

Symmetry Species of Overtones of Degenerate Vibrational Fundamentals

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course is not involved in the simplest cases (e.g., H+H). The case CH_3+CH_3 would appear to be of an intermediate nature.

The present model introduces another factor to be considered in the above connection. The (mean) activated state, in CH_3+CH_3 , comes at⁴ 5.90 Å. Ignoring the distribution of vibrational energy among other vibrational degrees of freedom, the lifetime of the associated molecule should be increased by virtue of this relatively large distance. We have calculated, using classical mechanics, the time necessary for two methyl radicals to go from $r=5.90$ Å to $r=r_0$ (see below) and back to $r=5.90$ Å for an average case. The location of the activated complex, $r=r^*$, depends on the value of $J(J+1)$. For the average case calculated, we have chosen that value of $J(J+1)$ which gives $r^{*2}=(5.90)^2$. The rotational energy U_R is then

$$U_R = [\hbar^2 J(J+1)/8\pi^2 \mu r^2]. \quad (10)$$

For the interaction energy U_I we have used $U_I = -\beta/r^6$ for $r > 4$ Å and a Morse curve (giving $r_e = 1.54$ Å, $\nu_{C-C} = 993$ cm^{-1} and $D_{C-C} = 79.1$ kcal./mole) for $r < 2.5$ Å. A smooth, arbitrary transition curve was used in the range $2.5 < r < 4$ Å. The time for a classical particle of average energy $\frac{3}{2}kT$ (rotation plus vibration) and mass μ to go from $r=5.90$ Å to $r=r_0$ and back to $r=5.90$ Å in the potential field $U = U_R + U_I$ was then computed by numerical integration, where $U(r_0) = \frac{3}{2}kT$ ($r_0 = 1.20$ Å; also, the potential barrier at $r=5.90$ Å turns out to be 101 cal./mole). For 120°C, this time was found to be 5.4×10^{-13} sec. The corresponding time for a harmonic oscillator of frequency $\nu = 993$ cm^{-1} is 0.34×10^{-13} sec., which is smaller by a factor of 16.

However, in the presence of acetone at 117.4 mm pressure,^{6,9} the mean interval between collisions of such an associated molecule with acetone molecules is 6.75×10^{-10} sec. Hence, in the lifetime 5.4×10^{-13} sec., the probability of deactivation by collision (assuming every collision is effective) is 8.0×10^{-4} . This value can probably be considered a lower limit for κ (at this pressure and temperature), as the effect studied by Kimball⁷ and Kassel⁸ will of course tend to increase κ .

The author is indebted to Professor W. A. Noyes, Jr., for suggesting this problem and to Professor Noyes, Professor W. D. Walters, and Dr. L. M. Dorfman for helpful discussions.

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¹ Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

² Kistiakowsky and Ransom, *J. Chem. Phys.* 7, 725 (1939).

³ Summarized on pp. 127-133, 260-261 of reference 1.

⁴ The mean square inter-radical distance in the activated complex, using k_J as a weighting function in computing the average, where k_J is the rate of the reaction for an activated complex with rotational quantum number J , turns out to be $2\Gamma(\frac{1}{2})/(\beta/kT)^{1/2}/\Gamma(\frac{1}{2})$. Using this for D^2 in Eq. (9) gives $P = \kappa[\Gamma(\frac{1}{2})]^2/\Gamma(\frac{1}{2})^2 = 0.49\kappa$ for any reaction of this type. For the combination of two methyl radicals at 120°C, and using the β mentioned, the root-mean-square inter-radical distance in the activated complex is 5.90 Å.

⁵ T. L. Hill, *J. Chem. Phys.* 16, 399 (1948).

⁶ T. L. Hill, *J. Chem. Phys.* (to be submitted).

⁷ G. E. Kimball, *J. Chem. Phys.* 5, 310 (1937).

⁸ L. S. Kassel, *J. Chem. Phys.* 5, 922 (1937).

⁹ Estimating kinetic theory collision diameters of 4.95 Å for acetone and 5.1 Å for a rather expanded ethane.

Symmetry Species of Overtones of Degenerate Vibrational Fundamentals

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THE symmetry species of overtones of degenerate vibrational fundamentals have been derived by Tisza,¹ whose calculation of the characters of such levels involved essentially a recursion relation between the characters of successive overtones. It is the purpose of this note to describe several closed expressions for such characters; the expressions are limited to the cases of double and triple degeneracy of the fundamental.

By choosing polar normal coordinates, defined in terms of the "cartesian" normal coordinates, Q_a , Q_b , and Q_c , the (unnormalized) wave functions assume the following forms:

(i) Doubly degenerate case:
 $\psi_{vi} = \exp(-\gamma\rho^2/2)F_{vi}(\gamma^{\frac{1}{2}}\rho)\exp(i\ell\phi). \quad (1)$

(ii) Triply degenerate case:

$$\psi_{vlm} = \exp(-\gamma r^2/2)G_{vl}(\gamma^{\frac{1}{2}}r)P_l^{|m|}(\cos\theta)\exp(im\phi). \quad (2)$$

The polar coordinates, ρ and ϕ ; r , θ , and ϕ , are defined by

$$(i) \quad Q_a = \rho \cos\phi \quad Q_b = \rho \sin\phi, \quad (3)$$

$$(ii) \quad Q_a = r \sin\theta \cos\phi \quad Q_b = r \sin\theta \sin\phi \quad Q_c = r \cos\theta. \quad (4)$$

The quantum numbers assume the following values: (i) $v=0, 1, 2, \dots$; $l=0, \pm 2, \pm 4, \dots \pm v$ if v even, $l=\pm 1, \pm 3, \pm 5, \dots \pm v$ if v odd; (ii) $v=0, 1, 2, \dots$; $l=0, 2, 4, \dots v$ if v even, $l=1, 3, 5, \dots v$ if v odd; $m=0, \pm 1, \pm 2, \dots \pm l$.

In order to determine the characters of overtones ($v=2, 3, \dots$) it is necessary to determine from a character table two properties of the doubly or triply degenerate fundamental species corresponding to $v=1$. These are: (a) whether the (irreducible) representation matrix has a positive or negative determinant; (b) an angle, α_R , such that

$$\chi_R^{(1)} = 2 \cos \alpha_R \quad (\text{doubly degenerate case}), \quad (5)$$

$$\chi_R^{(1)} = \pm 1 + 2 \cos \alpha_R \quad (\text{triply degenerate case}). \quad (6)$$

In (5) and (6), $\chi_R^{(1)}$ is the character of a group operation, R , for a doubly or triply degenerate species which corresponds with the fundamental level ($v=1$) in question. It is unnecessary to solve (5) if the matrix has a negative determinant; the choice of signs in (6) corresponds precisely to positive or negative determinants.

The criteria for the signs of the determinant are:

(i) Doubly degenerate case:

The sign is negative if $\chi_R^{(1)}=0$ and $\chi_R^{(1)}=+2$; otherwise positive.

(ii) Triply degenerate case:

The sign is positive if $\chi_R^{(1)} = (\chi_R^{(1)})^2 - 2\chi_R^{(1)}$ when $\chi_R^{(1)} \neq 0$, or if $\chi_R^{(1)} = +3$ when $\chi_R^{(1)} = 0$; otherwise negative.

In the above expressions, $\chi_R^{(1)}$ means the character of the n th power of the group operation, R .

The following character formulas can then be shown to hold (R^+ mean a group operation whose matrix in the given irreducible representation has a positive determinant, R^- a negative determinant):

(i) Doubly degenerate case:

$$\chi_R^{+(v)} = \frac{\sin(v+1)\alpha_R^+}{\sin\alpha_R^+}, \quad (7)$$

$$\chi_R^{-(v)} = \begin{cases} 0, & v \text{ odd} \\ 1, & v \text{ even} \end{cases}. \quad (8)$$

(ii) Triply degenerate case:

$$\chi_R^{+(v)} = \frac{\{\sin[(v+1)\alpha_R^+/2]\} \{\sin[(v+2)\alpha_R^+/2]\}}{[\sin(\alpha_R^+/2)][\sin\alpha_R^+]}, \quad (9)$$

$$v \text{ odd} \quad \chi_R^{-(v)} = \frac{\{\sin[(v+1)\alpha_R^-/2]\} \{\cos[(v+2)\alpha_R^-/2]\}}{[\cos(\alpha_R^-/2)][\sin\alpha_R^-]}, \quad (10)$$

$$v \text{ even} \quad \chi_R^{-(v)} = \frac{\{\cos[(v+1)\alpha_R^-/2]\} \{\sin[(v+2)\alpha_R^-/2]\}}{[\cos(\alpha_R^-/2)][\sin\alpha_R^-]}. \quad (11)$$

It is also possible to give character formulas for the sublevels of a given v , which will be useful particularly in studying the splitting of degeneracies when anharmonic potential terms and vibration-rotation interaction energies are included in the general molecular problem. Thus, in the doubly degenerate case, it is possible to express $\chi_R^{(v)}$ in the form:

TABLE I. Symmetry species of the overtone $v=6$ of E_g in the Group D_{4h} .

D_{4h}	E	$2C_4$	C_4^2	$2C_2'$	$2C_2''$	σ_h	$2\sigma_v$	$2\sigma_d$	$2S_4$	i	Species
$\chi_R^{(v)}, v=1$	2	0	-2	0	0	-2	0	0	0	2	E_g
Determinant sign	+	+	+	-	-	+	-	-	+	+	
α_R	0	$\pi/2$				π			$\pi/2$	0	
$\chi_R^{(l)}; l $	0	1	1	1	1	1	1	1	1	1	A_{1g}
$ l =2$	2	-2	2	0	0	2	0	0	-2	2	$B_{1g} + B_{2g}$
$ l =4$	2	2	2	0	0	2	0	0	2	2	$A_{1g} + A_{2g}$
$ l =6$	2	-2	2	0	0	2	0	0	-2	2	$B_{1g} + B_{2g}$
$\chi_R^{(v)}, v=6$	7	-1	7	1	1	7	1	1	-1	7	$2A_{1g} + A_{2g} + 2B_{1g} + 2B_{2g}$

TABLE II. Symmetry species of the overtone $v=7$ of F_2 in the group T_d .

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	Species
$\chi_R^{(v)}, v=1$	3	0	-1	1	-1	F_2
Determinant sign	+	+	+	-	-	
α_R	0	$2\pi/3$	π	0	$\pi/2$	
$\chi_R^{(l)}; l =1$	3	0	-1	1	-1	F_2
$ l =3$	7	1	-1	1	1	$A_1 + F_1 + F_2$
$ l =5$	11	-1	-1	1	-1	$E + F_1 + 2F_2$
$ l =7$	15	0	-1	1	1	$A_1 + E + 2F_1 + 2F_2$
$\chi_R^{(v)}, v=7$	36	0	-4	4	0	$2A_1 + 2E + 4F_1 + 6F_2$

$$\chi_R^{(v)} = \sum_{|l|} \chi_R^{(|l|)} \quad (12)$$

in which the permitted values of $|l|$ are as described above, and

$$\chi_R^{+ (|l|)} = 2 \cos \alpha_R \quad \chi_R^{- (|l|)} = 0 \quad \chi_R^{- (0)} = 1, \quad l \neq 0, \quad (13)$$

$$\chi_R^{- (0)} = 1. \quad (14)$$

Similarly, for the triply degenerate case,

$$\chi_R^{(v)} = \sum_l \chi_R^{(l)}, \quad (15)$$

where

$$\chi_R^{+ (l)} = \frac{\sin[(2l+1)\alpha_R/2]}{\sin(\alpha_R/2)}, \quad (16)$$

$$\chi_R^{- (l)} = \frac{\cos[(2l+1)\alpha_R/2]}{\cos(\alpha_R/2)}. \quad (17)$$

Examples of the application of these formulas are given in Tables I and II.

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¹ L. Tisza, *Zeits. f. Physik* **82**, 48 (1933).

Search for Short-Lived Y, ZR, and CB Fission Products*

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March 21, 1949

TABLE II of "Nuclei Formed in Fission," issued by the Plutonium Project,¹ is noteworthy for the great number of gaps it contains where one would expect fission products to exist. In most cases, these missing nuclei have not been identified yet because of their short half-lives and the relatively long time required for their chemical isolation. It has recently been shown² that, in certain cases, the chemical procedures can be shortened by effecting some separation of the fission products from each other during the bombardment

by utilizing their different recoil ranges in air. Collimated fission fragments from a thin Pu foil were allowed to pass through air at 140 mm pressure. By placing a few very thin zapon films at the appropriate distances from the Pu, selected fission fragments could be collected completely separated from fragments of very different masses and partially separated from fragments of neighboring mass numbers.

This procedure is most useful for the separation of yttrium from the rare earth activities, since the chemical separation is slow and difficult, and the range method permits a complete and automatic separation. Several runs were made using this technique plus the following chemical operations: one YF_3 precipitation, one $Sr(NO_3)_2$ scavenging precipitation from fuming nitric acid, another YF_3 precipitation, and a final yttrium oxalate precipitation. Counting was begun as soon as 10 minutes after a 5-minute irradiation. In no case was there a shorter-lived component than the previously reported 16.5-min. Y^{94} .³ Therefore, any short-lived unidentified Y fission products, with an appreciable fission yield, must have a half-life shorter than 3 minutes.

In the case of zirconium, it was found that the range separation technique offered no advantages over the chemical separation from neutron-irradiated solutions of uranium or plutonium. In the first few runs, when the standard chemical procedure⁴ was abbreviated slightly and the final precipitation of zirconium with cupferron was omitted, a new component with a 14-min. half-life appeared in the decay curves. This period was eliminated when four instead of three barium fluozirconate precipitations were performed and when the precipitation with cupferron was included. In the best two runs, counting was begun at 15 minutes after the end of 10-minute bombardments. The characteristic growth of 75-min. Cb from 17-hr. Zr was observed, but no short-lived activity was found. Thus, no zirconium isotopes with half-lives between 3 minutes and 17 hours result from fission in appreciable yield.

The experiments with columbium were performed both with and without the fission recoil apparatus. The chemical purifications consisted mainly of repeated Cb_2O_5 precipitations and Bi_2S_3 scavenging precipitations.⁵ Small amounts of short period activities were observed when the purely chemical method was used, but the half-lives and yields varied from run to run, thus indicating that these were contaminations. In the two runs in which the recoil method was used, counting started at about 16 minutes after 3-minute irradiations. Very little activity was found. Thus, any new Cb fission products with an appreciable yield must have shorter half-lives than 4 minutes.

* This document is based on work performed at Los Alamos Scientific Laboratory of the University of California under Government Contract W-7405-eng-36.

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¹ J. Am. Chem. Soc. **68**, 2411 (1946); J. C. Slater, *Rev. Mod. Phys.* **18**, 441 (1946).

² Katcoff, Miskel, and Stanley, Report La-659 (February, 1948).

³ L. Brown and S. Katcoff, Report LADC-568.

⁴ Hume, Ballou, and Glendenin, Report CN-2815 (June 30, 1945); D. N. Hume, Plutonium Project Record IX B, 8.8.4 (1946).

⁵ L. E. Glendenin, Plutonium Project Record IX B, 8.9.1 (1946).

The Dissociation Energy of the First N—H Bond in Ammonia

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January 5, 1949

TO determine experimentally the dissociation energy of the first N—H bond in ammonia we have used three different methods: the pyrolysis of NH_3 , the pyrolysis of N_2H_4 , and the pyrolysis of $C_6H_5 \cdot CH_2 \cdot NH_2$.