Resonant ion pair formation of HD^+: Absolute cross sections for the $H^- + D^+$ channel

Anita Neau, Alik Derkatch, Fredrik Hellberg, Stefan Rosén, Richard Thomas, and Mats Larsson*
Fysikum, SCFAB, Stockholm University, SE-106 91 Stockholm, Sweden

Nada Djurić, Duška B. Popović, and Gordon H. Dunn†
JILA, National Institute of Standards and Technology and University of Colorado, Boulder, Colorado 80309-0440

Jacek Semaniak
Institute of Physics, Świętokrzyska Academy, 25 406 Kielce, Poland
(Received 29 November 2001; published 4 April 2002)

Absolute cross sections for the production of $H^- + D^+$ in the collision of cold HD^+ with electrons have been measured in the storage ring CRYRING at Manne Siegbahn Laboratory, Stockholm University in Stockholm. The magnitude of this cross section ($\sim 3\times 10^{-19}$ cm^2 above threshold), as well as its interference pattern (14 peaks in the interaction energy region 0–16 eV) were found to be identical to that observed for the production of $D^- + H^+$, which was measured earlier in CRYRING.

DOI: 10.1103/PhysRevA.65.044701 PACS number(s): 34.80.Lx, 34.80.My, 34.90.+q

I. INTRODUCTION

Efforts in understanding collision processes for a molecular ion-electron system have mostly been directed to the study of dissociative recombination (DR) [1]. This very efficient process is one of the main destructive processes of molecular ions in cold plasma environments. An electron, impacting a molecular ion, can be resonantly captured into a doubly excited dissociative state of the neutral molecule. Dissociation times generally compete favorably with autoionization times, so a stable net neutral state is reached via dissociation. After passing the stabilization point where autoionization is no longer possible, there are many competing channels along which the resultant neutral may go—most of them yield neutral fragments, but a negative and a positive fragment may also result along some channels, and this is resonant ion pair formation or RIP. In an earlier study [2,3], we demonstrated that the resonant ion-pair formation of $D^- + H^+$ in the collision of HD^+ with electrons was governed by an interference mechanism which results in a series of 14 resonances in the cross section in the energy range 0–16 eV. Due to experimental constraints, we could not, at that time, study the complementary RIP channel, $H^- + D^+$. A factor of two difference was observed in an equivalent photoionization study of ion-pair formation from HD by Chupka *et al.* [4]: the H^-/D^- ratio was two just above threshold and decreased with decreasing wavelength. To verify whether there is or is not an isotope effect and to leave no doubt on the magnitude and shape of the total RIP cross section, improvements to the detection apparatus were made and it became possible to complete this study by measuring the reaction rate for the second RIP channel $H^- + D^+$.

II. EXPERIMENT

The experiment was performed at the storage ring facility CRYRING, at Manne Siegbahn Laboratory, Stockholm University, in Stockholm. A view of the facility is given in Fig. 1. The ions were produced by injecting HD neutral gas into a hot filament ion source (MINIS). After extraction from the source, HD^+ ions were mass selected, accelerated to 300 keV by a radio frequency quadrupole device, and injected into the ring. They were then further accelerated to an energy of 3.5 MeV/amu and circulated in the ring for about 10 s after each injection. One straight section of the ring is equipped with an electron cooler [5]. This device produces an electron beam with a velocity distribution that can be described by a flattened Maxwellian distribution

$$f(v) = \frac{m_e}{2\pi k T_{e\perp}} \left(\frac{m_e}{2\pi k T_{e\parallel}} \right)^{1/2} \exp\left(-\frac{m_e v_{e\perp}^2}{2kT_{e\perp}} - \frac{m_e v_{e\parallel}^2}{2kT_{e\parallel}} \right), \tag{1}$$

where $T_{e\parallel} \approx 0.1$ meV and $T_{e\perp} \approx 2$ meV are the longitudinal and transverse temperatures, respectively [5].

The electron cooler serves two purposes in recombination experiments. First, by Coulomb interaction, the translational heat from the molecular ions circulating in the ring is effectively transferred to the continuously renewed cold electron beam while both beams are velocity matched, a process known as phase-space cooling. The ion velocity distribution consequently becomes narrower and centered around the average electron velocity. Second, at each passage through the

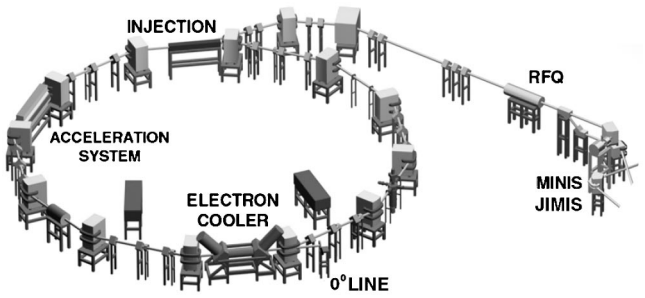

FIG. 1. View of the heavy-ion storage ring facility CRYRING, at Manne Siegbahn Laboratory in Stockholm, Sweden.

*Electronic address: Mats.Larsson@physto.se
†Electronic address: gdunn@jila.colorado.edu

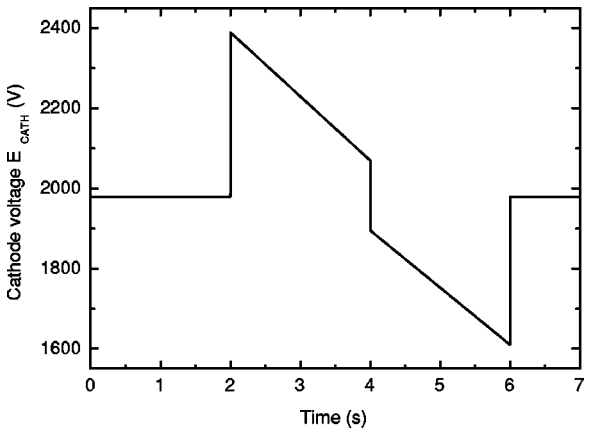

FIG. 2. The electron cathode voltage as a function of time for each injection cycle.

electron cooler, the ions interact with the electrons and the dissociative processes of interest here, DR and RIP, occur. The H^- fragments, as well as the D^- fragments, are deflected out from the center of the ring inside the dipole magnet immediately following the electron cooler. A movable energy-sensitive surface-barrier detector is set to intersect their trajectory inside this dipole chamber and collects all the H^- fragments produced from resonant ion-pair formation. Detection of the negative ion supplies a necessary and sufficient signature of the RIP process. Thus, the complementary positive D^+ fragments were not detected in this experiment, neither were the H^+ fragments in our earlier study of the $D^- + H^+$ channel.

III. DATA ACQUISITION AND ANALYSIS

The surface-barrier detector collects the H^- fragments with a 100% efficiency and converts each particle hit into an electric pulse. The height of the pulse is proportional to the energy deposited in the detector material, thus giving information about the mass of the detected ion. Recording of the number of pulses can be done either as a function of the deposited energy or as a function of storage time. This is achieved through the use of a multichannel analyzer (MCA) or scaler (MCS) card, respectively, installed in a PC. The technique we use to measure the rate coefficient and, subsequently deduce the cross section is that we vary the electron cooler cathode voltage as a function of storage time during each injection cycle. The interaction energy in the center-of-mass frame E_{cm} is given by

$$E_{cm}(t) = (\sqrt{E_{cath}(t)} - \sqrt{E_{cool}})^2, \tag{2}$$

where $E_{cath}(t)$ is the electron energy at time t, illustrated in Fig. 2, and E_{cool} is the electron energy corresponding to the cooling process, both defined in the laboratory frame of reference.

Each time window (~ 1 ms) in the recorded spectrum thus corresponds to a particular and well-defined cathode voltage and, consequently [Eq. (2)], to a specific interaction energy. The rate coefficient as a function of interaction energy can be deduced from the number of particles hitting the detector during each time window

$$\langle \sigma v \rangle = \frac{v_i e}{n_e l} \frac{N_{RIP}}{I_i}, \tag{3}$$

where N_{RIP} is the number of counts per second on the detector due to fragments produced via the RIP process, I_i is the ion current, measured simultaneously with a current transformer, v_i is the ion velocity, e is the electron charge, n_e is the electron density, and l the length of the interaction region, which is equal to 85 cm. The cross-section σ can be extracted by deconvolution via a Fourier transform technique from

$$\langle \sigma v_{cm} \rangle = \int_{-\infty}^{+\infty} v\, \sigma(v) f(v_{cm}, v)\, dv, \tag{4}$$

where $f(v_{cm}, v)$ is the electron velocity distribution defined in Eq. (1).

To obtain the correct value of the cross section, different effects must be accounted for in the data analysis procedure. First, the interaction energy must be corrected for the electron space charge. Second, due to the geometry of the electron cooler, some of the measured counts arise from reactions occurring at a different energy than that set in the center of the electron cooler: the ions interact with the electrons not only in the straight section but also in the merging and demerging parts of the cooler, where the relative velocity is different. An iterative procedure for this so-called toroidal effect is described by Lampert *et al.* [6]. More details about the analysis procedure can be found elsewhere [7].

IV. RESULTS AND DISCUSSION

The cross section for formation of $H^- + D^+$ from the collision of HD^+ with e^- was deduced from the measured rate coefficient in the electron cooler by using the analysis procedure described in the previous section. The results are shown in Fig. 3, together with our earlier measurement of the complementary channel $D^- + H^+$. As can be seen, these two channels are produced with the same probability over the whole studied energy range (0–16 eV collision energy). Exactly the same interference pattern as previously observed for the $D^- + H^+$ channel was found for production of $H^- + D^+$. It was proposed and confirmed [2] with a simple Landau-Zener-Stückelberg calculation that this pattern originates from quantum interference of the multiple dissociation pathways. A more complete time independent Landau-Zener-Stückelberg calculation [3] further established the validity of this hypothesis. In a diabatic representation the neutral dissociative state leading to the ion-pair limit crosses many Rydberg states twice, both at small and large internuclear distance; this opens two different possible routes to the ion pair limit, thus leading to the interference behavior observed in the cross section. In Ref. [3], six states were included: the lowest neutral $^1\Sigma_g^+$ dissociative state of HD, which is dominated by a $(2p\sigma_u)^2$ configuration at small internuclear distance and diabatically correlates with the ion-pair limit D^-

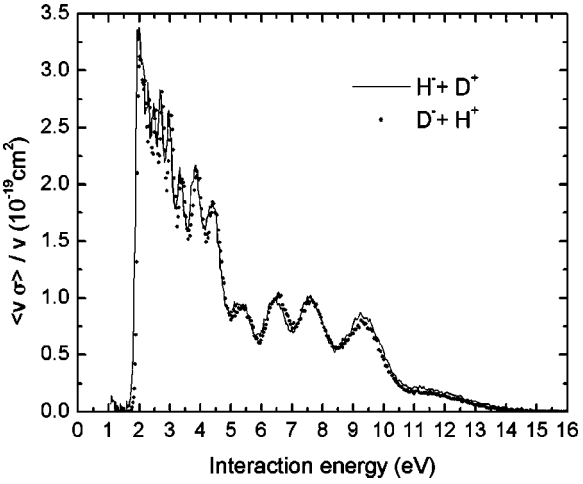

FIG. 3. Absolute cross section as a function of interaction energy. Dots, results from Ref. [2] (D^-+H^+); solid line, present results (H^-+D^+).

$+H^+$, the lowest $^1\Sigma_u^+(2p\sigma_u 2s\sigma_g)$ dissociative state, the second $^1\Sigma_g^+$ state $(2p\sigma_u 3p\sigma_u)$, the two Rydberg states $[(1s\sigma_g 2s\sigma_g)$ and $(1s\sigma_g 3d\sigma_g)]$ associated with the H($n=2$)+D($1s$) limit, and the lowest Rydberg state $(1s\sigma_g 3s\sigma_g)$ associated with the H($n=3$)+D($1s$) limit. For electron collision energies up to approximately 6 eV, the dissociation dynamics can be described by the lowest doubly excited state $^1\Sigma_g^+(2p\sigma_u)^2$ but for higher interaction energies, higher-excited neutral repulsive states $[^1\Sigma_u^+(2p\sigma_u 2s\sigma_g)$ and $^1\Sigma_g^+(2p\sigma_u 3p\sigma_u)]$ become important. A more complete theoretical study, using a time-dependent wave-packet approach, has now been reported by Larson and Orel [8].

As noted earlier, in the mid-1970s, Chupka *et al.* [4] observed in their photodissociation study of ion-pair formation for HD, that the H^-/D^- ratio was a factor 2 just above threshold and decreased with decreasing wavelength. To rationalize the difference, they noted that the H^-+D^+ pair correlates with $4f\sigma^1\Sigma_g^+$, while the H^++D^- pair correlates with the lower lying $3d\sigma^1\Sigma_g^+$ and speculated about different interactions along the various crossings. They also noted the possibility of their having detector discrimination between H^- and D^-. Their results covered an energy range of only about 0.6 eV above threshold. Our results show that production of H^- and D^- is equally probable for any interaction energy in the studied range 0–16 eV.

One can conclude that the total resonant ion pair formation cross section is simply twice the cross section for one of the channels ($\sim 4\times 10^{-19}$ cm^2 as a rough average over the studied energy range) and still only a few percent of the total dissociative recombination cross section ($\sim 10^{-17}$ cm^2) [9,10]. We also conclude that the different correlations speculated on by Chupka *et al.* [4] do not play a major role and that there is no isotope dependence between the two channels H^-+D^+ and H^++D^-.

ACKNOWLEDGMENTS

We wish to acknowledge the support of the Swedish Foundation for International Cooperation in Research and Higher Education (STINT) and the IHP Program of the EC under Contract No. HPRN-CT-2000-00142. G. H. Dunn, N. Djurić, and D. B. Popović were supported in part by the U.S. Department of Energy, Fusion Energy Branch, under Contract No. DE-A102-95ER54294. J. Semaniak was supported in part by the State Committee for Scientific Research (Poland), under Contract No. 146/E-346/SPUB-M/5. The authors gratefully acknowledge the staff from Manne Siegbahn Laboratory for their support during the experiment and Kjell Schmidt for the design of the new detection system.

[1] See e.g., *Dissociative Recombination: Theory, Experiment and Applications III*, edited by M. Larsson, J. B. A. Mitchell, and I. F. Schneider (World Scientific, Singapore, 2000).
[2] W. Zong *et al.*, Phys. Rev. Lett. **83**, 951 (1999).
[3] Å. Larson *et al.*, Phys. Rev. A **62**, 042707 (2000).
[4] W. A. Chupka *et al.*, J. Chem. Phys. **63**, 3929 (1975).
[5] H. Danared *et al.*, Nucl. Instrum. Methods Phys. Res. A **441**, 123 (2000).
[6] A. Lampert *et al.*, Phys. Rev. A **53**, 1413 (1996).
[7] C. Strömholm *et al.*, Phys. Rev. A **54**, 3086 (1996).
[8] Å. Larson and A. E. Orel, Phys. Rev. A **64**, 062701 (2001).
[9] C. Strömholm *et al.*, Phys. Rev. A **52**, R4320 (1995).
[10] L. H. Andersen *et al.*, Phys. Rev. A **55**, 2799 (1997).