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In the first successful reactive scattering study of nitrogen atoms, the angular and velocity distribution of the ND product from the reaction N(^2D)+D$_2$ at 5.1 and 3.8 kcal/mol collision energies has been obtained in a crossed molecular beam study with mass spectrometric detection. The center-of-mass product angular distribution is found to be nearly backward–forward symmetric, reflecting an insertion dynamics. About 30% of the total available energy goes into product translation. The experimental results were compared with those of quasiclassical trajectory calculations on an accurate potential energy surface obtained from large scale *ab initio* electronic structure computations. Good agreement was found between the experimental results and the theoretical predictions. © *1999 American Institute of Physics.* [S0021-9606(99)02118-2]

During the last decade, advancements in molecular beam and laser spectroscopic techniques, as well as in theoretical methodologies and computer capabilities, have produced exciting progress in the field of chemical reaction dynamics.[1–8] Pivotal to the advances in our current understanding of the dynamics of elementary reactions has been the strong synergism between experiment and theory, which has recently resulted in detailed comparisons between state-of-the-art experiments (state-to-state integral and differential reactive cross section measurements) and state-of-the-art theory [converged quantum mechanical scattering calculations and extensive classical simulations on accurate *ab initio* potential energy surfaces (PESs)] for the dynamics of the benchmark three-atom reactions H+H$_2$,[1–4] F+H$_2$,[5–7] and Cl+H$_2$.[8] These are all direct *abstraction*, collinearly dominated, reactions which have no well on the minimum energy path. Over the past few years there has also been a significant development, both experimental and theoretical, on one side for small radical (four-atom) reactions of great fundamental and practical interest, such as OH+H$_2$,[9] OH+CO,[10] and CN+H$_2$,[11] and on another side for more complex reactions involving three atoms, which occur on PESs with a deep potential well between reactants and products. Belonging to this category are O(^1D)+H$_2$ and S(^1D)+H$_2$, whose reaction intermediates are the bound species H$_2$O and H$_2$S, respectively, and which may involve multiple PESs and nona-

diabatic effects. In particular, considerable experimental and theoretical attention[12,13] is currently on the reaction O(^1D)+H$_2$→OH+H, which has long served as the prototypical *insertion* reaction; recently, scattering results have also been reported for S(^1D)+D$_2$.[14] A survey[15] of work since the development of the crossed molecular beam (CMB) technique reveals that the reaction dynamics of atoms belonging to nearly all groups of the Periodic Table has been explored using this technique. However, to date no investigations of the dynamics of atoms of group V, notably nitrogen, by the CMB technique have been reported, despite extensive literature on gas-phase reactions of ''active nitrogen,''[16] with the exception of a couple of pioneering efforts[17,18] in the late 1970s. Only recently, pump–probe laser-induced-fluorescence (LIF) studies of N(^2D) reactions have started to appear.[19,20] It is worth noting that studies of reactions of N atoms with inorganic and organic molecules are significant in a wide variety of systems: planetary and extraplanetary atmospheres, the chemistry of interstellar and circumstellar clouds, nitrogen chemistry in hydrocarbon combustion, and laboratory studies of the reactions of hydrocarbons with ''active nitrogen.''

In this communication, we present the results of a detailed dynamical investigation of the simplest N-atom reaction, that of excited atomic nitrogen, N(^2D), with molecular hydrogen:

$$N(^2D) + H_2(^1\Sigma^+) \rightarrow NH(X\,^3\Sigma^-) + H(^2S),$$

$$\Delta H_0^\circ = -33.2 \, \text{kcal mol}^{-1} \qquad (1)$$
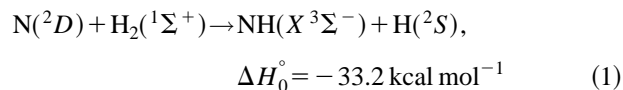
by combining experimental and theoretical techniques. Specifically, we have carried out CMB experiments and measured reactive double differential cross sections (DCSs), developed high quality PESs based on accurate *ab initio* electronic structure calculations and the reproducing kernel Hilbert space interpolation method,[21] and computed the dynamics on the ground state NH$_2$ surface by quasiclassical trajectory (QCT) methods. The aim of this combined effort is to assess the quality of the newly developed PES and to gain insight into the reaction micromechanism. We recall that the DCS is one of the most sensitive observables to the nature of the PES[22] and the QCT method has been demonstrated to be a reliable and powerful tool for describing the dynamics of many reactions involving light species such as H$_2$ and D$_2$.[23]

Reaction (1) has recently attracted significant experimental and theoretical attention since it is the prototype for excited state N-atom reactions and has also been seen as a useful prototype for *insertion* reactions, which are characterized by a deep potential well (corresponding to the bound NH$_2$ radical in this case) along the minimum energy path. Rate constants,[24] the product vibrational distribution from infrared chemiluminescence,[25] and product vibrational and rotational distributions from LIF measurements[19] have been reported. QCT as well as three-dimensional quantum scattering (total $J=0$) studies have been performed on a PES based on *ab initio* computations,[26] but the agreement between experiment and theory was poor due to inaccuracy in the calculated PES.

In the present study, experiments take advantage of the recently developed novel capability of generating intense continuous supersonic beams of atomic nitrogen[27] which are of sufficient intensity to carry out product angular and velocity distribution measurements in CMB experiments. On the theoretical side, we take advantage of recent advances in the accurate representation of PESs. The reproducing kernel Hilbert space interpolation method allows the surface to be represented in a straightforward and efficient manner without requiring a specific functional form to be chosen.[21] This allows highly accurate surfaces to be constructed without requiring the fine tuning and intuition that previously has been required.

The scattering experiments were performed at two different collision energies using a universal CMB apparatus which has been described elsewhere.[10] Two collimated supersonic beams of the reagents are crossed at 90° in a large scattering chamber maintained in the 10^{-7} mbar range and the product angular and velocity distributions are measured by an in-plane, rotatable, electron-impact quadrupole mass spectrometer using the pseudorandom time-of-flight (TOF) method. The study of reaction (1) has been particularly challenging because of the small reaction cross section,[28] the unfavorable N isotopic distribution, and the high inherent background at $m/e=16$ (due to CH$_4$) in any ultrahigh-vacuum chamber. This combination forced us to use isotopically labeled ^{15}N and D$_2$, which allowed us to detect the ND product at the mass-to-charge (m/e) ratio of 17 and so to

achieve a sufficiently good signal to noise. Continuous supersonic beams of N atoms are generated from a radio-frequency discharge beam source[10,27] starting from dilute (2.5%) mixtures of N$_2$ (50% isotopically enriched in ^{15}N$_2$) in He. This procedure leads to more than 60% dissociation of molecular N$_2$ and to a distribution of electronic states of atomic nitrogen. The latter has been characterized by Stern–Gerlach magnetic analysis:[27] 72% of the N atoms are found in the ground ^4S state, and 21% and 7% in the first excited ^2D and ^2P states (lying 55.1 and 82.1 kcal mol^{-1}, respectively, above the ground state). The N beam had an angular divergence of 2.3°, a peak velocity of 2579 m/s, and a velocity of spread of about 20%. A supersonic beam of D$_2$ is obtained by expanding pure *normal* deuterium at high pressure through a heatable stainless steel nozzle. The relative collision energy was varied by changing the nozzle temperature and, hence, the D$_2$ beam velocity. The D$_2$ beam angular divergence was about 4°, the peak velocity 2642 and 1896 m/s for the high ($E_c = 5.1$ kcal mol^{-1}) and low ($E_c = 3.8$ kcal mol^{-1}) collision energies, respectively, and the velocity spread about 10%. The presence in the nitrogen atom beam also of N(^4S) and N(^2P) does not represent a complication in the present studies since the reaction of N(^4S) with H$_2$ is strongly endoergic ($\Delta H_0^\circ = 21.7$ kcal mol^{-1}) and that of N(^2P) about two orders of magnitude slower[28] than that of N(^2D), so the measured ND product is all coming from the N(^2D) reaction, as confirmed by the extent of the product translational energy release. We recall that N(^2D) is the second most abundant metastable (radiative lifetime about 26 h) species, after O$_2(a\,^1\Delta)$, in the upper atmosphere[29] and, since N(^4S) is well known to be very little reactive, many reactive processes in various environments leading to N-containing compounds may well be due to reaction of N(^2D).

We have measured angular and TOF distributions in the laboratory frame of the ND product from the reaction N(^2D)+D$_2$ at two different E_c (the laboratory angular distribution at $E_c=5.1$ kcal mol^{-1} is shown in Fig. 1) and derived product angular, $T(\theta)$, and translational energy, $P(E_t)$, distributions in the center-of-mass (c.m.) frame (the results at $E_c=5.1$ kcal mol^{-1} are shown in Fig. 2) by forward convolution of the laboratory data. The c.m. angular distributions are nearly backward–forward symmetric [the ratio $T(0°)/T(180°)$ is 1.05 ± 0.05] at both E_c [see Fig. 2(a) for $E_c=5.1$ kcal mol^{-1}] and reflect an insertion dynamics via the ground state PES correlating with the ground state $1\,^2B_1$ of NH$_2$. About 31% of the total available energy is found to be channeled in translation, which points to high internal rovibrational excitation of the NH product, consistent with the results of a recent spectroscopic investigation of this reaction.[19,25]

The present *ab initio* calculations of the PES are multireference configuration interaction calculations employing a full-valence, complete active space reference wave function and a triple zeta basis set augmented with diffuse functions.[21(b)] A schematic of the PES derived from these calculations is shown in Fig. 3. The insertion pathway on the ground state PES leading to the $1\,^2B_1$ state of NH$_2$ has a barrier of about 2.4 kcal mol^{-1} in C_{2v} geometry and of about
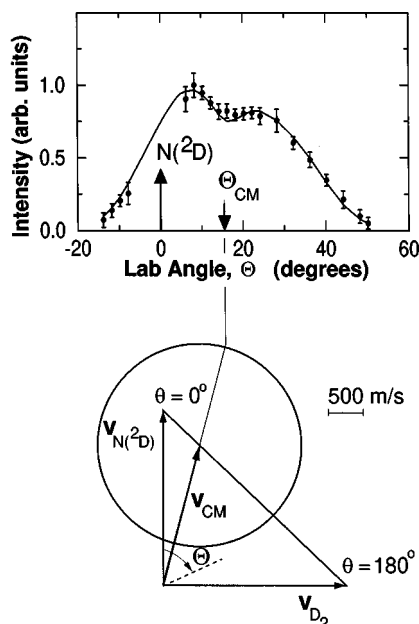
FIG. 1. The ND product laboratory angular distribution from the reaction $N(^2D)+D_2(X\,^1\Sigma^+)\rightarrow ND(X\,^3\Sigma^-)+D(^2S)$ at relative collision energy E_c = 5.1 kcal/mol and the corresponding canonical velocity vector ("Newton") diagram. $\mathbf{v}_{N(^2D)}$ and $\mathbf{v}_{D_2}$ are the laboratory beam velocity vectors, $\mathbf{v}_{c.m.}$ is the c.m. velocity vector; θ and Θ are c.m. and laboratory scattering angles, respectively. The circle in the Newton diagram indicates the maximum speed that the ND product can attain if all the available energy is channeled into translation. The solid line represents the angular distribution obtained from the best-fit c.m. angular and translational energy distributions of Fig. 2.
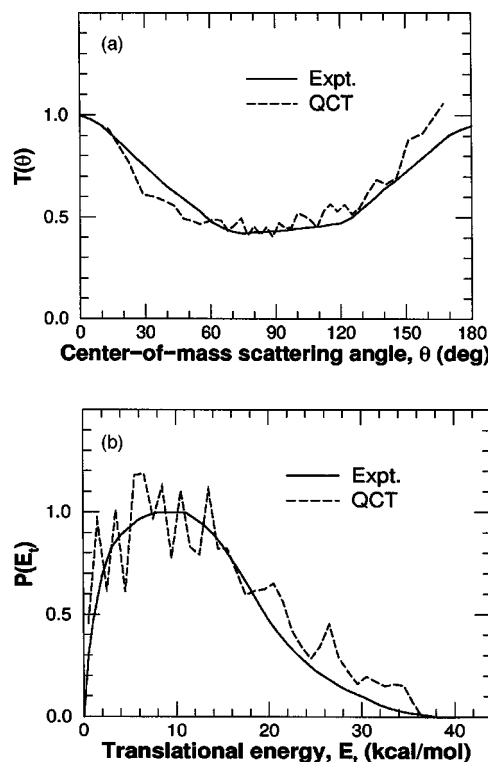

FIG. 2. Comparison between the experimental (solid lines) center-of-mass ND product angular (a) and translational energy (b) distribution for the $N(^2D)+D_2$ reaction at E_c = 5.1 kcal/mol and those calculated by the quasi-classical trajectory method (the dashed line) on a new potential energy surface based on accurate *ab initio* computations and the reproducing kernel Hilbert space interpolation method. The surface used to generate these results did not incorporate the Davidson correction, however, the results with this correction are virtually identical [Ref. 21(b)].

5.6 kcal mol^{-1} for collinear approach ($C_{\infty v}$ geometry). The first two excited PESs $^2A_1$ and $^2B_2$ do not correlate with ground state $NH(X\,^3\Sigma^-)$, but with $NH(a\,^1\Delta)$ and $NH(b\,^1\Sigma^+)$, respectively, so neither can contribute adiabatically to the formation of the ground state $NH+H$. Also, for the collinear approach the first excited PES $^2\Delta$ has a large barrier (> 20 kcal mol^{-1}) and the $^2\Pi$ PES is strongly repulsive. Thus, only insertion should play a role in $N(^2D)+H_2$ at thermal energies. Our calculations show that more than one PES may actually contribute to insertion, although the ground $^2B_1$ state should be dominant. The other possible pathway involves the $^2A_1$ PES which is adiabatically connected to the $^2B_2$ state via non-C_{2v} geometry (a conical intersection exists between $^2A_1$ and $^2B_2$ surfaces), and is coupled to $^2B_1$ via Renner–Teller interaction. The $^2B_2$ surface has a modest barrier of only 3.4 kcal/mol (for C_{2v} geometry).

QCT calculations were performed at the collision energies of the experiments on the ground state PES and the calculated product angular and translational energy distributions were compared with the experimentally derived quantities in the c.m. system. Quite good agreement is found for the angular distributions and very good accord exists for the translational energy distributions, as can be seen in Fig. 2. Analysis of the computed reactive trajectories revealed that $N(^2D)$ approaches almost perpendicularly the H–H bond and inserts into it forming the intermediate NH_2 (Fig. 3); if the initial approach is well away from perpendicular, then H_2 is able to reorient to the perpendicular direction before reaching the barrier top in the entrance channel. The lifetime of

the formed NH_2 is quite short (few vibrational periods), but a significant amount of scrambling of energy among different degrees of freedom takes place and, as a result, the product vibrational and rotational excitation are substantial, but only slightly hotter than is obtained by a phase-space theory that imposes conservation of angular momentum.[30] These findings are quite interesting since they help in understanding the dynamics of insertion reactions where the intermediate complex is a triatomic molecule with a few degrees of freedom.
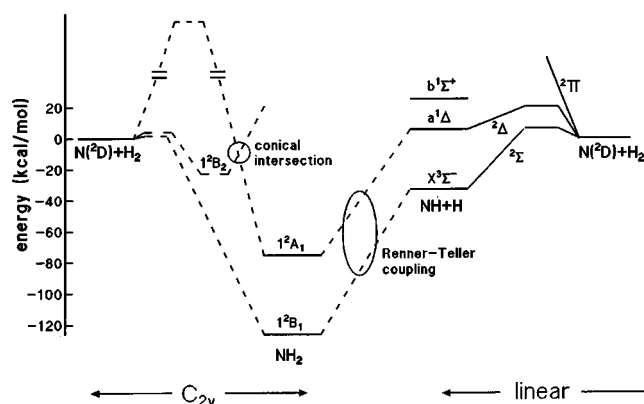

FIG. 3. Schematic energy level and correlation diagram for the reaction $N(^2D)+H_2$ based on *ab initio* electronic structure calculations (multireference configuration interaction) of the ground and first excited potential energy surfaces. The surfaces for both C_{2v} and linear geometry are shown.

It is instructive to compare the $N(^2D)+H_2$ reaction dynamics with that of the similar reaction $O(^1D)+H_2$. At the comparable E_c of 5.3 kcal mol^{-1}, experiments have shown[12(a)] for $O(^1D)+D_2$ an asymmetric c.m. angular distribution with more intensity in the backward direction, which has been interpreted[12(a),31] in terms of a direct abstraction mechanism (giving a backward scattered product angular distribution) superimposed with an insertion mechanism (giving a symmetric angular distribution), with abstraction taking place on the first excited PES $^1\Pi$ (in collinear geometry) which has a barrier of 2.4 kcal mol^{-1} and correlates with ground state OH.[13] In the case of $N(^2D)+H_2$, an analogous excited PES (in collinear geometry) correlating adiabatically with ground state products is not present (see Fig. 3), and this explains the absence of a direct abstraction contribution in this system in contrast to $O(^1D)+D_2$.

The dynamics of the $N(^2D)+H_2$ reaction has also been studied by QCT methods on an earlier *ab initio* PES,[26] and the results are quite different (backward scattered) since the insertion barrier is considerably higher than in the present PES. Very recently,[32] this surface has been modified to make the insertion barrier lower, and the new results are qualitatively similar to what we have obtained. Previously, dynamical calculations on $N(^2D)+H_2$ have been carried out by quantum scattering methods[26] for total angular momentum $J=0$. The results are generally quite similar to QCT results for the same PES, indicating that the QCT results should be accurate. Obviously, exact QM scattering calculations would be desirable for an unambiguous test of the PES. Such calculations on the present PES are currently under way.[33]

The good agreement between theory and experiment reported here shows we can model the PES well enough to predict detailed dynamical attributes of chemical reactions beyond direct *abstraction* reactions, such as $H+H_2$, $F+H_2$, and $Cl+H_2$, to encompass another important class of reactions, the perhaps more challenging *insertion* reactions, of which $N(^2D)+H_2$ represents a prototype. Finally, this study opens the way to the investigation of other important reactions of atomic nitrogen under the single collision conditions of crossed beam experiments.

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