

## Statistical Theory of Dissociation and Recombination for Moderately Complex Molecules\*

JAMES KECK

*Massachusetts Institute of Technology, Cambridge, Massachusetts*

AND

ASHOK KALELKAR

*Avco Everett Research Laboratory, Everett, Massachusetts*

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The dissociation and recombination of moderately complex molecules in a background of inert atoms has been investigated using a master equation with transition probabilities and spontaneous decay rates obtained from the statistical theory of reaction rates. A relatively simple expression has been derived for the steady-state dissociation rate constant which is valid at all pressures for molecules containing three or more atoms. This expression has been used with reasonable success to correlate the available experimental data for 21 molecules having from three to six atoms.

## I. INTRODUCTION

The dissociation and recombination of moderately complex polyatomic molecules is important in many chemical and aerodynamic problems including the pyrolysis of hydrocarbons, combustion, ablating boundary layers, and reacting wakes. Excellent summaries of previous experimental and theoretical work on this problem and references to original publications may be found in recent books by Nikitin<sup>1</sup> and Bunker.<sup>2</sup> Among the most successful theories are those of Rice, Ramsperger, Kassel, and Marcus<sup>3</sup> and of Troe and Wagner.<sup>4</sup> The former is valid at all pressures and has been used with reasonable success to correlate the experimental dissociation rate constants for a variety of polyatomic molecules. The latter is limited to low pressures but includes a discussion of adiabatic collisions and electronic transitions. It has been used, also with reasonable success, to correlate the dissociation rate constants for a number of small molecules having three or four atoms.

The present theory is similar to that of Rice, Ramsperger, Kassel, and Marcus and involves many of the same assumptions. However, it differs in detail and the results have been obtained in a somewhat simpler form which facilitates numerical computations. The analysis is based on an iterative solution of the one-dimensional master equation describing the excitation and dissociation of molecules in a background of inert atoms. The spontaneous decay rates and vibrational transition probabilities used were obtained from the

statistical theory of reaction rates.<sup>5-7</sup> The most important assumption made is that the spontaneous decay rate is a function only of the energy of a molecule. This involves neglecting conservation of total angular momentum in the application of the statistical theory and probably leads to an overestimate of the magnitude of the dissociation rate. Nevertheless, it is felt that the form of the results is basically correct and the theory has been used with considerable success to correlate the experimental dissociation rate constants for 21 molecules having from three to six atoms.<sup>8-31</sup>

<sup>5</sup> J. C. Keck, *J. Chem. Phys.* **29**, 410 (1958).<sup>6</sup> P. Pechukas and J. C. Light, *J. Chem. Phys.* **42**, 3281 (1965).<sup>7</sup> J. C. Keck, *Advan. Chem. Phys.* **13**, 85 (1966).<sup>8</sup> W. M. Jones and N. Davidson, *J. Am. Chem. Soc.* **84**, 2868 (1962).<sup>9</sup> S. W. Benson, and A. E. Axworthy, *J. Chem. Phys.* **42**, 2614 (1965).<sup>10</sup> P. Deklan and H. B. Palmer, *Symp. Combust.*, 8th, Pasadena, Calif., 1960, 139 (1962).<sup>11</sup> A. P. Modica and D. F. Hornig, *J. Chem. Phys.* **43**, 2739 (1965).<sup>12</sup> R. W. Diesen, *J. Chem. Phys.* **45**, 759 (1966).<sup>13</sup> R. E. Hoffman, and N. Davidson, *J. Am. Chem. Soc.* **81**, 2311 (1959).<sup>14</sup> A. P. Modica, *J. Chem. Phys.* **44**, 1585 (1966).<sup>15</sup> H. A. Olschewski, J. Troe, and H. Gg. Wagner, *Z. Phys. Chem.* **47**, 383 (1965).<sup>16</sup> H. A. Olschewski, J. Troe, and H. Gg. Wagner, *Z. Phys. Chem.* **44**, 173 (1965).<sup>17</sup> W. L. Patterson, Jr., and E. F. Greene, *J. Chem. Phys.* **36**, 1146 (1962).<sup>18</sup> D. Schofield, W. Tsang, and S. H. Bauer, *J. Chem. Phys.* **42**, 2132 (1965).<sup>19</sup> H. F. Cordes and H. S. Johnston, *J. Am. Chem. Soc.* **76**, 4264 (1954).<sup>20</sup> M. Volpe and H. S. Johnston, *J. Am. Chem. Soc.* **78**, 3903 (1956).<sup>21</sup> D. E. Hoare, J. B. Protheroe, and A. D. Walsh, *Trans. Faraday Soc.* **55**, 548 (1959).<sup>22</sup> T. A. Jacobs, *J. Phys. Chem.* **67**, 6651 (1963).<sup>23</sup> K. W. Michel and H. Gg. Wagner, *Symp. Combust.* 10th, Univ. Cambridge, Cambridge, England, 1964, 353 (1965).<sup>24</sup> W. Tsang, S. H. Bauer, and M. Cowperthwaite, *J. Chem. Phys.* **26**, 1768 (1962).<sup>25</sup> A. P. Modica, and J. E. LaGraff, *J. Chem. Phys.* **44**, 3375 (1966).<sup>26</sup> G. B. Skinner and R. A. Ruehrwein, *J. Phys. Chem.* **63**, 1736 (1959).<sup>27</sup> A. P. Modica and J. E. LaGraff, "Shock-Tube Kinetic Studies of the Tetrafluoroethylene-Oxygen System," Avco RAD-TM-65-29, Avco Corp. Wilmington, Mass., 1965.

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<sup>1</sup> E. E. Nikitin, *Theory of Thermally Induced Gas Phase Reactions* (Indiana University Press, Bloomington, Ind., 1966).<sup>2</sup> D. L. Bunker, *Theory of Elementary Gas Reactions Rates* (Pergamon Press, Inc., New York, 1966).<sup>3</sup> See G. M. Wieder and R. A. Marcus, *J. Chem. Phys.* **37**, 1835 (1962) for comparison with experiments and references to earlier work.<sup>4</sup> J. Troe, and H. Gg. Wagner, paper presented at the 28th Propulsion and Energetics Panel Meeting on "Recent Advances in Aerochemochemistry," Oslo, May 1966.

## II. MATHEMATICAL MODEL

We shall consider gas-phase reactions of the type



and



in which the atoms A are inert and the molecules  $M_1$  contain at least three atoms. We assume (1) the concentration of  $M_1$  is sufficiently small that isothermal conditions prevail, (2) electronic transitions do not occur, (3) the spontaneous decay rate of  $M_1$  molecules is a function only of their internal energy  $E$ , (4) the internal degrees of freedom of  $M_2$  and  $M_3$  molecules are in equilibrium at the temperature  $T$  of the A atoms, and (5) the level density of  $M_1$  molecules in the vicinity of the dissociation limit  $D$  is large compared to  $(kT)^{-1}$ . Under these conditions the progress of the reactions (2.1) and (2.2) can be described by the classical master equation

$$\frac{\partial N(\epsilon, t)}{\partial t} = \int_0^\infty [K(\epsilon, \epsilon')N(\epsilon', t) - K(\epsilon', \epsilon)N(\epsilon, t)]d\epsilon' + K_r(\epsilon)[M_2(t)][M_3(t)] - K_d(\epsilon)N(\epsilon, t), \quad (2.3)$$

where  $\epsilon \equiv E/kT$  is the energy in units of  $kT$ ,  $N(\epsilon, t)$  is the concentration of  $M_1$  per unit  $\epsilon$  and  $K(\epsilon', \epsilon)$  is the rate constant per unit  $\epsilon'$  for transition from  $\epsilon$  to  $\epsilon'$ , and  $[M_2(t)]$  and  $[M_3(t)]$  are, respectively, the concentrations of  $M_2$  and  $M_3$ .

Under steady-state conditions, the solution of (2.3) which satisfies the boundary condition

$$N(\infty, t)/[M_2(t)][M_3(t)] = N_e(\infty)/[M_2]_e[M_3]_e$$

is<sup>22</sup>

$$\frac{N(\epsilon, t)}{N_e(\epsilon)} = \left( \frac{N(0, t)}{N_e(0)} - \frac{[M_2(t)][M_3(t)]}{[M_2]_e[M_3]_e} \right) \chi(\epsilon) + \{ [M_2(t)][M_3(t)]/[M_2]_e[M_3]_e \}, \quad (2.4)$$

where the subscript  $e$  denotes equilibrium, and the distribution function  $\chi(\epsilon)$  satisfies the boundary conditions  $\chi(0) = 1$  and  $\chi(\infty) = 0$  and the integral equation

$$\chi(\epsilon) = [K_c(\epsilon) + K_d(\epsilon)]^{-1} \int_0^\infty K(\epsilon', \epsilon)\chi(\epsilon')k\epsilon', \quad (2.5)$$

where

$$K_c(\epsilon) = \int_0^\infty K(\epsilon', \epsilon)d\epsilon' \quad (2.6)$$

is the collision rate for molecules of energy  $\epsilon$ .

<sup>22</sup> T. Carrington and N. Davidson, *J. Phys. Chem.* **57**, 418 (1953).

<sup>23</sup> L. M. Brown and B. de B. Darwent, *J. Chem. Phys.* **42**, 2158 (1965).

<sup>24</sup> A. P. Modica and J. E. LaGraff, *J. Chem. Phys.* **43**, 3383 (1965).

<sup>25</sup> I. D. Gay, R. D. Kern, G. B. Kistiakowsky, and H. Kiki, *J. Chem. Phys.* **45**, 2371 (1966).

<sup>22</sup> J. Keck and G. Carrier, *J. Chem. Phys.* **43**, 2284 (1965).

Substituting (2.4) into (2.3), and integrating over  $\epsilon$  using the approximation

$$\frac{[M_1(t)]}{[M_1]_e} = \int_0^\infty \frac{N(\epsilon, t)d\epsilon}{[M_1]_e} \approx \frac{N(0, t)}{N_e(0)} \quad (2.7)$$

we obtain the phenomenological rate equation

$$\partial[M_1(t)]/\partial t = k_r[M_2(t)][M_3(t)] - k_d[M_1(t)], \quad (2.8)$$

where the steady-state rate constants for recombination  $k_r$  and dissociation  $k_d$  are given by

$$k_d[M_1]_e = k_r[M_2]_e[M_3]_e = \int_0^\infty K_d(\epsilon)N_e(\epsilon)\chi(\epsilon)d\epsilon. \quad (2.9)$$

## III. TRANSITION RATES

To obtain expressions for the transition rates  $K_d(\epsilon)$  and  $K(\epsilon', \epsilon)$  necessary to evaluate the steady-state rate constants, we shall use the statistical theory<sup>5-7</sup> of reaction rates. In this theory, it is assumed that the rate of decay of an unstable complex into a given final state is simply proportional to the rate of flow of states in phase space across the boundary of the complex into that state. This assumption is valid when the interactions are sufficiently strong to produce a uniform distribution of products in all final states. In practice it undoubtedly overestimates the relative importance of large energy transfers and this in turn will lead to an overestimate of the rate constants. Nevertheless, the theory represents an important limiting case and the rate constants obtained from it may be regarded as upper bounds to the true values.

### A. Spontaneous Dissociation Rate

According to the statistical theory, the rate constant for the spontaneous decay of  $M_1$  molecules is

$$K_d(\epsilon) = \Gamma_{23}(\epsilon)/\Omega_1(\epsilon), \quad (3.1)$$

where  $\Gamma_{23}(\epsilon)$  is the rate of flow of states of  $M_1$  into states of  $M_2 + M_3$  per unit  $\epsilon$  and  $\Omega_1(\epsilon)$  is the density of states of  $M_1$  per unit  $\epsilon$ .

If we assume that the rotational and vibrational motions of the molecules can be approximately separated, then the density of states can be written

$$\Omega_1(\epsilon) = \sum_{\epsilon_v \leq \epsilon} \Omega_{1r}(\epsilon - \epsilon_v), \quad (3.2)$$

where

$$\epsilon_v = \sum_{i=1}^v k_i \Theta_{v_i} \quad (3.3)$$

is the vibrational energy in units of  $kT$ ,

$$\Omega_{1r}(x) = h^{-2r} \frac{d}{dx} \int_{h_r \leq \epsilon} \prod_{i=1}^{2r} dp_i dq_i \quad (3.4)$$

is the density of rotational states at the energy  $x$  and the summation in (3.2) is over all vibrational states with  $\epsilon_v \leq \epsilon$ . In (3.3)  $v$  is the number of vibrational modes of  $M_1$ ,  $\Theta_{vi} = hc\omega_{vi}/kT$ , and  $k_i$  is the number of quanta in the  $i$ th mode. In (3.4)  $2r$  is the number of rotational modes and  $h_r = E_r(p, q)/kT$  is the rotational Hamiltonian in units of  $kT$ . If we assume the rotational Hamiltonian is that of a classical rigid rotor,<sup>33</sup> then (3.4) gives the familiar result

$$\Omega_{1r}(x) = Q_r x^{r-1}/(r-1)!, \quad (3.5)$$

where

$$Q_r = \pi^{r-1} \prod_{i=1}^{2r} \left( \frac{kT}{hcB_{ri}} \right)^{1/2} \\ \equiv \pi^{r-1} (kT/hcB_r)^r \quad (3.6)$$

is the rotational partition function and  $B_{ri}$  is the rotational constant for the  $i$ th principal axis.

Note that (3.3) is a reasonable approximation for polyatomic molecules for which the principal contribution to the sum in (3.2) comes from states of low vibrational energy, but is not valid for diatomic molecules for which the density of states is largest near the dissociation limit. This is the reason the theory is restricted to polyatomic molecules with three or more atoms.

For  $v > 1$ , the evaluation of the sum in (3.2) can become quite tedious. However, we can obtain a good approximation in the high-energy limit by converting the sum to an integral. This gives for  $\epsilon \gtrsim \epsilon_{v0}$

$$\Omega_1(\epsilon) \approx Q_r (\epsilon + \epsilon_{v0})^{N-1} / (N-1)! \Theta_v^v, \quad (3.7)$$

where

$$\Theta_v^v \equiv \prod_{i=1}^v \Theta_{vi} \quad (3.8)$$

is the reciprocal of classical vibrational partition function for  $M_1$  molecules,

$$\epsilon_{v0} = \frac{1}{2} \sum_{i=1}^v \Theta_{vi} \quad (3.9)$$

is the zero-point energy of the oscillators in units of  $kT$ , and  $N \equiv v + r$ . For most cases of interest,  $\epsilon > \epsilon_{v0}$  and (3.7) is satisfactory.

To calculate the flow rate  $\Gamma_{23}(\epsilon)$ , we consider a collision complex of radius  $a$  such that, if the separation  $r$  between  $M_2$  and  $M_3$  is greater than  $a$ , the interaction is negligible or repulsive for all orientations of the molecules, while, if the separation is less than  $a$ , the interaction is attractive at least for some orientations. We further assume that on the boundary  $r = a$  the interaction potential  $\Phi$  is independent of the internal vibrational state of  $M_2$  or  $M_3$  and is a function only of the position and orientation of  $M_3$  with respect to  $M_2$ .

Under these conditions<sup>7</sup>

$$\Gamma_{23}(\epsilon) = \int_0^{\epsilon-\delta} \int_0^x \Omega_2(x-y) \Omega_3(y) k_{23}(\epsilon, x) dy dx, \quad (3.10)$$

where  $\delta = D/kT$ ,  $D$  is the minimum value of  $\Phi$  on the boundary  $r = a$ ,  $\Omega_2$  and  $\Omega_3$  are the densities of states of  $M_2$  and  $M_3$  given by the appropriate form of (3.7),

$$k_{23}(\epsilon, x) = \sigma_{23} c_{23} Q_{23}(\epsilon - \delta - x) \quad (3.11)$$

is the rate of flow per unit  $\epsilon$  of a state of  $M_2 + M_3$  across the boundary  $r = a$ ,

$$Q_{23} = (2\pi\mu_{23}kT/h^2)^{3/2} \quad (3.12)$$

is the translational partition function per unit volume,  $\mu_{23} = m_2 m_3 / (m_2 + m_3)$  is the reduced mass of  $M_2$  and  $M_3$ ,

$$c_{23} = (8kT/\pi\mu_{23})^{1/2} \quad (3.13)$$

is the mean thermal speed for the collisions,

$$\sigma_{23} = \frac{ga^2}{32\pi^2} \int_{\phi \leq \epsilon - \chi} \left( \frac{\epsilon - \chi - \phi}{\epsilon - \chi - \delta} \right) d \cos\phi_1 d\phi_2 d \cos\phi_3 d\phi_4 d\phi_5 \quad (3.14)$$

is an effective decay cross section,  $\phi = \Phi/kT$ , and  $g$  is the number of ways  $M_1$  can decay into  $M_2 + M_3$ , e.g., four for the reaction  $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ . In (3.14)  $\phi_1$  and  $\phi_2$  are the two polar angles giving the direction of  $r$  with respect to the principal axes of  $M_2$  and  $\phi_3, \phi_4$ , and  $\phi_5$  are the three Euler angles giving the orientation of the principal axes of  $M_3$  with respect to those of  $M_2$ . Note that we have assumed  $M_2$  to be of lower symmetry than  $M_3$ .

In principle  $\sigma_{23}$  can be calculated if the potential  $\Phi$  is known. Since this is not usually the case, it is more realistic to assume  $\sigma_{23}$  is approximately a constant and regard it as an adjustable parameter to be determined by experiment. Fortunately in many practical cases, the dependence of the results on  $\sigma_{23}$  is quite weak and only its order of magnitude is required. This may be obtained from (3.14) by estimating the probability that  $\Phi$  is attractive for various orientations of the  $M_2$  and  $M_3$ . On this basis it is reasonable to anticipate that  $\sigma_{23}/\pi a^2$  will be of order  $(4\pi)^{-1}$  if  $M_3$  is spherically symmetric so that  $\phi$  is independent of  $\phi_3, \phi_4$ , and  $\phi_5$ , of order  $(4\pi)^{-2}$  if  $M_3$  has axial symmetry so that  $\phi$  is independent of  $\phi_5$ , and of order  $(2\pi)^{-1}(4\pi)^{-2}$  otherwise.

Evaluating (3.10) we obtain

$$\Gamma_{23}(\epsilon) = \sigma_{23} c_{23} Q_{23} Q_3 \sum_{\epsilon_u \leq \epsilon - \delta} [(\epsilon - \delta - \epsilon_u)^{s+1} / (s+1)!], \quad (3.15)$$

where

$$\epsilon_u = \sum_{i=1}^u k_i \Theta_{ui} \quad (3.16)$$

<sup>33</sup> J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940).

is the sum of the vibrational energies of  $M_2$  and  $M_3$ ,

$$Q_s = \pi^{s-1} \prod_{i=1}^{2s} \left( \frac{kT}{hcB_{si}} \right)^{1/2} \\ \equiv \pi^{s-1} (kT/hcB_s)^s \quad (3.17)$$

is the product of the rotational partition function for  $M_2+M_3$ .

The sum of the number of rotational degrees of freedom of  $M_2$  and  $M_3$  and

$$l=1 \quad \text{if } M_3 \text{ monatomic,} \\ =2 \quad \text{otherwise.} \quad (3.18)$$

Note that  $v+2r=u+2s+3=3n_1-3$  where  $n_1$  is the number of atoms in  $M_1$ .

Using (3.15) and (3.7), the spontaneous decay rate (3.1) is found to be

$$K_d(\epsilon) = \nu_d [(N-1)!/(s+1)!] [\Theta_v/(\epsilon+\epsilon_{v0})]^{N-1} \\ \times \sum_{\epsilon_u \leq \epsilon - \delta} [(\epsilon - \delta - \epsilon_u)/\Theta_u]^{s+1}, \quad (3.19)$$

where

$$\nu_d = \sigma_{23} c_{23} Q_{23} Q_s \Theta_u^{s+1} / Q_r \Theta_v^{r-1} \quad (3.20)$$

is a characteristic frequency which depends only on molecular parameters and

$$\Theta_u^u = \prod_{i=1}^u \Theta_{ui} \quad (3.21)$$

is the reciprocal of the classical vibrational partition function for  $M_2+M_3$ .

### B. The Transition Kernel

For the transition kernel the statistical theory gives<sup>7</sup>

$$K(\epsilon', \epsilon) N_e(\epsilon) = \{[A][M_1]_e / Q_{1A} Q_r Q_v\} \\ \times \int_{\epsilon'}^{\infty} e^{-x} \left( \frac{\gamma(x, \epsilon) \gamma(x, \epsilon')}{\Gamma(x)} \right) dx, \quad (3.22)$$

where  $\epsilon_>$  is the larger of  $\epsilon$  or  $\epsilon'$ ,

$$N_e(\epsilon) = [M_1]_e \Omega_1(\epsilon) e^{-\epsilon} / Q_r Q_v \quad (3.23)$$

is the equilibrium concentration of  $M_1$  per unit  $\epsilon$ ,

$$Q_v = \prod_{i=1}^v [1 - \exp(-\Theta_{vi})]^{-1} \quad (3.24)$$

is the vibrational partition function of  $M_1$ ,

$$Q_{1A} = (2\pi\mu_{1A}kT/h^2)^{3/2} \quad (3.25)$$

is the translational partition function for relative motion of  $M_1$  and A,  $\mu_{1A} = m_1 m_A / (m_1 + m_A)$  is the reduced mass of  $M_1$  and A,

$$\gamma(x, \epsilon) = \Omega_1(\epsilon) k_{1A}(x, \epsilon) \quad (3.26)$$

is the rate of flow per unit  $\epsilon$  and  $x$  of states of  $M_1$  at  $\epsilon$  across the boundary of the collision complex formed

by  $M_1$  and A at  $x$ ,

$$k_{1A}(x, \epsilon) = \sigma_{1A} c_{1A} Q_{1A}(x - \epsilon) \quad (3.27)$$

is the appropriate form of (3.11),  $c_{1A}$  is the mean speed for collisions of A and  $M_1$ ,  $\sigma_{1A}$  is an effective energy-transfer cross section, and

$$\Gamma(x) = \int_0^x \gamma(x, \epsilon') d\epsilon'. \quad (3.28)$$

Since we shall be interested in  $K(\epsilon', \epsilon)$  for values of  $\epsilon'$  and  $\epsilon$  of order  $\delta \gg 1$  we may use the approximation (3.7) for  $\Omega_1(\epsilon)$  in (3.23) and (3.26). Substitution into (3.22) then gives

$$K(\epsilon', \epsilon) = \nu_c [(N+1)!/(N-1)!] (\epsilon' + \epsilon_{v0})^{N-1} \\ \times \int_{\epsilon'}^{\infty} \exp(\epsilon - x) \left( \frac{(x - \epsilon)(x - \epsilon')}{(x + \epsilon_{v0})^{N+1}} \right) dx, \quad (3.29)$$

where  $\nu_c = \sigma_{1A} c_{1A} [A]$  is the collision frequency. Integrating (3.29) over  $\epsilon'$  we obtain the collision rate

$$K_c(\epsilon) = \int_0^{\infty} K(\epsilon', \epsilon) d\epsilon' = \nu_c. \quad (3.30)$$

The integral in (3.29) cannot be evaluated in terms of elementary functions. However, an excellent approximation can be obtained for  $\epsilon \sim \epsilon' \sim \delta \gg 1$  by making the substitution

$$(x + \epsilon_{v0})^{N+1} \approx (\epsilon + \epsilon_{v0})^{N+1} \exp[\eta(x - \epsilon)], \quad (3.31)$$

where  $\eta = (N+1)/(\delta + \epsilon_{v0})$ . This gives

$$K(\epsilon', \epsilon) / \nu_c = [\eta^2 / (1 + \eta)^3] [2 + (1 + \eta)(\epsilon - \epsilon')] \\ \times \exp[-\eta(\epsilon - \epsilon')]: \quad \epsilon' < \epsilon \\ = [\eta^2 / (1 + \eta)^3] [2 + (1 + \eta)(\epsilon' - \epsilon)] \\ \times \exp[-(\epsilon' - \epsilon)]: \quad \epsilon' > \epsilon, \quad (3.32)$$

where we have been careful to preserve the normalization (3.30).

It follows from (3.32) that  $K(\epsilon', \epsilon)$  has a relatively strong maximum at

$$\epsilon_m' = \epsilon - (1 - \eta) / (1 + \eta)\eta. \quad (3.33)$$

Thus the most probable result of a collision is de-excitation with an energy loss  $\Delta\epsilon \sim (1 - \eta) / (1 + \eta)\eta$ . The fraction  $\alpha$  of collisions leading to de-excitation can be obtained by integrating (3.32) over  $\epsilon'$  from 0 to  $\epsilon$ . This gives

$$\alpha = \int_0^{\epsilon} \frac{K(\epsilon', \epsilon)}{\nu_c} d\epsilon' \\ = (1 + 3\eta) / (1 + \eta)^3, \quad (3.34)$$

which is close to unity for conditions of experimental interest, i.e.,  $\eta \lesssim \frac{1}{2}$ . It should be borne in mind, however, that (3.34) is probably somewhat of an overestimate because, as previously observed, the statistical theory

undoubtedly gives too much weight to large energy transfers. It is in fact only the decreasing density of states at smaller  $\epsilon$  which limits the losses to reasonable values. A possible refinement of the theory which we shall not consider at present because of the additional complication it introduces would be to include an adiabaticity factor to cut off large energy transfers.

#### IV. STEADY-STATE DISTRIBUTION

For a relatively wide kernel of the form (3.32) a good approximation to the steady distribution function  $\chi(\epsilon)$  required to compute the rate constants from (2.9) may be obtained by iteration of (2.5). This leads to the recursion relation

$$\chi^{(i+1)}(\epsilon) = [\nu_c + K_d(\epsilon)]^{-1} \int_0^\infty K(\epsilon', \epsilon) \chi^{(i)}(\epsilon') d\epsilon', \quad (4.1)$$

in which we have used (3.30). If we start with the trial function  $\chi^{(0)}(\epsilon) = 1$  corresponding to an equilibrium distribution, we obtain the first iterate

$$\chi^{(1)}(\epsilon) = \nu_c [\nu_c + K_d(\epsilon)]^{-1}. \quad (4.2)$$

This is the form usually employed in theories of unimolecular decay. A better approximation may be obtained by substituting (4.2) back into (4.1) and observing that  $\chi^{(1)}(\epsilon)$  falls rapidly to zero for  $\epsilon > \delta^*$ , where  $\delta^*$  is the energy at which the collision frequency equals the spontaneous decay rate, that is

$$\nu_c = K_d(\delta^*). \quad (4.3)$$

This gives the second iterate

$$\chi^{(2)}(\epsilon) = \chi^{(1)}(\epsilon) \alpha(\delta^*, \epsilon), \quad (4.4)$$

where

$$\alpha(\delta^*, \epsilon) = \nu_c^{-1} \int_0^{\delta^*} K(\epsilon', \epsilon) d\epsilon' \quad (4.5)$$

is the fraction of collisions in which molecules of energy  $\epsilon$  are transferred to states of energy  $\epsilon' \leq \delta^*$ . Using (3.32) for  $K(\epsilon', \epsilon)$  we find from (4.5)

$$\begin{aligned} \alpha(\delta^*, \epsilon) &= 1 - \left( \frac{3\eta^2 + \eta^3}{(1+\eta)^3} + \frac{\eta^2(\delta^* - \epsilon)}{(1+\eta)^2} \right) \\ &\quad \times \exp[-(\delta^* - \epsilon)]: \quad \epsilon \leq \delta^* \\ &= \left( \frac{1+3\eta}{(1+\eta)^3} + \frac{\eta(\epsilon - \delta^*)}{(1+\eta)^2} \right) \\ &\quad \times \exp[-\eta(\epsilon - \delta^*)]: \quad \epsilon > \delta^*. \quad (4.6) \end{aligned}$$

It follows from (4.6) that for  $\epsilon < \delta^*$ ,  $\chi^{(2)}(\epsilon)$  is close to  $\chi^{(1)}(\epsilon)$  while for  $\epsilon > \delta^*$ ,  $\chi^{(2)}(\epsilon)$  decreases much more rapidly than  $\chi^{(1)}(\epsilon)$ . Thus the use of  $\chi^{(1)}(\epsilon)$  to calculate rate constants leads to something of an overestimate.

To show that the iteration procedure converges we can compute the third iterate in the same manner.

This gives

$$\chi^{(3)}(\epsilon) = [\nu_c + K_d(\epsilon)]^{-1} \int_0^{\delta^*} \alpha(\delta^*, \epsilon') K(\epsilon', \epsilon) d\epsilon', \quad (4.7)$$

which may be evaluated using (3.32) and (4.6) and gives for  $\epsilon > \delta^*$

$$\frac{\chi^{(3)}(\epsilon)}{\chi^{(2)}(\epsilon)} \approx 1 - \frac{2\eta^4(2+\eta)[2+(1+\eta)(\epsilon - \delta^*)]}{(1+\eta)^3[1+3\eta+\eta(1+\eta)(\epsilon - \delta^*)]}. \quad (4.8)$$

It can be seen from (4.8) that for small  $\eta$  the ratio of  $\chi^{(3)}(\epsilon)$  to  $\chi^{(2)}(\epsilon)$  is very close to unity for all  $\epsilon > \delta^*$ . In particular for  $\eta < \frac{1}{2}$ ,  $1 > \chi^{(3)}(\epsilon)/\chi^{(2)}(\epsilon) > 22/27$ , which is a negligible correction for our purposes. For  $\epsilon < \delta^*$  the correction is considerably smaller. We shall therefore use  $\chi^{(2)}(\epsilon)$  in our calculation of the rate constants.

#### V. DISSOCIATION RATE CONSTANT

Substituting (4.4) into (2.9) and using (4.2) we obtain the dissociation rate constant

$$k_d = (Q_r Q_v)^{-1} \int_\delta^\infty \left( \frac{\nu_c K_d(\epsilon)}{\nu_c + K_d(\epsilon)} \right) \alpha(\delta^*, \epsilon) \Omega_1(\epsilon) e^{-\epsilon} d\epsilon. \quad (5.1)$$

The corresponding recombination rate constant  $k_r$  can be obtained by reflection through the equilibrium constant as indicated in (2.9).

Since  $K_d(\epsilon) \ll \nu_c$  for  $\epsilon < \delta^*$  and  $K_d(\epsilon) \gg \nu_c$  for  $\epsilon > \delta^*$  we can obtain a reasonable approximation to  $k_d$  in the form

$$k_d = k_{d1} + k_{d2}, \quad (5.2)$$

where

$$k_{d1} = (Q_r Q_v)^{-1} \int_\delta^{\delta^*} \alpha(\delta^*, \epsilon) \Gamma_{23}(\epsilon) e^{-\epsilon} d\epsilon \quad (5.3)$$

is a unimolecular contribution and

$$k_{d2} = \nu_c (Q_r Q_v)^{-1} \int_{\delta^*}^\infty \alpha(\delta^*, \epsilon) \Omega_1(\epsilon) e^{-\epsilon} d\epsilon \quad (5.4)$$

is a bimolecular contribution to the total rate constant. Evaluating (5.3) and (5.4) using (3.7), (3.15), (4.6) and the approximation (3.31), we find

$$k_{d1} = \nu_d \alpha \left( \frac{Q_u \Theta_v^{-1}}{Q_v \Theta_u^{s+1}} \right) e^{-\delta} \sum_{\epsilon_u \leq \Delta} \exp(-\epsilon_u) \left( \frac{(s+1, \Delta - \epsilon_u)!}{(s+1)! Q_u} \right) \quad (5.5)$$

and

$$k_{d2} = \nu_c \alpha \beta_v \left( \frac{(\Delta + \delta + \epsilon_{v0})^{N-1}}{(N-1)!} \right) \exp[-(\Delta + \delta + \epsilon_{v0})], \quad (5.6)$$

where

$$\beta_v = \prod_{i=1}^v (2/\Theta_{vi}) \sinh(\Theta_{vi}/2) \quad (5.7)$$

is factor which is very close to unity in the classical limit but may be large in the quantum limit,

$$(s, x)! = \int_0^x y^s e^{-y} dy \quad (5.8)$$

is the incomplete factorial function, and  $\Delta = \delta^* - \delta$  satisfies the equation

$$\frac{\nu_c}{\nu_d} = \frac{(N-1)!}{(s+1)!} \left( \frac{\Theta_v}{\Delta + \delta + \epsilon_{v0}} \right)^{N-1} \left( \frac{\Delta}{\Theta_u} \right)^{s+1} G_u(s+1, \Delta), \quad (5.9)$$

where

$$G_u(s+1, \Delta) = \sum_{\epsilon_u \leq \Delta} (1 - \epsilon_u/\Delta)^{s+1}. \quad (5.10)$$

Using (5.9) and the recursion relation

$$(s+1)(s, \Delta)! = (s+1, \Delta)! + \Delta^{s+1} e^{-\Delta}, \quad (5.11)$$

(5.5) and (5.6) may be combined to give the total dissociation rate

$$k_d = \nu_c \alpha \beta_v \gamma [(\Delta + \delta + \epsilon_{v0})^{N-1} / (N-1)!] \exp[-(\Delta + \delta + \epsilon_{v0})] \quad (5.12a)$$

$$= \alpha \sigma_{23} c_{23} Q_{23} (Q_s Q_u / Q_r Q_v) e^{-\delta} \times \sum_{\epsilon_u \leq \Delta} \exp(-\epsilon_u) [(s, \Delta - \epsilon_u)! / s! Q_u], \quad (5.12b)$$

where

$$\begin{aligned} \gamma &= k_d / k_{d2} \\ &= \sum_{k=1}^{\infty} \frac{(s+1)! \Delta^k G_u(s+1+k, \Delta)}{(s+1+k)! G_u(s+1, \Delta)} \end{aligned} \quad (5.13)$$

is the ratio of the total rate constant to the bimolecular contribution.

These expressions are valid for molecules with  $D > E_{v0} = kT\epsilon_{v0}$  at all pressures and temperatures for which  $\Delta + \delta + \epsilon_{v0} > N + (N)^{1/2}$ . Equation (5.12a) is convenient for calculations at low pressures since it is relatively insensitive to  $\Delta$  under these conditions, and (5.12b) is convenient at high pressures for the same reason.

In general the calculation of  $k_d$  is sufficiently complicated to justify the use of a computer. However in several important special cases it can be simplified sufficiently to carry out with a slide rule. These cases are considered below.

### A. High-Pressure Limit

The high-pressure limit

$$k_{\infty} = \alpha \sigma_{23} c_{23} Q_{23} (Q_s Q_u / Q_r Q_v) e^{-\delta} \quad (5.14)$$

is approached in the region defined by  $\Delta > s+1$  and  $\epsilon_{v0} > u + s + 1 - \Delta$  in which

$$\sum_{\epsilon_u \leq \Delta} \exp(-\epsilon_u) (s, \Delta - \epsilon_u)! / s! \rightarrow Q_u. \quad (5.15)$$

It may be noted that  $k_{\infty}$  has a form similar to that given by the theory of absolute reaction rates<sup>34</sup> which differs from the high-pressure rate constant obtained in theories of isomerization.<sup>1,2</sup> In particular even in the

classical limit the pre-exponential factor is temperature dependent. This is due to the change in the number of translational and rotational degrees of freedom which occurs during dissociation but not during isomerization.

### B. Classical Limit

In the classical limit the sum in (5.10) may be approximated by an integral and we find

$$G_u(s+1, \Delta) \approx [(s+1)! / (M+1)!] \times (\Theta_u/\Delta)^{s+1} [(\Delta + \epsilon_{u0})/\Theta_u]^{M+1}, \quad (5.16)$$

where  $M = u + s$ . Using (5.16) we obtain from (5.9), (5.12), (5.13), and (5.14)

$$k_d \approx \nu_c \alpha \beta_u \gamma [(\Delta + \delta + \epsilon_{v0})^{N-1} / (N-1)!] \times \exp[-(\Delta + \delta + \epsilon_{v0})] \quad (5.17a)$$

$$\approx k_{\infty} (M, \Delta + \epsilon_{u0})! / M!, \quad (5.17b)$$

where  $\beta_u$  is given by the appropriate form of (5.7),

$$\gamma \approx [(M, \Delta + \epsilon_{u0})! (M+1) / (\Delta + \epsilon_{u0})^{M+1}] \exp[(\Delta + \epsilon_{u0})], \quad (5.18)$$

and  $\Delta$  satisfies the equation

$$\frac{\nu_c}{\nu_d} \approx \frac{(N-1)!}{(M+1)!} \left( \frac{\Theta_v}{\Delta + \delta + \epsilon_{v0}} \right)^{N-1} \left( \frac{\Delta + \epsilon_{u0}}{\Theta_u} \right)^{M+1}. \quad (5.19)$$

These approximations are valid in the region where  $\Theta_v < 1$ ,  $\Theta_u < 1$ , and  $\Delta > \Theta_u(s+1+u/2)$ .

### C. Quantum Limit

In practice it is found that much of the available experimental data fall in the low-pressure quantum-mechanical region defined by  $\Delta < s+1$ ,  $\Theta_u > \Delta / (s+1 + \frac{1}{2}u)$ . In this case only the lowest vibrational state of the product molecules makes an appreciable contribution sum in (5.10) so that  $G_u(s+1, \Delta) \approx 1$  and (5.12) becomes

$$k_d \approx \nu_c \alpha \beta_v \gamma [(\Delta + \delta + \epsilon_{v0})^{N-1} / (N-1)!] \times \exp[-(\Delta + \delta + \epsilon_{v0})] \quad (5.20a)$$

$$\approx k_{\infty} (s, \Delta) / s! Q_u, \quad (5.20b)$$

where

$$\gamma \approx [(s, \Delta)! (s+1) / \Delta^{s+1}] e^{\Delta} \quad (5.21)$$

and  $\Delta$  satisfies the equation

$$\frac{\nu_c}{\nu_d} \approx \frac{(N-1)!}{(s+1)!} \left( \frac{\Theta_v}{\Delta + \delta + \epsilon_{v0}} \right)^{N-1} \left( \frac{\Delta}{\Theta_u} \right)^{s+1}. \quad (5.22)$$

In many cases of interest  $\Delta \ll \delta + \epsilon_{v0}$  and (5.22) can be approximately solved to give

$$\frac{\Delta}{\Theta_v} \approx \chi^{1/(s+1)} + \left( \frac{N-1}{s+1} \right) \left( \frac{hc\omega_v}{D+E_{v0}} \right) \chi^{2/(s+1)}, \quad (5.23)$$

<sup>34</sup> S. Gladstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., New York, 1941).

where

$$\chi = \frac{\nu_c(s+1)! \left(\frac{\Theta_u}{\Theta_v}\right)^{s+1} (\delta + \epsilon_{v0})^{N-1}}{\nu_d(N-1)! \left(\frac{\Theta_v}{\Theta_u}\right)} = (\sigma_{1A\rho}/\sigma_{23\rho_{23}}) (kT/hc\omega_v)^{1/2} \quad (5.24)$$

is a density-dependent parameter having an almost negligible temperature dependence over the range of interest,

$$\rho_{23} = \frac{\rho_0(N-1)! \left(\frac{\mu_{1A}}{\mu_{23}}\right)^{1/2} \left(\frac{hc\omega_v}{D+E_{v0}}\right)^{N-1}}{\mathfrak{L}V_{23}(s+1)! (\mu_{23})} \quad (5.25)$$

is a critical density,

$$V_{23} = \left(\frac{h}{2\pi\mu c\omega_v}\right)^{3/2} \frac{\pi^{l-1}B_s^s}{(\pi\omega_v)^{s-r}B_r^r} \quad (5.26)$$

is a characteristic molecular volume, and  $\mathfrak{L}$  is Loschmidt's number.

### D. Apparent Activation Energy and Order of a Reaction

For comparison with experimental results over a limited range of temperature and density it is often convenient to approximate the rate constant in the standard form

$$k_d = C\rho^m \exp(-E_A/RT), \quad (5.27)$$

where  $C$  is a constant,

$$m = (\partial \ln k_d / \partial \ln \rho)_T \quad (5.28)$$

is the order of the reaction with respect to the A atoms, and

$$E_A = RT^2(\partial \ln k_d / \partial T)_\rho \quad (5.29)$$

is the apparent activation energy.

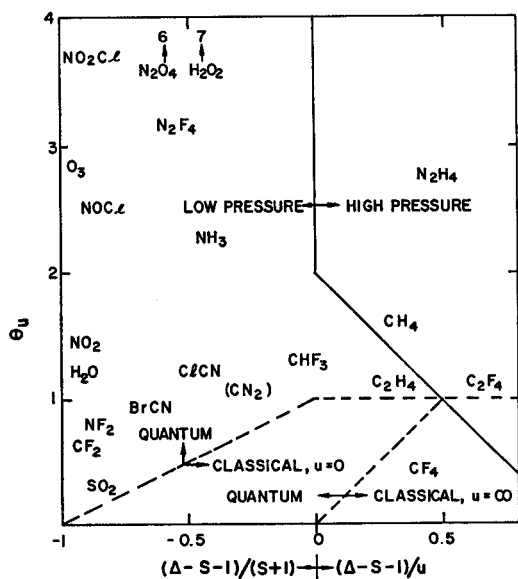


FIG. 1. Domain map showing approximate conditions under which dissociation experiments on various molecules have been carried out. Note the scale change at the origin. Also note that the boundary between the quantum and classical domain depends on the number  $u$  of vibrational modes of the products. See text for definition of symbols.

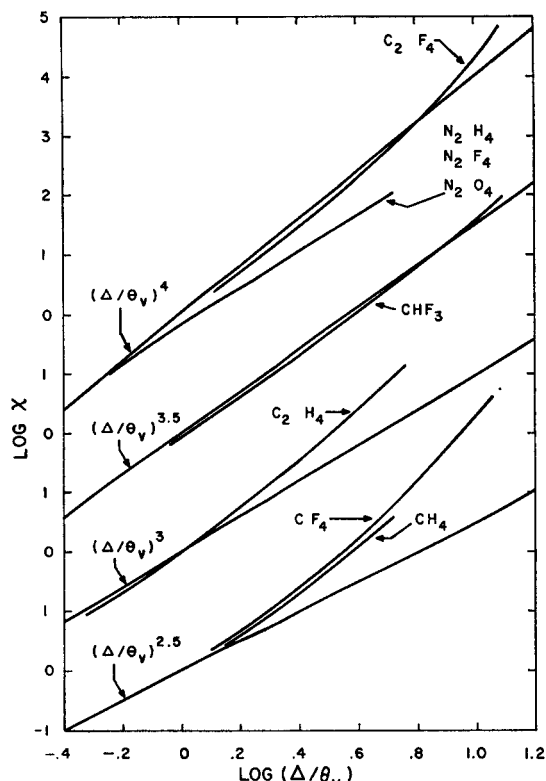


FIG. 2. Numerically computed curves relating  $\log \chi$  and  $\log(\Delta/\theta_v)$  for five- and six-atom molecules. The straight lines denoted  $(\Delta/\theta_v)^{s+1}$  are asymptotes for small  $\chi$ . The origin for different values of  $s$  has been displaced to avoid excessive overlapping. See text for definition of symbols.

Substituting (5.12) into (5.28) and (5.29) we find in general

$$m^{-1} = \gamma \left[ 1 - \left( \frac{N-1}{\rho+1} \right) \left( \frac{\Delta}{\Delta + \delta + \epsilon_{v0}} \right) \frac{G_u(s+1, \Delta)}{G_u(s, \Delta)} \right] \quad (5.30)$$

and

$$D - E_A = RT \{ \bar{v} + r - s + [(s+1)/\gamma] - (m/2) - 4 + (2/\alpha) - [\sum_{\epsilon_u \leq \Delta} \epsilon_u \exp(-\epsilon_u) (s, \Delta - \epsilon_u)!] \times [\sum_{\epsilon_u \leq \Delta} \exp(-\epsilon_u) (s, \Delta - \epsilon_u)!]^{-1} \}, \quad (5.31)$$

where

$$\bar{v} = \sum_{i=1}^v \Theta_{vi} [\exp(\Theta_{vi}) - 1]^{-1} \quad (5.32)$$

is essentially the number of classically excited vibrational modes of  $M_1$ .

In the classical domain where (5.16) applies

$$m^{-1} \approx \gamma \left[ 1 - \left( \frac{N-1}{M+1} \right) \left( \frac{\Delta + \epsilon_{v0}}{\Delta + \delta + \epsilon_{v0}} \right) \right] \quad (5.33)$$

and

$$D - E_A \approx RT \{ \bar{v} + r - s + [(M+1)/\gamma] - (m/2) - 4 + (2/\alpha) - \bar{u} \}, \quad (5.34)$$

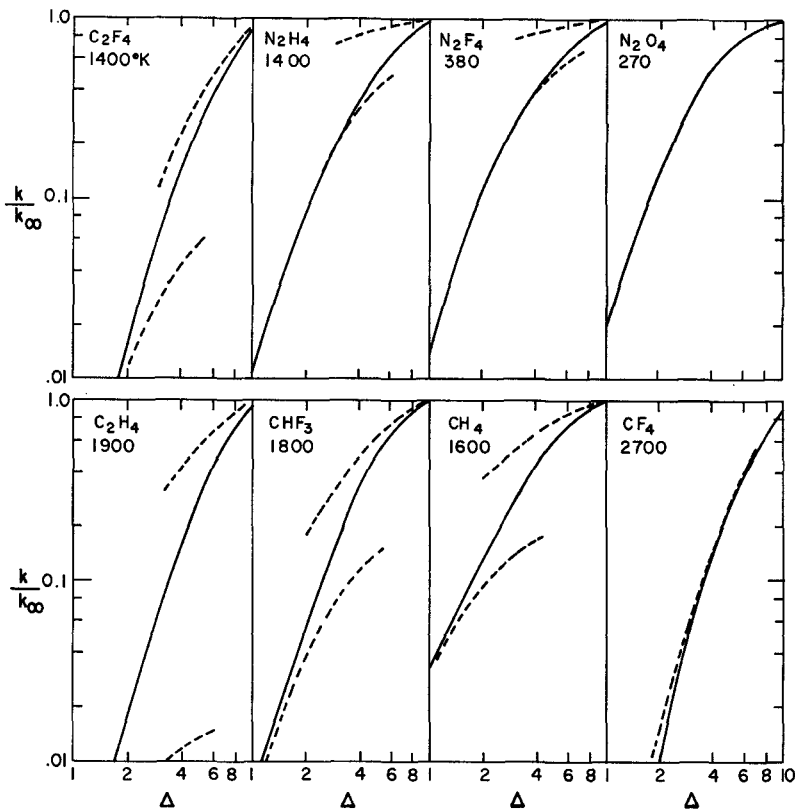


FIG. 3. Numerically computed values of  $k/k_\infty$  as a function of the parameter  $\Delta$  for five- and six-atom molecules. The upper and lower dashed curves are, respectively, the high-pressure classical and low-pressure quantum limits given by Eqs. (5.17) and (5.20).

where

$$\bar{u} = \sum_{i=1}^u \Theta_{ui} [\exp(\Theta_{ui}) - 1]^{-1} \quad (5.35)$$

is the number of classically excited vibrational degrees of freedom of the product molecules  $M_2$  and  $M_3$ .

In the high-pressure limit  $m \rightarrow 0$  and  $D - E_A \rightarrow RT[\bar{v} + r - s - 4 + (2/\alpha) - \bar{u}]$  while in the low-pressure quantum limit  $m \rightarrow 1$  and  $D - E_A \rightarrow RT(\bar{v} + r - \frac{1}{2} + 2/\alpha)$ .

## VI. COMPARISON WITH EXPERIMENTAL RESULTS

The molecular constants necessary to evaluate the dissociation rate constant were obtained from the JANAF Tables<sup>35</sup> and the AIP Handbook.<sup>36</sup> They are summarized in Table I for the reactions of interest. Two lines are used for each reaction. The top line of each pair lists the reactant molecule and catalyst and gives their properties; the bottom line lists the dissociation products and their properties. Note that we have omitted reactions in which a change in electronic state occurs on dissociation because the theory does not apply in this case. Such reactions have been treated by Troe and Wagner.<sup>4</sup>

For reactions such as  $C_2F_4 \rightarrow CF_2 + CF_2$  which involve

<sup>35</sup> JANAF Thermochemical Tables (Dow Chemical Co., Midland, Mich., 1965).

<sup>36</sup> American Institute of Physics Handbook, D. E. Gray *et al.*, Eds. (McGraw-Hill Book Co., New York, 1957).

only the breaking of a single bond, the true activation energy  $D$  is assumed to be the dissociation energy  $D_0$ . For reactions such as  $CHF_3 \rightarrow CF_2 + HF$  which involve the breaking of two bonds and the formation of a new one, we expect  $D > D_0$  and in these cases  $D$  was determined from the observed activation energy. The test of the theory is then the degree to which it predicts the magnitude and pressure dependence of the rate constant.

For reactions involving CN as a product, we have based our values of  $D_0$  on the value of 125 kcal/mole given by Tsang *et al.*<sup>24</sup> for  $(CN)_2 \rightarrow 2CN$  since this gives the best fit to the data. However a lower value of 111 kcal/mole also gives a reasonable fit and a higher value of 143 kcal/mole cannot be ruled out.

The temperature-, density-, and cross-section-dependent parameters which enter the calculations are summarized in Table II for mean experimental conditions. The energy exchange cross section  $\sigma_{1A}$  was assumed to be  $3 \times 10^{-16}$  cm<sup>2</sup> in all cases. The spontaneous decay cross section was assumed to be  $10^{-16}$  cm<sup>2</sup> if either product was monatomic,  $10^{-17}$  cm<sup>2</sup> if either product was linear and only a single bond broken, and  $2 \times 10^{-18}$  cm<sup>2</sup> otherwise. These values were chosen to fit the experimental data and are in rough accord with the discussion in Sec. III.

For three- and four-atom molecules, all of which fall in the low-pressure quantum domain, we have used the approximation (5.23) to determine the parameter  $\Delta$



TABLE I. Molecular parameters used to evaluate rate constants. The reaction is specified in the first column. Note that we have omitted the catalyst in the "products" column to save space. The values were computed from data in Refs. 35 and 36, and the experimental papers cited.

Reactants	$\mu_{1A}$	$2r$	$v$	$N$	$D_0$	$B_r$	$\omega_r$	$E_{v_0}$	$\log V_{23}$ (cm <sup>3</sup> )
Products	$\mu_{23}$	$2s$	$u$	$M$	$D$	$B_s$	$\omega_u$	$E_{u_0}$	$\log \rho_{23}/\rho_1$
					(kcal)	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	
O <sub>2</sub> +Ar	22	3	3	4.5	24.2	0.85	1050	1 660	-24.5
O <sub>2</sub> +O	11	2	1	2	24.2	1.45	1580	790	2.4
NOCl+Ar	25	3	3	4.5	37	0.46	760	1 360	-24.2
NO+Cl	16	2	1	2	37	1.70	1904	952	1.3
NF <sub>2</sub> +Ar	23	3	3	4.5	66	0.66	830	1 290	-24.5
NF+F	12	2	1	2	66	1.10	980	490	0.8
NO <sub>2</sub> +Ar	21	3	3	4.5	72	1.14	1190	1 890	-24.7
NO+O	10	2	1	2	72	1.70	1904	952	1.5
CF <sub>2</sub> +Ar	22	3	3	4.5	106	0.80	1050	1 660	-24.6
CF+F	12	2	1	2	106	1.43	1308	654	0.6
H <sub>2</sub> O+Ar	12	3	3	4.5	117	15.8	2790	4 500	-24.2
OH+H	1	2	1	2	117	18.9	3735	1 867	1.9
SO <sub>2</sub> +Ar	25	3	3	4.5	131	0.59	930	1 520	-24.3
SO+O	12	2	1	2	131	0.71	1124	562	0.2
BrCN+Ar	29	2	4	5	83	0.13	560	1 750	-23.8
CN+Br	20	2	1	2	83	1.90	2069	1 035	-1.4
ClCN+Ar	24	2	4	5	93	0.20	690	1 850	-23.9
CN+Cl	15	2	1	2	93	1.90	2069	1 035	-1.2
NO <sub>2</sub> Cl+Ar	27	3	6	7.5	29.5	0.21	740	2 600	-24.7
NO <sub>2</sub> +Cl	20	3	3	4.5	29.5	1.14	1190	1 890	1.0
H <sub>2</sub> O <sub>2</sub> +N <sub>2</sub>	15	3	6	7.5	50	1.9	1450	5 520	-25.8
OH+OH	9	4	2	4	50	18.9	3735	3 735	1.1
NH <sub>3</sub> +Ar	12	3	6	7.5	85	1.84	2240	7 530	-25.7
NH+H <sub>2</sub>	1.8	4	2	4	92	2.95	3820	3 850	-1.1
(CN) <sub>2</sub> +Ar	23	2	7	8	125	0.16	670	3 410	-27.9
CN+CN	13	4	2	4	125	1.90	2069	2 069	-1.2
CHF <sub>3</sub> +Ar	26	3	9	10.5	59	0.28	1050	5 470	-28.1
CF <sub>2</sub> +HF	14	5	4	6.5	70	2.25	1490	3 730	-0.2
CH <sub>4</sub> +Ar	11	3	9	10.5	101	5.30	1957	9 480	-25.2
CH <sub>3</sub> +H	1	3	6	7.5	101	7.40	1780	5 850	-1.1
CF <sub>2</sub> +Ar	28	3	9	10.5	122	0.19	766	3 760	-26.4
CF <sub>3</sub> +F	15	3	6	7.5	122	0.27	805	2 660	-4.3
N <sub>2</sub> O <sub>4</sub> +N <sub>2</sub>	18	3	12	13.5	12.7	0.13	601	4 970	-29.7
NO <sub>2</sub> +NO <sub>2</sub>	23	6	6	9	12.7	1.13	1200	3 780	3.3
N <sub>2</sub> F <sub>4</sub> +N <sub>2</sub>	18	3	12	13.5	19.8	0.12	604	4 160	-30.4
NF <sub>2</sub> +NF <sub>2</sub>	26	6	6	9	19.8	0.66	830	2 580	3.1
N <sub>2</sub> H <sub>4</sub> +Ar	18	3	12	13.5	58	1.60	1543	10 960	-28.6
NH <sub>2</sub> +NH <sub>2</sub>	8	6	6	9	58	6.40	2630	8 400	0.7
C <sub>2</sub> F <sub>4</sub> +Ar	29	3	12	13.5	75	0.11	619	4 670	-30.2
CF <sub>2</sub> +CF <sub>2</sub>	25	6	6	9	75	0.79	1080	3 320	-2.6
C <sub>2</sub> H <sub>4</sub> +Ne	12	3	12	13.5	44	1.60	1561	10 680	-25.4
C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub>	1.9	4	8	10	72	9.10	1440	7 850	-2.3

TABLE II. Temperature-, density-, and cross-section-dependent parameters used to evaluate rate constants. The values shown are based on molecular parameters in Table I and mean experimental temperatures and densities. The cross section  $\sigma_{1A}$  was assumed to be  $3 \times 10^{-16}$  cm<sup>2</sup> in all cases; the cross section  $\sigma_{23}$  was assumed to be  $10^{-16}$  cm<sup>2</sup> if either product was monatomic,  $10^{-17}$  cm<sup>2</sup> if either product was linear and only one bond is broken, and  $2 \times 10^{-18}$  otherwise. Note  $k_0 = \nu_e \alpha \beta \nu \gamma$ .

Reactants	$T$	$\theta_v$	$\epsilon_{v0}$	$\log Q_v$	$\log \beta_v$	$\bar{v}$	$\delta$	$\log \alpha$	$\log k_0$
Products	$\rho/\rho_0$	$\theta_u$	$\epsilon_{u0}$	$\log Q_u$	$\log \beta_u$	$\bar{u}$	$\Delta$	$\log \gamma$	$\log k_\infty$
	(°K)								(sec <sup>-1</sup> )
O <sub>3</sub> +Ar	800	1.89	3.0	0.28	0.16	1.1	15.1	-0.07	8.3
O <sub>2</sub> +O	0.2	2.84	1.4	0.02	0.13	0.2	0.1	0.01	6.4
NOCl+Ar	1100	1.00	1.8	0.77	0.10	1.7	16.8	-0.06	8.7
NO+Cl	0.5	2.50	1.3	0.04	0.14	0.2	0.3	0.05	5.1
NF <sub>2</sub> +Ar	1700	0.70	1.1	0.89	0.02	2.0	19.4	-0.05	8.5
NF+F	0.3	0.83	0.4	0.25	0.01	0.7	0.3	0.05	4.8
NO <sub>2</sub> +Ar	1900	0.90	1.4	0.71	0.05	1.8	18.9	-0.05	9.4
NO+O	0.4	1.44	0.7	0.12	0.04	0.4	0.2	0.03	5.1
CF <sub>2</sub> +Ar	3300	0.45	0.7	1.32	0.01	2.3	16.1	-0.06	7.7
CF+F	0.04	0.57	0.3	0.36	0.00	0.7	0.1	0.01	6.2
H <sub>2</sub> O+Ar	4500	0.89	1.4	0.71	0.05	1.8	13.0	-0.09	8.6
OH+H	0.2	1.19	0.6	0.16	0.03	0.5	0.1	0.01	7.9
SO <sub>2</sub> +Ar	6000	0.22	0.4	1.94	0.00	2.6	10.9	-0.10	9.2
SO+O	1.0	0.27	0.1	0.62	0.00	0.9	0.4	0.07	8.5
BrCN+Ar	3300	0.24	0.8	2.60	0.01	3.3	12.6	-0.10	7.6
CN+Br	0.03	0.90	0.5	0.23	0.01	0.6	0.5	0.09	5.7
ClCN+Ar	2600	0.40	1.1	2.00	0.03	3.1	17.8	-0.06	8.2
CN+Cl	0.1	1.20	0.6	0.16	0.03	0.5	1.2	0.15	4.0
NO <sub>2</sub> Cl+Ar	460	2.31	8.1	0.41	0.93	1.7	32.0	-0.05	7.2
NO <sub>2</sub> +Cl	0.005	3.72	5.9	0.05	0.80	0.3	0.2	0.03	-0.2
H <sub>2</sub> O <sub>2</sub> +N <sub>2</sub>	800	2.60	9.9	0.42	1.39	1.5	31.2	-0.05	9.7
OH+OH	0.1	6.73	6.7	0.00	1.06	0.0	1.4	0.18	-0.7
NH <sub>3</sub> +Ar	2500	1.29	4.4	0.95	0.25	2.8	18.4	-0.10	9.6
NH+H <sub>2</sub>	1.0	2.19	2.2	0.12	0.16	0.6	1.8	0.25	4.9
(CN) <sub>2</sub> +Ar	2600	0.37	1.9	3.75	0.05	5.3	24.0	-0.09	8.3
CN+CN	0.1	1.14	1.1	0.32	0.04	1.1	1.9	0.30	3.5
CHF <sub>3</sub> +Ar	1800	0.84	4.4	2.38	0.22	5.5	19.5	-0.14	8.8
CF <sub>2</sub> +HF	0.4	1.19	3.0	0.77	0.20	2.0	3.1	0.35	5.5
CH <sub>4</sub> +Ar	1600	1.77	8.6	0.86	0.65	3.3	31.6	-0.10	10.1
CH <sub>3</sub> +H	1.0	0.60	5.3	0.69	0.37	2.4	4.6	0.49	0.8
CF <sub>4</sub> +Ar	2700	0.41	2.0	4.32	0.01	7.1	22.6	-0.12	8.9
CF <sub>3</sub> +F	0.4	0.43	1.4	2.80	0.02	4.7	4.5	0.39	4.9
N <sub>2</sub> O <sub>4</sub> +N <sub>2</sub>	270	3.20	26.4	1.04	4.50	2.4	23.5	-0.15	13.3
NO <sub>2</sub> +NO <sub>2</sub>	1.0	6.37	20.1	0.02	3.83	0.2	2.0	0.20	4.3
N <sub>2</sub> F <sub>4</sub> +N <sub>2</sub>	380	2.28	15.8	0.95	1.55	3.1	26.0	-0.14	10.5
NF <sub>2</sub> +NF <sub>2</sub>	1.0	3.15	9.8	0.16	1.13	0.9	1.7	0.18	4.4
N <sub>2</sub> H <sub>4</sub> +Ar	1400	1.59	11.3	1.54	0.94	4.8	20.7	-0.18	10.5
NH <sub>3</sub> +NH <sub>3</sub>	1.0	2.71	8.7	0.24	0.91	1.2	6.5	0.71	5.0
C <sub>2</sub> F <sub>4</sub> +Ar	1400	0.65	4.8	4.24	0.17	8.2	26.8	-0.14	9.2
CF <sub>3</sub> +CF <sub>2</sub>	0.3	1.12	3.4	1.12	0.14	3.2	7.5	0.76	3.5
C <sub>2</sub> H <sub>4</sub> +Ne	1400	1.18	8.1	2.15	0.48	6.1	18.9	-0.20	8.9
C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub>	0.1	1.10	6.0	1.80	0.43	4.0	6.5	0.55	4.1

TABLE III. Comparison of experimental observations for mean conditions with theoretical calculations based on parameters in Tables I and II.  $m$  is the order of the reaction with respect to the catalyst,  $E_A$  is the apparent activation energy, and  $k$  is the first-order dissociation rate constant. Omissions of  $m_{\text{obs}}$  correspond to cases where the order was not determined experimentally. Omissions of  $(D-E_A)_{\text{obs}}$  correspond to cases where a double bond is broken and  $D$  was taken to be  $E_{A_{\text{obs}}} + (D-E_A)_{\text{theoret}}$ .

Reactants Products	$T$ $\rho/\rho_0$ (°K)	$m_{\text{theoret}}$ $m_{\text{obs}}$	$(D-E_A)_{\text{theoret}}$ $(D-E_A)_{\text{obs}}$ (kcal)	$\log k_{\text{theoret}}$ $\log k_{\text{obs}}$ (sec <sup>-1</sup> )	Ref.
O <sub>3</sub> +Ar	800	1.0	1.6	3.6	8
O <sub>2</sub> +O	0.2	~1	1.1	3.4	9
NOCl+Ar	1100	1.0	4	3.8	10
NO+Cl	0.5	...	6	3.9	
NF <sub>2</sub> +Ar	1700	1.0	8	3.2	11
NF+F	0.3	...	14	3.3	12
NO <sub>2</sub> +Ar	1900	1.0	8	3.8	13
NO+O	0.4	...	7	3.9	
CF <sub>2</sub> +Ar	3300	1.0	17	3.5	14
CF+F	0.04	...	16	3.8	
H <sub>2</sub> O+Ar	4500	1.0	19	5.1	15
OH+H	0.2	...	12	4.6	
SO <sub>2</sub> +Ar	6000	1.0	31	6.6	16
SO+O	1.0	~1	21	6.1	
BrCN+Ar	3300	0.8	20	4.5	17
CN+Br	0.03	~1	-7	2.3	
ClCN+Ar	2600	0.7	14	3.2	18
CN+Cl	0.01	...	13	3.5	
NO <sub>2</sub> Cl+Ar	460	1.0	1.8	-3.2	19
NO <sub>2</sub> +Cl	0.005	~1	2.0	-3.7	20
H <sub>2</sub> O <sub>2</sub> +N <sub>2</sub>	800	0.8	2	-1.2	21
OH+OH	0.1	~1	5	-0.7	
NH <sub>2</sub> +Ar	2500	0.7	12	4.2	22
NH+H <sub>2</sub>	1.0	~1	...	4.4	23
(CN) <sub>2</sub> +Ar	2600	0.6	22	2.8	18
CN+CN	0.1	...	25	3.3	24
CHF <sub>2</sub> +Ar	1800	0.6	18	4.6	25
CF <sub>2</sub> +HF	0.4	0.6	...	4.3	
CH <sub>2</sub> +Ar	1600	0.4	0	0.5	26
CH <sub>2</sub> +H	1.0	...	-1	0.6	
CF <sub>4</sub> +Ar	2700	0.5	25	4.1	27
CF <sub>2</sub> +F	0.4	...	24	3.9	
N <sub>2</sub> O <sub>4</sub> +N <sub>2</sub>	270	0.7	1.0	3.5	28
NO <sub>2</sub> +NO <sub>2</sub>	1.0	0.7	1.7	4.0	
N <sub>2</sub> F <sub>4</sub> +N <sub>2</sub>	380	0.7	2	3.3	29
NF <sub>2</sub> +NF <sub>2</sub>	1.0	0.5	2	3.7	
N <sub>2</sub> H <sub>4</sub> +Ar	1400	0.3	8	4.8	23
NH <sub>2</sub> +NH <sub>2</sub>	1.0	0.3	8	4.7	
C <sub>2</sub> F <sub>4</sub> +Ar	1400	0.3	12	3.3	30
CF <sub>2</sub> +CF <sub>2</sub>	0.3	...	18	3.7	
C <sub>2</sub> H <sub>4</sub> +Ne	1900	0.5	22	3.8	31
C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub>	0.1	0.5	...	3.5	

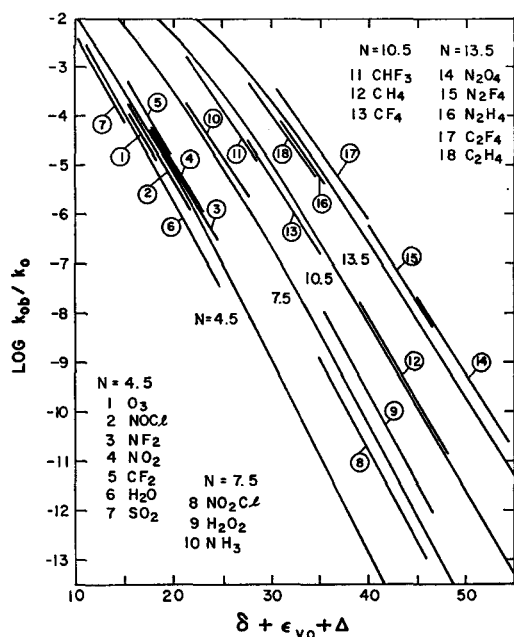


FIG. 4. Correlation of experimentally observed first-order dissociation rate constants with theoretical predictions based on Eq. (5.12) and molecular parameters given in Tables I and II. Note  $k_0 = \nu_0 \alpha \beta \gamma$ .

and Eq. (5.20a) to determine  $k_d$ . For five- and six-atom molecules the values of  $\Delta$  and  $k_d/k_\infty$  were determined from the curves in Figs. 1 and 2, which were calculated from (5.9) and (5.12b) using an IBM 650.

The locations of the various experiments<sup>8-31</sup> in the  $(\Theta_v, \Delta)$  plane are shown in Fig. 3 and it can be seen that most of them fall in the low-pressure quantum region. There is one case,  $\text{CF}_4$ , which falls in the classical region and three,  $\text{CH}_4$ ,  $\text{N}_2\text{H}_4$ , and  $\text{C}_2\text{F}_4$ , which fall in the high-pressure region.

The theory and experiments are compared in Table III and Figs. 4 and 5. The calculations for Table III and Fig. 4 are based on the parameters in Tables I and II. The curves in Fig. 5 have been adjusted to give a best fit with the data<sup>26</sup> and correspond to values of  $\sigma_{1A} = 1 \times 10^{-16} \text{ cm}^2$  and  $\sigma_{23} = 8 \times 10^{-19} \text{ cm}^2$  which are reasonable.

Considering the range of condition spanned, the difficulty of the experiments and the sensitivity of the calculation to the value of  $D$ , the over-all correlation is quite good. The only really exceptional case is  $\text{BrCN}^{17}$  which is far out of line both with the theory and the experiments on  $\text{ClCN}^{18}$  to which it should be similar. This may be due to the assumption made in the analysis of the experimental data that the excited state of CN was in equilibrium with the ground state.

It should also be mentioned in connection with our interpretation of the dissociation of  $\text{C}_2\text{H}_4$  as a simple unimolecular decomposition, that Gay *et al.*<sup>31</sup> were concerned about the rapid appearance of HD as a

product in their experiments with  $\text{C}_2\text{H}_4 + \text{C}_2\text{D}_4$  mixtures. A possible explanation of this which they do not discuss would be exchange reactions of the type  $\text{C}_2\text{H}_4 + \text{D}_2 \rightarrow \text{C}_2\text{H}_3\text{D} + \text{HD}$  and  $\text{C}_2\text{D}_4 + \text{H}_2 \rightarrow \text{C}_2\text{D}_3\text{H} + \text{HD}$  following the dissociation reactions.

## VII. SUMMARY AND CONCLUSIONS

Using the theory developed in this paper we have been able to obtain a reasonable fit to the experimental dissociation rate constants for 20 out of 21 moderately complex molecules containing from three to six atoms. The data cover the pressure range from low- to high-pressure limits and the temperature range from 250°–7500°K. The observed rate constants span 10 orders of magnitude. Examples of both classical and quantum-mechanical reactions are included.

For reactions involving only the breaking of a single bond the activation energy was taken equal to the dissociation energy and the fit was made using two adjustable parameters, the energy exchange cross section and the spontaneous decay cross section. For reactions involving the breaking of two bonds and the formation of a new one it was also necessary to fit the activation energy since it is no longer reasonable to assume it equal to the dissociation energy.

In all 20 cases where a fit was obtained, the observed temperature and pressure dependences were given within the estimated experimental uncertainties and the rate constant was given within a factor of  $\sim 3$ . Values of the cross sections and activation energies

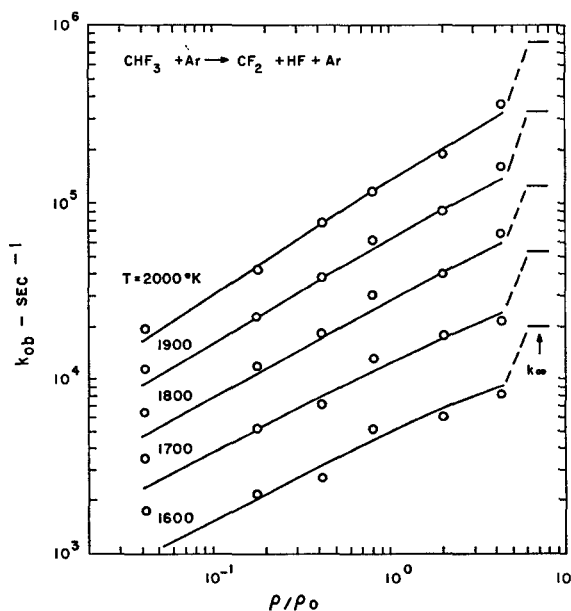


FIG. 5. Correlation of Modica's first-order rate constants for the dissociation of  $\text{CHF}_3$  in Ar with theoretical predictions based on Eq. (5.12). The curves were fit to the data using values of  $\sigma_{1A} = 10^{-16} \text{ cm}^2$  and  $\sigma_{23} = 8 \times 10^{-19} \text{ cm}^2$ .

obtained were in reasonable agreement with *a priori* expectations. The only molecule for which the theory failed badly was BrCN but there is reason to suppose that the experiments may be in error in this case.

We conclude that the theory provides a reasonable method for correlating and extrapolating experimental results for the dissociation rate of moderately complex molecules over the entire range between low- and high-pressure limits and that it may even be useful for

predicting rate constants in cases where the activation energy can be estimated or set equal to the dissociation energy as is reasonable when only a single bond is broken.

Possible refinements of the theory which could be considered include the introduction of the angular momentum constraint and the inclusion of an adiabaticity factor to reduce the probability of large energy transfers.

## Studies in Configuration Interaction. II. Determination of Charge- and Spin-Density Functions in $\pi$ -Electron Systems

I. L. COOPER\* AND R. McWEENY

*Department of Chemistry, The University, Sheffield 10, England*

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Results of calculations of spin- and charge-density functions are presented for some small  $\pi$ -electron systems, using a configuration-interaction procedure which applies equally well to both molecular-orbital and valence-bond approximation methods, and thus provides a direct comparison of the two methods.

### I. INTRODUCTION

The general configuration-interaction (CI) procedure described elsewhere<sup>1</sup> (hereafter Part I) is used in the present paper to obtain charge and spin densities for some small  $\pi$ -electron systems, and to compare the convergence of the CI expansions based on molecular orbitals (MO method) and atomic orbitals [AO's, as in the valence-bond (VB) method]. Earlier calculations of this kind, but not including the spin density, have been reported elsewhere.<sup>2</sup> The charge- and spin-density functions<sup>3</sup> are

$$P_1(r; r') = \sum_{a,b} [P_1]_{ab} a(r) b^*(r'), \quad (1.1)$$

$$D_s(r; r') = \sum_{a,b} [D_s]_{ab} a(r) b^*(r'), \quad (1.2)$$

and reduce to the charge density and (McConnell<sup>4</sup>) spin density, respectively, for  $r' = r$ .

The summations are over the set of basis orbitals  $\chi = \{a, b, c, \dots\}$  which will normally be assumed ortho-

normal; orthonormalized AO's can be obtained from ordinary Slater AO's,  $\chi' = \{a', b', c', \dots\}$  by the Löwdin prescription,

$$\chi = \chi' S^{-1/2}, \quad (1.3)$$

where  $S$  is the overlap matrix with elements  $S_{ab} = \langle a' | b' \rangle$ . The density matrix elements in  $P_1$  and  $D_s$  then allow us to estimate the charge and spin populations of the orbital and overlap regions defined by the basis. Matrices for the different bases are related by

$$\begin{aligned} P_1' &= S^{-1/2} P_1 S^{-1/2}, \\ D_s' &= S^{-1/2} D_s S^{-1/2}, \end{aligned} \quad (1.4)$$

and will be determined for a variety of approximate wavefunctions, and for singlet, doublet, and triplet states, using both MO and VB methods.

### II. Method

The CI wavefunction is

$$\Psi(x_1, x_2, \dots, x_N) = \sum_{\kappa} c_{\kappa} \Psi_{\kappa}(x_1, x_2, \dots, x_N), \quad (2.1)$$

where

$$\begin{aligned} \Psi_{\kappa}(x_1, \dots, x_N) &= (2^{m_{\kappa}}/N!)^{+1/2} \sum_{\mathcal{O}'} (-1)^{P'} \\ &\times \mathcal{O}' \Phi_{\kappa}(r_1, \dots, r_N) \Theta_{\kappa}(s_1, \dots, s_N). \end{aligned} \quad (2.2)$$

\* Present address: Department of Chemistry, University of Manchester, Manchester 13, England.

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