

# A metastable complex model for vibrational relaxation

Robert J. Gordon

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680  
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The probability of vibrational relaxation of a number of molecules is known to increase at lower temperatures. The role of intermediate complexes in such processes is discussed. A model similar to one previously introduced by Tully and co-workers is used to describe complex formation and decay. An orbiting capture cross section is assumed, and unimolecular theory is used to estimate the rate of vibrational predissociation. Fair agreement with a large body of experimental data is obtained.

## I. INTRODUCTION

The rates of most chemical processes increase with temperature. In a number of cases, however, the reverse is true. Inverse temperature behavior has been observed extensively in the gas phase for two types of bimolecular processes. One is a chemical reaction involving radicals such as NO, ClO, HO<sub>2</sub>, O, and S, for which little or no activation energy is expected. The other is vibrational energy transfer between molecules having strong van der Waals (VDW) or hydrogen bonding interactions. A mechanism frequently suggested to explain the anomalous behavior of these systems is the formation of long-lived intermediate complexes. Such a mechanism is plausible because both the capture cross section for attractive potentials and the lifetime of the complex vary inversely with collision energy. In the case of energy transfer, the longer the complex lives, the greater the opportunity for energy to flow into new degrees of freedom.

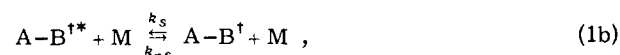
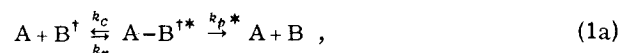
Recent molecular beam experiments<sup>1,2</sup> revealed an inverse temperature dependence for VT energy transfer, with large cross sections at low collision energies. Such behavior is incompatible with the usual Landau-Teller description of direct collisions, even when the attractive part of the potential is taken into account.<sup>1,3</sup> The most likely explanation for these experiments is the formation of a metastable intermediate. Further direct evidence for complex formation is seen in the trajectory calculations of Billing *et al.*<sup>4</sup> They found for HF relaxation that a major part of the VV and VT cross sections is due to the occurrence of orbiting collisions.

In this paper we develop a simple model for energy transfer based on the metastable complex mechanism. Consider the collision of unexcited molecule A with vibrationally excited molecule B<sup>†</sup> to form a complex A-B<sup>†\*</sup>. (Throughout this discussion a dagger refers to vibrational excitation of a chemical bond, while an asterisk refers to vibrational energy in the normal modes associated with the VDW bond.) This complex is metastable since it spontaneously dissociates when, through random fluctuation, sufficient energy resides in the VDW bond. van der Waals molecules have the unusual property that energy flows very inefficiently between the chemical and VDW modes. If this were not the case, the complex would dissociate almost immediately since the vibrational quanta of the chemical bonds are generally much larger than the VDW bond strength. The overall efficiency of energy transfer is neverthe-

less large because of the many internal collisions that A and B<sup>†</sup> undergo during the lifetime of the complex. This mechanism has also been used successfully to explain the large cross sections for the spin-forbidden quenching of O(<sup>1</sup>D) by atmospheric molecules.<sup>5(b),6,7</sup>

Recently, Coulson and Robertson,<sup>8</sup> Ewing,<sup>3,9</sup> and Beswick and Jortner<sup>10</sup> developed a theory of vibrational predissociation of VDW molecules. Ewing<sup>3</sup> used this theory to evaluate the role played by complexes in vibrational relaxation. Third body collisions were assumed to stabilize the metastable complex, producing a Boltzmann distribution in the VDW modes. The rate of vibrational predissociation (i.e., transfer from the chemical to the VDW bond, followed by dissociation) was found to have a negative temperature dependence, in qualitative agreement with experiment. However, Ewing noted that stabilization of the complex occurs only at very high pressures, and consequently he concluded that complexes do not play a significant role in vibrational relaxation under normal laboratory conditions.

We have re-examined Ewing's argument and conclude that he was overly pessimistic. It is true that very high pressures are required to obtain a stabilized, equilibrium concentration of complexes. In this limit the effective rate constant is independent of pressure. However, it is also true that at low pressures metastable complexes also can lead to a pressure independent rate constant. Consider the following "energy transfer model" of complex formation and decay:



Here  $k_c$  is the capture rate constant,  $k_r$  is the rate of dissociation back into the original reactants, and  $k_p^*$  is the rate of vibrational predissociation of the metastable complex. If the pressure is high enough, collision with bath molecule M stabilizes the complex at the gas kinetic rate  $k_s[M]$ . The rate of vibrational predissociation of the stabilized complex is denoted by  $k_p$ .

Assuming a steady state concentration of A-B<sup>†\*</sup> and A-B<sup>†</sup>, the overall relaxation rate is given by

$$\frac{d}{dt} [B] = k_{\text{eff}} [A] [B^\dagger], \quad (2)$$

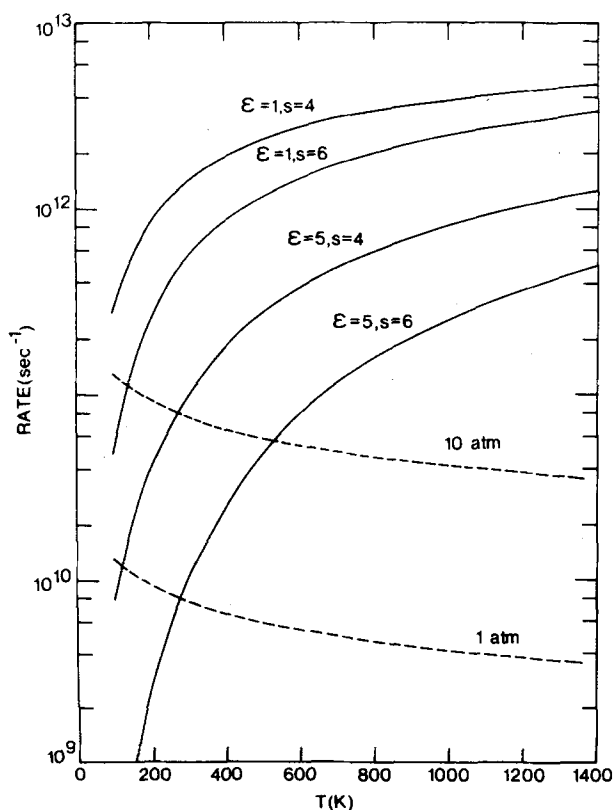


FIG. 1. Comparison of the average dissociation rate  $\langle k_r \rangle$  (solid) with the stabilization rate  $k_s[M]$  (dashed). The dissociation rate was calculated with the RRK theory for well depths  $\epsilon = 1$  and 5 kcal/mole and  $s = 4$  or 6 oscillators. The stabilization rate was calculated assuming a gas kinetic rate constant.

where  $k_{\text{eff}}$  is the effective bimolecular rate constant. We consider three pressure ranges: (i) For  $k_s[M] \gg k_p$ ,

$$k_{\text{eff}} = k_c k_p k_s / [k_p k_s + (k_p^* + k_r) k_s] \quad (3)$$

For  $k_r \gg k_p^*$  and  $k_r k_s \gg k_p k_s$ ,  $k_{\text{eff}}$  is the same as Ewing's high pressure limit. (ii) For  $k_s[M] \ll k_p$ , we obtain the pressure dependent result

$$k_{\text{eff}} = \frac{k_c k_s [M]}{k_r + k_p^*} + \frac{k_c k_p^*}{k_r + k_p^* + k_s [M]} \quad (4)$$

(iii) Finally, for  $k_s[M] \ll k_r + k_p^*$ , we obtain the single collision rate constant

$$k_{\text{eff}} = k_c \Gamma \quad (5)$$

where the branching ratio  $\Gamma$  is given by

$$\Gamma = \frac{k_p^*}{k_r + k_p^*} \quad (6)$$

Ewing showed that the high pressure limit has not been reached experimentally. In fact, most, if not all, experiments are conducted in the single collision limit. Using the RRK model<sup>11</sup> to estimate the complex lifetime [see Eq. (14)], we calculated the flux weighted Boltzmann average of  $k_r$ . The results for four and six effective oscillators, with VDW well depths of 1 and 5 kcal/mole, are plotted as functions of temperature in Fig. 1. Also shown in  $k_s[M]$ , assuming a stabilization rate of  $10^7 \text{ sec}^{-1}$  at 300 °K and 1 Torr. We note that

$k_s[M] > k_r$  can be achieved for polyatomic molecules at low temperatures and high pressures. Under these conditions the kinetic model predicts a pressure dependent effective rate constant. Under normal laboratory conditions, however, the single collision limit is maintained.

In the present study we examine in more detail the metastable complex model for vibrational energy transfer. In the following section a model is introduced for calculating  $k_c$ ,  $k_r$ , and  $k_p^*$ . In Sec. III the Boltzmann averaged transition probability is compared with a large body of experimental data, and in Sec. IV the validity of the model is critically examined.

## II. THE MODEL

The method used for calculating  $k_{\text{eff}}$  follows closely a model first described by Tully<sup>5</sup> for quenching of  $O(^1D)$  atoms. Consider a collision  $A + B^\dagger$  with initial velocity  $v$ , translational energy  $E$ , and impact parameter between  $b$  and  $b + db$ . The microscopic capture rate constant is given by

$$k_c(E, b) = 2\pi v P_c(E, b) b db \quad (7)$$

where  $P_c(E, b)$  is the capture opacity function (i. e., the probability of complex formation in a single collision). The total reaction cross section is given by

$$\sigma(E) = 2\pi \int_0^\infty P_c(E, b) \Gamma(E, b) b db \quad (8)$$

The macroscopic rate constant is the flux average of  $\sigma(E)$ :

$$k_{\text{eff}}(T) = \left(\frac{4}{\pi}\right)^{1/2} \alpha \int_0^\infty \sigma(E) x e^{-x} dx \quad (9)$$

where  $\alpha$  is the most probable Boltzmann velocity and  $x = E/kT$ . Finally, the thermally averaged transition probability is given by

$$P(T) = k_{\text{eff}}(T) / [(4\pi)^{1/2} \alpha d^2] \quad (10)$$

where  $d$  is the hard sphere diameter.

To complete the model it is necessary to specify  $P_c$  and  $\Gamma$ . For the capture probability we have used the Langevin<sup>12</sup> orbiting model, i. e.,

$$P_c = 1, \text{ for } b \leq b_0 \quad (11a)$$

and

$$P_c = 0, \text{ for } b > b_0 \quad (11b)$$

where  $b_0$  is the orbiting impact parameter. A steric factor could be introduced here by setting the right hand side of Eq. (11a) equal to a quantity less than unity. For an attractive potential of the form

$$V(r) = -C_m r^{-m} \quad (12)$$

the orbiting impact parameter is given by<sup>12</sup>

$$b_0 = \left(\frac{m}{m-2}\right)^{(m-2)/2m} \left(\frac{mC_m}{2E}\right)^{1/m} \quad (13)$$

Ignoring the repulsive core of the potential has little numerical effect on the capture cross section and greatly simplifies the subsequent calculations.

The branching ratio  $\Gamma$  was determined with the RRK

model assuming  $s$  classical oscillators. In evaluating  $\Gamma$  it is necessary to take into account the effect of orbital angular momentum on  $k_r$  and  $k_{p^*}$ . In one limit we assume that this effect is negligible (i. e., that the exit impact parameter is much smaller than  $b$ ). This case could arise, for example, if a large amount of orbital angular momentum were converted to rotation. In this case  $k_r$  is given by the RRK expression<sup>11</sup>

$$k_r(E) = \nu \left( \frac{E}{E + \epsilon} \right)^{s-1}, \quad (14)$$

where  $\epsilon$  is the well depth of the VDW potential, and  $\nu$  is the oscillator frequency. The predissociation rate  $k_{p^*}$  is equal to the internal conversion rate  $k_{ic}$  (i. e., the rate of converting chemical vibrational energy to vibration of the VDW bond) averaged over the vibrational states of the VDW oscillator, i. e.,

$$k_{p^*}(E) = \int_0^\epsilon k_{ic}(E, E_v) P_v(E_v) dE_v, \quad (15)$$

where  $P_v(E_v)$  is the distribution function for vibrational energy  $E_v$  in the  $s$  active modes. Expressions for  $k_{ic}$  have been given by Ewing<sup>3,9</sup> and Beswick and Jortner.<sup>10</sup> This quantity has a maximum at some internal energy  $E_{vm}$  which is due to a tradeoff between two competing factors.<sup>9</sup> At low  $E_v$ ,  $k_{ic}$  increases because of an improving Franck-Condon overlap between the bound and unbound wave functions. At high  $E_v$ ,  $k_{ic}$  decreases because of the increasing amount of vibrational energy which must be converted to translation (i. e., there is an "exponential gap" behavior). Generally,  $k_{ic}(E_v)$  is a sharply peaked function of width  $\Delta E_v$ , having a maximum value which we denote by  $\nu P_0$ . The RRK relation for the internal distribution function is

$$P_v(E_v) = (s-1) \frac{(E + \epsilon - E_v)^{s-2}}{(E + \epsilon)^{s-1}}. \quad (16)$$

Treating  $k_{ic}(E_v)$  as a delta function, we obtain for the predissociation rate

$$k_{p^*} = \nu(s-1) P_0 \Delta E_v \frac{(E + \epsilon - E_{vm})^{s-2}}{(E + \epsilon)^{s-1}}. \quad (17)$$

Finally, the branching ratio is given by

$$\Gamma(E) = \frac{(s-1) P_0 \Delta E_v (E + \epsilon - E_{vm})^{s-2}}{(s-1) P_0 \Delta E_v (E + \epsilon - E_{vm})^{s-2} + (E + \epsilon)^{s-1}}. \quad (18)$$

We refer to this result, which is independent of impact parameter, as model I.

In the other extreme, we assume that the initial and final orbital angular momenta are equal. In this case the centrifugal barrier increases the amount of internal energy needed to break the VDW bond. Let  $V_b$  be the barrier height measured with respect to the separated molecules, and let  $\epsilon_b$  be the effective well depth measured with respect to the barrier maximum. For the  $r^{-m}$  potential the barrier height is given by<sup>12</sup>

$$V_b = \left( \frac{m-2}{2m} \right) (m C_m)^{2/(2-m)} (2b^2 E)^{m/(m-2)}. \quad (19)$$

The dissociation rate of the complex is given by

$$k_r = \nu(E - V_b)^{s-1} / (E + \epsilon_b - V_b)^{s-1}. \quad (20)$$

A further consequence of the centrifugal barrier is that

effective well depth is smaller than  $\epsilon$ . Since the energy gap referred to previously is reduced, we may assume that  $E_{vm} \approx \epsilon_b$ . (See Table II of Ref. 3.) The predissociation rate is then given by

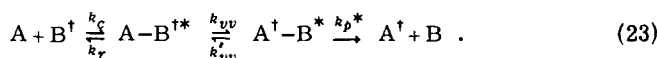
$$k_{p^*} = \nu(s-1) P_0 \Delta E_v (E - V_b)^{s-2} / (E + \epsilon - V_b)^{s-1}, \quad (21)$$

and the branching ratio is

$$\Gamma = (s-1) P_0 \Delta E_v / [(s-1) P_0 \Delta E_v + (E - V_b)]. \quad (22)$$

We refer to this limit as Model II. Note that the total cross section, given by Eqs. (8), (19), and (22), can be integrated analytically for  $m = 6$ .

A special situation arises for near-resonant  $VV$  transfer. In this case energy can be transferred between molecules A and B without predissociating the complex. An appropriate single collision mechanism then is



Assuming  $k_{vv} = k_{vv}^*$  and  $k_r = k_{p^*}$ , a steady state analysis gives, for the production of  $A^\dagger$ ,

$$\Gamma = \frac{k_{vv}}{k_r + 2k_{vv}}. \quad (24)$$

In our model we have assumed the same functional dependence for  $k_{vv}(E_v)$  as for  $k_{p^*}(E_v)$  in the predissociating case. Since there is no energy gap, we set  $E_{vm} = \epsilon$  (or  $\epsilon_b$ ).

The thermally averaged transition probability  $P(T)$  was calculated with models I and II for various values of  $s$ ,  $m$ ,  $P_0 \Delta E_v$ , and  $E_{vm}$ . In general,  $P(T)$  has a power law dependence, and can be accurately represented by the functional form

$$P(T) = AT^{-n}. \quad (25)$$

In comparing theory with experiment our procedure is to fit Eq. (25) to both the model calculations and the experimental data and then to compare the fitted parameters  $A$  and  $n$ . The dependence of the model calculation of  $n$  on  $P_0 \Delta E_v$  is shown in Fig. 2 for a typical calculation. As illustrated in the figure, the limiting value of  $n$  for small  $k_{p^*}$  is 2 for model I and  $1 + 2/m$  for model II.

### III. RESULTS

The empirical values of  $A$  and  $n$  are listed in Table I for a large number of experimental systems.<sup>13-28</sup> In selecting data for analysis, care was taken to use only low temperature points which show monotonic inverse temperature behavior. Many of the systems have normal behavior at higher temperature, where a direct mechanism is likely to prevail.

In applying the model to the data,  $P_0 \Delta E_v$  was treated as an adjustable parameter. The number of effective oscillators was assumed to be four for the diatom + diatom and diatom + linear triatom cases, and six otherwise. In model I we assumed  $E_{vm} = 0.8\epsilon$ , using either published values of  $\epsilon$  or reasonable estimates. The resulting value of  $n$  is not very sensitive to  $E_{vm}$ . In most calculations an  $r^{-6}$  potential was assumed. The  $C_6$  coefficient was calculated from dispersion and induction forces,<sup>29</sup> using published values of the dipole moments

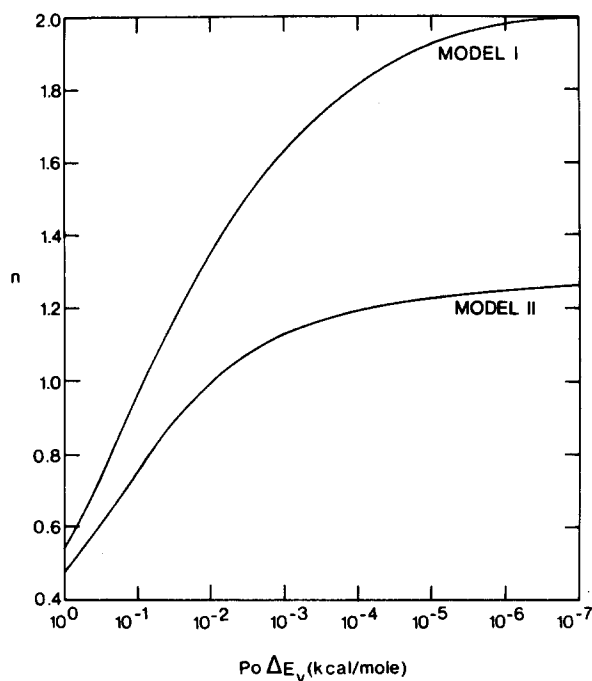


FIG. 2. Temperature exponent for VT relaxation of HCl as a function of the model parameter  $P_0 \Delta E_v$ . In model I the effect of the centrifugal barrier on dissociation is neglected, and  $\epsilon - E_{vm}$  is set at 0.13 kcal/mole. In model II the centrifugal barrier is included, and  $\epsilon - E_{vm} = 0$ .

and polarizabilities of the scattering partners. For molecules with large dipole moments an  $r^{-3}$  potential arising from the electrostatic interaction was also considered. In these cases the rms value of  $C_3$  was used. The results of model calculations for versions I and II are listed in Table I.

#### IV. DISCUSSION

As shown in Table I, the model is able to account for the large cross sections and negative temperature dependence of most of the experimental data. In most cases the experimental values of  $n$  are bracketed by the two model calculations. For the resonant processes the  $r^{-3}$  potential appears to be somewhat better, but this is probably fortuitous. There are some discrepancies between theory and experiment. For VT relaxation of HCl and HBr, and for the relaxation of ozone by water, the experimental values of  $n$  exceed the model limit of 2. Also, the model predicts that  $A$  and  $n$  are inversely correlated, whereas there appears to be a slight positive correlation between the experimental values.

There are two shortcomings of the model which may at least partially account for these discrepancies. First,  $k_c$  and  $k_r$  do not satisfy microscopic reversibility. At constant energy, microscopic reversibility implies that

$$\rho_1 k_{12} = \rho_2 k_{21},$$

where  $\rho_i$  is the density of state  $i$  and  $k_{ij}$  is the microscopic rate for the transition  $i \rightarrow j$ . In model I,  $k_c/k_r$  varies as  $E^{3/2-2/m-s}(E+\epsilon)^{s-1}$ , whereas the ratio of state densities varies as  $E^{1/2}(E+\epsilon)^{s-1}$ . It is implicitly as-

sumed in the model that a compensating error in  $k_p^*$  results in the proper energy dependence of  $\Gamma$ .<sup>30</sup>

A second shortcoming of the theory is the assumption of a Langevin capture cross section. Although the orbiting model has been used extensively for ion-molecule reactions, there is insufficient reason to believe that it holds for neutral collisions. The calculations of Billing and Poulsen<sup>4(b)</sup> for  $\text{HF}^+ + \text{HF}$  show that the fraction of orbiting collisions at translational energies between 200 and 4000  $\text{cm}^{-1}$  varies approximately as  $E^{-1}$ . They also point out that even at the lowest energies a significant part of the relaxation rate is due to direct collisions. In a trajectory study of  $\text{H}^+ + \text{D}_2$ , Gerlich *et al.*<sup>31</sup> found that the Langevin model breaks down. They obtained a capture cross section of the form  $\sigma_0 \exp(-E/E_0)$  for translational energy  $E$  between 0.1 and 2.0 eV.

Recently, Parmenter and Seaver<sup>32</sup> and Gordon<sup>33</sup> pointed out that the negative temperature dependence of the transition probability can be expressed in the form

$$P(T) = A \exp(\epsilon'/kT), \quad (26)$$

where  $\epsilon'$  is related to the strength of the attractive potential.<sup>34</sup> Moreover, they found that  $\epsilon'$  is the same for different processes occurring on a single potential energy surface (e.g., VV transfer, VT transfer, and energy exchange between different isotopic species), whereas  $A$  is process specific. An appealing interpretation of this observation is that the temperature dependence of  $P(T)$  is governed by the capture cross section, while  $A$  is determined by the branching ratio for the specific process of interest. In contrast, the present model predicts a power law dependence [Eq. (25)], with  $n$  tending to be larger for VT relaxation. Most experimental data are of insufficient quality to distinguish between the two functional forms. The very precise measurements by Horwitz and Leone<sup>14</sup> of isotopic VV transfer in HCl are somewhat better described by Eq. (25), but this is insufficient for choosing in general between the two functional forms.

A possible way of reconciling the present model with the observations of Parmenter and Seaver and Gordon is based on argument presented by Lin *et al.*<sup>35</sup> Suppose we take the thermal averages of  $k_c$ ,  $k_r$ , and  $k_p^*$  independently. The number density of complexes may be estimated by assuming that a complex forms whenever A and B<sup>†</sup> come within some critical distance  $r_c$  of each other. The density of molecules suffering such encounters is given by

$$[A-B^{\dagger*}] = [A][B^{\dagger}] \int_0^{r_c} 2\pi g(r) r^2 dr, \quad (27)$$

where  $g(r)$  is the pair correlation function.<sup>29</sup> For a square well potential the integral has the value  $(1/3)r_c^3 \times \exp(\epsilon'/kT)$ . However, from Reaction (1a),

$$[A-B^{\dagger*}] = [A][B^{\dagger}] k_c / (k_r + k_p^*), \quad (28)$$

and

$$k_{\text{eff}}(T) = k_c(T) \Gamma(T) = \frac{2}{3} \pi r_c^3 \exp(\epsilon'/kT) k_p^*(T). \quad (29)$$

The temperature dependence of  $k_{\text{eff}}(T)$  in Eq. (29) is

TABLE I. Comparison of experimental and theoretical rates.

System	Experimental parameters		Model I <sup>a</sup>		Model II <sup>a</sup>		References
	A	n	$P_0 \Delta E_v$ (kcal/mole)	n	$P_0 \Delta E_v$ (kcal/mole)	n	
Resonant VV transfer <sup>b</sup>							
DF	172	1.26 ± 0.05	1.7 - 2 <sup>c</sup> (4.3 - 3)	1.14 1.51	5.8 - 3	1.03	13
HCl <sup>d</sup>	976	1.64 ± 0.03	6.0 - 3 (6.4 - 3)	1.18 1.44	2.0 - 3	1.07	14
HCl	64.5	1.37 ± 0.05	1.5 - 3 (1.6 - 3)	1.27 1.54	3.9 - 4	1.15	15
HBr	112	1.38 ± 0.05	2.6 - 3 (4.8 - 3)	1.25 1.48	7.1 - 4	1.13	15
CO	2.68	0.89 ± 0.06	1.9 - 3	1.24	5.3 - 4	1.12	16
Nonresonant self-relaxation							
HF	139	1.65 ± 0.07	2.5 - 5 (3.8 - 7)	1.90 1.99	2.0 - 4	1.19	17
DF	80.5	1.77 ± 0.12	3.2 - 6 (2.7 - 8)	1.95 1.99	4.9 - 5	1.21	17
HCl	2.1 + 4	3.48 ± 0.05	5.1 - 8 (1.2 - 9)	1.99 2.00	1.3 - 6	1.24	18
HBr	91.7	2.48 ± 0.05	2.8 - 8 (1.5 - 9)	1.99 2.00	8.0 - 6	1.24	18
NO	0.66	1.43 ± 0.12	7.5 - 8	1.99	2.6 - 6	1.23	19
H <sub>2</sub> O (2ν <sub>2</sub> )	0.71	1.27 ± 0.16	1.4 - 3 (4.1 - 5)	1.52 1.85	1.0 - 2	0.96	20
H <sub>2</sub> O (ν <sub>1</sub> ν <sub>3</sub> )	1225	1.60 ± 0.44	5.8 - 5 (3.6 - 7)	1.79 1.95	1.4 - 3	1.09	20
NH <sub>3</sub> (ν <sub>2</sub> )	288	1.35 ± 0.08	9.0 - 5 (5.5 - 6)	1.76 1.91	1.7 - 3	1.08	20
HCN (ν <sub>1</sub> )	118	1.64 ± 0.11	1.1 - 5 (1.1 - 5)	1.92 1.92	9.0 - 5	1.20	21
CO <sub>2</sub> (ν <sub>1</sub> )	0.23	1.64 ± 0.19	<10 <sup>-10</sup>	2.00	2.2 - 7	1.25	22
N <sub>2</sub> O (ν <sub>1</sub> )	0.83	1.77	<10 <sup>-10</sup>	2.00	2.5 - 7	1.25	23
BF <sub>3</sub>	10.1	1.52 ± 0.07	1.1 - 8	1.98	1.8 - 5	1.21	24
CF <sub>3</sub> H	0.064	0.92 ± 0.07	<10 <sup>-10</sup>	2.00	2.4 - 6	1.23	25
Mixed systems							
HF <sup>†</sup> + CO <sub>2</sub>	38.9	1.51 ± 0.26	5.9 - 5	1.86	1.3 - 4	1.19	17
DF <sup>†</sup> + CO <sub>2</sub>	19.3	1.15 ± 0.24	5.2 - 4	1.71	7.2 - 4	1.15	17
CO <sub>2</sub> <sup>‡</sup> + HF	6.1	1.23 ± 0.06	4.8 - 5	1.88	1.0 - 4	1.20	17
CO <sub>2</sub> <sup>‡</sup> + DF	0.49	0.90 ± 0.07	2.0 - 5	1.92	5.6 - 5	1.21	17
HCl <sup>†</sup> + CO <sub>2</sub>	2.1	0.87 ± 0.09	3.7 - 4	1.69	2.8 - 4	1.18	26
HF <sup>†</sup> + HCN	175	1.55 ± 0.13	5.8 - 5	1.86	3.7 - 4	1.16	21
DF <sup>†</sup> + HCN	181	1.63 ± 0.17	2.7 - 5	1.89	2.2 - 4	1.18	21
HCN <sup>†</sup> + HF	34.2	1.53 ± 0.13	4.0 - 6	1.94	6.2 - 5	1.20	21
HCN <sup>†</sup> + DF	23.1	1.47 ± 0.17	3.6 - 6	1.95	5.8 - 5	1.20	21
O <sub>3</sub> <sup>‡</sup> + HCl	1.76	1.06 ± 0.05	1.2 - 6	1.96	4.8 - 5	1.19	27
O <sub>3</sub> <sup>‡</sup> + H <sub>2</sub> O	3.8 + 4	2.6 ± 0.3	1.8 - 7	1.96	7.8 - 5	1.19	28
O <sub>3</sub> <sup>‡</sup> + D <sub>2</sub> O	3.8 + 4	2.3 ± 0.4	3.1 - 5	1.87	2.3 - 3	1.26	28

<sup>a</sup>Quantities in parentheses were calculated with an  $r^{-3}$  potential. The rest were calculated with an  $r^{-6}$  potential.

<sup>b</sup>Relaxation is of the type  $2\text{CO}(v=1) \rightarrow \text{CO}(v=2) + \text{CO}(v=1)$  except where noted otherwise.

<sup>c</sup>1.7 - 2 means  $1.7 \times 10^{-2}$ .

<sup>d</sup>Resonant isotopic vibrational energy transfer.

dominated by the exponential factor. This argument is of course only heuristic, and an explicit dynamic justification is still required.

Finally, it is interesting to examine the role of complexes in radical reactions. The experimental reaction probabilities at low temperatures can be fitted to Eq. (25), with  $n$  generally less than 2. The most extreme cases we are aware of are S + tetramethylethylene<sup>36</sup> with  $n = 2.28$  and ClO + HO<sub>2</sub> (Ref. 37) with  $n = 3.06$ . In the single collision limit, the branching ratio in readily evaluated with the RRK formalism. Let us suppose that in general there is a potential energy barrier  $\Delta E_r$  in the reactant channel and  $\Delta E_p$  in the exit channel, both measured with respect to the zero point energy of the reactants. (Note that  $\Delta E_r > 0$ , while  $\Delta E_p$  may be negative.) Ignoring angular momentum effects, the branching ratio is

$$\Gamma = \frac{(E + E_i - \Delta E_p)^{s-1}}{(E + E_i - \Delta E_r)^{s-1} + (E + E_i - \Delta E_p)^{s-1}}, \quad (30)$$

where  $E_i$  is the internal energy of the reactants before collision. For  $\Delta E_r = 0$  and  $\Delta E_p < 0$ ,  $\Gamma$  is only weakly energy dependent, and the temperature dependence of  $k_{eff}$  is dominated by the capture rate. Further reflection, however, indicates that the single collision description is inappropriate here. The deep potential wells and large number of effective oscillators in these reactions result in much longer-lived complexes, which are readily stabilized by collisions.<sup>38</sup> The negative temperature dependence of  $P(T)$ , therefore, stems from the equilibrium concentration of complexes in the high pressure limit, and an exponential temperature dependence results.

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