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Including tunneling into the classical cross sections and rate constants for the $N(^2D)+H_2$ ($v=0, j=0$) reaction

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Abstract

The dynamics of the $N(^2D)+H_2(v=0, j=0)$ reaction has been theoretically studied between 200 and 300K by combining the classical trajectory method and the WKB penetration factor through the early barrier involved in this reaction. The resulting opacity functions, cross sections and rate constants are in reasonable agreement with accurate quantum wave packet results [S. Lin and H. Guo, *J. Chem. Phys.* 124, 031101 (2006)] and experimental measurements [T. Suzuki *et al.*, *J. Chem. Soc., Faraday Trans*, 1993, **89**, 995]. Nevertheless, our treatment tends to underestimate the importance of deep tunneling, probably due to the crude linear approximation of tunneling paths employed in our study.

Introduction

The dynamics of chemical elementary reactions should, in principle, be described within the framework of quantum mechanics. Unfortunately, the approach reveals cumbersome to implement, if not impossible, when the dimensionality to consider increases and/or the process involves long-lived intermediates. In such cases, classical trajectories, grounded when the de Broglie wavelength associated to the nuclear motions is small compared to the characteristic length on which the potential varies, are used [1]. These are indeed easily calculable whatever the size of the system under scrutiny, and they have a strong interpretative power [2,3]. Nevertheless, the classical approach ignores (1) the energy quantization of bound motions, (2) possible diffraction and interferences and (3) tunneling (we focus here on processes taking place in the electronic ground state). Works have thus been carried out, for decades, to include quantum corrections in the classical description, based on semi-classical treatments, or one-dimensional analytical quantum formula on parabolic, Eckart or Morse barriers [4]. Energy quantization can usually be reasonably recovered by non-uniform weighting of the trajectories [5-7] and diffraction has been the focus of recent works [8-10]. Both issues are beyond the scope of the present study. Tunneling, besides, may influence much reactivity, in particular when barriers show up along reaction paths and the motions of light atoms are involved. Consequently, corrections of various sophistication have been proposed to include tunneling in the calculation of VTST rate constants [11] or in dynamics simulations [12-16] by computation of classical phase integral on upside down potentials along rectilinear or optimized tunneling paths [17] or as average over relevant pathways [15].

Fig.1: Schematic representation of the potential energy, V_{RC} , along the reaction coordinate (RC). Energy is in eV.

The potential energy surface (PES) for the title reaction, $N(^2D)+H_2 \rightarrow NH+H$, is characterized by a small entrance barrier (0.08 eV), a deep well (5.48 eV) and a significant exothermicity towards the barrierless product channel (1.25 eV). Because of this last feature, back-scattering to the reactants is low, once the system has overcome the entrance barrier. A schematic representation of the potential energy along the reaction path is shown in Fig.1. We note that the saddle point of the entrance barrier has a T-shape geometry. To a good extent, total reactivity is governed by the entrance barrier crossing [18]. The process has been extensively studied both theoretically [19-29] and experimentally [30-43], in the last decades, because it is expected to play an important role in the chemistry of planetary atmospheres, in particular Titan's one. Besides, from a fundamental point of view, this process is a prototypical insertion reaction associated with a long-lived intermediate complex and has served as a test case for the development of statistical approaches [19]. Non-adiabatic Renner-Teller couplings with the first electronic excited state [44] have been shown to weakly influence the dynamics of the process as long as H_2 is not rotationally excited. [45]

Recently, we developed a capture model including a simple semi-classical tunneling correction to predict the rate constants of the title reaction, in reasonable agreement with new experiments [43]. The model relies on the propagation of quasi-classical trajectories coupled with the computation of the entrance channel barrier penetration factor, within the framework of the Wentzel-Kramers-Brillouin (WKB) semi-classical model [11,46]. The goal of the present paper is to compare its predictions with those of highly resolved exact quantum Wave Packet (WP) calculations previously obtained [18] on the same system. As far as we are aware, very few comparisons of this type can be found in the literature. We first present the model, then, extensively compare its predictions with the quantum results, and finally conclude.

Theoretical Method

Semi-Classical Capture Model

Quasi Classical Trajectory (QCT) calculations, including correction for tunneling, have been performed to predict the reactivity of the $N(^2D)+H_2(v=0, j=0)$ process. As mentioned above, since the reaction is highly exothermic with no exit-barrier, the probability that a trajectory recrosses the entrance-barrier towards the reagents after overcoming it, is quite low. The capture probability is thus a good approximation to the reaction probability. (We here only focus on total reactivity and do not deal with product dynamical attributes) Capture dynamics is simulated in the following, using the $1^2A''$ potential energy surface developed by *Ho et al* [24].

The initial conditions of the molecular system are selected in the same way as in ref. [47]: the relative velocity of the $N(^2D)$ atom with respect to the center-of-mass of H_2 , G , and the impact parameter corresponding to collision energy E and total angular momentum J are given by $v_{rel} = \sqrt{2E/\mu}$ and $b = \hbar\sqrt{J(J+1)}/(\mu v_{rel})$, respectively, where μ is the reduced mass of $N(^2D)$ with respect to H_2 . As $j=0$, the total angular momentum J equals the initial orbital angular momentum l . Considering $\sqrt{J(J+1)}$ instead of J in the expression of b is assumed to lead to a better description of the entrance centrifugal barrier, and hence, to a better approximation of the maximum J consistent with reaction. We consider the Jacobi vectors $\mathbf{R} = \mathbf{GN}$, and $\mathbf{r} = \mathbf{HH}$. The Cartesian coordinates (R_x , R_y , R_z) of $\mathbf{R}$ in the space-fixed frame (x , y , z) are given by $R_x = b$, $R_y = -15 \text{ \AA}$ and $R_z = 0$. The coordinates (P_x , P_y , P_z) of the momentum $\mathbf{P}$ conjugate to $\mathbf{R}$ are given by $P_x = 0$, $P_y = \mu v_{rel}$ and $P_z = 0$. The modulus r of $\mathbf{r}$ and its conjugate momentum $\mathbf{p}$ are deduced from taking the vibrational action of H_2 at 0, freezing its rotational motion and randomly selecting its vibrational phase q [47,48]. The polar angle θ of $\mathbf{r}$ is deduced from the random selection of $\cos \theta$ between -1 and $+1$ and since H_2 is homonuclear, the azimuthal angle φ is randomly selected between 0 and π . The passage from (r, p, θ, φ) to the Cartesian coordinates of $\mathbf{r}$ and $\mathbf{p}$ is achieved by the usual transformation from spherical to Cartesian coordinates.

When running N_{traj} trajectories from the above-described initial conditions, the capture probability $p_J(E)$ is computed as

$$p_J(E) = \sum_{n=1}^{N_{traj}} p_n / N_{traj} \quad (1)$$

where p_n is the capture probability assigned to the n^{th} trajectory. For a reaction with no entrance barrier, this probability is 1 if the trajectory enters the well, 0 otherwise. However, the process under scrutiny involves an entrance barrier of about 0.08 eV, thus requiring to account for tunneling in the capture dynamics as follows. The classical Hamiltonian for the molecular system reads:

$$H = \frac{p^2}{2\mu} + \frac{l^2}{2\mu R^2} + \frac{p^2}{2m} + \frac{j^2}{2mr^2} + V(R, r, \gamma) \quad (2)$$

where m is the H_2 reduced mass and γ the Jacobi angle between $\mathbf{R}$ and $\mathbf{r}$. If capture is classically allowed, *i.e.* if the trajectory overcomes the entrance barrier, p_n is taken to be one. Quantum reflection is thus neglected. In practice, each trajectory reaching $R_{min} = 3a_0$ is considered to be captured (the top of the minimum C_{2v} energy barrier lies at approx. $R=4a_0$). Because of the important depth of the intermediate NH_2 well (5.48 eV), at $R_{min} = 3a_0$, the potential energy along the reaction path is already 0.5eV lower than the reactant asymptote. Trajectories crossing the line $R_{min} = 3a_0$ thus form the intermediate complex. (we have checked that our results are not altered by lowering

R_{min} down to $1.5 a_0$, a value close to the equilibrium value ($1.20a_0$) [ref 24]). If capture is classically prohibited, a turning point along the R coordinate shows up at a given instant t . Still, capture may happen by tunneling through the barrier, the probability of which can be semi-classically evaluated. The trajectory is stopped at the turning point where the radial momentum $P=0$ and l_t, j_t, p_t, R_t, r_t and γ_t are respectively the values of l, j, p, R, r and γ . From this point inward, it is assumed that the vibrational motion can be decoupled from the ro-translational one. At the turning point, the potential energy thus reads:

$$V(R_t, r_t, \gamma_t) = V_t(R_t, r_{eq}, \gamma_t) + v_t(r_t) \quad (3)$$

where $v_t(r_t)$ and $V_t(R_t, r_{eq}, \gamma_t)$ are, respectively, the potentials for the diatom on one hand, and the remaining degrees-of-freedom on the other hand. r_{eq} , the equilibrium diatom distance is found to be almost constant from the reactant to the barrier top. At the turning point, the diatom vibrational energy can thus be approximated by

$$E_{vib}^t = \frac{p_t^2}{2m} + v_t(r_t) \quad (4)$$

and the H_2 rotational kinetic energy is

$$E_R^{K,t} = \frac{j_t^2}{2mr_t^2}. \quad (5)$$

As a consequence, the effective collision energy reads:

$$E^t = E + E_{ZPE} - E_{vib}^t - E_R^{K,t} \quad (6)$$

where we recall that E is the initial collision energy, and E_{ZPE} is the H_2 zero-point energy. Assuming that the rotational and vibrational motions are frozen during barrier crossing, tunneling is computed along the radial coordinate R , at collision energy E^t , through the effective potential

$$V_{eff}^t(R, r_{eq}, \gamma_t) = \frac{l_t^2}{2\mu R^2} + V_t(R, r_{eq}, \gamma_t) \quad (7)$$

The tunneling probability for the n^{th} trajectory, p_n , is estimated using the WKB semi-classical model [11,46] by

$$p_n = \frac{1}{1 + e^{2\theta(E^t, l_t)}} \quad (8)$$

where the phase integral $\theta(E^t, l_t)$ reads

$$\theta(E^t, l_t) = \int_{R_{min}}^{R_t} \sqrt{2\mu (V_{eff}^t(R, r_{eq}, \gamma_t) - E^t)} / \hbar^2 dR \quad (9)$$

This model is called the Semi-Classical Capture model in the following (SC-Capt). When tunneling is disregarded, *i. e.* if any trajectory which is not classically crossing the barrier is ignored in the numerator of eq. (1), the model is called the Classical Capture model (C-Capt). The correction for tunneling employed here is known as the zero curvature tunneling (ZCT) [15] since the minimum reaction path is accurately defined by the radial direction R in

the entrance channel (see Fig. 1 of ref 24). More sophisticated methods to optimize the tunneling path [17] have not been used in the present work, to keep the model as simple as possible, and because our separability assumption (eq. (3)) is quite reasonable (see further below).

As previously stated, quantum reflection over the barrier is neglected in our approach. A comment is in order regarding this approximation. The barrier in question is that of the effective potential energy given by eq. (7). For a given collision energy, there is a real value J_{cut} of J making the effective potential energy at the barrier saddle point equal to the collision energy. Therefore, right above J_{cut} , no trajectory can classically – by increasing time along the real axis – cross the barrier. Consequently, all the trajectories bounce back against the barrier (type 1 paths). Right below J_{cut} , a few trajectories can classically cross the barrier in the vicinity of its saddle point (type 2a paths). The remaining ones go up the barrier too far from the saddle point to be able to reach the well, and they eventually turn back to the reagents (type 2b paths). Right below J_{cut} , type 2b trajectories are obviously the majority. Now, our calculation of the tunneling probability p_n (eqs. (8) and (9)) is quite accurate for types 1 and 2b trajectories (we checked that on simple potentials for which analytical quantum probabilities are available). Moreover, by ignoring the possible reflection of type 2a paths, we clearly overestimate their contribution to the reactivity, but these trajectories being in negligible amount right below J_{cut} , this overestimation is expected to have no incidence on the capture probability $p_c(E)$ (see eq. (1)) whose value mainly depends on types 1 and 2b trajectories. Consequently, our treatment should be relatively accurate right below J_{cut} . Last but not least, if we decrease J , the amount of type 2a paths becomes significant, but owing to the narrowness of the barrier, their reflection probability should be closer to 0 than to 1. Once again, this tends to justify assigning the unit weight to type 2a trajectories.

The reagent state-resolved integral cross section (ICS) is computed from the reaction probability as:

$$\sigma(E) = \frac{\pi}{k^2} \sum_J (2J + 1) p_J(E) \quad (10)$$

with $k^2 = 2\mu E / \hbar^2$. The state-resolved rate constant is obtained as follows:

$$k_{vj}(T) = g \sqrt{\frac{8\beta^3}{\pi\mu}} \int_0^\infty \sigma(E) E e^{-\beta E} dE \quad (11)$$

where g is the electronic degeneracy (equal to 1/5 in this case) and $\beta = (k_B T)^{-1}$.

In the following, we compare the results of our two models with the benchmark Wave Packet calculations of Lin and Guo [18]. In order to predict the rate constants, the capture reagent state-resolved cross-sections $\sigma(E)$ were computed from 5 to 300 meV collision energies, every 5 (10) meV below (above) 200 meV. At each collision energy, the maximum value of the total angular momentum, J_M , was estimated in the following way. The tunneling

probability along the reaction path ($\gamma=90^\circ$), maximized as compared to that along any other path, was computed for increasing values of l (eq. 8 and 9), until it was found to be a thousand times lower than the overall tunneling probability at $l=0$. The given maximum value of l , l_M , is that of J , J_M . More than 2000 trajectories were run for each value of J with a 0.05 fs time step. Convergence was checked.

Results and Discussion

Fig. 2: Selected J-resolved total reaction probability as a function of collision energy for the WP calculations (bold lines), the C-Capture model (circles) and the SC-Capture model (squares)

J-resolved total reaction probabilities from the capture models and WP calculations [18] are displayed in Figure 2 as a function of collision energy E . As previously described [18], the quantum probabilities at $J=0$, 10, 20 and 29 show a threshold. At $J=0$, this feature is related to the potential energy barrier lying in the entrance channel. The threshold then shifts towards higher collision energy with increasing J because of the centrifugal barrier. As apparent from the figure, the SC-Capture reaction probabilities nicely reproduce the exponential rise at threshold, except from the broad oscillations of the WP probabilities, which were suggested to stem from short lived resonances[18]. The C-Capture probabilities, instead, suddenly rise at the thresholds as they ignore any tunneling. Consequently, threshold energies correspond to sensibly higher values than the WP ones. At increasing collision energies, the comparison between the C- and SC-Capture probabilities indicates that the effect of tunneling, at least described from the present semi-classical treatment, can be rapidly neglected above threshold. Nevertheless,

one should not discard the possibility that quantum reflection, which is here ignored in the SC-Capture model, might slightly lower capture probability at collision energies just above the thresholds. The quantum probabilities steeply rise at thresholds to approach the maximal values, somewhat lower than one, presumably because of non-reactive collisions back to the reactant channel. Conversely, C- and SC-Capture reaction probabilities rapidly rise to a value very close to one since recrossing of the entrance barrier is not accounted for in these models. As a matter of fact, however, the inclusion of tunneling into the capture model greatly improves the description of the reaction threshold, so that the global shapes of the quantum reaction probabilities are reasonably reproduced by the SC-Capture model. The fair quality of the predictions is probably related to the early character of the barrier. Indeed, the reaction coordinate is well defined by the Jacobi R coordinate down to $R=3a_0$ (see Fig. 1 of ref. 24). Possible couplings between the translation motion and the ro-vibrational ones does not seem to drastically affect the predictions around thresholds.

Fig. 3: Degeneracy weighted opacity functions for selected collision energies from WP calculations (bold lines), C-Capture (circles) and SC-Capture (squares) model.

Further insight can be gained from Figure 3, in which the degeneracy weighted opacity functions are displayed at 0.05, 0.1, 0.2 and 0.26 eV collision energies. At $E=0.05\text{ eV}$, the reaction is classically forbidden. The SC-Capture model nicely reproduces the shape of the WP opacity function but reactivity seems underestimated. Tunneling is thus less effective in the SC-Capture model. This is confirmed by the opacities at higher energies, for which the

SC-Capt tails at the highest J , though qualitatively well described, are always lower than WP ones (yet, they are much more realistic than the C-Capt opacity cut-off). The contribution of these high J s to the reactivity may be non-negligible due to the $2J+1$ degeneracy factor in the computation of the cross-sections (see eq. 10). Figure 4 displays the integral cross-sections from WP, C-Capt and SC-Capt models as a function of the collision energy (excitation function). Apart from the small oscillations appearing in the WP excitation function, the latter seems to be quite reasonably reproduced by both capture models, except in the region of the threshold (around 0.07eV) where the SC-Capt cross-section is significantly closer to the quantum one (see inset). One must, however, notice that the SC-Capt model leads to increased reactivity with respect to the C-Capt model even at energies well above threshold. This stems from the above-mentioned contribution of high J s.

Fig.4: Excitation function from WP calculations (bold line), C-Capture model (circles) and SC-Capture model (squares).

The difference between C-Capt and SC-Capt model may be significant when computing rate constants as the excitation function is weighted by the Boltzmann distribution (see eq. 11). This is illustrated in Figure 5, where the integrand of eq. 11 is displayed as a function of collision energy E for $T=200$ and 300K .

Fig.5: integrand of eq. 11 as a function of collision energy for WP calculations (bold lines), C-Capture (circles) and SC-Capture (squares) models. The red line corresponds to 70 meV collision energy, the approximate classical threshold.

From the figure, one can see that the differences between both capture models are significant only for energies below 100-120 meV. However, the contribution of such low energies represents an increasing contribution to total reactivity as temperature decreases, because of the Boltzmann weight. As an example, WP calculations show that collision energies below 100meV contribute to nearly 61% of the reactivity at $T=200\text{K}$, against only 36% at $T=300\text{K}$. The temperature dependence of the rate constants between 200 and $\sim 300\text{K}$ is illustrated in Figure 6 and Table 1.

Fig.6: rate constants as a function of inverse temperature from WP calculations (bold and dashed line), C-Capture (circles), SC-Capture (squares) models and experiments (dots)[49].

At the lowest temperature displayed, $T=200\text{K}$ ($1000/T=5$), the WP rate constant is 25 % higher than the SC-Capt one and 68% higher than the C-Capt one. This is in lines with what was mentioned above as 61% of the reactivity takes place at collision energies below 0.1eV for which tunneling plays a major role. At 300K, the differences are lower as the WP rate constant is only 13 % higher than the SC-Capt one and 34% higher than the C-Capt one. These results nevertheless suggest that tunneling, within the present semi-classical implementation, still plays a significant role at the highest temperatures of the range considered. It is responsible of an increase of 35, 24 and 18 % of reactivity at $T= 200, 250$ and 300K , respectively, with respect to classical capture. At high temperature, this increase of reactivity originates both from tunneling at low collision energies, favored by the Boltzmann factor, and by tunneling at the highest J s at collision energies above classical threshold. SC-Capture predictions are in very satisfying agreement with the experimental measurements of Suzuki et al. displayed in fig. 6 [49] though the reference comparison to consider is the one with the WP results for $H_2(v=0,j=0)$. Comparison between both capture models and experiments must be done with caution as calculations are only performed for $H_2(v=0,j=0)$. However, the comparison between QM thermal and $H_2(v=0,j=0)$ calculations suggests that the effect of initial rotational excitation is minor within the considered temperature range. The former were also found to be in reasonable agreement with measured rate constants at lower temperatures [43].

T [K]	$k_{WP} [10^{-12} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$ (% of tunnel reactivity)	$k_{SC-Capt} [10^{-12} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$ (% of tunnel reactivity)	$k_{Capt} [10^{-12} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$	$k_{WP}/k_{SC-Capt}$	k_{WP}/k_{C-Capt}	$k_{SC-Capt}/k_{C-Capt}$
200	0.67 (40.5)	0.54 (25.9)	0.40	1.24	1.68	1.35
215	0.884 (37.1)	0.726 (23.1)	0.556	1.21	1.59	1.3
230	1.137 (34.6)	0.952 (21.9)	0.745	1.19	1.53	1.28
250	1.53 (31.5)	1.30 (19.4)	1.05	1.18	1.46	1.24
265	1.86 (28.6)	1.61 (17.3)	1.33	1.15	1.4	1.21
280	2.24 (27)	1.96 (16.6)	1.63	1.14	1.37	1.20
300	2.78 (25.4)	2.46 (15.2)	2.08	1.13	1.34	1.18

Table 1: Calculated rate constants from WP, C-Capture and SC-Capture models at selected temperatures, and ratio of the rates from the different models. The data in parenthesis is the proportion of tunneling reactivity, estimated by difference with classical capture.

Conclusions

The classical trajectory method is a powerful and friendly alternative to quantum scattering approaches for the study of the dynamics of chemical reactions (state-resolved differential and integral cross sections). Moreover, rate constants can be straightforwardly deduced from the dynamics. This is particularly useful for processes involving multiple transition states, as VTST lacks accuracy in such a case (VTST assumes a microcanonical equilibrium between TS's which may not be achieved). In order to be predictive, however, the classical trajectory method must take into account quantum mechanical effects whenever they are not negligible. This is typically the case of tunneling for processes involving a barrier along the reaction path. In the present work, we have considered one such process, the atom-diatom insertion reaction $N(^2D) + H_2(v=0, j=0)$ within the temperature range 200-300K. This process involves an early barrier along the reaction path which can be approximated by the radial distance between $N(^2D)$ and the center-of-mass of H_2 . Moreover, the exothermicity of the reaction is sufficiently large for neglecting any recrossing back to the reagents once the system has reached the insertion well. Following previous studies, we have thus computed the WKB penetration factor through the early barrier at each turning point which occurs when the momentum conjugate to the radial distance is zero, and we have averaged this factor to obtain opacity functions, cross sections and rate constants. We have then compared these quantities to (i) accurate quantum wave packet results and (ii) experimental measurements. In both cases, the agreement with our semiclassical predictions was found to be satisfying. Last but not least, we have found that tunneling plays a non-negligible role at temperatures as large as 300K though the barrier height for the title process has only a moderate

value (0.08 eV). We wish to emphasize that if the theory used in the present work to treat tunneling is well established, very few comparisons with both quantum scattering and experimental results seem to be available in the literature. We also note that our treatment underestimates the importance of deep tunneling. This drawback, preventing from accurate predictions at low temperatures, is likely due to the crude linear approximation of tunneling paths employed in our study. We thus plan to look for more realistic tunneling paths in a near future.

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