

## ION-DIPOLAR MOLECULE RATE COEFFICIENTS

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### ABSTRACT

Using the semiclassical adiabatic invariance method, extensive computations are performed on the cross sections and rate coefficients for hitting collisions between ions and linear polar molecules. The results are parameterized so that the cross sections and rate coefficients for any polarizability, dipole moment, reduced mass, and temperature can easily be calculated. Some computations are also performed for collisions involving symmetrical top polar molecules in low ( $J, K$ ) levels. The results show that the (1, 1) rate coefficients are rather greater than are the (1, 0) rate coefficients (which are as for a linear polar molecule), especially at low temperatures.

*Subject heading:* molecular processes

### 1. INTRODUCTION

Sakimoto (1980) and Takayanagi (1982) have observed that calculations by the perturbed rotational state (PRS) method show that the rate coefficients for hitting collisions between ions and dipolar molecules in low  $J$  levels increase rapidly as the temperature  $T$  is decreased. As they have pointed out, this is of importance for interstellar cloud chemistry because, if an exothermic reaction is possible, its probability of occurrence in a hitting collision is likely to be very high. Clary (1985) has obtained rather similar results by his combined adiabatic capture and centrifugal sudden approximation (ACCSA or, briefly, AC). Clary, Smith, and Adams (1985) have made an impressive comparison between the AC results and SIFT measurements on the reactions of ionic species with HCN and HCl in the 205–450 K range, where their agreement with the PRS results is close. Furthermore, Adams, Smith, and Clary (1985) have employed the AC approximation to obtain rate coefficients for the reactions of  $H_3^+$  with the two molecules just mentioned and also with CS and  $HC_3N$  (all in the  $J = 0$  and  $J = 1$  levels) at cool interstellar cloud temperatures.

Some use has also been made of the adiabatic invariance method proposed by Bates (1982) and skillfully developed by Sakimoto (1984), who applied it in the linear molecule case, obtaining good agreement with his PRS results (which should be reliable). Bates and Mendaš (1985) have treated the linear quadrupole molecule case. The accord with the laboratory data available is satisfactory.

The adiabatic invariance method lends itself to systematic computation. With this in mind, we (Bates and Morgan 1986) have carried through the formulation for symmetrical top dipolar molecules (which includes linear dipolar molecules as a special case).

Our main objective here is to provide a simple parameterization which would enable the hitting collision rate coefficient  $k_D$  to be found easily for any combination of an ion and a linear dipole molecule. In order to eliminate the dependence on the reduced mass  $\mu$ , we will concentrate our attention on the ratio  $k_D/k_L$ , where  $k_L$  is the Langevin rate coefficient, which,

denoting the polarizability by  $\alpha$ , is given by

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

(Eyring, Hirschfelder, and Taylor 1936; Gioumousis and Stevenson 1958). A convenient form of equation (1) is

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

with tildes over  $\alpha$  and  $\mu$  to signify that the polarizability and the reduced mass are measured in units of  $10^{-24} \text{ cm}^3$  and amu, respectively.

In order to take full advantage of the main computational effort, we also parameterized  $Q_D/Q_L$ , where  $Q_D$  and  $Q_L$  are the cross sections corresponding to the rate coefficients  $k_D$  and  $k_L$ , so that

$$Q_L = \pi(2\alpha e^2)^{1/2} E^{-1/2}, \quad (3)$$

$E$  being the energy of relative motion. This ratio is of interest partly in itself and partly because

$$J_D/J_L = (Q_D/Q_L)^{1/2}, \quad (4)$$

where  $J_D$  is the greatest orbital angular momentum quantum number for a hitting collision and where

$$J_L = (8\mu^2\alpha e^2 E)^{1/4}/\hbar \quad (5)$$

is the Langevin value of this quantum number. Equation (5) may be written as

$$J_L = 5.35\tilde{\mu}^{1/2}\tilde{\alpha}^{1/4}\tilde{E}^{1/2}, \quad (6)$$

the tilde over the  $E$  indicating that the energy is here in inverse centimeters. The value of  $J_D$  is required for calculations on ion-dipolar molecule association rates.

Rather than attempt similar parameterizations for the general symmetrical top dipolar molecule, we judged it best to confine ourselves to treating  $NH_3$  (as an oblate example) and  $H_2CO$  (as an approximate prolate example). Note that a molecule may be an excellent approximation to a symmetrical top as far as its rotational constants are concerned yet have a different behavior with regard to hitting collisions. Thus the

rotational constants of CH<sub>3</sub>OH are such that it might be supposed that our results on H<sub>2</sub>CO would serve as a guide for this coincidental symmetrical top molecule. They do not do so, however, because a large component of the CH<sub>3</sub>OH dipole is perpendicular to the top axis.

## II. CALCULATIONS AND TEST RESULTS

The details of the adiabatic invariance method are described by Sakimoto (1984) for linear dipoles and by Bates and Morgan (1986) for symmetric top dipoles. Briefly, the method involves writing the total energy of relative motion, in units of  $B$ , as

$$u(r) = J^2 + (D/B) \cos \theta / r^2, \quad (7)$$

where

$$J^2 = p_\theta^2 + p_\psi^2 / \sin^2 \theta. \quad (8)$$

Noting that  $\psi$  is cyclic and, hence, that

$$p_\psi = m = \text{constant}, \quad (9)$$

and defining the adiabatic invariant

$$n + \frac{1}{2} \equiv \oint p_\theta d\theta / \pi, \quad (10)$$

an application of the Bohr-Sommerfeld quantization rule yields, for  $r \rightarrow \infty$ ,

$$n + \frac{1}{2} = u(\infty)^{1/2} - |m|. \quad (11)$$

Since

$$u(\infty) = (J + \frac{1}{2})^2, \quad (12)$$

we obtain

$$J = n + |m|. \quad (13)$$

This condition along with equation (7) yields a transcendental equation for  $u_{J,m}(r)$ , the adiabatic potential. This equation is solved iteratively starting at large  $r$ . Details of the numerical methods involved are given in the aforementioned papers.

The total interaction potential is the sum of the ion-permanent dipole term above, an ion-induced dipole term, and a centrifugal term. That is (in units of  $B$ ),

$$V = -\frac{\alpha e^2}{2r^4 B} + \eta \frac{b^2}{r^2} + [u(r) - u(\infty)], \quad (14)$$

where  $\eta$  is the energy of relative motion in units of  $B$ , and  $b$  is the impact parameter. The impact parameter and energy for hitting collisions satisfy the equations

$$\frac{dV(r)}{dr} = 0, \quad \eta = V(r). \quad (15)$$

Given  $r$ ,  $b$  and  $\eta$  can be determined. The hitting cross section is then given by

$$Q(J, m) = \pi b^2. \quad (16)$$

The rate coefficient is then the integral of the cross section over all  $\eta$ :

$$\frac{k(J, m)}{k_L} = \left( \frac{2D^2}{\pi \alpha \beta} \right)^{1/2} \left( \frac{B}{kT} \right)^{3/2} \int_0^\infty \eta b^2 \exp\left(-\frac{\eta B}{kT}\right) d\eta. \quad (17)$$

For small collision energies,  $\eta < 1$ , which correspond to collisions at large  $r$ , we use the second-order Stark cross section,

as discussed by Sakimoto (1984) and references contained therein. The cross sections are

$$Q_{\text{Stark}}(J, m) = \begin{cases} \pi(2C/\eta)^{1/2} & \text{for } C > 0, \\ 0 & \text{for } C < 0, \end{cases} \quad (18)$$

where

$$C = \frac{\alpha B}{D^2} - \frac{J(J+1) - 3m^2}{J(J+1)(2J-1)(2J+3)}, \quad J > 0, \\ = \frac{\alpha B}{D^2} + \frac{2}{3}, \quad J = 0. \quad (19)$$

We have performed test calculations on HCl, CS, and HCN for comparison with the PRS computations of Sakimoto (1980) and the AC calculations of Adams, Smith, and Clary (1985). We set

$$\tilde{k}(1) = [2k(1, 1) + k(1, 0)]/3. \quad (20)$$

Figure 1 shows our graphs of  $\tilde{k}(0, 0)/k_L$  and  $\tilde{k}(1)/k_L$  versus  $T$  with the results of Sakimoto (1980) and Adams, Smith, and Clary (1985) also marked. For temperatures of 20 K and above, the agreement between the adiabatic invariance, the PRS, and the AC results is excellent. The agreement between the adiabatic invariance and the PRS results continues at lower temperatures, but the AC results become rather high. This may be seen by noting that in the case of HCN at 12.3 K the parameter  $\alpha kT/D^2$  has the value  $4.88 \times 10^{-4}$ , for which Sakimoto (1984) shows a graph of  $\tilde{k}(1)/k_L$  versus  $kT/B$  for the PRS approximation (his Fig. 3). The adiabatic invariance and PRS results are both about 20, whereas the AC result is 32.5.

## III. PARAMETERIZED RESULTS FOR LINEAR MOLECULES

We have performed a large number of calculations of cross sections and rate coefficients for a wide range of parameters for  $J = 0, 1$ , and 2 and have parameterized them for ease of application. For each  $(J, m)$  a set of cross sections was computed for 17 values of  $y$  in the range  $0.35 \leq y \leq 355$ , where the dimensionless quantity  $y$  is defined by

$$y = D/(\alpha B)^{1/2} \\ = 71.0 \tilde{D}/(\tilde{\alpha} \tilde{B})^{1/2}, \quad (21)$$

where the tildes signal to  $D$ ,  $\alpha$ , 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  $1 \leq |\eta| \leq 8200$ , the upper limit of  $\eta$  being chosen so that  $Q \approx Q_L$  at this energy, and two-parameter least-squares fits were made of  $Q/Q_L$  (averaged over  $m$  values for each  $J$ ) versus  $y$  for each  $\eta$ . The functional form used for the fitting is the same as that used by Su and Chesnavich (1982) for fitting ion-polar molecule rate coefficients. If  $y = y_0$  is chosen as the break point between a quadratic fit and a linear fit, then the fitting function is

$$Q(y)/Q_L = \begin{cases} a + by, & y \geq y_0, \\ (y+c)^2/d + (1-c^2/d), & y < y_0. \end{cases} \quad (23)$$

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:

$$c = \frac{by_0^2 + 2(a-1)y_0}{2(1-a)}, \quad (24)$$

$$d = y_0^2/(1-a). \quad (25)$$

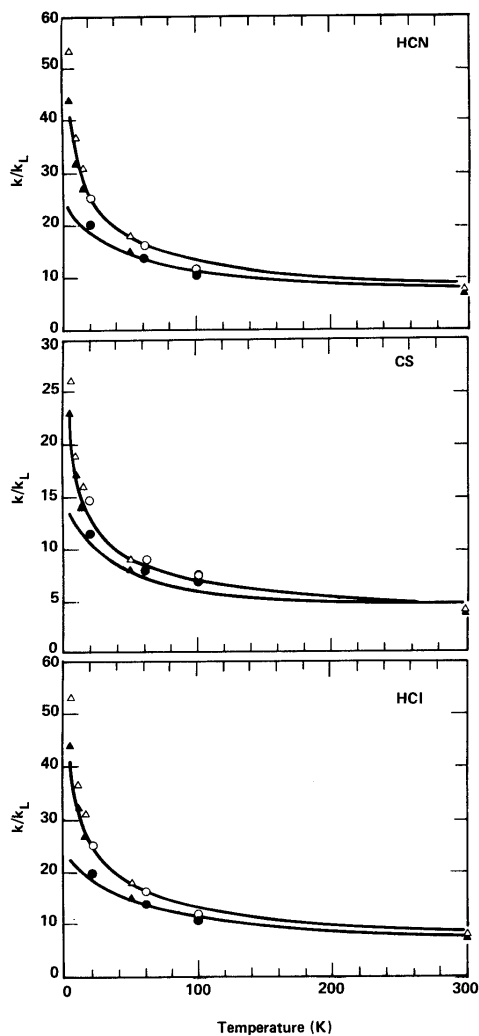


FIG. 1.—Comparison of adiabatic invariance results with other calculations. Solid lines are our calculations; open and filled triangles are the AC results of Adams, Smith, and Clary (1985); open and filled circles are the PRS results of Sakimoto (1980). Open symbols denote  $J = 0$ , and filled symbols denote  $J = 1$ .

After the cross sections were fitted in this manner for each  $\eta$ , the  $a$  and  $b$  coefficients appearing in equations (23)–(25) were then fitted by a least-squares quartic polynomial:

$$a(\eta), b(\eta) = \sum_{i=1}^5 p_i (\ln \eta)^{i-1}, \quad (26)$$

where the  $p_i$  are the polynomial coefficients shown in Table 1. The rms error in the fitting is about  $\frac{1}{2}\%$ , 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 linear dipolar molecules.

Rate coefficients were also computed and fitted with the same functional forms used for the cross sections. Defining the following dimensionless quantities,

$$\beta \equiv kT/B = 0.695T/\bar{B}, \quad \zeta \equiv y/(2\beta)^{1/2}, \quad (27)$$

with  $y$  as in equation (21), we were able to fit, in the same manner as we did the cross sections, the rate coefficients  $k(\zeta)/k_L$  for a number of values of  $\zeta$  with two parameters  $a$  and  $b$ . Here

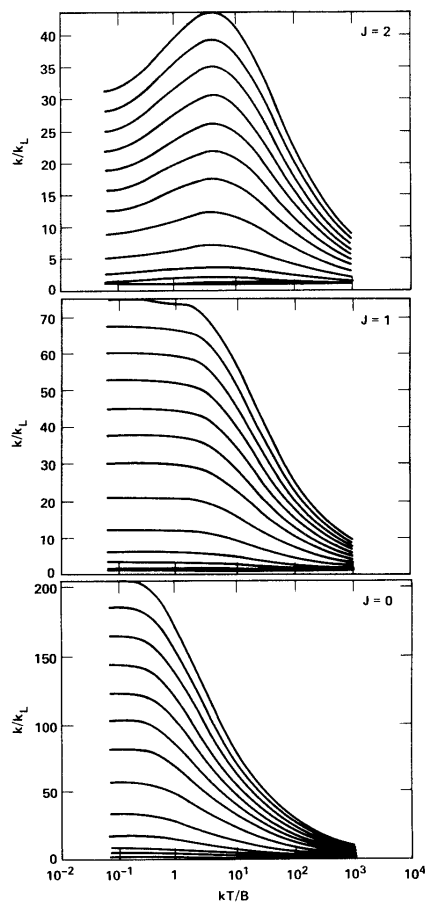


FIG. 2.—Temperature dependence of rate coefficients parametric in  $y = D/(\alpha B)^{1/2}$ . Values of  $y$  shown are 2.8, 7.1, 14, 28, 57, 99, 142, 177, 213, 248, 284, 319, and 355.

TABLE 1  
 FITTING COEFFICIENTS FOR CROSS SECTIONS\*

Coefficient	$p_1$	$p_2$	$p_3$	$p_4$	$p_5$
$J = 0, y_0 = 3$					
$a$ .....	1.660(-1)	3.912(-1)	-7.071(-2)	5.713(-3)	-1.717(-4)
$b$ .....	4.650(-1)	-1.175(-1)	2.454(-4)	2.056(-3)	-1.406(-4)
$J = 1, y_0 = 3$					
$a$ .....	6.496(-1)	-1.511(-1)	1.003(-1)	-1.556(-2)	7.518(-4)
$b$ .....	1.793(-1)	5.387(-2)	-3.713(-2)	5.565(-3)	-2.604(-4)
$J = 2, y_0 = 3$					
$a$ .....	7.574(-1)	-1.067(-1)	4.615(-2)	-4.793(-3)	1.431(-4)
$b$ .....	9.513(-2)	4.047(-2)	-1.801(-2)	2.019(-3)	-7.055(-5)

\* The notation  $(-n)$  means  $\times 10^{-n}$ .
 TABLE 2  
 FITTING COEFFICIENTS FOR RATE COEFFICIENTS\*

Coefficient	$p_1$	$p_2$	$p_3$	$p_4$	$p_5$
$J = 0, \xi_0 = 3$					
$a$ .....	1.764(-1)	9.538(-3)	5.364(-2)	-5.962(-3)	3.327(-5)
$b$ .....	6.631(-1)	1.757(-1)	-1.044(-2)	-3.189(-3)	3.507(-4)
$J = 1, \xi_0 = 5$					
$a$ .....	1.695(-1)	-1.120(-1)	2.612(-2)	6.204(-3)	-8.184(-4)
$b$ .....	3.090(-1)	1.653(-1)	1.684(-2)	-5.081(-3)	2.330(-4)
$J = 2, \xi_0 = 5$					
$a$ .....	3.517(-1)	-1.743(-1)	7.731(-3)	9.265(-3)	-8.500(-4)
$b$ .....	1.607(-1)	1.179(-1)	2.327(-2)	-1.879(-3)	-1.612(-4)

\* The notation  $(-n)$  means  $\times 10^{-n}$ .
 TABLE 3  
 RATE COEFFICIENTS,  $k/k_L$ , FOR SYMMETRICAL TOP MOLECULES

		$T$ (K)									
$J$	$K$	5	10	15	20	30	50	100	150	200	300
NH <sub>3</sub>											
0	0	12.6	11.4	10.5	9.78	8.78	7.57	6.09	5.33	4.85	4.24
1	0	4.77	4.76	4.76	4.76	4.72	4.58	4.23	3.95	3.74	3.43
1	1	8.27	7.05	6.52	6.20	5.80	5.33	4.67	4.28	4.00	3.62
H <sub>2</sub> CO											
0	0	32.9	26.0	22.4	20.5	17.1	14.0	10.6	9.12	8.20	7.10
1	0	18.9	17.4	16.1	15.1	16.6	11.7	9.34	8.18	7.45	6.55
1	1	22.4	19.4	17.5	16.2	14.4	12.2	9.65	8.40	7.63	6.68

the break between quadratic and linear fits is at  $\xi_0$  instead of  $y_0$ . The parameters  $a(\beta)$  and  $b(\beta)$  were then fitted by the quartic polynomial shown in equation (26) with  $\beta$  instead of  $\eta$ . The coefficients of the polynomials are tabulated in Table 2. A total of 306 values of  $k/k_L$  were used in the fitting, with the temperature range defined by  $0.07 \leq \beta \leq 1100$ . The range of  $\xi$  covered, which varies with  $\beta$ , is determined by the range of  $y$ ,  $0.35 \leq y \leq 355$ , and the value of  $\beta$ . The rms fitting errors are less than 1%, the maximum individual errors being about 10% for the smallest  $\xi$  and smallest  $\beta$ . Graphs of  $k(\beta)/k_L$  parametric

in  $y$  are shown in Figure 2. Note that we found it advantageous to change  $\xi_0$  in going from the  $J = 0$  case to the  $J = 1$  and  $J = 2$  cases.

To illustrate the procedure, suppose that we wish to determine the  $J = 1$  rate coefficient for  $H^+ - HCN$  hitting collisions at 100 K. We have

$$\bar{D} = 2.98, \quad \bar{\alpha} = 2.59, \quad \bar{B} = 1.478, \quad \bar{\mu} = 0.963, \quad (28)$$

whence, from equation (22),

$$y = 108.1, \quad (29)$$

and from equation (27),

$$\beta = 47.0, \quad \xi = 11.15. \quad (30)$$

Substitution in the  $\xi$ -polynomial companion to the  $\eta$ -polynomial of equation (26) with the coefficients from Table 2 yields

$$a(47.0) = 0.299, \quad b(47.0) = 0.956. \quad (31)$$

Since  $11.15 > \xi_0$ , we use the first of equations (23) to obtain

$$k(1)/k_L = 10.9, \quad (32)$$

while from equation (2) we have  $k_L = 3.84 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .

#### IV. SYMMETRICAL TOP CALCULATIONS

Using the adiabatic invariance formulation for a symmetrical top dipolar molecule (Bates and Morgan 1986), we computed the rate coefficients for hitting collisions, for  $\text{NH}_3$ , an oblate top, and for  $\text{H}_2\text{CO}$ , an approximate prolate top. The

rate coefficients  $k(T)/k_L$  for  $(J, K) = (0, 0)$ ,  $(1, 0)$ , and  $(1, 1)$  are tabulated in Table 3. The main interest attaches to  $k(T)/k_L$  in the  $(1, 1)$  case, the values in the  $(0, 0)$  and  $(1, 0)$  cases being exactly as for the linear dipole molecule having the same rotational constant, polarizability, and dipole moment. It may be seen from Table 3 that the  $(1, 0)$  values of  $k(T)/k_L$  provide quite a good approximation to the  $(1, 1)$  values: thus the  $(1, 0)$  and  $(1, 1)$  values at 20 and 50 K differ by only 32% and 16% for ammonia and by only 7% and 4% for formaldehyde. The usefulness of our parameterization is not confined to linear molecules.

Further computations on symmetrical top molecules are under way (Bates and Morgan 1986).

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