

Temperature dependence for the CN+NH₃ reaction under interstellar conditions: beyond capture theories?

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Received 3 March 1999 / Accepted 28 May 1999

Abstract. The reaction between the radical CN and NH₃ is representative of the important class of radical-neutral reactions that proceed rapidly at low temperature, due to strong inverse temperature dependences. Such reactions are assumed to be of great importance in the gas-phase chemistry of dense interstellar clouds; unfortunately, their temperature dependence is poorly understood theoretically. We estimated the rate constant for the CN+NH₃ reaction as a function of temperature in the range 25–300 K, using the classical trajectory Monte Carlo approach. Employing an accurate *ab initio* potential energy surface, we confirm that capture approximations lead to a flat temperature dependence for the rate constant, in severe disagreement with the strong inverse temperature dependence observed experimentally. In order to understand the cause of this severe discrepancy, we investigated the possible influence of the rotation of reactants on the short-range dynamics. We present a crude illustrative model which reproduces both magnitude and temperature dependence of the experimental rate constant. This study emphasizes the importance of the formation conditions of the reaction complex and constitutes a first attempt to evaluate the relevance of processes subsequent to capture.

Key words: molecular processes – scattering – ISM: clouds – ISM: molecules

1. Introduction

Until recently, the chemical models of cold interstellar clouds were dominated by processes involving electrically charged species, such as ion-molecule reactions and dissociative recombinations (Herbst, 1995). Neutral-neutral reactions were supposed to be slow at low temperatures because they are generally dominated by activation barriers at short-range. This assumption is now being questioned, owing to recent experiments showing that certain classes of neutral-neutral reactions proceed rapidly at low temperatures (Herbst et al., 1994; Bettens et al., 1995; Lee et al., 1996). All these rapid reactions involve at least one radical (species with a nonsinglet ground electronic state). In particular, Sims et al. showed that several reactions between CN, OH and CH radicals and neutral species occur rapidly at

temperatures as low as 13 K, with unexpected inverse temperature dependences of the rate constants (Sims & Smith, 1995; Canosa et al., 1997).

For such rapid reactions, capture theories were expected to be successful (Clary, 1990). The *capture approximation* assumes (a) that the reaction rate is controlled by the dynamics in the long-range part of the entrance channel to the reaction and (b) that reaction occurs with unit probability once the molecules pass over the effective barrier to reaction. A large number of capture treatments have been developed and used with success for most ion-molecule reactions (see, e.g., Herbst (1996)). Recently, neutral-neutral reactions have been investigated with long-range potentials that contain both electrostatic, induction and dispersion terms. The use of capture theories for these reactions has been questioned because it generally leads to large overestimations of the measured rate constant values, particularly at room temperature (Stoecklin et al., 1991; Clary et al., 1994; Liao & Herbst, 1995). Moreover, the experimental temperature dependences are not reproduced by the calculations, especially when the dispersion term is included (Stoecklin et al., 1991).

The reaction of CN with NH₃ provides a striking example of a system having a large experimental rate that strongly increases with decreasing temperature (Sims et al., 1994):

$$k(T) = 2.77 \times 10^{-11} \left(\frac{T}{298}\right)^{-1.14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (1)$$

The products of reaction are presumably HCN+NH₂ (Meads et al., 1993) but Herbst et al. (1994) also mentioned the thermodynamically possible set of products NH₂CN+H.¹ Stoecklin & Clary (1995) applied the rotationally adiabatic capture theory (AC) on the CN+NH₃ reaction using a long-range potential built as the sum of dipole-dipole, induction and dispersion multipolar contributions. They predicted a rate constant larger than the experimental value by a factor of 10 at 300 K, and pointed out the possible limitations of the potential used. In a recent paper (Faure et al., 1999), we investigated the long- and medium-range parts of the CN-NH₃ interaction in order to assess the use of multipolar approximations. We computed an accurate capture potential energy surface using *ab initio* quantum chemical techniques, and found that, although the dispersion term is

¹ The cyanamide molecule is an observed interstellar species (Turner et al., 1975).

large and competes with electrostatic interactions, the potential presents no unusual behaviour that could be responsible for the anomalous temperature dependence observed experimentally.

As discussed by Woon & Herbst (1997), the detailed temperature dependence for neutral reactions might depend on short-range processes, which are ignored by usual capture theories. The long-range interactions for neutral systems are relatively weak (in contrast to ion-molecule systems) and short-range forces could play an important role, which might increase in importance with increasing temperature (Klippenstein & Kim, 1993).

In the present paper, we report classical trajectory calculations which include short-range rotational effects, in a first attempt to evaluate the relevance of processes occurring subsequent to capture. The purpose of our study is (a) to confirm the failure of the capture approximation for the CN-NH₃ system and (b) to investigate the influence of short-range rotational barriers on reactivity, in order to evaluate the importance of the formation conditions of the reaction complex. In Sect. 2, we present the potential and Hamiltonian used in this work, and describe the computational technique. The results of classical trajectory calculations are presented and compared with experiment in Sect. 3. Concluding remarks concerning future works are made in Sect. 4.

2. Details of scattering calculations

2.1. Potential energy surface and Hamiltonian

The potential energy surface used in this work is a fit to accurate *ab initio* data², as described in our previous study (Faure et al., 1999). Both molecules were treated as rigid rotors as geometry relaxation was shown to affect the short-range reactive domain only. We obtained an analytical expansion of the capture potential surface V_{capt} at long- and intermediate range (namely for intermolecular separations larger than 4 Å), as the sum of dipole-dipole, CN dipole-NH₃ quadrupole and dispersion interactions:

$$V_{capt} = \frac{C_{d-d}}{R^3} + \frac{C_{d-q}}{R^4} + \frac{C_{disp}}{R^6} \quad (2)$$

The magnitudes and angular dependences of C_{d-d} , C_{d-q} and C_{disp} are given explicitly in Faure et al. (1999), in terms of body- and space-fixed coordinates.

In the present study, we performed classical trajectory calculations over V_{capt} . We used the space-fixed coordinates which describe the orientation of both molecules as follows:

- (R, θ, ϕ) describe the norm and direction of \mathbf{R} , the intermolecular vector which joins the centers of mass of both molecules. \mathbf{R} is the coordinate of *relative motion*.
- $(\alpha_1, \beta_1, \gamma_1)$ are Euler angles which describe the orientation of NH₃ with respect to an arbitrary space-fixed system.
- (α_2, β_2) are Euler angles which describe the orientation of CN with respect to an arbitrary space-fixed system.

² Calculations were performed at the ROMP2/6-311+G(3d,3p) level of theory (including counterpoise corrections).

In the center of mass frame, the total hamiltonian takes the form:

$$H = H_{rel.} + H_{rot1} + H_{rot2} + V_{capt} \quad (3)$$

where

$$H_{rel.} = \frac{p_R^2}{2\mu} + \frac{1}{2\mu R^2} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta} \right) \quad (4)$$

is the Hamiltonian of the relative motion,

$$H_{rot1} = \frac{1}{2I_{B1}} \left(p_{\beta_1}^2 + \frac{(p_{\alpha_1}^2 - \cos\beta_1 p_{\gamma_1})^2}{\sin^2\beta_1} \right) + \frac{p_{\gamma_1}^2}{2I_{C1}} \quad (5)$$

is the Hamiltonian of free NH₃ and

$$H_{rot2} = \frac{1}{2I_2} \left(p_{\beta_2}^2 + \frac{p_{\alpha_2}^2}{\sin^2\beta_2} \right) \quad (6)$$

is the Hamiltonian of free CN. The p_i are the generalized conjugated momenta, μ is the reduced mass, I_{B1} and I_{C1} are the principal moments of inertia of NH₃ and I_2 is the principal moment of inertia of CN.

The equations of motion of both molecules were derived from Hamilton's equations:

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \quad \text{and} \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i, \quad (7)$$

which were numerically integrated with an extrapolation algorithm (Bulirsch & Stoer, 1966). The conservation of energy and momentum resulted from the integration of Eqs. (7), and provided a numerical consistency check for the whole procedure. We achieved an accuracy of 10^{-10} over typical trajectories.

2.2. The Classical Trajectory Monte Carlo method

In the Classical Trajectory Monte Carlo (CTMC) method, one examines a batch of trajectories sampled with random initial conditions, and makes a statistical analysis of the outcome.

In the present study, we calculated the rate constant $k(T)$ for five different temperatures T , namely 25, 50, 100, 200 and 300 K. For each temperature, five relevant collision velocities v_c were selected (in the range $0.1 \leq v_c \leq 1.5$ km s⁻¹) to obtain the cross section as an analytic function of v_c (see below). Batches of 1000 trajectories were run for each value of the collision velocity. For each temperature, the initial rotational energies of both molecules were assigned to correspond to quantum states (using the correspondence principle) and were weighted according to the Boltzmann distribution (using the von Neumann rejection technique, see e.g. Mayne (1996)). Concerning ammonia, the statistical weight due to nuclear spin was neglected because classical trajectories were found to be insensitive to the ortho-para distinction. All angular variables were Monte Carlo selected from appropriate distributions, as described in Levine & Bernstein (1974). The initial values of R were chosen sufficiently large to neglect the residual interaction potential between CN and NH₃ ($R_{init.} \approx 100$ Å). Finally, the sample of impact parameters b was constructed from a uniform distribution in b^2 in the range $[0, b_{max}]$, where b_{max} is the upper limit beyond which no reaction occurs.

The probability of reaction for each individual trajectory was defined as the unit step function (Levine & Bernstein, 1974):

$$P_R = \begin{cases} 1, & \text{if reaction occurs} \\ 0, & \text{otherwise} \end{cases} \quad (8)$$

Different criteria for P_R were used in Sect. 3, depending on various approximations (Eqs. (13), (17), (18)).

According to the Monte Carlo sampling, the total cross section was calculated as:

$$\sigma_R(T, v_c) = \frac{N_R}{N} \pi b_{max}^2, \quad (9)$$

where N_R is the total number of reactive trajectories sampled over the initial conditions, and N is the total number of trajectories sampled. The cross section has a standard deviation of:

$$\Delta\sigma_R = \sigma_R \times \left(\frac{N - N_R}{N N_R} \right)^{1/2}, \quad (10)$$

For each temperature, we found that a good fit of the resulting cross sections is obtained using the non-linear functional form:

$$\sigma_R(T, v_c) = A(T) v_c^{B(T)} \quad (11)$$

where $A(T)$ and $B(T)$ are the fitting parameters.

Finally, the reaction rate constant at a temperature T was evaluated as an appropriate integral of the cross section over a Maxwell-Boltzmann distribution of collision velocities. Analytical integration using Eq. (11) gives:

$$k(T) = A(T) \sqrt{\frac{8}{\pi}} 2^{\frac{B(T)}{2}} \Gamma\left(2 + \frac{B(T)}{2}\right) \left(\frac{k_b T}{\mu}\right)^{\frac{1+B(T)}{2}} \quad (12)$$

where k_b is the Boltzmann's constant, μ is the reduced mass and Γ is the Euler gamma function.

3. Results

3.1. Capture calculations

In accordance with the usual capture approximation, we defined the probability of reaction for an individual trajectory as:

$$P_R = \begin{cases} 1, & \text{if the reactive region is reached, i.e. } R \leq 4 \text{ \AA} \\ 0, & \text{otherwise} \end{cases} \quad (13)$$

Within the AC theory, the simplest approach is the infinite-order sudden approximation (ACIOSA) (Clary, 1984). For each long-range interaction term, the ACIOSA provides a simple analytical prediction of the temperature dependence expected for capture rate constants (Clary, 1990). For most interactions (except the highly anisotropic ion-dipole potential), the ACIOSA was shown to give results in good agreement with the more accurate partial and global centrifugal sudden approximations (ACPCSA and ACGCSA) (Clary, 1984; Stoecklin et al., 1991).

In Fig. 1, we present a comparison between experimental and capture rate constants for the CN+NH₃ reaction. ACIOSA and CTMC calculations use the potential given by Eq. (2). Since the three interactions do not present the same dependence on R ,

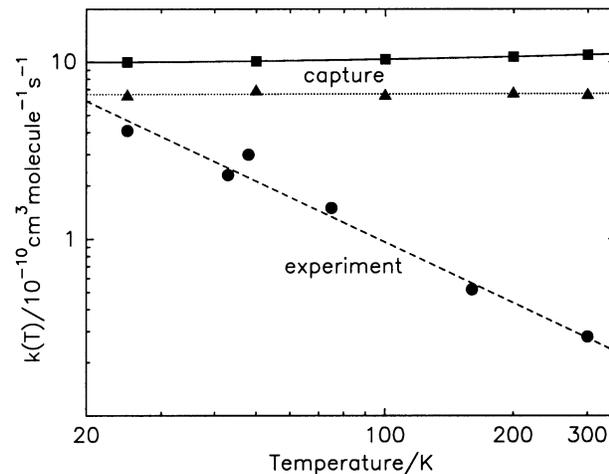


Fig. 1. The rate constant k for the reaction CN+NH₃ as a function of temperature. Capture calculations are compared to experiment. (■): ACIOSA calculations; (▲): CTMC calculations; (●): experimental data (from Sims et al. (1994)). The solid line is the analytic ACIOSA, dashed and dotted lines are least-squares fits of experimental data and CTMC calculations, respectively. CTMC errorbars (corresponding to 2 standard deviations) are of the size of the triangles.

it is not possible to obtain an analytical ACIOSA rate constant including simultaneously the three contributions. An approximate solution to this problem is to sum the different contributions, as discussed by Stoecklin et al. (1991). This analytical approach was shown to give a good approximation of the temperature dependence of the rate constant (in comparison with more elaborate calculations), but to overestimate its magnitude.

We calculated ACIOSA rate constants for each term of Eq. (2), using the formulae (47b), (48b) and (77) given in Stoecklin et al. (1991). We obtained:

$$k_{d-d}(T) = 6.0 \times 10^{-10} T^{-1/6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (14)$$

$$k_{d-q}(T) = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (15)$$

$$k_{disp}(T) = 2.5 \times 10^{-10} T^{1/6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (16)$$

As illustrated in Fig. 1, both CTMC and analytical ACIOSA methods lead to a flat behaviour of the rate constant as a function of temperature. We notice in Eqs. (14–16) that the *ab initio* dispersion contribution is dominant even at very low temperatures (from $T > 14$ K). The slight increase of the ACIOSA rate constant with increasing temperature is due to this dispersion contribution. Moreover, our CTMC calculations illustrate the overestimation of the analytical ACIOSA prediction.

Thus, the predicted temperature dependences of both methods are in excellent agreement, indicating that the CTMC method provides an excellent and simple approach to investigate capture processes. However, both methods are in strong disagreement with experiment, indicating that capture alone cannot account for the experimental behaviour of $k(T)$, except possibly at very low temperatures.

3.2. Effect of reactants rotation on reactivity

As the temperature of a molecular system is increased, the distribution of molecules over rotational energy levels changes and the average rotational energy rises. As discussed by Sims & Smith (1995), for reactions remaining rapid at low temperatures, rotational excitation could reduce reactivity because the rotational motion might prevent the reactants to find the most favorable orientation to react.

The influence of reactant rotation on reactivity was actually studied experimentally³ and theoretically (Sathyamurthy, 1983). In both cases, rotation was related to the initial rotational state j of the reactants. From the experimental point of view, both increase and decrease in reactivity with increasing rotational excitation were observed. A general qualitative result is that the influence of rotation can be connected with the anisotropy of the potential on the way to the barrier (Hochman-Kowal & Persky, 1997).

Theoretically, Clary (1984) showed that a negative temperature dependence of $k(T)$ may be due to the sensitivity of the rotationally selected rate constants $k_j(T)$ on j . Indeed, he applied the ACPCSA theory on dipole-dipole and dipole-quadrupole potentials and showed that the rate constant slightly decreases with increasing temperature, as opposed to the $k_j(T)$ temperature dependence. He also noticed that the $k_j(T)$ decreases with increasing j for a given temperature. He concluded that the weak negative temperature dependence of $k(T)$ is due to the Maxwell-Boltzmann average over the $k_j(T)$, and is strongly connected with the dependence of $k_j(T)$ on j .

Accordingly, the large inverse temperature dependence observed experimentally for the CN+NH₃ reaction could reflect a strong dependence of the reactivity on the reactants rotational excitation. We investigate hereafter a crude model of rotational selectivity, in order to assess such an assumption.

A simple model of rotational selectivity

The correspondence principle permits to define the classical rotational motion of molecules in terms of quantum numbers \tilde{j}_1 and \tilde{j}_2 ⁴. The flat temperature dependence of $k(T)$ predicted by our capture calculations indicates a weak dependence of $k_{\tilde{j}_1, \tilde{j}_2}(T)$ on \tilde{j}_1 and \tilde{j}_2 . However, the capture approximation neglects the effects of short-range interactions, which are highly anisotropic. These interactions may induce orienting forces and cause the reactivity to increase with decreasing rotational excitation (see *e.g.* Hochman-Kowal & Persky (1997)).

Selection on initial rotational states

A simple way to estimate the influence of rotational effects on reactivity is to connect the probability of reaction with the rotational state of the reactants. We can assume, for instance, that the

³ Most of the experimental studies were performed on atom-diatom reactions.

⁴ The tilde indicates that classical calculations does not necessarily yield an integer value for j .

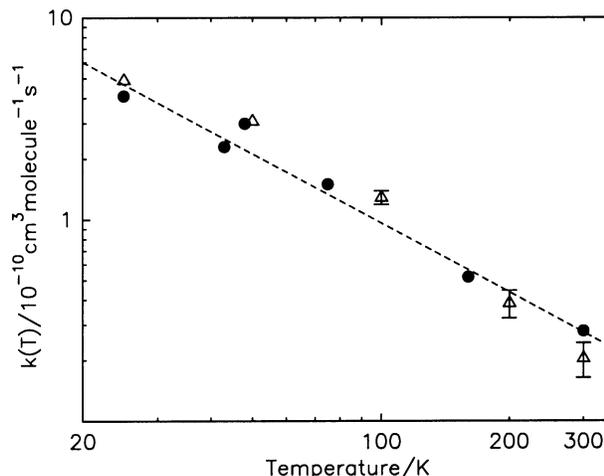


Fig. 2. Rate constant k for the reaction CN+NH₃ as a function of temperature. Comparison between CTMC calculations (Δ) and experiment (\bullet). Eq. (17) is applied for each trajectory. The dashed line is a least-squares fit of experimental data. CTMC errorbars correspond to 2 standard deviations.

reaction will occur only if reactants have small initial rotational quantum numbers (*i.e.* slow initial rotational motions):

$$P_R = \begin{cases} 1, & \text{if } R \leq 4 \text{ \AA} \text{ and} \\ & \tilde{j}_1(R_{init}) \leq \tilde{j}_1^{max}, \tilde{j}_2(R_{init}) \leq \tilde{j}_2^{max} \\ 0, & \text{otherwise} \end{cases} \quad (17)$$

This model assumes that the appearance of anisotropic (chemical) forces at short-range causes a strong dependence of reactivity on rotation. We were able to fit the experimental data with $\tilde{j}_1^{max} = 2$ and $\tilde{j}_2^{max} = 3$. As shown in Fig. 2, calculations are in good agreement with experiment, indicating the possible influence of such a selection mechanism on the reactivity.

However, in Eq. (17) the reaction criterion involves the initial rotational states of the molecules. Since an *effective* rotational selection can occur at short-range only, the use of initial rotational quantum numbers is consistent providing that rotational states are unchanged along a collision.

Evolution of the rotational motion

As illustrated in Fig. 3, short-range values of \tilde{j}_1 and \tilde{j}_2 can greatly differ from their initial asymptotic values. There is indeed a strong rotational coupling between the reactants for intermediate intermolecular separations, particularly at low temperatures (*i.e.* for low collision energies), where molecules are more sensitive to the anisotropies of the potential. The appearance of chemical forces at shorter-range might exacerbate this effect and could effectively lead to a strong dependence of reactivity on rotation. Thus, if we assume that the reaction rate is controlled by the dynamics in the short-range part of the potential, Eq. (17) is inadequate.

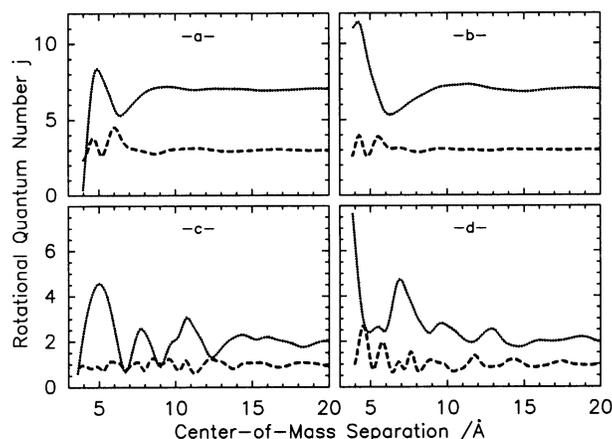


Fig. 3. Evolution of the classical rotational states of CN (dotted lines) and NH₃ (dashed lines) during typical trajectories at 300 K (-a- and -b-) and 25 K (-c- and -d-), in terms of quantum numbers \tilde{j}_1 and \tilde{j}_2 (see text).

Selection on effective rotational states

We therefore suggest that the influence of rotation must be related to the short-range rotational states of reactants. We assumed that once the reactive region is reached, reaction occurs only for reactants with small *effective* rotational quantum numbers:

$$P_R = \begin{cases} 1, & \text{if } R \leq 4 \text{ \AA} \text{ and} \\ & \tilde{j}_1(4 \text{ \AA}) \leq \tilde{j}_1^{max}, \tilde{j}_2(4 \text{ \AA}) \leq \tilde{j}_2^{max} \\ 0, & \text{otherwise} \end{cases} \quad (18)$$

We were able to fit the experimental data with $\tilde{j}_1^{max} = 3$ and $\tilde{j}_2^{max} = 4$. As shown in Fig. 4, calculations are in very good agreement with experiment, suggesting the probable existence of *effective* short-range rotational barriers. Moreover, the rotational selection is less drastic and more realistic than in the previous model⁵.

3.3. Perspectives

In contrast to the usual capture approximation which assumes that the reaction complex “forgets” all details about its formation, our model emphasizes the influence of short-range rotational effects on the complex formation. In view of our crude rotational selection model, further investigations are needed to identify in more details the relevant short-range processes, and to develop a predictive theory. It seems probable that orienting chemical forces, which are topological features of the potential surface at short-range, can play such a role (Sathyamurthy, 1983). Moreover, our model neglects the relative orientation of the rotational angular momenta \tilde{j}_1 and \tilde{j}_2 . This relative orientation might influence the above rotational selection mechanism (Faure et al., submitted). Therefore, the present study provides only *strong indications* that rotational excitation could play a key role in the reactivity of radical-neutral reactions, and urges the need for more detailed studies.

⁵ Note that the rotational energy is proportional to $j(j+1)$

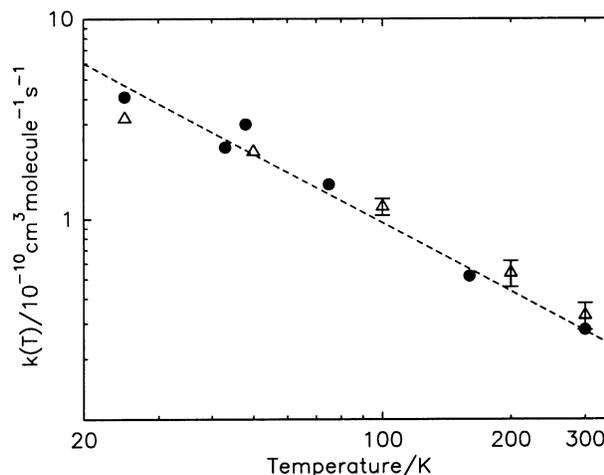


Fig. 4. Rate constant k for the reaction CN+NH₃ as a function of temperature. Comparison between CTMC calculations (Δ) and experiment (\bullet). Eq. (18) is applied for each classical trajectory. The dashed line is a least-squares fit of experimental data. CTMC errorbars correspond to 2 standard deviations.

4. Discussion

The rate constant for the radical-neutral reaction CN+NH₃ has been estimated as a function of temperature in the range 25–300 K, using the classical trajectory Monte Carlo approach. The potential surface used in the calculations has been taken from our earlier *ab initio* quantum chemical study (Faure et al., 1999). We showed that a capture approximation predicts a flat temperature dependence of the rate constant, in agreement with the analytic adiabatic capture theory, but in severe disagreement with the strong inverse temperature dependence observed experimentally. An illustrative model, which takes into account the influence of the rotation of reactants on short-range dynamics, was shown to give results in quantitative agreement with experiment in the whole temperature range.

Thus, although capture theories have been used with success for ion-molecule reactions, they prove unreliable to predict the temperature dependence of rate coefficients for radical-neutral reactions and more detailed kinetics treatments are required. In contrast to long-range theories, the present work emphasizes the importance of the formation conditions of the reaction complex and suggests that rotational selection effects could explain the strong inverse temperature dependence measured for the CN+NH₃ reaction. Further modeling of the kinetics of the complex would require an accurate description of the relevant hypersurface, including the symmetry-breaking of ammonia in the crucial region of the hydrogen transfer. Other processes may prove relevant to consider for quantitative predictions, especially for reactions involving two radicals (relative population of spin-orbit states, non adiabatic couplings between relevant surfaces, etc...).

Given the striking agreement between our results and experiment, *ab initio* investigations are in progress, in search of the eventual presence of a short-range barrier in the entrance or exit channel to reaction. Such a barrier must be small enough

to allow reaction at very low temperatures but large enough to influence the dynamics and to drive rotational selection effects. Short-range interactions are also expected to induce orienting forces (towards reaction path), which become probably less effective with an increase of the rotational motion. In order to explore such short-range processes, we also carried on simple dynamics calculations for an atom-diatom exchange reaction based upon empirical potentials, and we emphasize the importance of vector correlations between angular momenta (Faure et al., submitted).

Concerning interstellar chemistry, in addition to their influence on cold interstellar clouds (Herbst et al., 1994), neutral-neutral reactions are of great importance in the chemistry of species such as silicon- and sulfur-bearing molecules, which are tracers of shocks in interstellar clouds (Schilke et al., 1997; Charnley S.B., 1997). It is important to note that only one half of the neutral-neutral reactions included in the UMIST database have been measured in the laboratory, and that most of them were measured above room temperature (Millar et al., 1997). Moreover, for all experiments measured at low temperature, it was not possible to determine the products. There is therefore an important challenge for theory in predicting low-temperature rate coefficients as well as the reaction products. Such predictive models involve quantum chemical techniques (Woon & Herbst, 1997) and will probably require a detailed understanding of the formation conditions of the reaction complex.

Acknowledgements. Calculations were carried out on the workstations of the "Service Commun de Calcul Intensif de l'Observatoire de Grenoble". This work was partly supported by the CNRS program "Physique et Chimie du Milieu Interstellaire". One of us (A.F.) is supported by a fellowship of the Ministère de l'Enseignement Supérieur et de la Recherche.

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