Quasiclassical trajectory study of the dynamics of the H + N 2 O reaction on a new potential energy surface


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Quasiclassical trajectory study of the dynamics of the \( \text{H} + \text{N}_2\text{O} \) reaction on a new potential energy surface

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A new \textit{ab initio} potential energy surface (PES) for the \( \text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2 \) reaction has been constructed using the GROW package of Collins and co-workers. The \textit{ab initio} calculations have been done using the Becke three-parameter nonlocal exchange functional with the nonlocal correlation of Lee, Yang, and Parr density functional theory. A detailed quasiclassical trajectory study of integral and differential cross sections, product rovibrational populations, and internal energy distributions on the new PES is presented. The theoretical integral cross sections as a function of collision energy are in qualitative agreement with the experimental measurements. A good correspondence is found between the calculated \( \text{OH}(v^r = 0,1) \) rovibrational populations and the recent measurements of Brouard and co-workers at 1.48 eV collision energy. In particular, the calculated kinetic energy release distributions for state resolved \( \text{OH}(v^r, N^r) \) products predict a substantial fraction of total energy going into rotational excitation of the \( \text{N}_2 \) co-product, in good agreement with the experimental findings. © 2003 American Institute of Physics.

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I. INTRODUCTION

The reaction

\[
\text{H}(2\Sigma) + \text{N}_2\text{O}(1\Sigma) \rightarrow \text{OH}(\tilde{X}^2\Pi) + \text{N}_2(1\Sigma^+_g),
\]

\[
\Delta H^0_0 = -2.706 \text{ eV}
\]

has been the subject of considerable experimental research for over a decade. This reaction is important in the combustion of \( \text{H}_2/\text{N}_2\text{O} \) mixtures, and is one of the few known reactions where the \( \text{N}_2\text{O} \) greenhouse molecule is decomposed into \( \text{N}_2 \). Relevant to the present work are the pioneering studies of the photoinitiated reaction between translationally hot \( \text{H} \) atoms and \( \text{N}_2\text{O} \) molecules by Hollingsworth \textit{et al.} \cite{1} and Wittig and co-workers.\textsuperscript{2–4} These studies have determined the \( \text{OH}(\tilde{X}) \), \( \text{OH}(\tilde{A}) \), and \( \text{NH}(\tilde{X}) \) branching ratios, \( \text{OH} \) product quantum state populations, and kinetic energy release fractions of the \( \text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2 \) and \( \text{H} + \text{N}_2\text{O} \rightarrow \text{NH} + \text{NO} \) reactions. One of the most intriguing findings of these experiments has been the high \( \text{N}_2 \) internal excitation, observed indirectly via \( \text{OH} \) Doppler-resolved laser induced fluorescence (LIF) measurements using photolysis of \( \text{HI} \) as an \( \text{H} \)-atom precursor.\textsuperscript{3} In that study, it was speculated that vibrationally excited \( \text{N}_2 \) products were produced by a reaction mechanism in which a HNNO complex is formed and undergoes a 1, 3-hydrogen shift to the \( \text{N}_2 \rightarrow \text{OH} \) product channel.

The first study of the stationary points of the potential energy surface (PES) for reaction (1) was due to Marshall et al.\textsuperscript{5} using the bond additive corrections Möller–Plesset 4 (BAC-MP4) methodology. This study predicted that the reaction can take place either via a \textit{direct} process, in which the \( \text{H} \) attacks the \( \text{O} \)-end of \( \text{N}_2\text{O} \), or via an \textit{indirect} process, in which the \( \text{H} \) attaches to the terminal \( \text{N} \) to form a HNNO complex, and then a 1, 3-hydrogen migration occurs yielding \( \text{N}_2 + \text{OH} \). This early \textit{ab initio} calculation\textsuperscript{5} predicted a N–N bond length of 1.23 Å for the \textit{cis}-HNNO intermediate, which is about 0.13 Å larger than the \( \text{N}_2 \) equilibrium distance, and it was suggested that this may lead to vibrationally excited \( \text{N}_2 \) products, as proposed by Wittig and co-workers.\textsuperscript{4}

A more reliable characterization of the \( \text{HN}_2\text{O} \) PES was performed by Walch\textsuperscript{6} using high level \textit{ab initio} methods, i.e., complete active space self-consistent field /internally contracted configuration interaction (CASSCF/ICCI) method. Walch’s calculations predicted that the indirect pathway has a lower overall barrier and should be the more likely process at low temperatures. Later \textit{ab initio} calculations of transition states by Durant\textsuperscript{7} using the GAUSSIAN2 method were found to be in good agreement with Walch’s results.

Theoretical studies of the dynamics of the \( \text{H} + \text{N}_2\text{O} \) and its reverse \( \text{NH} + \text{NO} \) reactions have been performed using the quasiclassical trajectory method (QCT) by Bradley \textit{et al.}\textsuperscript{8,9} The dynamical calculations were mainly performed using a global PES, hereafter denoted as the BS PES, based on the \textit{ab initio} calculations of Walch\textsuperscript{6} and on the calculation and addition of more, less accurate, \textit{ab initio} data for a better description of the reaction path for 1,3-hydrogen migration and for the \( \text{H} \) addition to \( \text{N}_2\text{O} \) \textit{via} the \( \text{H} \rightarrow \text{ON} \) transition state.\textsuperscript{8} The energetics of the stationary points of the BS PES was modified with respect to the original calculations of Walch by fixing the difference between \( \text{NH} + \text{NO} \) and \( \text{H} \)
+ N₂O at the experimental exoergicity.⁸ The QCT study of the H + N₂O reaction on that PES by Bradley and Schatz⁹ showed that the direct mechanism for production of OH + N₂ was dominant for collision energies above 0.8 eV. However, these calculations predicted that OH and N₂ products were born with low rotational and vibrational excitation, with most of the available energy going into translation, in clear disagreement with the experimental observations of Böhmer et al.⁴

Recently, Fletcher and Wocjick¹⁰ have measured the total reaction cross section, as a function of the collision energy, σₚ(É), of the photon initiated H + N₂O→OH + N₂ reaction in a bulk experiment over collision energies in the range 0.87–1.95 eV. Laser-induced fluorescence was used to detect of the OH reaction product. Several different H-atom precursors were used to span the range of collision energies. In this study, absolute values of σₚ were obtained by calibration with the photodissociation of HNO at 266 nm as a standard, for which the absorption cross section and quantum yield for the production of OH are very well known. The σₚ were found to be about four times smaller that those calculated by Bradley and Schatz.⁹ The large discrepancies found between the QCT predictions and the experiments seem to indicate that the PES used in Ref. 9 is not accurate enough to capture the underlying dynamics of the reaction.

Also recently, Brouard and co-workers have studied the product state-resolved dynamics of the title reaction using a pump and probe experiment with sub-Doppler resolution at a mean collision energy of 1.48 eV in a series of experiments.¹¹–¹⁴ These studies have provided a great deal of new data about reaction (1) through the measurement of OH rovibrational quantum-state populations, quantum-state resolved differential cross sections (DCS), kinetic energy release distributions for a selected quantum state of the OH (thus providing information about the internal energy distribution of the undetected N₂ partner formed in coincidence with that internal state of OH), and the rotational angular momentum polarization of the OH.

The observed kinetic energy distributions for OH(ν’ =0, J’=13) turned out to be particularly interesting, showing a clear bimodal character, which was attributed to the existence of two microscopic pathways: a direct process, yielding products with a high kinetic energy release, corresponding to very cold internal excitation in the N₂ co-product, and a major indirect process which generates N₂ molecules with very high internal excitation. The similarities found between the energy disposal for the indirect channel of the reaction and the photodissociation of N₂O from its first absorption band lead the authors to suggest that N₂ generated via reaction (1) was born highly rotationally, rather than vibrationally excited. However, none of the previous theoretical studies could account for these experimental findings, perhaps due to inaccuracies in the PES, and the matter remained without theoretical confirmation.

In this paper, we present a QCT study of the title reaction at collision energies in the range É=0.6–1.48 eV, based on a new ab initio PES. The PES has been developed using the iterative interpolation methods devised by Collins and co-workers¹⁵–¹⁷ and recently implemented in the GROW package. These methods have proved to be very successful in constructing highly accurate PESs for the H + H₂O→OH + H₂ reaction.¹⁸,¹⁹ In the present case, we have employed Becke three-parameter nonlocal exchange functional with the nonlocal correlation of Lee, Yang, and Parr (B3LYP) hybrid density functional theory (DFT) method for the ab initio calculations, which is quite an efficient and economical technique to calculate energy, gradients, and second derivatives.²⁰ B3LYP performance in comparison with higher level methods, such as quadratic configuration interaction with singles and doubles plus perturbative contribution of triples, QCISD(T), has been tested for transition states and barriers for reactions such as H + OCS,²¹ with quite encouraging results. On the contrary, it is known that the B3LYP DFT method predicts activation barriers of reactions such as H + CH₂ and OH with fluorinated methanes which are 1–2 kcal mol⁻¹ lower than the experimental values.²² There have been only few attempts to construct a global PES for a reaction using DFT methods.²³ Thus little is known about their accuracy for dynamical calculations. The present study can shed some light on the performance of the DFT methodology to describe the dynamics of a reaction with a complex mechanism such as that of the title reaction.

II. POTENTIAL ENERGY SURFACE

All ab initio calculations were performed using the GAUSSIAN 98 suite of programs.²⁴ The basis set used in the DFT B3LYP calculations is the Dunning correlation consistent triple zeta basis (cc-pVTZ).²⁵ Table I compares the present DFT B3LYP/ccc-pVTZ energetics [see also Fig. 1(a)]

<table>
<thead>
<tr>
<th>Species</th>
<th>B3LYP</th>
<th>CASSCF/CCI⁺</th>
<th>G2/QCISD⁺</th>
<th>BAC-MP²⁺</th>
<th>MRD-Cl/HF²⁺</th>
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<td>H–ONN</td>
<td>0.55(0.32)</td>
<td>0.78</td>
<td>0.86</td>
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<tr>
<td>H–NNO</td>
<td>0.25(0.32)</td>
<td>0.45</td>
<td>0.40</td>
<td>0.16</td>
<td>0.82</td>
</tr>
<tr>
<td>[NNOH]</td>
<td>0.71(0.39)</td>
<td>0.71</td>
<td>0.72</td>
<td>0.72</td>
<td>0.99</td>
</tr>
<tr>
<td>cis-HNNO</td>
<td>-0.88(0.55)</td>
<td>-0.63</td>
<td>-0.62</td>
<td>-0.63</td>
<td>-1.27</td>
</tr>
<tr>
<td>trans-HNNO</td>
<td>-1.12(0.54)</td>
<td>-0.86</td>
<td>-0.93</td>
<td>-0.50</td>
<td>-1.28</td>
</tr>
<tr>
<td>cis-to-trans TS</td>
<td>-0.13(0.48)</td>
<td>-0.16</td>
<td>-0.16</td>
<td>-0.095</td>
<td></td>
</tr>
<tr>
<td>OH + N₂</td>
<td>-2.56(0.38)</td>
<td>-2.71</td>
<td>-2.87</td>
<td>-2.67</td>
<td></td>
</tr>
</tbody>
</table>

⁺CASSCF/CCI/cc-pVTZ, Ref. 6.
⁺⁺G2/QCISD,b-31G(d,p), Ref. 7.
²⁺MRD-Cl/HF/4-31G(d,p), Ref. 26.

Reference 5.
of the optimized stationary points of the HN$_2$O ($\tilde{A}^1$) PES with those previously reported. As can be seen, there is a wide variation in the \textit{ab initio} values. Nevertheless, B3LYP, CASSCF/ICCI, and BAC-MP4 calculations predict that the H–NN NO transition state barrier is considerably lower than the H–ON N barrier. The $\tilde{N}$NOH (1,3-hydrogen migration) saddle point energies obtained by the different methods agree very well with the exception of the MRC-CI calculation by Fueno et al.\textsuperscript{26} Interestingly, the B3LYP H–ON N barrier is noticeably smaller than that of the $\tilde{[}NNOH]$ saddle point, whereas the opposite occurs in the CASSCF/ICCI calculations. As it will be shown below, this has relevant consequences on the dynamics of the title reaction. The trans-HNNO structure is found to be below the cis-HNNO minimum in accordance with all previous calculations, except the BAC-MP4 prediction of Marshall and co-workers,\textsuperscript{5} who found the reverse order. The B3LYP/cc-pVTZ calculations underestimate by 5\% the experimental exothermicity $\Delta H^\circ = -2.706 \pm 0.04$ eV (Ref. 27).

Tables II and III give the B3LYP computed frequencies and geometries of the stationary points. It should be noted that all the transition states have a planar geometry. The reactant N$_2$O and products OH + N$_2$ geometries are in very good agreement with experimental determinations with a relative error no larger than 0.5\%. However, the N$_2$O and N$_2$ vibrational frequencies are about 5\% larger than the experimental values. The comparison with the CASSCF/ICCI calculations by Walch\textsuperscript{6} and the GAUSSIAN2 calculations by Duran\textsuperscript{7} is fairly good, except for the DFT B3LYP imaginary frequencies of the H–ON N and H–NNO saddle points, which are about 45\% smaller than the CASSCF frequencies. Recently, Laursen et al.\textsuperscript{28} have investigated the NH+NO re-

![Energy Diagram](image-url)

FIG. 1. (a) Energy diagram showing the location of the stationary points obtained in the present B3LYP \textit{ab initio} calculations. The energies include the zero point energy correction and are listed in Table I. (b) Minimum energy paths (MEP) of the H+N$_2$O $\rightarrow$OH + N$_2$ reaction computed at the B3LYP/cc-pVTZ level of theory. Energies are relative to the H+N$_2$O asymptote ($-185.237 \pm 0.311$ hartrees). Solid line: H+N$_2$O $\rightarrow$OH + N$_2$ direct mechanism MEP. Dotted line: H+N$_2$O $\rightarrow$H–NN NO $\rightarrow$OH + N$_2$ direct mechanism MEP. Dashed line: cis-HNNO $\rightarrow$[HONN] $\rightarrow$OH + N$_2$ migration MEP. Dotted–dashed line: cis-HNNO $\rightarrow$trans-HNNO isomerization MEP.
TABLE II. Geometries and vibrational frequencies of the stationary points of the H\textsubscript{2}O \textsubscript{2} PES obtained in the present work. Distances (r) are in Å, angles in deg, and frequencies (\omega) in cm\textsuperscript{-1}.

<table>
<thead>
<tr>
<th></th>
<th>cis-to-trans HNNO</th>
<th>[NNOH]</th>
<th>OH + N\textsubscript{2}</th>
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<tr>
<td>r\textsubscript{HN}</td>
<td>1.64</td>
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<tr>
<td>r\textsubscript{NN}</td>
<td>1.12</td>
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<td>1.18</td>
<td>1.18</td>
<td>1.21</td>
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<td>r\textsubscript{OH}</td>
<td>2.98</td>
<td>1.38</td>
<td>0.97</td>
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<tr>
<td>H\textsubscript{NN}</td>
<td>111.2</td>
<td>90.2</td>
<td></td>
</tr>
<tr>
<td>NNO</td>
<td>177.3</td>
<td>96.5</td>
<td></td>
</tr>
<tr>
<td>N\textsubscript{OH}</td>
<td>76.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH\textsubscript{N}</td>
<td>96.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>\omega\textsubscript{1}</td>
<td>2899.3</td>
<td>2053.1</td>
<td>3699.6(OH)</td>
</tr>
<tr>
<td>\omega\textsubscript{2}</td>
<td>1951.9</td>
<td>1652.9</td>
<td>2450.1(N\textsubscript{2})</td>
</tr>
<tr>
<td>\omega\textsubscript{3}</td>
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<td>859.5i</td>
<td>1838.2i</td>
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<td>\omega\textsubscript{6}</td>
<td>501.3</td>
<td>1011.3</td>
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</table>

action in a solid xenon matrix and have detected the HNNO intermediate by infrared spectroscopy. Two isomers were identified that can be associated with cis-HNNO and trans-HNNO structures. The assigned experimental frequencies for these structures are in quite good agreement with the present results, with the CASCCF/ICC1 by Walch,\textsuperscript{6} and with the GAUSSIAN2 calculations by Durant.\textsuperscript{7}

From the transition states, i.e., H–NNO, H–ONN, [NNOH], and cis-to-trans isomerization, the intrinsic reaction coordinate (IRC) or minimum energy paths (MEP) have been calculated using the Berny algorithm implemented in GAUSSIAN 98.\textsuperscript{8,9} The MEPs are displayed in Fig. 1(b). Clearly, the H–NNO transition state is connected to the cis-HNNO minimum. The [NNOH] transition state leads to cis-HNNO and to the OH + N\textsubscript{2} products. The sets of points that define the reaction paths shown in Fig. 1(b) have been used to calculate the initial surface. A total of 200 points for the reaction paths have been calculated and used as initial guess for developing the PES. The self-consistent field (SCF) wave function has been required to be converged tight to 10\textsuperscript{-10} and to be stable for all points. The final PES has been grown using the iterative methods implemented in the GROW script. The methods for choosing a new data point at each iteration have been discussed in detail elsewhere. The “variance sampling”\textsuperscript{20} and “\textit{h} weight” methods\textsuperscript{30,31} have been used alternatively for each additional data point. The classical trajectory calculations, which are performed in order to select new data points, have been run under the following conditions. A ground state zero-point energy has been given to N\textsubscript{2}O with coordinates and momenta corresponding to a microcanonical distribution. A relative translational energy of 1.48 eV and a maximum impact parameter of 2.0 Å was chosen for the initial conditions of the trajectories. The initial distance from the H-atom to the N\textsubscript{2}O molecule was set to 6 Å, and the final relative separation between the OH and N\textsubscript{2} products was set to 6 Å. A total of 1400 data points that include energy, gradient, and Hessian have been calculated for the present PES and are available from the authors upon request or as an EPAPS document.\textsuperscript{37} The convergence of the total integral cross section has been monitored while the surface was being developed by running batches of 2000 trajectories. The cross section only changes by 0.5% when the number of data points is increased from 1200 to 1400. By maintaining the collision energy below 1.5 eV, no attempt has been made to calculate data at configurations relevant to the NH + NO channel of the reaction.

III. QUASICLASSICAL TRAJECTORY CALCULATIONS

The method of QCT calculations followed in this work has been described in our recent studies on the H + H\textsubscript{2}O reaction,\textsuperscript{32–34} and references therein. Batches of 5 \texttimes 10\textsuperscript{5} trajectories with a maximum impact parameter \textit{b}\textsubscript{max} = 2.00 Å have been run for each translational energy in the range \textit{E}_{t} = 0.6–1.48 eV. At \textit{E}_{t} = 1.48 eV, an additional batch of 2.3 \texttimes 10\textsuperscript{5} trajectories was run to improve the product state resolved statistics. Initial conditions for the rotationless N\textsubscript{2}O molecule in the (000) vibrational state have been determined using a microcanonical normal mode sampling. Integration of the equations of motion was carried out using an adapted version of the VENUS 96 program\textsuperscript{35} with at time step of 0.05 fs. The typical conservation of energy was better than 1 in 10\textsuperscript{3}. For the assignment of diatomic products quantum numbers, the classical diatomic molecule rotational angular momentum is equated to \textit{j} = \textit{j}'(\textit{j}' + 1)/2. With the (real) \textit{j}' value so obtained, the vibrational quantum number \textit{v}' is found by equating the internal energy of the outgoing molecule to the corresponding rovibrational Dunham expansion in (\textit{v}' + 1/2) and \textit{j}'(\textit{j}' + 1), whose coefficients are calculated by fitting the semiclassical or quantum rovibrational energies given by the asymptotic diatomic potentials of the PES. The values of \textit{v}' and \textit{j}' found in this way are then rounded to the nearest integer. The calculation of the kinetic energy release distributions \textit{f}(\textit{s}), where \textit{f} = \textit{E}_{t}/\textit{E}_{avail} is the fraction of the total available energy channeled into product relative translation, has been carried out by using the state resolved integral cross sections as described in recent works.\textsuperscript{33,34}

In order to calculate the DCSs, the scattering angle in the center-of-mass (CM) frame has been defined as follows: If
the OH molecule is detected, as is the case in the experiments of Brouard and co-workers, the usual convention, followed by these authors, defines the scattering angle as that formed between the incoming H atom and the outgoing OH radical. Therefore, if the OH CM velocity is $w_{\text{OH}}$ and that of the H atom is $w_{\text{H}}$, the definition of the scattering angle $\theta$ is given by

$$\cos \theta = \frac{w_{\text{H}}}{|w_{\text{H}}|} \cdot \frac{w_{\text{OH}}}{|w_{\text{OH}}|}. $$

(2)

The DCSs are calculated by the method of moments expansion in Legendre polynomials. The Smirnov–Kolmogorov test is used to decide when to truncate the series. Significance levels higher than 95% can be achieved using 5–6 moments, ensuring good convergence, such that the inclusion of more terms does not produce significant change.

IV. RESULTS AND DISCUSSION

A. Total reaction cross sections and average energy disposals

Figure 2 shows the present QCT calculated total reaction cross section as a function of collision energy, $\sigma_R(E_t)$, for the title reaction. As can be seen the QCT $\sigma_R$ overestimate the absolute values measured by Fletcher and Wocjick at translational energies below 1.3 eV and indicates a threshold for reaction near 0.6 eV, whereas the experimental threshold seems to be located at about 0.97 eV. The present calculations are restricted to collision energies below 1.48 eV and thus we cannot confirm the maximum in $\sigma_R(E_t)$ observed experimentally at about 1.5 eV. Nevertheless, the present results are in much better agreement with the experiment than the previous QCT $\sigma_R$ calculated by Bradley and Schatz, also shown in the figure. It should be noted that the QCT $\sigma_R$ calculated in Ref. 9 shown in Fig. 2 correspond to calculations imposing a somewhat ad hoc zero point energy (ZPE) constraint to both OH and N$_2$ product molecules; those trajectories yielding OH or N$_2$ with internal energy below their respective zero point energies are simply discarded. The values of $\sigma_R$ obtained without the ZPE constraint obtained in Ref. 9 are considerably larger than those represented in the figure. In the present case, no ZPE constraints have been considered.

As commented on above, considering the various reaction paths, there are two possible mechanisms for the reaction: one in which the H atom attacks the O-side of the N$_2$O molecule, forming H--ONN to yield products, and a second one, more complex, in which the H atom approaches first the terminal N atom, forming either the cis or trans H--N--N--O and, after surmounting a barrier migrates to a [NOOH] structure, finally decomposes into products. Undoubtedly, the first mechanism, which is basically an abstraction, is more direct than the second, which implies the formation of a complex and subsequent atom migration. The choice of one of these two mechanisms would be governed to a large extent by the direction of approach and the distance of the H-atom to the N- or O-side of the molecule. Following the prescription of Bradley and Schatz, it seems sensible to label the reactive trajectories as direct or indirect according to which distance, O--H or N--H, first reaches a given small value. Considering the geometries of the stationary points shown in Table II, this value could be approximately established in 1.6 Å. Hereafter the analysis of the trajectories will be done following this criterion.

Table IV presents the $\sigma_R$, energy partitioning and the fraction of trajectories going through the direct and indirect mechanisms. Note that as in previous works the fractions for vibration and rotation have been obtained from the rovibrational energies calculated by rounding off the vibrational and rotational actions of the products. This implies to assume

<table>
<thead>
<tr>
<th>$E_t$/eV</th>
<th>$\sigma_R$/Å$^2$</th>
<th>$\langle f_d \rangle$</th>
<th>$\langle f_i \rangle$</th>
<th>$\langle f_{\text{ah}}^{\text{OH}} \rangle$</th>
<th>$\langle f_{\text{ah}}^{\text{H}} \rangle$</th>
<th>$\langle f_{\text{ah}}^{\text{NNOH}} \rangle$</th>
<th>$\langle f_{\text{ah}}^{\text{trans}} \rangle$</th>
<th>$\langle f_{\text{ah}}^{\text{cis}} \rangle$</th>
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<td>0.61</td>
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<td>0.03</td>
<td>0.91</td>
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<td>0.10</td>
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<td>0.03</td>
<td>0.73</td>
<td>0.27</td>
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<tr>
<td>1.18</td>
<td>0.179</td>
<td>0.54</td>
<td>0.06</td>
<td>0.09</td>
<td>0.27</td>
<td>0.03</td>
<td>0.73</td>
<td>0.27</td>
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<tr>
<td>1.48</td>
<td>0.294</td>
<td>0.53</td>
<td>0.08</td>
<td>0.10</td>
<td>0.25</td>
<td>0.04</td>
<td>0.70</td>
<td>0.30</td>
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</table>
that the zero point energies of N2 and OH molecules are taken in $v' = 0$. About 52% of the available energy goes into translation of the products, 20%–10%, depending on the collision energy, appears as vibrational energy of OH, and only a tiny amount (3%–8%) goes into OH rotation. In contrast, a very significant amount of the available energy was channelled into N2 rotation, ~25%, whereas only 3% goes into vibrational energy of this molecule. This result is at variance with the QCT calculations performed by Bradley and Schatz on the BS PES, who found that about 70% of the available energy in channelled into translation of the products and that the internal energy of the nascent N2 molecule is very small, in clear disagreement with the experimental findings and the present calculations.

The analysis of trajectories in terms of the preferential approach of the H-atom to the O- or N-side of the N2O reveals that the direct abstraction mechanism (H–ONN) is dominant at all energies, although the indirect mechanism becomes more important as the collision energy increases. This behavior is the opposite to that found by Bradley and Schatz in their QCT study. However, it is consistent with the fact that, in the current PES, indirect trajectories have to overcome a barrier of 0.62 eV in the [NNOH] H-migration transition state, while the barrier for the H–ONN transition state is 0.17 eV lower. This is in contrast to the BS PES, for which the H–ONN barrier is larger than the [NNOH] H-migration transition state by 0.13 eV.9

A detailed comparison of the OH state-averaged energy disposal data with the experimental values obtained by Brouard and co-workers12 at $E_t = 1.48$ eV is presented in Table V. The main discrepancy between the present QCT results and the experiment lies in the fact that the experimentally inferred internal excitation of N2 is about 47% of the total available energy, whereas it is only 29% in the present QCT calculations. It must be pointed out that the present QCT calculations show that the direct mechanism is responsible for most of the rotational excitation of the N2 molecule. On the contrary, the indirect mechanism accounts for very little rovibrational excitation of N2 and most of the available energy goes into translation. The large amount of N2 rotational excitation predicted by the direct mechanism is somewhat surprising at first sight because the NNO angle in the H–ONN transition state is about 161°, so a torque on the departing N2 seems to be unlikely. However, an inspection of the NNO angle along the reaction coordinate shows that the NNO angle varies widely, from 160° to 120°, as the OH and N2 fragments separate. On the contrary, the NNO angle along the MEP that contains the [NNOH] transition state just changes from 95° to 110°. Thus, it seems that strong repulsive forces are at work along the H+ON2→[H–ONN]→OH+N2 path, exerting a significant torque on the N2 molecule. Note that this proposed mechanism is consistent with the fact that the rotational excitation of the N2 and OH molecules is largely independent on collision energy as shown in Table IV. It thus can be concluded that momentum transfer from the incoming H-atom is very inefficient as a mechanism for rovibrational excitation in this reaction.

In the QCT calculations on the BS PES at $E_t = 1.5$ eV (Ref. 9) also a high percentage (84%) of the reactive trajectories follow the direct mechanism. However, the fraction of the available energy going into rotation of the N2 fragment is only 0.04.9 Therefore, in the case of a PES based on ab initio calculations of higher accuracy, for which the order of the H–ONN and [NNOH] barrier heights is the opposite to that found in the present DFT calculations, the same direct mechanism is predicting a cold rotational distribution for N2. Dynamical results are then affected not only by the relative energies of the stationary points but also by the overall topology of the PES.

### B. Product population distributions and OH state-specific energy disposals

The OH and N2 vibrational populations at $E_t = 1.48$ eV relative to $v' = 0$ are shown in Figs. 3(a) and 3(b), respectively. The OH $P(v' = 1)/P(v' = 0)$ ratio is compared in Fig. 3(a) with the experimental determinations of Brouard et al.12 The experiments by Brouard and co-workers, with a single collision energy (1.48 eV), give a ratio $P(v' = 1)/P(v' = 0) = 0.28 ± 0.05$, which differs from that obtained in the present calculations. We note in passing that Wittig and co-workers4 obtained an experimental value of 0.5 which is quite close to the present theoretical data of 0.55. However, it should be born in mind that in the experiments of Ref. 4, translationally excited H atoms were produced by HI photolysis at 244.7 nm, which generates two-component H-atom velocity distributions due to the population of both iodine spin–orbit states. Consequently, in those experiments two collision energies (0.9 and 1.9 eV) are involved. In this figure, the contributions of the direct and indirect mechanism are also portrayed. As can be seen, the predominant direct mechanism does not show any population inversion, whereas for the reaction through the minor indirect mechanism the population of $v' = 0$ is slightly smaller than that of $v' = 1$. The calculated N2 vibrational distribution at this collision energy is represented in Fig. 3(b), showing a
similar pattern to that of OH. Neither of the two mechanisms yield population inversion for this product, although that from the indirect mechanism is somewhat hotter. As mentioned in the Introduction, the experiments by Brouard and co-workers allow a precise determination of the OH($v' = 0$) rotational distributions at $E_t = 1.48$ eV. In Fig. 4, the present QCT rotational distributions for $v' = 0$ and $v' = 1$ are compared with the experimental data. For this and following comparisons we have considered that $N'$, the OH total angular momentum apart from electron spin, can be equated to $j'$, the rotational angular momentum employed in the QCT calculations, which treat OH as a closed shell species. As it has been shown previously \cite{ref34}, this is a good approximation for high enough $N'$ levels ($N' \geq 5$) in terms of rotational energy. The agreement between theory and experiment is quite fair, although the QCT distributions show some structures which are not observed in the experimental distributions. At present, we do not have an explanation for these structures, though they could be caused by imperfections of the present PES.

Figure 5 displays the calculated $N_2(v' = 0)$ and $N_2(v' = 1)$ rotational distributions for which no direct experimental data are available. The rotational distributions are clearly bimodal, peaking around $j' = 20$ and $j' = 85$. As shown in the plots, the indirect mechanism leads to low rotational levels of $N_2$, while the direct mechanism generates $N_2$ in high rotational states.

The evidence for the high internal excitation of $N_2$ products and the concurrence of two microscopic reaction mechanisms is clearly provided experimentally by the kinetic energy release distributions for specific rovibrational states of the OH product determined by Brouard and co-workers \cite{ref11, ref12} by deconvolution of the Doppler contours of several rotational lines. Figure 6 compares the present QCT $P(f_t)$, where $f_t$ is the fraction of the total energy going into translation, for state-resolved OH($v', N'$) with the experimental distributions. Both QCT and experimental distributions are bimodal and agree qualitatively. The figure shows that the peak at $f_t = 0.5$ is only due to the direct mechanism while the high $f_t$ component is accounted for by the indirect mechanism. Brouard et al. compared the OH($v' = 0$, $N' = 5$) $P(f_t)$ for the H$+N_2$O reaction with that obtained in the photodissociation of N$_2$O from the first absorption band \cite{ref36} and observed an excellent agreement. It is known that the nascent $N_2$ fragment from the photodissociation of N$_2$O is born in high rotational states, showing a distribution peaking around $j' = 100$. \cite{ref36} Therefore, it seems very likely that $N_2$ molecules from the reaction are generated in high rotational states, showing a distribution peaking around $j' = 100$. \cite{ref36} Therefore, it seems very likely that $N_2$ molecules from the reaction are generated in high rotational states, although a direct experimental proof is still waiting. As shown above, the present QCT calculations support the conclusion that the $N_2$ product must appear rotationally excited rather than vibrationally excited as was conjectured previously. \cite{ref3, ref4} It
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should be pointed out that Brouard et al., when discussing about the existence of two mechanisms, attributed the formation of translationally hot N₂ (thus emerging with low \( j' \)) to a “direct process,” presumably occurring by the attack of the H to the O end of the N₂O molecule, whereas the rotationally excited N₂ formation was ascribed to an “indirect process” occurring via H approach to the nitrogen side of the NNO. The present study provides additional support for the existence of two mechanisms, but it differs from the interpretation by Brouard and coworkers in that the direct mechanism (i.e., H attacking the O side) is the one that produces rotationally hot N₂, whereas it is the indirect mechanism (H attacking the N end) which causes the N₂ molecules to appear translationally excited. The plausible explanation of this behavior have been discussed above; in any case, there is no reason why rotationally excitation must necessarily imply the existence of an indirect mechanism.

C. Differential cross sections

Figure 7 shows the total and OH vibrationally state-resolved (summed on all N₂ final states) DCSs calculated for the title reaction at 1.48 eV collision energy. In all cases, the contributions from the direct and indirect mechanisms are also depicted. The total DCS is predominantly backward with a large contribution in the sideways region for scattering angles larger than 60° and a small isotropic contribution in the forward hemisphere. The analysis of trajectories in terms of the direct and indirect mechanisms at this collision energy indicates that the direct mechanism yields a purely backward DCS, whereas the DCS corresponding to the indirect mechanism is very isotropic. This same behavior, observed for the total DCS, is also obtained for the \( v' \) state-resolved DCS.

As mentioned above the experiments of Brouard et al.12 probed in detail the OH(\( v' =0, N' =5,9,14 \)) and OH(\( v' =1, N' =6 \)) rovibrational levels, which were found to be amongst the most populated at \( E_i =1.48 \) eV for this reaction. The experimental DCSs for these levels are compared in Fig. 8 with the present QCT DCSs. Note that the DCSs are normalized by the factor \( 2π/\sigma \) and represented against cos \( \theta \), which is convenient for a proper comparison of the shapes of the experimentally determined DCS and the theoretical ones. The agreement found between theory and experiment is mostly unsatisfactory with the possible exception of \( v' =0, N' =5 \). The most noticeable disagreement can be observed for OH(\( v' =0,N' =9 \)) and OH(\( v' =0,N' =14 \)), where the experimental DCSs are fairly isotropic, whereas the QCT DCSs are sharply sideways peaking in the backward hemisphere. The backward–forward symmetry of the experimental DCS has been proposed as an evidence of a mechanism that involves a relatively long-lived NNO–H complex,12 but this is not well reproduced by the QCT calculations performed on the present PES. For the rest of rotational levels...
of OH, the agreement between experiment and theory is only qualitative. However, the experimental DCSs show a trend of shifting from forward-backward symmetry at low \( N \) to more sideways at high \( N \). The QCT DCSs have a similar behavior.

V. CONCLUSIONS

A detailed quasiclassical trajectory study has been carried out for the H+N\(_2\)O→OH+N\(_2\) reaction employing a new \textit{ab initio} potential energy surface. DFT B3LYP/cc-pVQZ theory has been used to calculate the relevant transition states and reaction paths for the reaction. The final surface has been constructed using the iterative and interpolation methods implemented in the GROW package by Collins and co-workers. The calculated total reaction cross sections vs collision energy are found in qualitative agreement with the most recent experimental measurements. The OH rotational populations and kinetic energy release distributions at the collision energy \( E_t = 1.48 \) eV reproduce most of the important features of the experimental data. It is found that there are two mechanisms contributing to the reaction, which are labeled as \textit{direct} or \textit{indirect} according to whether the H attacks the O side or the N side of the N\(_2\)O molecule. The former (direct attack of the H to the O end) constitutes the main mechanism for the reaction, and accounts for the considerable amount of internal excitation of N\(_2\) observed in the experiments of Böhmert et al. and of Brouard and co-workers. The predicted N\(_2\) vibrational distribution is \textit{cold}, while the rotational distribution is quite \textit{hot}, corroborating the inferences of Brouard and co-workers. The second, indirect, mechanism by which the H atom attacks the N end of the NNO molecule, yields translationally hot N\(_2\), explaining the bimodality of the recoil energy distributions found experimentally. Nevertheless, the QCT calculations on the present \textit{ab initio} potential energy surface do not yield results that match all the available experimental measurements quantitatively or even qualitatively, in the case of the state-resolved differential cross sections. Therefore, further refinements of the potential energy surface are warranted. Work is in progress to construct a potential energy surface employing an \textit{ab initio} method of a higher level of accuracy.

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