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Excitation and Dissociation of Molecules Due to β Decay of a Constituent Atom*

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The theory of electronic, vibrational, and rotational excitation of a molecule, specifically a diatomic molecule, due to β decay of a substituent atom is presented. The nature of the vibrational and rotational excitation for certain specific cases is mathematically investigated. The problem of dissociation arising from the excitation of rotations is discussed. It is shown that it is very difficult to obtain exact figures on the probability of dissociation due to the excitation of vibrations and rotations. Molecular orbital wave functions are employed to gain some insight into the electronic excitation of the daughter molecule. A very rough calculation is made of the probability of nondissociation in the decay of C^{14} labeled ethane.

INTRODUCTION

EXCITATION of atoms caused by β^\pm decay and K -capture has been considered by several authors¹ and has been experimentally verified by a number of investigators.² In the sudden perturbation approximation, the theory of which as applied to β decay has been extensively discussed,¹ the matrix element which connects a given parent electronic state $\psi_i(P)$ with a given daughter electronic state $\psi_f(D)$ is taken to be $\int \psi_f^*(D) \psi_i(P) d\tau$. The effect of the nuclear recoil in causing electronic excitation was shown by Levinger^{1(c)} to be negligible. In the case of molecules, the consideration of this recoil should however be quite important. Recent careful experiments by Wolfgang, Anderson, and Dodson³ on the formation of labeled methyl amine ($C^*H_3NH_2$) from the β decay of doubly labeled ethane ($C^*H_3C^*H_3$) serve as a stimulus for a more detailed investigation of the effect of the β decay of a substituent atom on a molecule.

THEORY

We consider now the case of β^- decay. The case of β^+ decay or of orbital capture will be quite similar. Take for the initial wave function of the system consisting of a molecule and an antineutrino

$$\psi_i = \phi z_i \theta_{\text{int.}, z_i} \frac{\exp[-(i/\hbar)K \cdot r_{cm_i}]}{V^{1/2}} \frac{\exp[(i/\hbar)k \cdot r_\nu]}{V^{1/2}}, \quad (1)$$

where ϕz_i is the nucleon wave function,

$$\exp[-(i/\hbar)K \cdot r_{cm_i}]/V^{1/2}$$

describes the motion of the center of mass of the molecule moving with a momentum K , $\theta_{\text{int.}, z_i}$ is the internal

wave function of the molecule (describing the electronic state, the vibration, and the rotation), $\exp[(i/\hbar)k \cdot r_\nu]$ describes the antineutrino with momentum k . One may rewrite Eq. (1):

$$\psi_i = \phi z_i \theta_{\text{int.}, z_i} \frac{\exp[-(i/\hbar)K \cdot r_{cm_i}]}{V^{1/2}} \times \frac{\exp[(i/\hbar)k \cdot (r_\nu - R_A)]}{V^{1/2}} \exp[(i/\hbar)k \cdot R_A], \quad (2)$$

where R_A refers to the coordinate of the nucleus which is decaying. In a similar manner, one may write for the final state consisting of the molecule and an escaping β particle, neglecting the Coulomb interaction of the β particle with the emitting nucleus and also with the other nuclei and electrons in the molecule (i.e., sudden perturbation approximation),

$$\psi_f = \phi z_f \theta_{\text{int.}, z_f} \frac{\exp[-(i/\hbar)M \cdot r_{cm_f}]}{V^{1/2}} \times \frac{\exp[-(i/\hbar)l \cdot (r_\beta - R_A)]}{V^{1/2}} \exp[-(i/\hbar)l \cdot R_A]. \quad (3)$$

Take the perturbing part of the Hamiltonian which leads to transition between ψ_i and ψ_f to be of the usual form $M = M_{\text{nuclear}} \delta(r_\beta - r_A) \delta(r_\nu - R_A)$, where M_{nuclear} is the nuclear perturbation which also transforms antineutrinos into electrons. One then finds, in the sudden perturbation approximation, for the probability, per β decay with given electron and neutrino momentum, of a transition between given initial and final molecular states

$$P_{i \rightarrow f} = \left| \int \frac{1}{V} \exp\left(\frac{i}{\hbar} M \cdot r_{cm_f}\right) \exp\left(-\frac{i}{\hbar} K \cdot r_{cm_i}\right) \times \exp\left(\frac{i}{\hbar} (l+k) \cdot R_A\right) \theta_{\text{int.}, z_f}^* \theta_{\text{int.}, z_i} d\tau \right|^2. \quad (4)$$

Take now

$$r_{cm} = r_{cm_f} \approx r_{cm_i}. \quad (5)$$

* Research carried out under the auspices of the U. S. Atomic Energy Commission.

¹ (a) A. Migdal, J. Phys. (U.S.S.R.) IV, 449 (1941). (b) E. L. Feinberg, J. Phys. (U.S.S.R.) IV, 423 (1941). (c) J. S. Levinger, Phys. Rev. 90, 11 (1953). (d) H. M. Schwartz, J. Chem. Phys. 21, 45 (1953). (e) H. Primakoff and F. T. Porter, Phys. Rev. 89, 930 (1953).

² For instance, M. Perlman and J. Miskel, Phys. Rev. 94, 1683 (1954); W. Robinson and J. J. Howland, Jr., Phys. Rev. 96, 1610 (1954).

³ Wolfgang, Anderson, and Dodson, J. Chem. Phys. 24, 16 (1956).

Then

$$\mathbf{r}_{cm} = \frac{\sum_X M_X \mathbf{R}_X + m \sum_i^N \mathbf{r}_i}{\sum_X M_X + Nm}, \quad (6)$$

where M and R refer to the mass and position coordinates of the nuclei, and m and r refer to the corresponding quantities for the electrons.

Consider now the case of a diatomic molecule, AB . Define the electronic coordinates in terms of the distance of the electrons from one or the other nucleus (as is done in setting up molecular wave function based on atomic orbitals):

$$\begin{aligned} \omega_1 &= r_1 - R_A \\ \omega_2 &= r_2 - R_A \\ &\vdots \\ \omega_f &= r_f - R_A \\ \omega_{f+1} &= r_{f+1} - R_B \\ &\vdots \\ \omega_N &= r_N - R_B. \end{aligned} \quad (7)$$

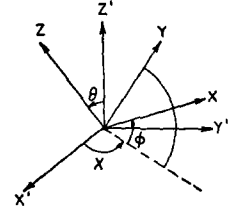
$$\begin{aligned} P_{i \rightarrow f} &= \left| \int \frac{1}{V} \exp[(i/\hbar) \mathbf{M} \cdot \mathbf{r}_{cm}] \exp[-(i/\hbar) \mathbf{K} \cdot \mathbf{r}_{cm}] \exp[(i/\hbar) \mathbf{t} \cdot \mathbf{r}_{cm}] d\tau_{cm} \right. \\ &\quad \times \left[\int \int \psi_f^*(\omega_1, \dots, \omega_N, R) \exp\left[-\left\{ \frac{i}{\hbar} \frac{m}{M_A + M_B + Nm} \sum_i^N \omega_i \right\} \right] \psi_i(\omega_1, \dots, \omega_N, R) d\tau_{\omega_1} \dots d\tau_{\omega_N} \right. \\ &\quad \times \left. \int \int \psi_f^*(\theta, \phi, \chi, R) \exp\left[-\frac{i \{M_B + (N-f)m\} R}{\hbar M_A + M_B + Nm} t_x \sin\theta \cos\chi + t_y \sin\theta \sin\chi + t_z \cos\theta \right] \right. \\ &\quad \left. \left. \times \psi_i(\theta, \phi, \chi, R) R^2 dR \sin\theta d\theta d\phi \right]^2 \right|, \quad (9) \end{aligned}$$

where t_x, t_y, t_z are the components of the vector t with respect to the fixed coordinate system.

The first integral merely expresses the fact that linear momentum is conserved in the decay process and will be omitted from now on. i and f will then only refer to the electronic, vibrational, and rotational states of the system. The magnitude of $\psi_i(\theta, \phi, \chi, R)$ will usually be appreciable only over a sufficiently small region R that one can neglect the variation of the electronic wave function $\psi(\omega_1, \dots, \omega_N, R)$ with internuclear distance and simply evaluate the electronic integral for the equilibrium value of R corresponding to the initial system, R_0 . Take, moreover, for the sake of convenience, t directed along the Z' -axis, $t_z = t$. Remembering that the electronic mass is negligible compared to nuclear masses, one obtains from Eq. (10)

$$\begin{aligned} P_{i \rightarrow f} &= \left| \int \psi_f^*(\omega_1, \dots, \omega_N) \psi_i(\omega_1, \dots, \omega_N) d\tau_{\omega_1} \dots d\tau_{\omega_N} \right. \\ &\quad \times \int \psi_f^*(\theta, \phi, \chi, R) \exp\left(-\frac{i M_B}{\hbar M_A + M_B} R t \cos\theta \right) \\ &\quad \left. \times \psi_i(\theta, \phi, \chi, R) R^2 dR \sin\theta d\theta d\phi \right|^2. \quad (10) \end{aligned}$$

FIG. 1. Coordinate system of molecule with respect to stationary X', Y', Z' -axes.



Take also

$$R = R_a - R_b$$

and define the position of the molecule with respect to a fixed coordinate system X', Y', Z' by means of the Eulerian angles θ, χ , and ϕ as in Fig. 1. Let the resultant of l and h be designated as t . Employing the Born-Oppenheimer approximation, one may separate the nuclear and the electronic motion, writing

$$\theta_{int.} = \psi(\omega_1, \dots, \omega_N, R) \psi(\theta, \phi, \chi, R).^4 \quad (8)$$

Substituting into Eq. (5), one obtains

The first integral is the overlap between the electronic functions of the initial and final state evaluated at the equilibrium internuclear distance of the initial state, in complete analogy with the result in the corresponding atomic problem. The second integral represents the probability of rotational and vibrational excitation. As Eq. (11) is written, the electronic excitation and the vibrational and rotational excitations may be evaluated separately, and one may write

$$P_{mj \rightarrow gh} = P_{m \rightarrow g}^{\text{elec.}} P_{j \rightarrow h}^{\text{v.r.}}. \quad (11)$$

$P^{\text{elec.}}$ is, as has already been pointed out, an overlap integral and presents no special difficulty beyond the general problem of obtaining molecular electronic wave functions. $P^{\text{v.r.}}$ is a new type of probability and does introduce some new problems.

Vibrational and Rotational Excitation⁵

The first difficulty encountered in the calculation of vibrational and rotational excitation is the problem

⁴ The nuclear spin which may give rise to some complications in homonuclear diatomic molecules is being completely neglected here.

⁵ Previous work on this topic has been carried out by H. Steinwedel and J. H. D. Jensen, *Z. Naturforsch.* **2a**, 125 (1947), who have determined, among other things, the various average excitations.

of wave functions. At present no very good wave functions have been formulated for systems in highly excited rotational and vibrational states. If one is interested in dissociation, one is of course extremely interested in these states. This problem will be discussed further in the next section. As a first approximation, assume a harmonic potential and no interaction between rotation and vibration. Then

$$\psi(\theta, \phi, \chi, R)_{n, l, m} = C_n e^{im\phi} P_l^{|m|}(\cos\theta) \times \exp\left(-\frac{1}{2}b^2x^2\right) \frac{H_n(bx)}{R_0+x}, \quad (12)$$

where $P_l^{|m|}(\cos\theta)$ is an associated Legendre polynomial, H_n is the n th Hermite polynomial, $b^2 = (4\pi^2\mu\nu/\hbar)$, ν is the classical vibrational frequency of the molecule, μ is the reduced mass, $R = R_0 + x$, and R_0 is the equilibrium internuclear distance. The normalizing factor C_n is given by

$$C_n^2 = \frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \frac{b/\sqrt{\pi}}{n!2^n}. \quad (13)$$

The approximate energy levels of this system will be given by

$$E_{n,l} = \hbar\nu(n + \frac{1}{2}) + \frac{\hbar^2}{2\mu R_0^2} l(l+1). \quad (14)$$

This system of eigenfunctions and corresponding energy levels is accurate only for small n and l . The spacing of rotational levels, depending on l , will usually be much smaller than the spacing of vibrational levels, depending on n , which implies $bR_0 \gg 1$.

Make now the simplifying assumption that the parent and the daughter molecule both have the same equilibrium internuclear separation and the same vibrational force constant. With this assumption the integral involved in $P_{00 \rightarrow nl}^{v,r}$ becomes very similar to that involved in the excitation of rotation and vibration by electron impact, and methods similar to those used by Morse⁶ in his treatment of this subject may be employed. It is immediately obvious that the selection rule $\Delta m = 0$ is operative. Suppose now that the parent molecule has no rotational or vibrational excitation ($n, l = 0$), one then obtains

$$P_{00 \rightarrow nl}^{v,r} = \frac{2l+1}{4\pi n!2^n} \int_{-\infty}^{\infty} \exp(-b^2u^2) H_n(bu) d(bu) \times \int_{-\infty}^{\infty} \exp(-b^2v^2) H_n(bv) d(bv) \times \int_{-1}^1 P_l^0(y) \exp\left[-\frac{i}{\hbar} \frac{M_B}{M} (R_0+u)ty\right] dy \times \int_{-1}^1 P_l^0(z) \exp\left[-\frac{i}{\hbar} \frac{M_B}{M} (R_0+v)tz\right] dz, \quad (15)$$

⁶ P. M. Morse, Phys. Rev. **90**, 51 (1953).

where M is the mass of the molecule, and the integration over bu and bv has been extended to minus infinity since $bR_0 \gg 1$.

The average vibrational and average rotational excitation is obtained from (16) by determining the average value of n (n_{av}) and the average value of $l(l+1)$ ($l(l+1)_{av}$). In doing so, use will be made of the quantity $\sum_l P_{00 \rightarrow nl} = 1/(2dn!) \int_0^{d^2/2} e^{-s} s^{n-1} ds$ where $d = M_B t / \hbar M b$, a relation which will be proved later.

$$n_{av} = \sum_{n,l} n P_{00 \rightarrow nl} = \sum_n n \sum_l P_{00 \rightarrow nl} = \frac{1}{\sqrt{2}d} \int_0^{d^2/2} e^{-s} s^{\frac{1}{2}} \sum_{n=1}^{\infty} \frac{s^{n-1}}{(n-1)!} ds = \frac{1}{\sqrt{2}d} \int_0^{d^2/2} s^{\frac{3}{2}} ds = \frac{d^2}{4}, \quad (16)$$

$$l(l+1)_{av} = \sum_{n,l} l(l+1) P_{00 \rightarrow nl} = \sum_n \frac{1}{2\pi n!2^n} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-1}^1 \exp(-b^2u^2) \times \exp(-b^2v^2) H_n(bu) H_n(bv) \times \exp\left[-\frac{i}{\hbar} \frac{M_B}{M} (R_0+u)ty\right] sd(bu) d(bv) dy, \quad (17)$$

where

$$s = \int_{-1}^1 \sum_l (2l+1) l(l+1) P_l^0(y) P_l^0(z) \times \exp\left[-\frac{i}{\hbar} \frac{M_B}{M} (R_0+v)tz\right] dz = -\frac{d}{dy} \left[(1-y^2) \frac{d}{dy} \exp\left(-\frac{i}{\hbar} \frac{M_B}{M} (R_0+v)ty\right) \right]^7 = -e^{-dv} \{2dy - d^2y^2 + d^2\}. \quad (18)$$

Substituting back in Eq. (18), and using the expansion theorem for Hermite polynomials, one obtains

$$l(l+1)_{av} = \frac{2}{3} \frac{M_B^2}{M^2} \frac{t^2}{\hbar^2} \left[R_0^2 + \frac{1}{2b^2} \right] \simeq \frac{2}{3} \frac{M_B^2}{M^2} \frac{t^2}{\hbar^2} [R_0^2] \quad (19)$$

for $bR_0 \gg 1$.

One finds then for the average energies

$$E_{vibr, av} = \frac{1}{6} \frac{M_B}{M M_A} t^2 \quad (20)$$

$$E_{rot, av} = \frac{1}{3} \frac{M_B}{M M_A} t^2.$$

⁷ Reference 5, equation above Eq. (21). There is a minus sign missing in Morse's equation.

These are just the quantities which one would expect classically. In the case that the molecular constants of the parent and the daughter molecule are not the same, one obtains by methods which shall not be elaborated here:

$$E_{\text{vib},Av} \geq -\frac{1}{6} \frac{M_B}{MM_A} l^2 + \frac{1}{2} h(\nu_f - \nu_i) \quad (21)$$

$$E_{\text{rot},Av} \geq -\frac{1}{3} \frac{M_B}{MM_A} l^2 + \frac{1}{2} h(\nu_f - \nu_i),$$

where ν_f and ν_i refer to the vibrational frequencies of the final and initial systems, respectively.

A quantity which is of some interest is the probability of exciting to a given vibrational state but summing over all rotational states. If one could neglect rotational dissociation, this would give one a good method of determining the amount of dissociation occurring as a result of the recoil process (but see next section). It will be assumed here that the molecules are initially in the lowest-lying vibrational state of the parent molecule, but with a Boltzman distribution over the various rotational states. This probability shall be called $P_{0 \rightarrow n \Sigma l^{\nu, r}}$.

$$P_{0 \rightarrow n \Sigma l^{\nu, r}} = \frac{\frac{1}{\pi n! 2^n} \sum_{l, m, l', m'} \exp\left[-\frac{\hbar^2 l'(l'+1)}{2IkT}\right] \frac{2l'+1}{4\pi} \frac{(l'-|m'|)!}{(l'+|m'|)!} \frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}{\sum_{l'} (2l'+1) \exp\left[-\frac{\hbar^2 l'(l'+1)}{2IkT}\right]}$$

$$\times \int_{-\infty}^{\infty} \exp(-b^2 u^2) H_n(bu) d(bu) \int_{-\infty}^{\infty} \exp(-b^2 v^2) H_n(bv) d(bv)$$

$$\times \int_0^\pi \int_0^{2\pi} P_{l', |m'|}(\cos\theta) \exp(im'\phi) P_{l, |m|}(\cos\theta) \exp(im\phi) \exp\left\{\frac{i}{\hbar} \left[\frac{M_B}{M} (R_0 + u)t \cos\theta\right]\right\} \sin\theta d\theta d\phi$$

$$\times \int_0^\pi \int_0^{2\pi} P_{l', |m'|}(\cos\psi) \exp(-im'\alpha) P_{l, |m|}(\cos\psi) \exp(-im\alpha)$$

$$\times \exp\left\{-\frac{i}{\hbar} \left[\frac{M_B}{M} (R_0 + v)t \cos\psi\right]\right\} \sin\psi d\psi d\alpha. \quad (22)$$

Here I is the moment of inertia of the molecule.

Using the expansion theorem for Legendre polynomials, this expression reduces to

$$P_{0 \rightarrow n \Sigma l^{\nu, r}} = \frac{1}{\pi n! 2^n} \left\{ \sum_{l'} (2l'+1) \exp\left[-\frac{\hbar^2 l'(l'+1)}{2IkT}\right] \right\}^{-1}$$

$$\times \sum_{l', m'} \exp\left[-\frac{\hbar^2 l'(l'+1)}{2IkT}\right] \frac{2l'+1}{4\pi} \frac{(l'-|m'|)!}{(l'+|m'|)!}$$

$$\times \int_{-\infty}^{\infty} \exp(-b^2 u^2) H_n(bu) d(bu)$$

$$\times \int_{-\infty}^{\infty} \exp(-b^2 v^2) H_n(bv) d(bv)$$

$$\times \int_0^\pi \int_0^{2\pi} P_{l', |m'|}(\cos\psi) P_{l, |m'|}(\cos\psi)$$

$$\times \exp\left\{-\frac{i}{\hbar} \left[\frac{M_B}{M} (u-v)t \cos\psi\right]\right\}$$

$$\times \sin\psi d\psi d\alpha. \quad (23)$$

Next, using the addition theorem for Legendre polynomials,

$$P_{0 \rightarrow n \Sigma l^{\nu, r}} = \frac{1}{2\pi n! 2^n} \int_{-\infty}^{\infty} \exp(-b^2 u^2) H_n(bu) d(bu)$$

$$\times \int_{-\infty}^{\infty} \exp(-b^2 v^2) H_n(bv) d(bv)$$

$$\times \int_0^\pi \exp\left[\frac{i}{\hbar} \left[\frac{M_B}{M} (u-v)t \cos\psi\right]\right] \sin\psi d\psi. \quad (24)$$

Employing the expansion

$$\exp(ixz) = \exp(-\frac{1}{4}x^2) \sum_{n=0}^{\infty} (ix)^n H_n(z) / 2^n n! \quad (25)$$

and making use of the orthonormality expression for Hermite polynomials, one obtains the result

$$P_{0 \rightarrow n \Sigma l^{\nu, r}} = \frac{1}{\sqrt{2} n!} \int_0^{d/2} \exp(-k) k^{n-1} dk. \quad (26)$$

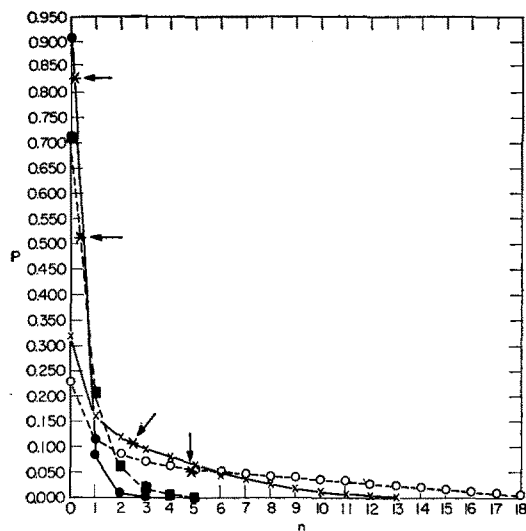


FIG. 2. $P_{00 \rightarrow \Sigma l}$ vs n for various d . * (marked by arrow) corresponds to n_{Av} for that value of d .

● $d=0.78$ × $d=1.56$
 ■ $d=3.90$ ○ $d=5.46$.

Since this probability is independent of the temperature T , it is obvious that the same result would be obtained if the initial state had been confined to the zeroth rotational level.

The function (27) has been plotted in Fig. 2 for various values of d . The average value of n corresponding to each value of d has been indicated on the respective plots. In Table I are indicated the percentage of the processes having less than the average value of n (since this value is usually noninteger the percentage is interpolated). It is seen that the transition to the zeroth vibrational state is the most probable one, but a significant fraction of the events give rise to daughter molecules with more vibrational excitation than the value classically expected.

Some computations of Eq. (16) have been carried out for low values of d . Using Eq. (16) in its absolute square form and employing Eq. (26) and the orthogonality expression for Hermite polynomials, one finds

$$P_{00 \rightarrow n l}^{r,r} = \frac{2l+1}{4n!2^n} \left| \int_{-1}^1 \exp\left(-\frac{1}{4}d^2y^2\right) (dy)^n \times \exp(idbR_0y) P_l^0(y) dy \right|^2. \quad (27)$$

Since $P_l^0(y)$ is of the form $\sum a_k y^k$, and since $\exp[-(1/4)d^2y^2]$ may be expanded in the same form, Eq. (28) may be evaluated by computing integrals $\int y^n \cos ay dy$ and $\int y^n \sin ay dy$. These integrals present no difficulties. Since, however, the number of terms in the expansion of $\exp[-(1/4)d^2y^2]$ grows larger as d increases, the computations here have been restricted to small values of d . These results are tabulated in Fig. 3. All computations were made for $bR_0=23$ which can

TABLE I.^a

d	E (ev)	% with n less than n_{Av}
0.78	0.049	91.6
1.56	0.196	79.2
3.90	1.227	65.3
4.68	1.766	63.3
5.46	2.404	61.4
6.24	3.140	61.0
6.52	3.431	60.7
7.80	4.905	59.8

^a Percentage of recoil processes giving rise to daughter molecules with less than the average value of n . E is the energy of the recoiling atom in electron volts where $M_B=20$, $M=34$, and b corresponds to a homonuclear C_2^{14} molecule with $R_0=1.51$ Å, $\nu=900$ cm^{-1} .

correspond to $\nu=1829$ cm^{-1} , $M=26$, $M_A=14$, and $R_0=1.23$ Å. The star on each plot indicates $l(l+1)_{Av} = 2/3d^2(bR_0)^2$, corresponding to the given value of d . The behavior of the probability of exciting to a value of l at a given n has interesting oscillating characteristics which should arouse even more interest if methods are devised for actually measuring these probabilities experimentally. It is seen that for a given value of d , the probability of exciting higher values of l decreases as n increases. This is also demonstrated in Table II. From the data which we have available now, it seems that any computation based only on the average amounts of rotational and vibrational excitation would give results which could be much in doubt.

Rotational Dissociation

When one takes rotation into account, the potential energy for the diatomic vibrator becomes $V'(r) = V(r) + (k^2/8\pi^2\mu r_e^2)(l(l+1)/(r/r_e)^2)$,⁸ where $V(r)$ is the electronic potential energy, μ is the reduced mass, r is the internuclear separation, and r_e is the equilibrium internuclear separation corresponding to $V(r)$. The potential $V(r)$ will be taken here to be the Morse potential

$$V(r) = D\{1 - \exp[-\beta r_e(r/r_e - 1)]\}^2, \quad (28)$$

where D is the total amount of energy which one must put into vibrations to dissociate a molecule if it is in

TABLE II.^a

d	n	% with $l(l+1)$ less than $l(l+1)_{Av}$
0.1	0	76.8
0.2	0	55.3
	1	86.8
0.75	0	43.31
	1	88.94
	2	90.95

^a Percentage of transitions to a given value of n with $l(l+1)$ less than $l(l+1)_{Av}$.

⁸ L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

⁹ G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

TABLE III.^a

Molecule	βr_e
H ₂ ⁺	1.40
H ₂	1.44
HCl ⁺	2.20
OH	2.24
O ₂	2.37
HCl	2.38
HBr	2.56
HeH ⁺	2.60
BN	2.89
N ₂	3.38
N ₂ ⁺	3.47
NO	3.49
C ₂	3.72
Br ₂	4.48

^a Values of βr_e for various diatomic molecules. The data are taken from G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), except for the data for HeH⁺, which were taken from S. Toh, Proc. Phys. Math. Soc. Japan 22, 119 (1940).

the ground rotational state, and $\beta = C\nu(\mu/D)^{1/2}$ (C is a constant determined by the units employed). Values of βr_e for various diatomic molecules are listed in Table III.

It is obvious that, as l increases, the equilibrium internuclear distance of $V'(r)$ shifts to larger distances with respect to that of $V(r)$, until finally, when the molecule has more than a certain amount of rotational excitation, there is no longer a potential minimum at all, and a stable molecule can no longer exist. The amount of energy which must be put into internal energy by the recoil process in order to accomplish dissociation is equal to the infinite separation energy $V'(r)$ measured with respect to the minimum of $V(r)$ taken as zero. This energy may be divided into three parts: (1) the energy

TABLE IV.^{a,b}

	$R(r_e)$	r_{\min}/r_e	$R(r_{\min})$	D'	E_∞
(A) $\beta r_e = 3.76$	0.000	1.00	0.000	1.000	1.000
	0.140	1.00	0.140	0.875	1.015
	0.281	1.00	0.281	0.758	1.039
	0.561	1.05	0.508	0.558	1.094
	1.122	1.10	0.928	0.224	1.250
	1.684	1.20	1.169	0.018	1.467
	2.245 no minimum				
(B) $\beta r_e = 2.0$	0.000	1.00	0.000	1.000	1.000
	0.136	1.05	0.123	0.872	1.005
	0.272	1.05	0.246	0.756	1.011
	0.543	1.10	0.449	0.549	1.030
	1.086	1.30	0.643	0.238	1.083
	1.629	1.50	0.724	0.041	1.164
	2.172 no minimum				
(C) $\beta r_e = 1.0$	0.000	1.00	0.000	1.000	1.000
	0.136	1.10	0.112	0.879	1.000
	0.272	1.20	0.189	0.781	1.003
	0.543	1.40	0.277	0.620	1.005
	1.086	1.60	0.424	0.389	1.016
	1.629	1.90	0.451	0.229	1.032
	2.172	2.20	0.449	0.113	1.051
	2.716	2.50	0.434	0.035	1.073

^a Characteristics of the $V'(r)$ potential energy curves. Symbols are defined in the text.

^b All quantities were evaluated for r/r_e at intervals of 0.05. The quantities given are for the point which seemed closest to the minimum of the curve.

necessary to stretch the molecule from r_e to the equilibrium internuclear distance of $V'(r)$; (2) the rotational energy of the molecule corresponding to the equilibrium internuclear distance of $V'(r)$; (3) the vibrational dissociation energy corresponding to the potential energy curve $V'(r)$ which is the energy distance from the minimum of the potential curve to its infinite separation value. Listed in Table IV are the rotational energy corresponding to r_e [$R(r_e)$], the ratio of r_e of the internuclear separation corresponding to the minimum of $V'(r)$ which is called r_{\min} (r_{\min}/r_e), the rotational energy

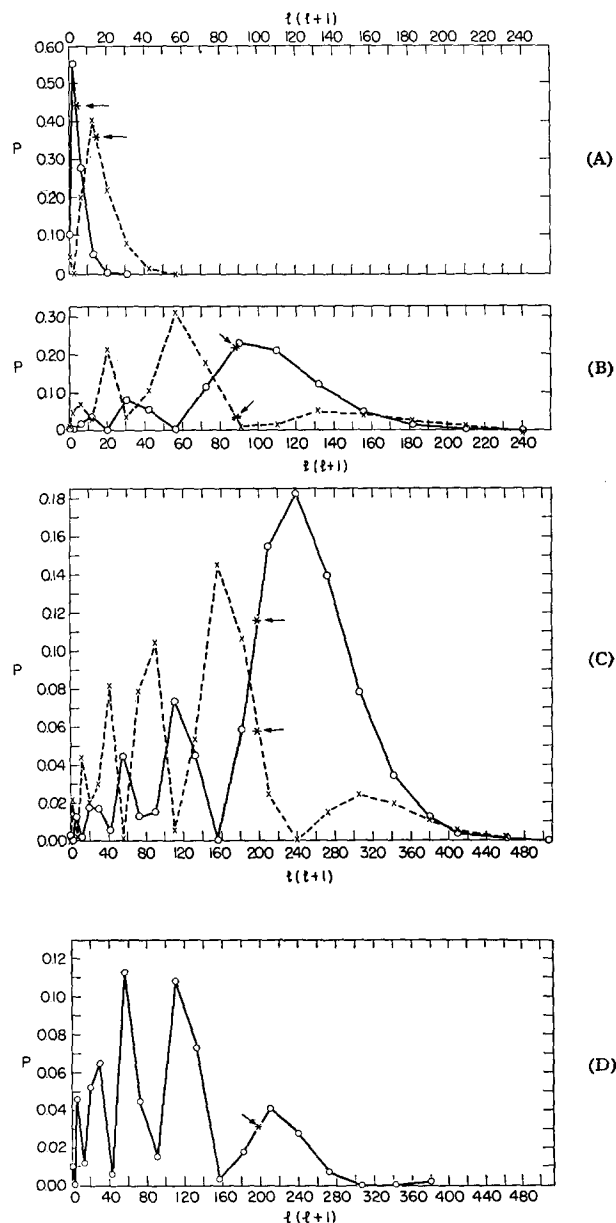


FIG. 3. $P_{00 \rightarrow nl}$ vs $l(l+1)$. * (marked by arrow) corresponds to $l(l+1)_{Av}$ for that value of d with $bR_0 = 23$. (A) $\circ d=0.1$; $n=0$. $\times d=0.2$; $n=0$. (B) $\circ d=0.5$; $n=0$. $\times d=0.5$; $n=1$. $P \times 30$ is plotted. (C) $\circ d=0.75$; $n=0$. $\times d=0.75$; $n=1$. $P \times 10$ is plotted. (D) $\circ d=0.75$; $n=2$.

corresponding to $r_{\min} [R(r_{\min})]$, the vibrational dissociation energy corresponding to $V'(r)$ (D'), and the total energy of $V'(r)$ at infinite separation with respect to the minimum of $V(r)$ (E_∞). These quantities are listed for various amounts of rotational energy and for several values of β . All the energies are normalized with respect to $D'=1$ for no rotation. Table IV shows that rotational excitation can be important in causing dissociation in a molecule. Moreover this study also emphasizes the interplay between rotations and vibrations in molecules which possess large amounts of rotational excitation. In the recoil process, a large proportion of the recoil energy goes into rotations; as a matter of fact, for the case considered previously, on the average two-thirds of the energy which goes into vibrations and rotations, goes into rotational excitation. However, no thorough attempt appears to have been made to study rotational and vibrational eigenfunctions and eigenvalues for high rotational excitation.

Electronic Excitation

It has been shown that the probability of finding the daughter molecule in the electronic state m , if the parent molecule was in the state j , is given by

$$P_{j \rightarrow m}^{\text{elec.}} = \left| \int \psi_m^* \psi_j d\tau \right|^2, \quad (29)$$

the integral being evaluated at the equilibrium internuclear distance of the parent molecule. At the present time, there appears to be only one case where Eq. (30) may be evaluated with great accuracy. This is the case of the ground state of H_2 going to the ground state of HeH^+ , where good James Coolidge type molecular wave functions are available. This case will not be considered here. Instead, some molecular orbital functions will be considered, and the results obtained by them compared with the results obtained for atoms.

Consider C_2 in its $(\pi)^4 1\Sigma_g^+$ state as the parent, and ask for the probability that the daughter CN^+ molecule be also in the $(\pi)^4$ state.

$$\begin{aligned} \psi_j &= (1s_A)^2(1s_B)^2(2s_A)^2(2s_B)^2 \\ &\times \left\{ \frac{1}{N}(\pi x_A + \pi x_B) \right\}^2 \left\{ \frac{1}{N}(\pi y_A + \pi y_B) \right\}^2 \\ \psi_m &= (1s_A)^2(1s_B)^2(2s_A)^2(2s_B)^2 \\ &\times \left\{ \frac{1}{N'}(a\pi x_{A'} + b\pi x_B) \right\}^2 \left\{ \frac{1}{N'}(a\pi y_{A'} + b\pi y_B) \right\}^2. \quad (30) \end{aligned}$$

The orbital nomenclature here is the usual one. N and N' are proper normalizing factors, A is the carbon atom which decays into a nitrogen atom, while B is

TABLE V.*

$ 1/N'N(a\pi x_{A'} + b\pi x_B)(\pi x_A + \pi x_B) ^2$	
(A) $\text{C}-\text{N}^+$	
$a/b=1$	0.966
$a/b=2$	0.866
$a/b=\sqrt{3}$	0.896
(B) C^+-N	
$a/b=\sqrt{3}$	0.920

* Molecular orbital overlap integrals. These values must be compared with the atomic overlap integral $\int 2p x_A' 2p x_A d\tau = 0.956$. The molecular calculations were made for an internuclear distance of 1.31 Å.

the other carbon atom. a and b are undetermined and depend on how much of the time the electron spends on the N atom and how much on the C atom. The s functions on one atom will be taken as orthogonal to those on the other. Moreover, $1s_{A'}$ and $2s_{A'}$ will be taken as orthogonal to $1s_B$ and $2s_B$. The functions (31) may be thought to be properly antisymmetrized. $P_{j \rightarrow m}^{\text{elec.}}$ becomes then simply a product of one-electron integrals over the electronic functions which change.

$$\begin{aligned} P_{j \rightarrow m}^{\text{elec.}} &= \left| \int 1s_{A'} 1s_A d\tau \right|^4 \left| \int 2s_{A'} 2s_A d\tau \right|^4 \\ &\times \left| \frac{1}{N'N} \int (a\pi x_{A'} + b\pi x_B)(\pi x_A + \pi x_B) d\tau \right|^8. \quad (31) \end{aligned}$$

The corresponding integral for the probability of a C atom in an $s^2 p^2$ configuration decaying into an N^+ atom in the same configuration is

$$\begin{aligned} P_{j \rightarrow m}^{\text{elec.}}(\text{atom}) &= \left| \int 1s_{A'} 1s_A d\tau \right|^4 \left| \int 2s_{A'} 2s_A d\tau \right|^4 \\ &\times \left| \int 2p x_{A'} 2p x_A d\tau \right|^4. \quad (32) \end{aligned}$$

The first two integrals are the same in both Eqs. (32) and (33). The expressions differ only in the last integral, where each atomic overlap integral is replaced by the square of a molecular orbital overlap integral. Thus only this last integral will have to be considered in determining how the probability that the molecule remains in the same configuration compares with the probability that the atom remains in the same configuration.

The molecular overlap integrals may be readily evaluated using the method of Mulliken¹⁰ and his co-workers. Slater type atomic orbitals were employed. In Table V are listed results obtained for different values of a and b , and also using different atomic orbitals for the C and N atoms in the $\text{C}-\text{N}^+$ molecule.

¹⁰ R. S. Mulliken *et al.*, J. Chem. Phys. 17, 1248 (1949).

TABLE VI.*

		X^2
(A) C-N ⁺ $a/b=1$	$R=1.31$ A	0.965
(B) C ⁺ -N $a/b=\sqrt{3}$ $a/b=\sqrt{3}$	$R=1.31$ A	0.942
	$R=1.54$ A	0.936

* Molecular overlap integrals for σ orbitals. R is the internuclear separation.

Z -values for a neutral carbon atom were employed in C_2 . For CN^+ , two cases were considered: (1) neutral C and positive N, (2) neutral N and positive C. The second choice probably corresponds more nearly to the actual situation.¹¹ It is to be noted that, if the π electrons are divided between the nitrogen and the carbon in a ratio of a^2/b^2 , then $a/b=\sqrt{3}$ leads to leaving the nitrogen neutral and the carbon with one positive charge. The values of the integrals are sensitive to the ratio of a/b and also to the atomic orbitals involved in the molecular wave function. While the values seem to tend somewhat lower than the value of 0.956 for the corresponding atomic integral, the final $P_{j \rightarrow m}^{elec.}$ will be of the same order of magnitude as the atomic one. Molecular calculations were also undertaken with the σ orbital of the type $a2p\sigma_A + b2p\sigma_B$. Let $X^2 = |(1/NN') \int (a2p\sigma_A + b2p\sigma_B)(2p\sigma_A + 2p\sigma_B) d\tau|^2$, where the designations are the same as for the π orbitals. The results obtained are shown in Table VI. They do not differ much from those obtained for π orbitals. In one case a variation of internuclear separation was also tested with the effect found not to be very large.

A lower limit for the probability of ending up in a stable electronic molecular state after the β -decay process will usually be given by the probability that the molecule remains in the same configuration since this configuration will usually also correspond to the ground state of the daughter molecule ion. Of course, many of the other states to which a transition is possible may also be stable but these have not been considered here. In the case of the homonuclear diatomic molecule decay, both parent and daughter wave functions must belong to the same irreducible representation of the lower symmetry molecule $C_{\infty v}$. They must also have the same electron spin. These electronic selection rules may be generalized to any polyatomic system.¹²

β Decay of Doubly Labeled Ethane

As mentioned in the Introduction, this work was undertaken largely because of the experimental

¹¹ It must be admitted that if one makes this choice, the $2s_A$ orbital should probably be taken as that for neutral N in which case $\int 2s_A 2s_A d\tau$ will not be the same for the molecule as for the atom.

¹² The polyatomic problem will be further discussed in a subsequent note.

work on the production of labeled methyl amine from the β decay of doubly labeled ethane. One might make the primary assumption that the labeled methyl amine is formed if the C-N bond does not break as a result of the process. This assumption makes the problem essentially a diatomic one, although the nondissociation in the molecule would probably be larger since the recoil of the atom may be distributed over more degrees of freedom. Moreover, the probability of breaking carbon-hydrogen bonds and what may happen as a result is ignored. Even, however, in the diatomic case, a rather large difficulty is faced because of the problem of rotational dissociation to which no adequate solution seems to exist at the present time.

One finds that, if the recoil energy of the carbon-14 atom is larger than 3.57 ev, the vibrational and rotational energy of the daughter molecule will be larger than 2.1 ev assuming that the mass of the molecule in atomic units is 34, that the parent molecule is in the ground rotational vibrational state, and that the dimensions and force constants of both parent and daughter molecule are the same. 2.1 ev is taken as the C-N bond energy.¹³ Formulas for recoil spectra in β decay have been given by Kofoed-Hansen.¹⁴ Kofoed-Hansen's equation leaves out the coulomb correction, which has been included in the computations reported here. One finds, assuming no correlation between the electron and neutrino, that only approximately 26% of the recoils in C^{14} have energies larger than 3.57 ev. This answer is very little affected by including some correlation between the electron and neutrino.

Taking a bond distance of 1.51 A (intermediate between C-C and C-N) and a frequency of 900 cm^{-1} , one may also calculate, using Eq. (27) and the above recoil spectrum, the probability of finding daughter molecules with more than 2.1 ev of vibrational energy. In the absence of rotational dissociation, this would be the probability of dissociation aside from that due to nonbonding electronic states. This number comes out to be only 0.074.

For the electronic probability, the probability of a $1s^2 2s 2p^3$ C atom becoming a $1s^2 2s 2p^3$ positive N atom will be taken as a lower limit for nondissociation, as justified previously. This probability is found to be 0.815.

In order to make a rough guess at the probability of nondissociation, combine the above 0.815 with the 74% probability of having recoils equal to or less than 3.57 ev to arrive at a figure of 0.60 for the probability of nondissociation. It would probably not be too far-fetched to give for the expected probability of non-

¹³ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1948).

¹⁴ O. Kofoed-Hansen, *Phys. Rev.* **74**, 1785 (1948).

dissociation 0.60 ± 0.20 . This compares with the experimental value of 0.51. The important matter is that one expects a fairly large fraction of the processes to lead to nondissociation as is found experimentally. The problem of subsequent reactions that the "hot" protonated methyl amine molecule ion may undergo is completely ignored here.

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Halogen Catalyzed Decomposition of Nitrous Oxide

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The thermal decomposition of N_2O in the presence of added Cl_2 , Br_2 , I_2 , and C_2H_5I was studied over the temperature range 876 to 1031°K. The catalytic reaction was found to be first order in N_2O and in atomic halogen concentration. The rate constants are in the order $Cl > Br > I$. Activation energies of 33.5, 37, and 38 kcal and pre-exponential factors of 1.3, 2.0, and 2.8×10^{14} cc mole⁻¹ sec⁻¹ were found for the Cl, Br, and I reaction. A probable mechanism is discussed and qualitative evidence provided for a high rate constant for the dissociation of Cl_2 , analogous to reported values for Br_2 and I_2 .

INTRODUCTION

THE strong catalytic effect of the halogens in the thermal decomposition of nitrous oxide was first described by Musgrave and Hinshelwood¹ and by Volmer and Bogdan.² Musgrave and Hinshelwood studied the effect of added isopropyl iodide, bromine, and chlorine in the temperature ranges 625 to 700°C, 680 to 745°C, and 682 to 744°C, respectively. They observed a limiting value of the rate with increasing iodine atom concentration, a similar but weaker effect with bromine, and a linear dependence of rate on atomic chlorine concentration. At a constant temperature, they found the order of rates per unit halogen atom concentration to be $I > Cl > Br$. Surprisingly high activation energies (I —51.5, Br —48.5, Cl —46.5 kcal) were calculated for the N_2O —halogen atom reactions and an unsatisfactory picture of the reaction resulted.

Volmer studied only the influence of iodine and bromine at much higher pressures and lower temperatures (450 to 530°C and 520 to 595°C) and found the rate to be proportional to the halogen atom concentration. Both Musgrave and Hinshelwood and Volmer reported the catalytic reaction to be first order with N_2O concentration.

In the course of extensive study of the thermal decomposition of nitrous oxide, we investigated the weak chemiluminescence of decomposing N_2O and its inhibition by halogens.³ In order to show the relation of this effect to the catalytic N_2O decomposition, we reinvesti-

gated the halogen- N_2O reaction using iodine, ethyl iodide, bromine, and chlorine.

EXPERIMENTAL

A 500-cc spherical quartz vessel served as reaction flask. In all cases, rates of pressure increase were measured with a calibrated oil manometer, and the reaction was usually followed over 20 to 30% of its total extent. A conventional gas system was used. Matheson N_2O was purified by freezing out at liquid nitrogen temperature and pumping to remove noncondensable gases. Its reaction rate was equal to that of unpurified N_2O . Tank chlorine and liquid bromine were treated similarly. Cp iodine was used without purification. Ethyl iodide was carefully distilled and the middle fraction used. Initial rates were determined by taking readings every 10 to 15 seconds for 3 to 5 minutes, plotting and extrapolating to zero time. Total experimental error was estimated at ± 3 to 4%.

The temperature and pressure of added halogen were varied in such a way that the catalyzed reaction was 2 to 40 times faster than the blank N_2O decomposition. At constant initial pressure of N_2O , halogen pressures were varied over a factor of 10 to 20 in several steps. Runs with similar variation of N_2O concentration at constant added halogen were also performed. The halogen catalyzed decomposition of N_2O gives only N_2 and O_2 as products. The formation of NO is inhibited as will be described in a later paper.³

RESULTS

The catalytic reaction was found to be first order in N_2O in every instance. This is shown in Table I for ethyl

¹ F. F. Musgrave and C. N. Hinshelwood, Proc. Roy. Soc. (London) A137, 25 (1932).

² M. Volmer and M. Bogdan, Z. physik. Chem. B21, 257 (1933).

³ To be submitted to J. Chem. Phys.