limits on n and l' follows from those in Eq. (A2) and from the transformation given by Eq. (A1).] Integration over n yields

$$N_s^l(E)$$
$$= \left[\int_0^{E/h\nu} dl'(E - l'h\nu)^{s-1}\delta(l' - l)/2(s-1)!h\nu\Pi_i h\nu_i \right]. \tag{A5}$$

Integrating over l' yields Eq. (2) of the text. A similar argument applies to the case $l < 0$. One then uses in Eq. (A4) the limits $(-l', E/h\nu)$ for n and $(-E/h\nu, 0)$ for l'. For $l = 0$, the delta function occurs at an endpoint in Eq. (A5) and in a corresponding expression for $l' \leqslant 0$. Integrals over the $l' < 0$ and $l' > 0$ domains each yield $1/2$ and so Eq. (2) of the text is once again obtained.

In modifying Eq. (2) so as to yield Eq. (3) we have done so in a way which permits the standard Whitten–Rabinovitch expression[5] to be recovered from Eq. (3) with only a minor approximation. If we integrate the right-hand side of Eq. (3) over all l, we first reexpress $(\epsilon + aE_{z,s} - lh\nu)^{s-1} dl$ for all l positive as $-d[(\epsilon + aE_{z,s} - lh\nu)^s]/sh\nu[1 + E_{z,s}(da/d\epsilon)]$. [We have used the fact that $da/d(-lh\nu)$ equals $da/d\epsilon$]. An analogous change is made in the domain of l negative. We then note that the dominant contribution of the original integrand occurs at $l = 0$ and then replace the $da/d\epsilon$ by its value at $l = 0$, i.e., at the "reduced energy" of $\epsilon/E_{z,s}$. This derivative is negligible at the E's we have investigated (a is close to unity there) and so the standard[5] Whitten–Rabinovitch expression is obtained after integration over l.

APPENDIX B: DERIVATION OF EQ. (6)

Let $n_1 h\nu_1$ and $n_2 h\nu_2$ denote the classical energies in the two pairs of degenerate modes, and let $n_1^a h\nu_1$ and $n_1^b h\nu_1$ denote the classical energies of each member of the first pair and similarly for the second pair. We define

$$l_1' = n_1^a - n_1^b, \quad l_2' = n_2^a - n_2^b,$$
$$n_1 = n_1^a + n_1^b, \quad n_2 = n_2^a + n_2^b. \tag{B1}$$

As independent variables in the integration domain we use n_1, n_2, l_1', and l' (instead of l_1' and l_2'), where l' equals $l_1' l_2'$. The volume element $dn_1^a\, dn_1^b\, dn_2^a\, dn_2^b$ becomes $dl_1'\, dn_1\, dl'\, dn_2/4$.

The equation analogous to Eq. (A2) is found to be

$$N_s^l(E) = \frac{1}{4} \int\int\int\int dl'\, dl_1'\, dn_1\, dn_2$$
$$\times N_{s-4}(E - n_1 h\nu_1 - n_2 h\nu_2)\delta(l' - l) \tag{B2}$$

where $N_{s-4}(x)$ is the number of states of the $s - 4$ oscillators with energy equal to or less than x:

$$N_{s-4}(x) = x^{s-4}/(s-4)!\Pi_i h\nu_i. \tag{B3}$$

Here, i goes from 5 to s throughout, the oscillators $i = 1$–4 being the two pairs of degenerate bending vibrations. The l in the delta function is a particular value of l'. The limits on the variables are as follows: n_1 goes from $|l_1'|$ to $(E - n_2 h\nu_2)/h\nu_1$

and n_2 from $|l'_2|$ (*i.e.*, $|l' - l'_1|$) to $(E - |l'_1|hv_1)/hv_2$. For example, the lower limit just cited for the n_1 integral $|l'_1|$ is seen by noting that $n_1 = l'_1 + 2n_1^b = 2n_1^a - l'_1$ and observing that when $l'_1 > 0$ the smallest value of n_1 is obtianed by making $n_1^b = 0$ and hence $n_1 = l'_1$, and that when l'_1 is negative, the smallest value of n_1 is obtained by making $n_1^a = 0$ and hence making $n_1 = -l'_1$. That is, for both cases, we have $n_1 \geqslant |l'_1|$. The limits on l'_1 and l' in Eq. (B2) are given later:

$$N_s^l(E)$$

$$= \frac{\iint (E - |l'|hv_1 - |l' - l'_1|hv_2)^{s-2}\delta(l' - l)dl'_1 dl'}{4(s-2)!hv_1 hv_2 \Pi_i hv_i}.$$

(B4)

The limits on l_1 and l' are found by noting that the quantity in parentheses in Eq. (B4) must be nonnegative. Because of the absolute value signs, it is convenient to divide the integration region into several subdomains, in each of which the integral over l'_1 can be easily evaluated. For example, we let $v_2 > v_1$ and let the most negative and most positive values of l'_1 for which the quantity in parentheses in Eq. (B4) is nonnegative be denoted by l_1^{min} and l_1^{max}. Then, for the domain with $l' > 0$, the l'_1 domains are found to be as follows:

When $l' < E/hv_2$, there are three subdomains of l'_1, namely $(l_1^{min}$ to $0)$ $(0$ to $l')$ and $(l'$ to $l_1^{max})$. Here, l_1^{min} is given by $E - l'hv_1 - (l' - l_1^{min})hv_2 = 0$; and l_1^{max} is given by $E - l'hv_1 - (l_1^{max} - l')hv_2 = 0$. (We have used the fact that l'_1 can exceed l' since l'_2 can be negative.)

When $l' > E/hv_2$ (its maximum value is E/hv_1) one finds that the above l_1^{min} is positive rather than negative and so now there are only two subdomains of l'_1 namely $(l_1^{min}$ to $l')$ and $(l'$ to $l_1^{max})$. Furthermore, when l is positive, we need only use the positive l' integration domain, because of the delta function. One thus finds, for $l > 0$, an expression identical with Eq. (6), but with $|l|$ replaced by l. Similar remarks apply for the case when l is negative, with an obvious change in limits, and once again obtains Eq. (6), but with $|l|$ replaced by $-l$. Equation (6) still applies when $l = 0$.

APPENDIX C: DERIVATION OF EQ. (1b) FOR ROVIBRATIONAL STATES

In what follows, we use the notation and method of paper I. For group I molecules (defined there) we showed that a vibrational state with several quanta in at least one degenerate mode has a ratio of 1:1:3 for A labels to E labels to T labels ("labels" defined there). This symmetry species of the vibrational state was represented as equivalent to $A + E + 3T$. If we couple this symmetry species for the vibrational state to a rotational state having a general symmetry species $lA + mE + nT$ in the molecular point group,

where l, m, and n are zeros or integers, the overall symmetry of the coupled state is

$$(A + E + 3T)(lA + mE + nT)$$

$$= (l + 2m + 3n)A + (l + 2n + 3n)E$$

$$+ (3l + 6m + 9n)T$$

$$\equiv A + E + 3T.$$

(C1)

(The equivalent sign is defined in Ref. 1). Thus, the ratio of A labels to E labels to T labels of the coupled rovibrational state is 1:1:3, as it was for the vibrational state alone. If we assume a randomization of the labels among all of the symmetry species as in Ref. 1, the analysis is identical to that given for vibrational states alone there and yields the value of f_T given by Eq. (1b). It is of interest to note, though the results are independent of this, that if one averages over the rotational symmetry species given by Weber[15] by averaging over all K's, one obtains the same results as the averaged overtone rules given in Table I of Ref. 1 for vibrational state alone.

Similar arguments are applicable to groups 2 and 3 in Ref. 1, and so Eq. (1b) applies to rovibrational states of these molecular point groups as well.

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