F+OH reactive collisions on new excited $^3A''$ and $^3A'$ potential-energy surfaces

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(Received 28 June 2005; accepted 8 August 2005; published online 22 September 2005)

Global three-dimensional adiabatic potential-energy surfaces for the excited $2^3A''$ and $1^3A'$ triplet states of OHF are obtained to study the $F(^2P)+OH(^2\Pi)\rightarrow O(^3P)+HF(^1\Sigma^+)$ reaction. Highly accurate *ab initio* calculations are obtained for the two excited electronic states and fitted to analytical functions with small deviations. The reaction dynamics is studied using a wave-packet treatment within a centrifugal sudden approach, which is justified by the linear transition state of the two electronic states studied. The reaction efficiency presents a marked preference for perpendicular orientation of the initial relative velocity vector and the angular momentum of the OH reagent, consistent in the body-fixed frame used with an initial collinear geometry which facilitates the access to the transition state. It is also found that the reaction cross section presents a rather high threshold so that, in an adiabatic picture, the two excited triplet states do not contribute to the rate constant at room temperature. Thus, only the lowest triplet state leads to reaction under these conditions and the simulated rate constants are too low as compared with the experimental ones. Such disagreement is likely to be due to nonadiabatic transitions occurring at the conical intersections near the transition state for this reaction. © 2005 American Institute of Physics. [DOI: 10.1063/1.2046669]

I. INTRODUCTION

The reaction dynamics of open-shell reactants to form open-shell products involves several electronic states correlating the two rearrangement channels. As an example, in atmospheric chemistry open-shell species, such as oxygen atoms, play an important role. Among others, the reactions of hydrogen halides, HX, with oxygen atoms are interesting because of their contribution to the catalytic ozone destruction cycle.¹ Because of its larger abundance, the chlorinated compounds have been the most widely studied,^{2–13} normally on single adiabatic potential-energy surfaces (PESs). However,

open-shell states may eventually cross along the reaction path, so that nonadiabatic events may become important. The realistic modelization of three-dimensional coupled potential-energy surfaces for studying reaction dynamics requires high-level *ab initio* calculations of large complexity and the development of new methods for their fitting and for the study of the dynamics. Presenting most of the features of the O+HX family and because of its relatively simple electronic structure, the O+HF system may be considered as a benchmark model system for this kind of reaction.

The $O+HF(^3P)\rightarrow O(^3P)+HF$ reaction is very endoergic, about 1.5 eV, in contrast to the analogous $O+HCl(^3P)\rightarrow O(^3P)+HCl$ reaction, which is nearly thermoneutral. The reverse F+OH reaction involves two radical species and, until now, only few experimental kinetic studies on the temperature effect on the rate constants¹⁴ and infrared chemilu-

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miniscence spectra for final vibrational states of HF products¹⁵ are available, albeit under multiple collision conditions.

An alternative source of experimental information on this system was provided by the photoelectron detachment spectroscopic studies performed by Bradforth *et al.*¹⁶ In these experiments, the OHF⁻ anion, of linear equilibrium configuration, is excited by detaching an electron, and several electronic states of the neutral OHF system are reached in the region of the transition state. Until recently, theoretical simulations of the experiment^{16,17} had been restricted to collinear OHF geometries and the ground electronic state.

Later, a three-dimensional PES for the lowest triplet $1^3A''$ state has been proposed¹⁸ and the photodetachment spectrum was simulated.¹⁹ In contrast to previous two-dimensional (2D) simulations, the spectrum showed many resonances. Below the F+OH threshold, the resonances were attributed to the collinear O+HF products well. Above this threshold, however, the resonances correspond to the light hydrogen atom oscillating between the heavier atoms, exploring the two wells existing in the entrance and exit channels, respectively, and the in-between region of the saddle point. Such resonances also appeared in the F+OH reactive collisions,¹⁸ both in wave-packet (WP) and quasiclassical trajectory (QCT) simulations, thus demonstrating the importance of quasiperiodic orbits at the transition state for low translational kinetic energies. After average over partial waves, the individual trace of these heavy-light-heavy (HLH) resonances disappears but, due to the presence of those HLH resonances, the total cross section showed a fast increase as the translational energy decreased. The good agreement obtained in the total reaction cross sections between WP and QCT calculations¹⁸ justifies the use of the last method for comparing with the available experimental data. Thus, the experimental final vibrational and rotational distributions of HF products at nearly room temperature¹⁵ were very nicely reproduced by QCT results.²⁰ Also, the thermal rate constant obtained on the $1^3A''$ electronic state was only slightly larger than the experimental one.¹⁴ Neglecting the spin-orbit effects and assuming that the three triplet states have the same reactivity, multiplying by the electronic degeneracy factor for triplets, 9/24, the simulated rate constant becomes, instead, slightly lower than the experimental one.

The aim of the present work is to check the reactivity of the excited triplet states for the F+OH(reactants)→O+HF(products) reaction. For this purpose, as discussed in Sec. II, PESs are developed based on accurate *ab initio* calculations, as those previously described for the $1^3A''$ triplet state. Actually, all three triplet states, $1^3A''$, $2^3A''$, and $1^3A'$, have already been used to simulate¹⁹ the photodetachment spectrum of OHF⁻, reaching a very good agreement with the experimental result of Bradforth *et al.*¹⁶ Moreover, very recently new experimental data have been published on the photodetachment spectrum of this system,^{21,22} showing an excellent agreement with our previous simulations.

In particular, the detection of electrons and neutral fragments in coincidence as used by Deyerl and Continetti²² provides a deeper insight into the reaction dynamics and would be especially useful if the authors extend their research to the

higher energies where the F+OH(reactants) channel opens.²² In any case, the agreement justifies the use of our surfaces to simulate the F+OH→O+HF reaction dynamics on the two excited triplet states, a topic not studied until now. For this, a wave-packet treatment was used, as described in Sec. III. Finally, in Sec. IV some conclusions are extracted on the validity of the use of uncoupled adiabatic surfaces for the study of reactions in the presence of conical intersections.

II. *AB INITIO* CALCULATIONS AND FIT OF THE SURFACES

Three triplet states, two $^3A''$ and one $^3A'$, correlate adiabatically with F(2P)+OH($^2\Pi$) and with O(3P)+HF($^1\Sigma^+$). However, the $1^3A''$ and the $1^3A'$ states also correlate with H(2S)+FO($^2\Pi$) channel while the excited $2^3A''$ state connects with H(2S)+FO($^4\Sigma^-$) dissociation limit. The lowest $1^3A''$ state was already presented in a previous work.^{18,20} In this paper, the details of the two new triplet surfaces, $2^3A''$ and $1^3A'$, are introduced.

Correlation-consistent polarized valence triple zeta basis sets of Dunning and co-workers^{23,24} augmented with diffuse functions for F, O, and H atoms, denoted aug-cc-pVTZ or AVTZ, are used in this work. These extra diffuse functions were further optimized to reproduce the lowest state of the anion.

All *ab initio* electronic structure calculations were carried out with the MOLPRO suite of programs.²⁵ As a starting point, a full valence state-averaged complete active space calculation^{26,27} (SA-CASSCF) was performed, including all molecular orbitals arising from the valence atomic orbitals (14 electrons in 9 orbitals). All calculations were performed in C_s symmetry. The two lowest a' CASSCF molecular orbitals (approximately 1s orbitals on fluorine and oxygen atoms) have been optimized, but maintaining them doubly occupied. The SA-CASSCF wave function used¹⁸ in the $1^3A''$ state included three $^1A'$, two $^1A''$, one $^3A'$, and two $^3A''$. Nevertheless, these previous calculations sampling a large range of geometry configurations showed that the excited PESs are not smooth enough. So, finally, the number of states included in the SA-CASSCF calculation was increased, in order to describe properly these excited states, being six $^1A'$, five $^1A''$, five $^3A'$, and five $^3A''$. This state-averaged selection yields the correct asymptotic degeneracy of the reactants F(2P)+OH($^2\Pi$) and products in the ground O(3P)+HF($^1\Sigma^+$) and excited O(1D)+HF($^1\Sigma^+$) states. In addition, at collinear geometries, the Π - or Δ -degenerated states calculated as A' and A'' become degenerate.

Internally contracted multireference configuration-interaction (icMRCI) calculations,^{28,29} with single and double excitations, have been done, using the CSFs obtained from the SA-CASSCF calculations as reference functions. Finally, the Davidson correction (+ Q) (Ref. 30) was applied to the final energies in order to approximately account for unlinked cluster effects of higher excitations. In this case, preliminary calculations of the two-degenerate states of Π symmetry (or Δ) show a small difference of about 0.1 mE_h (ca. 3 meV). The accuracy of the *ab initio* computations at the dissociation asymptotes was assessed in a previous paper¹⁸

FIG. 1. Global minimum-energy paths for the three three-dimensional triplet states for the $F(^2P)+OH(^2\Pi)\rightarrow O(^3P)+HF(^1\Sigma^+)$ reaction.

by comparing some calculated equilibrium spectroscopic data with experimental values for the OH, HF, and FO diatoms.

A. Triatomic *ab initio* calculations

Ab initio calculations have been performed over an initial grid in the internal coordinates r_{HF} , r_{OH} , and OHF bond angle. The general grid is as follows:

$$r_{HF} = 1.2 - 7.0a_0 \text{ (25 values),}$$

$$r_{OH} = 1.3 - 7.2a_0 \text{ (25 values),}$$

TABLE I. Energies and geometries icMRCI+*Q* of the stationary points of the $2^3A''$ PES for several AVnZ basis sets and extrapolation to the complete basis set (CBS). Energies and distances are given in eV and Å, respectively.

	r_{OH}	r_{HF}	θ	Energy
AVTZ				
Reactant	0.9731	...	...	0.000
Product	...	0.9179	...	-1.466
Minimum M1	0.9730	2.2839	180.0	-0.047
Transition state	1.0429	1.2657	180.0	0.512
AVQZ				
Reactant	0.9700	...	...	0.000
Product	...	0.9145	...	-1.459
Minimum M1	0.9703	2.2859	180.0	-0.042
Transition state	1.0431	1.2576	180.0	0.533
AV5Z				
Reactant	0.9700	...	...	0.000
Product	...	0.9140	...	-1.451
Minimum M1	0.9700	2.3093	180.0	-0.037
Transition state	1.0438	1.2586	180.0	0.550
CBS				
Reactant	...	...	...	0.000
Product	...	...	...	-1.446
Minimum M1	...	...	...	-0.034
Transition state	...	...	...	0.560

TABLE II. As Table I for the $1^3A'$ PES.

	r_{OH}	r_{HF}	θ	Energy
AVTZ				
Reactant	0.9731	...	...	0.000
Product	...	0.9181	...	-1.452
Minimum M1	0.9730	2.2983	180.0	-0.043
Transition state	1.0275	1.3441	180.0	0.258
AVQZ				
Reactant	0.9700	...	...	0.000
Product	...	0.9147	...	-1.445
Minimum M1	0.9704	2.3038	180.0	-0.039
Transition state	1.0271	1.3356	180.0	0.269
AV5Z				
Reactant	0.9695	...	...	0.000
Product	...	0.9140	...	-1.451
Minimum M1	0.9700	2.3178	180.0	-0.035
Transition state	1.0279	1.3318	180.0	0.281
CBS				
Reactant	...	...	...	0.000
Product	...	...	...	-1.454
Minimum M1	...	...	...	-0.033
Transition state	...	...	...	0.288

$$\theta(\text{OHF}) = 0^\circ - 180^\circ \text{ (10 values),}$$

$\theta=180^\circ$ corresponding to collinear OHF and $\theta=0^\circ$ to both collinear HOF and OFH structures. Moreover, in order to increase the accuracy of the fit for the minimum-energy path (MEP) and the energetically low-lying regions for every surface, additional points along the reaction path, using the MEP from preliminary fits, were computed. Additional points have been selected in order to take into account all the asymptotic channels shown in Fig. 1 of Ref. 18 up to 4.5 eV with respect to the zero of energy, located at the reactants F+OH asymptote, the origin of energy hereafter used in this work. All in all, a total of 6514 and 7372 points were used to fit the first excited $3A''$ and the $3A'$ potential-energy surfaces, respectively, as described below.

As used before,¹⁸ in order to estimate the effect of higher angular momentum functions, geometries of the stationary points as well as of the reactant and product channels have been optimized with the more extended basis sets aug-cc-pVnZ or AVnZ (with $n=Q$ and 5) (for quadruple and quintuple zeta, respectively). The inclusion of higher angular momentum functions in the basis sets shows that the AVTZ basis provides results accurate enough, as can be seen in Tables I and II for the $2^3A''$ and $1^3A'$ states, respectively, where the computed relative energies and optimized geometries are compared. The energy difference between the AVTZ and AV5Z results is only about 0.01 eV, and the geometry difference is, in general, less than 0.01 Å for the distances or 0.1° for the OHF angle. Note that the icMRCI+*Q* calculations with the AVQZ and AV5Z basis sets (with 206 and 334 contracted functions, respectively) involve a number of contracted (uncontracted) configurations of the order of 1 000 000 (82 000 000) and 2 500 000

(225 000 000), respectively, making the calculation of the whole surface at those levels computationally too expensive.

In view of the regular variation with n of the stationary energy values calculated with the different AVnZ ($n=T$, Q , and 5) basis sets, we used the expression³¹

$$E(n) = E_{\text{CBS}} + Be^{-(n-1)} + Ce^{-(n-1)^2}$$

to calculate E_{CBS} , the extrapolated infinity ($n=\infty$) basis set limit energy. As seen in the last column of Tables I and II, the energy differences between the CBS and AVTZ stationary points values do not exceed 30 meV, thus showing the accuracy of the AVTZ results used in this work.

Finally, the calculated exoergicity for the reaction $F(^2P) + \text{OH}(^2\Pi) \rightarrow \text{O}(^3P) + \text{HF}(^1\Sigma^+)$, obtained from the energy dissociation for the diatoms, is 1.416 eV, including the harmonic zero-point energies (ZPEs). The experimental exoergicity, 1.477 or 1.454 eV, corresponding to the two experimental results for OH (Refs. 32 and 33) (see Table I of Ref. 18), is in good agreement with the calculated one, better than 4%.

B. Global potential-energy surface

The *ab initio* icMRCI+ Q energies for these two triplet states, $2^3A''$ and $1^3A'$, have been fitted using the procedure introduced in Refs. 34 and 35 and also used for the lowest $1^3A''$ state.¹⁸ The PESs are represented by a many-body expansion

$$V_{\text{OHF}} = \sum_A V_A + \sum_{AB} V_{AB}^{(2)}(r_{AB}) + V_{ABC}^{(3)}(r_{AB}, r_{AC}, r_{BC}).$$

The diatomic terms are written as a sum of short- and long-range contributions. The long-range term is a linear combination of modified Rydberg functions¹⁸ defined as

$$\rho_m(R_m) = R_m e^{-\beta_m^{(N)} R_m}, \quad m = AB, BC, \text{ or } AC,$$

$$\text{and } \beta_m^{(N)} > 0,$$

with $N=2$. The root-mean-square (rms) errors of the fitted potentials from *ab initio* values are 1.6, 2.2, 6.1, and 1.3 meV for OH, HF, FO($^2\Pi$), and FO($^4\Sigma^-$), respectively. Note that the FO diatom is energetically not accessible in the energy range of interest. The agreement of the basic spectroscopic constants of the ground electronic states for the diatomic molecules is good, as shown in Table I of Ref. 18. For FO($^4\Sigma^-$) there are no available experimental data so far.

The three-body term is expressed as the expansion

$$V_{ABC}^{(3)}(r_{AB}, r_{AC}, r_{BC}) = \sum_{ijk} d_{ijk} \rho_{AB}^i \rho_{AC}^j \rho_{BC}^k$$

in the same Rydberg functions ρ with $N=3$.¹⁸ The linear parameters d_{ijk} ($i+j+k \leq K$) and the three nonlinear parameters $\beta_{AB}^{(3)}$, $\beta_{AC}^{(3)}$, and $\beta_{BC}^{(3)}$ are determined by fitting to the last equation the 6514 (for the $2^3A''$ state) or 7372 (for the $1^3A'$ state) calculated *ab initio* energies after the subtraction of the total two-body contributions. The overall root-mean-square deviations from the *ab initio* values of the fitted $2^3A''$ and $1^3A'$ surfaces are 42 and 37 meV, respectively. The maxi-

TABLE III. Root mean square (rms) and maximum error (E_{max}) in eV of the $2^3A''$ fitted PES for the OHF system for several energy ranges and geometry ranges. N is the number of *ab initio* points.

Energy range	N	rms	E_{max}
$E > 0.70$	3411	0.050	0.27
$-0.30 < E < 0.70$	1706	0.039	0.20
$-1.15 < E < -0.30$	632	0.026	0.21
$E < -1.15$	765	0.016	0.12
All data points	6514	0.042	0.27
Geometry range	N	rms	E_{max}
Long distances	401	0.024	0.19
Intermediate distances	3078	0.046	0.23
Short distances	775	0.061	0.27
OH channel	894	0.023	0.16
HF channel	1106	0.026	0.20
FO channel	260	0.055	0.20

um error (E_{max}) amounts to 27 meV for the $2^3A''$ state and 26 meV for the $1^3A'$ state, and both of them are located in a repulsive region, as shown in Tables III and IV. The energy range of both fitted PESs goes from -1.30 eV up to values over the three atom ($\text{H} + \text{F} + \text{O}$) dissociation limit (4.5 eV).

In order to have a more detailed view of the accuracy of the fitted PESs, we also report in Tables III and IV the rms errors and maximum deviations subdivided in several energy regions. In the lower part of every table, the rms errors and E_{max} values are shown, ordered following a geometrical criterion, namely, long-, intermediate-, and short-distance regions, as well as according to the different chemical arrangements.

C. Topological characteristics

The main topological characteristics of the three triplet surfaces are shown in the MEPs displayed in Fig. 1. They were obtained following the gradient extremal path^{36,37} as a function of the arclength s defined as the sum of the displacements ds between two consecutive points of the surface in terms of the three internuclear distances.³⁷ By convention, we take ds positive from the saddle point toward products

TABLE IV. As Table III for the $1^3A'$ PES.

Energy range	N	rms	E_{max}
$E > 0.48$	4645	0.044	0.26
$-0.30 < E < 0.48$	1708	0.020	0.18
$-1.14 < E < -0.30$	482	0.017	0.06
$E < -1.14$	537	0.012	0.06
All data points	7372	0.037	0.26
Geometry range	N	rms	E_{max}
Long distances	498	0.015	0.13
Intermediate distances	2537	0.039	0.22
Short distances	1449	0.055	0.26
OH channel	1340	0.020	0.18
HF channel	1257	0.016	0.06
FO channel	291	0.039	0.13

TABLE V. Geometries and energies of the adiabatic stationary points of OHF as calculated from the global fits of the $1^3A''$, $2^3A''$, and $1^3A'$ potential-energy surfaces. The (ν, n, b) notation corresponds to the harmonic normal modes for OH and HF stretching and OHF bending, respectively. Bond lengths are in Å, angles $\theta(\text{O-H-F})$ in degree, frequencies (ω) in cm^{-1} , and energies (V) in eV.

	$1^3A''$		$2^3A''$		$1^3A'$	
	icMRCI+ Q	Fitted	icMRCI+ Q	Fitted	icMRCI+ Q	Fitted
<i>Reactant</i>						
r_{OH}	0.9737	0.9735	0.9731	0.9735	0.9731	0.9735
r_{HF}	...	...	...	...	...	...
θ	...	...	...	...	...	...
ω	3723	3723	3717	3728	3718	3723
V	0.000	0.000	0.000	0.000	0.000	0.000
$V+\text{ZPE}$	0.230	0.231	0.230	0.231	0.230	0.231
<i>Product</i>						
r_{OH}	...	...	...	...	...	...
r_{HF}	0.9165	0.9166	0.9179	0.9166	0.9181	0.9166
θ	...	...	...	...	...	...
ω	4154	4170	4160	4170	4158	4170
V	-1.443	-1.443	-1.466	-1.443	-1.452	-1.443
$V+\text{ZPE}$	-1.185	-1.184	-1.208	-1.185	-1.194	-1.185
<i>Minimum M1</i>						
r_{OH}	0.9822	0.9864	0.9730	0.9776	0.9730	0.9750
r_{HF}	2.0924	2.1794	2.2839	2.0440	2.2983	2.1461
θ	66.4	59.7	180.0	180.0	180.0	180.0
ω_{ν}	3617	3557	3729	3871	3729	3801
ω_n	344	331	90	158	90	143
ω_b	575	570	388	247	154	166
V	-0.230	-0.230	-0.047	-0.037	-0.043	-0.046
$V+\text{ZPE}$	0.052	0.048	0.238	0.243	0.213	0.219
<i>Minimum M2</i>						
r_{OH}	1.9214	1.9177	...	...	...	...
r_{HF}	0.9308	0.9285	...	...	...	...
θ	180.0	180.0	...	...	...	...
ω_{ν}	158	180	...	...	...	...
ω_n	4031	3750	...	...	...	...
ω_b	402	341	...	...	...	...
V	-1.589	-1.587	...	...	...	...
$V+\text{ZPE}$	-1.279	-1.301	...	...	...	...
<i>Transition state</i>						
r_{OH}	1.0330	1.0270	1.0429	1.0426	1.0275	1.0161
r_{HF}	1.3494	1.3753	1.2657	1.3357	1.3441	1.3651
θ	109.2	109.6	180.0	180.0	180.0	180.0
ω_{ν}	2646	2536	772	810	1381	1464
ω_n	1418i	1425i	3976i	2221i	958i	964i
ω_b	450	336	1365	1062	434	505
V	-0.002	0.007	0.512	0.447	0.258	0.276
$V+\text{ZPE}$	0.190	0.185	0.644	0.767	0.457	0.489

(O+HF) and negative toward reactants (F+OH). In contrast to the lowest $1^3A''$ state that presents two rather deep hydrogen-bonded wells (see Fig. 1), the other two surfaces exhibit only a rather shallow well in the reactant channel.

In Table V we present the geometries and energies of the stationary points of the three triplet states. The lowest triplet state $1^3A''$ is included for comparison with the other two excited ones. *Ab initio* and fitted data are shown. The reactant and the product channels of the excited states are well described, being the equilibrium distances and harmonic vi-

brational frequencies in good agreement with the experimental ones.³²

The $2^3A''$ surface presents a shallow well (*M1* minimum) in the entrance channel located at a collinear configuration at ≈ 0.04 eV, being the r_{OH} distance close to the equilibrium geometry of the OH-free diatom. Unlike the lowest $1^3A''$ state¹⁸ where the transition state was located at an angular configuration, in this excited state $2^3A''$ the transition state is collinear. As expected for an exoergic reaction³⁸ the transition state (TS) is placed in the reactant channel, as

FIG. 2. Contour plots of the three fitted triplet potential-energy surfaces for three cuts. The energy contours are $-1.5, -1.0, -0.6, -0.2, 0.0, 1.0, 2.0$, and 4.0 eV, the solid lines corresponding to zero (F+OH asymptote) or positive values.

shown in the corresponding panel of Fig. 2; the r_{OH} distance is slightly greater than for free OH, and the r_{HF} distance is much greater than for free HF. The agreement between the fitted and the *ab initio* geometry is good, being the greater difference in the r_{HF} distance of the minimum $M1$. The fitted barrier height of 0.447 eV (0.767 eV with the zero-point energy) is much higher than for the $1^3A''$ state practically has no barrier. This will affect the reaction dynamics as will be shown in Sec. III. Finally, note that this excited state $2^3A''$ does not present van der Waals well in the O+HF product channel.

A normal-mode analysis has been performed both for the analytical fit and for the *ab initio* calculations in the vicinity of the stationary points. To assess the accuracy of the fitted PES, both *ab initio* and fitted harmonic normal modes are shown in Table V. They are denoted as (ν, n, b) , and it turns out that for the well $M1$ the $\omega_v \approx 3800 \text{ cm}^{-1}$ corresponds approximately to the OH stretching, the $\omega_n \approx 150 \text{ cm}^{-1}$ to the F–OH stretching, and the $\omega_b \approx 250 \text{ cm}^{-1}$ to the OHF bending, as shown in the panel (a) of Fig. 3. The transition state has a fitted imaginary frequency of $\omega_n \approx 2200i \text{ cm}^{-1}$ corresponding to the HF stretching, as also shown in the panel (a) of Fig. 3. The imaginary normal mode is the reaction coordinate s in the transition state where the hydrogen atom is transferred from the OH reactant to the HF product. This value is not in agreement with the calculated one. This can be explained by the presence of the conical intersection that appears in the MEP at collinear configurations, near the transition state, see Fig. 4. The real frequencies for the transition state, $\omega_v \approx 800 \text{ cm}^{-1}$ and $\omega_b \approx 1100 \text{ cm}^{-1}$, correspond to the O–HF stretching and to the OHF bending, respectively.

The $1^3A'$ state also presents a shallow well ($M1$ minimum) in the entrance channel located at a collinear configuration at ≈ 0.04 eV. This collinear minimum must be degenerate with the $M1$ minimum of the $2^3A''$ because they correlate with the $^3\Pi$ state (see Table V and the bottom panel of Fig. 4). The transition state is also collinear but it is located at a lower energy (0.28 eV) than the transition state of

FIG. 3. Normal modes at the stationary points of the $2^3A''$ and $1^3A'$ excited states, (a) and (b), respectively. In every picture, the atoms are oxygen (left), hydrogen (middle), and fluorine (right).

the $2^3A''$ state. This transition state is also located in the reactant channel, as shown in the right top panel of Fig. 2. Finally, as for $2^3A''$ this excited state $1^3A'$ does neither present van der Waals well in the O+HF product channel.

In the minimum $M1$ the normal-mode analysis yields a frequency $\omega_v \approx 3800 \text{ cm}^{-1}$, corresponding to the OH stretching. $\omega_n \approx 140 \text{ cm}^{-1}$ is associated essentially with the symmetrical stretching F–H–O, where the greater movements are of F and O atoms. Because at collinear geometries the $M1$ minimum of the $1^3A'$ is degenerate to the $M1$ minimum of the $2^3A''$ state, the two vibrational frequencies corresponding to the stretching movements must also be degenerated, as can be seen in Table V. Nevertheless, the $\omega_b \approx 160 \text{ cm}^{-1}$ that corresponds to the OHF bending is not degenerate with the bending frequency of the $2^3A''$, because the bending motion breaks the degeneration of these two excited states. In the transition state, the imaginary frequency $\omega_n \approx 960i \text{ cm}^{-1}$ corresponds to the F–OH motion while the real ones, $\omega_v \approx 1400 \text{ cm}^{-1}$ and $\omega_b \approx 500 \text{ cm}^{-1}$, are associated with the O–HF stretching and the OHF bending, respectively. The normal modes at the stationary points of the $1^3A'$ state are displayed in the panel (b) of Fig. 3.

III. WAVE-PACKET DYNAMICS

A. Calculation details

The wave-packet calculations are done as described previously;^{18,39} reactant Jacobi vectors are used, the vector $\mathbf{r}$, pointing from the O to the H nucleus, and the vector $\mathbf{R}$ that points from the OH center of mass to the F atom. The com-

FIG. 4. $3\Sigma^-$ and 3Π states (top and middle panels, respectively), with the broader line showing the intersection seam between both states. In the lower panel, a cut to the three adiabatic surfaces is shown for the region of the top of the barrier as a function of the OHF angle.

ponents of these vectors are expressed in a body-fixed frame with the three atoms in the xz plane and the z axis parallel to $\mathbf{R}$. Three Eulerian angles (ϕ, θ, χ) determine the orientation of the body-fixed axes with respect to a space-fixed frame and three internal variables define the nuclear configuration of the system: r , the internuclear H–O distance, R , the modulus of $\mathbf{R}$, and the angle γ , with $\cos \gamma = \mathbf{r} \cdot \mathbf{R} / rR$.

The internal coordinates are represented in the grids described previously for the lowest $1^3A''$ state,^{18,39} in which an exhaustive convergence analysis was done. 90×490 equidistant points in the intervals $0.4 \leq r \leq 5.5$ Å and $0.75 \leq R \leq 13$ Å are used for the radial coordinates. The angle γ is described by 100 Gauss-Legendre quadrature points. The two new surfaces for the excited electronic states present rather similar features to those of the lowest $1^3A''$ state, thus allowing the use of similar parameters. The main differences are the practical absence of wells in the excited surfaces, either in the reactants or products valley, and the higher barrier with linear geometry, while for the $1^3A''$ electronic state it is bent. In all the cases, because of the HLH character, the skew angle is very small thus requiring very dense angular grids (100 points in this case) to properly describe products up to a rather short r value (of ≈ 5 Å).

FIG. 5. Reaction probabilities obtained for the F+OH ($v_0=0, j_0=0, \Omega_0=0, J=40$) collisions with the CS approach and a converged calculation including $\Omega=0, 1, \dots, 5$ for the $1^3A'$ electronic state.

Ω , the projection of the total angular momentum $\mathbf{J}$ on the body-fixed z axes and the OH angular momentum $\mathbf{j}$ are fixed equal to their respective initial values. This centrifugal sudden (CS) approach^{40–42} works very well in this system. First, for long distances in the entrance channel the system is well approximated by a quasidiatomic system, because of the light H atom, as compared to the heavier F and O, which minimizes the Coriolis couplings among different Ω , since $\mathbf{R}$ is essentially parallel to the principal axis of inertia. Second, in the product channel, the exit angular cone is very narrow around collinear geometries, as a consequence of the small skew angle, and the Coriolis couplings become again very small. For the $1^3A''$ electronic state, several converged calculations were performed^{18,39} including $\Omega=0, 1, \dots, 5$. It was found that at moderately high energies, the CS approach worked very well. The only significant disagreement was found at low energies where many HLH resonances appeared. Those resonances were due to the two wells of the $1^3A''$ electronic state absent in the other excited electronic states. As a consequence, the CS approach is expected to work even better for the two new surfaces treated here. To check this assumption, in Fig. 5 the CS results are compared with converged results including $\Omega=0, 1, \dots, 5$ for the $1^3A'$ surface and $J=40$ for the F+OH ($v=0, j=0$) reactive collisions. As clearly seen the agreement is even better than for the lowest $1^3A''$ state (see Fig. 12 of Ref. 18).

A Chebyshev propagator^{43,44} is used to integrate the Schrödinger equation in time, with a small time step of 2.5 fs, to resolve the reaction probabilities over the large energy range shown in Fig. 5. The initial wave packet is built as an incoming complex Gaussian function multiplied by the initial rovibrational state (v_0, j_0, Ω_0) of the OH reactant. Body-fixed Bessel functions are used in the CS approach, as described previously.^{45,46} The Gaussian wave packet is initially placed at relatively long distances, around $R=10$ Å, because of the long-range character of the PES. In the course of the propagation the total reaction probability, $P_{v,j,\Omega}^J(E)$, is obtained using the flux method,^{47–51} for each OH(v_0, j_0, Ω_0) initial state. The energy distribution of the final OH(v, j) rovibrational states is obtained by the method of Balint-Kurti and co-workers.^{52,53} The total flux (reactant and product channels) is used as a test to check the accuracy of the calculation.

The z body-fixed axis or $\mathbf{R}$ is parallel to the incident wave vector $\mathbf{k}_0$ (proportional to the relative velocity) in the

asymptote. The projection of $\mathbf{j}$ is Ω , and the $(\mathbf{k}_0, \mathbf{j}_0)$ correlations are quite naturally expressed in this frame. For a particular entrance channel, (v_0, j_0, Ω_0) , the same spherical harmonic $Y_{j_0\Omega_0}$ is used for all J values, and the information about the correlation between the initial directions of $\mathbf{j}_0$ and $\mathbf{k}_0$ can be obtained from the helicity-dependent reaction cross section,⁴⁵ $\sigma_{v_0j_0\Omega_0}$, defined as

$$\sigma_{v_0j_0\Omega_0}(E) = \frac{\pi}{k_0^2} \sum_{J=\Omega_0}^{\infty} (2J+1) P_{v_0j_0\Omega_0}^J(E), \quad (1)$$

where k_0 is the wave number of the collision process.

Sometimes, specially for high j_0 , it is convenient to express the $2j_0+1$ values of $\sigma_{v_0j_0\Omega_0}$ in terms of state multipoles, whose components provide the relative contributions of different polarization of $\mathbf{j}_0$ on the reaction.^{54,55} The monopole moment is proportional to $\sigma_{v_0j_0}$, the total reaction cross section, given by

$$\sigma_{v_0j_0}(E) = \frac{1}{2j_0+1} \sum_{\Omega_0=-j_0}^{j_0} \sigma_{v_0j_0\Omega_0}(E), \quad (2)$$

corresponding to an isotropic distribution of $\mathbf{j}_0$. In analogy to rotational alignment parameter frequently used in photodissociation,⁵⁶ the quadrupole moment, defined as⁴⁵

$$\mathcal{A}_{v_0j_0}(E) = \sum_{\Omega_0} \left[\frac{3\Omega_0^2}{j_0(j_0+1)} - 1 \right] \rho_{v_0j_0\Omega_0} \quad (3)$$

with $\rho_{v_0j_0\Omega_0} = \sigma_{v_0j_0\Omega_0} / \sum_{\Omega_0} \sigma_{v_0j_0\Omega_0}$, provides information about the preferred initial alignment of $\mathbf{j}_0$ with $\mathbf{k}_0$ to produce the reaction. For high j_0 the semiclassical limit can be used in which $\cos \theta_j = \Omega / \sqrt{j_0(j_0+1)}$ (θ_j being the angle between $\mathbf{j}_0$ and the z axis), and $\mathcal{A}_{v_0j_0}(E) \propto \langle 2P_2(\cos \theta_j) \rangle$ [being $P_2(x)$ the second-order Legendre polynomial in x] provides an idea of the most favorable angle between $\mathbf{j}_0$ and $\mathbf{k}_0$ yielding to products. In the semiclassical limit the $\mathcal{A}_{v_0j_0}$ parameter takes values between -1 and 2 . $\mathcal{A}_{v_0j_0} = -1$ and 2 means that the reaction is more likely when $\mathbf{j}_0$ is perpendicular or parallel to the z axis, respectively, while $\mathcal{A}_{v_0j_0} = 0$ means that the reactivity is independent of Ω .

Also, the initial relative orientation distribution between the Jacobi vectors $\mathbf{r}$ and $\mathbf{R}$ is given by spherical harmonics $Y_{j_0\Omega_0}(\gamma, 0)$, giving physical insight on the role of the diatomic axis orientation with respect to the initial velocity vector within the body-fixed frame used. As an example, for $j_0=1$, $\Omega_0=0$, $\mathbf{r}$ is mainly parallel to $\mathbf{k}_0$, while, on the contrary, for $\Omega_0=\pm 1$ they are perpendicular.

B. Results and discussion

In this work, the F+OH reactive collisions have been simulated on the $2^3A''$ and $1^3A'$ electronic states. The results for the $1^3A''$ state were already reported,^{18,39} but they will also be shown here to compare the reaction dynamics to that on the excited states. The total reaction probabilities calculated for several initial energy selections OH($v_0=0$, $j_0=0, 1, 2, 3$, $J=0$) are shown in Fig. 6 for the three lowest triplet states.

FIG. 6. F+OH ($v_0=0$, $j_0=0, 1, 2$, and 3 , $J=0$) collision reaction probabilities obtained for the $1^3A''$ (from Refs. 18 and 39), $2^3A''$, and $1^3A'$ electronic states. Notice the change in the ordinate scale on going from ground to excited PES.

As expected, the $2^3A''$ and $1^3A'$ states present a higher threshold to reaction and lower reaction probabilities than the lowest $1^3A''$ state. The top of the barriers of the $2^3A''$ and $1^3A'$ electronic states lies above the OH($v_0=0$, $j_0=0$) energy level, by 0.216 and 0.045 eV, respectively, while for the $1^3A''$ it is well below, by 0.224 eV. The reaction thresholds of the two excited states are, however, shifted to higher energies because some zero-energy effects are important. For the $1^3A'$, the threshold at ≈ 0.2 eV is approximately equal to the barrier height including the harmonic zero-point energy in Table V, 0.258 eV with respect to the OH($v_0=0$, $j_0=0$) energy level. For the $2^3A''$ state, however, such comparison is rather bad; the real threshold is at ≈ 0.3 eV while the harmonic estimation leads to 0.536 eV. Such large disagreement is due to the appearance of several crossings with some other excited states in the case of the $2^3A''$, which introduces important difficulties for the fitting of the surface and makes the harmonic approximation become very poor.

The larger reactivity of the lowest $1^3A''$ state, as compared with those of the excited electronic states, is related to its larger angular cone of acceptance of the reaction. The two excited electronic states present a collinear barrier with a rather small cone of acceptance (see the bottom panel of Fig.

4). The lowest electronic state $1^3A''$ at collinear geometry is degenerate with the $1^3A'$ state in the region of the barrier, because the two states correspond to $^3\Pi$ states at the barrier. These degenerate $^3\Pi$ surfaces cross with a $^3\Sigma^-$ state at collinear geometry which presents two wells in the reactant and product channels, as pointed out in Ref. 57. When the system bends, the $^3\Sigma^-$ and $^3\Pi$ states interact, splitting into the two $^3A''$ and one $^3A'$ states described in that paper. As a consequence of such interaction, the resulting lowest electronic state presents a minimum as a function of the angle, which becomes the effective barrier, leading to a much broader angular cone of acceptance than the two excited electronic states.

The wells of the collinear $^3\Sigma^-$ state appear only in the resulting $1^3A''$ state because of the necessity of continuity condition to form the adiabatic surfaces. Such wells are responsible for the appearance of resonance structures in the $1^3A''$ electronic state, which are essentially absent in the other excited electronic states. Such resonances mediate the reaction at low energies, below 0.1 eV of translational energy for $j_0=0$, for the lowest $1^3A''$ state, and have a classical periodic orbit counterpart as already discussed in detail in Ref. 18. They also appear in the simulated photodetachment spectrum of OHF^- , see Refs. 19 and 57 where the structure of the spectrum was discussed.

The important differences in the reaction probabilities at low energies for different j_0 in the $1^3A''$ states are due to these resonances. At higher energies for $1^3A''$ the dependence is weaker and shows a similar pattern as for the excited $2^3A''$ and $1^3A'$ states. As for the effect of the initial rotational $\text{OH}(j_0)$ excitation, the reaction probability is first enhanced, and for the excited states this phenomenon is followed by a decrease, a behavior consistent with the sliding mass model.⁵⁸

The influence of the initial rotational excitation is linked to the amplitude of the angular cone of acceptance. When this cone is small, the reaction efficiency must strongly depend on the initial vector correlation between the relative initial velocity of reactants $\mathbf{k}_0$ and their rotational angular momentum $\mathbf{j}_0$. Such stereodynamical effects are very neatly observed in the body-fixed frame; for a particular j_0 , Ω_0 channel, the initial angular distribution is given by $Y_{j_0,\Omega_0}(\gamma,0)$, providing a particular initial distribution between the $\mathbf{r}$ and $\mathbf{R}$ vectors, independent of the total angular momentum. Thus, for a given $j_0 > 0$, the distributions associated with $\Omega_0=0$ present the maximal amplitude for collinear configurations, while for $\Omega_0=j_0$, they peak at an angle of $\pi/2$. Thus, these initial distributions might influence a lot the reaction efficiency provided they do not change during the approach of the reactants. In the present case, the two excited electronic states present a collinear geometry, which suggests that for $\Omega_0=0$ the reactivity must be enhanced. Such effect is clearly observed in Fig. 7 for $v_0=0$, $j_0=0, 1, 2$, and 3 , and $J=40$ and $0 \leq \Omega_0 \leq j_0$.

Such effect alone is not enough to explain all the stereodynamics, because the lowest $1^3A''$ also shows such a behavior for high translational energies while the transition state corresponds to a bent barrier. This was explained³⁹ by the small skew angle associated with $\text{H}+\text{LH}' \rightarrow \text{HL}+\text{H}'$ reac-

FIG. 7. Same as Fig. 6 but for $J=40$ and several Ω_0 . The different values of Ω_0 are distinguished at high energies where the reaction probabilities decrease when increasing Ω_0 .

tions; as the products fly apart, the reactant Jacobi angle γ tends to zero, geometry at which the CS approach becomes very good. Since the amplitude of the wave packet at collinearity varies as $\sin^{\Omega}\gamma$, low Ω collisions present a clear preference to react as compared with high Ω ones. This effect corresponds thus to a kinematic constraint completely general associated with $\text{H}+\text{LH}' \rightarrow \text{HL}+\text{H}'$ reactions.

In order to calculate cross sections from probabilities, several total angular momentum ($J=\Omega_0, 20, 40, 60$, and 80) calculations were performed for each j_0, Ω_0 channel, for $j_0=0, 1, 2$, and 3 and $0 \leq \Omega_0 \leq j_0$. The required reaction probabilities for intermediate J were obtained using an interpolation procedure based on the J -shifting approach. Thus, the total reaction cross sections obtained for several initial rotational and electronic states are shown in Fig. 8 as a function of translational energy. The behavior of the lowest $1^3A''$ state is very different from that of the excited states. Thus, cross sections are much larger and present some oscillations at low energies. The first peaks are associated with the resonance-mediated mechanism at low energies for the $1^3A''$ state.^{18,39} At high energies, the cross sections for $1^3A''$ state decrease with energy and the behavior is very similar for any j_0 .

For the $1^3A''$ electronic state the quantum results were compared in Ref. 39 (see Fig. 6) with the quasiclassical ones,

FIG. 8. State-to-all reaction cross sections for the F+OH ($v_0=0$, $j_0=0, 1, 2$, and 3) collisions on the three electronic states. The solid and dashed lines correspond to quantum wave packets and quasiclassical results, respectively. Notice the change in the ordinate scale.

obtained with the VENUS code.⁵⁹ The QCT results also show the fast decay with energy at low energies for low j_0 , but the cross section is lower, because this approach subestimates the reaction probabilities at the resonances.¹⁸ As j_0 increases, however, the agreement between quantum and classical results improves, just because at the higher initial rotational energy the region dominated by resonances becomes closed.

Figure 8 also shows that for $1^3A'$ the cross sections are very similar for all j_0 , presenting an increasing trend with energy, because the cone of acceptance opens up. For the $2^3A''$ state, the cross sections also increase with energy, but their absolute values progressively decrease with increasing j_0 .

In order to better describe the stereodynamical effect discussed previously, helicity-dependent cross sections were calculated and, from them, the alignment parameter defined in Eq. (3) was obtained. Results are shown in Fig. 9. The alignment parameter for the two excited $2^3A''$ and $1^3A'$ states presents a value of -1 just at threshold and beyond it increases slightly with energy. Such behavior corresponds to a marked preference of reaction when $\mathbf{j}_0$ is perpendicular to $\mathbf{k}_0$, the initial relative velocity between reactants, i.e., for low Ω_0 values. This strong preference for low Ω_0 is related to the

FIG. 9. Alignment parameter for the F+OH ($v_0=0$, $j_0=1, 2$, and 3) collisions on the three electronic states.

well-known $\ell \rightarrow \ell'$ angular momentum propensity rule for $H+LH' \rightarrow HL+H'$ reactions. Since Ω is the projection of $\mathbf{j}$ it must remain very low because $j \leq l$ and $j' \leq l'$. For the $1^3A''$ state a similar trend toward negative values of the alignment parameter is obtained for high energies while for low energies, the resonance-mediated region, the mechanism is completely different.

To finish we compare quantum and QCT results on the $1^3A''$ state for more averaged quantities. Thus, state specific rate constants are obtained for several rotational OH ($v_0=0$, j_0) initial states. The quantum results are obtained as

$$K_{v_0 j_0}(T) = \frac{1}{2\pi\hbar} \left(\frac{\mu k_B T}{2\pi\hbar^2} \right)^{-3/2} \int dE \sigma_{v_0 j_0}(E) \frac{k_0^2}{\pi} e^{-E/k_B T} \quad (4)$$

by numerical integration over the translational energy E . The quasiclassical results are obtained by running batches of 50 000 trajectories for each temperature and initial rotational state. The QCT calculations have been performed for $j_0=0, 1, 2, \dots, 10$, while the quantum calculations have been conducted only up to $j_0=3$. In any case, $v_0=0$, i.e., no vibrational averaging was taken (the thermal population of vibrationally excited states of OH is non-negligible beyond around $T=1000$ K). The quantum and QCT results between 100 and 1000 K are compared in Fig. 10(a), showing an increasingly better agreement as j_0 increases, as it was also the case for the corresponding cross sections in the $1^3A''$ state (left column panels of Fig. 8). In view of these results, we will assume that the agreement is good for $j_0 > 3$ that allow us to calculate only the QCT rate constants for OH ($v_0=0$, $j_0=4, 5, 6, 7, 8, 9$, and 10), as shown in Fig. 10(b).

FIG. 10. Specific rate constants for $\text{OH}(v_0=0, j_0=0, 1, 2, \text{ and } 3)$ states for the $1^3A''$ state: (a) comparison of quantum wave-packet results (solid lines) and quasiclassical results (points) for $j_0=0, 1, 2, \text{ and } 3$, and (b) quasiclassical results for $j_0>3$.

In a previous work,²⁰ rotationally averaged rate constants for the $1^3A''$ state were obtained using exclusively quasiclassical trajectories. It was assumed that the three triplet states contribute in a similar way, so that considering the 24 degenerate electronic states in the entrance channel, and without considering spin-orbit effects, the electronic degeneracy factor is 9/24. When this factor is considered, the simulated rate constant becomes slightly smaller than the experimental one at room temperature and nearby.

However, in this work, it has been found that the cross section for the excited states is negligible for energies below

FIG. 11. Rotationally averaged rate constant for the F+OH collision obtained for the $1^3A''$ electronic state with or without an electronic degeneracy factor of 3/24. The filled triangles correspond to purely quasiclassical results (QCTs), while the filled circles are the mixed quantum/classical curves (WP-QCT), as explained in the text. QCT value of the rate constant at $T=2500$ K of $18.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ is too large to fit in the figure and is not plotted. The experimental data (EXP) are from Ref. 14.

0.2 eV or more. Therefore, at room temperature all F+OH reactivity must be due to only the lowest $1^3A''$ electronic state. The real electronic degeneracy factor should thus be 3/24. In Fig. 11 the rotationally averaged rate constant obtained by a QCT approach using the $1^3A''$ PES and multiplied by this 3/24 factor is compared with the experimental data. It should be noted that the QCT results shown slightly differ from those previously shown in Ref. 20 because longer integration times have been considered here to properly account for the reactivity at low energies, where resonances or quasiperiodic orbits dominate the dynamics. Anyway, the theoretical result is much lower than the experimental one.

The pure quantum rotationally averaged rate constant has not been calculated because it becomes computationally very expensive. Instead, since the agreement of quantum and QCT results for $j_0 \approx 3$, or larger, is good, as already stated (see Fig. 10), we used a mixed quantum/QCT description to obtain the rotational averaged rate constant: for $j_0=0, 1, 2$, and 3 we used the quantum results, while for $j_0>3$ the QCT results are used. Since the QCT results seem to underestimate the reactivity in the region mediated by resonances, while on the contrary the quantum CS results overestimate the reactivity at those resonances,¹⁸ the two theoretical results in Fig. 11 can be considered as lower and upper limits in the present adiabatic model. However, both kinds of theoretical results are too low as compared with the experimental results.

It should be noted that at low temperatures the quantum results are not well converged. All reaction probabilities have been calculated starting at a very low kinetic energy, 1 meV, but the error in the 1–10-meV energy range of the reaction probabilities is rather high, of the order of 50%. Such error is evaluated analyzing the total flux both towards products and reactants and should be the reason why the pure QCT and the mixed quantum/QCT cross at a temperature of 100 K. Since the low-energy regime is dominated by resonances, it would be interesting to analyze their effect at cold or ultracold temperatures.

A final comment regarding the overall shape of the calculated curves in Fig. 11 is not out of place. Both quantum and QCT curves feature, in fact, a marked non-Arrhenius

behavior in the investigated temperature range. This finding is qualitatively consistent with the change in mechanism¹⁸ at the microscopic level, namely, from a resonance-enhanced reactivity at low collision energies to a direct, over the barrier mechanism at high energies (see Figs. 6, 8, and 9). In fact, it is apparent from Fig. 11 not only a quantitative but even a qualitative change of slope, reaching an inverted Arrhenius trend (reactivity increases as temperature goes down) below 200 K.

Finally, several reasons could explain the disagreement between experimental and calculated (when the 3/24 factor is included) rate constants. First the potential-energy surfaces may introduce some errors. However, the high accuracy of the *ab initio* points and fit procedure makes improbable that this is the reason. Second, in the entrance channel there are spin-orbit couplings, which may change the electronic partition function as a function of energy and also the reaction efficiency. However, the effects which are considered to be the most important are the nonadiabatic transitions due to the conical intersections appearing along the minimum-energy reaction path at collinear geometries, which play a singular role in the reaction dynamics. In fact, some of the inaccuracies of the fits arise because of the cusps introduced by the conical intersections, which are somehow avoided in the fit of the adiabatic surface.

For treating the reaction dynamics at the conical intersections, electronic diabatic states are required. Some preliminary calculations on approximated diabatic states⁶⁰ have shown that the wave packet splits at the two conical intersections among the different electronic states, yielding to final electronic populations of nearly the same value. Work in this direction is now in progress to analyze this effect.

IV. CONCLUSIONS

In this work, global three-dimensional adiabatic potential-energy surfaces for the excited $2^3A''$ and $1^3A'$ states of OHF system have been obtained to study the $F(^2P) + OH(^2\Pi) \rightarrow O(^3P) + HF(^1\Sigma^+)$ reaction. Highly accurate *ab initio* calculations at MRCI level, using the MOLPRO suite of programs,²⁵ were first obtained at ≈ 6000 nuclear configurations for the two excited electronic states. These points were fitted to an analytical function using the method of Aguado and Paniagua.³⁴ These fits present small errors, ≈ 0.037 eV for the $1^3A'$ (lowest state in its symmetry) and ≈ 0.042 eV for the $2^3A''$ state. The error of the $2^3A''$ state is slightly larger because this state presents several avoided crossings either with the lowest $1^3A''$ or with other excited electronic states, specially in the $F(^2P) + OH(^2\Pi)$ entrance channel.

The $2^3A''$ and $1^3A'$ surfaces present a rather high barrier to reaction at collinear configurations amounting to 0.45 and 0.28 eV, respectively, while that of the lowest $1^3A''$ surface is much lower, ≈ 0.07 eV, and it is bent. These surfaces were already recently used to simulate the photodetachment spectrum of the parent anion, OHF⁻, yielding results¹⁹ in very good agreement with the experimental ones by Bradforth *et al.*¹⁶

The $F + OH \rightarrow O + HF$ reactive collisions were simulated using a wave-packet treatment in the centrifugal sudden ap-

proach on the two excited states and for different rotational states of the OH reactant. Total reaction cross section was obtained and the k_0-j_0 correlation was analyzed to get information of the stereodynamics. In all the cases, the reaction is more efficient for low Ω_0 values, thus indicating that the reaction proceeds through a collinear geometry and that during the approach of reactants and separation of products this trend does not change. The reaction cross section for the two excited electronic states presents a relatively high threshold, >0.2 eV, so that they cannot contribute at thermal energies.

At thermal energies only the lowest $1^3A''$ state contributes. Since there are 24 electronic states in the entrance channel, the electronic degeneracy factor is thus 3/24. When it is taken into account, the simulated thermal rate constants become too small as compared with the experimental ones.¹⁵ With or without consideration of any electronic degeneracy factor, the overall shape of the $k(T)$ curves between 100 and 1000 K is clearly non-Arrhenius.

The disagreement between experimental and calculated (when the 3/24 factor is included) rate constants is attributed to important nonadiabatic transitions at the conical intersections appearing along the reaction path. Some preliminary calculations on coupled diabatic states clearly show an important electronic mixing when passing near conical intersections.⁶⁰ Such transitions are expected to introduce important effects on the reaction dynamics, which may explain the disagreement with the experimental results. Work in this direction is now in progress.

ACKNOWLEDGMENT

This work has been supported by DGICYT (Ministerio de Educación y Ciencia, Spain) under Grant Nos. BQU2002-04462-C02-01, CTQ2004-06615/BQU, and CTQ2004-02415/BQU.

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