

## Lifetimes of Unstable Molecules

N. Rosen

Citation: *J. Chem. Phys.* **1**, 319 (1933); doi: 10.1063/1.1749296

View online: <http://dx.doi.org/10.1063/1.1749296>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v1/i5>

Published by the American Institute of Physics.

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT

**physicstoday**

Comment on any  
*Physics Today* article.

The advertisement shows a screenshot of a *Physics Today* article titled "Measured energy in Japan" by David von Seggern. A red arrow points from the article to a comment box. The comment box contains a comment by Edgar McCarroll dated 14 July 2012 19:59, discussing the energy release of a 100-megaton explosion and the damage caused by a nuclear device.

## Lifetimes of Unstable Molecules

N. ROSEN,\* *University of Michigan*

(Received February 1, 1933)

The mechanism of the decomposition of a molecule formed by the collision between a molecule and another particle is discussed qualitatively. Calculations are then carried through to determine the lifetime of a simple linear triatomic molecule formed by the collision of an atom with a

diatomic molecule. The results are applied to the short-lived molecule  $\text{HO}_2$  to determine the order of magnitude of its lifetime in a number of different states, although it does not conform strictly to the idealized conditions for which the calculation was made.

### I.

THERE is evidence that, as intermediate steps in certain chemical reactions, molecules are formed of extremely short lifetime, decomposing spontaneously unless they can react with other molecules before this happens. In some cases the molecules are known to be intrinsically stable. The question naturally arises as to the mechanism of this unimolecular decomposition. While this type of phenomenon has been treated by other writers,<sup>1</sup> it is the purpose of the present paper to discuss it in slightly greater detail than has been done hitherto and from a somewhat different point of view.

Let us first consider the formation of a molecule from two colliding particles. In order that they may form a stable system after the collision two conditions must be satisfied. First the force between the particles must be such that their potential energy as a function of the distance between them must have a minimum, that is, its graph must have the form of a valley. Then, the sum of this potential energy and the energy of relative motion of the particles must be less than the top of either side of the potential valley. It is evident that since the particles were originally free and therefore had energy above the outer wall of the potential valley there must be

something to take up some energy in order to bind the particles to each other. As is well known, this can be done by a third particle (triple collision), the wall of the containing vessel, etc.

It must be remembered, however, that it is not necessary to remove this energy completely from the system. It is sufficient merely to transfer it from the degrees of freedom corresponding to the relative motion of the two particles to some other part of the system. Thus, if the colliding particles are both atoms the energy might go to excite the electrons in one or both of them, producing a molecule in an excited electronic state. If one of the particles is a molecule there is an additional way of disposing of this energy. It might be taken up by the internal degrees of freedom of this molecule as vibrational energy. It is this case that interests us in the present paper, namely, that in which a collision takes place between a molecule and an atom or another molecule so that some vibrations are excited in the former and a binding to the latter thus produced.

With this picture it is easy to see why the molecule, if left to itself, eventually may decompose. Just as the energy was able to flow from the coordinates of relative motion to some other portion of the system, so it may sometimes also flow back. If it does this, the energy of relative motion assumes its original value, the particles are once again free, and they promptly separate.

This sort of explanation appears quite reasonable, but how does one account for the ability of the energy to flow in this way? The answer is to be found in the type of force existing in a molecule. It is known that the forces between atoms

\* National Research Fellow.

<sup>1</sup> For example, Roginsky and Rosenkewitsch, *Zeits. f. physik. Chemie* **B10**, 47 (1930), Langer, *Phys. Rev.* **34**, 92 (1929), Kassel, *J. Phys. Chem.* **32**, 1065 (1928), etc., Rice, *Phys. Rev.* **34**, 1451 (1929), etc. The paper of Roginsky and Rosenkewitsch treats the problem from the standpoint of the Auger effect as is done in the present paper.

do not add vectorially and are not central.<sup>2</sup> The potential energy of a group of atoms is a complicated function of all the coordinates and, strictly speaking, cannot be written as a sum of functions of individual distances between pairs of atoms. Even if one assumes as an approximation that the last is possible—so that one can use for the individual functions those of the type occurring in diatomic molecules, as approximated by Morse<sup>3</sup> for example—one is still faced with the  $n$ -body problem. These facts imply that the wave equation for a group of atoms is not separable for any choice of coordinates. Now if the equation were separable in some set of coordinates the energy of the system would be the sum of a number of energies each due to motion involving one coordinate. Each of these energies would be constant in time and hence there would be no possibility of energy flowing from one coordinate to another. Since the equation is not separable, however, this is not the case. In solving the equation one must use approximate methods. One can choose a set of coordinates which render the equation nearly separable—that is, make it separable if one neglects some of the smaller quantities in the equation. If one solves this approximate equation and then introduces the previously neglected terms as perturbations one finds in certain cases just the flow of energy described before. This may occur, for example, if there are degeneracies in the unperturbed problem.

It is rather a coincidence for a degeneracy to occur in the discrete states of a vibrating system, that is, for two energy levels belonging to two different modes of vibration to coincide, although this is known to occur.<sup>4</sup> That discrete levels should coincide with continuous is quite common. In fact if the system contains two or more internal degrees of freedom the energy spectrum of each consisting of a group of discrete levels surmounted by a region of continuous energy, there *must* be certain discrete energy levels which coincide with continuous energies. This can be

seen in Fig. 1, where hypothetical potential curves have been drawn for two coordinates so that the zero of each is taken as the value of the potential energy at an infinite distance from the origin. The total energy is the sum of the energies for the two coordinates. If now we take a

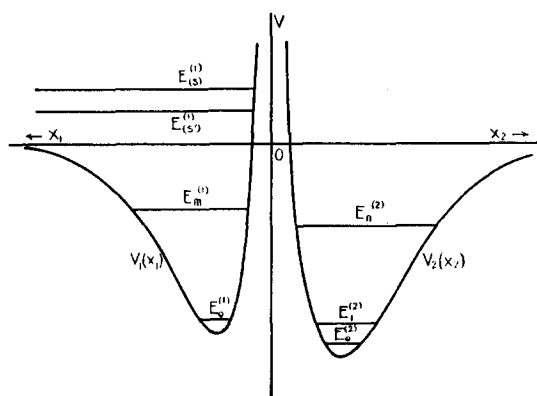


FIG. 1. Some energy levels in a system of two degrees of freedom, illustrating degeneracies between discrete and continuous states.

pair of energy levels  $E_m^{(1)}$  and  $E_n^{(2)}$  such that their sum is greater than  $E_0^{(2)}$ , one can always find a continuous level  $E_{(s)}^{(1)}$  such that

$$E_{(s)}^{(1)} + E_0^{(2)} = E_m^{(1)} + E_n^{(2)}.$$

If  $E_m^{(1)} + E_n^{(2)}$  is sufficiently high there may be a number of such levels. Thus in Fig. 1,  $E_{(s)}^{(1)}$  and  $E_1^{(2)}$  represent another such pair.

In the problem we are considering, since the molecule was formed through a collision of two free particles, the "bound" or discrete state into which it goes (neglecting the possibility of energy being radiated, which is slight) must coincide in energy with at least one continuous state, namely, that in which the particles were before the molecule was formed.

That being the case, there is a certain probability for a transition from the discrete state to a continuous one of the same energy—which is a dissociation of the system. This effect in a polyatomic molecule is analogous to the Auger effect for an atom or "predissociation" for a diatomic molecule, and the method of calculating transition probabilities is therefore already available.<sup>5</sup> The molecule may be said to have a

<sup>2</sup> London, *Probleme der modernen Physik*, p. 103, Leipzig (1928), Slater, *Phys. Rev.* **38**, 1109 (1931), Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

<sup>3</sup> Morse, *Phys. Rev.* **34**, 57 (1929).

<sup>4</sup> For example in CO<sub>2</sub>, cf. Fermi, *Zeits. f. Physik* **71**, 250 (1931).

<sup>5</sup> Wentzel, *Phys. Zeits.* **29**, 321 (1928).

certain lifetime, i.e., the mean time required for it to dissociate. If this lifetime is sufficiently long so that the molecule can collide with other particles before dissociating it may give up its excess energy and become a completely stable system.

A case closely related to the one being considered at present is the following. There are many polyatomic molecules the atoms of which are arranged in groups such that the atoms in each group are bound together rather tightly but the groups are held together quite loosely. By a tight binding is ordinarily meant that a plot of the potential has a large curvature near its minimum. This in general implies that the potential valley is deep; whereas a loose binding has a shallow minimum and relatively little energy is required to cause dissociation. Now if such a molecule takes part in a collision as a result of which it receives sufficient energy to break one of the weak bonds, it may happen that this energy is first taken up by one of the strong bonds and is present as vibrational energy. After some time has elapsed this energy may reach the weak bond (in the manner discussed before) and cause a decomposition of the molecule. Such an effect is of rather frequent occurrence because the weak bonds are often in the interior of the molecule and thus less exposed to direct effects of collisions than some of the strong bonds. This process represents a very general type of unimolecular reaction. It is not easy to do much of a detailed quantitative nature for this case as yet, but perhaps the simple example treated in the following section may throw some light on the more general problem.

## II.

### 1. General treatment

We now proceed to treat quantitatively a very simple idealized case, our purpose being to determine the order of magnitude of the lifetime of a molecule having an excess of energy. It is hoped that in spite of the simplification the essential features of the problem are retained.

Let us suppose a triatomic molecule with atoms of masses  $m_1$ ,  $m_2$  and  $m_3$ , restricted to move along a single straight line and let their distances from some fixed point on the line be  $x_1$ ,  $x_2$  and  $x_3$  ( $x_1 < x_2 < x_3$ ). We make the simplifying assumption that the potential energy

$$U = V_1(x_2 - x_1) + V_2(x_3 - x_2) + V_3(x_3 - x_1), \quad (1)$$

where, for an equilibrium configuration,  $|V_1|$  and  $|V_2|$  are large compared to  $V_3$ . It is to be expected that  $V_1$  and  $V_2$  will have forms similar to those of stable diatomic-molecule potentials, whereas in general  $V_3$  will correspond to a repulsive force.

If we write the wave equation for the system, introduce new variables

$$\left. \begin{aligned} r_1 &= x_2 - x_1, \\ r_2 &= x_3 - x_2, \\ \rho &= (m_1 x_1 + m_2 x_2 + m_3 x_3) / (m_1 + m_2 + m_3), \end{aligned} \right\} \quad (2)$$

and take the wave function as a product  $\psi(r_1, r_2)\chi(\rho)$ , the terms depending on  $\rho$  can be separated off (giving the usual equation for the center of gravity of the system) and the equation for  $\psi$  becomes

$$\left\{ -\frac{\hbar^2}{8\pi^2} \left[ \frac{1}{\mu_1} \frac{\partial^2}{\partial r_1^2} + \frac{1}{\mu_2} \frac{\partial^2}{\partial r_2^2} - \frac{2}{m_2} \frac{\partial^2}{\partial r_1 \partial r_2} \right] + V_1(r_1) + V_2(r_2) + V_3(r_1 + r_2) \right\} \psi = E\psi, \quad (3)$$

where  $E$  is the internal energy of the system and

$$\mu_1 = m_1 m_2 / (m_1 + m_2), \quad \mu_2 = m_2 m_3 / (m_2 + m_3). \quad (4)$$

To solve this equation exactly is impossible.<sup>6</sup> One notices however that if one omits the terms  $(\hbar^2/4\pi^2 m_2) \partial^2 \psi / \partial r_1 \partial r_2$  and  $V_3$  the problem reduces

<sup>6</sup> For small vibrations one could introduce normal coordinates to get a good approximation. This cannot be done in the present case where dissociation is considered.

to solving the two ordinary equations

$$-(\hbar^2/8\pi^2 \mu_1) d^2 \phi_m^{(1)} / dr_1^2 + V_1 \phi_m^{(1)} = E_m^{(1)} \phi_m^{(1)}, \quad (5)$$

$$-(\hbar^2/8\pi^2 \mu_2) d^2 \phi_n^{(2)} / dr_2^2 + V_2 \phi_n^{(2)} = E_n^{(2)} \phi_n^{(2)}, \quad (6)$$

the solution of (3) being then

$$\left. \begin{aligned} \psi_{mn}^0 &= \phi_m^{(1)} \phi_n^{(2)}, \\ E_{mn}^0 &= E_m^{(1)} + E_n^{(2)}. \end{aligned} \right\} \quad (7)$$

These quantities will be the more nearly equal to the correct ones the larger  $m_2$  and the smaller  $V_3$ . The operator

$$T = (\hbar^2/4\pi^2m_2)\partial^2/\partial r_1\partial r_2 + V_3, \quad (8)$$

which has been omitted can now be introduced as a perturbation.

The quantity  $V_3$ , as has already been said, is in general small. Its effect as a perturbation will be to change the energy levels somewhat and it will also act to some extent as a coupling between the two vibrations characterized by Eqs. (5) and (6). However there are few cases in which one knows the value of  $V_3$ . Since furthermore its presence is hardly likely to affect the order of magnitude of the result we shall not give it much attention, but shall center our interest on the first term of  $T$ . The effect of this on the energy is zero by a first-order calculation if the wave functions are real, as is the case here. Its principal rôle is as a coupling between the vibrations, the physical interpretation being that, as the central atom moves in both vibrations, it transfers energy from one to the other.

To calculate the rate of transition from a discrete state to one in the continuous spectrum of the same energy we use the relation<sup>5</sup>

$$\Gamma = (4\pi^2/\hbar) \left| \int \psi_{mn}^0 T \psi_{(s)k}^0 dr_1 dr_2 \right|^2, \quad (9)$$

where  $\psi_{mn}^0$  is the wave function for the discrete state and  $\psi_{(s)k}^0$  for the continuous state

$$\psi_{(s)k}^0 = \phi_{(s)}^{(1)} \phi_k^{(2)}, \quad (7a)$$

$\phi_{(s)}^{(1)}$  denoting a wave function which is a solution of Eq. (5) for continuous energy  $E_{(s)}^{(1)}$ , (i.e.,  $E_{(s)}^{(1)} > 0$ ). The transition rate  $\Gamma$  is related to the mean lifetime of the molecule  $\tau$  by

$$\tau = 1/\Gamma. \quad (10)$$

## 2. Numerical calculation

In order to evaluate (9) we must first get solutions of (5) and (6). For  $V_1$  and  $V_2$  we take the form suggested by Morse<sup>3</sup> for diatomic molecules

$$\left. \begin{aligned} V_1 &= D_1 e^{-2a_1(r_1-r_{01})} - 2D_1 e^{-a_1(r_1-r_{01})}, \\ V_2 &= D_2 e^{-2a_2(r_2-r_{02})} - 2D_2 e^{-a_2(r_2-r_{02})}. \end{aligned} \right\} \quad (11)$$

Further we might choose

$$V_3 = D_3 e^{a_3(r_1+r_2)} \quad (12)$$

in accordance with our general ideas about interatomic forces.

In solving (5) and (6) we need our function in a somewhat different form from that given by Morse and therefore briefly re-derive the solution of the equation

$$d^2\psi/dr^2 + (8\pi^2\mu/\hbar^2)(E - De^{-2a(r-r_0)} + 2De^{-a(r-r_0)})\psi = 0. \quad (13)$$

We make the following substitutions:

$$z = (4\pi/ah)(2\mu D)^{1/2} e^{-a(r-r_0)}, \quad (14)$$

where we assume that the range of  $z$  is 0 to  $\infty$  (instead of 0 to  $(4\pi/ah)(2\mu D)^{1/2} e^{ar_0}$ ), the error being small as Morse pointed out,

$$\left. \begin{aligned} \psi &= z^{-1/2} y, \\ k &= (2\pi/ah)(2\mu D)^{1/2}, \\ m &= (2\pi/ah)(-2\mu E)^{1/2}, \end{aligned} \right\} \quad (15)$$

and (13) becomes

$$d^2y/dz^2 + \{-1/4 + k/z + (1/4 - m^2)/z^2\}y = 0, \quad (16)$$

which is the confluent hypergeometric equation.<sup>7</sup>

For large values of  $z$  one solution is  $W_{k,m}(z)$  which has the asymptotic form

$$W_{k,m}(z) \sim e^{-z/2} z^k \{1 + [m^2 - (k - \frac{1}{2})^2]/z + \dots\}, \quad (17)$$

and the other independent solution is  $W_{-k,m}(-z)$  which obviously does not have the proper behavior. We therefore take for our wave function  $z^{-1/2} W_{k,m}(z)$ .

We next consider small values of  $z$ . The two solutions there are  $M_{k,m}(z)$  given by

$$\begin{aligned} M_{k,m}(z) &= e^{-z/2} z^{m+1/2} \\ &\quad \{1 + [(\frac{1}{2} + m - k)/(2m+1)!]z + \dots\}, \end{aligned} \quad (18)$$

and  $M_{k,-m}(z)$ . If  $E < 0$ , so that  $m$  is real and positive, the appropriate solution is  $M_{k,m}(z)$ , since the other function causes a singularity in  $\psi$  at the origin. Now we have the relation<sup>7</sup>

$$\begin{aligned} W_{k,m}(z) &= [\Gamma(-2m)/\Gamma(\frac{1}{2} - m - k)] M_{k,m}(z) \\ &\quad + [\Gamma(2m)/\Gamma(\frac{1}{2} + m - k)] M_{k,-m}(z), \end{aligned} \quad (19)$$

<sup>7</sup> Whittaker and Watson, *Modern Analysis*, p. 337, Cambridge, 1927.

and so our quantization condition is

$$\Gamma(2m)/\Gamma(\frac{1}{2}+m-k)=0,$$

or

$$\frac{1}{2}+m-k=-n \quad (n=0, 1, 2, \dots) \quad (20)$$

subject to the restriction  $m>0$ .

We have then for the discrete states

$$\begin{aligned} \psi_n &= z^{-\frac{1}{2}} W_{k, k-n-\frac{1}{2}}(z) = (-1)^n [\Gamma(2k-n)/\Gamma(2k-2n)] z^{-\frac{1}{2}} M_{k, m}(z), \\ &= (-1)^n \Gamma(2k-n) e^{-z/2} z^{k-\frac{1}{2}-n} \sum_{j=0}^n (-1)^j \binom{n}{j} z^j / \Gamma(2k-2n+j), \end{aligned} \quad (21)$$

which is essentially the same as the solution used by Morse.

For  $E>0$ ,  $m$  is imaginary and there is no restriction on it. We need the asymptotic form of  $\psi$  as  $r \rightarrow \infty$  or  $z \rightarrow 0$ . Expanding (19) and keeping terms of greatest order of magnitude, one finds

$$\psi_{(s)} \sim 2G \cos(sar - s\lambda + \gamma), \quad (22)$$

where

$$\left. \begin{aligned} s &= m/i = (2\pi/ah)(2\mu E)^{\frac{1}{2}}, \\ \Gamma(2is)/\Gamma(\frac{1}{2}-k+is) &= Ge^{i\gamma} \\ \text{and } \lambda &= ar_0 + \ln(4\pi(2\mu D)^{\frac{1}{2}}/ah). \end{aligned} \right\} \quad (23)$$

If one now normalizes the wave function with respect to the energy (Appendix, 1, 2) the normalizing factor by which it must be multiplied is found to be

$$N_{(s)} = (4/h)(\mu \sinh 2\pi s |\Gamma(\frac{1}{2}-k+is)|^2/a)^{\frac{1}{2}}. \quad (24)$$

To normalize the discrete wave function, we first evaluate a general integral we shall need. We find (Appendix, 3)

$$\int \psi^{(m)} \psi_n z^\lambda dz/z = n! \Gamma(2k-n) \sum_{j=0}^n \frac{(-1)^j \Gamma(k-\frac{1}{2}-m+\lambda-j) \Gamma(k-\frac{1}{2}+m+\lambda-j)}{j!(n-j)! \Gamma(2k-n-j) \Gamma(\lambda-j)}, \quad (25)$$

where  $\psi_n$  is a discrete wave-function and  $\psi^{(m)}$  an arbitrary one.<sup>8</sup> For  $m=k-\frac{1}{2}-n$  and  $\lambda=0$  one finds that the normalizing factor for the discrete function is

$$N_n = [(2k-2n-1)a/(n!\Gamma(2k-n))]^{\frac{1}{2}}. \quad (26)$$

If now one makes use of the easily derivable relation

$$\begin{aligned} \int \psi_k (d\psi_n/dr) dr \\ = \int \psi_k \psi_n (dV/dr) dr / (E_n - E_k), \quad (E_n \neq E_k) \end{aligned} \quad (27)$$

and observes that

$$dV/dr = (a^2 h/2\pi) [(D/2\mu)^{\frac{1}{2}} z - (ah/8\pi\mu) z^2], \quad (28)$$

<sup>8</sup> The notation here is exceptional because the wave function is intended to correspond to either a discrete or a continuous state and the superscript is the  $m$  defined in (15). Everywhere else as far as the appendix, a subscript in parentheses indicates a continuous state and is the value of  $s$  as defined in (23); without parentheses it indicates a discrete state and is the value of the integer in (20).

one finds with the help of (25) that the transition rate from a discrete state with approximate wave function  $\psi_{pm}^0$  to a continuous state with function  $\psi_{(s)n}^0$  (if we neglect  $V_3$  in (8))<sup>9</sup> is

$$\Gamma = (h\mu_1 a^2/4m_2^2) F_1(s) F_2(m) G_1(p) G_2(n), \quad (n < m) \quad (29)$$

where

$$\left. \begin{aligned} F_1(s) &= |\Gamma(k_1 + \frac{1}{2} + is)|^2 \sinh 2\pi s \\ &\quad \div (\sinh^2 \pi s + \cos^2 \pi k_1), \\ &\sim 2 |\Gamma(k_1 + \frac{1}{2} + is)|^2 \quad \text{for } s \gg 1, \\ F_2(m) &= m! \Gamma(2k_2 - m) (2k_2 - 2m - 1), \\ G_1(p) &= (2k_1 - 2p - 1)/(p! \Gamma(2k_1 - p)), \\ G_2(n) &= (2k_2 - 2n - 1)/(n! \Gamma(2k_2 - n)). \end{aligned} \right\} \quad (30)$$

<sup>9</sup> If one wished to take into account the effect of  $V_3$  on the rate of transition, it could be done by writing (12) in terms of  $z_1$  and  $z_2$  (in analogy with (14)) and then making use of the integral (25). This is not done here for the reasons previously stated.

The quantities  $s$ ,  $n$ ,  $p$  and  $m$  are connected by the fact that the energy of the two states must be the same, which leads to the relation

$$(a_1^2/\mu_1)(s^2 + (k_1 - p - \frac{1}{2})^2) = (a_2^2/\mu_2)((k_2 - n - \frac{1}{2})^2 - (k_2 - m - \frac{1}{2})^2). \quad (31)$$

To evaluate (30) we need to know that<sup>10</sup>

$$|\Gamma(k_1 + \frac{1}{2} + is)|^2 = [\Gamma(k_1 + \frac{1}{2})]^2 / \prod_{j=0}^{\infty} (1 + s^2 / (k_1 + \frac{1}{2} + j)^2). \quad (32)$$

It can be seen from (30) and (32) that if there are several continuous states to which the system can go, the transition probability is by far the greatest to that state which involves the least change in the energy of either individual vibration (except that if  $s$  is very small there is a strong dependence on  $\cos \pi k_1$ , and predictions are difficult, but this is rather unusual).

Let us now suppose that the molecule was formed by the collision of atom 1 with the diatomic molecule  $A$  consisting of atoms 2 and 3,

each having kinetic energy of the order of magnitude of that for room temperature; and let us suppose further that as result of the collision the vibration of 2 and 3 changed from  $n=0$  to some quantum number  $m$ , and a vibration of 1 and 2 with quantum number  $p$  was set up. We must assume that the original relative kinetic energy is such that it matches with the molecular levels, i.e., (31) is satisfied. We are not concerned with the details of the molecule formation, and if we like can assume that a large number of elastic collisions take place until the energy match occurs.<sup>11</sup>

Then in the decomposition of the molecule the process is uniquely defined. We have  $n=0$ ,  $s$  is proportional to the initial relative momentum of the particles 1 and 2, as in (23), and  $p$  is an integer satisfying (31). For this case the transition rate becomes

$$\Gamma = (h\mu_1 a_2^2 / 4m_2^2) F_1(s) G_1(p) F_2(m) / \Gamma(2k_2 - 1). \quad (29a)$$

If further we neglect the denominator of (32) this can be written

$$\Gamma = \frac{h\mu_1 a_2^2 (2k_1 - 2p - 1) [\Gamma(k_1 + \frac{1}{2})]^2 m! (2k_2 - 2m - 1) \Gamma(2k_2 - m)}{2m_2^2 p! \Gamma(2k_1 - p) \Gamma(2k_2 - 1)}. \quad (29b)$$

If we set  $k_1 - p - \frac{1}{2} = t$  we get

$$\Gamma = \frac{h\mu_1 a_2^2 t (2k_2 - 2m - 1) [\Gamma(k_1 + \frac{1}{2})]^2 m! \Gamma(2k_2 - m)}{m_2^2 \Gamma(k_1 + \frac{1}{2} - t) \Gamma(k_1 + \frac{1}{2} + t) \Gamma(2k_2 - 1)}. \quad (29c)$$

In this form we see that  $\Gamma$  is not as sensitive in the dependence of its order of magnitude on  $k_1$  and  $k_2$  as appeared in the earlier formula. An estimate of  $\Gamma$  may have some reliability (as far as order of magnitude) even if there are moderate uncertainties in these constants.

A compound  $\text{HO}_2$  is believed to be formed bimolecularly by the reaction of atomic hydrogen with molecular oxygen. It is probably not a linear molecule and one does not know what the constants of its potential functions are. We shall assume that the above model can be used nevertheless; and for potential functions we use those supposed to exist in the lowest electronic states of  $\text{OH}$  and  $\text{O}_2$  on the basis of their vibrational spectra. It is hoped that the order of

magnitude of the result will not be changed very much by these approximations.

We take therefore  $\mu_1, \mu_2, m_2 = (16/17, 8, 16) \times 1.65 \cdot 10^{-24}$  g,  $k_1 = 25.5$ ,  $k_2 = 68.5$ ,  $a_1 = 2.0 \cdot 10^8$  cm<sup>-1</sup>,  $a_2 = 2.34 \cdot 10^8$  cm<sup>-1</sup>. At ordinary temperatures  $s$  is of the order of magnitude of 1. A simple calculation leads to the results in Table I.

We see that for  $m=1$ , the calculated lifetime is so short that one really cannot speak of the molecule having existed, for the entire process could not be distinguished from an elastic collision. For  $m$  greater than 4, the lifetime is very long compared to the average time between

<sup>10</sup> Nielsen, *Handbuch der Gammafunktion*, p. 23, Leipzig (1906).

<sup>11</sup> This matching of energy is not very difficult because of the broadening of the levels due to the finite lifetimes of the molecular states. Roughly the ratio of favorable to total number of collisions is of the order of magnitude of  $h\Gamma/\Delta E$  where  $\Delta E$  is the spacing of the vibrational levels in the energy region involved.

collisions at moderate pressures. The mean lifetime would depend on the collision process which would determine the relative frequency of occurrence of the various values of  $m$ . Because collisions (and consequent reactions) would play a part in determining the actual lifetime for the larger values of  $m$ , an experimentally obtained value for the mean lifetime would involve a certain amount of arbitrariness in its interpretation. The results calculated here are at any rate consistent with available chemical data.<sup>12</sup>

TABLE I.

$m$	$p$	$t$	$s$	$\Gamma(\text{sec.}^{-1})$
1	21	4	2.4	$2 \cdot 10^{14}$
2	19	6	2.7	$2 \cdot 10^{12}$
3	17	8	0.5	$2 \cdot 10^{10}$
4	16	9	2.0	$4 \cdot 10^8$

### 3. Conclusion

Aside from the simplification of the conditions in the previous calculation, a further difficulty is

that the unperturbed wave functions do not describe the actual situation very well (especially for the continuous states) and the perturbation may be quite large so that a first order method of treatment may be inaccurate. However, one would expect the order of magnitude to be unchanged in a more accurate treatment. Also it must be stressed that the purpose of the calculation is mainly to see how the process can come about. The particular type of coupling between the two unperturbed vibrations does not matter very much. The essential point is that in any treatment of the problem some sort of coupling will be found to exist—and it is to be expected that it will in general play a part in bringing about the decomposition of the molecule.

In conclusion the writer wishes to express his indebtedness to Professor J. R. Bates, who called attention to this type of problem, for discussions on the chemical aspects of the subject, and to Professor D. M. Dennison for discussions on the physical aspects.

## APPENDIX

### 1. Normalization of continuous wave functions

The well-known condition for normalization of a continuous wave function in a one-dimensional problem where the variable has a range 0 to  $\infty$  is:

$$J = \lim_{\Delta \rightarrow 0} (1/\Delta) \int_0^\infty \left[ \int_{p-\Delta/2}^{p+\Delta/2} \psi_p(x) dp \right] \left[ \int_{p-\Delta/2}^{p+\Delta/2} \psi_p(x) dp \right] dx = 1, \quad (33)$$

where  $p$  is a continuous parameter used to order the wave functions.

Let us write

$$\psi_p = \phi_p + \chi_p, \quad (34)$$

where  $\chi_p$  is that part of the wave function which goes to zero with sufficient rapidity as  $x \rightarrow \infty$  so that  $\int_0^\infty \chi_p \chi_p dx$  and  $\int_0^\infty \phi_p \chi_p dx$  are both convergent. Let us now write  $J$  as the sum of two integrals, one for a finite range 0 to  $a$  and the second for the range  $a$  to  $\infty$ . Then in the first integral and in all the terms of the second which involve  $\chi_p$  or  $\bar{\chi}_p$  the order of integration can be interchanged and these quantities are seen to vanish. We have therefore

$$J = \lim_{\Delta \rightarrow 0} (1/\Delta) \int_a^\infty \left[ \int_{p-\Delta/2}^{p+\Delta/2} \bar{\phi}_p(x) dp \right] \left[ \int_{p-\Delta/2}^{p+\Delta/2} \phi_p(x) dp \right] dx, \quad (35)$$

where  $a$  is finite but can be made as large as one pleases. Practically this means that one can use the *asymptotic form* of the wave function in carrying out a normalization.

### 2. Normalization with respect to energy

The normalizing factor for a continuous wave function depends on the parameter used. Care must be taken to use the same parameter consistently. Thus in the original

derivation of (9) the energy was the parameter and integrations were carried out with respect to it. It is therefore necessary to use the energy in normalizing the function in our case.

If we consider the wave function for a free particle  $e^{2\pi i k x}$  where

$$k = P/\hbar = (2\mu E)^{1/2}/\hbar, \quad (36)$$

$P$  is the momentum of the particle and the range of  $x$  is 0 to  $\infty$ , the usual normalization with respect to  $k$  leads to a normalizing factor,  $2^{1/2}$ . If, instead, we use  $E$  as parameter

<sup>12</sup> Bates and Lavin, J. Am. Chem. Soc. 55, 81 (1933); Bates and Salley, *ibid.*, p. 110.



the integration is somewhat more complicated and leads to a normalizing factor

$$N = (1/h)(2\mu/k)^{\frac{1}{2}} = (2\mu/P\hbar)^{\frac{1}{2}}. \quad (37)$$

For  $\cos 2\pi kx$  this is to be multiplied by  $2^{\frac{1}{2}}$ . Use was made of it in (24).

### 3. Evaluation of an integral

To evaluate the integral (25) use is made of Eq. (19). In

the course of the calculation one obtains two hypergeometric series for argument 1. These can be summed if  $\lambda < 1$ . If  $1 < \lambda < 2$ , one can make use of the well-known relations between hypergeometric functions and by letting the argument approach 1, one obtains the same result as before. One thus finds that (25) is valid for  $\lambda < 1$  and  $1 < \lambda < 2$ . But since (25) is analytic for  $0 \leq \lambda \leq 2$  it must give the correct values at  $\lambda = 1$  and  $\lambda = 2$  also.