

# Adiabatic invariance treatment of hitting collisions between ions and symmetrical top dipolar molecules

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The adiabatic invariance method of calculating the rate coefficient  $k_D(J,K)$  for hitting collisions between ions and symmetrical top dipolar molecules in level  $(J,K)$  is formulated. The rate coefficient for a particular quantum level does not depend on the rotational constant  $A$  of the symmetrical top molecule. This facilitates parametrization of the results.

Representative results on  $\text{NH}_3$  and  $\text{CH}_3\text{F}$  including the thermal average  $\bar{k}_D$  are presented. A formula that Su and Chesnavich obtained for linear molecules reproduces  $\bar{k}_D$  for  $\text{NH}_3$  and  $\text{CH}_3\text{F}$  quite well. Measured rate coefficients  $k_r$  for reactive collisions between several species of ion and  $\text{NH}_3$  yield collision efficiencies  $k_r/\bar{k}_D$  that are rather less than unity and temperature independent in the low temperature region. Corresponding results involving  $\text{H}_2\text{O}$  suggest that the linear molecule formula is useful even for an asymmetrical top molecule.

## I. INTRODUCTION

The rate coefficients for ion-molecule collisions, variously called hitting, intimate, close, capture, or orbiting (of which the Langevin rate coefficient is the archetype) are of interest primarily because the probability of many exothermic chemical reactions is almost unity in such collisions. Their calculation is troublesome when the interaction is non-spherical. For interactions of this type, rate coefficients have been evaluated mainly by trajectory analysis (Dugan and Magee,<sup>1</sup> Su and Chesnavich<sup>2</sup>); the average dipole orientation approximation (Su and Bowers<sup>3</sup>); the perturbed rotational states (PRS) method (Takayanagi<sup>4</sup> and Sakimoto<sup>5</sup>); variational rate theory (Chesnavich *et al.*<sup>6</sup>); an average free energy approach (Celli *et al.*<sup>7</sup>); and a quantal centrifugal sudden approximation (Clary<sup>8</sup>).

We are here concerned with the adiabatic invariance method proposed by Bates<sup>9</sup> and skillfully developed by Sakimoto<sup>10</sup> who applied it to linear dipole molecules and showed that it gives good agreement with the more elaborate perturbed rotational states method. Bates and Mendaš<sup>11</sup> have applied it to linear quadrupolar molecules. We shall use the method to treat symmetrical top dipolar molecules.

## II. THEORY

Denote the two equal moments of inertia of the symmetric top molecule by  $I_B$  and the third moment of inertia by  $I_A$  and let  $(\theta, \phi, \psi)$  be the Eulerian angles. The kinetic energy of rotation is then

$$T = 1/2I_B [\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta] + 1/2I_A [\dot{\psi} + \dot{\phi} \cos \theta]^2 \quad (1)$$

(cf. Landau and Lifshitz<sup>12</sup>). The conjugate momenta indicated by the subscripts are

$$p_\theta = I_B \dot{\theta}, \quad (2)$$

$$p_\phi = (I_A \cos^2 \theta + I_B \sin^2 \theta) \dot{\phi} + (I_A \cos \theta) \dot{\psi} = m\hbar \quad (\text{say}), \quad (3)$$

$$p_\psi = I_A (\dot{\psi} + \dot{\phi} \cos \theta) = K\hbar \quad (\text{say}), \quad (4)$$

in which  $m$  and  $K$  are constants because  $\phi$  and  $\psi$  are cyclic coordinates. Combination of Eqs. (1)–(4) yields

$$T = \left[ \frac{Bp_\theta^2}{\hbar^2} + \frac{B(m - K \cos \theta)^2}{\sin^2 \theta} + AK^2 \right], \quad (5)$$

where

$$A \equiv \hbar^2/2I_A \quad \text{and} \quad B \equiv \hbar^2/2I_B \quad (6)$$

are the rotational constants of the molecule. Following Sakimoto,<sup>10</sup> the effective contribution to the potential of the angular part of the field is  $[E(r) - E(\infty)]$  in which  $E(r)$  is the energy of the molecule in this part. The permanent dipole moment  $D$  lies along the axis of symmetry so that if an ion of charge is distance  $r$  away,

$$E(r) = T + De \cos \theta / r^2. \quad (7)$$

It is convenient to change the variable  $r$  to the dimensionless  $x$ , where

$$Dex^2 \equiv Br^2, \quad (8)$$

to introduce

$$v(x) \equiv [E(r) - E(\infty)]/B \quad (9)$$

and to put

$$\cos \theta \equiv \rho. \quad (10)$$

Taking<sup>13</sup>

$$E(\infty) = B(J + 1/2)^2 + (A - B)K^2, \quad (11)$$

we find from Eqs. (5) and (7) that

$$p_\theta = h \left[ v(x) + (J + 1/2)^2 - K^2 - \rho x^{-2} - \frac{(m - k\rho)^2}{1 - \rho^2} \right]^{1/2}. \quad (12)$$

The adiabatic invariance method of determining  $v(x)$  exploits the result that

$$I = 1/\pi \int p_\theta d\theta \quad (13)$$

is a constant of the motion, the integration involved being carried out over accessible  $\theta$ , that is, over all  $\theta$  when the axis of the molecule rotates and over the range in which  $p_\theta$  is real when the axis librates. Equation (13) may with advantage be written

$$I = \frac{\hbar}{x\pi} \int \frac{[f(\rho)]^{1/2} d\rho}{1 - \rho^2} \quad (14)$$

with

$$f(\rho) \equiv \rho^3 - \rho^2 x^2 [v(x) + (J + 1/2)^2] - \rho [1 - 2mKx^2] + x^2 [v(x) + (J + 1/2)^2 - (m^2 + K^2)]. \quad (15)$$

The evaluation of  $I$  from Eq. (14) in the  $x \rightarrow \infty$  limit is simple. Letting  $|l|$  be the larger of  $|K|$  and  $|m|$ , we obtain

$$I/\hbar = J + 1/2 - |l|. \quad (16)$$

On writing Eq. (15) in the form

$$f(\rho) = (\rho - a)(\rho - b)(\rho - c) \quad (17)$$

with

$$a > b > c, \quad (18)$$

the integral involved for finite  $x$  may be expressed in terms of the complete elliptic integrals of the first, second, and third kinds (for which we adopt the notation of Milne-Thomson<sup>14</sup>). From the derived expression for  $I/\hbar$  and Eq. (16), we get that

$$v(x) = \pi(J + 1/2 - |l|)(a - c)^{1/2}/2xK(q) - (a - c)E(q)/x^2K(q) - \{(J + 1/2)^2 - ax^{-2}\} + \left[ \frac{(m - K)^2}{1 - c} \Pi(p_1, q) + \frac{(m + K)^2}{1 + c} \Pi(p_2, q) \right] / 2K(q), \quad (19)$$

in which

$$q = (b - c)/(a - c), \quad p_1 = (b - c)/(1 - c), \quad p_2 = (c - b)/(1 + c). \quad (20)$$

Equation (19) allows  $v(x)$  to be computed by an iterative procedure. Computation of  $dv/dx$  must also be performed. Differentiation of Eq. (13) with respect to  $x$  and use of Leibnitz's rule gives, after some reduction,

$$\frac{dv}{dx} = 2x^{-3} [(a - c)E(q)/K(q) - a]. \quad (21)$$

Unexpectedly, Eq. (21) is identical with the corresponding relation for the case of a linear molecule (obtained in the

same way by Sakimoto). Observe that Eq. (19) also applies to linear molecules if we take  $K = 0$  throughout.

Introducing the contribution from the ion-induced dipole interaction for a molecule of polarizability  $\alpha$  and the centrifugal term for impact parameter  $b$ , in units  $(De/B)^{1/2}$ , in units  $B$ , we have that the effective potential is

$$V_{\text{eff}} = -Px^{-4} + \eta b^2 x^{-2} + v(x) \quad (22)$$

with

$$P \equiv \alpha B / 2D^2. \quad (23)$$

Equation (22) shows that  $V_{\text{eff}}$  does not depend on the value of the rotational constant  $A$  of the symmetrical top molecule. Hence, neither does the hitting collision rate coefficient for a particular quantum state. This curious lack of dependence on  $A$  facilitates the presentation of some of the results.

The usual equation determining the separation at the maximum of  $V_{\text{eff}}$  gives

$$\eta b^2 = 2Px^{-2} + \frac{1}{2} x^3 \frac{dv}{dx}. \quad (24)$$

The energy of relative motion, which is just enough to enable the maximum to be traversed, is

$$\eta = V_{\text{eff}} + \frac{x}{2} \frac{dV_{\text{eff}}}{dx} \quad (25)$$

$$= Px^{-4} + \frac{x}{2} \frac{dv}{dx} + v(x). \quad (26)$$

The cross section  $\pi b^2$  for hitting collisions between ions and polar symmetrical top molecules at energy of relative motion  $\eta$  may be computed from Eq. (24), having first computed  $x$  as a function of  $\eta$  from Eq. (26) by inverse interpolation. Instead of giving the rate coefficient  $k_D$  for hitting collisions, it is neater to give the ratio  $k_D/k_L$ , where, if  $\mu$  is the ion-molecule reduced mass,

$$k_L = 2\pi(\alpha e^2/\mu)^{1/2} \quad (27)$$

is the Langevin rate coefficient.<sup>15,16</sup> we find that

$$k_D/k_L = [B^3/\pi P(kT)^3]^{1/2} \int \eta b^2 \times \exp(-\eta B/kT) d\eta, \quad (28)$$

$T$  being the temperature. It may be noted that Eq. (27) may be written

$$k_L = 2.34 \times 10^{-9} \tilde{\alpha}^{1/2} \tilde{\mu}^{-1/2} \text{ cm}^3/\text{s}, \quad (29)$$

the tilde over  $\alpha$  and  $\mu$  indicating that these quantities are here in the usual practical units ( $10^{-24} \text{ cm}^3$  and amu, respectively).

### III. RESULTS AND DISCUSSION

Calculations have been carried out on collisions between ions and the symmetrical top molecules  $\text{NH}_3$  and  $\text{CH}_3\text{F}$  taking the molecular constants to be as in Table I. Representative results for the two molecules are presented in Tables II and III for the same value of the parameter

TABLE I. Molecular constants.

Species	Rotational constants		Polarizability (Ref. 17) $\alpha$ ( $10^{-24}$ cm <sup>3</sup> )	Dipole moment (Ref. 17) $D$ ( $10^{-18}$ esu)
	$A$	$B$ (cm <sup>-1</sup> )		
NH <sub>3</sub>	6.196	9.443 (Ref. 18)	2.26	1.47
CH <sub>3</sub> F	5.10	0.8496 (Ref. 17)	2.97	1.85

$$\xi \equiv D / (2\alpha kT)^{1/2}. \quad (30)$$

The entries show that  $k_D(J, K)$  at fixed  $K$  decreases as  $J$  is increased and at fixed  $J$  increases as  $K$  is increased. Both variations are more pronounced for NH<sub>3</sub> than for CH<sub>3</sub>F because the rotational constant  $B$  is much larger for the former than for the latter. As already noted, the rotational constant  $A$  does not affect the hitting cross sections and rate coefficients.

### A. Thermal average rate coefficients

For many purposes, the entity of interest is the thermal average

$$\begin{aligned} \bar{k}_D = & \left\{ \sum_{J,K=3n} \omega(J,K) k_D(J,K) \right. \\ & \times \exp[-E(J,K)/kT] \Big\} / Q_q(T) \\ & + \left\{ \sum_{J,K \neq 3n} \omega(J,K) k_D(J,K) \right. \\ & \times \exp[-\{E(J,K) - E(1,1)\}/kT] \Big\} / Q_d(T), \end{aligned} \quad (31)$$

TABLE II. Ratio  $k_D(J, K)/k_L$  for NH<sub>3</sub>. Parameter  $\xi$  is defined by Eq. (30) or (A7) and  $T$  is in K.

$\xi =$	16	14	12	10	8	6	4
$T =$	13.5	17.6	23.9	34.6	53.8	96.0	215
$J K$	$k_D(J, K)/k_L$						
0 0	10.7	10.1	9.33	8.44	7.40	6.17	4.73
1 0	4.76	4.76	4.75	4.69	4.55	4.25	3.68
1 1	6.64	6.34	6.02	5.67	5.26	4.71	3.93
2 0	2.59	2.67	2.76	2.86	2.94	2.97	2.85
2 1	3.62	3.51	3.42	3.36	3.30	3.21	2.98
2 2	6.40	5.95	5.49	5.02	4.52	3.96	3.27
3 0	1.66	1.73	1.83	1.94	2.07	2.19	2.25
3 1	2.41	2.35	2.30	2.29	2.31	2.34	2.34
3 2	4.22	3.95	3.68	3.42	3.18	2.92	2.62
3 3	5.84	5.40	4.95	4.50	4.05	3.57	3.02
4 0	1.33	1.37	1.43	1.50	1.60	1.73	1.85
4 1	1.82	1.77	1.73	1.73	1.75	1.82	1.90
4 2	2.97	2.75	2.55	2.36	2.22	2.12	2.07
4 3	4.22	3.87	3.52	3.18	2.86	2.58	2.34
4 4	5.45	4.97	4.49	4.01	3.55	3.10	2.68
5 0	1.09	1.12	1.17	1.23	1.31	1.42	1.56
5 1	1.47	1.43	1.40	1.40	1.43	1.49	1.60
5 2	2.37	2.20	2.03	1.89	1.77	1.72	1.72
5 3	3.36	3.08	2.80	2.53	2.27	2.06	1.92
5 4	4.35	3.97	3.57	3.19	2.82	2.47	2.18
5 5	5.32	4.83	4.34	3.85	3.37	2.90	2.48

in which  $\omega(J, K)$  is the statistical weight,<sup>13</sup>  $E(J, K)$  is the energy of the  $(J, K)$  level, and  $Q_q(T)$  and  $Q_d(T)$  are rotational partition functions of the nuclear spin quartets and doublets, respectively. Thermal averages for NH<sub>3</sub> and CH<sub>3</sub>F have been obtained, the summations over  $J$  in the numerators of Eq. (31) being truncated beyond  $J = 10$  and  $J = 23$ , respectively (which at the higher temperatures may cause an error 3%–5%). For a given  $\xi$ , the difference between the values for NH<sub>3</sub> and CH<sub>3</sub>F is quite small.

Su and Cheshavich<sup>2</sup> have found that the results of their trajectory calculations on the rate coefficients for collisions between ions and linear dipolar molecules may be represented by

$$k_D/k_L = 0.4767\xi + 0.6200, \quad \xi \geq 2. \quad (32)$$

As may be seen from Table IV, this equation fits our results on symmetrical top polar molecules satisfactorily, as Sakimoto<sup>19</sup> has observed, it fits his corresponding PRS results. The excellence of the fit is unexpected in view of  $k_D(J, K)$  at fixed  $J$  increasing as  $K$  is increased and is certainly partly fortuitous. At very low temperatures, the fit is rather better for CH<sub>3</sub>F than it is for NH<sub>3</sub>, probably mainly because the lower rotational constants ensure that a larger number of rotational levels contribute appreciably to the rate coefficient.

TABLE III. Ratio  $k_D(J, K)/k_L$  for CH<sub>3</sub>F. Parameter  $\xi$  is defined by Eq. (30) or (A7) and  $T$  is in K.

$\xi =$	16	14	12	10	8	6	4
$T =$	16.3	21.3	29.0	41.8	65.3	116	261
$J K$	$k_D(J, K)/k_L$						
0 0	16.8	15.1	13.4	11.6	9.71	7.81	5.87
1 0	12.8	12.0	10.9	9.79	8.49	7.04	5.46
1 1	13.7	12.7	11.5	10.2	8.78	7.23	5.56
2 0	9.66	9.29	8.79	8.13	7.30	6.27	5.04
2 1	10.1	9.68	9.09	8.36	7.46	6.38	5.10
2 2	11.6	10.9	10.0	9.06	7.96	6.70	5.27
3 0	7.39	7.56	7.30	6.92	6.39	5.42	4.40
3 1	7.72	7.56	7.30	6.92	6.39	5.65	4.68
3 2	8.56	8.11	7.60	6.99	6.27	5.42	4.40
3 3	9.94	9.29	8.57	7.75	6.83	5.79	4.61
4 0	5.82	5.85	5.82	5.69	5.43	4.97	4.28
4 1	6.04	6.03	5.96	5.80	5.50	5.02	4.31
4 2	6.71	6.57	6.38	6.12	5.73	5.18	4.40
4 3	7.76	7.44	7.08	6.65	6.12	5.43	4.54
4 4	9.06	8.54	7.99	7.37	6.65	5.79	4.75
5 0	4.70	4.78	4.84	4.83	4.72	4.45	3.95
5 1	4.86	4.92	4.94	4.91	4.78	4.49	3.95
5 2	5.37	5.33	5.26	5.15	4.95	4.60	4.04
5 3	6.18	5.99	5.79	5.56	5.24	4.80	4.15
5 4	7.20	6.85	6.49	6.10	5.65	5.07	4.31
5 5	8.31	7.82	7.31	6.76	6.15	5.42	4.51

TABLE IV. Thermal average  $\bar{k}_D/k_L$  for  $\text{NH}_3$  and  $\text{CH}_3\text{F}$  as calculated by adiabatic invariance methods and for linear dipolar molecules as given by the parametric formula (32) of Su and Chesnavich (Ref. 2).

$\xi$	$\text{NH}_3$		$\text{CH}_3\text{F}$		Linear $\bar{k}_D/k_L$
	$T(\text{K})$	$\bar{k}_D/k_L$	$T(\text{K})$	$\bar{k}_D/k_L$	
4	215	2.39 [2.50] <sup>a</sup>	261	2.55	2.53
6	96	3.35 [3.33]	116	3.60	3.48
8	54	4.33 [4.14]	65.3	4.62	4.43
10	34.6	5.33 [4.74]	41.8	5.66	5.39
12	24.0	6.36 [5.12]	29.0	6.72	6.34
14	17.6	7.44 [5.36]	21.3	7.78	7.29
16	13.5	8.52 [5.55]	16.3	8.84	8.25

<sup>a</sup>The entries in brackets refer to the fictitious planar  $\text{NH}_3$  molecule.

cients. In consequence, the influence of the distinctive statistical weight difference between symmetrical top and linear molecules is less marked. To illustrate the effect of the low rotational levels we obtained the thermal average for the fictitious planar  $\text{NH}_3$  system. The results are given in Table IV. Note that in the low temperature limit, half of normal  $\text{NH}_3$  is in (0,0) and half is in (1,1), these being the lowest quartet and doublet levels. While the (1,1) level is also the lowest doublet for planar  $\text{NH}_3$ , the (0,0) level does not occur and (1,0) is the lowest quartet.

As already noted the specific ( $J,K$ ) rate coefficients are independent of  $A$ , but because the energy depends on  $A$  so do the thermal averages. This is shown in Fig. 1. The linear

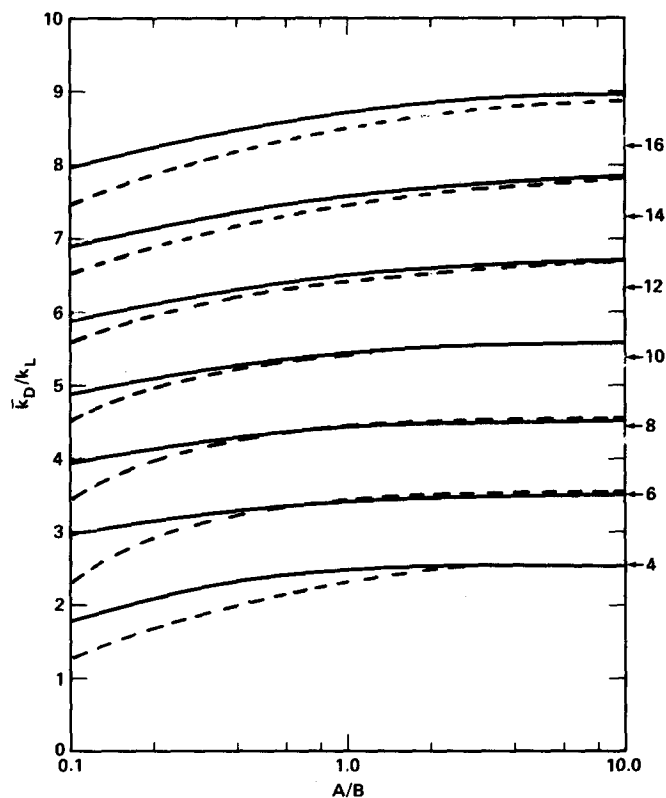


FIG. 1. Thermal average rate coefficients using  $B$ ,  $\alpha$ , and  $D$  for  $\text{NH}_3$  (solid curve) and  $\text{CH}_3\text{F}$  (dashed curve) and varying rotational constant  $A$ . These are plotted parametric in  $\xi = D/(2\alpha kT)^{1/2}$  with the value of  $\xi$  and  $\bar{k}_D/k_L$  from Eq. (32) shown along the right-hand axis of the graph.

TABLE V. Collision efficiencies  $k_r/\bar{k}_D$  deduced from reaction rates  $k_r$  of Marquette *et al.* (Ref. 20) and calculated values of  $\bar{k}_D/k_L$ .

Reaction	163 K	68 K	27 K
$\text{He}^+ + \text{NH}_3$	...	0.39	0.38
$\text{C}^+ + \text{NH}_3$	...	0.62	0.57
$\text{N}^+ + \text{NH}_3$	0.38	0.65	0.68
$\text{He}^+ + \text{H}_2\text{O}$	...	0.18	0.29
$\text{C}^+ + \text{H}_2\text{O}$	...	0.76	1.2
$\text{N}^+ + \text{H}_2\text{O}$	0.90	0.93	1.04

molecule corresponds to  $A$  infinite and at the higher temperatures, where the statistical weight effect is unimportant, there is virtually perfect agreement between the linear molecule results of Su and Chesnavich and our results for  $A$  large. The dependence on  $A$  is rather slight in the region  $A > B$  as shown in Fig. 1, but for  $A < B$  it is quite pronounced. This should be born in mind when using formula (32).

## B. Comparison with measured rate coefficients

Marquette *et al.*<sup>20</sup> have used their CRESU technique to determine the rate coefficients  $k_r$  for reactive collisions between  $\text{He}^+$ ,  $\text{C}^+$ , and  $\text{N}^+$  ions and  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules. Their results expressed as the collision efficiency  $k_r/\bar{k}_D$  are given in Table V. The value of  $\bar{k}_D/k_L$  was obtained from our adiabatic invariance calculations in the  $\text{NH}_3$  case. It was obtained from Eq. (32) for the  $\text{H}_2\text{O}$  case to test whether this relation has any validity when the dipolar molecule is an asymmetric top. The rotational constant  $B$  was taken to be the geometrical mean of the rotational constants associated with the two principal axes perpendicular to the axis of the dipole yielding  $A/B = 0.9$ . It is satisfactory that the  $\text{NH}_3$  collision efficiencies are less than unity and for each species of ion are effectively the same at the two lower temperatures. The  $\text{H}_2\text{O}$  results suggest that Eq. (32) is useful even for asymmetric top dipolar molecules. There is need, however, for further experimental data.

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## APPENDIX: PARAMETRIZATION OF RESULTS FOR SMALL $J$

In connection with interstellar cloud chemistry, it is of interest to have general results for the low rotational levels. Fortunately  $k_D(J,0)$  is identical with  $k_D(J)$  for the linear molecule with the same  $B$ ,  $D$ , and  $\alpha$ . Morgan and Bates<sup>21</sup> have already parametrized  $k_D(J)$  for  $J = 0, 1, 2$  and the corresponding cross sections. The absence of a dependence on the rotational constant  $A$  makes a similar parametrization for  $K \neq 0$  feasible.

For the sake of accuracy in fitting cross sections and rate coefficients, calculations were performed at 400 values of the

TABLE VI. Fitting coefficients for cross sections. The notation  $(-n)$  means  $\times 10^{-n}$ .

$J = 1, K = 1, y_0 = 3$					
a:	9.142(-1)	-8.663(-2)	4.527(-2)	-6.714(-3)	3.190(-4)
b:	2.767(-1)	-7.197(-2)	2.323(-3)	7.734(-4)	-5.746(-5)
$J = 2, K = 1, y_0 = 3$					
a:	8.223(-1)	-1.484(-1)	5.928(-2)	-6.628(-3)	2.330(-4)
b:	1.327(-1)	1.285(-2)	-1.051(-2)	1.140(-3)	-3.324(-5)
$J = 2, K = 2, y_0 = 3$					
a:	8.049(-1)	7.743(-2)	-2.903(-2)	5.159(-3)	-2.938(-4)
b:	2.381(-1)	-5.194(-2)	8.508(-4)	5.072(-4)	-3.093(-5)

dimensionless radius  $x$ , defined by Eq. (8), on a logarithmic mesh. The cross section for each value of  $(J, m, K)$  required an average of 0.20 s, or 0.05 s per 100 mesh points, to compute on a CRAY 1 computer. The number of values of  $(J, m, K)$  for the range  $0 < J < J_{\max}$  is equal to  $(J_{\max} + 1)(J_{\max} + 2)(4J_{\max} + 3)/6$ . Test calculations have shown that rate coefficients of reasonable accuracy can be obtained using only 50 to 100 mesh points, which reduces computation time substantially.

We have performed a large number of calculations of cross section and rate coefficients for a wide range of parameters for  $(J, K) = (1, 1), (2, 1),$  and  $(2, 2)$  and have parameterized them for ease of application. For each  $(J, m)$  a set of cross sections was computed for seventeen values of  $y$  in the range  $0.35 < y < 355$ , where the dimensionless quantity  $y$  is defined by

$$y = D / (\alpha B)^{1/2} \quad (\text{A1})$$

$$= 71.0 \tilde{D} / (\tilde{\alpha} \tilde{B})^{1/2}, \quad (\text{A2})$$

where the tildes signal that  $D$ ,  $\alpha$ , and  $B$  are in  $10^{-18}$  esu,  $10^{-24}$  cm<sup>3</sup>, and cm<sup>-1</sup>, respectively. Fourteen values of  $\eta$  were then chosen with  $1 < \eta < 8200$ , the upper limit of  $\eta$  being chosen so that  $Q \approx Q_L$  at this energy, and two parameter least-square fits were made of  $Q/Q_L$  (averaged over  $m$  values for each  $J$ ) vs  $y$  for each  $\eta$ . The functional form used for the fitting is the same as that used by Su and Chesnavich<sup>2</sup> for fitting ion-polar molecule rate coefficients. If  $y = y_0$  is cho-

sen as the break point between a quadratic fit and a linear fit, then the fitting function is

$$Q(y)/Q_L = \begin{cases} a + by & y \geq y_0 \\ (y+c)^2/d + (1-c^2/d) & y < y_0 \end{cases} \quad (\text{A3})$$

Note that at  $y = y_0$ , both the fitting function and its derivative are continuous. Because of this,  $c$  and  $d$  can be expressed in terms of  $a$ ,  $b$ , and  $y_0$  as follows,

$$c = \frac{by_0^2 + 2(a-1)y_0}{2(1-a)}, \quad (\text{A4})$$

$$d = y_0^2 / (1-a). \quad (\text{A5})$$

After the cross sections were fit in this manner for each  $\eta$ , the  $a$  and  $b$  coefficients appearing in Eqs. (A3) and (A5) were then fit by a least-square quartic polynomial:

$$a(\eta), b(\eta) = \sum_{i=1}^5 p_i (\ln \eta)^{(i-1)}, \quad (\text{A6})$$

where the  $p_i$  are the polynomial coefficients shown in Table VI. The rms error in the fitting is less than 3% and the largest individual fitting errors, which occur for small  $\eta$  and small  $y$ , are less than 10%. The range of  $y$  chosen covers most symmetrical tops.

Rate coefficients were also computed and fit with the same functional forms used for the cross sections. Using the dimensionless quantities

TABLE VII. Fitting coefficients for rate coefficients. The notation  $(-n)$  means  $\times 10^{-n}$ .

$J = 1, K = 1, \xi_0 = 5$					
a:	9.637(-1)	-1.640(-1)	-7.520(-3)	1.461(-2)	-3.004(-3)
b:	4.116(-1)	1.057(-1)	-7.343(-3)	-4.235(-3)	1.226(-3)
$J = 2, K = 1, \xi_0 = 5$					
a:	2.175(-1)	-1.473(-1)	3.911(-2)	1.131(-2)	-3.662(-3)
b:	2.486(-1)	1.364(-1)	7.159(-3)	-7.605(-3)	1.702(-3)
$J = 2, K = 2, \xi_0 = 5$					
a:	4.807(-1)	3.175(-3)	-2.562(-3)	9.948(-3)	-2.887(-3)
b:	3.888(-1)	1.101(-1)	-1.504(-3)	-6.057(-3)	1.518(-3)

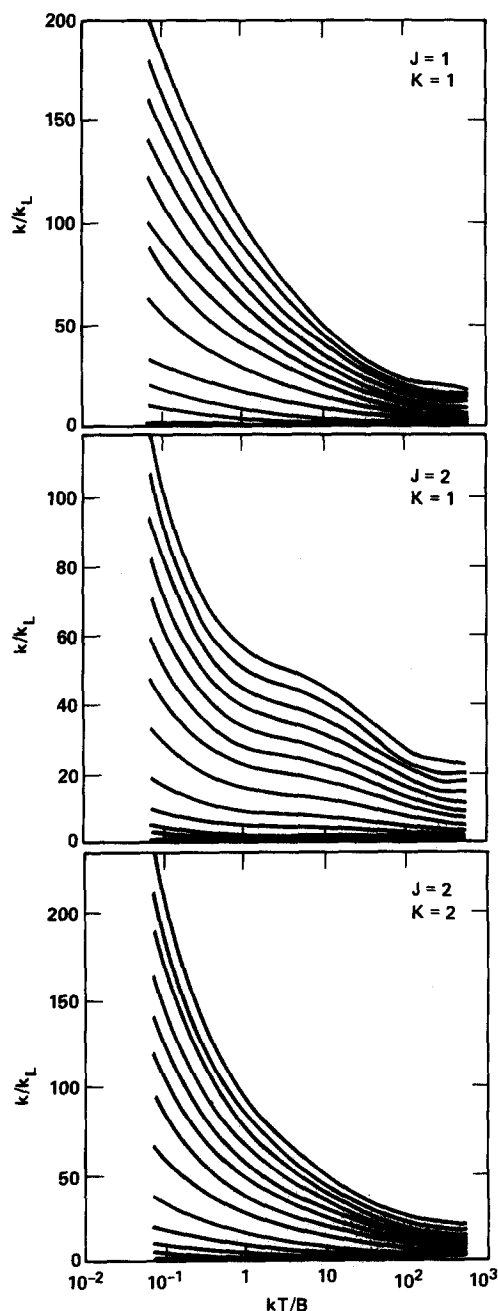


FIG. 2. Temperature dependence of rate coefficients parametric in  $y = D / (\alpha B)^{1/2}$ . Values of  $y$  shown are 2.8, 7.1, 14, 28, 57, 99, 142, 177, 213, 248, 284, 319, and 355.

$$\beta \equiv kT/B = 0.695T/\bar{B} \quad \text{and} \quad \xi \equiv 60.2\bar{D}/\bar{\alpha}^{1/2}T^{1/2}, \quad (\text{A7})$$

we were able to fit, in the same manner as we did the cross sections, the rate coefficients  $k(\xi)/k_L$  for a number of values of  $y$  with two parameters  $a$  and  $b$ . Here the break between quadratic and linear fits is at  $\xi_0$  instead of  $y_0$ . The parameters  $a(\beta)$  and  $b(\beta)$  were then fit by a quartic polynomial as in Eq. (A6) with  $\beta$  instead of  $\eta$ . The coefficients of the polynomials are tabulated in Table VII. A total of 306 values of  $k/k_L$  were used in the fitting with the temperature range defined by  $0.07 \lesssim \beta \lesssim 1000$ . The range of  $\xi$  covered, which varies with  $\beta$ , is determined by the range of  $y$ ,  $0.35 < y < 355$ , and the value of  $\beta$ . The rms fitting errors are less than 1% with the maximum individual errors being about 20% for the smallest  $\xi$  and smallest  $\beta$ . Graphs of  $k(\beta)/k_L$  parametric in  $y$  are shown in Fig. 2.

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