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# The $O(^1D) + H_2$ reaction at 56 meV collision energy: A comparison between quantum mechanical, quasiclassical trajectory, and crossed beam results

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Quantum mechanical and quasiclassical trajectory reactive scattering calculations have been performed for the  $O(^1D) + H_2$  ( $v=0, j=0$ ) reaction on the Dobbyn–Knowles *ab initio*  $1^1A'$  and  $1^1A''$  potential energy surfaces (PES) at the mean collision energy  $E_{\text{col}} = 56$  meV (1.3 kcal/mol) of a crossed beam experimental study based on H-atom Rydberg “tagging” time-of-flight detection. Novel data from this latter experiment are presented and compared with the theoretical results at the level of state-resolved integral and differential cross sections and product recoil energy distributions. A good overall agreement with small discrepancies is found between the experimental data and the results of the two theoretical approaches. The main conclusion of the present work is that the contribution of the ground state  $1^1A'$  PES to the global reactivity accounts for the experimental observations and that, at the title collision energy, the participation of the  $1^1A''$  PES in the reaction is negligible for all practical purposes. © 2002 American Institute of Physics.

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## I. INTRODUCTION

The detailed understanding of the dynamics of bimolecular reactions is presently limited to a few three atom systems. Among these systems, the  $O(^1D) + H_2$  reaction, which plays an important role in combustion and in atmospheric chemistry, has become the best prototype of a simple chemical process taking place via an insertion mechanism and has attracted much theoretical and experimental attention.<sup>1–50</sup> In contrast to the best known benchmark reactions  $H + H_2$  and  $F + H_2$ , which are dominated by repulsive interactions and characterized by direct abstraction mechanisms, the ground state potential energy surface (PES) of the  $O(^1D) + H_2 \rightarrow OH + H$  system is barrierless for most atom-molecule orientations, favors the insertion of the  $O(^1D)$  atom into the  $H_2$  molecular bond, and has a deep attractive well ( $\sim 7.3$  eV) corresponding to the ground state of water. The presence of this attractive well, supporting many bound

states, makes particularly difficult an exact theoretical study of the dynamics. The  $O(^1D) + H_2$  system presents additional complications from the theoretical point of view due to the fact that the fivefold degeneracy of the  $O(^1D)$  atom gives rise to five PESs of which at least three, the ground state PES,  $1^1A'$ , and those corresponding to the two excited states  $1^1A''$  and  $2^1A'$ , can contribute to the global reactivity at some of the collision energies accessed thus far in the experiments. Since the latter PES only correlates with electronically excited products, it can only contribute to the reaction via nonadiabatic effects by means of coupling with the  $1^1A'$  PES, thus constituting an additional difficulty for theoretical treatments.

The search of a proof for the possible participation of excited electronic states in the observed reaction dynamics has stimulated intensive investigations by different research groups and has led also to some controversy over the last years.<sup>6,8,9,15,17,21,29,32–38,42,44,48–50</sup> A critical summary of

experimental and theoretical work can be found in Refs. 42, 45, 48.

The general picture emerging from these works indicates that the reactivity of the title reaction is governed by the ground state  $1^1A'$  PES for collision energies below 100 meV, which corresponds to the approximate height of the barrier for reaction on the two excited surfaces.<sup>29</sup> At higher collision energies, a fraction of the reactive yield comes from a direct abstraction reaction taking place over the  $1^1A''$  surface. It is precisely the different reaction mechanism, leading to a concentration of the scattered products in the backward direction and in a few rovibrational states of OH, which has allowed the assessment of the participation of this PES in the reaction. The relative contribution of the  $1^1A''$  excited PES to the total reactivity increases with growing collision energy, but in any case, the overall reactivity is largely determined by the ground state PES, even at the highest collision energies investigated experimentally ( $E_{\text{col}}=250$  meV).<sup>27</sup> The possible contribution of the  $2^1A'$  PES is more difficult to ascertain. This contribution would require a nonadiabatic transition from  $2^1A'$  to  $1^1A'$ , and although this transition is possible due to the existence of a region of avoided crossing between the two surfaces, the reactive yield predicted for this pathway is even smaller than that over the  $1^1A''$  PES.<sup>38,42</sup>

A significant progress towards a rigorous understanding of the reaction dynamics of this system has been brought about in latter times by a remarkable improvement in the experimental resolution, and also by an increase in the accuracy of the theoretical calculations and of the degree of detail in the simulation of the experiments.

In a recent bulk experiment, Brouard and co-workers<sup>50</sup> generated  $O(^1D)$  atoms by photolysis of  $N_2O$  in a mixture of this gas with  $H_2$ . The  $O(^1D)$  atoms thus formed react with  $H_2$  to yield  $OH+H$ . Product rovibrational state populations,  $P(v',N')$ , and rotational angular momentum alignment parameters,  $a_0^{(2)}$ , were reported. The average collision energy of this experiment was 120 meV with a full-width-at-half-maximum (FWHM) of 160 meV. A significant fraction of the collisions takes place at energies higher than the threshold for reaction on the  $1^1A''$  surface. Under these experimental conditions, detailed quasiclassical trajectory (QCT) and quantum mechanical (QM) scattering calculations on the ground  $1^1A'$  and first excited  $1^1A''$  *ab initio* PES developed by Dobbyn and Knowles (DK) (Ref. 29) predicted a noticeable influence of the abstraction mechanism on the higher vibrational states ( $v'=3,4$ ) of the OH product and, in fact, the simulation of the experimental  $P(v',N')$  and  $a_0^{(2)}$  for  $v'=3,4$  required the theoretical contribution from the  $1^1A''$  PES.

A large increase in the experimental resolution has been achieved by the group of Yang,<sup>38,43,44,49</sup> who used a crossed molecular beam set-up with laser photolysis of  $O_2$  (at 157 nm) for the generation of  $O(^1D)$ , and the Rydberg-atom "tagging" technique for the detection of the H(D) atoms generated in the  $O(^1D)+H_2(D_2,HD)$  reactions. The highest energy resolution achieved thus far for this system corresponds to the  $O(^1D)+H_2(v=0,j=0)$  isotopic variant of the reaction at a collision energy of 56 meV (1.3 kcal/mol).<sup>44</sup> A first theoretical analysis of these results led to the somewhat

unexpected conclusion that a small contribution from the collinear abstraction mechanism over the  $1^1A''$  PES could be identified in the measurements, even at this low collision energy.<sup>44</sup> This analysis was based on the discrepancies found between the experimentally deduced and QCT state-resolved DCS calculated on the  $1^1A'$  PES, especially for  $v'=4$ . Although these calculations indicated that the cross section on the  $1^1A''$  PES at the collision energy of the experiment was negligible, in order to bring experiment and those QCT calculations into a better agreement, the theoretical results were corrected by using the cross sections obtained at the collision energy of 2.5 kcal mol<sup>-1</sup> (0.11 eV), substantially higher than the experimental one and above the barrier. In addition, these results on the  $1^1A''$  surface were multiplied by an empirical factor adjusted to fit the integral cross section for  $v'=4, N'=4$ . It was argued that QM calculations could make the contribution of the  $1^1A''$  upper PES detectable, especially if the barrier on this PES would be somewhat lower.

In this work we present a full account of these experimental results together with detailed QM and QCT calculations performed on the  $1^1A'$  and  $1^1A''$  DK PESs. Special attention has been paid to the direct simulation of the angle- and state-resolved experimental data with the theoretical cross sections. In this way, the possible ambiguity associated with the comparison between theory and experiment is much diminished. The results are discussed and contrasted with previous works on the reaction dynamics of this system.

## II. EXPERIMENT

The  $O(^1D)+H_2(v=0,j=0)\rightarrow OH(^2\Pi,v',N')+H$  reaction has been investigated using the high resolution Rydberg-atom "tagging" time-of-flight (TOF) technique, originally developed by Welge and co-workers.<sup>51-53</sup> Note that hereafter primed quantities will refer to quantum numbers of the reaction products. The study has been carried out in a newly built crossed molecular beam apparatus shown schematically in Fig. 1(a). The present experimental investigation was performed at a collision energy of 56 meV (1.3 kcal/mol), which is significantly below the 100 meV (1.8 kcal/mol) barrier for the abstraction channel (barrier of the  $1^1A''$  PES) inferred from previous experimental and theoretical studies.<sup>15,26,29</sup> A description of the apparatus used in this work can be found in Refs. 44 and 49. Briefly, product H-atoms are detected through a two-step excitation scheme to a Rydberg state. The 121.6 nm VUV light used in the first step excitation is generated with a two-photon resonant ( $2\omega_1-\omega_2$ ) four wave mixing scheme in a Kr/Ar gas cell.<sup>54</sup> After this first excitation step, the H-atoms are sequentially promoted to a high Rydberg state with  $n\approx 50$  using 365 nm laser light. The two excitation laser beams must overlap exactly both in space and time. The neutral Rydberg H-atoms fly then a certain distance until they reach a microchannel plate (MCP) detector with a grounded fine metal grid in the front. After passing through the grid, the Rydberg H-atoms are immediately ionized by the electric field applied between the front plate of the Z-stack MCP detector and the fine metal grid. The signal received by the MCP is then amplified by a fast pre-amplifier, and counted by a multichannel scaler.

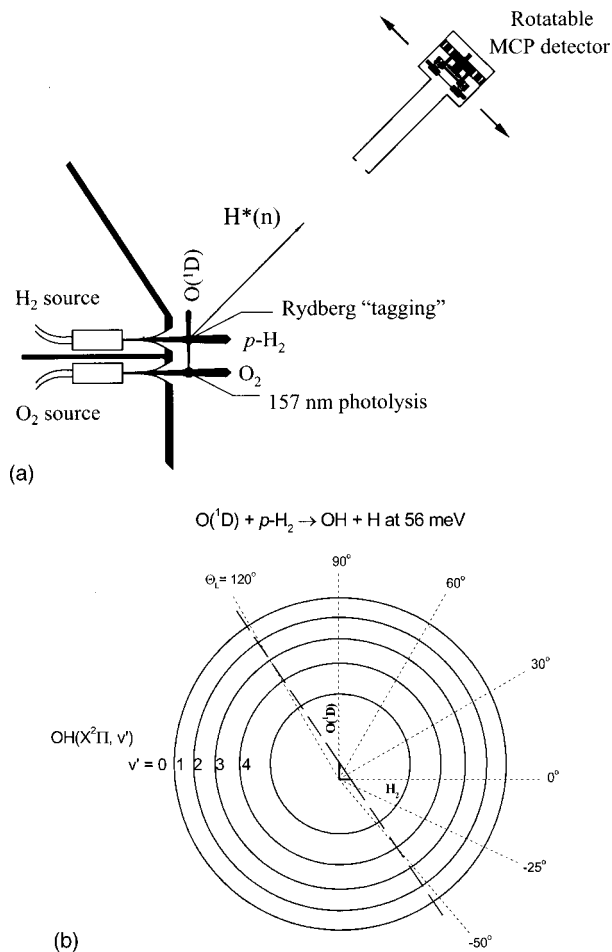


FIG. 1. (a) Scheme of the experimental setup. (b) Newton diagram of the title reaction at the collision energy of 56 meV (1.3 kcal/mol).

Two parallel molecular beams ( $p\text{-H}_2$  and  $\text{O}_2$ ) were generated with similar pulsed valves [see Fig. 1(a)]. The  $\text{O}(^1D)$  atomic beam was produced by photolysis of  $\text{O}_2$  with the 157 nm radiation from an  $\text{F}_2$  laser (Lambda Physik LPX 2101). The generated  $\text{O}(^1D)$  beam crossed at right angles the  $\text{H}_2$  molecular beam. The  $\text{H}_2$  beam was formed by expanding  $p\text{-H}_2$  through a pulsed nozzle cooled to the temperature of liquid nitrogen. This cooling reduces significantly the uncertainty in the collision energy by minimizing the beam velocity spread. In addition, practically all the  $\text{H}_2$  molecules in the beam are in the  $j=0$  rotational state.<sup>52,53</sup> A small aperture placed between the  $\text{O}_2$  and  $p\text{-H}_2$  beams was used for the geometrical definition of the  $\text{O}(^1D)$  beam. Product H-atoms were detected using the technique described above with a rotatable MCP detector. The velocity of the  $\text{O}(^1D)$  beam has been measured to be  $2050 \text{ m s}^{-1}$  with a very narrow spread ( $v/\delta v > 50$ ), while the velocity of the liquid nitrogen cooled  $p\text{-H}_2$  beam was  $1384 \text{ m s}^{-1}$  with a speed ratio ( $v/\delta v$ ) of about 15. In order to illustrate the kinematics of reactive scattering in the experiment, the Newton diagram corresponding to the present experimental conditions is shown in Fig. 1(b).

### III. THEORETICAL METHODS

#### A. Quantum mechanical methods

QM calculations were performed for the  $\text{O}(^1D) + \text{H}_2$  ( $v=0, j=0$ ) reaction at  $E_{\text{col}}=56 \text{ meV}$  collision energy on both the ground,  $1^1A'$ , and first excited,  $1^1A''$  DK PESs.

The relevant details of the QM scattering calculations on the  $1^1A'$  PES are given in Refs. 46 and 50. Briefly, the QM calculations employ a time-independent method and body-frame democratic hyperspherical coordinates to represent the nuclear wave function. In a first step, a set of eigenstates of a simplified Hamiltonian  $H_0 = T + V$  were determined, where  $V$  is the potential energy and  $T$  the kinetic energy arising from deformation and rotation around the principal axis of least inertia at fixed hyperradius. The full scattering wave function, which is the solution of the exact Hamiltonian, is then expanded in a basis of eigenstates of  $H_0$  that dissociate at large hyperradius into the  $\text{H}_2$  (14, 12, 8, 2) and OH (40, 38, 36, 33, 30, 28, 24, 21, 17, 11) rovibrational sets (this notation indicates the largest rotational level  $j$  for each vibrational manifold). The expansion coefficients are the solutions of a set of second order differential equations with couplings arising from the difference between the exact Hamiltonian and  $H_0$ . The QM scattering study on this PES is quite demanding due to the extensive Coriolis coupling taking place within the deep well ( $\sim 7.3 \text{ eV}$ ) of the surface in the transition state region. Therefore, no restrictions were placed on the helicity quantum number  $\Omega$  (the projection of the total angular momentum  $J$  of the system on each of the atom-diatom axes). Thus  $\Omega_{\text{max}} = J$  and the number of coupled equations increases from 310 for  $J=0$  to 4505 for  $J=25$ . As many as 4505 close-coupling equations were solved for the highest partial wave considered,  $J=25$ . Further aspects about the fundamentals of the QM time-independent methodology employed can be found in Ref. 55.

The QM calculations on the excited  $1^1A''$  DK PES were performed following a different hyperspherical coordinate scheme described in detail elsewhere.<sup>56</sup> In this case, the convergence of the calculations is less costly than on the ground state PES and only requires helicity quantum numbers  $\Omega = 0-3$ . All reactant and product channels with diatomic rotational quantum number  $j_{\text{max}}=16$ ,  $\Omega_{\text{max}}=3$  and total energies  $E_{\text{max}}=1.4 \text{ eV}$  were included in the basis set. This results in 294 coupled channels for calculations at total angular momentum  $J > 3$ . Calculations with  $J \leq 17$  were necessary to obtain converged results.

Since the calculations have been carried out without consideration of spin-orbit and  $\Lambda$ -doublet effects, the OH product is treated as a closed shell molecule. Although there is no general and unambiguous procedure to make the correspondence between the  $j'$  and  $N'$  quantum numbers, a comparison of the experimental energies of the OH rotational levels for the  $F_1$  and  $A'$  states ( $^2\Pi_{3/2}$ ) with the energy of the  $\text{OH}(v', j')$  levels calculated using the Dunham expansion obtained with the OH diatomic potential of the PES indicates that the correspondence rule  $N' = j'$  represents a good approximation. This procedure is alternative to the usual correspondence rule  $N' = j' + 1$ . Actually, on the basis of comparison of rotational energies, the  $N' = j' + 1$  rule is only valid

for the first levels and rapidly deviates to the  $N'=j'$  rule as  $N'$  increases. Therefore, in order to obtain  $N'$  quantum numbers we have equated  $N'=j'$ . Notice that the use of the correspondence rule  $N'=j'$  effectively implies to neglect the cross section of the  $v', j'=0$ , states, which, in any case, represent an almost negligible contribution to the total cross section.

### B. Quasiclassical trajectory method

The general method for the calculation of quasiclassical trajectories has been described in previous publications (see, for instance, Ref. 57, and references therein). In particular, the methodological details relevant to the present work are given in Refs. 34, 42 and only a brief description is presented here.

A batch of 200 000 trajectories was run for initial  $j=0$  at  $E_{\text{col}}=56$  meV on the ground  $1^1A'$  PES. The initial  $O(^1D)-H_2$  distance was set at 8 Å and a time step of  $5 \times 10^{-17}$  s was used, which guarantees an energy conservation better than 1 in  $10^5$ . The maximum impact parameter was 3.1 Å. The assignment of the rovibrational energies of the  $H_2$  and OH molecules was carried out by semiclassical quantization of the classical action fitted to a Dunham expansion as described in Ref. 42; the asymptotic diatomic potential of the PES was employed in each case. Nevertheless, for the simulation of the recoil energy distributions of the products (see below), the experimental energies of the different  $N'$  levels have been used.

A batch of 100 000 trajectories was run for initial  $j=0$  on the first excited  $1^1A''$  PES as a function of collision energy between 30 meV up to 0.5 eV following the procedure described in Ref. 57. No reactive trajectories were found below 70 meV collision energy, which is the classical threshold for the reaction.

### C. Theoretical simulation of the experimental product kinetic energy distributions

In order to reduce the possible ambiguity associated with the comparison of the theoretical and experimentally deduced reaction cross sections, the experimental observables can be simulated using the QM or QCT state-resolved center-of-mass (CM) cross sections. The present experimental investigation has yielded a set of H-atom TOF spectra at different scattering angles that could be converted to CM product kinetic energy (recoil energy) distributions,  $P(E_T')$ , in a straightforward way.

The simulation of the experimentally derived  $P(E_T')$  with the theoretical integral or differential cross sections has been carried out using the experimental rovibrational energies of the OH product and the resolution of the measurements. In particular, the simulations were performed by averaging the theoretical DCSs over an angular range of  $3^\circ$ , which is approximately the angular resolution of the experiment in the CM frame. More important, due to the high energy resolution of the Rydberg-atom “tagging” technique employed in the experiments ( $\Delta E_T' \leq 70 \text{ cm}^{-1}$ ), which is roughly independent of  $E_T'$  in the CM frame, the measured spectra are sensitive to the splitting of the  $N'$ -state quadruplets of the OH products due to  $\Lambda$ -doubling and spin-orbit coupling, especially for the peaks associated to the least exothermic states  $v'=3,4$ . Thus, in our simulation of the experimental  $P(E_T')$  we have assigned the same cross section to the four states within each  $N'$ -manifold (i.e., one fourth of the cross section calculated for the  $N'$  state) and we have used the experimental rovibrational energies corresponding to each level. Finally, the theoretical recoil energy distributions derived from the QM and QCT calculations were scaled to the corresponding experimental  $P(E_T')$  by means of a least-squares procedure. The scaling factors (one for QCT and one for QM) so obtained were also used for the simulation of the

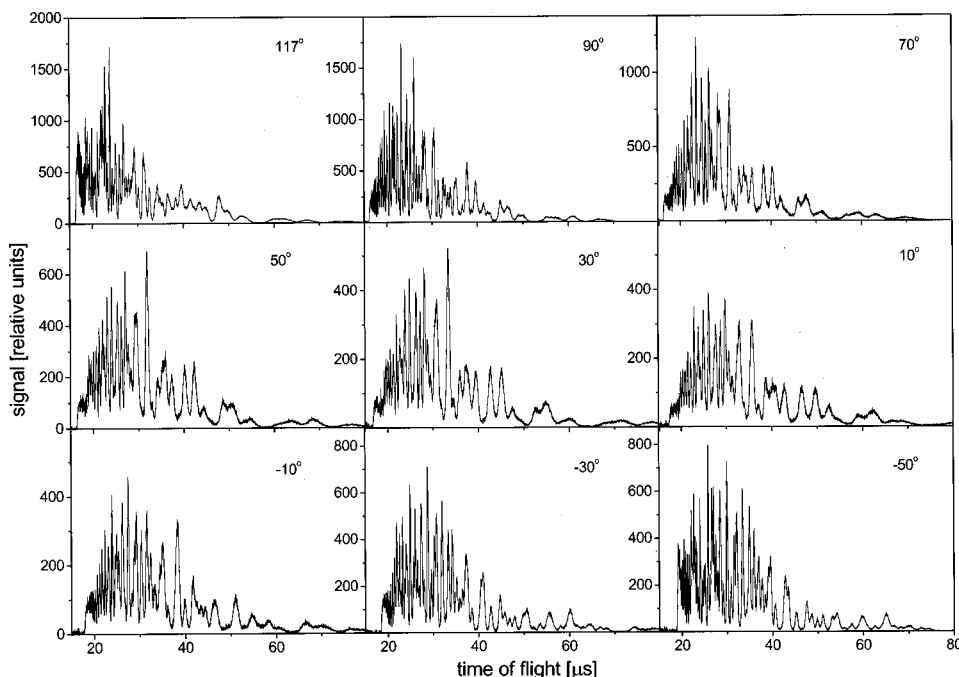


FIG. 2. H-atom time-of-flight spectra at nine different laboratory angles from the  $O(^1D)+H_2$  ( $v=0, j=0$ ) reaction.

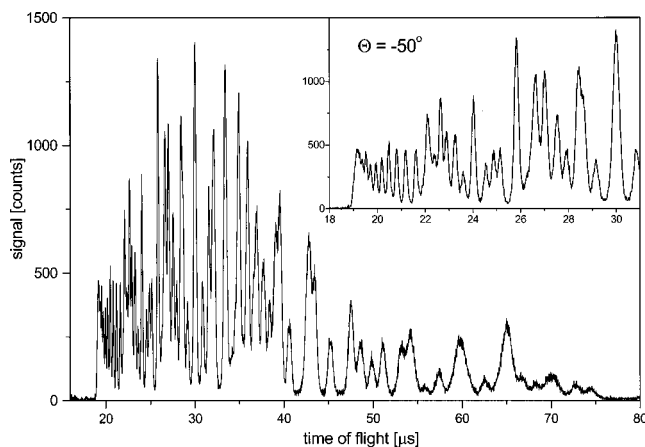


FIG. 3. Expanded plot of the TOF spectrum at a laboratory angle  $\Theta = -50^\circ$ .

whole set of scattering angle-resolved recoil energy distributions,  $P(E_T', \theta)$ , considered in this work (see below). Throughout the paper, the symbol  $\Theta$  will be used to denote laboratory (LAB) scattering angles and  $\theta$  will refer to scattering angles in the CM frame.

## IV. RESULTS AND DISCUSSION

### A. Experimental results

TOF spectra of the H-atom products have been measured at 18 laboratory angles (from  $117.5^\circ$  to  $-50^\circ$  with an approximate  $10^\circ$  interval) using the technique described above. Figure 2 shows nine of these TOF spectra in which many sharp features are clearly observed. These features correspond to the different rovibrational states of the nascent OH product molecule. Low time-of-flight values correspond to OH molecules produced in low vibrational states, whereas the largest time-of-flight values are related with high OH vibrational states. These structures can be better seen in Fig. 3, where an expanded plot of the TOF spectrum at  $-50^\circ$  in the TOF range 18–31  $\mu\text{s}$  is shown. Given the large number

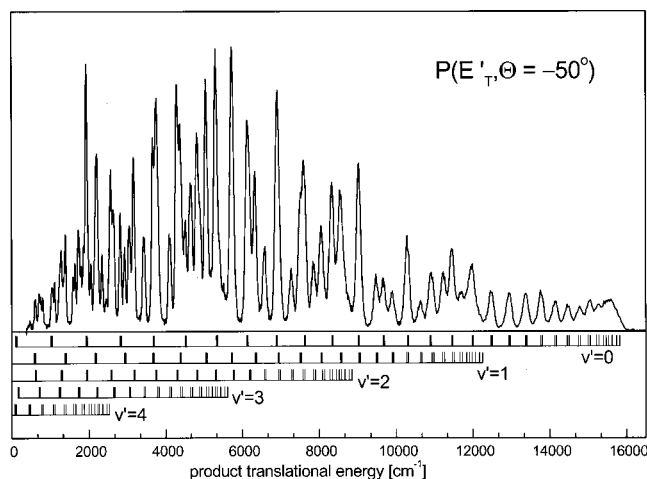


FIG. 4. Products' translational energy distribution at a laboratory angle  $\Theta = -50^\circ$ . The energy levels of the OH internal states are also represented in order to facilitate the assignment of the sharp structures in the translational energy spectrum to the different rovibrational states.

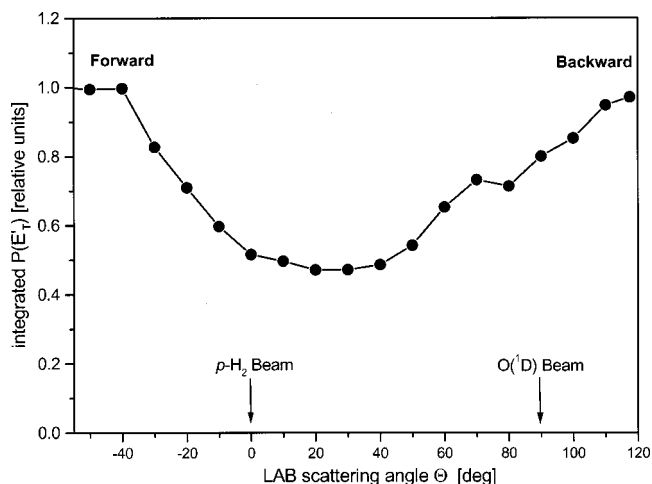


FIG. 5. Total angular distribution of the H-atom product in the laboratory frame. The directions of the  $O(^1D)$  and  $p\text{-H}_2$  beams are indicated by arrows.

of rovibrational states of the OH molecule populated and the resolution of the present experiment, most of the  $v'$ ,  $N'$  states are only partially resolved in each TOF spectrum. However, by combining all the measured TOF spectra, it has been possible to extract the populations of most of the rovibrational states<sup>44,53</sup> of OH at each LAB angle. LAB angles that correspond roughly to forward, backward, and sideways scattering in the CM frame are  $-60^\circ$ ,  $117^\circ$ , and  $40^\circ$ , respectively [see Fig. 1(b)]. In the following, the forward and backward directions of OH are defined relative to the  $O(^1D)$  beam direction or, equivalently, by the direction of the outgoing H-atoms with respect to the direction of the  $\text{H}_2$  beam.

By converting these TOF spectra from the LAB to the CM frame using a standard Jacobian transformation and taking into account the different detection efficiency of the H-atom at different angles and different velocities, the products' translational energy distribution  $P(E_T'; \Theta)$  can be obtained at different LAB angles. These  $P(E_T'; \Theta)$  exhibit many sharp structures that can often be correlated with individual rovibrational states of OH, as exemplified in Fig. 4, where the  $P(E_T'; \Theta = -50^\circ)$  is displayed. Given the resolution of the present experiment, the spin-orbit doublets cannot be neatly separated except for some states in  $\text{OH}(v' = 4)$ .

The total angular distribution of the H-atom product in the LAB frame is shown in Fig. 5. This angular distribution has been obtained by integrating the total intensity of the translational energy distribution at each LAB angle. From this angular distribution it is apparent that the H-atom product is scattered with an approximate forward-backward symmetry with respect to the  $\text{H}_2$  beam direction. This result is in agreement with previous experimental studies and is a clear indication of the dominant role of insertion in this reaction.

Since the CM scattering angle varies with the (H-atom) product velocity for a given LAB angle, a translational energy distribution obtained from the direct conversion of the TOF spectra contains information from a range of CM scattering angles. For the conversion of LAB translational energy distributions into CM recoil energy distributions, the

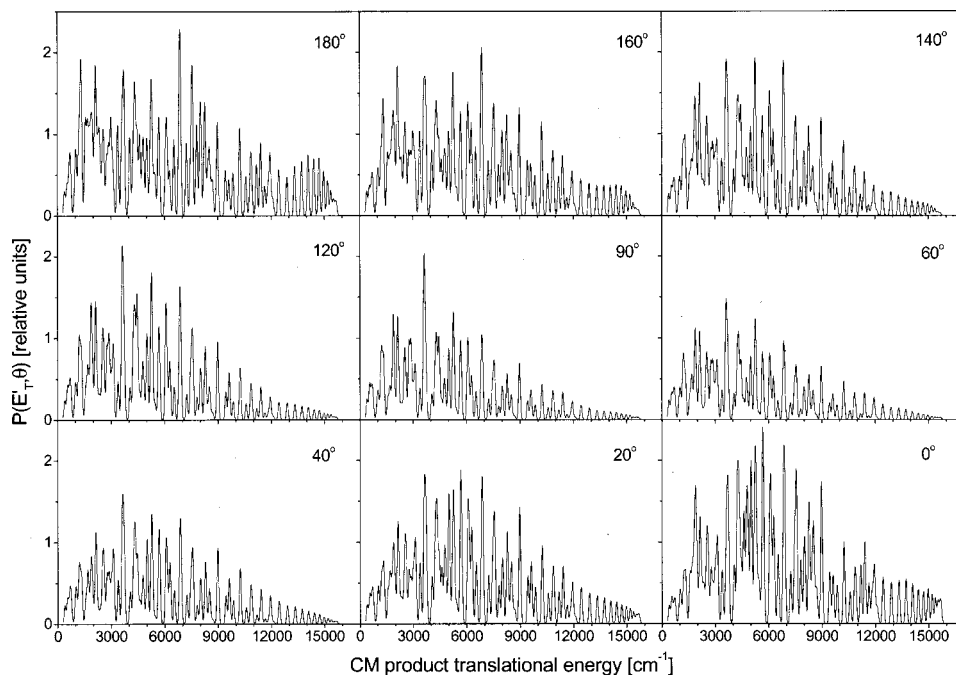


FIG. 6. Products' translational energy distributions at nine different angles in the CM frame.

former are fitted taking into account the energetics of all rovibrational states ( $v' \leq 4$ ) of the OH product. From these fits, the recoil distributions at 19 different CM angles ( $\theta = 0^\circ$  to  $180^\circ$  in  $10^\circ$  steps) and, thus, the  $v'$ ,  $N'$  state-resolved differential cross sections (DCS) have been determined. Figure 6 shows the product kinetic energy distribution of the scattered H-atoms at nine different angles in the CM frame relative to the H<sub>2</sub> beam direction.

The  $v'$  state-resolved DCSs can be determined by integrating the peaks assigned to each vibrational state of the OH molecule. Likewise, the experimental  $v'$ ,  $N'$  state-resolved integral cross sections are derived by integration over scattering angles. Finally, by integration of the experimental  $P(E_T', \theta)$  over the whole recoil energy range, the total (summed on all final states) CM DCS can be obtained. These results will be presented along with the corresponding theoretical ones in the next section in order to compare both sets of data.

## B. Theoretical results and comparison with experiment

Table I lists the QM (on the  $1^1A'$  and  $1^1A''$  DK PESs) and QCT (on the  $1^1A'$  PES) total and  $v'$  state-resolved integral cross sections (ICS) and compares the corresponding product vibrational branching ratios with those obtained ex-

perimentally. The values of the QM and QCT total ICSs obtained on the ground  $1^1A'$  PES are practically coincident. The QM total ICS calculated on the  $1^1A''$  PES is more than two orders of magnitude lower than that obtained for the reaction on the ground state PES. As commented on above, no reactive trajectories were found on the  $1^1A''$  at this collision energy. Whereas the vibrational distribution is nearly statistical on the  $1^1A'$  ground state PES, on the first excited state surface,  $1^1A''$ , there is a strong population inversion and only  $v' = 3, 4$  have appreciable cross sections, which are in any case much smaller than those of the ground state surface.

The  $v'$  state-resolved ICS, calculated on the ground state PES, are additionally displayed in Fig. 7 together with the experimental data. In this figure, the experimental ICS summed on all vibrational states has been equated to the absolute value of the total QM ICS ( $1^1A' + 1^1A''$ ) and the factor thus obtained has been used to scale both the vibrationally and rovibrationally state resolved integral and differential cross sections. In this way the three sets of vibrationally state-resolved ICSs can be compared simultaneously in an absolute scale. The agreement between the experimental and QM  $v'$  state-resolved ICSs is fairly good and only for  $v' = 3, 4$  the QM results are slightly larger than the experimental values; notice that the QM contribution of the  $1^1A''$

TABLE I. QM and QCT integral cross sections (in  $\text{\AA}^2$ ) for the O( $^1D$ ) + H<sub>2</sub>( $v=0, j=0$ ) reaction at 56 meV collision energy. The values in parentheses denote the theoretical and experimental vibrational branching ratios defined as  $\sigma(v')/\sigma(v'=0)$ .

	Total	$v'=0$	$v'=1$	$v'=2$	$v'=3$	$v'=4$
QM $1^1A'$	23.31	6.58 (1.00)	5.62 (0.85)	5.01 (0.76)	4.02 (0.61)	2.06 (0.31)
QCT $1^1A'$	23.72	8.05 (1.00)	6.34 (0.79)	5.05 (0.63)	3.06 (0.38)	1.22 (0.15)
QM $1^1A''$	0.134	$2.1 \times 10^{-5}$	$3.6 \times 10^{-5}$	$1.29 \times 10^{-3}$	0.041	0.0916
Experiment	...	(1.00)	(0.86)	(0.77)	(0.52)	(0.26)

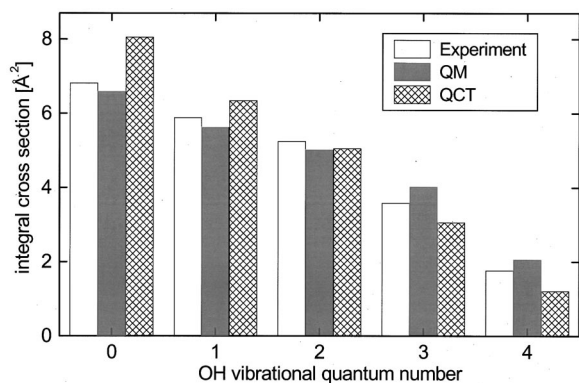


FIG. 7. Vibrationally state-resolved integral cross sections for the  $\text{O}(^1D) + \text{H}_2$  ( $v=0, j=0$ ) reaction at 56 meV collision energy. The (relative) experimental cross sections are brought to an absolute scale by setting the total reactive cross section equal to that of the QM calculation on the  $1^1A'$  +  $1^1A''$  DK PESs.

surface to the population of the  $v'=4$  state is  $\approx 5\%$  and is even less for the rest of the vibrational states. The QCT  $v'$  state-resolved ICSs agree qualitatively with the QM and experimental ones, but predict a somewhat colder vibrational distribution of the OH products.

Figures 8(a) and 8(b) compare the theoretical and experi-

mentally deduced ICSs resolved into individual rovibrational states  $v', N'$  of the OH products. For each  $\text{OH}(v')$  state, the experimental ICS increases smoothly with  $N'$ , reaches a maximum at one of the higher states energetically allowed, and falls sharply to negligible values within the last few states accessible. Both the QM and QCT rotational distributions for the different  $v'$  states, shown in Figs. 8(a) and 8(b), respectively, are in good agreement with the experimentally deduced data. The QM calculation yields somewhat broader  $N'$  state distributions with less differentiated maxima in comparison with the experiment, especially for  $v'=0, 1, 2$ . Interestingly, the QCT  $N'$  state-resolved ICSs for these low  $v'$  states agree better with experiment than the QM ones, although the  $v'=0$  yield is overestimated, as already observed in Fig. 7. On the other hand, the ICSs of the less exothermic states  $\text{OH}(v'=3, N')$  and  $\text{OH}(v'=4, N')$  are better reproduced by the QM calculation, whereas the QCT predicts a hotter  $N'$  distribution for these  $v'$  states. It should be recalled here that a single scale factor has been used for the comparison of theory (both QM and QCT) and experiment.

Figure 8(a) also shows the  $v', N'$  state-resolved QM ICSs obtained on the first excited  $1^1A''$  PES. The contribution of the  $1^1A''$  PES to the total reactivity into  $v'=4, N'=5$ , which is the most populated state on the excited PES, is

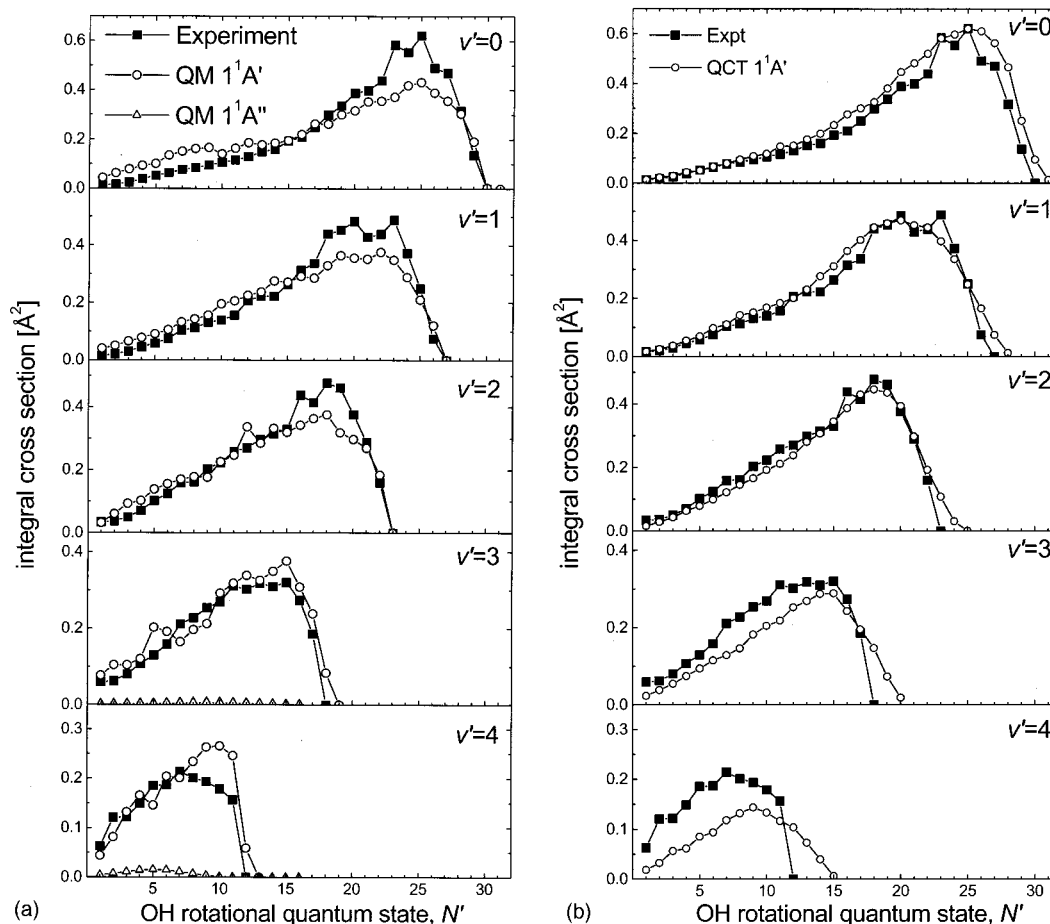


FIG. 8. (a) Experimental vs QM rotationally state-resolved integral cross sections for the  $\text{O}(^1D) + \text{H}_2$  ( $v=0, j=0$ ) reaction at 56 meV collision energy. The absolute scaling of the experimental data is the same as in Fig. 7. (b) Same as (a) but for the QCT results. The correspondence  $N'=j'$  has been employed to relate the (closed-shell) theoretical quantum states to the OH levels.



less than 10%. Therefore, in general the neglect of the reactivity on the  $1^1A''$  surface has no consequences in the comparison with the experimental results.

As already mentioned in the Method, an alternative way of comparing theory and experiment is via simulation of the CM product recoil energy distributions  $P(E_T')$ , evaluated in the experiment from the measured TOF spectra by transforming from the LAB to the CM system, with the calculated  $OH(v', N')$  state-resolved integral and/or differential cross sections. Figures 9(a) and 9(b) compare the experimental  $P(E_T')$  derived from the  $P(E_T', \theta)$ , shown in Fig. 6 (by multiplying by  $2\pi \sin \theta$  and integrating in scattering angles), with those obtained using the QM and QCT state-resolved ICSs. The contribution of each vibrational state to the recoil energy distribution is also shown in the lower part of this figure. The details of the simulation procedure were discussed previously in the Method.

Figures 9(a) and 9(b) show that both the QM and QCT calculations on the ground state  $1^1A'$  DK PES lead to a very good agreement with the experimental  $P(E_T')$ . A close inspection of both figures reveals that the QCT simulation reproduces the high energy part (12 000–16 000  $\text{cm}^{-1}$ ) of the experimental distribution better than the QM one. These high recoil energies correspond to the production of only  $OH(v' = 0, 1)$  in low rotational states. The lower energy region ( $E_T' < 9000 \text{ cm}^{-1}$ ) of the experimental  $P(E_T')$ , associated to  $OH(v' = 2, 3, 4)$  products, is reproduced with a similar level of accordance by the QM and QCT calculations.

The experimentally deduced DCS summed over all final states is compared in Fig. 10 with the corresponding QM and QCT DCSs on the  $1^1A'$  PES. In the same figure the QM DCS calculated on the  $1^1A''$  PES is also portrayed. As in the previous Figs. 7 and 8, the experimental DCS has been brought to an absolute scale by equating the experimental and QM total ICSs. Considering the degree of uncertainty necessarily implied in the derivation of the experimental DCS, the three curves are in good agreement. Perhaps the most noticeable differences are the sharp edges at  $0^\circ$  and  $180^\circ$  found in the QM DCS calculated on the ground state PES. The QM DCS also shows some forward-backward asymmetry, favoring the scattering into the forward hemisphere. It should be recalled however, that the experimental evaluation of the DCSs includes some degree of angular smearing, whereas no attempt of smoothing has been made in the theoretical curves. The QCT DCS agrees somewhat better with that deduced from the experiment, especially in the forward hemisphere. At  $\approx 150^\circ$  the classical DCS shows a shoulder which is only slightly hinted at in the QM and does not appear in the experimentally deduced DCS.

The vibrationally state-resolved DCSs are displayed in Fig. 11. Notice again the sharper features of the theoretical DCSs, especially for extreme forward and backward scattering in the QM case. Despite some apparent differences, the shapes and the relative contributions of the various vibrational states to the total DCS are similar in the three cases. The contribution of the  $1^1A''$  PES is nearly negligible and affects only  $OH(v' = 4)$ .

The  $O(^1D) + H_2$  reaction on the ground state PES is well known to proceed via an insertion mechanism involving a

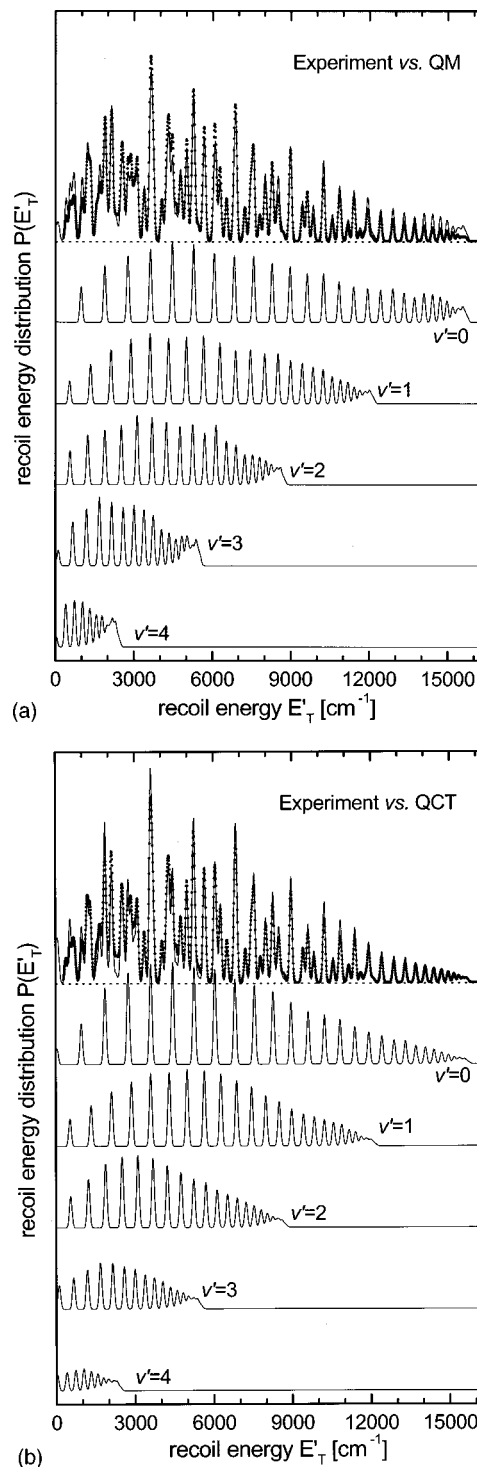


FIG. 9. Experimental product recoil energy distribution for the  $O(^1D) + H_2$  ( $v=0, j=0$ ) reaction at 56 meV collision energy compared to simulations carried out with (a) the QM state-resolved integral cross sections shown in Figs. 8(a) and (b) the QCT state-resolved integral cross sections shown in Fig. 8(b). Each theoretical distribution is independently scaled to the experimental data with a least-square factor. The theoretical  $v'$  state-resolved recoil distributions are also shown in the lower part of the figures to guide the assignment of the experimental spectrum.

HOH intermediate (superexcited ground-state water). Within this dynamical picture, an approximately forward-backward symmetric DCS is expected for the reaction. This is in fact the overall behavior of the theoretical and experimentally

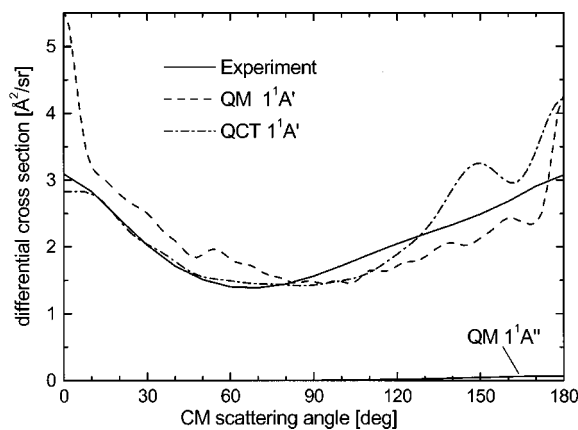


FIG. 10. Experimental total reactive differential cross section for the  $O(^1D)+H_2$  ( $v=0, j=0$ ) reaction at 56 meV collision energy compared to the QM and QCT calculations on the  $1^1A'$  and  $1^1A''$  DK PESs. The absolute scaling of the experimental curve is consistent with Fig. 7.

deduced total and vibrationally state-resolved DCS (Figs. 10 and 11). For the lowest  $v'$  states, the QM DCS shows a propensity for scattering into the forward hemisphere; as  $v'$  increases the CM angular distributions become more symmetric. It is worth noticing that both theoretical DCS show a local minimum for the lowest vibrational states at about  $160^\circ$ – $170^\circ$ . The shoulder at  $140^\circ$ – $150^\circ$  present in the total QCT DCS is found to be essentially due to scattering into the  $v'=0, 1$  states.

The comparison between experiment and theory can be extended to a higher level of detail by considering the recoil energy distributions of the H-atom product resolved into scattering angles,  $P(E_T', \theta)$ , presented in Fig. 6. This is done in Figs. 12 and 13 for the QM and QCT results, respectively. As mentioned above, no attempt has been made to scale individually the experimental and theoretical  $P(E_T', \theta)$  at the different scattering angles; instead of that, a single scaling factor, obtained from Figs. 9(a) and 9(b), has been used for the whole angular range within each theoretical approach.

Figure 12 compares the QM  $P(E_T', \theta)$  with the experimental ones at six different angles. As can be seen, the global agreement is good, especially in the intermediate angular region (sideways scattering). The most noteworthy discrepancies correspond to the QM overestimation of the reactive forward scattering, which was also apparent in the DCSs represented in Figs. 10 and 11. Figure 12 shows that this theoretical excess of forward scattering corresponds to the lower  $N'$  levels of the  $v'=0$  state. A similar discrepancy, but smaller in magnitude, is also observed at  $\theta=180^\circ$ . Although the QM DCSs used in the simulation have been smoothed by averaging in a range of  $3^\circ$  (see Method) one should take into account that the experimental  $P(E_T', \theta)$  have been derived from the recoil energy distributions in the LAB frame  $P(E_T', \Theta)$  like that shown in Fig. 4 (which correspond to different CM scattering angles depending on each  $v'$ ,  $N'$  state), by interpolation in the whole range of available scattering angles. As a result of this procedure, it is conceivable that the extent of blurring would have been larger in the derivation of the experimental data. This might explain, at

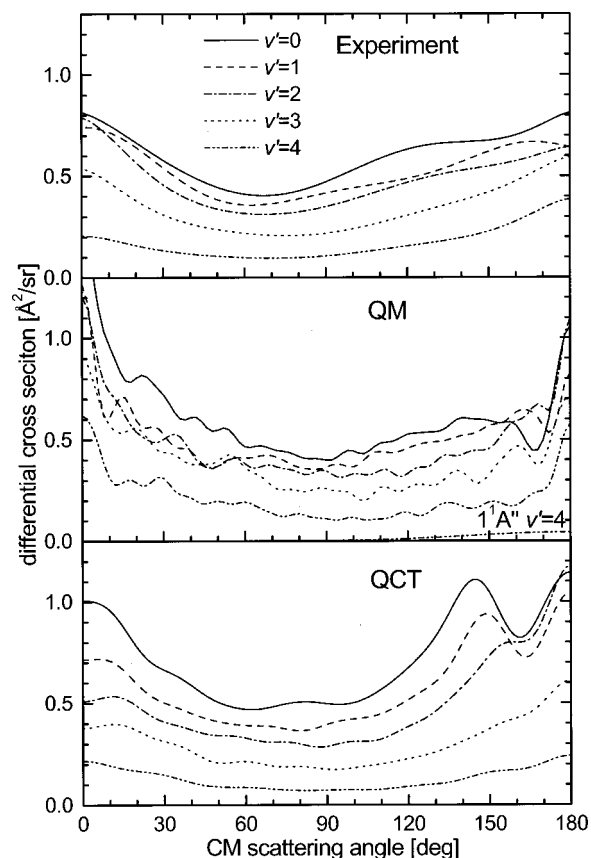


FIG. 11. Vibrationally state-resolved differential cross sections for the  $O(^1D)+H_2$  ( $v=0, j=0$ ) reaction at 56 meV collision energy. (Top panel) Experimental cross sections. (Middle panel) QM calculations on the  $1^1A'$  and  $1^1A''$  DK PESs. (Bottom panel) QCT calculation on the  $1^1A'$  DK PES. The absolute scaling of the experimental data is the same as in Fig. 7.

least in part, the discrepancies observed at the forward and backward ends of the CM scattering angular range.

In Fig. 13, the analogous comparison is carried out for the QCT results. Here, the accordance with the experimental data is good over most of the angular range. Nevertheless, at  $\theta=180^\circ$  the QCT calculations yield too much reactive scattering into some of the  $v'$ ,  $N'$  levels corresponding to relatively low  $P(E_T')$  (below  $7000\text{ cm}^{-1}$ ). For low rotational levels of the  $v'=0$  state, and in contrast to the QM case, just a small discrepancy is found between experiment and theory. The reason of the better agreement between experiment and QCT as compared with that between experiment and QM lies most probably in the fact that the QCT DCSs are smoother than those from the QM calculations. It should be stressed that the reactive yield predicted by the QCT calculations into  $v'=3$  and  $v'=4$  (the states preferentially populated by the reaction taking place on the  $1^1A''$  PES at higher collision energies) is either in good agreement or even overestimated with respect to the experimental one. This buttresses the asset that, from a theoretical point of view, it is not necessary to invoke the contribution of the  $1^1A''$  PES to the reactivity in order to obtain good accordance with the experimental data.

As mentioned above, for the  $v'=4$  level of the scattered OH, the resolution of the present experiment allows the identification in the recoil energy distributions of the two spin-

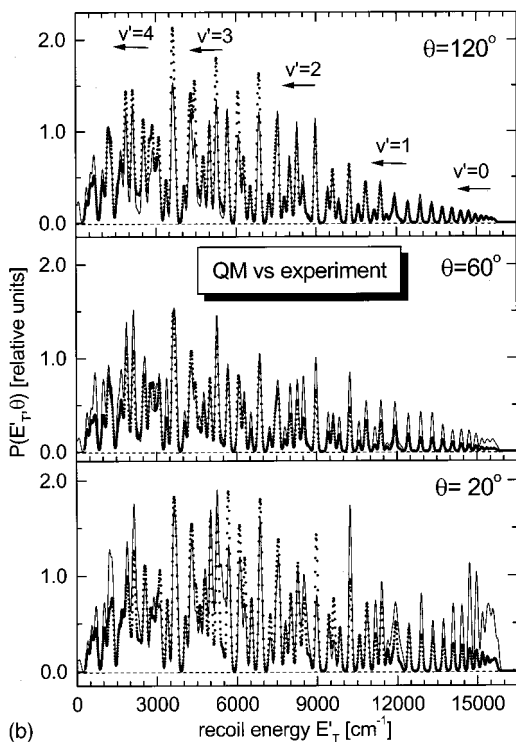
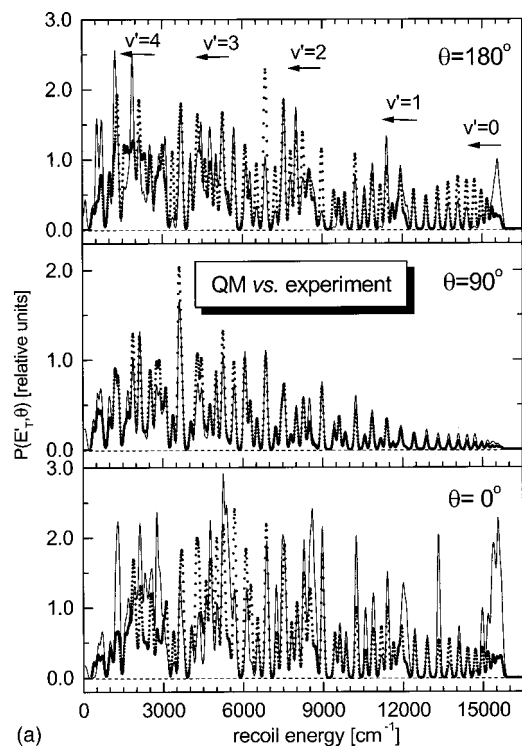


FIG. 12. Experimental (dots) vs QM (solid curve) product recoil energy distributions for the  $O(^1D)+H_2$  ( $v=0, j=0$ ) reaction at 56 meV collision energy at the indicated selected CM scattering angles. The same factor employed in Fig. 9 has been used to scale all the theoretical curves. The onset of the different OH vibrational levels is indicated by arrows.

orbit states  $F_1$  and  $F_2$ . Figure 14 shows the experimental rotational distributions corresponding to these spin-orbit components. The overall shape of the  $N'$  distributions is similar, but the population of the  $F_1$  state is somewhat higher than that of  $F_2$  except for  $N'=7$ . The curves correspond to the experimental cross section of the total (i.e., including

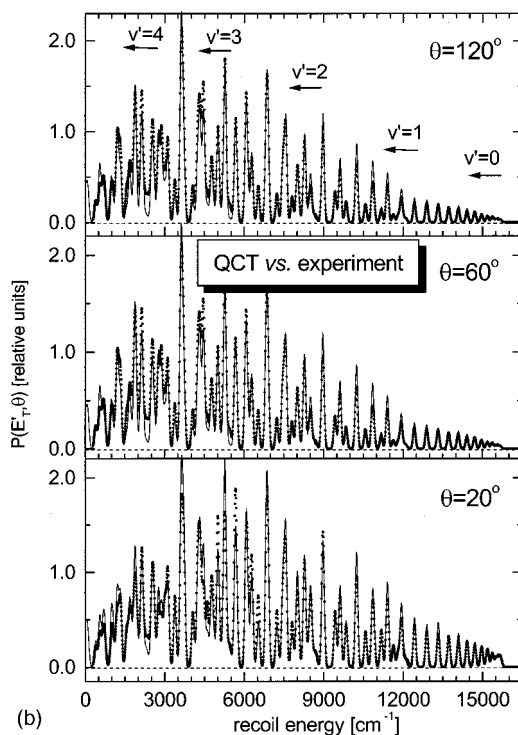
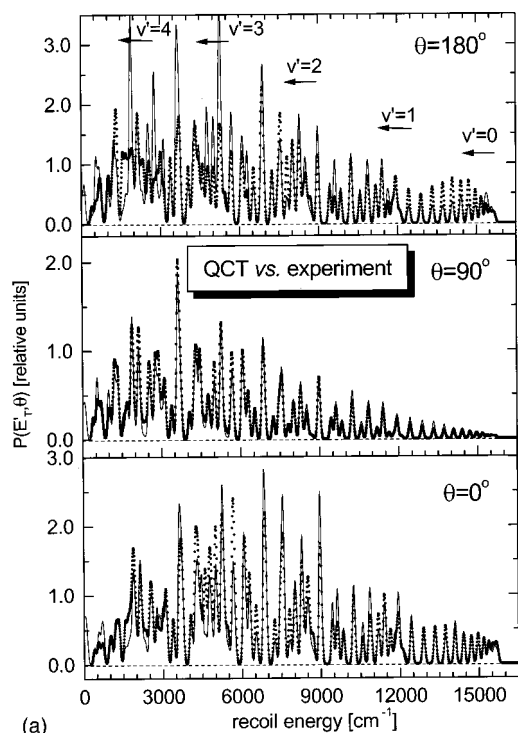


FIG. 13. Same as Fig. 12 but for the QCT simulation of the product recoil energy distributions.

both  $F$  states)  $N'$  distribution of the  $v=4$  level weighted with the degeneracy,  $2J+1$ , of the respective  $F_1$  and  $F_2$  states, where  $J=N'+1/2$  for  $F_1$  and  $J=N'-1/2$  for  $F_2$ . As can be seen, these lines can account for the observed differences in the two  $N'$  distributions; this indicates that the populations of the two spin-orbit components are essentially statistical. This can be expected for a reaction dominated by an insertion mechanism with a relatively long lived complex

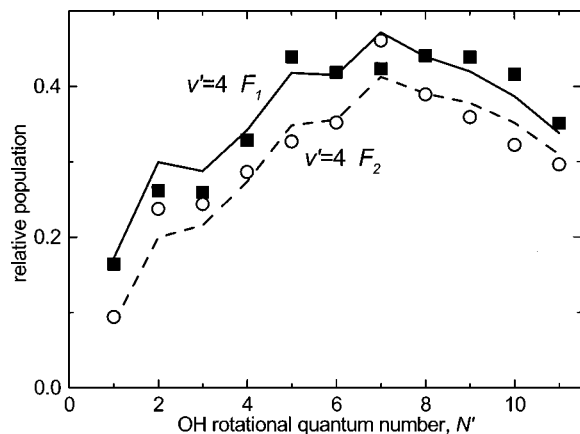


FIG. 14. Experimental rotational distributions of the  $F_1$  (solid squares) and  $F_2$  (open circles) spin-orbit components of the  $\text{OH}(v'=4)$  product. The curves correspond to the experimental total (i.e., including both components) cross section weighted with the degeneracy of the  $F_1$  (solid line) and  $F_2$  (dashed line) states.

whose dynamics is well accounted for by statistical capture models based on phase space theory.<sup>58</sup>

## V. CONCLUSIONS

In this work, a full account of high resolution experimental data for the title reaction at a collision energy of 56 meV has been presented. These data include angle-resolved TOF spectra of the scattered H-atoms, which allow the determination of state-resolved integral and differential cross sections. Accurate, fully converged QM as well as extensive QCT calculations have been performed on the most recent and supposedly most accurate potential energy surfaces (the  $1^1A'$  and  $1^1A''$  DK PESs) available for this reaction. Theoretical results have been compared not only with the experimentally deduced integral and differential cross sections, but also, via simulation, with the angle-resolved products' translational energy distributions obtained in the experiment. An overall good agreement with just small discrepancies has been found at all levels.

Present accurate QM calculations on the first excited  $1^1A'$  PES clearly indicate that its contribution is indeed negligible when compared with that due to the ground  $1^1A'$  PES, even for those rovibrational states which are preferentially populated by the reaction on the  $1^1A''$  PES. In fact, the agreement of the present QM and QCT calculations on the  $1^1A'$  PES with the experimental measurements is almost quantitative, especially when the respective recoil energy distributions (total and for fixed CM scattering angles) are compared. The most important discrepancies between the QM and experimental results occur in the scattering into the extreme backward and forward regions where the QM calculations show large peaks which are not present in the experimental data.

Up to date, several *ab initio* calculations of the first excited electronic PES have been performed. The most recent ones due to Schatz, Harding and co-workers<sup>15</sup> and to Dobbyn and Knowles<sup>29</sup> yielded barrier heights which differ by less than 0.2% ( $2.3067 \text{ kcal mol}^{-1}$  in the former and

$2.3211 \text{ kcal mol}^{-1}$  in the latter), and entrance channels almost identical.<sup>42</sup> In any case, the present results on the available  $1^1A''$  PES do not suggest that the barrier height should be modified.

The possible contribution of the  $2^1A'$  PES can be disregarded at the collision energy of the present experiments given the fact that the barrier for this latter PES is very similar to that of the  $1^1A''$  PES. Approximate nonadiabatic calculations by Drukker and Schatz<sup>32</sup> considering all PES correlating with the  $\text{O}(^1D)+\text{H}_2$  reagents ( $1^1A'$ ,  $1^1A''$ ,  $2^1A'$ ,  $2^1A''$ , and  $3^1A'$ ) proved that the total reactivity so obtained was the same as that obtained considering just the ground adiabatic PES at energies well below the barrier of the  $1^1A''$  (or  $2^1A'$ ) PES.

Therefore, the conclusion to be drawn is that the detailed experimental measurements with rovibrational state resolution at 56 meV collision energy can be explained by resorting to adiabatic calculations on the ground  $1^1A'$  PES, without invoking the necessity of the contribution of excited state PESs.

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