

Absolute cross sections for dissociative recombination of HD^+ : Comparison of experiment and theory

C. Strömholm,¹ I. F. Schneider,² G. Sundström,¹ L. Carata,² H. Danared,³ S. Datz,⁴ O. Dulieu,⁵ A. Källberg,³
M. af Ugglas,³ X. Urbain,⁶ V. Zengin,¹ A. Suzor-Weiner,⁷ and M. Larsson¹

¹Department of Physics I, Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden

²Laser Department, Institute for Physics and Technology of Radiation Devices, Bucarest, Romania

³Manne Siegbahn Laboratory at Stockholm University, S-104 05 Stockholm, Sweden

⁴Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6377

⁵Laboratoire Aimé Cotton, Université de Paris XI, Orsay, France

⁶Laboratoire des Collisions, Université Catholique de Louvain, Louvain-la-Neuve, Belgium

⁷Laboratoire de Photophysique Moléculaire, Université de Paris XI, Orsay,

and Laboratoire de Chimie Physique, Université de Paris VI, Paris, France

(Received 29 June 1995)

Absolute cross sections for dissociative recombination of HD^+ were measured in the ion storage CRYRING for incident electron energies in the range 0.01–20 eV. The ions were stored for about 25 s before data taking, which is several orders of magnitude longer than their vibrational lifetimes towards spontaneous emission of infrared radiation. A broad resonance in the cross section at 5–12 eV is due to recombination into a manifold of doubly excited states. Multichannel quantum-defect theory was used to calculate the absolute cross section of this resonance. The calculations required inclusion of different mechanisms, such as dissociative autoionization, and many molecular states in order to reproduce the resonance region. Very good agreement of experiment and theory is found, and the results strongly reinforce that vibrationally cold ions were used in the experiment.

PACS number(s): 34.80.Ht, 34.80.Gs, 34.80.Kw

The advent of using ion storage rings for atomic physics has opened new possibilities for studies of dissociative recombination (DR) of molecular ions. In the first-generation storage ring experiments, broad resonances at high-incident electron energies (5–25 eV) were found in HeH^+ [1], HD^+ [2], and H_3^+ [3]. The origins of these resonances, however, differ among the three molecules. The resonances in HeH^+ and H_3^+ have their origin in electron capture to doubly excited valence states of HeH and H_3 [4,5], but the HD^+ resonances do not fit into a similar framework. Figure 1 shows potential curves of H_2^+ [6] (and, apart from the vibrational spacing, of HD^+ and D_2^+). It has been suggested that the high-energy resonances found in HD^+ are due to capture into Rydberg states with dissociative ($2p\sigma_u$) and ($2p\pi_u$) ion cores [2,7], but only relative cross sections are supplied as support. Theoretical arguments for [8,9] and against [10] the effectiveness of this mechanism have been put forward, but a stringent calculation has never been performed. Recent storage ring experiments using H_2^+ [11] and D_2^+ [12] give cross sections somewhere between the crude theoretical estimates [8–10]. Neither H_2^+ nor D_2^+ , however, are ideally suited for a comparison of experiment and theory. A storage ring experiment using the infrared inactive homonuclear isotopomers invariably leads to the presence of ions in vibrationally excited levels. The remedy for this is to use the mixed HD^+ molecule, which is infrared active. In the present work we compare absolute cross sections measured in the ion storage ring CRYRING [13] at the Manne Siegbahn Laboratory in Stockholm, with cross sections calculated by means of multichannel quantum-defect theory for the electron energy range 3–18 eV.

Narrow resonances in the DR cross section of H_2^+ at low incidence electron energy (<1 eV) were observed in single-pass merged-beams experiments [14,15]. They have been assigned to the so-called indirect recombination process [16] due to temporary capture into bound Rydberg states

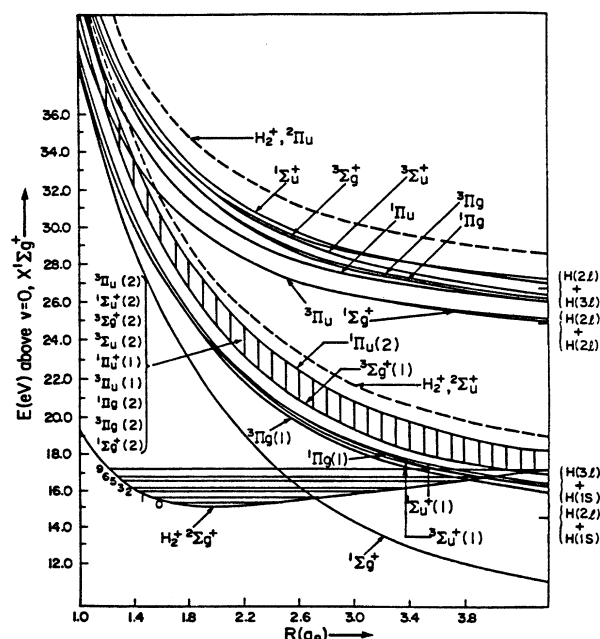


FIG. 1. Potential-energy curves for H_2 and H_2^+ reproduced from Ref. [6] by permission of S. L. Guberman.

converging to the ion ground state. These states interact both with the electronic continuum (entrance channel) through non-Born-Oppenheimer vibrational coupling, and with the doubly excited dissociative states of the same symmetry (exit channel) via electronic interaction. This process cannot be treated independently of the direct capture into the dissociative states because both interfere and result in a very complex structure in the DR cross section with many interfering and overlapping resonances [17–19]. The cross section was calculated by means of multichannel quantum-defect theory (MQDT) [17], and a comparison of experiment and theory revealed good agreement [18]. More recently it has become clear that rotational-electronic coupling is important for dissociative recombination at low energy [19], and MQDT calculations with rotational motion for DR of HD^+ have been performed in the energy range 0.001–0.9 eV [20]. The calculated cross section was in quite good qualitative agreement with the relative cross section measured in the TARN II storage ring [20], using an adiabatically expanded low-temperature electron beam [21,22]. In the present work we present an absolute cross section for low-energy DR of HD^+ . The electron beam in CRYRING has an electron-velocity distribution that is similar to the one in TARN II, hence a qualitative comparison of low-energy resonances is possible.

The HD^+ ions were extracted at 30 keV from an electron-impact ion source operated with HD gas. After injection in the ring, the ions were accelerated to an energy of 18 MeV (6 MeV/u) and electron cooled for 25 s prior to measurement. This is much longer than the vibrational lifetimes in HD^+ due to radiative relaxation [23,24]. After the electron-cooling phase, the energy of the electrons in the laboratory reference frame was increased from $E_{\text{cool}}=3.27$ keV to E_{meas} for ten time intervals of 100 ms each. The time windows of 100 ms were separated by 200 ms, during which time the electron cooler was switched back to E_{cool} . The two laboratory energies are related to a detuning energy E_d , which can be expressed as $E_d=(E_{\text{meas}}^{1/2}-E_{\text{cool}}^{1/2})^2$ and associated with a detuning velocity $v_d=2(E_d/m_e)^{1/2}$. In the present experiment, $E_d \geq kT_{e\perp} \approx 0.01$ eV, which means that the detuning energy to a good approximation is equal to the collision energy in the center-of-mass frame.

Neutral particles produced in the straight section of the storage ring hosting the electron cooler were detected by an ion-implanted silicon particle detector positioned after the dipole (bending) magnet of the electron-cooler section. H_3^+ is a potential contaminant in a beam of HD^+ . We used a combination of a “translucent” grid [25] and a copper foil absorber [26] in front of the particle detector to get access to a clear “fingerprint” of H_3^+ in the pulse-height spectrum. No contamination of H_3^+ was found at any time during the experiment.

The absolute cross section was measured using the technique described in Ref. [12]. The results are shown in Fig. 2. The two high-energy resonances agree well in position and relative strength with those observed in the earlier experiment at the Test Storage Ring (TSR) [2,7] and TARN II [20]. The difference is that the absolute cross sections of the peaks also are obtained in the CRYRING experiment.

The low-energy cross section contains several resonances. The long storage time suggests that the data were obtained

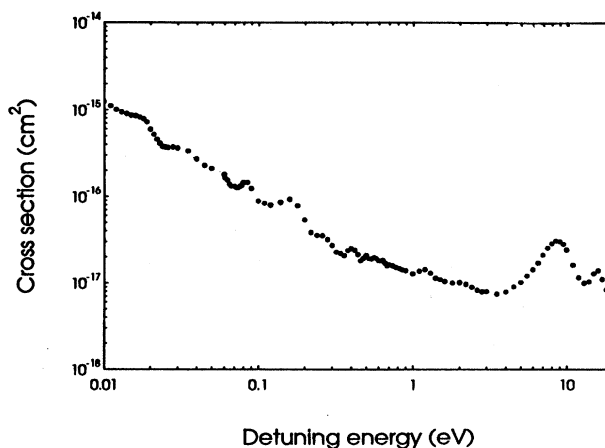


FIG. 2. Cross section for dissociative recombination of HD^+ measured in the CRYRING.

for HD^+ populating only its zeroth vibrational level. The rotational distribution is not known, but a reasonable assumption is that the rotational temperature is in equilibrium with the beam tube, which is kept at room temperature. The resonances are not as deep and narrow as those observed in the single-pass experiment of H_2^+ [15]. This is not expected at a transverse electron temperature of 10 meV.

The experimental energy range (0.01–20 eV) can be divided into two zones, depending on the value of the energy of the incident electron with respect to the dissociation limit of the ion ground state (see Fig. 1). For an ion initially in the lowest ($\nu=0, N=0$) level of the ground state of HD^+ , the frontier is around 2.7 eV. Below 2.7 eV, only the lowest $(2p\sigma_u)^2 \ ^1\Sigma_g^+$ dissociative state contributes to DR, but the process is complicated by the infinite series of Rydberg series of same symmetry converging to the ion ground state and responsible for the indirect process. The multichannel quantum-defect-theory calculations presented here concern the broad resonance at 9 eV. As HD and H_2 have similar electronic structure except at very long range near their dissociation limit, we used a set of molecular data obtained for H_2 . In addition to potential curves (Fig. 1), the calculations require autoionization (or “capture”) widths, proportional to the square of the electronic matrix elements coupling the doubly excited configurations to the electronic continuum of the ion ground state. These data are available for a few dissociative states only, usually the lowest state of each symmetry. Most of the data we have used come from electron scattering studies using the R -matrix method [27–29] or linear algebraic methods [29], but these calculations are performed only at rather short internuclear distances where the doubly excited states lie above the ion ground state and appear as resonances in electron scattering. At longer ranges, the doubly excited configurations cause double minima in the potential-energy curves obtained in fully adiabatic structure calculations [30]. By diabatically correlating monoexcited configurations on the one hand, and doubly excited ones on the other in the region of the avoided crossings, both autoionization widths and quasidiabatic potential curves may be extracted at large internuclear distance and connected with the short-range scattering results.

In the high-energy region above the ion dissociation limit,

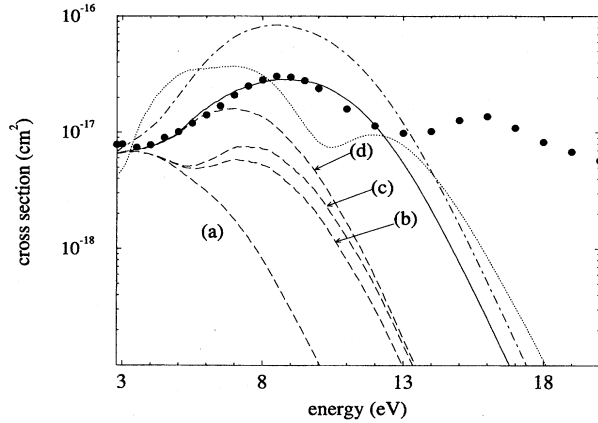


FIG. 3. Cumulative contributions of dissociative states of HD to the theoretical DR cross section compared with experimental results. (a) theory, contribution of $(2p\sigma_u)^2\ ^1\Sigma_g^+$ state only; (b) same as (a) plus contribution of the lowest $\ ^1\Pi_g$ dissociative state; (c): same as (b) plus contribution of the lowest $\ ^1\Sigma_u^+$ state; (d) same as (c) plus contribution of the lowest $\ ^3\Pi_g$ state; —, contribution of entire series of Rydberg dissociative states for the 4 symmetries added (i.e., the final theoretical result for $\nu=0, N=0$); — — —, same, without including dissociative autoionization (see text); - - - - -, theoretical result for $\nu=1$; ●, experimental results. The second peak observed at higher energy is probably due to the second group of dissociative states with a $2p\pi_u$ ion core, which are not included in the calculations.

capture in bound Rydberg levels is no longer possible, and DR proceeds through direct electronic recombination in doubly excited dissociative states. Additional dissociative states contribute with increasing energy, as shown in Fig. 1. A first group of states, which may be considered as Rydberg states with the dissociative $(2p\sigma_u)$ ion core, begins to contribute beyond 3 eV. Figure 3 shows the contribution of the lowest members of three series, with symmetries $\ ^1\Pi_g, \ ^1\Sigma_u^+, \ ^3\Pi_g$. Their potential curves and electronic widths have been deduced from various sources [27–30], which indicate that they are the dominant symmetries for the recombination process (the smaller width of the $\ ^3\Pi_g$ state is compensated for by its large statistical weight). The other symmetries have much smaller widths and have been shown to contribute very little. Together with the lowest $\ ^1\Sigma_g^+$ dissociative state, these states reproduce correctly the first part of the broad resonance observed in the cross section between 5 and 12 eV, but clearly more states are needed to fully reproduce the entire resonance region.

Actually, the whole dissociative Rydberg series for each molecular symmetry should be included, but precise molecular data are lacking, except for the $(2p\sigma_u n l \sigma)^1\Sigma_g^+$ series [28]. The contribution of this entire Rydberg series was introduced using data calculated in [28] for the lowest members ($n=3-5$). The higher members of the series are very close, and we represent them by a single effective state with an energy corresponding to $n^* \approx 6$ and a total width

$$\Gamma_{\text{eff}} = \sum_{n=6}^{\infty} \Gamma_n = \left(\sum_{n=6}^{\infty} \frac{2 \text{ Ry}}{n^{*3}} \right) \bar{\Gamma}, \quad (1)$$

where $\bar{\Gamma}$ is a dimensionless width parameter deduced from

the lowest-state values. We have also included the approximate contribution to DR of other dominant series of dissociative states (symmetries $\ ^1\Pi_g, \ ^3\Pi_g, \ ^1\Sigma_u^+$) for which, to our knowledge, no data are published: The potential curves and electronic widths of the second to fifth members of the series are deduced from those of the lowest, using Rydberg state properties (energy splitting decreasing as n^{*-2} , width as n^{*-3}), and an effective state represents the higher members, as described above. Note that states of *same symmetry* must be included simultaneously in a single calculation, even if they are not directly coupled, because they can interact indirectly by being coupled to the same set of bound Rydberg states or ionization continuum.

At high electron energy (≥ 13 eV), a second group of dissociative Rydberg states with a $(2p\pi_u)$ ion core (denoted Q_2 states in [6]) should be included. However, there is a lack of molecular data for these states, in particular, for the capture width, and we did not perform calculations in this energy range.

Besides these infinite series of dissociative states, another feature specific to the high-energy range is autoionization into the vibrational continuum of the ion ground state ($\text{H}_2^{**} \rightarrow \text{H} + \text{H}^+ + e^-$). Dissociative ionization is a three-particle fragmentation whose exact treatment requires integration over correlated electron and nuclei kinetic energies. Here we estimate the reduction factor of the DR cross section from the first-order expression [17] of the “survival factor” [16]

$$S = \frac{1}{(1 + \sum_{\nu} \xi_{\nu}^2)^2}, \quad \xi_{\nu} = \pi \langle \chi_{\nu} | V | F_d \rangle, \quad (2)$$

where χ_{ν} is a vibrational wave function of the ion ground state, F_d is the dissociative nuclear wave function, and V stands for the electronic coupling. The summation in the denominator involves all open vibrational channels at a given energy, and we extend it above the dissociation limit by adding to the discrete summation the integral

$$\pi \int |\langle \chi_E | V | F_d \rangle|^2 dE, \quad (3)$$

where χ_E is the energy-normalized nuclear wave function in the continuum of the ion ground state. The energy E is the kinetic energy that the dissociating nuclei may acquire, sharing with the departing electron, and varies from zero to $E_{\text{tot}} - D_0(\text{HD}^+)$, where E_{tot} is the total energy and D_0 the dissociation energy of $\text{HD}^+(\ ^2\Sigma_g^+)$. The reduction in the DR cross section due to this competing dissociative autoionization process is shown in Fig. 3 (dash-dotted line versus solid line). This process is also responsible for the dissociative excitation cross section [2,7,31].

Figure 3 also shows the cross section for dissociative recombination of HD^+ between 3 and 20 eV (dots). From 3 eV to about 12 eV the measured cross section is very well reproduced, both in shape and magnitude, by the calculations for ions initially in the $\nu=0, N=0$ level of the ground state, and it seems clear that the first peak is due to the cumulative contribution of the various states described above.

Similar results obtained for the initial $\nu=1$ ion level disagree in shape and magnitude with the experimental results

in the same 3–12-eV energy range (see Fig. 3), a good indication that only $\nu=0$ ions are present in the cooled beam after 25 s residence time. Finally, calculations were also performed for initial rotational levels $N=1,2, \dots, 10$; the effect of rotational excitation is very small for the lowest rotational levels, which are those that can be expected to be populated in the experiment.

In summary, we report absolute cross sections for dissociative recombination of HD^+ for the electron energy range 0.01–20 eV measured in the ion storage ring CRYRING. Resonances are present in both the low- and high-energy parts of the cross section. Multichannel quantum-defect theory was used to calculate the DR cross section of a broad resonance at 9 eV for HD^+ in its zeroth vibrational level of the electronic ground state. The very good agreement of experiment and theory suggests that the mechanism for DR at high incident electron energy now is well understood and underscores that vibrational cooling is obtained when the ions are stored in the ring for tens of seconds. Recent relative cross sections [20] from the TARN II storage ring are in good qualitative agreement with the present results over the entire 0.01–20-eV energy range. MQDT calculation, includ-

ing rotational electronic coupling [20], is in reasonable agreement with the present experimental results for the general shape of the cross section, but is larger by about a factor 2.5 for the energy range 0.01–0.1 eV. Further theoretical study is underway for this low-energy range.

The authors would like to thank R. Kennedy, A. E. Orel, T. Tanabe, and P. Forck for communicating unpublished results, and the staff members of the Manne Siebahn Laboratory for valuable help with the experiment. This work was supported by the Swedish Natural Science Research Council (NFR) and the Göran Gustafsson Foundation. I.F.S. acknowledges financial support from the International Atomic Energy Agency and the SOROS Foundation, and thanks B. and C. Bahrim for their hospitality. Grants from the CNRS-Romanian Academy exchange program and from EC HCM Contract No. ERB CHRX CT920013 are gratefully acknowledged. S.D. was sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Division Chemical Sciences, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. M.L. acknowledges financial support from the JILA Visiting Fellow Program.

-
- [1] T. Tanabe *et al.*, Phys. Rev. Lett. **70**, 422 (1993).
 [2] P. Forck *et al.*, Phys. Rev. Lett. **70**, 426 (1993).
 [3] M. Larsson *et al.*, Phys. Rev. Lett. **70**, 430 (1993).
 [4] A. E. Orel and K. C. Kulander, Phys. Rev. Lett. **71**, 4315 (1993).
 [5] A. E. Orel, K. C. Kulander, and T. N. Rescigno, Phys. Rev. Lett. **74**, 4807 (1995).
 [6] S. L. Guberman, J. Chem. Phys. **78**, 1404 (1983).
 [7] P. Forck *et al.*, Nucl. Instrum. Methods Phys. Res. B **79**, 273 (1993).
 [8] V. P. Zhdanov and M. I. Chibisov, Zh. Éksp. Teor. Fiz. **74**, 75 (1978) [Sov. Phys. JETP **47**, 38 (1978)].
 [9] V. P. Zhdanov, J. Phys. B **13**, L311 (1980).
 [10] C. Derkits, J. N. Bardsley, and J. M. Wadehra, J. Phys. B **12**, L529 (1979).
 [11] M. Larsson *et al.*, J. Phys. B **27**, 4915 (1994).
 [12] M. Larsson *et al.*, Phys. Scr. **51**, 354 (1995).
 [13] K. Abrahamsson *et al.*, Nucl. Instrum. Methods Phys. Res. B **79**, 269 (1993).
 [14] H. Hus, F. Yousif, C. Noren, A. Sen, and J. B. A. Mitchell, Phys. Rev. Lett. **60**, 1006 (1988).
 [15] P. Van der Donk, F. B. Yousif, J. B. A. Mitchell, and A. P. Hickman, Phys. Rev. Lett. **67**, 42 (1991).
 [16] J. N. Bardsley, J. Phys. B **1**, 349 (1968); **1**, 365 (1968).
 [17] A. Giusti, J. Phys. B **13**, 3867 (1980); S. L. Guberman and A. Giusti-Suzor, J. Chem. Phys. **95**, 2602 (1991).
 [18] I. F. Schneider, O. Dulieu, and A. Giusti-Suzor, J. Phys. B **24**, L289 (1991).
 [19] H. Takagi, J. Phys. B **26**, 4815 (1993).
 [20] T. Tanabe *et al.*, Phys. Rev. Lett. **75**, 1066 (1995).
 [21] H. Danared, Nucl. Instrum. Methods Phys. Res. A **335**, 397 (1993).
 [22] H. Danared *et al.*, Phys. Rev. Lett. **72**, 3775 (1994).
 [23] Z. Amitay, D. Zajfman, and P. Forck, Phys. Rev. A **50**, 2304 (1994).
 [24] R. Kennedy (private communication).
 [25] S. Datz *et al.*, Phys. Rev. Lett. **74**, 896 (1995).
 [26] S. Datz *et al.*, Phys. Rev. A **52**, 2901 (1995).
 [27] J. Tennyson and C. J. Noble, J. Phys. B **18**, 155 (1985).
 [28] I. Shimamura, C. J. Noble, and P. G. Burke, Phys. Rev. A **41**, 3545 (1990).
 [29] L. A. Collins, B. I. Schneider, D. L. Lynch, and C. J. Noble, Phys. Rev. A **52**, 1310 (1995).
 [30] W. Kolos and J. Rychlewski, J. Mol. Spectrosc. **66**, 428 (1977); L. Wolniewicz and K. Dressler, J. Chem. Phys. **88**, 3861 (1988); L. J. Lembo, N. Bjerre, D. L. Huestis, and H. Helm, *ibid.* **92**, 2219 (1990); L. Wolniewicz and K. Dressler, *ibid.* **100**, 444 (1994); W. Kolos and J. Rychlewski, J. Mol. Spectrosc. **166**, 12 (1994).
 [31] P. Forck, Ph.D. thesis, Universität Heidelberg (1994); P. Forck *et al.* (unpublished).