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Influence of Internal Rotation on Exothermic Reactions between Neutral Molecules at Low Temperatures[†]

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A Langevin-type transition state model is developed to take account of the internal rotation energy in exothermic reactive collisions between neutral molecules. Energy and total angular momentum are both rigorously conserved. Reactive rate coefficients attain a maximum of a few 10^{-10} cm^3/s at temperatures in the range 10−30 K decreasing rapidly at higher temperatures. Results for a representative selection of well-studied systems, Si−O_2, CN−O_2, Si−NO, are in good agreement with experimental observations. At higher temperatures, typically around 100 K or greater, the rate coefficient exhibits a $T^{-1/3}$ dependence.

1. Introduction

Exothermic reactions in ion−molecule collisions tend to be very rapid at low temperatures and their measured rate coefficients are generally in good agreement with the predictions of the simple Langevin capture model[1,2] for nonpolar reactants. In ion reactions with polar molecules, the adiabatic capture centrifugal approximation (ACCSA)[3,4] and variants thereof[5−9] have proved to be satisfactory.[10,11] This led the way to great advance in our understanding of the photochemistry of the interstellar medium, where ion−molecule reactions play a major role.

The Langevin capture model appears to be much less satisfactory for treating exothermic reactions between neutral molecules. In general, the measured rate coefficients of neutral−neutral reactions, only agree with the capture model predictions for extremely low temperatures of around 10−20 K, where rate coefficients of a few10^{-10}cm^{3}s^{-1} are attained.[12−15] However, at higher temperatures, the rate coefficients decrease rapidly to values of a few 10^{-11} cm^3 s^{-1} for temperatures of the order of 100 K or more. Of course, the range of validity of a capture model is expected to be more restricted than that for ion−molecule reactions since the attractive long-range interaction potential between neutral reactants is much weaker than that for ion−neutral systems. But, even making allowance for a weaker long-range interaction, it is clear that, as formulated, the Langevin capture model is unable to explain the experimental results. The aim of this work is to understand why.

One obvious weakness of the Langevin capture model stems from its neglect of the internal rotation of the reactants. It is known from the work of Troe[7] and of Phillips[16] that the internal rotation energy can have a profound influence on ion−molecule reactions. So it is to be expected that the angular momentum conservation of the collision complex may also modify the rate coefficient when one or both of the reactants has internal rotational energy.

To simplify the presentation, we shall first consider a reaction between atom A, in its ground state (with no fine structure), and molecule M in its ground vibrational state but in some excited rotational quantum state j with energy $E_j = Bj(j + 1)$, where B is the rotation constant of M. The relative kinetic energy of the reactants is denoted by E_t. The method can, of course, be generalized to treat the case when the atom has a fine structure or when both reactants are molecules with internal rotation.

Except for the case of j =0, to each j level, there correspond $(2j + 1)$ degenerate states$|jm\rangle$. We adopt the standard convention that the average cross section $\bar{\sigma}_j(E_t)$ for a molecule in a rotation level j, as a sum over all possible m and an average over the $(2j + 1)$ initial states. Unfortunately, there are no available data on such cross sections in the 1−100 meV energy range and there is, at present, no way of testing calculated cross sections. However, rate coefficients measurements offer a means to test some aspects of the theoretical model.

Rate coefficients are obtained from cross sections by averaging over the distribution of the internal rotational states and the kinetic energy of the reactants. In this work, it will be assumed that the reactants are in thermal equilibrium, where the rotational state distribution is characterized by the kinetic temperature T of the reactants. (It may be remarked that this condition may not be satisfied in certain applications, for example, in dilute interstellar space. However, most laboratory experiments are carried out under thermal conditions. See Sims et al.[12] for a discussion of this point). We note that for a given total energy E of the reactants, there is an equipartition of energy between the internal energy states $E_j$and the kinetic energy E_t with the condition that $E = E_t + E_j$.

Atomic units are used throughout except where otherwise stated.

2. Calculation of Reactive Cross Section

First of all, let us recall the basic hypothesis of the capture model, when applied to exothermic reactions involving neutral molecules with no internal rotation This is, of course, a rather academic exercise since many excited rotational levels of typical interstellar molecules, such as CN, O_2, or CO, are significantly populated even at relatively low temperatures. So the theoretical model assuming no internal rotation will only be valid for temperatures $T < B/k$ where k is the Boltzmann constant and B the rotational constant of the reactant molecule..

For relative kinetic energies of the reactants up to about 50 meV, the reactive cross section collisions are governed by the

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long-range interaction between the reactants. (1 meV corresponds roughly to a temperature of 10 K). In the classical trajectory model of Langevin,[1,2] the initial state of the system is characterized by the relative kinetic energy of the reactants E_t and the impact parameter b. Denoting the interaction potential by$V(R)$, the effective radial potential may then be considered as a function of (b,E_t,R)

$$V_{\text{eff}}(b, E_t, R) = V(R) + \frac{E_t b^2}{R^2} \tag{1}$$

where R is the intermolecular distance. At this stage, it is not necessary to specify the exact form of$V(R)$. But for the capture model to be valid, the distance R_0 *at* which orbiting of the reactants occurs, must be greater than about 5−6, where the interaction is known with some precision. In this work, we shall represent $V(R)$ by its asymptotic form

$$V(R) = -\frac{C_6}{R^6} \qquad \text{for} \qquad R < R_0 \tag{2}$$

where C_6 is some known constant but the method can be applied to any form of potential.

The usual procedure is to calculate, for some given the value of $R = R_{\text{mx}}$ for which $V_{\text{eff}}(E_t,b,R)$ is maximum. Then considering R_{mx} as a function of E and b, we determine the value of $b = b_c$ for which $V_{\text{eff}}(R_{\text{mx}}) = E_t$. We observe now that b_c is a function ofE_t. In the capture model, it is assumed that the reaction proceeds with unit probability if$b < b_c$ but forbidden if $b > b_c$. In other words, the centrifugal barrier can only be crossed if $b < b_c$. Then, the reactive cross section is given by

$$\sigma(E_t) = 2\pi \int_0^{\infty} bP(E_t, b)\,\mathrm{d}b = 2\pi \int_0^{b_c} b\,\mathrm{d}b = \pi b_c^{\,2} \tag{3}$$

This calculation is simple for interaction potentials of the form R^{-n}, when expressions both R_{mx} and b_c can readily be obtained in analytic form. For more general interaction potentials, numerical procedures are required.

However, when as is usually the case, the main aim is to determine rate coefficients, it is actually much simpler to characterize the initial state of the collision system by E_t and the angular momentum by $L = b(2\mu E_t)^{1/2}$ where μ is the reduced mass.

$$V_{\text{eff}}(L, R) = V(R) + \frac{L^2}{2\mu R^2} \tag{4}$$

The advantage of this procedure is that it is readily adaptable to a semiclassical quantification of the relative angular momentum and, as will become apparent later, makes it much simpler to enforce angular momentum conservation.

As before, we determine, for a given value of L the radial distance R_{mx} for which the effective potential $V_{\text{eff}}(L,R)$ is maximum. Now R_{mx} is a function of only one variable, which makes the subsequent calculations simpler. In conformity with the capture model, the reaction for any given L is assumed to proceed with unit probability if $E_t > V_{\text{eff}}(L,R_{\text{mx}}))$ but is forbidden if $E_t < V_{\text{eff}}(L,R_{\text{mx}})$. To obtain the cross section, then if L is treated as a continuous variable, we integrate over all possible L to obtain

$$\sigma(E_t) = \frac{\pi}{\mu E_t} \int_0^{\infty} LP_{\text{L}}(E_t)\,\mathrm{d}L \tag{5}$$

where

$$\begin{aligned} P_{\text{L}} &= 1 \quad \text{if} \quad E_t \geq V_{\text{eff}}(r_{\text{mx}}) \\ &= 0 \quad \text{if} \quad E_t < V_{\text{eff}}(r_{\text{mx}}) \end{aligned} \tag{6}$$

For molecules with no internal rotation, a classical description of L is satisfactory since the values of L which contribute most to the cross section are large (of the order of 50−150). But when we treat molecules with internal rotation, the rotational quantum number j of a rotation state is quite small, in the range ranging from 0 to 15, for which a semiclassical quantification is preferable. So treating L as a semiclassical quantized variable $L_{\text{sc}} = L + 1/2$, then the effective radial potential may be defined as

$$V_{\text{eff}}^{\text{sc}}(L_{\text{sc}}, R) = V(R) + \frac{L_{\text{sc}}^{\;2}}{2\mu R^2} = V(R) + \frac{(L + 1/2)^2}{2\mu R^2} \approx V(R) + \frac{L(L + 1)}{2\mu R^2} \tag{7}$$

The total cross section can be expressed as a sum over all possible values of L.

$$\sigma(E_t) = \frac{\pi}{2\mu E_t} \sum_{L=0}^{\infty} (2L + 1)P_L(E_t) \tag{8}$$

The dependence of R_{mx} on L obtained from (7) differs a little compared with the classical value obtained from (5), but since subsequently the sum in (8) over all possible values of L, the end result is not significantly affected.

In practice, for molecules with no internal rotation, it makes little difference whether we use (5) or (8). But as we shall see in the next section, when account must be taken of the internal rotation, it is more convenient to use (8).

3. Calculation of the Rate Coefficient at Very Low Temperatures

The rate coefficient can always be defined, but it is only when the reactants are in thermal equilibrium that a practical calculation is simple. In this section, we determine the rate constant when only the ground rotational state ($j = 0$) of the molecule is significantly populated. In this case the kinetic energy of the reactants, $E_t = E$.

We first define the transition rate $K_0\ (E)$ at a specific energy E

$$K_0(E) = \sqrt{(2E/\mu)}\sigma_0(E) \tag{9}$$

The rate coefficient at a temperature T is then given by integrating over the Maxwell distribution of E.

$$K_0(T) = \frac{1}{kT}\left(\frac{8}{\pi\mu kT}\right)^{1/2} \int_0^{\infty} E\sigma_0(E) \exp\left(-\frac{E}{kT}\right) \mathrm{d}E \tag{10}$$

from which, using (8), we obtain

$$K_0(T) = \frac{1}{2\mu}\frac{1}{kT}\left(\frac{8}{\pi\mu kT}\right)^{1/2}\int_0^\infty \pi\sum_{L=0}^{\infty}(2L+1)P_L(E)\exp\left(-\frac{E}{kT}\right)\mathrm{d}E \qquad (11)$$

Now, it is convenient to permute the integration over E with the sum over L

$$K_0(T) = \frac{1}{kT}\left(\frac{2\pi}{\mu^3 kT}\right)^{1/2}\sum_{L=0}^{\infty}(2L+1)\int_0^\infty \mathrm{d}E P_L(E)\exp\left(-\frac{E}{kT}\right) \qquad (12)$$

Using (6), it is elementary to carry out the integration over E. This leads to

$$K_0(T) = \frac{1}{kT}\left(\frac{2\pi}{\mu^3 kT}\right)^{1/2}\sum_{L=0}^{\infty}(2L+1)\int_{E_L^*}^{\infty}\mathrm{d}E\exp\left(-\frac{E}{kT}\right) \qquad (13)$$

$$= \left(\frac{2\pi}{\mu^3 kT}\right)^{1/2}\sum_{L=0}^{\infty}(2L+1)\exp(-E_L^*/kT)$$

where

$$E_L^* = V_{\mathrm{eff}}(L, R_{\mathrm{mx}}) \qquad (14)$$

This expression was used by Ramillon and McCarroll[17] to study ion−molecule reactions. We may remark that (14) is identical to the result of the statistical capture model[7,8] based on the assumption that the reaction proceeds via an energetically accessible transition state. For every value of L, there exists a quasi-stationary transition state, and if accessible, the reaction proceeds with unit probability. However, (13) is only valid at very low temperatures T for which$T < B/k$. So, we would not expect (13) to be valid for temperatures exceeding 10−20 K when the population of excited rotational states becomes significant.

4. Calculation of the Rate Coefficients Including Rotation

Other considerations become important when the reactant molecule has internal rotational energy. In section 3, the reactant molecule has no internal rotation energy and the relative angular momentum of the system **L** is conserved. But when the molecule possesses an internal angular momentum **j**, the conservation of the total angular momentum imposes additional constraints. A general discussion of this problem is given by Levine.[18]

Fortunately, in the asymptotic region, where the interaction potential is purely radial, the internal rotation is not coupled to the relative angular momentum and so in this region the initial relative angular momentum L is still conserved. Then, as in the preceding section, the transition states can be labeled by a value of L from 0 up to L_{mx} and their energies are determined uniquely by the asymptotic potential and L. All transition states which can contribute effectively to the reaction for temperatures less than 300 K are defined by the asymptotic potential. It is this simplification that makes the simple calculation possible for exothermic reactions at low temperatures. The model would not be valid for endothermic reactions, at least not in such simple form.

So let us now consider the cross section as in section 3, when the reacting molecule is in a specific initial rotation state j. First of all, recalling the standard definition of the cross section for a transition from a degenerate state, and by analogy with (10), we may deduce that

$$\bar{\sigma}_j(E_t) = \frac{\pi}{2\mu E_t}\frac{1}{2j+1}\sum_{L=0}^{\infty}\sum_{m=-j}^{m=+j}(2L+1)P_L^{jm}(E_t) \qquad (15)$$

where E_t is, as before, the kinetic energy of the reactant molecule initially in state j, but now the probability, denoted by P_L^{jm}depends not only on L but also on j and m.

In the interaction region, that is to say for short intermolecular distances, the interaction potential will involve all internal coordinates of the reactants. This leads to a strong mixing of all possible channels. However, not all states can be mixed. In particular, there are restrictions related to the conservation of total angular momentum. So, only states belonging to the manifold of states of a given J can be coupled. On the other hand, there is no coupling between states of different J. For a transition state corresponding to a specific J, the strong coupling theory assumes statistical mixing of the components of the J manifold. So, a transition state corresponding to angular momentum J will dissociate to reaction products with unit probability.

Corresponding to a set of initial conditions specified by j, L there are $(2j + 1)(2L + 1)$ states. From this ensemble of states we can construct a number of J states with values in the range

$$|L - j| \le J \le L + j \qquad (16)$$

The probability of forming a specific J state is therefore[18]

$$\frac{2J+1}{(2L+1)(2j+1)} \qquad (17)$$

from which we may deduce that

$$\sum_{m=-j}^{m=j} P_L^{jm}(E_t) = \sum_{J=L-j}^{J=L+j}\frac{2J+1}{(2L+1)(2j+1)}P_L(E_t) = P_L(E_t) \qquad (18)$$

$$\bar{\sigma}_j(E_t) = \frac{\pi}{2\mu E_t}\frac{1}{2j+1}\sum_{L=0}^{\infty}(2L+1)P_L(E_t) \qquad (19)$$

We may observe that J states can be formed from other combinations of j and L. So when we sum over L, all possible combinations of j and L are taken into account.

The rate constant for a reactant in state j is then given by

$$K_j(T) = \frac{1}{2\pi Q_T}\frac{1}{2j+1}\int_0^\infty\sum_{L=0}^{\infty}(2L+1)P^J(E_t)\exp\left(-\frac{E_t}{kT}\right)\mathrm{d}E \qquad (20)$$

where Q_T is the partition function of the translation motion given by

$$Q_T = \left(\frac{2\pi}{\mu kT}\right)^{-3/2} \tag{21}$$

When there is no internal energy, that is for $j = 0$, the result is identical to expression 10.

As before, it is convenient to permute the integration over E with the sum over L

$$K_j(T) = \frac{1}{2\pi Q_{\mathrm{T}}}\frac{1}{2j+1}\sum_{L=0}^{\infty}(2L+1)\int_0^{\infty}\mathrm{d}EP^L(E)\exp\left(-\frac{E}{kT}\right) \tag{22}$$

Integration over E as in section 3 leads to

$$K_j(T) = \frac{1}{2\pi Q_{\mathrm{T}}}\frac{1}{2j+1}\sum_{L=0}^{\infty}(2L+1)\int_{E_j*}^{\infty}\mathrm{d}E_{\mathrm{t}}\exp\left(-\frac{E_{\mathrm{t}}}{kT}\right) \tag{23}$$

$$= \frac{1}{2\pi Q_{\mathrm{T}}}\frac{1}{2j+1}\sum_{L=0}^{\infty}(2L+1)\exp(-E_L{*}/kT)$$

where

$$E_L^{\;*} = V_{\mathrm{eff}}(L, R_{\mathrm{mx}}) \tag{24}$$

The total reaction rate is then given by

$$K(T) = \frac{1}{Q_{\mathrm{r}}(T)}\sum_{j=0}^{\infty}K_j(T)(2j+1)\exp(-\varepsilon_j/kT) = \frac{S_{\mathrm{r}}(T)}{2\pi Q_{\mathrm{T}}Q_{\mathrm{r}}(T)}\sum_{L=0}^{\infty}(2L+1)\exp(-E_L{*}/kT) \tag{25}$$

where $S_{\mathrm{r}}(T)$ is given by

$$S_{\mathrm{r}}(T) = \sum_{j=0}^{\infty}\exp(-\varepsilon_j/kT) \tag{27}$$

and $Q_{\mathrm{r}}(T)$ is the partition function of the reactant molecule. In the case of a diatomic molecule whose electronic ground state is of Σ symmetry, $Q_{\mathrm{r}}(T)$ is defined as

$$Q_{\mathrm{r}}(T) = \frac{1}{\sigma_{\mathrm{r}}}\sum_{j=0}^{\infty}(2j+1)\exp(-E_j/kT) \tag{26}$$

where E_j is the energy of the jth rotational level and $\sigma_{\mathrm{r}} = 2$ for symmetric diatomic molecules and is unity for nonsymmetric species.

Note also that in the case of molecules, whose ground state is of Π symmetry, there is no rotational state with $j = 0$.

It is of interest to compare (25) with the result of Quing Liao and Herbst[23] where the rate coefficient is expressed in an analogous way as a sum over the angular momentum L, but without the constraint of angular momentum conservation. However, their rate coefficient is independent of the rotation constant B, whereas in (25) the ratio $S_{\mathrm{r}}(T)/Q_{\mathrm{r}}(T)$ exhibits a strong dependence on B.

5. Calculation for Interaction Potentials Varying as R^{-6}

To illustrate some general features of the model, we shall consider the case, where the long-range interaction potential between the reactants can be expressed in the form

$$V(R) = -C_6/R^6 \tag{27}$$

The effective radial potential $V_{\mathrm{eff}}(R)$ has a maximum at $R = R_{\mathrm{mx}}$, where

$$R_{\mathrm{mx}} = \left(\frac{6C_6u}{L^2}\right)^{1/4} \tag{28}$$

$$V_{\mathrm{eff}}(R_{\mathrm{mx}}) = \frac{L^3}{3\sqrt{6C_6u^3}} = \frac{L^3}{\beta}$$

$$\beta = \frac{1}{3\sqrt{6C_6u^3}}$$

Approximating the sum over L by an integral, we obtain

$$K_0(T) = \int_0^{\infty}2\,\mathrm{d}L\exp[-\beta L^3/kT] = 2\sqrt{\frac{2\pi}{\mu}}(2C_6)^{1/3}(kT)^{1/6}\Gamma\left(\frac{2}{3}\right) \tag{29}$$

and the total rate coefficient can then be expressed as

$$K(T) = \frac{S_{\mathrm{r}}(T)}{Q_{\mathrm{r}}(T)}K_0(T) \tag{30}$$

Formula 30 for a reactant molecule with no internal rotation reduces to the Langevin capture model. But, to our knowledge, (30) does not seem to have been used previously to calculate rate coefficients when the reactants have internal rotational energy.

6. Rate Coefficient at High T

The quantities $S_{\mathrm{r}}(T)$ and $Q_{\mathrm{r}}(T)$ must be calculated specifically for each specific molecule at low temperatures when only a few rotational levels contribute to the reaction rate. But for molecules with small rotational constants, it is possible to obtain expressions for $S_{\mathrm{r}}(T)$ and $Q_{\mathrm{r}}(T)$ which are valid at temperatures greater than 50−100K, by approximating the sum over j by an integral. Then we have

$$Q_{\mathrm{r}}(T) = \frac{1}{\sigma_{\mathrm{r}}}\sum_{j=0}^{\infty}(2j+1)\exp(-E_j/kT) \simeq \frac{1}{\sigma_{\mathrm{r}}}\int_0^{\infty}(2j+1)\exp\left(-B\frac{j(j+1)}{kT}\right)\mathrm{d}j \tag{31}$$

If we set $y = (j + 1/2)^2$ we obtain

$$\int_0^{\infty} (2j+1)\exp\left(-B\frac{j(j+1)}{kT}\right)\mathrm{d}j \simeq \int_{1/4}^{\infty}\exp\left(-\frac{By}{kT}\right)\mathrm{d}y = \frac{kT}{B}\exp(-B/4kT) \simeq \frac{kT}{B} \qquad (32)$$

Similarly, to evaluate Sr(T), we set $z = j + 1/2$

$$S_r(T) = \sum_{j=0}^{\infty}\exp(-E_j/kT) \approx \int_0^{\infty}\exp\left(-B\frac{j(j+1)}{kT}\right)\mathrm{d}j \simeq \frac{1}{2}\sqrt{\frac{\pi kT}{B}} \qquad (33)$$

Finally, we obtain

$$\frac{S_r(T)}{Q_r(T)} = \frac{1}{\sigma_r}\frac{B}{kT}\sqrt{\frac{\pi kT}{B}} = \frac{1}{\sigma_r}\sqrt{\frac{\pi B}{kT}} \qquad (34)$$

It is thus seen that combining (32) and (34) the total rate coefficient is expected to decrease as $T^{-1/3}$ in the higher temperature range. For very low temperature, when only the ground rotational is populated, the rate coefficient will increase with temperature as $T^{1/6}$. But as the temperatures increase, the rate coefficient will attain a maximum around 10−20 K, and then turn over to a $T^{-1/3}$ dependence at higher temperatures. Of course, the temperature where the maximum occurs will depend on the particular nature of the reactant. But it is worth remarking that the overall features of this simple model agree with experimental observations.

8. Results and Discussion

To illustrate the consequences of angular momentum conservation, we present a small selection of results for some representative systems, CN-O_2, Si−O_2, and Si-NO, which have been the subject of much experimental and theoretical investigation. The rate coefficients are calculated in the interesting temperature range from 0 to 300 K, where it is verified that all transition states which contribute to the total rate corresponding to values of L less than 150, which corresponds to a value of R_{mx}> 6 b. The C_6 coefficients for each system have been have been estimated by the formula using the best experimental and/or theoretical values of the dipole polarizability and dipole moment. These are listed together with the experimental rotation constants in Table 1.

In the case of the Si−O_2 and Si−NO reactions, we have taken account of the fine structure of the ^{3}P ground state of the Si atom using the procedure of Graff and Wagner[21] adopted by Dayou and Spielfiedel[22] and Le Picard et al.[29] The experimental energies of the $^3P_0$, $^3P_1$, and $^3P_2$ fine structure levels have been adopted.

TABLE 1: Values of the Atomic and Molecular Parameters Required for the Calculation of the Rate Coefficient[a]

parameters	Si	CN	O_2	NO	ref
ionization potential I (e^2/a_0)	0.300	0.521	0.443	0.340	24
dipole moment μ (ea_0)	0	0.57	0	0.224	28
dipole polarizability α (a_0^3)	37.4	25.4	10.6	14.7	25, 26
rotation constant B (e^2/a_0)	0	8.97×10^{-6}	6.58×10^{-6}	7..77	24

[a] All quantities are expressed in atomic units.

TABLE 2: Rate Coefficients (in units of 10^{-11} cm^3 s^{-1}) of Si with O_2

temperature (K)	Langevin rate constant	calcd reaction rate constant	exptl reaction rate constant (ref 27)
1	34.44.	36.44	
2	40.90	40.91	
5	47.65	46.70	
10	53.68	46.32	25.3
20	60.26	41.16	31.9
30	64.48	36.19	34.1
40	67.34	31.62	30.0
60	72.38	24.72	
80	75.92	20.25	
100	78.80	17.26	25.6
150	84.32	12.97	
200	88.46	10.81	22.5
300	94.64	8.77	17.4

In the CN−O_2 reaction, the generalization of formula 30 to the case of two rotors has been used. The anisotropic contribution from the dipole quadruple interaction has been neglected, since its effect is only likely to be important for the low rotational levels ($j = 0, 1$) of CN. Its effect on the more highly excited rotational levels is minimal. Symmetry effects for the O_2 molecule are taken into account in the calculation of the partition function. And in the case of NO, care must be taken to exclude the $j = 0$ rotational level, since the ground electronic state is of Π symmetry.

The C_6 coefficient if the long-range interaction is estimated by the relation used by Woon and Herbst[24]

$$C_6 = \frac{3}{2}\frac{I_A I_B}{I_A + I_B}\alpha_A\alpha_B + {\mu_A}^2\alpha_B + {\mu_B}^2\alpha_A \qquad (39)$$

It may be remarked that the main contribution to the C_6 coefficient comes from the first term. Besides, since the rate coefficient is proportional to $(C_6)^{1/3}$ the results are not sensitive to errors in the C_6 coefficient. The main temperature dependence of the rate coefficient is governed by the rotation constant, which is given to high precision by spectroscopic measurements.

The anisotropic dipole−quadrupole interaction has not been taken into account in the present calculations. Its effect may be significant on the low rotation states $j = 0-2$ but is much weaker for the higher j states. So the overall effect is expected to be weak for molecules with small rotational constants, which is the case in this work. In any case, its inclusion should not affect the main conclusions on the influence of internal rotation on the reaction rate.

The results are presented in Tables 2−4. In all cases, we observe a maximum of the rate coefficient at temperatures around 10−20 K falling off rapidly between 20 and 100 K. It is seen that the calculated rate coefficients reproduce the overall features of the experimental measurements, whereas the simple Langevin capture theory gives a slow $T^{1/6}$ increase with temperature for all T and overestimates the experimental rate by more than a factor of 10 for temperatures of 100 K or higher.

Of course, we cannot expect perfect agreement since theory assumes complete thermalization of the reactants, which may not always be achieved in the experiments. But the results do seem to indicate that the basic assumption of transition state

TABLE 3: Rate Coefficients (in units of 10^{-11} cm^3 s^{-1}) of Si with NO

temperature (K)	Langevin rate constant	calcd reaction rate constant	exptl reaction rate constant (ref 27)
1	19.96	19.96	
2	22.40	22.29	
5	26..10	23.93	
10	29.30	23.14	25.1
20	32.88	21.02	30.0
30	35.18	18.82	34.1
40	36.91	16.67	31.3
60	39.49	13.26	28.6
80	41.43	10.99	25.0
100	43.00	9.44	
150	46.00	7.18	14.6
200	48.27	5.99	
300	51.64	4.77	8.2

TABLE 4: Reaction Rates (in units of 10^{-11} cm^3 s^{-1}) of CN with O_2

temperature (K)	Langevin rate constant (10^{-11} cm^{3}s $^{-1}$)	calcd reaction rate constant (10^{-11} cm^3 s^{-1})	exptl reaction rate constant (10^{-11} cm^3 s^{-1}) (ref 12)
10	53.86	21.08	
13			13.4
20	60.46	13.50	
25			12.8
26			10.8
30		10.121	
40	67.86	8.19	
44			8.86
48			9.26
49			8.29
60	72.61	6.02	
75			5.75
80	76.16	4.05	
100	79.06	4.12	
150	84.58	2.95	
170			3.24
200	88.74	2.37	
295			2.27 −2.48
300	94.95	1.78	

theory, namely, the statistical mixing of channels states of a specific total angular momentum, provides a satisfactory model for the reaction.

Our results underline another important point. It is clear that the rapid decrease of the rate coefficient with increasing T is due to the increasing population of excited rotational states. This may raise some questions about the use of experimental rate coefficients in astrochemical modeling. The density of interstellar clouds is much lower than that in laboratory experiments and it may be expected that the rotational temperature of interstellar molecules may be quite different from the kinetic temperature of the interstellar gas. Under these conditions, the reactive rate coefficient should be computed using reactive cross sections given by (19) and not from (30).

9. Conclusion

It has been shown that the rate coefficient of exothermic reactions involving neutral molecules is profoundly influenced by the internal rotational energy of the reactants. Calculations using transition state theory, which ensure the conservation of angular momentum in the reaction, are successful in reproducing the main characteristics of the measured rate coefficients in the temperature range from 0 to 300K.

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References and Notes

(1) Langevin, P. *Ann. Chim. Phys.* **1905**, *5*, 245.

(2) Clary, D. C. *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Kluwer: Dordrecht, 1988.

(3) Clary, D. C. *Mol. Phys.* **1985**, *54*, 605.

(4) Dateo, C. E.; Clary, D. C. *J. Chem. Phys.* **1989**, *90*, 7216.

(5) Sakimoto, K. *Chem. Phys.* **1981**, *63*, 419.

(6) Bates, D. R. *Proc. R. Soc. London, Ser. A* **1982**, *384*, 289.

(7) Troe, J. *Chem. Phys. Lett.* **1987**, *122*, 425.

(8) Troe, J. *Chem. Phys.* **1987**, *87*, 2773.

(9) Smith, S. J.; Troe, J. *J. Chem. Phys.* **1992**, *97*, 5451.

(10) Dubernet, M. L.; McCarroll, R. *Z. Phys.D* **1989**, *13*, 255.

(11) Dubernet, M. L.; Gargaud, M.; McCarroll, R. *Astron. Astrophys.* **1992**, *259*, 373.

(12) Sims, I. R.; Queffelec, J.-L.; Defrance, A.; Rebrion-Rowe, C.; Travers, D.; Bocherel, P.; Rowe, B. R.; Smith, I. W. M. *J. Chem. Phys.* **1994**, *100*, 4229.

(13) Le Picard, S. D.; Canosa, A.; Travers, D.; Chastaing, D.; Rowe, B. R. *J. Phys. Chem. A* **1999**, *101*, 9988.

(14) Naulin, C.; Costes, M. *Chem. Phys. Lett.* **1999**, *310*, 231.

(15) Le Picard, S. D.; Canosa, A.; Reignier, D.; Stoecklin, T. *Phys. Chem. Chem. Phys.* **2002**, *2*, 3659.

(16) Phillips, L. F. *J. Comput. Chem.* **1990**, *11*, 88.

(17) Ramillon, M.; McCarroll, R. *J. Chem. Phys.* **1994**, *101*, 8697.

(18) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge University Press: Cambridge, 2009.

(19) Herbst, E. In *Springer Handbook of Atomic, Molecular and Optical Physics*; Drake, G., Ed.; Springer Science + Business Media: New York, 2006.

(20) Light, J. C. *Discuss. Faraday Soc.* **1967**, *44*, 14.

(21) Graff, M. M.; Wagner, A. F. *J. Chem. Phys.* **1990**, *92*, 2423.

(22) Dayou, F.; Spielfiedel, A. *J. Chem. Phys.* **2003**, *119*, 4237.

(23) Quing Liao Herbst, E. *Astrophys. J.* **1995**, *444*, 694.

(24) Woon, D. E.; Herbst, E. *Astrophys. J.* **1997**, *477*, 204.

(25) Huber, K. P.; Herzberg, G. *Molecular Structure: IV Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.

(26) Neogrády, P.; Medved, M.; Černušák, I.; Urban, M. *Mol. Phys.* **2002**, *100*, 541.

(27) Andersson, S.; Marković, N.; Nyman, G. *Phys. Chem. Chem. Phys.* **2000**, *2*, 613.

(28) NIST Data Base (http://physics.nist.gov/PhysRefData/).

(29) Le Picard, S. D.; Canosa, A.; Reignier, D.; Stoecklin, T. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3659.

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