RESONANT ION PAIR FORMATION (RIP) IN ELECTRON-MOLECULAR ION COLLISIONS

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Resonant ion pair formation (RIP) has been observed and measured in the Stockholm heavy-ion storage ring, CRYRING for electrons impacting on HD^+ and HF^+, and an upper limit was put on RIP for OH^+. The HD^+ results are characterized by a spectacular set of 14 resonances which we divide into three groups. We can speculate on the formation mechanisms for two of the groups, but for the third group any reasonable hypothesis escapes us. The HF^+ ion is particularly interesting because of certain degeneracies that occur.

Resonant ion pair formation (RIP) can be represented by e + $XY^+ \rightarrow XY^{**} \rightarrow X^+ + Y^- + KER$, where KER is the kinetic energy of release. Clearly, it is resonant capture into compound states of the type operative in dissociative recombination (DR) except that there is only a single, well-defined and easy-to-detect final channel for the stabilization products. Thus, measurements of this process should provide valuable information in the quest to fully understand dissociation dynamics of compound states involved with DR. For H_2^+ RIP calculations were made[1] many years ago and RIP experiments[2] conducted on 'hot' ions of both H_2^+ and H_3^+. Later experiments[3] on cool H_3^+ have also been done.

The present experiments were undertaken to take advantage of the time available in a heavy-ion storage ring to obtain a vibrationally cold target beam with an eye toward obtaining data which will be beneficial in unraveling the dissociation dynamics of doubly - excited autoionizing states. The heavy-ion storage ring CRYRING in Stockholm was used, and detectors were mounted which could detect the heavier of the negative fragments from the collision. The HD^+ ion was chosen because it is the simplest heteronuclear diatomic molecular ion in nature, and thus serves as a paradigm for such studies. The HF^+ ion was chosen because the ground vibrational state of the molecular ion is effectively degenerate with the ion pair state of $H^+ + F^-$ and it thus represents a totally different case from that of HD^+ where an energy threshold of $E_T = D_{ion} - A_D = l .913$ eV is expected.

The HD+ cross section greets us with a sharp rise at the expected threshold, followed by 14 spectacular resonances superimposed on a generally declining envelope which starts near 4 x 10^{-19} cm^2 and is near zero past 14 eV. The resonance positions are shown in Table 1, which also shows the separation between adjacent resonances.

It is seen that the first five resonances (1-5) lie below the dissociation energy of HD^+ (2.668 eV) and have a spacing of around 0.2 eV, which is in the neighborhood of what is expected for vibrational spacing of Rydberg of HD which lie close to HD^+. Thus, one may speculate that the mechanism here is capture by depositing the electron energy into vibrational excitation, followed by dissociation via coupling to the $(2p\sigma_u)^2$ repulsive state.

Table 1. Observed peaks in RIP for HD^+

Peak #	Energy (eV) of Peak	Interval (eV)
l	1.94	
2	2.09	0.15
3	2.25	0.16
4	2.46	0.21
5	2.66	0.20
6	2.93	0.27
7	3.30	0.37
8	3.76	0.46
9	4.29	0.53
10	5.28	0.99
11	6.43	1.15
12	7.47	1.04
13	9.09	1.62
14	11.83	2.74

The resonant peaks 10-14 are broad and separated by 1-3 eV. The Peak l0 position is precisely at the position one would expect if a Franck-Condon transition is made from the ground state of the ion to the $(2p\sigma_u)^2$ state, and the Peak 14 energy just matches such a transition to a state just below the $2p\pi_u$ state of the ion. Peaks 6–9 seem entirely anomalous to us. We have no hypothesis for peaks in the range of energies just above D_{ion} and below the vertical energy difference to the $(2p\sigma_u)^2$ state. We speculate that the dynamics of separation leads to such peaks.

For HF^+ the RIP cross section correlates with the total DR cross section (also measured), as is about 26% as large. 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^-.

References

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