A direct, local model of dissociative recombination of HF$^+$

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Abstract. The direct mechanism of dissociative recombination of HF$^+$ have been studied by propagating wave packets on 30 resonant states. The relevant electronic states have been calculated $ab\ initial$ with electron scattering calculations and multireference configuration interaction calculations. We obtain a qualitative good agreement with experiments for energies in the range from 0.04 eV to 10 eV. Some of the structures in the experimental cross section can be explained by the direct capture and dissociation along the resonant states. To fully describe the measured cross section, the electronic couplings between the neutral states cannot be neglected.

1. Introduction

Dissociative recombination (DR) is the key process in the physics of plasmas where molecular ions are present. Resonant ion-pair formation (RIP) and DR have two modes. The direct mode of DR and RIP of HF$^+$ can be represented by

$$HF^+(v = 0) + e^- \rightarrow HF^{**} \rightarrow \{ H^+ + F, H + F^- \}, \quad (1)$$

and the indirect mode by

$$HF^+(v = 0) + e^- \rightarrow HF_{Ryd}^{**} \rightarrow HF^{**} \rightarrow \{ H^+ + F, H + F^- \}. \quad (2)$$

In the present model only the direct process is considered and no electronic couplings between the neutral states are included. We then obtain the total cross section that is the sum of the two reactions in (1). When the electron is captured into the resonant state it can either autoionize (re-emit the electron) or dissociate. Autoionization is possible until the neutral state has crossed the ionic ground state and after that the resonant state becomes electronically stable. This study includes wavepacket propagation on 30 resonant states and the total cross section is obtained by summing up the individual cross sections. The cross sections for DR and RIP of HF$^+$ have been measured in the ion-storage ring CRYRING [1]. The cross section for DR of HF$^+$ is smaller than for other diatomic molecules and the ratio between RIP and DR is relatively large. Both cross sections also show structures that were attributed to competition between the direct and indirect processes [1].
2. Potential energy curves and autoionization widths

We have determined the relevant electronic state potentials in all symmetries. The resonance energy and autoionization width are obtained from electron scattering calculations using the complex Kohn variational method [2]. In the region where the resonant states become electronically stable we have carried out a set of multireference configuration interaction (MRCI) calculations. To be able to merge the results of the different calculations we have used the same basis sets and target wave function in both the MRCI and the complex Kohn calculations.

The quasidiabatization of the resonant states relative to the continuum and the Rydberg states are performed by tracking the dominant configurations when the internuclear distance, $R$, is varied. Both the ionization continuum and the Rydberg states will have a configuration corresponding to the ground state of the ion \[ (1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^3 \] plus an electron in an outer orbital. The resonant states are Rydberg states converging to electronically excited ionic cores and all of these have the $(3\sigma)$ orbital singly excited. The structure calculations do not show any indications of avoided crossings between the resonant states in any of the symmetries. They are well separated in energy so the diabatization is made by following the configuration of the excited core towards larger internuclear distances assuming no crossing between the resonant states. Also it is assumed that there is no crossing among the Rydberg states.

Outside the region where scattering calculations and structure calculations have been performed, we extrapolate autoionization widths and potentials. It is important to have a good representation of the autoionization widths in the Franck-Condon region where the overlap between the ground vibrational wave function of the HF$^+$ ion is nonzero out to the point where the resonant state crosses the ion potential energy curve. In this region we have performed scattering calculations and outside we extrapolate the autoionization widths smoothly towards zero. The potential energy curves are extrapolated towards their asymptotic limits which are determined from spectroscopic data for the separated atoms [3]. The Wigner-Witmer rules [4] give us the number of electronic states, of a given symmetry, that is associated with a specific asymptotic limit. The quasidiabatic potential curves are displayed in figure 1.

Figure 1. (a)-(e): Quasidiabatic potential energy curves of HF and HF$^+$
3. Wave packet dynamics
The electron capture induces a wave packet on the resonant state \[ \Psi_i(t = 0, R) = \sqrt{\frac{\Gamma_i(R)}{2\pi}} \chi_{v=0}(R), \] \[ (3) \]
where \( \chi_{v=0} \) is the vibrational wave function of the ground state of HF\( ^+ \), calculated with a finite-difference method [6]. \( \Gamma_i \) is the autoionization width of the resonant state \( i \). The wave packet is then propagated by solving the time dependent Schrödinger equation with a Crank-Nicholson propagator [7]. Autoionization is included by letting the potentials become complex above the crossing point with the ground state of HF\( ^+ \)
\[ \tilde{V}_i(R) = V_i(R) - i \frac{\Gamma_i(R)}{2}. \] \[ (4) \]
This is the so called Boomerang approximation [8] that assumes that the total energy of the system is high enough to allow autoionization into a complete set of vibrational eigenstates. When this approximation breaks down, i.e. for the lower resonant states, a non-local operator [9; 10] for treating autoionization has to be used. This will be addressed in a future study.

4. The total cross section
When the wave packets have been propagated out in the asymptotic region they are projected onto energy normalized wave functions for the separated atoms. This gives us the transition matrix element which for the resonant state \( i \) is given by \( T_i \)
\[ T_i(E) = \lim_{t \to \infty} \langle \Phi_E(R) | \Psi_i(R, t) \rangle_R. \] \[ (5) \]
The cross section for state \( i \) is given by[8; 11]
\[ \sigma_i(E) = \frac{2\pi^3}{E} g |T_i(E)|^2, \] \[ (6) \]
where \( g \) is the multiplicity ratio of the neutral resonant state to the ionic state with the free electron. The total cross section is given by the sum of the cross section of the individual states.

5. Results and conclusions
The calculated cross sections are shown in figure 2 where also the measured cross sections for DR and RIP [1] are included. Figure 2(a) and (b) show the partial cross sections for the four lowest resonant states of singlet and triplet multiplicities. In figure 2(c) we show the contributions from the resonant states with threshold energies around 1.94 eV. Finally in figure 2(d) we compare the calculated total cross section with the measured. As can be seen in figure 2(d), we have reasonably good agreement in magnitude with the experimental cross section and we find that many resonant states contribute to the total cross section. The vertical lines in figure 2(d) correspond to energies where the different resonant states become energetically open for dissociation. In agreement with our calculated cross section the experimental cross section shows a clear threshold at \( E = 1.94 \) eV and broad peaks in the partial cross section can be seen when the Franck-Condon overlap has a maximum for several of the resonant states. Below \( E = 0.04 \) eV we believe that electronic couplings need to be included in the model to reproduce the experimental cross section. Flux captured into resonant states that are energetically closed for dissociation can then leak out via the Rydberg states to states that are energetically open for dissociation. In a future study, the electronic couplings will be determined. By propagating wave packets on coupled potentials we will be able to calculate the cross section for ion-pair formation and DR branching ratios.
Figure 2. (a)-(c): Partial cross sections. (d): Calculated total cross section. The experimental results for DR (△) and RIP (○) measured at CRYRING are included in the figures for comparison [1].

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