Transition state spectroscopy of open shell systems: Angle-resolved photodetachment spectra for the adiabatic singlet states of OHF

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Abstract

In this work three-dimensional potential energy surfaces of the first five singlet states of OHF are developed based on fits of more than 10,000 highly accurate *ab initio* points. An approximate treatment is presented for the calculation of the anisotropy parameter describing the electron angular distribution photodetached from a molecular anion. This method is used to calculate the angle-resolved photoelectron spectra in the photodetachment of OHF^-. The wave packet formed in the neutral OHF system is placed at the transition state region, and yields the formation of $OH + F$ and $HF + O$ products. The results are compared with the recent experimental measurements published by Neumark [D.M. Neumark, Phys. Chem. Chem. Phys. 7 (2005) 433]. The intensity found at low electron kinetic energy including these five states and the three lower triplet states is found to be low. To analyze the effect of higher electronic states more excited $^1\Sigma^-$, $^3\Sigma^+$ and $^3\Delta$ states are calculated at collinear geometry. The agreement with the experimental data improves, thus demonstrating that the correct simulation of the photodetachment spectrum at 213 nm involves at least 12 electronic states. All the structures of the experimental spectra are semiquantitatively reproduced finding an overall good agreement. It is concluded that the main problem of the simulation is in the intensity and anisotropy parameters. An alternative to their calculation would be to fit their values to reproduce the experimental results, but this would require to separate the contribution arising from different final electronic states.
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1. Introduction

Chemical reactions involve a drastic change in the electronic structure from reactants to products. The adiabatic potential energy surfaces (APESs) involved can be viewed as resulting from the diagonalization of a Hamiltonian matrix represented in a crude basis of "diabatic" states correlating to the asymptotic states of reactants and products, and their mutual crossings create barriers along the minimum energy paths (MEP). Such singular regions, or transition states (TSs), act as bottlenecks for the reaction, determining mechanisms and many of the properties of the measured quantities.

The nature of the reactive TS were first studied in molecular beam studies [1] under single collision conditions, studying the effect of pre- and post-collision variables such as quantum state specification, angular and rotational polarization. Very valuable information of the TS was indirectly obtained with the help of

theoretical dynamical simulations and *ab initio* calculations of the intermolecular potential, giving rise, for example, to the so-called Polanyi rules [2–4].

Several spectroscopic techniques have been developed to obtain more direct information about the structure and dynamics at the TS, giving rise to the so-called transition state spectroscopy (TSS) [5–7]. Recently, the development of ultrafast lasers also allows probing of the dynamics in real time [8,9], and if the pulse is properly designed it may be used to control the outcome of the reaction [10,11]. Moreover, some promising new directions in the field of TSS fill the gap between gas and condensed phases, through the study of solvation effects in mass selected clusters [7,12–14] or heterogeneous chemistry on metal surfaces [15].

In these spectroscopic studies, the TS is reached via photon excitation from a specific precursor, usually a van der Waals complex between the two reactants [7,16–27] or a stable negative ion [6,28–33]. Using van der Waals complexes as precursors, one alternative developed by Wittig and co-workers [7,26,27] consists in photodissociating one of the reactants ejecting one fragment towards the second partner at restricted geometry conditions, imposed by the structure of the initial van der Waals

precursor. In a second possibility, one of the partners within the complex is promoted to excited electronic states where the reaction takes place, as first done by Soep and co-workers [16–20], and lately applied by Polanyi and co-workers [21–23] and González-Ureña and co-workers [24,25]. These complexes are typically formed by a halide molecule (RX) and a metal atom (M), which acts as chromophore. In the case of complexes of alkali atoms, the measured electronic spectra have been well reproduced by theoretical simulations [34–36]. Reaction dynamics involve non-adiabatic transitions towards the ground electronic state, as recently simulated for Li–HF [37], and product detection in the ground state is complicated. In complexes containing alkali-earth atoms, however, the MX products are electronically excited and are more easily detected because they fluoresce. Nevertheless, the higher number of excited states and their complicated sequence of curve crossings appearing in this last case, makes their theoretical simulation very difficult.

On the other hand, TSS studies from an anion as a precursor are feasible if it is stable and its equilibrium geometry is similar to the TS of the neutral system of interest. Thus very interesting information about the TS on the ground electronic state and some dynamical resonances linked to it (otherwise very elusive to detect), has been obtained from photoelectron detachment spectra for many benchmark reactions such as $OH + H_2$ and $F + H_2$, recently reviewed [38]. Reactions involving open shell reactants and products are particularly interesting because they are very common in atmospheric and interstellar chemistry. The presence of several electronic states, crossing along the reaction path with significant non-adiabatic effects, complicates the interpretation of the results: the selection rules involved in electric dipole transitions, angular distributions and rotational polarization of products make of TSS studies a source of data to unravel the dynamics.

This is the situation of the $O(^3P, {}^1D) + HF(^1\Sigma^+) \rightarrow OH(^2\Pi) + F(^2P)$ reaction, whose MEP for some of the states involved are shown in Fig. 1, for collinear geometries. This reaction can be considered a model system of the more general reactions involving halogen atoms that play an important role in the catalytic ozone destruction cycle [39]. The reaction involving chlorine atoms has been the most widely studied [40–50], typically in single adiabatic potential energy surfaces (APES).

Experimental information about OHF was obtained in the photoelectron detachment spectroscopic studies performed by Neumark and co-workers [51]. 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 TS. For this reason several theoretical simulations [51,52] restricted to collinear OHF geometries and the ground electronic state were performed.

Later, three-dimensional PESs for the ground triplet 1 $^3A''$ state [53] and two first excited triplet states, 2 $^3A''$ and 1 $^3A'$, were obtained [54]. The simulated photodetachment spectra [55], obtained using these three three-dimensional APESs of the lower triplet states, and four two-dimensional PESs for singlet states, reproduced qualitatively rather well all the structures of the experimental photoelectron detachment spectrum [51].
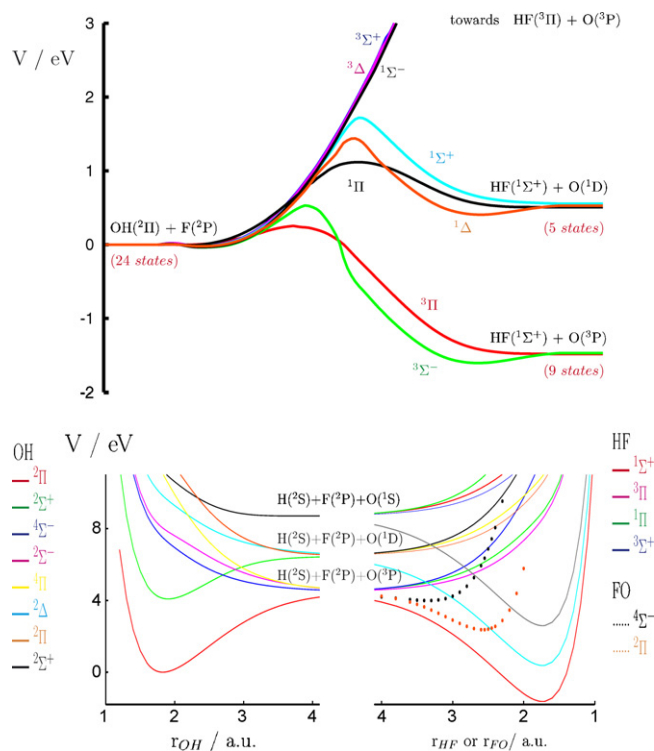

Fig. 1. Collinear minimum energy paths for the states that correlate with $F(^2P) + OH(^2\Pi)$ asymptotic limit (top panel). Asymptotic energy curves corresponding to the F + OH, O + HF and H + FO rearrangements (bottom panel).

The exploration of non-adiabatic mechanisms has become accessible by two new sets of photodetachment spectroscopy experiments, which allow the probing of conical intersections as has already been reported for other systems [56–58]. In one case, Neumark published [38] the photoelectron spectra recorded some years before [59] at two angles with respect to the polarization vector of the incident light. The analysis of these data can help to separate the contribution arising from different electronic states, as will be treated in detail in the present work. Moreover, since the initial wave packet is sitting on the top of the two conical intersections [60], these spectra provide direct spectroscopic data about the region of the crossings. Second, Continetti and co-workers [61,62] have detected in coincidence the electron and neutral fragments. Since, the formation of products requires that the wave packet passes through the conical intersections, such kind of experiments would provide information about non-adiabatic transitions induced by conical intersections in the reaction dynamics.

In addition, the reaction cross-section simulated for the OH + F collision on the excited adiabatic triplet states was found to be too low [54]. Thus, with only the ground triplet state contributing to the reaction the simulated rate constant is too small with respect to the experimental one [63]. This could be attributed to inaccuracies of the APESs. However, the high quality of the *ab initio* calculations and the accuracy of the fits indicate that this is probably not the only reason for the disagreement.

Very recently, new-coupled diabatic potential energy surfaces have been proposed to describe the first three triplet states and to