4.8. RESONANT ION PAIR FORMATION IN ELECTRON COLLISIONS WITH GROUND STATE MOLECULAR IONS

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Resonant ion pair formation (RIP) has been observed and cross sections measured in CRYRING for electrons impacting on HD^+ and HF^+ and an upper limit was set for the RIP cross section for OH^+. A sharp threshold and a spectacular set of 14 peaks characterize the HD^+ cross section. The HF^+ cross section is interesting because of some degeneracies that occur. The measurements are the first ever for diatomic molecular ions in their ground states.

Resonant ion pair formation can be represented by $e + XY^+ \rightarrow XY^{**} \rightarrow X^+ + Y^- + KER$, where KER is the kinetic energy of release. Thus, RIP represents one stabilization channel of the compound states that are active in dissociative recombination. A study of RIP, which is characterized by only one final state, should lead to better understanding of the dynamics of stabilization of compound states. The measurements on CRYRING were carried out by detecting the heavy negative ion fragment resulting from RIP, i.e. D^-, F^- or O^-. Storage times were made commensurate with having ion targets in their ground vibrational levels.

The HD^+ cross section presents us with a sharp rise at the expected threshold, followed by 14 stunning peaks superimposed on a generally declining envelope. The cross section is shown in fig. 1. The first five resonances lie below the dissociation energy of HD^+ (2.668 eV) and are spaced about 0.2 eV apart, a value in the neighborhood of what is expected for vibrational spacing of Rydberg states of HD which lie close to HD^+. Thus, it is appealing to attribute the mechanism here to capture by depositing the electron energy into vibrational excitation, followed by dissociation via coupling to the $(2p\sigma_u)^2$ repulsive state which correlates diabatically to $H^+ + D^-$ at infinity. Peaks at higher energies, 5.28 eV and above could be resonant capture to various repulsive Doubly-excited Rydberg states. However, the group of peaks between 2.66 eV and 5.28 eV are in an energy range where no traditional hypothesis can be invoked.

We are thus led submit a hypothesis that these

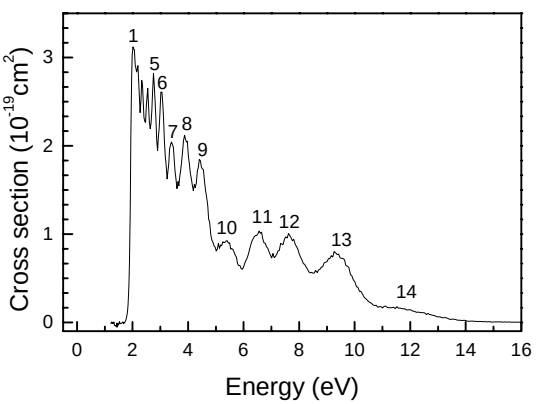

Figure 1. RIP Cross Section for HD^+.

peaks and possible others, which we already discussed, are due to non-adiabatic coupling of states, which occur at pseudo-crossings of the molecular potentials at large internuclear separations, leading to coherent phase interference in the product amplitudes, thus yielding so-called Rosenthal oscillations [1]. Such oscillations have

been seen in ion-atom scattering for a number of cases [2], and since there are curve crossings both at small and large distances in this experiment, this type of mechanism seems quite plausible.

For HF^+ the RIP cross-section correlates with the DR cross section (also measured). The ratio of RIP/DR is about 0.3 at zero energy. The cross section is large at zero energy and declines with energy, showing some resonances in the interval of measurement.

No RIP could be found for OH^+, and a preliminary upper limit of 10^{-21} cm^2 is attached for the cross section for forming O^-.

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