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# Influence of rotation and isotope effects on the dynamics of the $N(^2D)+H_2$ reactive system and of its deuterated variants

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Integral cross sections and thermal rate constants have been calculated for the  $N(^2D)+H_2$  reaction and its isotopic variants  $N(^2D)+D_2$  and the two-channel  $N(^2D)+HD$  by means of quasiclassical trajectory and statistical quantum-mechanical model methods on the latest *ab initio* potential-energy surface [T.-S. Ho *et al.*, *J. Chem. Phys.* **119**, 3063 (2003)]. The effect of rotational excitation of the diatom on the dynamics of these reactions has been investigated and interesting discrepancies between the classical and statistical model calculations have been found. Whereas a net effect of reagent rotation on reactivity is always observed in the classical calculations, only a very slight effect is observed in the case of the asymmetric  $N(^2D)+HD$  reaction for the statistical quantum-mechanical method. The thermal rate constants calculated on this Potential-Energy Surface using quasiclassical trajectory and statistical model methods are in good agreement with the experimental determinations, although the latter are somewhat larger. A reevaluation of the collinear barrier of the potential surface used in the present study seems timely. Further theoretical and experimental studies are needed for a full understanding of the dynamics of the title reaction.

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## I. INTRODUCTION

The reactions of nitrogen atoms in metastable electronic states, with molecular hydrogen, are important in interstellar chemistry<sup>1</sup> and in technologically relevant plasmas.<sup>2</sup>

In 1991, an investigation of the dynamics of the  $N(^2D)+H_2 \rightarrow NH+H$  reaction was carried out by Dodd *et al.*<sup>3</sup> In this work inverted vibrational distributions of NH, characteristic of a direct abstraction mechanism, were derived from time-resolved infrared emission measurements following the pulsed bombardment of a  $N_2/H_2$  mixture with an electron beam. In 1993 Suzuki *et al.*,<sup>4</sup> using a pulsed radiolysis-resonance absorption technique, obtained an approximate Arrhenius functionality for the temperature-dependent rate constants of the reactions of  $N(^2D)$  with  $H_2$  and  $D_2$ .

The first theoretical calculations on the title reaction supported the preponderance of the direct abstraction mechanism. The activation energies derived by Suzuki *et al.*<sup>4</sup> and the inverted vibrational populations measured by Dodd *et al.*<sup>3</sup> could be reproduced by quasiclassical trajectory (QCT) calculations on a suitable potential-energy surface (PES) of the London-Eyring-Polanyi-Sato (LEPS) type.<sup>4</sup> On the other hand, the *ab initio* PES for the ground electronic state of the  $N(^2D)+H_2$  system built by Kobayashi *et al.*,<sup>5</sup>

using first-order-configuration-interaction (FOCI) calculations, had a deep well for  $C_{2v}$  HNH configurations, but the reaction path had the lowest barrier for a collinear ( $C_\infty$ ) geometry. Quantum-mechanical (QM) calculations<sup>6</sup> on this *ab initio* surface led also to an inverted vibrational state distribution characteristic of a direct abstraction mechanism.

However, since the mid-1990s this picture changed markedly. In a series of experiments, Umemoto and co-workers<sup>7-10</sup> measured the rovibrational state distributions of the nascent NH molecules with improved experimental resolution. In their experiments, the  $N(^2D)$  atoms were generated from two-photon dissociation of NO, and the NH molecules were detected by laser-induced fluorescence (LIF). The product internal state distributions derived from these measurements were found to be similar to those obtained in typical  $H_2$  insertion reactions (see, for instance, Refs. 11 and 12 and the references cited therein): The population of vibrational levels,  $P(v')$ , was not inverted and the rotational distributions,  $P(j')$ , within each vibrational state were broad, with maxima at high  $j'$ .

Kobayashi *et al.*<sup>13</sup> modified empirically their previous FOCI PES (Ref. 5) in order to change the entrance channel barrier from a  $C_\infty$  to a  $C_{2v}$  configuration. QCT calculations performed on the modified PES could reproduce the noninverted vibrational populations of Umemoto and Matsumoto<sup>7</sup> and Umemoto *et al.*<sup>8</sup>

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Casavecchia and co-workers<sup>14,15</sup> carried out crossed molecular-beam experiments with mass spectrometric detection of the products, on the  $N(^2D)+D_2$  isotopic variant of the reaction at collision energies of 165 and 220 meV, higher than those of the thermal energy experiments commented on thus far. The center-of-mass differential cross sections (DCSs) derived from the measurements were backward-forward symmetric like those characteristic of insertion reactions, and only about 0.3 of the available energy went into products translation, reflecting a substantial internal excitation.

A new and more refined *ab initio* surface for the ground electronic state ( $1^2A''$ ) of the  $N(^2D)+H_2$  system was calculated by Pederson *et al.*<sup>16</sup> The results of this calculation at the second-order configuration-interaction level (with Davidson correction) gave a lowest barrier of 83.5 meV for a  $C_{2v}$  nuclear geometry. QCT (Refs. 14–16) as well as exact<sup>17</sup> and approximate<sup>18,19</sup> QM calculations performed on this PES yielded differential cross sections in good accordance with the measurements of Casavecchia and co-workers and internal state distributions in approximate agreement with those of the experiments of Umemoto *et al.*<sup>8</sup> and Umemoto.<sup>9</sup> The QCT calculations showed that the preponderant reaction mechanism was certainly an insertion of the  $N(^2D)$  atom into the molecular bond giving rise to a short-lived complex (of the order of hundreds of femtoseconds) and to a roughly statistical distribution of energy between the various energetic modes, before reaching the exit channel. The range of angles of attack leading to reaction broadens with increasing collision energy,  $E_c$ , but only for  $E_c$  values larger than  $\approx 200$  meV, it is collinear abstraction is allowed. As often found in atom-diatom reactive systems, the global dynamics is well described within the QCT approach<sup>20</sup> and quantum effects play a relatively minor role. For the present reaction, quantum effects, most probably tunneling, were identified in a thorough comparison of experimental, QCT, and exact QM differential cross sections.<sup>21</sup>

Among the known insertion reactions of  $H_2$  with nonmetallic electronically excited atoms [i.e., those with  $C(^1D)$ ,  $N(^2D)$ ,  $O(^1D)$ , and  $S(^1D)$ ],<sup>11,12</sup> that with  $N(^2D)$  is the only one having a barrier in the entrance channel for all interatomic orientations and consequently a relatively small thermal rate constant,  $k(T)$  (see Ref. 22 for a critical review on rate constants measurements since the 1970s). The rest of the mentioned reactions are barrierless and have near gas-kinetic rate coefficients. QCT calculations for  $N(^2D)+H_2$  on the surface of Pederson *et al.*<sup>16</sup> gave, as expected, a translational excitation function,  $\sigma_R(E_c)$ , with a threshold followed by a rapid rise and a stabilization. Later measurements by Liu<sup>12</sup> confirmed the shape of  $\sigma_R(E_c)$  in the post-threshold region. In a later work,<sup>23</sup> Pederson *et al.* concluded that excited electronic states of the system should not play a significant role on the reactivity at thermal energies.

QCT and accurate QM calculations of  $k(T=300\text{ K})$  on this surface led to values of  $1.90 \times 10^{-12}$  and  $2.51 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , respectively,<sup>21</sup> suggesting that tunneling may play a role in the reactivity at this temperature. Further support for this hypothesis has been found in the analysis of the differential cross sections.<sup>21</sup> In any case, both the QCT

and QM  $k(T=300\text{ K})$  values are not too far from the current experimental data [the  $k(T=300\text{ K})$  derived from the Arrhenius fit of Suzuki *et al.*<sup>4</sup> is  $2.45 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and the recommended room-temperature rate constant of Herron<sup>22</sup> is  $2.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ].

In a recent article, Ho *et al.*<sup>24</sup> have provided an improved surface for the  $1^2A''$  state of  $NH_2$  based on a larger set of *ab initio* points, with a fast algorithm for the computation of the PES and of its gradients, whose fast evaluation is essential for large-scale QCT calculations. There is a good general concordance between this surface and the previous one,<sup>16</sup> but the new PES is free from small spurious features and is in better agreement with the *ab initio* points in some key regions including the collinear and  $C_{2v}$  barriers. QCT calculations on the improved surface of Ho *et al.*<sup>24</sup> led to somewhat larger thermal rate constants. At  $T=300\text{ K}$ , the new QCT rate constant for  $N(^2D)+H_2$  has a value of  $2.19 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ,<sup>24</sup> closer to the experimental measurements. As far as we know, QM calculations on this surface have not yet been reported. The slightly lower threshold and the more pronounced positive influence of initial rotation on reactivity are probably the causes of the higher QCT rate constant.

The effect of rotational excitation on reactivity in atom-diatom reactions with a barrier has been a matter of study since the 1970s (see, for instance, Refs. 25–30 and the references cited therein). The influence of rotation on reactivity is determined by the features of the PES and by the kinematics (i.e., masses and velocities) of the colliding partners and is thus sensitive to isotopic substitution. This sensitivity is especially pronounced in the case of reactions involving deuterated variants of the  $H_2$  molecule. From a theoretical point of view, the combination of rotational and isotopic effects on  $H+H_2$  and  $F+H_2$ , the most prototypical atom-diatom reactions of  $H_2$ , has been thoroughly investigated by different groups (see Refs. 30–51 and references therein) and has provided both a sensitive probe of different energy surfaces and a detailed insight into the reaction dynamics. In common with these reactions, the  $N(^2D)+H_2$  system has also a barrier in the entrance channel, but in contrast to them the lowest barrier height corresponds to a perpendicular insertion geometry. The availability of an accurate PES for this peculiar “activated insertion” reaction, and the apparently pronounced sensitivity of rotational effects to the features of the potential evinced by the differences in the  $\sigma_R(E_c)$  and  $k(T)$  values obtained on the two (similar) versions of the PES,<sup>16,24</sup> render worthwhile a more thorough investigation of the role of rotational excitation.

In this work, we report a comparative study of rotational effects for the  $N(^2D)+H_2$ ,  $N(^2D)+D_2$ , and  $N(^2D)+HD$  systems. Two theoretical treatments have been used in the present investigation: the QCT method and a statistical quantum-mechanical (SQM) model for insertion reactions. Within these two approaches, reaction cross sections as a function of initial rotational excitation and thermal rate constants have been calculated for the three isotopic variants. Inter- and intramolecular isotopic effects have been addressed. The results are discussed and compared to previous experimental and theoretical works.

## II. METHOD

### A. Quasiclassical trajectory calculations

The quasiclassical trajectory method used for the calculations has been described in previous publications (see Ref. 52 and references therein) and only the details relevant to the present work will be given here.

Batches of  $2 \times 10^5$  trajectories were run on the  $1^2A''$  PES of Ho *et al.*<sup>24</sup> for individual rotational states,  $j$ , of the molecule between 0 and 4 and for randomly sampled collision energies,  $E_c$ , between threshold and 0.6 eV for all isotopic variants of the reaction, N(<sup>2</sup>D)+H<sub>2</sub>, N(<sup>2</sup>D)+D<sub>2</sub>, and N(<sup>2</sup>D)+HD. Trajectories were started at a N(<sup>2</sup>D)-H<sub>2</sub>(D<sub>2</sub>, HD) distance of 8 Å and a time step of 0.05 fs was used for the integration of the equations of motion. Under these conditions total energy was conserved to better than one part in  $10^4$ .

The maximum impact parameter,  $b_{\max}$ , for this insertion reaction increases with collision energy due to the presence of a barrier for C<sub>2v</sub> geometry. Thus, the impact parameter for each trajectory at a given collision energy  $E_c$  and initial rotational quantum number  $j$  was chosen by randomly sampling between zero and a maximum value  $b_{\max}(E_c, j)$  given by the expression

$$b_{\max}(E_c, j) = D(1 - E_D/E_c)^{1/2}, \quad (1)$$

where the parameters  $D$  and  $E_D$  were obtained previously by fitting the values of the maximum impact parameters found by running small batches of trajectories at several selected  $E_c$  and  $j$  to the functionality of Eq. (1). Over the range of  $E_c$  investigated,  $b_{\max}$  was always found to grow with  $E_c$ . The parameters used, ensure that no reaction occurs at a given  $E_c$  for values of the impact parameter larger than  $b_{\max}(E_c, j)$ . With this kind of energy-dependent sampling of the maximum impact parameter, each trajectory was weighted by  $w_i = b_{\max}^2/D^2$ . The  $j$  specific excitation functions,  $\sigma_R(E_c, j)$ , were subsequently calculated by selecting the set of trajectories with a given  $j$  and using the method of moments expansion in Legendre polynomials, as described elsewhere.<sup>52</sup>

Rate coefficients were calculated from the  $\sigma_R(E_c, j)$  using the usual formula.<sup>52</sup> In all cases, a statistical factor of 1/5 was considered to account for the fact that the  $1^2A''$  is just one of the five surfaces resulting from the degeneracy of the <sup>2</sup>D state of N.

### B. Statistical quantum-mechanical model

Details of the quantum statistical method employed in this work have been largely discussed previously,<sup>18,19</sup> so here we will only provide the most general and relevant aspects of the theory. The model assumes that the atom-diatom reactive process involves the formation of an intermediate collision complex with a long enough lifetime to treat its creation and decay as independent events. Thus no direct reactive transitions will be taken into account within this model. Under these two basic assumptions, the state-to-state reaction probability between an initial  $vjk$  state in the arrangement  $\alpha$  and a final  $v'j'k'$  state in the arrangement  $\alpha'$ , for a total angular momentum  $J$  and a parity eigenvalue  $I$ , can be approximated in the helicity representation as

$$|S_{\alpha'v'j'k',\alpha vjk}^{IJ}(E)|^2 \simeq \frac{P_{v'j'k'}^{IJ\alpha'}(E)P_{vjk}^{IJ\alpha}(E)}{\sum_{\alpha''v''j''k''} P_{v''j''k''}^{IJ\alpha''}(E)}, \quad (2)$$

where  $v$  and  $j$  are the diatomic vibrational and rotational quantum numbers, respectively, and  $k$  is the modulus of the projection of the diatomic rotational angular momentum on the atom-diatom axis. In Eq. (2),  $P_{vjk}^{IJ\alpha}$  is the capture probability or probability of forming the collision complex from the reactant channel  $vjk$  and  $P_{v'j'k'}^{IJ\alpha'}$  is the capture probability from the product channel  $v'j'k'$ , i.e., the probability for the collision complex to decay to that product channel. The capture probabilities can be written as

$$P_{vjk}^{IJ\alpha}(E) = 1 - \sum_{v'j'k'} |S_{v'j'k',vjk}^{IJ\alpha}(E)|^2, \quad (3)$$

where the sum runs over all the energetically open channels. The scattering matrix in Eq. (3) is obtained by solving, for each chemical arrangement within the centrifugal-sudden approximation, the close-coupled equations

$$\Psi''(R) = W(R)\Psi(R), \quad (4)$$

with the matrix  $W(R)$  expressed as

$$W(R) = \frac{2\pi}{\hbar^2}(\epsilon - E) + \frac{l(l+1)}{R^2} + \frac{2\mu}{\hbar^2}V(R), \quad (5)$$

where  $\mu$  is the atom-diatom reduced mass,  $\epsilon$  is a diagonal matrix with the diatomic rovibrational energies,  $V(R)$  is the potential-energy matrix, and

$$l = \sqrt{J(J+1) + j(j+1) - 2k^2 + 1/4} - 1/2. \quad (6)$$

Recently, an alternative approach, where the capture probabilities are calculated by means of time-dependent wave-packet propagation, has been proposed.<sup>53-55</sup>

The statistical integral cross section can be then evaluated using the exact quantum-mechanical expression

$$\sigma_{\alpha'v'j'k',\alpha vjk}(E) = \frac{\pi}{gk_{\alpha vj}^2(2j+1)} \sum_{lkk'} (2J+1) \times |S_{\alpha'v'j'k',\alpha vjk}^{IJ}(E)|^2, \quad (7)$$

where  $k_{\alpha vj}^2 = 2\mu(E - E_{vj})/\hbar^2$ ,  $g$  is the electronic degeneracy, and the reactive probability  $|S_{\alpha'v'j'k',\alpha vjk}^{IJ}(E)|^2$  is calculated using Eq. (2).

The application of statistical-model-based methods to insertion reactions<sup>18,19,53-56</sup> has revealed that processes where an  $X(^{2S+1}D)$  atom (with  $X$  being O, C, S, or N) collides with H<sub>2</sub> seem to satisfy, to some extent, the requirements mentioned above concerning the formation of an intermediate collision complex. Due to the presence of deep potential-energy wells, exact QM calculations for this sort of reactions are computationally too expensive, specially for large translational energies or collisions with diatoms where at least one of the hydrogen atoms has been substituted by heavier isotopic variants such as D. The statistical method provides then a very advantageous quantum approach for the study of these insertion reactions.

For the present study of the  $N(^2D)+H_2$ ,  $N(^2D)+D_2$ , and  $N(^2D)+HD$  reactions, the values considered for the mass-scaled capture radii, which define the entrance to the collision complex in the chemical arrangement of the capture calculation, were  $3a_0$  and  $3.5a_0$  for the reactant and product channels, respectively. Calculations have been performed at collision energies from threshold up to 0.6 eV at 0.01 eV intervals and for initial rotational quantum numbers of the diatom  $j$  between 0 and 3.

As in previous works,<sup>18,19,56</sup> the centrifugal-sudden (CS) approximation has been employed in the calculation of the integral cross sections. The use of this approximation does not produce any significant effect on the calculated cross sections when compared with those obtained by the accurate coupled-channel (CC) treatment.<sup>18,19,56</sup> In particular, integral cross sections for the  $N(^2D)+H_2$  reaction at  $E_{\text{coll}}=165$  meV obtained by means of both versions of the SQM were in a quite remarkable accord for all final vibrational  $v'$  states (see Fig. 2 of Ref. 18). Discrepancies between the CS and CC approaches, only found for the highest final NH rotational states  $j'$ , were always smaller than 15% in all cases. The accuracy of the CS approximation has also been tested previously for the  $C(^1D)+H_2$  reaction<sup>56</sup> with a time-dependent version of the SQM of Ref. 18. Capture probabilities calculated for a broad range of values of the total angular momentum  $J$  within such approximation showed a total agreement with those obtained by means of a CC calculation. As pointed out in the conclusions of Ref. 19, where the insertion reactions between  $H_2$  and electronically excited atoms [ $C(^1D)$ ,  $N(^2D)$ ,  $O(^1D)$ , and  $S(^1D)$ ] were studied by means of the SQM approach, the same good accord with the CC results is achieved when the CS treatment is employed to calculate DCSs. Nonpublished results for the  $C(^1D)+H_2$  system at  $E_{\text{coll}}=80$  meV (see Fig. 4 of Ref. 19) reveal that the largest difference between both approaches, found for the backward and forward peaks, does not exceed 5%. Such small margins of error justify, in our opinion, the use of the computationally more economical CS version of the SQM for this kind of insertion reactions.

The rate coefficients were calculated from the corresponding  $\sigma_R(E_c, j)$  in a similar way as in the QCT case (see above).

### III. RESULTS AND DISCUSSION

The present QCT and SQM translational excitation functions for the  $N(^2D)+H_2$  and  $N(^2D)+D_2$  reactions as a function of initial rotational quantum number are depicted in Fig. 1. As can be seen, all the excitation functions have a similar shape. The QCT  $\sigma_R(E_c, j)$  present a threshold at about  $E_c=70-75$  meV, then rise abruptly until approximately 0.25 eV, and beyond this value grow slower with increasing collision energy. Rotational excitation of the  $H_2$  and  $D_2$  molecules has no appreciable effect on the location of the reaction threshold, but causes an increase of the cross section, specially in the post-threshold region below 0.25 eV. As noted by Pederson *et al.*,<sup>16</sup> only  $C_{2v}$  insertion is possible for energies very close to the threshold. With increasing  $E_c$  broader angles of attack are also allowed since the potential

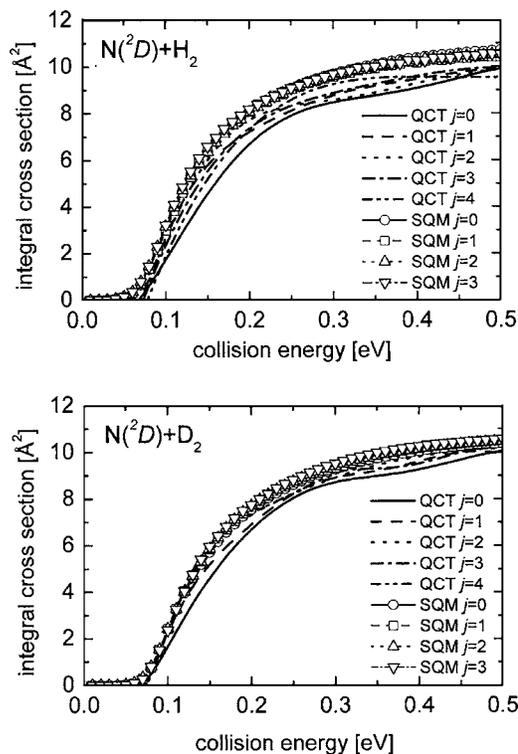


FIG. 1. QCT (curves) and SQM (curves and symbols) excitation functions for the  $N(^2D)+H_2(v=0, j=0-4)$  (top panel) and  $N(^2D)+D_2(v=0, j=0-4)$  (bottom panel) reactions calculated on the PES of Ho *et al.*

surface reorients the molecular axis towards a perpendicular (lowest barrier) geometry with respect to the direction of the incoming atom. Molecular rotation contributes to this reorientation of the molecular axis and thus leads to an enhancement of the reactivity. A similar, but even more marked positive influence of rotation on reactivity was observed in QCT calculations for the abstraction  $F+H_2$  and  $F+D_2$  reactions.<sup>43,48</sup>

The SQM cross sections are somewhat larger, especially for the lower rotational quantum numbers, and extend below the corresponding classical threshold. Surprisingly, and in contrast to the QCT results, the SQM excitation functions do not practically depend on the rotational state of the reacting molecule, even at the highest collision energies.

A close inspection to the region below 0.2 eV shows that for a given  $E_c$  the QCT cross section does not increase monotonically with  $j$ . This is best seen in the upper panel corresponding to the  $N(^2D)+H_2$  reaction, where the QCT cross section reaches maximum values for  $j=1,2$  and then decreases for  $j=3$  and 4, indicating that a too fast rotation is not so efficient for the adequate reorientation in the course of the collision. In the reaction with deuterium molecules, which have a smaller rotational constant, the favorable influence of rotation extends to higher values of  $j$  and although  $\sigma_R(E_c)$  does not decrease over the range of rotational numbers sampled, a stagnation in the value of the cross section is observed for  $j=3,4$ . For collision energies higher than 0.2 eV the steric restrictions and orientational properties of the PES have less importance and the relative contribution of rotational excitation to the cross section is much smaller. None of this classical rotation-dependent effects is reflected in the outcome of the SQM calculations.

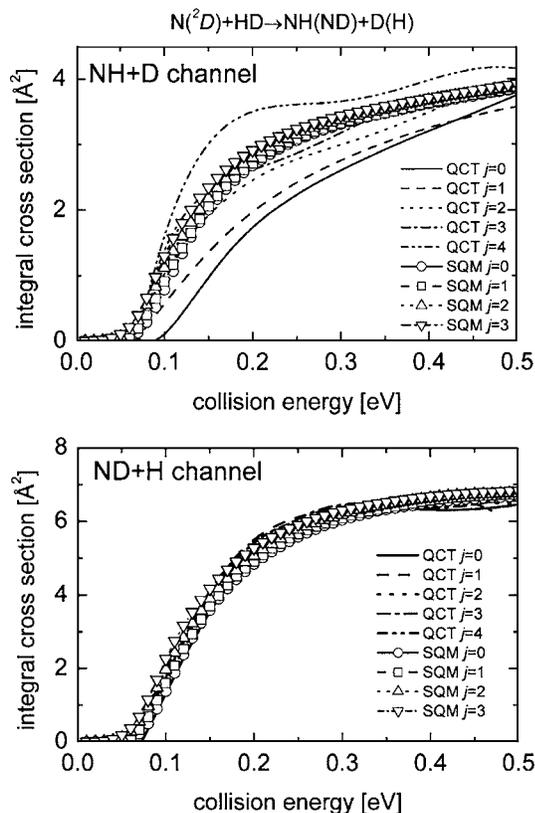


FIG. 2. Same as Fig. 1 but for the two channels of the  $N(^2D)+HD(v=0, j=0-4)$  reaction as indicated.

The only accurate QM integral cross sections for different values of the initial rotational quantum number  $j$  of  $H_2$  were reported in Ref. 21 corresponding to calculations on the previous PES by Pederson *et al.*<sup>16</sup> at the collision energy of 0.165 eV. The values of the cross sections were 6.69, 6.69, and 6.71  $\text{\AA}^2$  for  $j=0$ ,  $j=1$ , and  $j=2$ , respectively. Thus, no effect of  $H_2$  rotation on the cross sections was observed at this single collision energy. SQM calculations performed on the Pederson *et al.* PES (not shown) render similar results to those obtained from the accurate QM calculations; i.e., no effect of  $H_2$  rotation is observed. However, the SQM cross sections are slightly larger than the accurate QM ones by 3% at  $E_c=0.165$  eV and by 11% and 36% at  $E_c=0.11$  and 0.07 eV, respectively. It is expected that the same kind of results would be obtained on the newest PES, for which no accurate QM calculations have been performed so far. The fact that similar effects of  $H_2$  rotation are observed in the QM and SQM calculations indicates that the centrifugal-sudden approximation employed in the SQM calculations is adequate to yield accurate results on integral cross sections.

For the  $N(^2D)+HD$  reaction, a clear difference exists between the cross sections of the two output channels, as shown in Fig. 2. In the absence of molecular rotation, the QCT  $\sigma_R(E_c)$  for the channel leading to  $NH+D$  is always smaller and has a higher threshold and a slower post-threshold rise than that of the channel yielding  $ND+H$ . Rotational excitation of the  $HD$  molecule leads to a lowering of the threshold and to a pronounced increase in the cross section for the production of  $NH+D$  and has only a small (positive) effect in the  $ND+H$  channel. In the SQM calculations a

qualitatively analogous positive effect of rotation on reactivity is observed. Interestingly, the magnitude of this effect is similar to the classical one for the  $ND+H$  channel, but much smaller for the production of  $NH+D$ .

A contrasting effect of rotation in the cross sections of the two output channels of the abstraction  $F+HD$  reaction was also obtained in QCT and accurate QM calculations<sup>49,50</sup> carried out on the accurate Stark-Werner *ab initio* PES (see Fig. 1 of Ref. 49 and Fig. 1 of Ref. 50). In the reaction with fluorine, the effect was found to be even more extreme. With growing  $HD$  rotation, the reactivity of the  $HF+D$  channel increased markedly to the point of becoming preponderant, whereas that of the  $DF+H$  channel decreased slightly. Except for a resonant peak observed in the QM  $\sigma_R(E_c, j=0)$  for the  $HF+D$  exit channel, essentially the same features were observed in the classical and quantum-mechanical calculations. These results support the adequacy of the QCT method for the description of the effects of initial rotation in reactions with a barrier. Although the geometric location of their respective barriers is different, the  $F+HD$  and  $N(^2D)+HD$  reactions have both low thresholds and similar kinematic properties, which render likely a similar influence of reagents' rotation on reaction dynamics, as predicted by the present QCT calculations. On the other hand, though no accurate QM results have been reported on the effect of initial rotation on the reactivity of  $N(^2D)+HD$ , the comparison of accurate QM dynamical observables with those derived from the SQM approach has led in general to a very good agreement.<sup>18,19</sup> The discrepancy between the QCT and SQM results for the  $NH+D$  exit channel shown in the upper panel of Fig. 2 deserves, no doubt, a further study.

The decisive influence of the mass asymmetry on the dynamics of  $F+HD$  has been thoroughly discussed in the literature (see, for instance, Refs. 40, 42, 50, and 58–61 and references therein) and the basic concepts drawn from these studies can be applied to the reaction of  $HD$  with  $N(^2D)$  atoms. The geometry of the triatomic system in the course of the collision is conveniently described by the Jacobi coordinates for the entrance channel  $r, R, \gamma$ , where  $r$  is the  $HD$  internuclear distance,  $R$  the distance between the atom and the center-of-mass of the molecule, and  $\gamma$  the angle between the directions of  $r$  and  $R$ . Due to asymmetric location of the center of mass within the molecular axis, collisions with the  $H$  atom will correspond to lower  $R$  values. For a given  $E_c$  the range of angles of attack leading to reaction will be more restricted for the  $H$  than for the  $D$  end of the molecule and the cross section for the production of  $NH$  will be smaller. In the classical picture, the beneficial reorienting effect of rotation, which in the case of the  $NH+D$  channel is much more marked, helps us overcome the steric restrictions from the potential in the post-threshold region and expands the range of possible geometries leading to  $NH+D$ . This picture is, however, not borne out by the SQM calculations, which predict a small effect of  $HD$  rotation for this channel, as seen in Fig. 2 and commented on in the previous paragraph. In any case, for  $N(^2D)+HD$ , the effect of the mass asymmetry prevails over rotational excitation for the whole range of conditions sampled in this work. For the highest collision energy and rotational quantum number studied, the cross section for

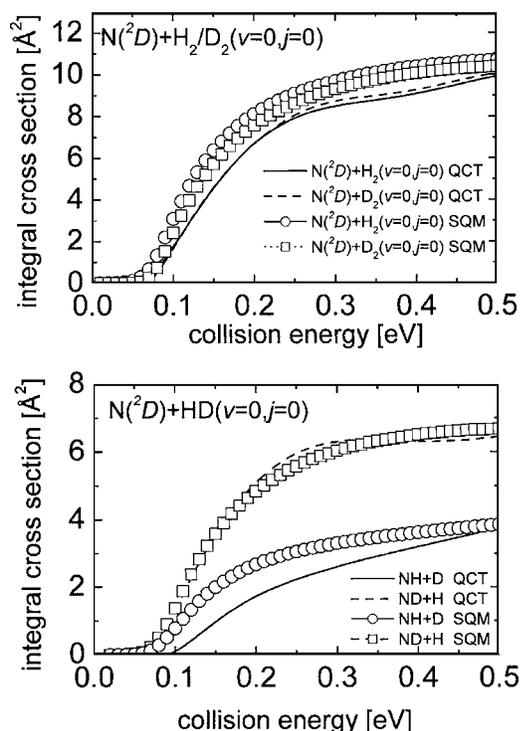


FIG. 3. Comparison between the QCT and SQM excitation functions for the  $N(^2D) + H_2 (v=0, j=0)$  and  $N(^2D) + D_2 (v=0, j=0)$  reactions (top panel) and the two channels of the  $N(^2D) + HD (v=0, j=0)$  reaction (bottom panel).

the generation of  $NH+D$  has a value of  $\approx 4 \text{ \AA}^2$ , as compared with the  $6 \text{ \AA}^2$  cross section for the  $ND+H$  channel.

The different behavior between the reactivity of the symmetric and asymmetric isotopic variants of the reaction under consideration is clearly displayed in Fig. 3, where the  $\sigma_R(E_c)$  for reaction with rotationless molecules have been represented. As indicated above, the SQM cross sections for  $j=0$  are somewhat larger. Within each (QCT or SQM) theoretical approach, the virtual identity between the cross section for reactions with  $H_2$  and  $D_2$  indicates that the different kinematics has no influence in the reactivity of the two symmetric variants. On the contrary, the outcome of the reaction with  $HD$  is determined by the kinematic peculiarities of the mass asymmetry.

As far as we know, no absolute values of the reaction cross section have been measured for any of the isotopic variants of the reaction under consideration, but as mentioned in the Introduction, relative values of  $\sigma_R(E_c)$  have been reported by Liu<sup>12</sup> for the  $N(^2D) + D_2 \rightarrow ND+D$ . Figure 4 shows a comparison between the present QCT and SQM translational excitation functions and the experimental data of Liu.<sup>12</sup> The measured points have been scaled to the theoretical values in the post-threshold region. For collision energies lower than 0.2 eV, the observed trend in  $\sigma_R(E_c)$  is well reproduced by the theoretical calculations. However, for higher collision energies the measured values grow faster than the theoretical ones. Although a possible explanation for this deviation could be an increasing contribution from the  $1A'$  excited state to the reactivity,<sup>23</sup> which is not included in the present calculations, a more likely explanation of purely experimental nature was already suggested in the work of Liu.<sup>12</sup> The experiment is based on the detection of the  $D$

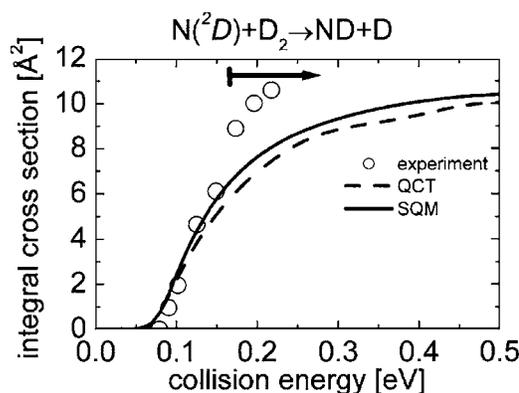


FIG. 4. Excitation function for the  $N(^2D) + D_2$  reaction. Open circles: experimental results taken from Ref. 12. The arrow indicates the collision energy from what the participation of the  $OH+H_2$  reaction cannot be disregarded in the experimental results. Dashed curve: QCT results. Solid curve: SQM result. The experimental results have been scaled to the SQM excitation function. The theoretical excitation functions have been obtained by averaging the different  $j$  contributions of the  $D_2$  reagent taking into account the rotational temperature of  $D_2$  in the molecular beam estimated experimentally (Ref. 12).

atoms formed in the reaction. The excited  $N(^2D)$  species is generated in the photolysis of a mixture of gases containing  $HNO_3$  and  $H_2$ . In this mixture  $OH$  radicals are also formed and, for collision energies larger than  $\approx 0.2$  eV, these radicals can lead to the production of  $D$  atoms via the  $OH+D_2$  reaction.

The reaction cross sections of Fig. 1 have been used for the calculation of the  $N(^2D) + H_2$  and  $N(^2D) + D_2$  rate coefficients, which show the approximate Arrhenius dependence typical for reactions with a barrier. The results are displayed in Fig. 5. The QCT rate coefficients are lower than those from the SQM calculations, as expected from the higher threshold and smaller values of the classical cross sections. Tunneling might explain part of the differences between the QM and QCT rate coefficients, especially at the lowest collision energies (note that in Figs. 1 and 2 the low energy tails in the QM cross sections extend below the classical threshold).

The experimental data of Suzuki *et al.*<sup>4</sup> lie between the QCT and the SQM results, but mostly closer to the classical ones. The best accordance over the whole temperature range is obtained for  $N(^2D) + D_2$ . In the case of  $N(^2D) + H_2$ , the calculated QCT  $k(T)$  are somewhat smaller than the experimental ones at the lower temperatures. The room-temperature rate coefficient evaluation based on accurate QM calculations of integral cross sections at three collision energies<sup>21</sup> on the PES of Pederson *et al.*,<sup>16</sup> which has a larger collinear barrier than that of the PES of Ho *et al.*,<sup>24</sup> was found to be in excellent agreement with the experiment.<sup>21</sup> However, the rate coefficients calculated from the SQM excitation functions on the PES of Pederson *et al.* (not shown) are somewhat larger than the QM evaluation. As commented on above, the SQM integral cross sections obtained on this PES are slightly larger than the accurate QM ones, especially in the region close to the threshold where the SQM cross section is about 30% larger than the QM one. Same behavior is expected in the PES of Ho *et al.* Thus, somewhat smaller

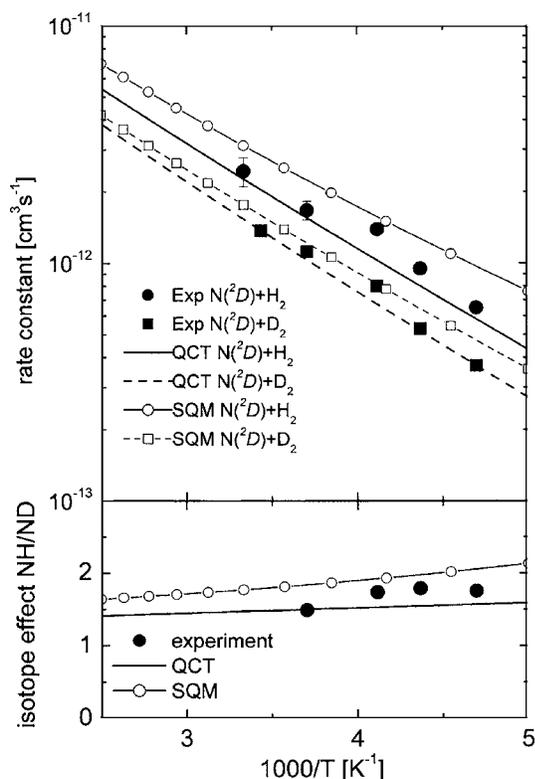


FIG. 5. Thermal rate constants (top panel) and intermolecular isotope effect (bottom panel) for the  $N(^2D)+H_2$  and  $N(^2D)+D_2$  reactions. Closed symbols: experimental results taken from Ref. 4. The lines and lines with symbols correspond to the QCT and SQM results, respectively, as indicated.

values of  $k(T)$  are expected if QM calculations were eventually performed on the latter PES. In any case, the comparatively high values of the SQM  $k(T)$  suggest that it might be worth investigating the threshold region of the surface of Ho *et al.*<sup>24</sup> in more detail.

The intermolecular NH/ND isotopic ratio for  $N(^2D)+H_2$  and  $N(^2D)+D_2$  is also displayed in Fig. 5. For the whole interval of temperatures considered, the QCT calculations yield a nearly constant value of  $\approx 1.5$ , close to the experimental data. The SQM results give a somewhat higher value, but approach also the experimental value in the low-temperature range. These values of the isotopic ratio are essentially due to the higher collision frequency of  $N(^2D)+H_2$ , since the cross sections for the two reactions are very similar, as shown in Figs. 1 and 3. Assuming a line-of-centers functionality for  $\sigma_R(E_c)$ , which should be a good approximation for the post-threshold region, the rate coefficient can be expressed as

$$k(T) = C \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \exp[-(E_0/k_B T)], \quad (8)$$

where  $C$  is a constant related to the size of the cross section,  $k_B$  is the Boltzmann constant, and  $\mu$  is the reduced mass of the colliding partners. For a given  $T$ , assuming equal cross sections for the two isotopic variants,

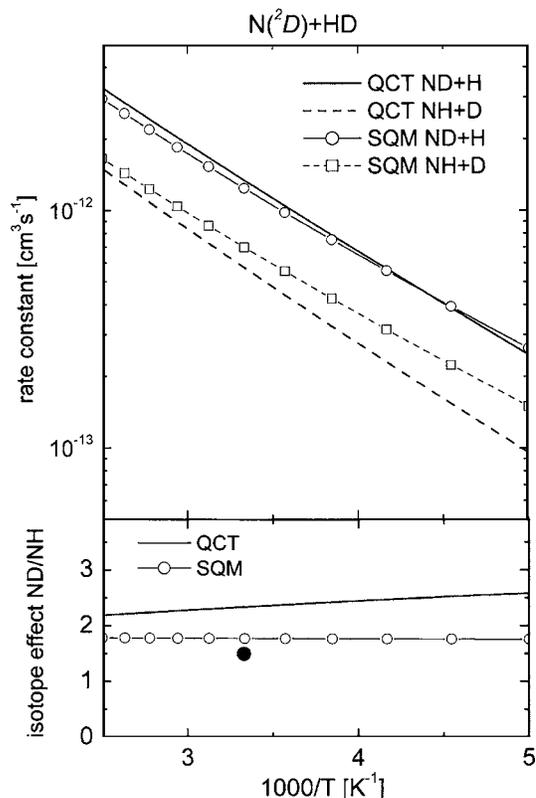


FIG. 6. Same as Fig. 5, but for the two channels of the  $N(^2D)+HD$  reaction. The bottom panel corresponds to the intramolecular ND/NH isotope effect. Closed circle in the bottom panel: experimental result taken from Ref. 9. The lines and lines with symbols correspond to the QCT and SQM results, respectively, as indicated.

$$\frac{k_{N(^2D)+D_2}}{k_{N(^2D)+H_2}} = \sqrt{\frac{\mu(N(^2D)+H_2)}{\mu(N(^2D)+D_2)}}, \quad (9)$$

which gives a value of 1.33 for the NH/ND branching ratio, not too far from the calculated ones. With decreasing temperatures, the experimental and SQM ratios grow slightly faster, possibly due to the contribution of tunneling, which should be more pronounced for the lighter  $N(^2D)+H_2$  isotopic variant.

Figure 6 shows the  $k(T)$  for each of the two output channels of the  $N(^2D)+HD$  reaction calculated with the  $\sigma_R(E_c)$  represented in Fig. 2. As expected from these cross sections, the largest differences between QCT and SQM rate coefficients are found in the low-temperature  $k(T)$  for the NH+D channel. For this isotopic variant of the reaction, experimental data are more scarce. At room temperature, Umemoto *et al.*<sup>57</sup> have reported a rate constant of  $1.83 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  (not shown in Fig. 6), in good agreement with the sum of the theoretical (both QCT and SQM) rate coefficients for the two channels.

The QCT ND/NH intramolecular branching ratio, represented also in the lower panel of Fig. 6, increases slightly (from 2.2 to 2.6) over the temperature range studied; its SQM counterpart remains practically constant at 1.75. These values of the branching ratio reflect the preponderance of the ND+H exit channel commented on above in the discussion of the reaction cross sections. The experimental room-

temperature measurement of 1.5 reported by Umemoto<sup>9</sup> is in good agreement with the SQM value, but lower than the corresponding QCT result.

From a dynamical point of view, asymmetric isotopic variants are the most interesting ones and have provided in general the richest dynamical information both on abstraction<sup>40,42,58–61</sup> and on insertion<sup>62–71</sup> reactions. Very similar rotational state distributions were measured by Umemoto<sup>9</sup> for the two exit channels of the  $N(^2D)+HD$  reaction at thermal collision energies. This absence of leaving-atom isotope effect on the  $P(j')$  of NH and ND indicates that the rotational distributions do not reflect the geometry at the entrance channel, where the H–D bond is not yet broken, but are rather determined by the internuclear dynamics in the potential well behind the barrier. This conclusion had been already advanced by Kobayashi *et al.*,<sup>13</sup> who performed QCT calculations on model  $NH_2$  surfaces and found that the calculated rotational distributions were relatively insensitive to the location of the entrance barrier. Whereas the rotational energy disposal is quite similar for the two exit channels of the  $N(^2D)+HD$  reaction, the rotational energy requirements at the entrance channel, for which no experimental data have been yet reported, are less clear (see Fig. 2 and discussion above).

In spite of recent progress, the dynamical characterization of the title reaction is far from complete. Besides the contrasting QCT and SQM results on the effect of rotation on reactivity, the likelihood of tunneling for the lower-temperature rate constants and the intramolecular isotope effect in the  $N(^2D)+HD$ , are worth investigating in more detail. In addition the nascent rotational state distributions measured at thermal collision energies<sup>8,9</sup> have not yet been satisfactorily reproduced by theoretical calculations on any of the existing potential-energy surfaces. Clearly more theoretical and experimental work is needed in order to clarify these points. In this respect, the performance of crossed molecular-beam experiments with resolution in the internal states of the products, similar to those already available for the  $O(^1D)+H_2$  system,<sup>68,72–74</sup> would certainly be most valuable.

#### IV. SUMMARY AND CONCLUSIONS

Translational excitation functions and rate coefficients for the  $N(^2D)+H_2(v=0,j)$  reaction and its deuterated isotopic analogs have been calculated using the QCT method and a statistical quantum-mechanical model on the most recent *ab initio* potential-energy surface for the  $NH_2$  system. In all cases the classical excitation functions rise from a threshold value at about 0.075 eV and become stabilized at collision energies close to 0.5 eV. The quantum-mechanical cross sections extend below the classical threshold and are usually somewhat larger than their classical counterparts. Although the differential cross sections and products' state distributions are determined by the deep potential well characteristic of insertion reactions of  $H_2$ , the value of the cross section and thus the "reactive size" depend essentially on entrance channel properties.

In the QCT calculations, rotational excitation of  $H_2$  is found to have a positive influence on the reactivity of all the isotopomers; the similitude between the classical rotational excitation features and those of the  $F+H_2$  system is worth noting. In the statistical QM calculations, the effect of reagent rotation is much smaller and restricted to the asymmetric  $N(^2D)+HD$  isotopic variant. The most dramatic effect of rotation is observed in the QCT results for the  $NH+D$  exit channel of this reaction. Classical and accurate QM calculations on the analogous  $F+HD \rightarrow HF+D$  system show a similar strong dependence of the cross section on the initial rotational state of HD. The contrasting weak dependence on  $j$  predicted by the statistical QM model for  $N(^2D)+HD \rightarrow NH+D$  invites further investigation, including accurate QM calculations.

The experimental rate constants lie above the classical results and below those from statistical quantal calculations, but closer to the classical values, which suggests that a reconsideration of the barrier region of the potential-energy surface might be worthwhile. For a given temperature, the calculated rate constants decrease with increasing reduced mass of the colliding partners. This intermolecular isotope effect is essentially caused by the higher collision frequency associated with the lower mass. In the mass asymmetric  $N(^2D)+HD$  reaction, the  $ND+H$  exit channel is always favored.

Further theoretical and experimental information is needed about the dynamics of this interesting reaction that combines typical features of insertion reactions, dominated by a deep attractive well, with other characteristics pertaining to reactions with a barrier, most of which are of the abstraction type.

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