

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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Quasiclassical trajectory study of the dynamics of the H+N₂O reaction on a new potential energy surface

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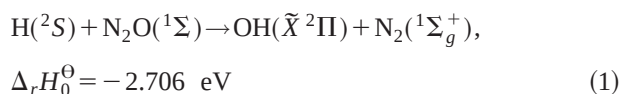
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A new *ab initio* potential energy surface (PES) for the H+N₂O→OH+N₂ reaction has been constructed using the GROW package of Collins and co-workers. The *ab initio* calculations have been done using the Becke three-parameter nonlocal exchange functional 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 OH(*v*'=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 OH(*v*',*N*') products predict a substantial fraction of total energy going into rotational excitation of the N₂ co-product, in good agreement with the experimental findings. © 2003 American Institute of Physics.

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I. INTRODUCTION

The reaction



has been the subject of considerable experimental research for over a decade. This reaction is important in the combustion of H₂/N₂O mixtures, and is one of the few known reactions where the N₂O greenhouse molecule is decomposed into N₂. Relevant to the present work are the pioneering studies of the photon initiated reaction between translationally hot H atoms and N₂O molecules by Hollingsworth *et al.*¹ and Wittig and co-workers.^{2–4} These studies have determined the OH(*X̃*), OH(*Ã*), and NH(*X̃*) branching ratios, OH product quantum state populations, and kinetic energy release fractions of the H+N₂O→OH+N₂ and H+N₂O→NH+NO reactions. One of the most intriguing findings of these experiments has been the high N₂ internal excitation, observed indirectly via OH Doppler-resolved laser induced fluorescence (LIF) measurements using photolysis of HI as an H-atom precursor.⁴ In that study, it was speculated that vibrationally excited N₂ products were produced by a reaction mechanism in which a HNNO complex is formed and undergoes a 1, 3-hydrogen shift to the N₂–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.*⁵ using the bond additive corrections Möller–Plesset 4 (BAC-MP4) methodology. This study predicted that the reaction can take place either *via* a *direct* process, in which the H attacks the O-end of N₂O, or *via* an *indirect* process, in which the H attaches to the terminal N to form a HNNO complex, and then a 1, 3-hydrogen migration occurs yielding N₂+OH. This early *ab initio* calculation⁵ predicted a N–N bond length of 1.23 Å for the *cis*-HNNO intermediate, which is about 0.13 Å larger than the N₂ equilibrium distance, and it was suggested that this may lead to vibrationally excited N₂ products, as proposed by Wittig and co-workers.⁴

A more reliable characterization of the HN₂O PES was performed by Walch⁶ using high level *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 *ab initio* calculations of transition states by Durant⁷ using the GAUSSIAN2 method were found to be in good agreement with Walch's results.

Theoretical studies of the dynamics of the H+N₂O and its reverse NH+NO reactions have been performed using the quasiclassical trajectory method (QCT) by Bradley *et al.*^{8,9} The dynamical calculations were mainly performed using a global PES, hereafter denoted as the BS PES, based on the *ab initio* calculations of Walch⁶ and on the calculation and addition of more, less accurate, *ab initio* data for a better description of the reaction path for 1,3-hydrogen migration and for the H addition to N₂O *via* the H–ONN transition state.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 NH+NO and H

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+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, $\sigma_R(E_t)$, 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 σ_R were obtained by calibration with the photodissociation of HNO₃ 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 σ_R were found to be about four times smaller than 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(v' = 0,1, $j' \leq 13$) 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 $E_t = 0.6$ –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-workers^{15–17} 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+CH₄ 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/cc-pVTZ energetics [see also Fig. 1(a)]

TABLE I. Energies of the stationary points of the H+N₂O PES including the zero-point energy correction. All energies are in eV relative to H+N₂O. Values in parentheses are the zero point energies (in eV) of the corresponding stationary points.

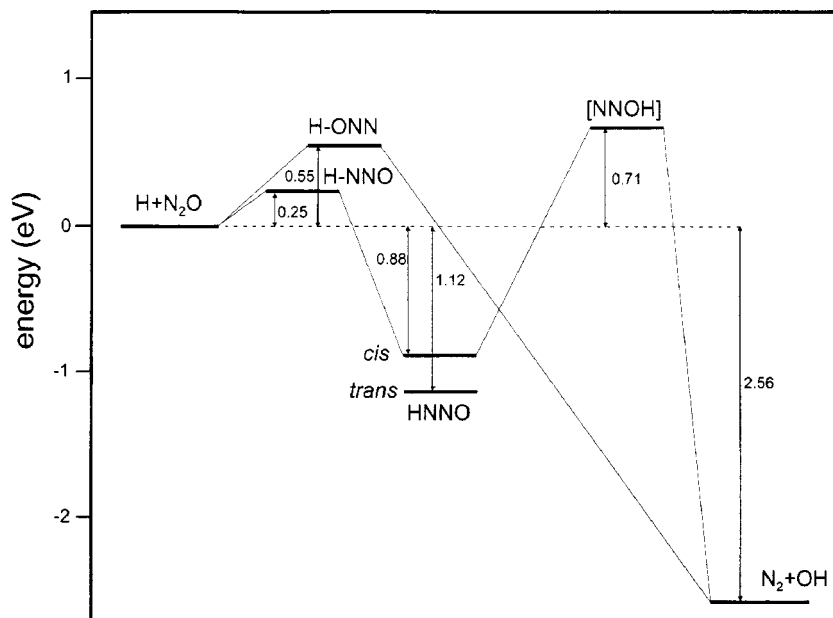
Species	B3LYP	CASSCF/ICCI ^a	G2//QCISD ^b	BAC-MP4 ^c	MRD-CI//HF ^d
H–ONN	0.55(0.32)	0.78		0.86	
H–NNO	0.25(0.32)	0.45	0.40	0.16	0.82
[NNOH]	0.71(0.39)	0.71	0.72	0.72	0.99
<i>cis</i> -HNNO	−0.88(0.55)	−0.63	−0.62	−0.63	−1.27
<i>trans</i> -HNNO	−1.12(0.54)	−0.86	−0.93	−0.50	−1.28
<i>cis</i> -to- <i>trans</i> TS	−0.13(0.48)		−0.16		−0.095
OH+N ₂	−2.56(0.38)		−2.71	−2.87	−2.67

^aCASSCF/CI/cc-pVTZ, Ref. 6.

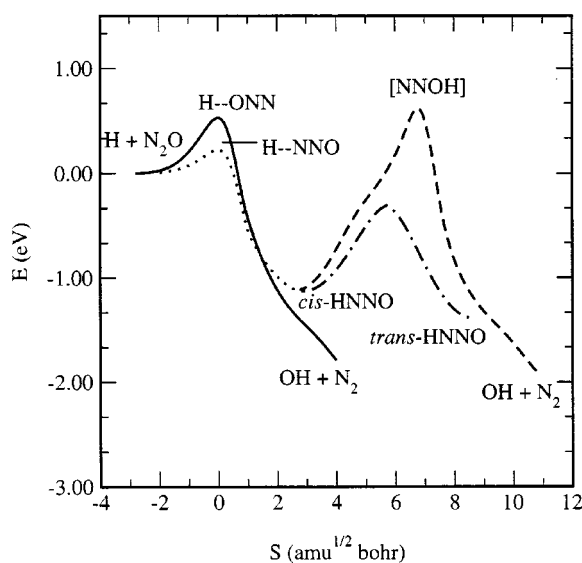
^bG2//QCISD/6-31G(*d,p*), Ref. 7.

^cReference 5.

^dMRD-CI//HF/4-31G(*d,p*), Ref. 26.



(a) reaction coordinate



(b)

FIG. 1. (a) Energy diagram showing the location of the stationary points obtained in the present B3LYP *ab initio* calculations. The energies include the zero point energy correction and are listed in Table I. (b) Minimum energy paths (MEP) of the $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$ reaction computed at the B3LYP/cc-pVTZ level of theory. Energies are relative to the $\text{H} + \text{N}_2\text{O}$ asymptote ($-185.237\,351$ hartrees). Solid line: $\text{H} + \text{N}_2\text{O} \rightarrow \text{H-ONN} \rightarrow \text{OH} + \text{N}_2$ direct mechanism MEP. Dotted line: $\text{H} + \text{N}_2\text{O} \rightarrow \text{H-NNO} \rightarrow \text{cis-HNNO}$ MEP. Dashed line: $\text{cis-HNNO} \rightarrow [\text{NNOH}] \rightarrow \text{OH} + \text{N}_2$ migration MEP. Dotted-dashed line: $\text{cis-HNNO} \rightarrow \text{trans-HNNO}$ isomerization MEP.

of the optimized stationary points of the HN_2O ($^2A'$) PES with those previously reported. As can be seen, there is a wide variation in the *ab initio* values. Nevertheless, B3LYP, CASSCF/ICCI, and BAC-MP4 calculations predict that the H-NNO transition state barrier is considerably lower than the H-ONN barrier. The [NNOH] (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.*²⁶ Interestingly, the B3LYP H-ONN barrier is noticeably smaller than that of the [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,⁵

who found the reverse order. The B3LYP/cc-pVTZ calculations underestimate by 5% the experimental exothermicity [$\Delta_r H_0^\circ = -2.706 \pm 0.04$ 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_2O and products $\text{OH} + \text{N}_2$ geometries are in very good agreement with experimental determinations with a relative error no larger than 0.5%. However, the N_2O and N_2 vibrational frequencies are about 5% larger than the experimental values. The comparison with the CASSCF/ICCI calculations by Walch⁶ and the GAUSSIAN2 calculations by Durant⁷ is fairly good, except for the DFT B3LYP imaginary frequencies of the H-ONN and H-NNO saddle points, which are about 45% smaller than the CASSCF frequencies. Recently, Laursen *et al.*²⁸ have investigated the $\text{NH} + \text{NO}$ re-

TABLE II. Geometries and vibrational frequencies of the stationary points of the H+N₂O PES obtained in the present work. Distances (*r*) are in Å, angles in deg, and frequencies (ω_i) in cm⁻¹.

	H+N ₂ O	H-NNO	<i>cis</i> -HNNO	<i>trans</i> -HNNO	H-ONN
r_{NH}		1.64	1.03	1.02	
r_{NN}	1.12	1.14	1.22	1.24	1.13
r_{NO}	1.18	1.18	1.21	1.20	1.22
r_{OH}					1.47
$\widehat{\text{HNN}}$		113.8	110.6	108.0	
$\widehat{\text{NNO}}$	180.0	172.2	139.6	132.5	161.0
$\widehat{\text{HON}}$					115.45
ω_1	2350.8	2229.8	3233.2	3440.4	2175.5
ω_2	1329.1	1293.7	1731.7	1714.2	1199.6
ω_3	619.0	624.0	1337.9	1364.1	806.6
ω_4	619.0	389.1	1222.4	1271.2	470.1
ω_5		965.2 <i>i</i>	594.0	671.3	1327.6 <i>i</i>
ω_6		677.8	760.2	777.5	578.3

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 CASSCF/ICCI by Walch,⁶ and with the GAUSSIAN2 calculations by Durant.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 98.²⁴ 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+N₂ 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 10⁻¹⁰ and to be stable for all points. The final PES has been grown

TABLE III. Geometries and vibrational frequencies of stationary points of the H+N₂O PES obtained in the present work. Distances (*r*) are in Å, angles in deg, and frequencies (ω_i) in cm⁻¹.

	<i>cis</i> -to- <i>trans</i> HNNO	[NNOH]	OH+N ₂
r_{NH}	1.05	1.26	
r_{NN}	1.21	1.20	1.09
r_{NO}	1.20	1.43	
r_{OH}	2.98	1.38	0.97
$\widehat{\text{HNN}}$	111.2	90.2	
$\widehat{\text{NNO}}$	177.3	96.5	
$\widehat{\text{NOH}}$		76.7	
$\widehat{\text{OHN}}$		96.6	
ω_1	2899.3	2053.1	3699.6(OH)
ω_2	1951.9	1652.9	2450.1(N ₂)
ω_3	1269.7	898.4	
ω_4	1158.1	607.1	
ω_5	859.5 <i>i</i>	1838.2 <i>i</i>	
ω_6	501.3	1011.3	

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”²⁹ and “h weight” methods^{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 N₂O 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 N₂O molecule was set to 6 Å, and the final relative separation between the OH and N₂ 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.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+H₂O reaction,^{32–34} and references therein. Batches of $5 \cdot 10^4$ trajectories with a maximum impact parameter $b_{\text{max}} = 2.00$ Å have been run for each translational energy in the range $E_t = 0.6$ –1.48 eV. At $E_t = 1.48$ eV, an additional batch of $2.3 \cdot 10^5$ trajectories was run to improve the product state resolved statistics. Initial conditions for the rotationless N₂O 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 program³⁵ with a time step of 0.05 fs. The typical conservation of energy was better than 1 in 10⁵. For the assignment of diatomic products quantum numbers, the classical diatomic molecule rotational angular momentum is equated to $[j'(j'+1)]^{1/2}\hbar$. With the (real) j' value so obtained, the vibrational quantum number v' is found by equating the internal energy of the outgoing molecule to the corresponding rovibrational Dunham expansion in $(v'+1/2)$ and $j'(j'+1)$, whose coefficients are calculated by fitting the semiclassical or quantum rovibrational energies given by the asymptotic diatomic potentials of the PES. The values of v' and j' found in this way are then rounded to the nearest integer. The calculation of the kinetic energy release distributions $P(f_i)$, where $f_i = E'_i/E_{\text{avail}}$ 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.^{33,34}

In order to calculate the DCSs, the scattering angle in the center-of-mass (CM) frame has been defined as follows: If

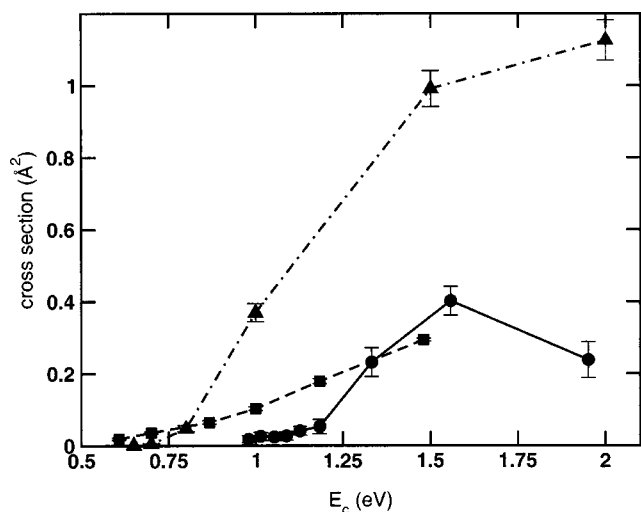


FIG. 2. Total reaction cross section (in $\text{\AA}^2$) as a function of collision energy (in eV) for the $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$ reaction. Solid squares and dash line: present QCT results. Solid circles and solid line: experimental results from Ref. 10. Solid triangles and dot-dashed line: QCT results from Ref. 9.

the OH molecule is detected, as is the case in the experiments of Brouard and co-workers,^{11–14} 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 $\mathbf{w}_{\text{OH}}$ and that of the H atom is $\mathbf{w}_{\text{H}}$, the definition of the scattering angle θ is given by

$$\cos \theta = \frac{\mathbf{w}_{\text{H}} \cdot \mathbf{w}_{\text{OH}}}{|\mathbf{w}_{\text{H}}| |\mathbf{w}_{\text{OH}}|}. \quad (2)$$

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 σ_R overestimate

the absolute values measured by Fletcher and Wojcik¹⁰ 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 σ_R calculated by Bradley and Schatz,⁹ also shown in the figure. It should be noted that the QCT σ_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 σ_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_2O 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 [NNOH] 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,⁹ 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 σ_R , energy partitioning and the fraction of trajectories going through the *direct* and *indirect* mechanisms. Note that as in previous works³⁴ 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 IV. QCT total reaction cross sections (σ_R) and energy partitioning data for the $\text{H} + \text{N}_2\text{O}$ reaction at different collision energies. f_d and f_i are the fractions of reactive trajectories going through the *direct* and *indirect* mechanisms, respectively (see text of details). Statistical uncertainties are $\pm 0.003 \text{ \AA}^2$ in the cross sections.

E_t/eV	$\sigma_R/\text{\AA}^2$	$\langle f_i \rangle$	$\langle f_r^{\text{OH}} \rangle$	$\langle f_v^{\text{OH}} \rangle$	$\langle f_r^{\text{N}_2} \rangle$	$\langle f_v^{\text{N}_2} \rangle$	f_d	f_i
0.61	0.019	0.51	0.03	0.20	0.23	0.03	0.91	0.09
0.69	0.036	0.51	0.03	0.17	0.26	0.03	0.95	0.05
0.87	0.065	0.56	0.04	0.12	0.25	0.03	0.77	0.23
1.00	0.103	0.56	0.05	0.10	0.26	0.03	0.73	0.27
1.18	0.179	0.54	0.06	0.09	0.27	0.03	0.73	0.27
1.48	0.294	0.53	0.08	0.10	0.25	0.04	0.70	0.30

TABLE V. OH state-averaged energy disposal data for the $\text{H} + \text{N}_2\text{O}$ reaction at $E_t = 1.48$ eV.

$\langle f_t \rangle$	$\langle f_r^{\text{OH}} \rangle$	$\langle f_v^{\text{OH}} \rangle$	$\langle f_{\text{int}}^{\text{N}_2} \rangle$	$\langle f_r^{\text{N}_2} \rangle$	$\langle f_v^{\text{N}_2} \rangle$	
0.45 ± 0.04	0.06 ± 0.01	0.02 ± 0.01	0.47 ± 0.04			Experiment ^a
0.53	0.08	0.10	0.29	0.25	0.04	total
0.48	0.07	0.07	0.37	0.33	0.04	direct
0.66	0.09	0.16	0.08	0.04	0.04	indirect
0.74	0.08	0.07	0.11	0.04	0.07	QCT BS96 ^b

^aReference 12.^bReference 9.

that the zero point energies of N_2 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 N_2 rotation, $\approx 25\%$, 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 N_2 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 N_2O 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.⁹ 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 N_2 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 N_2 molecule. On the contrary, the *indirect* mechanism accounts for very little rovibrational excitation of N_2 and most of the available energy goes into translation. The large amount of N_2 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 N_2 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 N_2 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 $\text{H} + \text{ONN} \rightarrow [\text{H–ONN}] \rightarrow \text{OH} + \text{N}_2$ path, exerting a significant torque on the N_2 molecule. Note that this proposed mechanism is consistent with the fact that the rotational excitation of the N_2 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 N_2 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 N_2 . 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 N_2 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 $P(v' = 1)/P(v' = 0) = 0.28 \pm 0.05$, 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 N_2 vibrational distribution at this collision energy is represented in Fig. 3(b), showing a

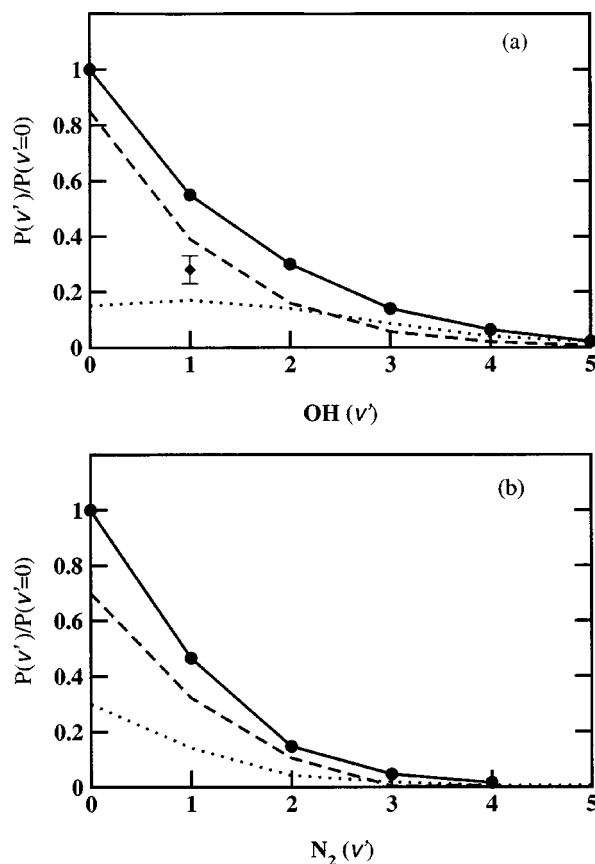


FIG. 3. (a) OH vibrational distribution relative to $v'=0$ at $E_t=1.48$ eV. Solid circles: present QCT results. Solid diamond with error bar: experimental result from Ref. 12. (b) Present N_2 vibrational distribution relative to $v'=0$ calculated at $E_t=1.48$ eV. The contributions from the *direct* and *indirect* mechanisms are depicted with dashed and dotted lines, respectively.

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 $\text{OH}(v'=0,1)$ 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,³⁴ 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 $\text{N}_2(v'=0)$ and $\text{N}_2(v'=1)$ 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

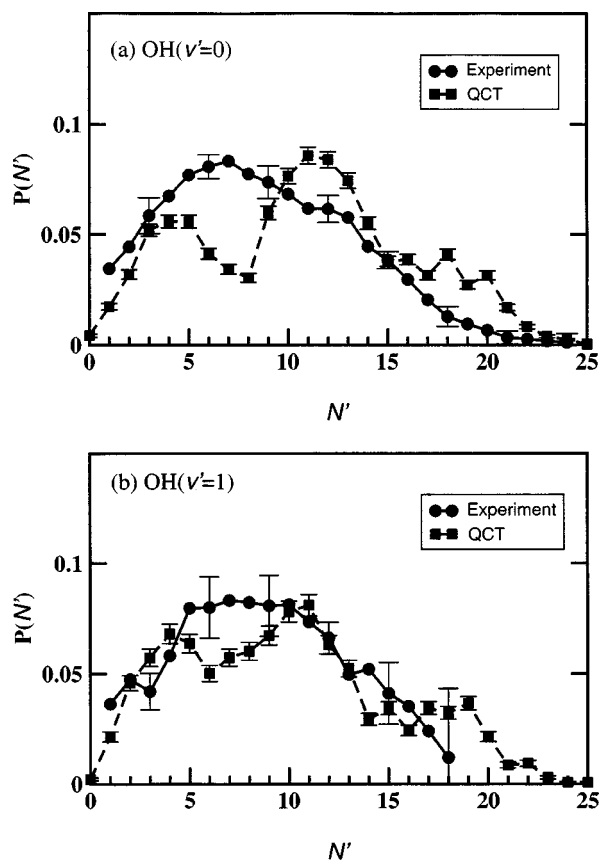


FIG. 4. (a) $\text{OH}(v'=0)$ rotational distribution at $E_t=1.48$ eV. Solid squares: present QCT results. Solid circles: experimental results from Ref. 12. (b) Same as (a) but for $\text{OH}(v'=1)$.

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^{11,12} 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 $\text{OH}(v', N')$ with the experimental distributions.¹² 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 $\text{OH}(v'=0, N'=5)$ $P(f_t)$ for the $\text{H} + \text{N}_2\text{O}$ reaction with that obtained in the photodissociation of N_2O from the first absorption band³⁶ and observed an excellent agreement. It is known that the nascent N_2 fragment from the photodissociation of N_2O is born in high rotational states, showing a distribution peaking around $j'=100$.³⁶ 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.^{3,4} It

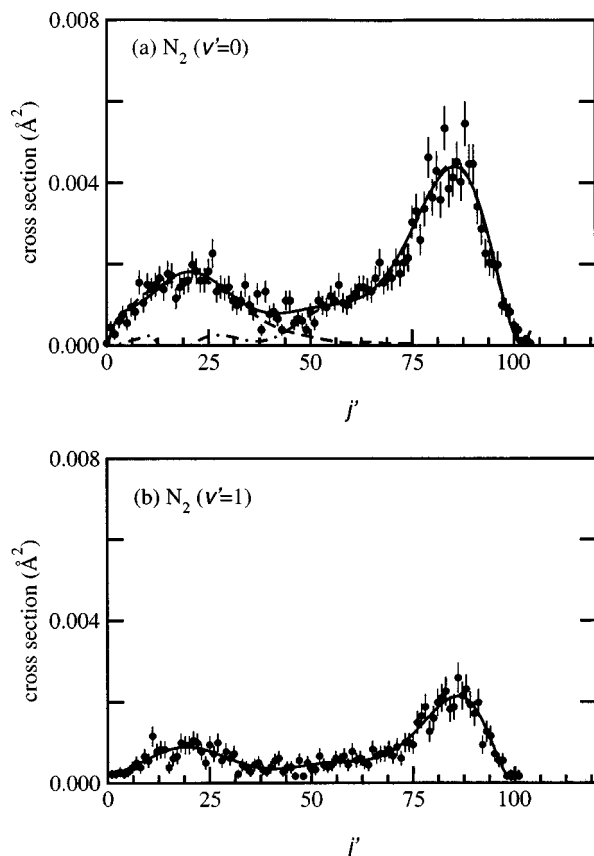


FIG. 5. (a) Solid circles with error bars: QCT rotational distribution for $N_2(v'=0)$ products at $E_t=1.48$ eV. The solid line is an eighth degree polynomial fit to the QCT distribution. Dashed line: contribution from the *indirect* mechanism. Dot-dashed line: contribution from the *direct* mechanism. (b) QCT rotational distribution for $N_2(v'=1)$ products at $E_t=1.48$ eV.

should be pointed out that Brouard *et al.*, when discussing about the existence of two mechanisms, attributed the formation of translationally hot N_2 (thus emerging with low j') to a “direct process,” presumably occurring by the attack of the H to the O end of the N_2O molecule, whereas the rotationally excited N_2 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 N_2 , whereas it is the *indirect* mechanism (H attacking the N end) which causes the N_2 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 N_2 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 scatter-

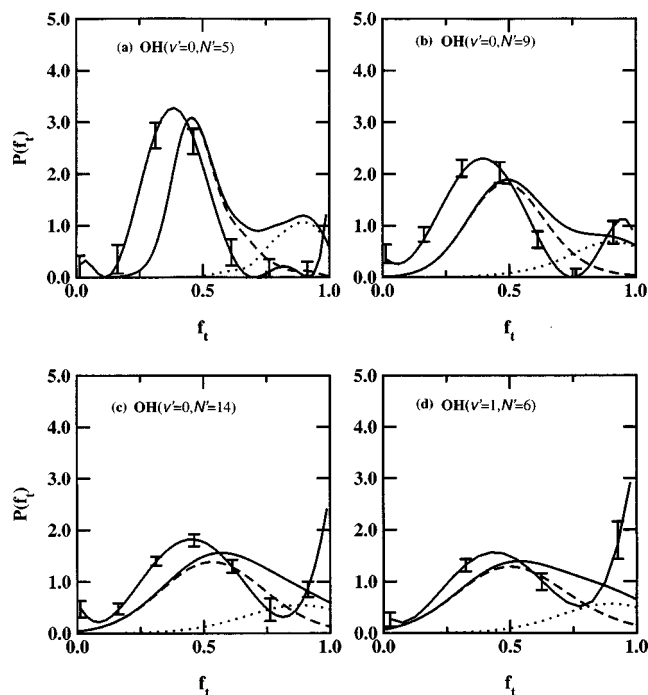


FIG. 6. Distributions of the fraction of the available energy appearing as product translation, $P(f_t)$, for selected OH rovibrational states. (a) Solid line: QCT results for $OH(v'=0, j'=5)$. Dotted line: contribution from the *direct* mechanism. Dot-dashed line: contribution from the *indirect* mechanism. Solid line with error bars: experimental results for $OH(^2\Pi_{3/2}; A'', v'=0, N'=5)$ from Ref. 12. (b), (c), and (d) same as (a) but for $OH(v'=0, j'=9)$, $OH(v'=0, j'=14)$, and $OH(v'=1, j'=6)$, respectively.

ing 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 $E_t=1.48$ 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 $2\pi/\sigma$ 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

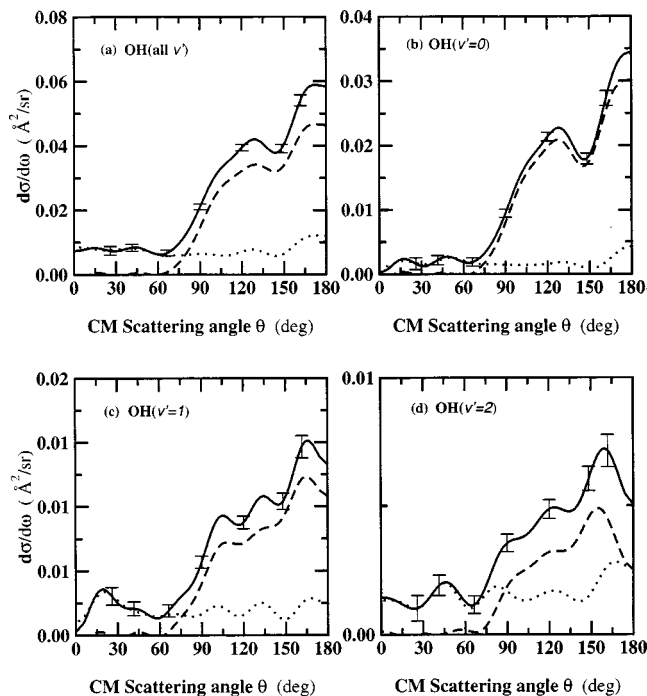


FIG. 7. Total (a) and vibrationally state-resolved (b, c, d) differential cross sections calculated for the title reaction at $E_t = 1.48$ eV. The contributions from the *direct* (dashed line) and *indirect* (dotted line) mechanisms are also depicted.

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 behav-

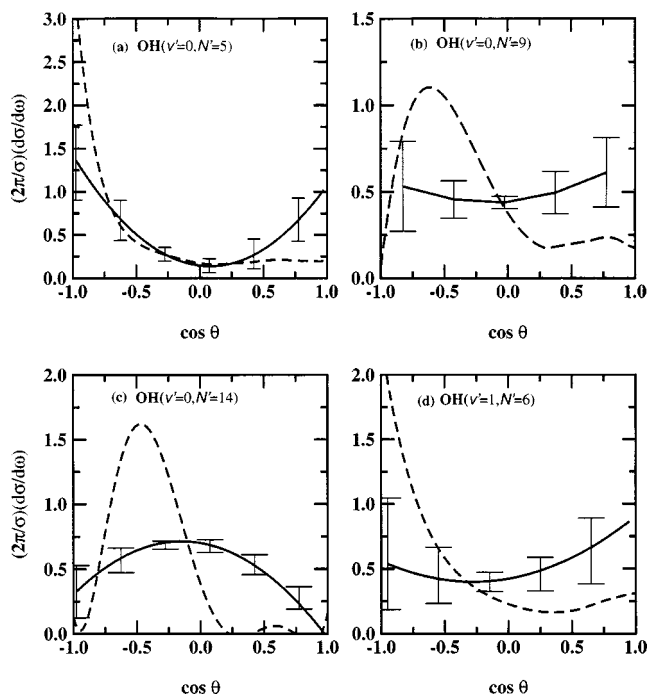


FIG. 8. Comparison between experimental and QCT $\text{OH}(v', N')$ state-resolved DCSs for the $\text{H} + \text{N}_2\text{O}$ reaction at $E_t = 1.48$ eV. Solid lines with error bars: experimental DCSs from Ref. 12. Dashed lines: present QCT calculations.

ior although the angular distributions are clearly more asymmetric than the experimental DCSs.

V. CONCLUSIONS

A detailed quasiclassical trajectory study has been carried out for the $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$ reaction employing a new *ab initio* potential energy surface. DFT B3LYP/cc-pVTZ 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 *direct* or *indirect* according to whether the H attacks the O side or the N side of the N_2O 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 Böhmer *et al.* and of Brouard and co-workers. The predicted N_2 vibrational distribution is *cold*, while the rotational distribution is quite *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 *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 *ab initio* method of a higher level of accuracy.³⁷

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