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Dynamics and kinetics of the F + OH reaction on the ground triplet potential energy surface

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Abstract

MRCI electronic energy calculations have been carried out for the ground triplet state of the OHF reactive system. 8069 ab initio points have been fitted with a two- and three-body polynomial expansion in modified Rydberg coordinates and a high quality global potential energy surface (PES) was thus generated. On the PES, quasiclassical trajectory calculations were run to simulate existing kinetic and dynamic experimental data for the title reaction. The calculated and measured trends with temperature of the thermal rate coefficient and rovibrational energy distribution of the HF molecule satisfactorily compare and discrepancies are explained.

1. Introduction

Due to the atmospheric abundance of oxygenated compounds, reactions involving atomic oxygen either as reactant or as product, are exceedingly important [1]. This applies to both the first electronically excited level, $O(^1D)$, and the ground state species, $O(^3P)$. The ca. 2 eV of electronic energy excitation of $O(^1D)$ over $O(^3P)$ makes that reactions which are possible with the former species as reagent, do not occur under thermal conditions with the latter one, as they are too endoergic. The opposite is, of course, true for the corresponding reverse reactions, i.e. those yielding $O(^3P)$ as a product. An example is the title reaction.

Some of us [2–4] have been recently concerned with $O(^1D) + HX(X = Cl, Br)$ reactions, and, in this work, we deal with the 'reverse' $F(^2P) + OH(^2\Pi) \rightarrow O(^3P) + HF(^1\Sigma^+)$ reaction. This exoergic (about 1.5 eV) [5] reaction has been the object, some years ago, of dynamic [1] [8] and kinetic [9] experiments with more or less thermalized reagents. Also, the authors of [8] performed some ab initio calculations in an attempt to rationalize their experimental results. The scarce (inappropriate basis sets, limitation to collinear geometries) theoretical information thus gained, and, in particular the appearance of a noticeable (ca. 0.5 eV) calculated barrier, led authors of [8] to conclude that a nonadiabatic mechanism (inter system crossing (ISC) from the ground singlet $^1A'$ to the ground triplet $^3A''$ PES) was necessary to account, at least qualitatively, for the experimental findings. These, however, remained in fact largely unexplained.

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[1] But not actual single-collision, beam conditions; in fact, due to lack of clean and efficient sources of beams of radicals, there have been up-to-date very few examples of experimental studies of atom + 'radical' reactions in beams. The situation may be changing [6] also because of increased sensibility for products with the help of the new soft electron impact ionization methods [7].

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Beyond the accurate calculation of ground and excited electronic triplet and singlet states, other motivations for our theoretically revisiting this system are: first the heavy-light-heavy mass nature, the exoergicity and the possible insertion mechanism of the reaction makes its quantum dynamics calculations computationally challenging and lets expect interesting quantum effects, and second, there exist, in addition to the above mentioned reactivity experiments, photodetachment electron spectrum experiments by Neumark and coworkers [10] not yet fully understood. Therefore, we undertook the theoretical investigation of the dynamics and kinetics on the ground triplet $^3A''$ PES of OHF. Although, as already stated, we are actually carrying out MRCI, large basis sets simultaneous calculations of excited singlet and triplet PES for this system, here we just refer to results on the ground triplet PES. As it will be shown this mere adiabatic surface seems to suffice for reasonably understanding the available dynamic [8] and kinetic [9] data.

A full account of the ab initio calculations of ground and excited surfaces [11] and a simulation [12] of the photodetachment electron spectrum experiment of Neumark et al. [10] will follow.

2. The ab initio and dynamics calculations

As a support to Sloan's group experiment they also performed some [8] ab initio calculations for the OHF *reactive* system. [2] These MRDCI single point calculations, however, did not give any functional form to fit the obtained energy values. Moreover, as a rule, only collinear geometries were considered for the calculations which , however, included both the ground ($^3\Pi$) and the excited ($^3\Sigma^-$) triplet PES correlating reactants and products. These calculations give a very high collinear barrier due to the small size of the basis sets (4-31G and DZP) and number of selected configurations (<1500). Thus, the authors considered that the barrier heights on triplet surfaces are too high to provide a reaction path, and conclude that the reaction might proceed first on a singlet surface to produce an HOF insertion complex, followed by rearrangement and a nonadiabatic transition to the triplet surface correlating with products.

In this Letter, we deal with a new three-dimensional ground, triplet potential energy surface that has been computed using highly correlated ab initio wavefunctions. However, we have not taken into account the spin-orbit splitting of the fluorine atom. All calculations have been performed with the MOLPRO [14] package of ab initio programs. The basis set used is the aug-cc-pVTZ [15,16] of contracted Gaussian functions. This basis set is a much more extended one than that used in the previous collinear calculation by Sloan et al. [8]. The effect of higher angular momentum functions was found to be very small. The orbitals were optimized in a complete active space (CASSCF) procedure [17,18] including all valence electrons and orbitals. These CASSCF wavefunctions were used as reference in subsequent internally contracted multireference configuration interaction [19,20] (MRCI) calculations. The Davidson correction [21] was applied in order to approximately account for unlinked cluster effects of higher excitations.

In order to test the accuracy of the calculated PES we have studied the basis set superposition error (BSSE). This is usually estimated with the well-known counterpoise (CP) procedure, proposed by Boys and Bernardi [22]. Nevertheless, the CP implementation in multireference methods is not straightforward, because they are not size consistent [23]. Also, there are serious problems in the definition of monomers when CP is applied to the calculation of a reaction's PES [24]. Here, we have used a modification of the CP procedure, proposed by Paniagua et al. [25], that allows us to estimate the accuracy of the ab initio calculations. We have applied this BSSE estimation at several configurations along the reaction path shown in Fig. 1, being the BSSE of the order of 0.006 eV and, accordingly, it was ignored in the remaining of the calculation.

Using the electronic wavefunctions described above, 8069 points were computed on the whole configurational space. The general data set has been obtained as a subset of the following grid:

$R_{\mathrm{HF}} = 1.2\text{–}7.0a_0$ (25 values),

$R_{\mathrm{OH}} = 1.3\text{–}7.2a_0$ (25 values),

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

corresponding $\theta = 180^\circ$ to collinear OHF and $\theta = 0^\circ$ to collinear HFO and HOF structures. These energies were fitted to a global analytical function using the method of Aguado and Paniagua [26,27] including expansions up to 9th order. Moreover, in order to obtain an accurate fit for the minimum energy path (MEP) and the energetically low lying regions, we have computed many additional points in the geometries, corresponding to these regions, obtained using preliminary fits to the general data set. The root mean square error of the fit was 0.043 eV for the global surface, which reduced to a mere 0.014 eV for geometries corresponding to the MEP regions.

The spectroscopic constants for the fitted HF and OH diatomic potentials ($r_e = 1.732$ and $1.840a_0$,

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[2] There also exist ab initio calculations for the ground (and first five excited) *singlet* PES relevant to the UV *photodissociation* process of hypofluorous acid, HOF, leading to $F(^2P) + OH(^2\Pi)$ [13]. These calculations, however, do not take care of the HF + O channel and are, therefore, only marginally relevant to the present work.

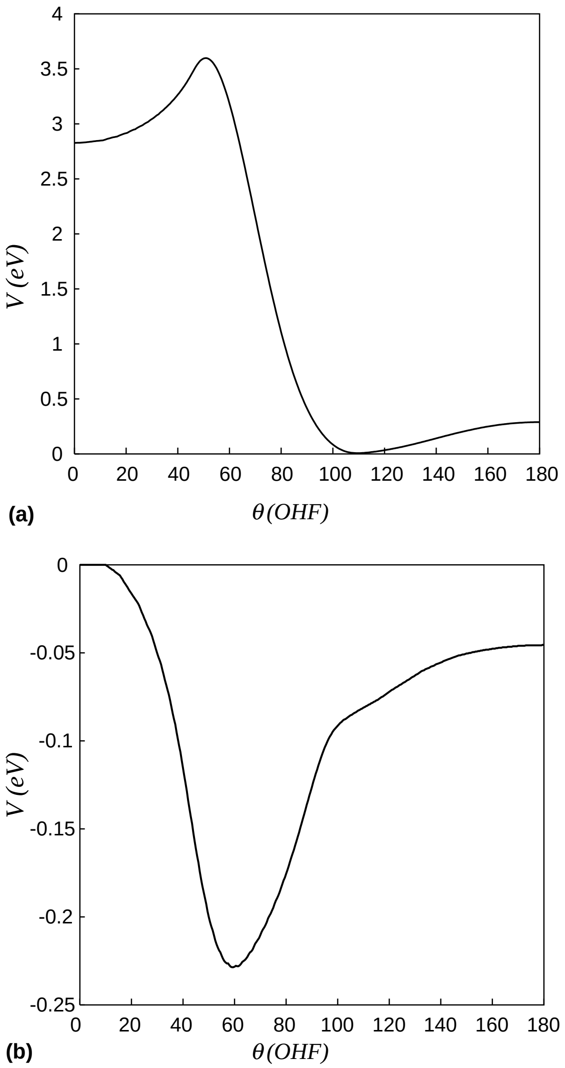

Fig. 1. Barrier height (a) and reactants valley van der Waals well (b) as a function of the angle θ (OHF). $\theta = 180°$ represents collinear OHF and $\theta = 0^o$ collinear HFO and HOF structures.

$\omega_e = 4170$ and 3723 cm^{-1}, respectively), are in good agreement with the experimental data [5] ($r_e = 1.733$ and $1.832a_0$, $\omega_e = 4138$ and 3738 cm^{-1}, respectively). Also, the fitted exoergicity, 1.45 eV, compares very well with the values obtained from the dissociation energy of diatomics fragments, namely our calculated value(1.45 eV) and the experimental (1.50 eV) result [5].

Special attention was paid to accurately represent the barrier region. Thus, the collinear barrier is 0.291 eV high over asymptotic reagents, to be compared with results of previous calculations (from 0.481 to 0.537 eV) [8]. Moreover, we have found practically no barrier for several non-collinear angles of approach, as shown on Fig. 1a, where the fixed angle barrier heights are plotted. It is important to stress that the reaction practically has no barrier, as we can also see in Fig. 2 where the global (three-dimensional) MEP of the PES, which includes the lowest barrier (saddle to reaction), has been plotted. It was obtained following the gradient extremal path [28,29] as a function of the arc length s, defined [29] as the square root of the sum of the three internuclear distances with respect to the corresponding values for the saddle point. This is then the origin of coordinates for this plot and s is, by convention, negative toward reactants (OH + F) and positive toward products (O + HF).

The saddle to reaction is located in the entrance channel ($R_{HF} = 1.934a_0$, $R_{OH} = 2.752\ a_0$, and $\theta = 109°$) Fig. 1b also shows the dependence of the reactant's van der Waals well with the angle θ, being the minimum at 60°. This van der Waals well is expected to lead to important stereodynamic reaction effects. Further details of the ab initio calculations and the fit will be published elsewhere [11,12].

The fitted ground $^3A''$ PES was tested against experimental results by running on it quasiclassical trajectory (QCT) calculations. A modified [4] version of the VENUS program [30] was used with this scope. The reagent vibrational quantum number was set to 0, the rotational energy was selected randomly from a Boltzmann 300 K distribution and the relative translational energy was also randomly selected with the Maxwell–Boltzmann temperature set at values ranging from

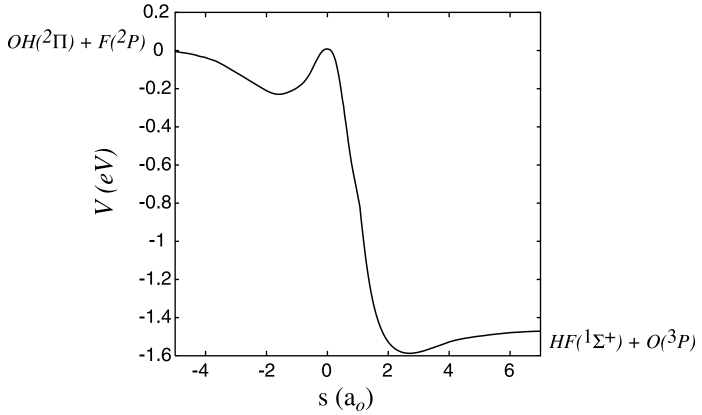

Fig. 2. Minimum energy path of the three-dimensional $^3A''$ ground state PES for the F + OH → O + HF reaction.

200 up to 1000 K. Other parameters of the simulation were chosen in a standard way [4]. After optimization of the impact parameter batches of 200 000 trajectories at each rotational and/or translational energy or temperature were run. At the end of each trajectory, an histogrammic binning method as implemented in Venus was used for estimating the product's internal energy. Finally, an electronic degeneracy partition factor of 9/24 was used for $k(T)$ as derived from 3 triplet surfaces correlating with the products and 6 triplet plus 6 singlet surfaces correlating with reagents [11].

3. Results and discussion

We first make a brief account of the conditions and results of the experiments by Sloan and coworkers [8] and by Walther and Wagner [9]. In fact, as remarked above, our reaction has been the subject of 'indirect' kinetic [9] and flow [8] but no actual beam (collision-free) experimental studies. 'Indirect' means here that both groups used the pre-reaction $F(^2P) + H_2O(^1A_1) \rightarrow OH(^2\Pi) + HF(^1\Sigma^+)$ to produce the OH reagent with the consequence of having to take somehow into account the simultaneous occurrence of both reactions. Walther and Wagner operating between 243 and 369 K obtained for this temperature range a simple Arrhenius-like behavior, namely $k(T)$ (cm^3 s^{-1}) $= 7.5 \times 10^{-11}$ exp $(-180/T)$. Sloan's experiment [8], on the other hand, was apparently done under the following conditions: for OH, $v = 0$ and $T_{\mathrm{rot}} = 300$ K, and $T_{\mathrm{transl}} = 300$ K for the F–OH relative kinetic energy. Further, they used an arrested relaxation technique to detect the infrared emission from HF. Working also under low pressure conditions (10^{-3} down to 10^{-5} Torr) they expected to see nascent internal energy distributions of HF. As stated, vibrational and rotational energy distributions for HF were measured by Sloan and coworkers by IR emission spectroscopy. This means they were unable to detect any HF($v' = 0$) population. They were not able to estimate it, either [31]. Instead, what the experiment gives are relative populations of the vibrationally excited states. All this also means that the recent contention [32] that the whole vibrational distribution (including a maximum in P($v = 0$)) is statistical, is not supported (nor rejected) by the experiment [8] as stated. Fig. 3 is a plot of the calculated and experimental [9] rate coefficient values as changing with temperature. Experimental data are plotted with ±30% error bars as estimated by us from reported incertitude ranges. Errors (±1 standard deviation) of the calculation are within the circles size. The values directly obtained from Venus were also multiplied by the electronic degeneracy factor 9/24 as explained above. Although points calculated in this way clearly fall outside the ±30% estimated incertitude of the experiment, within the range of the experimental temperatures (243–369 K) rate coefficients are well represented by a simple Arrhenius form both for experimental and for calculated values and, in fact, a sensible parallelism between both lines is seen in the figure, an activation energy of 165 K resulting from both fits (this is the value, in fact, which results us – instead of their 180 K value – also from fitting the three $k(T)$ data reported in [9]). However, a noticeable deviation from that simple form (i.e. a non-linear plot) is observed for temperatures far from room temperature. Thus, the whole interval between 200 and 1000 K is best fitted by the following three parameter modified Arrhenius form

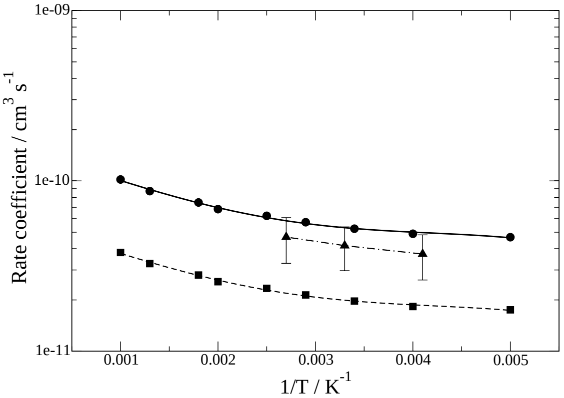

Fig. 3. Arrhenius plot of the rate coefficient dependence with temperature. Calculated values, circles (direct value from QCT calculations) and squares (QCT values per 9/24); experimental values [9], triangles (with estimated error bounds). Lines are best fit modified Arrhenius (for the calculation) and simple Arrhenius (for the experiment) lines. See the text for further explanations.

$$k = A \times T^b \exp(E^*/T) \qquad (1)$$

with $A = 9.55 \times 10^{-13}$ cm^3 s^{-1}, $b = 0.67$ and $E^* = 67$ K. This would imply an 'activation energy' equal to 400 K between 500 and 1000 K of temperature more than twice our room temperature value of 165 K.

Fig. 4 shows calculated and measured HF vibrational distributions. On top of the figure the whole calculated P(v') function is plotted. A clear *non-statistical* (inverted) distribution peaking at $v' = 1$ is obtained, a non unexpected result in view of the exoergicity of the reaction. Beyond this point, the distribution could be statistical. In fact, the bottom part of the figure shows a comparison between our calculated (renormalized to be compared with [8]) and Sloan's et al. [8] experimental data (including a ±5% error bounds [31]). Both sets of data were normalized at the total population *excluding* vibrationally ground HF, thus enabling a fair comparison. A good agreement is obtained.

In Fig. 5, finally, a comparison between calculated and measured HF rovibrational distributions is represented. Curves are normalized to the overall vibrational populations as given on Fig. 4. A very good agreement is obtained for $v' = 2$ and $v' = 3$ rotational populations

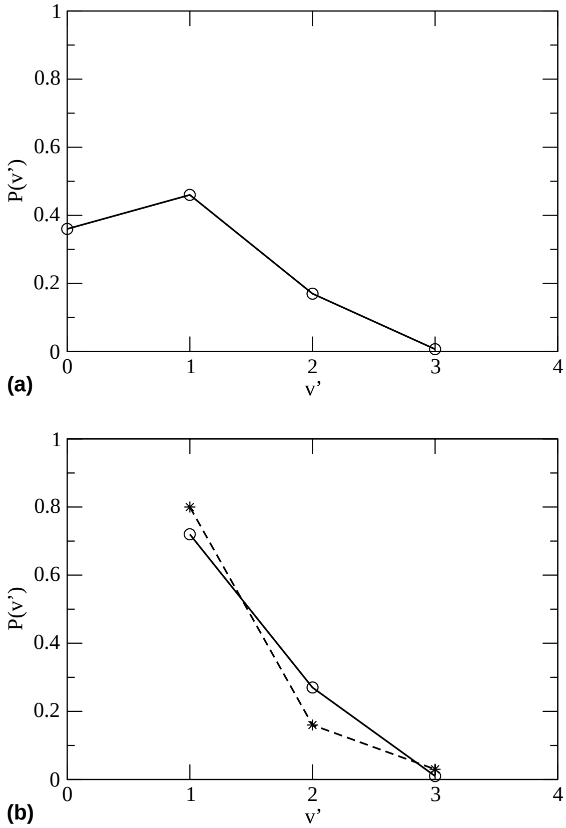

Fig. 4. (a) Calculated HF vibrational distribution for $F + OH(v = 0, T_{rot} = T_{transl} = 298$ K) $\rightarrow O(^3P) + HF(v')$. Points have been normalized to 1 for $v' = 0$–3. (b) Same as above but for points normalized to 1 for $v' = 1$–3 to allow comparison between calculation (circles, solid line) and experiment (stars, dashed line [8]).

but the agreement is poor for $v' = 1$. In fact, experimental results from [8] are well fitted up to $j' = 4$ by a thermalised rotational population with $T = 300$ K while the higher part of the distribution is hotter and it could be the unrelaxed component [31]. Our calculated distribution crosses the experimental one at the same $j' = 4$ value and is, beyond this point, still hotter than the hot component of the experimental spectrum. A working hypothesis is, therefore, that, in spite of the arrested relaxation technique, the *whole* HF rotational population for $v' = 1$ is relaxed to a more or less extent in the experiment [8]. In other words, the true nascent population is not obtained under the experimental conditions.

Responsible for the relaxation of $HF(v' = 1$, high $j')$ molecules are most probably, because of the quasi-matching of internal energy and the small inelasticity, $HF(v' = 0)$ molecules according to the energy transfer steps $HF(v' = 1$, high $j') + HF(v' = 0$, low $j') \rightarrow HF(v' = 1$, low $j') + HF(v' = 0$, high $j')$. Recall that the IR emission technique of Sloan and coworkers does not allow to detect HF molecules in their ground vibrational state. Thus, the authors of [8] suspect that unreacted H_2O (from the pre-reaction) would be the major relaxer because of 'serious doubts' that enough $HF(v' = 0)$ were produced [31]. In fact, however, our calculations lead to about 36% HF in this state (see Fig. 4b) almost as much as the 45% $HF(v' = 1)$. These figures thus lend support to our hypothesis.

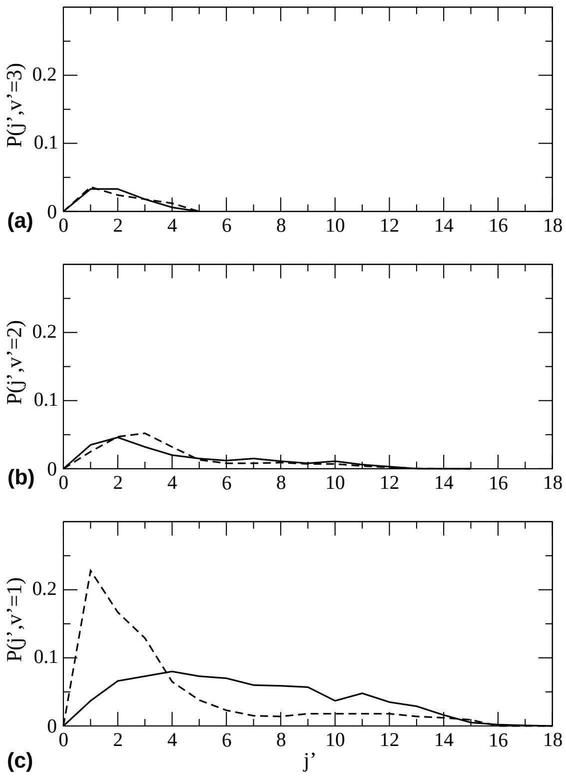

Fig. 5. Calculated (solid line) versus experimental (dashed line [8]) HF rovibrational distributions for $F + OH(v = 0, T_{rot} = T_{transl} = 298$ K) $\rightarrow O(^3P) + HF(j';v')$ and $v' = 1$ (c), 2 (b) and 3 (a) panels. Curves on the top panel have been magnified (3 times) for the sake of clarity.

4. Summary

Highly correlated ab initio electronic energy data (MRCI) have been calculated for the OHF system and subsequently fitted to a functional form appropriate to describe the $X(^3A'')$ adiabatic ground potential energy surface (PES) for the $F(^2P) + OH(^2\Pi) \rightarrow O(^3P) + HF(^1\Sigma^+)$ chemical reaction. On this PES quasiclassical trajectory calculations have been used to simulate the existing kinetic and dynamical experiments. Good agreement between theory and experiment was obtained for the variation with temperature of the rate coefficient and for the vibrational and rovibrational product distributions. The differences found are tentatively explained as due to failures of the experimental method to capture the whole unrelaxed rotational distribution of HF.

Notwithstanding the quantitative agreement of calculated and experimental trends with temperature of the rate coefficient, the calculated absolute values are smaller than the experimental ones. Also, although there are indications that differences between calculated and experimental final rovibrational distributions could be due to the experimental artifacts introduced by secondary collisions, there is further theoretical work to be done. In particular, it has been assumed that the three triplet states present the same reactivity. Such assumption is now being scrutined and the two other triplet PES are being calculated. Also, quantum effects could be important and non-adiabatic couplings (including spin-orbit couplings among triplet and singlet states) could play an important role in the dynamics. A full account of the ab initio calculations of ground and excited surfaces and the quantum dynamics calculation, including non-adiabatic effects, will follow. Moreover, the simulation of the photodetachment electron spectrum experiment by Neumark et al. [10], already in progress, will provide a complementary information about the title system.

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