

A comparison between experimental and theoretical excitation functions for the $O^+ + H_2$ ($^4A''$) system using trajectory calculations over a wide energy range

Miguel González,^{a)} Miquel Gilibert, Antonio Aguilar, and R. Sayós

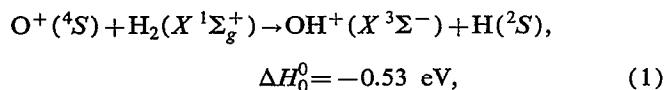
Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès, 1, 08028 Barcelona, Spain

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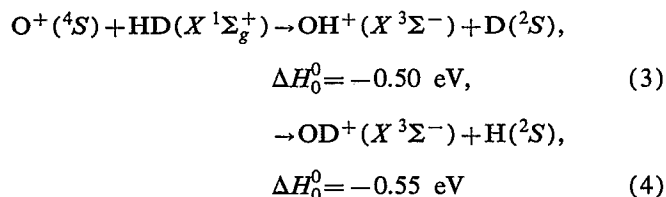
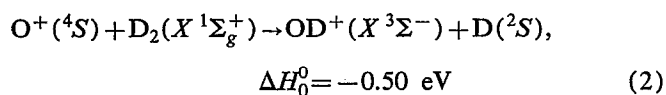
The $O^+ + H_2$ prototypic ion-molecule reaction was recently studied in our group using the quasiclassical trajectory method on a ground model potential-energy surface of the system inferred from both experimental and theoretical information and reasonable assumptions, fitted using a London-Eyring-Polanyi-Sato surface modified to include an ion-induced-dipole interaction term. The theoretical results previously reported agreed rather well with the available experimental information. In view of the latest experimental findings, we present in this contribution the results of new trajectory calculations on the above-mentioned surface, covering a wide range of relative translational energies of reactants. The accord between the experimental determinations and the present theoretical evaluations is excellent at relative energies below 1.0 eV, while for higher energies the potential-energy surface, even though still yielding reasonably good results, provides a worse agreement. The observed discrepancies should be attributed either to the too attractive character of the surface or to the interfering influence of the competing $O^+ + H_2 \rightarrow O + H_2^+$ charge-transfer process.

I. INTRODUCTION

The moderately exothermic hydrogen-atom transfer ion-molecule reaction:



and its isotopic variants:



provide a good opportunity of studying an ion-molecule system for which, unlike other similar related reactions,^{1,2} only the ground $^4A''$ potential-energy surface (PES) is likely to be necessary to achieve a reasonably accurate description of the dynamical features of this system. Most of the experimental³ as well as the theoretical^{4,5} data available about the lowest-lying $^4A''$ PES pointed towards the existence of a well on the collinear path leading from reactants to products which disappears for insertion geometries, giving rise to a barrier of about 4 eV.³ With this in mind, we

derived recently⁶ a plausible analytical PES for this system, assuming that it must proceed mainly through $C_{\infty v}$ configurations, only beginning to deviate from collinearity for moderate or high relative energies. The only structural information available about the $^4A''$ surface that could be used to construct the analytical PES, was the geometry and energy of the $C_{\infty v}$ $1^4\Sigma^-$ minimum. Given that for this stationary point, there was also a certain discrepancy as to its geometry and exact energetic placement,^{4,5} they had to be corrected to match the asymptotic spectroscopic data available. Finally, values of $R_{OH} = 1.191 \text{ \AA}$, $R_{HH} = 1.058 \text{ \AA}$, and an energy of 8.8 kcal/mol below products were adopted⁶ as a reasonable guess for the collinear minimum to build the PES. In a subsequent work,⁷ we reexamined the energy change of reaction (1) (ΔE) as well as the geometry and energy of the $OH_2^+(^4\Sigma^-)$ collinear minimum of the ground PES using large basis sets and accurate *ab initio* configuration-interaction (CI) calculations, calibrating the CI expansions against the full CI solution for the atoms and molecules involved. According to these findings, the *ab initio* CI ΔE value (-0.30 eV) was still 0.15 eV above the experimental determination (-0.45 eV , obtained by correcting the reaction enthalpy change with the zero-point energies of reactants and products), mainly due to the error in the ionization potential of oxygen. Thus, as the theoretical energy of the $O^+ + H_2$ asymptote has a substantial error, the $1^4\Sigma^-$ collinear minimum depth was determined with respect to the $OH^+ + H$ product asymptote, calculated with very little error. Optimizing the geometry for this minimum led to R_{OH} and R_{HH} distances of $1.12 \pm 0.01 \text{ \AA}$ and $1.23 \pm 0.01 \text{ \AA}$, respectively, in good agree-

^{a)} Author to whom correspondence should be addressed.

ment with the results of Ref. 5, and an actual depth of 7.79 kcal/mol with respect to products. These high-quality *ab initio* CI values confirmed our previous suppositions about the geometry and energy of the minimum. Taking into account the large computational cost necessary for an adequate extensive *ab initio* calculation to take place, as well as the large errors in the reactant asymptote, as will be proven below our PES represents a good starting point from which to obtain a better PES for this system.

For the analytical functional form, a fit of the geometry and energy of the collinear minimum using a London–Eyring–Polanyi–Sato (LEPS) surface with an ion-induced-dipole correcting term (hereafter termed LEPS–IDI) described elsewhere⁸ was employed. The PESs satisfying the necessary requirements were then tested to reproduce the different experimentally determined dynamical properties available. Harris and Leventhal⁹ measured the translational exoergicity $Q(0^\circ)$ in laboratory for reaction (2). The experimental data follows the spectator stripping model¹⁰ (SSM) quite well and evidence a high degree of vibrational excitation for the OD^+ molecules produced. The quasiclassical trajectory (QCT) results on our LEPS–IDI surface also exhibit a good agreement with the SSM expectations at energies above 3.1 eV, while fitting well to this model at lower energies if the electronic exoergicity is added to the SSM values. The ratio of cross sections for reactions (3) and (4) determined by Gillen, Mahan, and Winn at 6.3 eV (Ref. 12) also match well the QCT results obtained on this PES.¹¹ In accordance with the experimental findings,^{3,9,12} a reaction-mode analysis of this system evidenced a direct character for the trajectories over almost the whole energy range explored. Using the experimental rate-constant measurement of Smith, Adams, and Miller¹³ and approximating the rate constant at 300 K as the product of the cross section (S_r) by the relative velocity of reactants (v_r), the estimated S_r (83 \AA^2) and those obtained from QCT (86.4 \AA^2) fall very near each other and also not far from the value resulting from the Langevin model¹⁰ (LGS) (75 \AA^2). Also, on plotting the S_r vs E_T dependence for the QCT results, a behavior of the type $S_r \propto E_T^{-m}$ is found, with $m=0.60$, 0.63 , and 0.59 for H_2 , D_2 , and HD , respectively, not very far from the expected 0.50 if the system was to behave according to the LGS assumptions. The behavior of the fitted PES agreed also with the experimental observation by Gillen, Mahan, and Winn¹² that the forward/backward ratio of trajectories scattered in the center-of-mass system (f/b) was always greater for reaction (3) than for reaction (4). The different f/b values observed in reactions (1) to (4) as well as the strikingly different behavior of the opacity function for reactions (3) and (4) were explained in terms of angular momentum constraints.¹¹ Similarly, the enhancing effect of vibrational energy on promoting reaction (3) over (4) was explained¹¹ by taking into account the different shapes of the PESs for both reactions when considering a skewed-scaled representation of the collinear PES.

There exist several recent experimental contributions on the dynamics of the $O^+ + H_2$ system and isotopic variants. The most comprehensive ones are those of Armen-

trout and co-workers^{14,15} using guided-ion-beam mass spectrometry (GB) between 0.01 and 10 eV translational energy in the center-of-mass framework. In the lower E_T range, these results match quite well those of Dateo and Clary¹⁶ obtained within the adiabatic capture centrifugal sudden approximation (ACCSA) approach. Another experimental work by Flesch and Ng (Ref. 17) suggests that a charge-transfer process may play an important role in determining the behavior of S_r with E_T . The results in Ref. 14 are, in general, consistent with earlier molecular-beam determinations of Johnson and Henschman (B).¹⁸ A plot of the different theoretical and experimental information available about this system and isotopic variants is presented in Figs. 2(a)–2(d).

In view of these recent theoretical and experimental developments, it seems clear that a reevaluation of the validity and accuracy of the LEPS–IDI surface used in our previous contributions^{6,8} is opportune.

II. CALCULATION METHOD

A. Analytical potential-energy surface

To understand better the results of the trajectory calculations, it may be interesting to describe first in some

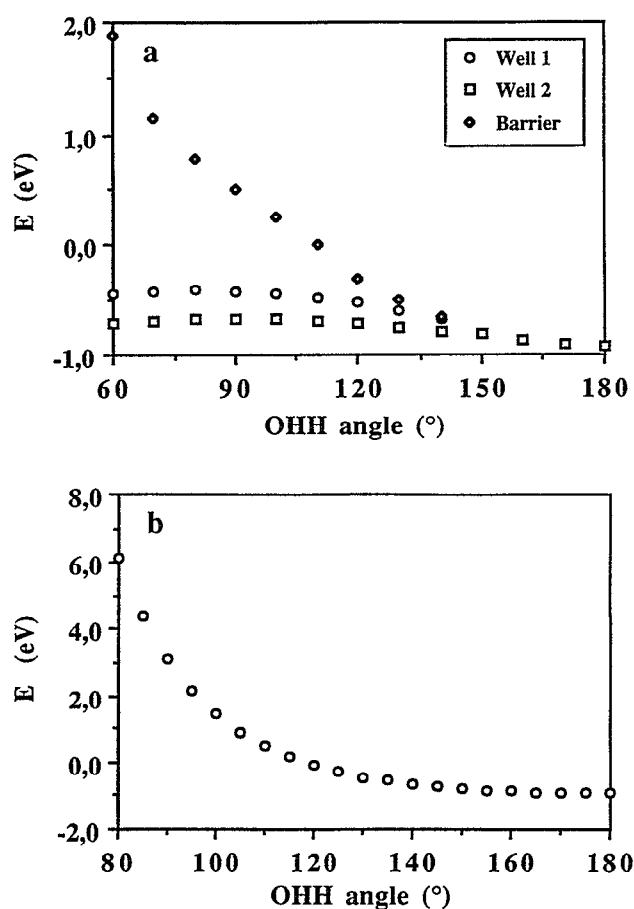


FIG. 1. (a) Evolution of the energy of the two wells and the barrier on the $4A''$ LEPS–IDI surface with the OHH angle. (b) Bending potential with the R_{OH} and R_{HH} interatomic distances held fixed at their values for the $C_{\infty v}$ minimum. Energies referred to reactants.

detail the main topological features of the analytical PES. As stated in the Introduction, in the present work we make use of the LEPS-IDI function already employed in other ion-molecule works in our group.^{19,20} Also, as it can be inferred from the Introduction, the behavior of this PES with respect to the different dynamical features of the system seems to be quite good.

We have performed an analysis of the behavior of the PES with the OHH angle by carrying out reaction coordinates at fixed OHH angular values and also by monitoring the bending potential with both interatomic distances fixed at the $C_{\infty v}$ ($O-H-H$)⁺ minimum values ($R_{OH}=1.191$ Å, $R_{HH}=1.058$ Å). Figure 1 shows the evolution of the most relevant stationary points on the LEPS-IDI surface as the OHH angle is narrowed from 180° to 60°. For collinear $C_{\infty v}$ geometries, the OHH minimum referred to above, lying 8.8 kcal/mol below products, is observed. As the OHH angle is closed down to narrower values, the depth of this collinear well diminishes, becoming shallowest for OHH angles about 90° and going down again very slightly afterwards.

At about 130°, the (OHH)⁺ minimum breaks in two. In terms of contour plots, the -0.43 eV equipotential curve (with energy referred to reactants), which for $C_{\infty v}$ arrangements goes far into the valley of reactants, breaks down giving rise to an additional well (well 1). The depth of this accident on the PES is shifted approximately 0.2 eV above that of the one coming from $C_{\infty v}$ configurations (well 2). Its evolution with the OHH angle, after appearing on the PES, runs almost parallel with that of well 2. Both wells on the PES become separated by a barrier which increases in height as the OHH angle is closed down. For OHH configurations near 60° the barrier for the passage from well 2 to well 1 nears 2.0 eV. For well 1, the R_{OH} bond length varies between 2.2 Å (for an OHH angle of 30°) and 1.5 Å (at an OHH angle of 140°), whereas the R_{HH} interatomic distance (0.775 and 0.799 Å for OHH angles of 30° and 140°, respectively) remains quite near the R_{HH} equilibrium value of 0.741 Å. Conversely, we observe a rather late character for well 2, with the R_{OH} bond length moving between 1.2 and 1.0 Å for OHH angles from 180° to 60° (the R_{OH} equilibrium bond distance is 1.029 Å), while the R_{HH} distance takes corresponding values between 1.040 and 2.718 Å. Figure 1(b) shows the evolution of the OHH bending potential at the R_{OH} and R_{HH} interatomic distance values of the $C_{\infty v}$ minimum on the PES. As can be seen, the bending potential rises steeply after 120°, eventually attaining 6.0 eV with respect to reactants for OHH angles of about 80°. It is to be noted, however, that both Figs. 1(a) and 1(b) evidence a markedly isotropic behavior of the potential between 180° and 115°. It is not until approximately this OHH angle value that the energy of the barrier to reaction overcomes that of reactants. Hence, all OHH configurations from 115° to 180° will be open for reaction at any E_T considered. Also, according to Fig. 1(a), there is a moderate increase in the height of the barrier between both wells (which represents in fact the barrier to reaction) on closing the angle further to 60°. This means that for $E_T \geq 2.0$ eV, which is quite a moderate value

in the energy range considered in the present and former works, in principle, a great deal of OHH angles (from 60° up to 180°) may lead to reaction.

Thus, for all energetic conditions explored, the energy of reactants is placed well above that of the $C_{\infty v}$ minimum, implying that even if collinear configurations are most favorable for reaction and we should expect a certain orientational effect of the PES in this sense, the number of trajectories spending a long time in the vicinity of the minimum will be low and most trajectories will proceed in a direct manner. In fact, this is observed when performing a reaction-mode analysis.⁸ Also, even though it gives rise to very few complex trajectories, the well on the PES may exert a certain influence as to the final energy partitioning in products. In fact, as evidenced from the data in Ref. 8, we observe an almost constant percentage of the accessible energy going into translation of products which in the $E_T = 0.25$ –2.0 eV energy range, deviates from the SSM expectations. Since this PES does not exhibit any energy threshold and becomes only moderately repulsive, one should expect (as it was observed in Ref. 8), a decreasing behavior of the excitation function, with a steep initial fall due to several concomitant factors, such as the lower maximum impact parameter b_{max} leading to reaction as E_T increases and the growing number of trajectories bouncing back without reacting because more repulsive zones of the PES are explored. At higher E_T the details of the PES become less relevant in the sense that almost all OHH configurations are open for reaction. Also, as observed in Ref. 8 the f/b ratio is expected to decrease with E_T , because exploring more repulsive configurations on the PES implies that the probability of OH^+ (OD^+) products being scattered back in the center-of-mass framework increases. At the higher E_T considered in our studies, (4.5 eV and above), one should also expect insertion of O^+ into the H_2 bond to be energetically allowed and thus that some trajectories proceed this way. We have not been able, however, to observe this behavior in our reaction-mode analysis.⁸

B. Initial conditions and QCT computational procedure

The calculations have been performed according to the quasiclassical trajectory method^{21,22} as implemented in a three-dimensional (3D) QCT program developed in our laboratory.²³ The accuracy of the coupled classical mechanics differential equations has been checked by verifying the conservation of total energy and momentum along each trajectory as well as through back integration of representative samplings of trajectories.

Our goal in performing the present study was to carry out a comparison of the QCT excitation function as a function of E_T with the diatomic molecules at $T_{rot}=T_{vib}=300$ K, with the existing experimental data. For the three isotopic mass combinations (H_2 , D_2 , and HD), an extensive QCT calculation focused mainly on the most populated rovibrational levels of each diatomic molecule at 300 K ($v=0$, $J=0$, 1, 2 for H_2 and D_2 , and $v=0$, $J=1$ for HD) as well as for the $v=1$, $J=1$ state of H_2 and HD , has been previously reported.¹¹ However, for an accurate compari-

son between the QCT data and those corresponding to thermal (300 K) cross sections to take place, it is necessary that a significant amount of the H_2 , D_2 , and HD molecule populations at this temperature be taken into account when averaging the S_r values for the different specific rovibrational states of the molecules, and more so for the low

E_T values. Therefore, we have set out to complete the previous existing QCT calculation, whose results are also used in the present work, to acquire a better description at those low E_T conditions for which no calculations at v, J levels other than the most populated one at 300 K existed. Thus, for $\text{O}^+ + \text{H}_2$, the $v=0, J=0, 1, 2, 5, 8$ and $v=1, 2, J=1$

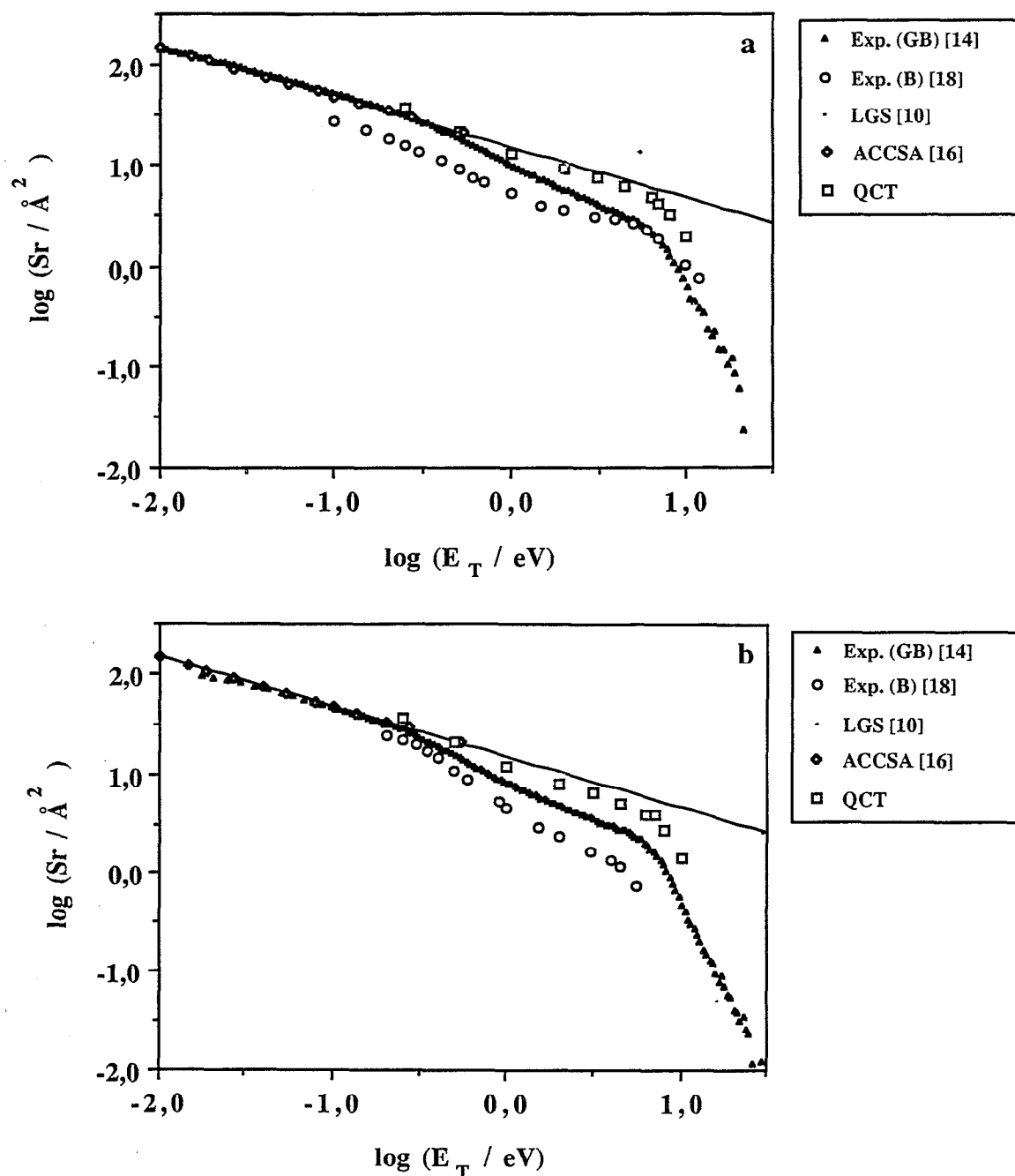


FIG. 2. Cross sections for the reaction of O^+ with H_2 (a), D_2 (b), and HD (c) and fraction of OH^+ produced in the reaction of O^+ with HD (d) as a function of the relative translational energy of reactants at 300 K. Solid triangles correspond to the guided beam (GB) data of Armentrout and co-workers (Ref. 14), circles denote the beam (B) results of Johnson and Henschman (Ref. 18), while lozenges represent the ACCSA theoretical results of Dateo and Clary (Ref. 16). The solid line included shows the Langevin model (LGS) cross-section behavior (Ref. 10). The QCT data from the present calculation and Ref. 11 are shown as squares. In (d) the crossed molecular beam (CB) $f(\text{OH}^+)$ results of Mahan and co-workers (Ref. 12) are also shown as solid squares.

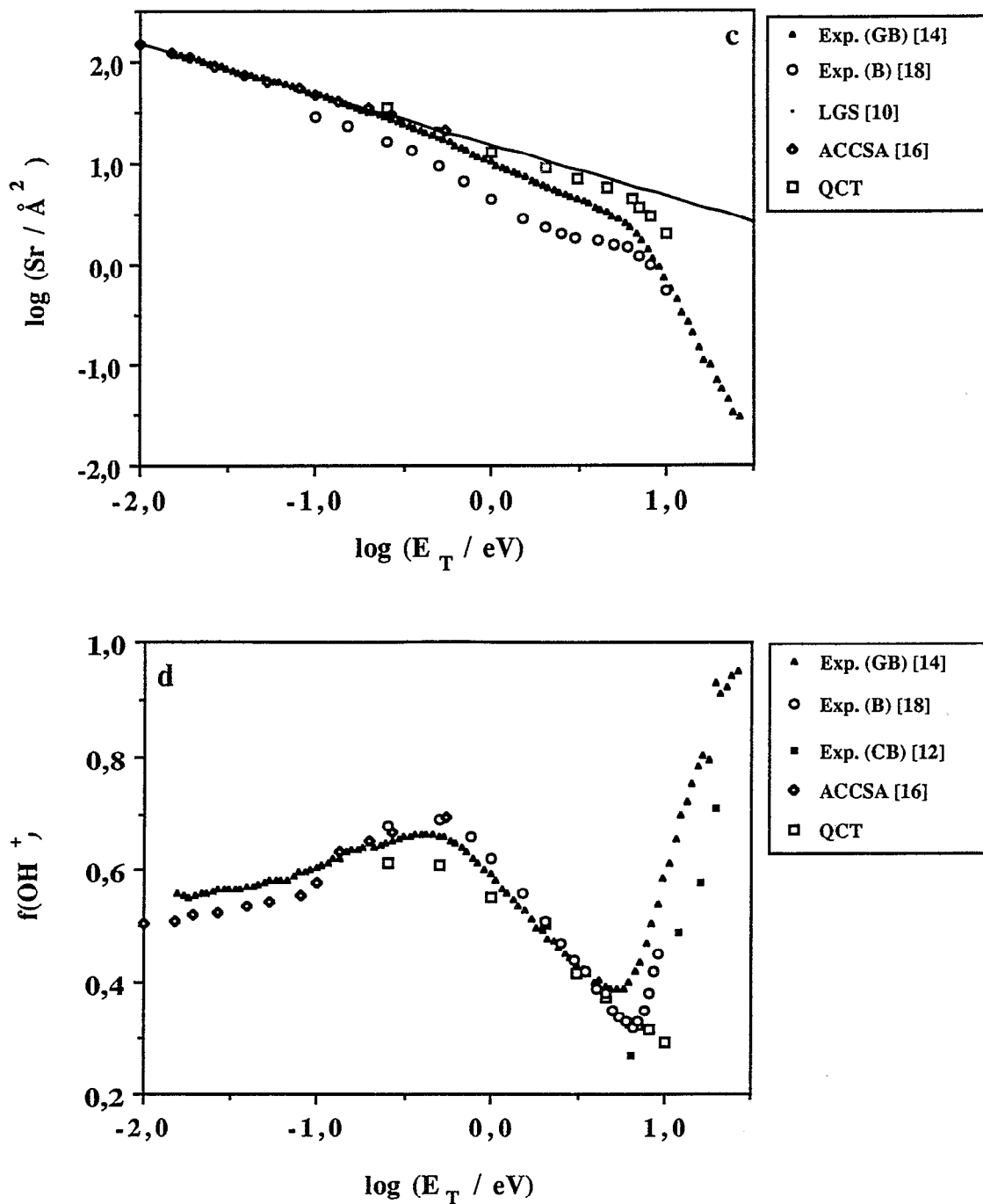


FIG. 2. (Continued.)

rovibrational states of H_2 at $E_T = 0.25$ eV have been considered, and also the $v=0, J=0, 2, 5, 8$ and $v=1, 2, J=1$ states of H_2 at $E_T = 0.5$ and 1.0 eV. An average of 500 trajectories per condition were integrated which, due to the high reactivity of this system, enables errors in S_r (one standard deviation) to fall below 10%. Similarly, for O^+

$+ \text{D}_2$, the $E_T = 0.25, 0.50$, and 1.0 eV initial energies for the $v=0, J=0, 1, 2, 6, v=1, J=1, 2$, and $v=2, J=2$ rovibrational states of D_2 , also with an average of 500 trajectories per condition were used in the present calculation. For the third isotopic combination, values of $v=0, J=0, 1, 2, 5$ and $v=1, 2, J=1$ for HD were selected to run an

average of 500 trajectories per condition at $E_T = 0.25, 0.5$, and 1.0 eV. Besides, in order to explore the high-energy range, where the initial rovibrational level of the diatomic molecule at 300 K is very little relevant, calculations were performed for $E_T = 7.0, 8.0$, and 10.0 eV with the H_2 , D_2 , and HD molecules placed in their most populated rovibrational levels at 300 K ($v=0, J=1, 2$, and 1 , respectively).

III. RESULTS

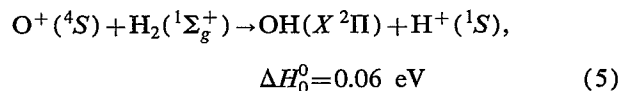
The different data available about the S_r vs E_T dependence for $O^+ + H_2$, D_2 , and HD are plotted in Figs. 2(a)–2(c), respectively. The behavior of $f(OH^+)$ with E_T , where $f(OH^+)$ stands for the ratio of S_r for reaction (3) and the sum of S_r for reactions (3) and (4), is depicted in Fig. 2(d).

For QCT results to be compared with the thermal $S_r(E_T, T_{rot} = T_{vib} = 300 \text{ K})$ given in Refs. 14–16 and 18, it is necessary to average the different S_r values for the various initial rotational levels of $H_2(v=0)$, $D_2(v=0)$, and $HD(v=0)$ over the relative populations of these levels at 300 K, taken usually to follow a Maxwell–Boltzmann distribution. This averaging is especially necessary in the low- E_T range, for which changes in the initial rotational state of the diatomic molecule imply significant changes in the magnitude of S_r .

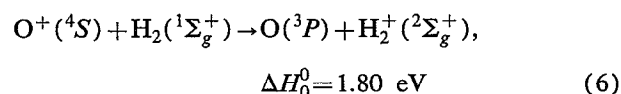
The experimental data depicted in Figs. 2(a)–2(c) clearly show three well-defined zones. In the first zone, corresponding to energies between 0.01 eV and roughly 0.3 eV, both three excitation function plots fit excellently well to the LGS model, even though for Fig. 2(a) it seems that the experimental values are very slightly above the LGS predictions, a fact that Burley, Ervin, and Armentrout¹⁴ attribute to experimental error. In fact, these authors estimate the accuracy in the absolute magnitude of their S_r to be of about $\pm 20\%$. At the same time, the ACCSA data of Dateo and Clary,¹⁶ obtained using an intramolecular potential based upon the LGS model but corrected to incorporate anisotropy effects, superimpose on the LGS and experimental estimates in this low-energy range. The only existing overlapping QCT point in this zone of the excitation function, that corresponding to 0.25 eV, falls in all three cases a bit above the LGS limit.

In the second zone of the S_r vs E_T curves, which comprises an energy range from 0.3 to roughly the thermodynamic onset for dissociation of the product molecules, the experimental data deviate considerably from the LGS predictions, following a steeper decreasing behavior. In this zone also [see Figs. 2(a)–2(c)], the other existing experimental data of Johnson and Henschman¹⁸ exhibit a similar trend. For these latter results, the behavior of S_r with E_T does not follow the LGS model in the low-energy range. In the case of the $O^+ + H_2$ reaction, the curves of Johnson and Henschman and of Burley, Ervin, and Armentrout do almost overlap if the former is just shifted up a bit, beginning only to deviate from each other after roughly 3.2 eV. In view of the lower accuracy of the results in Ref. 18, it might well be that the observed diverging behavior when

both curves are superimposed arises mainly from experimental uncertainties (ion collection efficiencies). The behavior of Johnson and Henschman's data¹⁸ in the case of the $O^+ + D_2$ [Fig. 2(b)] and $O^+ + HD$ systems [Fig. 2(c)] do not match so well when shifted the more recent determinations of Burley, Ervin, and Armentrout.¹⁴ For $O^+ + D_2$, the behavior of the S_r vs E_T plot corresponding to Johnson and Henschman's data approaches the limiting LGS model at low E_T , while falling significantly below Burley, Ervin, and Armentrout's determinations at higher relative energies. Thus, a simple shift of Johnson and Henschman's results to superimpose them to the ones by Burley, Ervin, and Armentrout, shows that they have a more concave behavior at low energies with S_r rising above the LGS limit. A similar behavior is observed for the $O^+ + HD$ system. In this case, the shape of the S_r vs E_T curve from Johnson and Henschman's data shows a bow followed by a shoulder in sharp disagreement with the more recent measurements of Burley, Ervin, and Armentrout. However, as pointed out in Ref. 18 there may be several sources of error for the different data. Armentrout and co-workers¹⁴ explain the deviation from the LGS limit as well as the preferred formation of OH^+ in the reaction of $O^+ + HD$ in terms of angular momentum constraints in the exit channel, even though still S_r falls apparently more rapidly than it should. Various explanations based upon competition from the spin-forbidden process



have been put forward.^{14,16} In a recent experimental work, Flesch and Ng¹⁷ have pointed out that the charge-transfer (CT) reaction,



does in fact play a much more important role than reaction (5), hinting also that to achieve an accurate description of the experimental S_r , it is necessary to take into account reaction (6).

On the other hand, the present QCT calculation results do in this intermediate energy range (0.3 to roughly 7 eV) fall a bit below the LGS estimate, even though they do not follow such a sharper decrease as is found experimentally. The slight deviation of the QCT results from the theoretical LGS model probably arises from the fact that one of its basic premises, that is, that all trajectories surmounting the effective potential will lead to reaction, no longer holds since more repulsive zones of the PES are explored and the probability of trajectories bouncing back into reactants increases accordingly. Also, the experimental charge-transfer [reaction (6)] cross sections of Flesch and Ng¹⁷ do not pay a significant contribution to S_r until E_T up to about 6 eV, where the most important process apart from reactions

(1)–(4) is the dissociation of the product molecule. Summing the CT cross sections with the experimental ones for the reactive process by Burley, Ervin, and Armentrout does not bring the resulting summed curves significantly closer to the QCT plotted one. Therefore, it seems that the experimental downhill shape of the excitation functions in the intermediate energy range cannot be attributed at least solely to the opening of the CT channel.

At energies between 5.6 and 6.25 eV, the experimental excitation function curves of Burley, Ervin, and Armentrout¹⁴ and Johnson and Henschman¹⁸ show a new change in steepness, going down much steeper than in the intermediate energy region [see Figs. 2(a)–2(c)] at approximately the same E_T values. This behavior has been attributed to the increasing number of OH^+ and OD^+ molecules appearing with enough internal energy to be dissociated, even though the experimentally derived onsets for dissociation of the product molecules appear between 1.14 and 2.34 eV higher in energy (depending on the isotopic variant considered) than the thermodynamically expected values. The high percentage of energy going into translation of products, in qualitative agreement with the SSM model, has been invoked to account for this fact. As evidenced by these plots, the QCT data begin to bend down at approximately the same energy as do the experimental results. The fact that we do not observe dissociated trajectories below 6.3 eV, the moderate product dissociated trajectories found below 6.3 eV, and the moderate product translational excitation observed throughout the calculations seem to support this hypothesis. It must be pointed out that some of the results of Flesch and Ng¹⁷ would indicate, however, that product dissociation begins to occur indeed at the thermodynamic dissociation onset values, in apparent disagreement with the data mentioned above. On examining the data in Fig. 2 it is worth remarking that the QCT results do always fall above the experimental ones. As commented above, it should also be noted that the results of Ref. 18, except in the case of the $\text{O}^+ + \text{H}_2$ system, deviate considerably from the more accurate ones of Burley, Ervin, and Armentrout.¹⁴ As pointed out by Johnson and Henschman,¹⁸ there is about a 25% scatter in the high-energy structure of the excitation function, which might account for the observed differences between the experimental works in this region.

Overall, it seems interesting to indicate also that in the intermediate zone, the experimental cross-section magnitude for $\text{O}^+ + \text{D}_2$ falls a little below that of the $\text{O}^+ + \text{H}_2$, with the $\text{O}^+ + \text{HD}$ one coming between both. The QCT data, giving S_r about 16% lower for deuterium than for hydrogen in this region, fully support the experimental results. However, in the lowest energy range explored in the present QCT study, from 0.25 to 0.5 eV, we find a value of 1.0 for the ratio of cross sections for H_2 and D_2 , in full agreement with the theoretical results of Dateo and Clary,¹⁶ but deviating a little from the experimental value of 1.2. Thus, a weak intermolecular isotopic effect is reported in the experiments^{14,18} in the low E_T zone which is absent from all the theoretical calculations.

Figure 2(d) shows a plot of the $f(\text{OH}^+)$ produced in

the reaction of O^+ with HD. The experimental results point once again to the existence of three well-defined zones. In the first zone, up to approximately 0.4 eV, $f(\text{OH}^+)$ grows with E_T . This behavior is also observed for the ACCSA results in this zone. In the second one there is a fall in $f(\text{OH}^+)$, while in the third $f(\text{OH}^+)$ rises up again. In this latter region, the crossed-beam results of Mahan and co-workers¹² at high E_T have also been considered. The behavior in the low-energy zone has been explained^{14,16} by considering that the incoming O^+ atom exerts a torque on HD as it approaches forcing the HD molecule into an orientation with H directed towards the incoming O^+ atom, thus causing it to react preferentially over D. As E_T rises, orbital angular momentum conservation criteria¹⁴ as well as effects based upon the anisotropy of the potential¹⁶ have been invoked to account for the increment in S_r . The decline in $f(\text{OH}^+)$ after 0.4 eV has been accounted for by taking into account the skewed-scaled¹⁰ PES, for which reactions to give OD^+ are more favorable,^{11,14} given the more open nature of the skewed PES leading to OD^+ formation. In the high-energy range, $f(\text{OH}^+)$ goes up again probably due to the higher internal energy contents of the OD^+ molecules formed which favors dissociation in this channel with respect to the one giving OH^+ . This higher internal energy contents of the OD^+ product molecules is also observed in the present QCT calculations.

As evidenced by the plot in Fig. 2(d), all three experimental data sets behave similarly. The results of Johnson and Henschman¹⁸ seem to indicate a sharper decrease in $f(\text{OH}^+)$ than those of Burley, Ervin and Armentrout,¹⁴ even though once errors are taken into consideration, both data sets are probably in good agreement. The crossed-beam data of Gillen, Mahan, and Winn¹² at $E_T \geq 6.3$ eV deviate a bit and run almost parallel to those reported in Ref. 14, but once again they may become relatively near once errors are taken into consideration. The QCT results also shown in Fig. 2(d) follow a simpler behavior. The QCT $f(\text{OH}^+)$ curve goes down more smoothly than the experimental data. In the declining zone of the $f(\text{OH}^+)$ plot, the QCT data behave very much like the experimental ones, even though they do not afterwards show a sharp increase at high E_T . Instead, $f(\text{OH}^+)$ remains almost constant between 8.0 and 10.0 eV. It must, however, be taken into consideration that the LEPS–IDI surface proposed is, in principle, only adequate for low and moderate energies and may give rise to faulty results at energies well above the dissociation energy of reactants and products. Besides, at these high energies, describing reactions (1)–(4) using only the ground $^4A''$ PES is no longer an appropriate approximation, since reaction may take place nonadiabatically, involving excited PESs of the system. In fact, as evidenced by the data in Ref. 17, the CT process at these energies dominates over reaction on the ground PES.

In Ref. 15, S_r values at $T = 105$ K are reported, comparing well with the data of Dateo and Clary.¹⁶ According to these results, the S_r values do not differ substantially at 105 and 305 K, while for the reaction of O^+ with HD, it seems that lower T favors a slightly higher $f(\text{OH}^+)$.

IV. DISCUSSION

The results presented in the preceding section clearly evidence that, while reproducing the overall dynamical properties of the system on the whole with quite a reasonable accuracy, the PES used in the trajectory calculations lacks the ability to mimic the excitation function in the intermediate energy zone. As stated above, several explanations have been put forward to account for the decline of S_r in this zone. One of them is competition of the spin-forbidden process (5) to the main reactive one. However, the experimental findings of Flesch and Ng¹⁷ seem to rule out this possibility, given the extremely low cross sections for H^+ appearance reported in their work, at least compared to other contributions such as that of the CT process (6). On the other hand, the energy threshold for reaction (5), 0.06 eV, would seem to suggest that the effects of this alternative reaction channel should become evident at considerably lower energies than the ones at which a significant deviation from the LGS model begins to take place.

The charge-transfer process (6) might be another possible explanation for the observed discrepancies between theory and experiment. However, as was already pointed out in Sec. III, the contribution of the CT channel to reactivity is rather low even at considerably high relative energies. Hence, the effect of the CT process, if any, would perhaps have to be understood as a deflecting one, that is, that it contributed mainly to scattering back towards reactants a significant part of the $O^+ + H_2$ (D_2 , HD) reactive events taking place on it. Unfortunately, to our knowledge no *ab initio* or model calculations whatsoever have been performed on this surface so that this hypothesis cannot be confirmed.

Another possible explanation, in our opinion the most plausible one, would be that the present LEPS-IDI PES behaves in too attractive a manner, at least at energies for which the CT channel is closed. In fact, as pointed out in the preceding section, the structure of the potential is such that at energies above 2.0 eV OHH angles from 180° to 60° are open for reaction. The rather isotropic behavior of the potential would thus cause an overestimation of the reactivity over the whole energy range. In fact, as pointed out before, the QCT results at low energies do in fact fall a little above those determined experimentally and also a bit above the LGS model ones.

A comparison between the present theoretical and the experimental data evidences a rather good quantitative agreement between theory and experiment, partly because the experimental errors (about $\pm 20\%$) cause the QCT results to fall close to the experimental values once the error intervals for these latter have also been taken into account. However, the shape of the experimental excitation functions in the intermediate energy region is not quite reproduced in the QCT calculation.

V. CONCLUDING REMARKS

In the present work, we have presented an extensive QCT calculation on a previously described LEPS-IDI an-

alytical PES for the lowest energy $^4A''$ surface of the $O^+ + H_2$ system and its isotopic variants to compare it with the latest experimental determinations available. The LEPS+IDI surface used exhibits a rather isotropic behavior on going away from the preferred collinear $C_{\infty v}$ configuration. The structure of the excitation function at 300 K found in the experimental determinations is fairly well described even though still not quite completely reproduced in the QCT calculations, which overestimate cross sections for all three isotopic combinations in the $0.5 \leq E_T \leq 4.5$ eV energy range, even though the QCT cross-section values agree rather well with those obtained experimentally when both uncertainties are included. On the other hand, the intramolecular isotopic effect in the case of the $O^+ + HD$ reaction is quite well reproduced. In view of the low probability that other competing reactive processes may be responsible for the observed decay in S_r in this energy range, it is concluded that the PES used is probably too attractive, but that nevertheless it may serve as a reasonably good starting point to obtain a better representation of the $^4A''$ PES for this system.

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