Production of D* ($n = 4$) from electron-D_2^+ dissociative recombination*

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Crossed beams of electrons and D_2^+ ions were used to measure absolute cross sections for the dissociative recombination process, $e + D_2^+ (X\ ^2\Sigma_g^+) \rightarrow D + D^* (n = 4)$ over a range of electron energies extending from 0.6 to 7 eV. The process was monitored by detecting a known portion of the 485.9-nm emission resulting from radiative decay of the product $D^* (n = 4)$ atoms. The cross sections, which correspond to a known vibrational-state distribution of the target ions, exhibit the same dependence on electron energy as recent measurements of the total dissociative recombination cross section reported by Peart and Dolder, and have a magnitude of about 10% of the total cross section, suggesting that the product D atoms are formed in excited states with a variety of principal quantum numbers. Systematic measurement uncertainties at high confidence are about 14%, and random uncertainties are at the 25% (standard deviation) level. The calculation of cross sections from the observed light intensities depends on the mean lifetimes and branch ratios for 485.9-nm emission, whose evaluation in turn requires assumptions concerning the recombination process. The situation is complicated by the presence of an electron-beam-confining magnetic field in the collision volume, which causes the incident ions and product atoms to experience a transverse motional electric field. A time-independent perturbation calculation of the weak-field Stark and Zeeman effects was performed and mean lifetimes and branch ratios were estimated under different assumptions concerning the recombination process. Assuming that all perturbed product $n = 4$ states are equally populated by dissociative recombination yields an experimental cross section of 1×10^{-16} cm^2 at 0.7 eV, decreasing to 3.3×10^{-17} cm^2 at 3 eV, and to 1×10^{-17} cm^2 at 7 eV. Assuming that only the perturbed $4s$ states are initially populated results in cross sections larger by some 50%.

I. INTRODUCTION

The dissociative recombination of electrons with positive molecular ions is an important process in upper atmospheric physics and astrophysics, as well as in laboratory plasmas such as gas lasers. This reaction is known to strongly influence the charge density and chemistry of the ionsophere, and its significance was first noted in 1931 by Kaplan,[1] who attributed observations of the strong auroral green line to the formation of excited oxygen atoms by dissociative recombination of electrons with O_2^+ ions. Dissociative recombination involving H_2^+ and its isotopes is of potential interest in controlled thermonuclear research as a possible method of preparing fast and highly excited deuterium atoms for injection into plasmas. Also, being the simplest of molecular ions, H_2^+ and its isotopes are the molecules most often studied in *ab initio* theoretical calculations of cross sections for the recombination process.

The first laboratory measurements of dissociative recombination were made in 1949 by Biondi and Brown[2] using microwave plasma afterglow techniques, variations of which have been employed in many subsequent investigations. The method involves determination of the decay of the electron and/or positive-ion concentrations in the plasma after the source of ionization has been removed. A comprehensive summary of the various experimental methods, results, theory, and applications is provided in a review by Bardsley and Biondi.[3] Other methods which have been employed include the colliding beam method,[4-8] in which beams of electrons and molecular ions are made to intersect at some angle, and the fast neutral atoms produced by dissociative recombination are detected, or, alternatively, photons resulting from the radiative decay of the excited product atoms are detected.[9] Very recently, ion storage techniques have also been applied with success to the study of dissociative recombination of electrons with various molecular ions.[10]

Much of the theoretical effort to date on dissociative recombination has concerned the H_2^+ ion. The first calculations were reported by Bauer and Wu,[11] who used the Born approximation, neglecting the long-range Coulomb interaction. They considered capture to the $(2p\sigma_u 2s\sigma_g)\,^3\Sigma_u^+$ and $(2p\sigma_u 2p\pi_u)\,^3\Pi_g$ states of H_2, and estimated cross sections of the order of 10^{-16} cm^2. Their calculation was improved upon by Wilkins,[12] who employed a Coulomb-Born treatment and obtained cross sections of comparable magnitude. A similar procedure was employed by Dubrovsky and Ob'edkov[13] for capture into the $(2p\sigma_u)^2\,^1\Sigma_g^+$ state; it predicts cross sections of the order of 10^{-17} cm^2 for this channel. Nielsen and Berry[14] considered direct capture into the $(1s\sigma_g 4s\sigma_g)\,^1\Sigma_g^+$ state, which does not cross the

ionic curve, and estimated cross sections of about 10^{-18} cm^2 at 0.3 eV. More accurate potential-energy curves for the relevant autoionizing states of H_2 and the required matrix elements have recently been computed by Bottcher and Docken[15] and have lead to further theoretical estimates of total cross sections for dissociative recombination.[16] These calculations indicate that the lowest $^1\Sigma_g^+$ resonance is almost entirely responsible for dissociative recombination, and cross sections in reasonable agreement with experiment[7,8] have been predicted for H_2^+ and D_2^+.

Experimental measurements on H_2^+ ions using afterglow techniques are somewhat uncertain, since, as Bardsley and Biondi[3] point out, most of the afterglow measurements refer to one or more of the ions H^+, H_3^+, or H_5^+. Recently, Peart and Dolder[7,8] have employed an inclined beam technique to determine accurate cross sections for dissociative recombination of electrons with H_2^+ and D_2^+ ions for interaction energies ranging from 0.3 to 5 eV. Their experiments yielded total recombination cross sections of 6.3×10^{-16} and 9.2×10^{-16} cm^2 for H_2^+ and D_2^+ ions, respectively, at an interaction energy of 1 eV. Their results for D_2^+ are about an order of magnitude larger than measurements by Vogler and Dunn,[9] who measured cross sections for electron dissociative recombination of D_2^+ ions in which one of the product D atoms was in the $2p$ state. Employing crossed ion and electron beams, they monitored the recombination process by detecting the Lyman-α radiation resulting from the decay of the excited $2p$ atoms. They also observed a decrease in the cross section with increasing ion velocity, which suggested that a substantial contribution to the observed Lyman-α intensity was due to cascade transitions from longer-lived states for which $n>2$. This effect, and the fact that the $2p$ dissociation channel accounts for less than 10% of the total recombination cross section as measured by Peart and Dolder, suggests that channels for which product D atoms occupy excited states with $n>2$ are important.

In the present experiment, absolute cross sections for the process

$$e + D_2^+ (X^2\Sigma_g^+) \rightarrow D^*(n=4) + D(1s) \qquad (1)$$

have been measured using crossed beams of electrons and D_2^+ ions for interaction energies ranging from 0.6 to 7 eV. The recombination process was monitored by measuring the intensity of Balmer-β radiation arising from spontaneous decay of the excited product D atoms,

$$D^*(n=4) \rightarrow D^*(n=2) + h\nu\,(485.9\text{ nm}). \qquad (2)$$

The $n=4$ dissociation channel was selected since the D($n=4$) states have mean lifetimes which are short enough to make photon detection feasible in a fast crossed-beam experiment. Also, the 485.9-nm transition has a relatively favorable branch ratio, and this wavelength was convenient for an absolute calibration of the optical detection system.

II. EXPERIMENT

The experimental procedure is to collide a mass-analyzed beam of D_2^+ ions of known vibrational-state population distribution at right angles with a magnetically confined beam of electrons of variable energy, and measure the photon flux into a cone along the third orthogonal direction. The method and apparatus have been described in detail in previous reports[17-19] on electron-impact excitation of Ca^+ and Ba^+, and only details peculiar to the present experiment will be discussed.

The dissociative recombination cross section σ_R is calculated from measured quantities using the equation

$$\sigma_R = \frac{1}{Y_\Omega}\,\frac{\mathcal{R}}{I_i I_e}\,\frac{e^2 v_i v_e}{(v_i^2+v_e^2)^{1/2}}\,\frac{\mathcal{F}}{D(z_0,\lambda)}\,\frac{1}{b(\lambda)}\,. \qquad (3)$$

Here $\mathcal{R}$ is the recorded count rate of photons, e is the electronic charge, I_i and I_e are the total currents of ions and electrons, and v_i and v_e are the respective velocities. The anisotropy correction factor Y_Ω, which includes allowance for the finite solid angle Ω of the detection system, is given in terms of the angle θ between the direction of photon emission and the electron beam axis by

$$Y_\Omega = (1 - P\langle\cos^2\theta\rangle_\Omega)/(1-\tfrac{1}{3}P), \qquad (4)$$

where P is the polarization of photons emitted along the observation axis and $\langle\cos^2\theta\rangle_\Omega$ is the average value of $\cos^2\theta$ over the detection solid angle. The ion and electron beams are traveling in the x and y directions, respectively, and photons are observed in a cone along the z axis. The form factor $\mathcal{F}$ which accounts for the spatial overlap of the ion- and electron-beam density distributions, $R(z)$ and $G(z)$, with the relative detection sensitivity profile $\eta(z,\lambda)$ can be written

$$\mathcal{F} = \int R(z)\,dz \int G(z)\,dz \Big/ \int R(z)G(z)\eta(z,\lambda)\,dz\,, \qquad (5)$$

where

$$\eta(z,\lambda) = D_R(z,\lambda) - I_1 + (e^{w_e/v_i\tau} - 1)I_2\,, \qquad (6)$$

and here

$$I_1 = \int_0^{w_e} e^{-x/v_i\tau}\,D_R(x,z,\lambda)\,dx \Big/ \int_0^{w_e} D_R(x,z_0,\lambda)\,dx \qquad (7)$$

and

$$I_2 = \int_{w_e}^{\infty} e^{-x/v_i\tau} D_R(x, z, \lambda)\, dx \Big/ \int_0^{w_e} D_R(x, z_0, \lambda)\, dx . \tag{8}$$

The quantity $D(z_0, \lambda)$ [$D(z_0, 485.9) = 0.75 \times 10^{-3}$ counts/photon] in Eq. (3) is the absolute average probability that a photon emitted in an arbitrary direction from the $z = z_0$ plane inside the collision volume will be recorded, and $D_R(z, \lambda)$ in Eq. (6) is the relative variation of that probability with height z such that $D_R(z_0, \lambda) = 1$. $D_R(x, z, \lambda)$ is the relative probability averaged over the width of the ion beam that a photon emitted from a line parallel to the electron beam will be detected; w_e is the mean width of the electron beam, and τ is the lifetime of the transition yielding photons of wavelength λ. The subtraction of I_1 accommodates for the fact that some particles do not radiate while within the limits of the electron beam. The term containing I_2 is added to account for those which radiate beyond the limits of the electron beam but are still detected. For 500- and 2000-eV incident D_2^+ ions, the terms I_1 and I_2 give corrections to $\eta(z, 485.9)$ of about 40% and 60%, respectively. The final factor $b(\lambda)$ in Eq. (3) is the fraction of excited D ($n = 4$) atoms created by dissociative recombination which decay by giving off light of wavelength λ [$b(485.9) \approx 0.3$]. Measurement of the quantities in Eqs. (3)–(8) is discussed elsewhere,[17–19] as noted.

The D_2^+ ions are formed by electron bombardment in an ion source which is similar to a Bayard-Alpert ionization gauge, and which has been described previously.[20] Typical operating pressure in the source is about 1 Pa (8×10^{-3} Torr), and the mean energy of the bombarding electrons is about 300 eV. Under these conditions the vibrational-state populations of the ions are expected to correspond to those measured by von Busch and Dunn.[21] The ions are mass analyzed, and the well-collimated beam (~0.6 μA) intersects the electron beam in a region where the background pressure is typically 1.3×10^{-7} Pa (1×10^{-9} Torr).

The ion and electron beams were square-wave modulated at frequencies f and $2f$, respectively ($f \sim 1$ kHz), and background and signal plus background were recorded in dual scalers gated according to the scheme of Bacon and Hooper.[22] Typical signal count rates were of the order of 0.1 sec^{-1}; background count rates ranged from 15 to 20 sec^{-1} and resulted mainly from detection of stray light from the hot cathode of the electron gun. The interference filter transmission had its peak at 487 nm, a full width at half-maximum of 5 nm, and transmitted 72.6% at 485.9 nm. The absolute sensitivity function $D(z, 485.9)$ was estimated by interpolating between calibrations made on the system at 452.5 and 490.0 nm.[19] The uncertainty associated with the interpolation procedure is estimated to be about 3%.

Extremely low signal levels made determination of the polarization P of the emitted radiation impractical. Previous measurements[23] of the polarization of H_β resulting from dissociative excitation of H_2 indicate that P is small (~0.08), and if the same states of H_2^* are responsible for dissociative recombination, one would expect a similarly small polarization in the present case. Consequently, the anisotropy factor Y_Ω has been taken to be 1.0.

III. MEASUREMENTS AND ANALYSIS

As noted in Sec. II, the motion of excited product D atoms along the ion-beam direction beyond the field of view of the detection system necessitates substantial corrections to the observed count rates according to Eqs. (6)–(8). Consequently, the decay of the intensity of Balmer-β radiation must be known. The situation is complicated by the presence of a fixed magnetic field of 0.02 T, which confines the electron beam, and without which the experiment would be unfeasible. The fast excited D atoms produced by dissociative recombination travel perpendicularly to the magnetic-field direction, and thus experience a motional electric field (about 3000 V/m for 500-eV D_2^+) directed along the axis of observation. This electric field is of sufficient magnitude to cause Stark mixing of the Zeeman-shifted D ($n = 4$) states, and depends linearly on the atom velocity. As a result, both the decay rate of Balmer-β intensity and the fraction $b(485.9)$ of D ($n = 4$) atoms which decay giving off Balmer-β light (branch ratio) depend on the degree of Stark mixing, and hence the incident-ion velocity.

Since the external magnetic field is uniform along the ion beam axis over the entire field of view of the detection system and dissociative recombination takes place in the field, ordinary time-independent perturbation theory of the weak-field Stark and Zeeman effects was employed to calculate the approximate eigenfunctions and eigenvalues of D ($n = 4$) atoms in the fields, and from them the mean lifetimes and branch ratios were deduced for each of the perturbed $n = 4$ states. Details of the calculation are outlined in the Appendix. The estimates of lifetimes and branch ratios were first based on the assumption that each of the 32 perturbed D ($n = 4$) eigenstates has an equal probability of being populated by the dissociative recombination process in the absence of definitive theoretical evidence to the contrary. An alternative

calculation was performed assuming that excited D (n = 4) atoms are produced only in the perturbed 4s states by dissociative recombination. The mean lifetimes and branch ratios calculated on the basis of these two assumptions are listed in Table I for the ion-beam energies used in the present experiment. Although the calculated expressions for the decay of the total intensity of the Balmer-β radiation were not purely exponential (rather a weighted sum of exponential decay terms for each of the perturbed states), deviations resulting from the use of an exponential decay with the calculated mean lifetime were at most a few percent, and, consequently, the lifetimes listed in Table I were used in conjunction with Eqs. (6)–(8) to correct the observed signal count rates. The magnitudes of these corrections for ion velocities used in the present experiment are also listed in Table I. The experimental situation is depicted graphically in Fig. 1, where the measured relative spatial sensitivity function and the calculated relative Balmer-β intensity [corresponding to part (a) of Table I] are plotted against distance from the center of the interaction region along the path of the ion beam.

The experimental dissociative-recombination cross-section data calculated from Eqs. (3)–(8) using the mean lifetimes and branch ratios quoted in parts (a) and (b) of Table I are presented in Figs. 2(a) and 2(b), respectively. Measurements taken at three different ion energies are distinguished in the graphs. Each data point represents 25–30 h of integration time, and bars are statistical, designating one standard deviation of the mean. The energy spread of the electron beam ranged from 0.5 eV at the lowest energy of 0.6 eV to 0.9 eV at 7 eV. It should be borne in mind that the data in Figs. 2 correspond to the particular

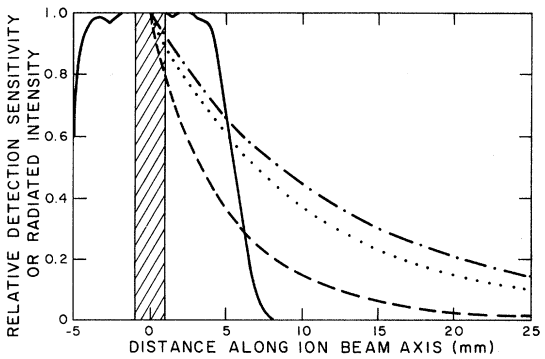

FIG. 1. Superimposed plots of the spatial variations along the ion beam axis of the measured relative detection sensitivity (solid curve) and the calculated relative intensities of Balmer-β radiation. (The dashed, dotted, and dot-dashed lines represent the calculated 485.9-nm intensities for 463, 1901, and 2933-eV incident D_2^+ ions, respectively, and correspond to data in part (a) of Table I. The cross-hatched region represents the extent of the electron beam.

vibrational-state distribution of our target D_2^+ beam, which is expected to correspond to that determined by von Busch and Dunn,[21] as noted previously.

IV. UNCERTAINTIES AND DISCUSSION

In Fig. 2(a), in which the data have been reduced according to the assumption that all perturbed D (n = 4) states are equally likely to be populated, the data points taken at ion energies of 1901 and 2933 eV lie about 50% above those taken with 463-eV ions. Although the discrepancies are within statistical uncertainties at the 95% confidence level, the trend seems to be genuine, and suggests that perhaps the assumption of equal initial popu-

TABLE I. Computed mean lifetimes and branch ratios for D (n = 4).

Assumption about initial conditions	Incident ion energy (eV)	Electric field (V/m)	Mean lifetime τ (nsec)	Balmer-β branch ratio b(485.9)	Finite lifetime correction to $\eta(z_0, 485.9)$ [Eq. (6)]
(a) All perturbed n = 4 states assumed equally populated by dissociative recombination	0	0	35.0	0.291	...
	463	2980	34.7	0.288	37%
	1901	6040	34.5	0.287	61%
	2933	7500	34.4	0.286	66%
(b) Only perturbed 4s states assumed populated by dissociative recombination	0	0	230	0.575	...
	463	2980	39.3	0.194	43%
	1901	6040	26.1	0.199	53%
	2933	7500	24.2	0.206	57%

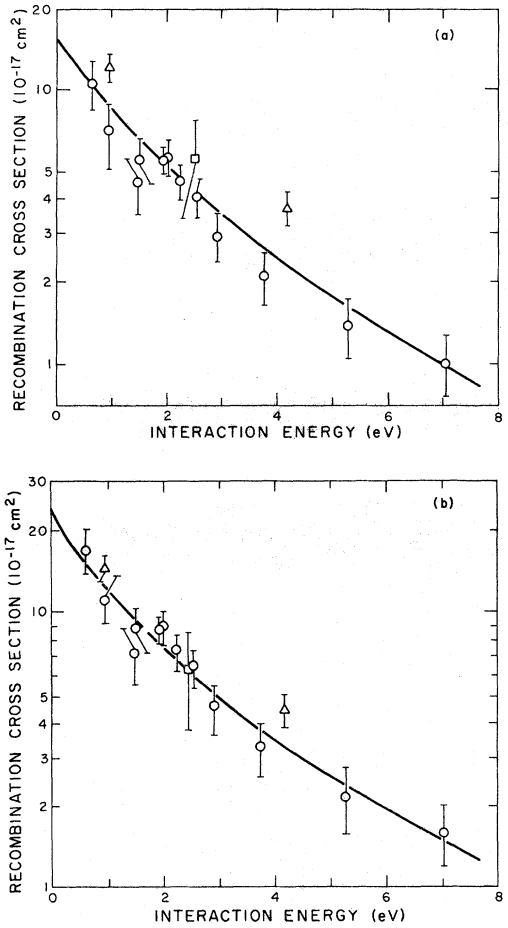

FIG. 2. Experimental cross sections vs electron energy for the process $e + D_2^+ (X\,^2\Sigma_g^+) \rightarrow D + D^*$ ($n=4$). Points ○, △, and □ represent data for 463-, 1901-, and 2933-eV incident D_2^+ ions, respectively. Error bars indicate one standard deviation of the mean. (a) Cross sections obtained from Eqs. (3)–(8) using calculated mean lifetimes and branch ratios listed in Table I(a), which result from the assumption that all perturbed D* ($n=4$) states are equally populated. (b) Cross sections obtained from Eqs. (3)–(8) using calculated mean lifetimes and branch ratios listed in Table I(b), which result from the assumption that only the perturbed 4s states are populated.

lations in all states may not be valid.

Recent calculations of Bottcher[16] predict that dissociative recombination goes almost exclusively through the lowest $^1\Sigma_g^+$ resonance. It has been noted by Bardsley[24] that if the electron is captured into this $^1\Sigma_g^+$ state, a transition to a second state of D_2^* is required to give the observed final D* state, and this transition probably occurs through a curve crossing, implying that the second molecular state should also be a $^1\Sigma_g$. Consequently, product states of D* for which $m_j = \pm\frac{1}{2}$ might be favored. An analogous calculation of the mean lifetimes and branch ratios was performed in which only the perturbed states for which $m_j = \pm\frac{1}{2}$ were assumed to be populated. The resulting cross sections were found not to differ from those presented in Fig. 2(a) by more than a few percent. Figure 2(b) shows the data as reduced assuming that only the perturbed 4s states are populated by dissociative recombination. This latter assumption was not based on any known theoretical model for the recombination process, but was made in order to establish a limit on the uncertainty in the data analysis which can arise from our lack of specific knowledge about the interaction itself. The discrepancies between the data taken at different ion energies are seen to be essentially removed, although the magnitudes of the recombination cross sections are larger than those of Fig. 2(a) by some 50% mainly owing to the decrease in the calculated branch ratio $b(485.9)$. The interpretative analysis which is required to extract the recombination cross sections from the experimental measurements gives rise to uncertainties which are not well defined in the absence of detailed knowledge of the recombination mechanism. The experimental results presented in Figs. 2(a) and 2(b) have been arrived at on the basis of two quite different assumptions concerning the recombination process. These particular assumptions would be expected to result in mean lifetimes and branch ratios, and thus magnitudes of the cross sections, which exhibit maximum differences from one another. Consequently, the actual magnitude of the recombination cross sections is expected to lie somewhere within the limits established by the plots of Figs. 2(a) and 2(b).

The extremely low signal levels limited the number of systematic checks which could be performed. The dependences of the cross sections on the background pressure in the interaction volume and on ion source pressure were investigated by changing each by a factor of 2, and negligible differences were observed under such conditions. The inherent systematic uncertainties of measurement are essentially the same as have been carefully outlined in previous reports,[17–19] with the few exceptions noted below. Corrections for increases in electron path lengths in traversing the ion beam due to spiraling about the confining magnetic field lines are somewhat larger than those of previous experiments due to the lower electron energies. These corrections were estimated from results of an experimental and theoretical analysis of the problem by Taylor *et al.*,[25] and ranged from 15% at the lowest electron energy of 0.6 eV to 1.4% at 7 eV. The corrections have been estimated to be accurate to within a factor of 2. As has been already noted, an additional uncertainty of about 3%

is introduced as a result of the interpolation of the absolute optical calibration from previous measurements. A combination in quadrature of uncorrelated systematic uncertainties leads to values of 14% and 8% at electron energies of 0.6 and 7 eV, respectively. The precision of the cross-section data is about 25%, which corresponds to one standard deviation of the mean.

Figure 3 shows for comparison curves representing the present experimental results for the D*(n = 4) channel and also the experimental cross sections measured by Peart and Dolder[7] for total electron dissociative recombination of D_2^+, as well as the data of Vogler and Dunn,[9] which refer to the particular channel in which one of the product D atoms is in the $2p$ state. All three sets of data are expected to correspond to the target-D_2^+ vibrational-state population distributions measured by von Busch and Dunn.[21] The results of Peart and Dolder for the total recombination cross section and the present results are seen to exhibit a similar behavior with electron energy. The results for the $2p$ channel were likely influenced by cascade from higher excited states and are considered to be an upper limit for the cross section. The fact that the n = 4 and n = 2 channels each account for only about 10% of the total cross section suggests that deuterium atoms formed by dissociative recombination are likely to be found in excited states with a variety of principal quantum numbers.

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APPENDIX

In order to correct the observed Balmer-β intensities to account for excited atoms which radiate downstream beyond the field of view of the detector, and to deduce the n = 4 state populations from observed photon count rates, knowledge is required of the time behavior of the decay of 485.9-nm intensity and of the fraction of D (n = 4) atoms which radiate at this wavelength. Since the excited atoms are produced and the detected photons are emitted in a region of uniform transverse magnetic field, these atoms experience a constant motional electric field. Consequently, we use the usual time-independent perturbation theory of the weak-field Stark and Zeeman effects to calculate the approximate perturbed eigenfunctions and eigenenergies for each m_j sublevel of the D (n = 4) states, and from them deduce the mean lifetimes and branch ratios for the perturbed states. The calculation is generally similar to that employed by Sellin *et al.*[26] in their analysis of periodic intensity fluctuations of Balmer lines from foil-excited hydrogen atoms.

The Hamiltonian H for a D (n = 4) atom is written

$$H = H_0 + H_{\text{f.s.}} + H_{\text{rad.}} + H_{\text{Stark}} + H_{\text{Zeeman}} . \tag{A1}$$

The Pauli eigenfunctions of the unperturbed Hamiltonian H_0 form the basis set for the calculation and should be adequate for the present case; since the electric fields in the experiments are not sufficiently strong to mix the n = 4 states with levels of different n. The fine-structure and radiation Hamiltonians, $H_{\text{f.s.}}$ and $H_{\text{rad.}}$, are treated phenomenologically as perturbations by including exact fine-structure splittings and Lamb shifts in the appropriate diagonal terms of H.

The coordinate system for the calculation (which differs from that referred to in the main text) was chosen such that the incident ion beam travels in the y direction, and the magnetic and motional electric fields are directed along the z and x axes, respectively. Considering only terms to first order in the field strengths, we have

$$\begin{aligned} H_{\text{Stark}} &= -e\vec{F}\cdot\vec{r} = -eFx = -eFr\sin\theta\cos\phi , \\ H_{\text{Zeeman}} &= -\vec{\mu}\cdot\vec{B} = -\mu_z B = g_j \mu_B B J_z , \end{aligned} \tag{A2}$$

where F is the motional-electric-field strength, given by

$$F = vB . \tag{A3}$$

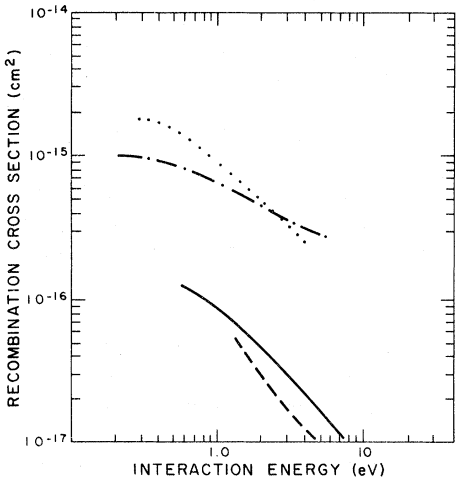

FIG. 3. Experimental and theoretical cross sections for electron-D_2^+ dissociative recombination. Dotted line: $e + D_2^+ \rightarrow D + D^*$ [experimental, Ref. 8]; Dot-dashed: $e + D_2^+ \rightarrow D + D^*$ [theoretical Ref. 16]; dashed: $e + D_2^+ \rightarrow D + D^*(2p)$ [experimental, Ref. 9]; solid: $e + D_2^+ \rightarrow D + D^*$ (n = 4) [this work, representing the curve in Fig. 2(a)].

B is the magnetic flux density (0.02 T); $\vec{\mu}$ is the atomic magnetic moment; μ_B is the Bohr magneton; g_j is the Landé factor, and v is the atomic velocity. The values of F for the different target-ion energies used in the experiments are listed in Table I.

The matrix H_{Zeeman} is diagonal, and matrix elements of H_{Stark} vanish except between states for which $\Delta l = \pm 1$, $\Delta m_j = \pm 1$. The total Hamiltonian H was diagonalized and the approximate perturbed eigenfunctions and eigenvalues were calculated by a standard computer analysis.

The stationary eigenstates of the system in the presence of the external fields are given by the time-independent perturbation expansion

$$\psi_j(\vec{r}) = \sum_i a_{ij}\phi_i(\vec{r}), \tag{A4}$$

where the coefficients a_{ij} are determined by diagonalization of H, and $\{\phi_i\}$ represents the set of 32 Pauli ($n=4$) eigenfunctions. The corresponding time-dependent wave function for an atom in the fields can be written

$$\Psi(\vec{r}, t) = \sum_j c_j\psi_j(\vec{r})\exp\left[-\frac{(iE_j + \Gamma_j/2)t}{\hbar}\right] \tag{A5}$$

where the coefficients c_j are determined by the initial conditions on the system, and E_j and Γ_j are, respectively, the energy and width of perturbed eigenstate ψ_j.

The target D_2^+ ions travel in a region of uniform magnetic field for some 16–40 nsec (depending on the beam energy) before interacting with the electron beam, and this field remains uniform along the ion beam path over the entire range of the photon-detection system. Since these transit times in the field are large compared to the time scale of the Stark mixing ($\hbar/H_{\text{Stark}} \sim 0.1$ nsec), we assume that an excited D ($n=4$) atom produced by dissociative recombination at $t=0$ occupies one of the perturbed stationary states $\psi_j(\vec{r})$. For an atom formed in the kth stationary state, this gives $c_j = \delta_{jk}$, and for the time-dependent wave function

$$\Psi_k(\vec{r}, t) = \psi_k(\vec{r})\exp\left[-\frac{(iE_k + \Gamma_k/2)t}{\hbar}\right] = \sum_i a_{ik}\phi_i(\vec{r})\exp\left[-\frac{(iE_k + \Gamma_k/2)t}{\hbar}\right]. \tag{A6}$$

Ignoring hyperfine structure and the relatively small differences in the photon frequencies due to differences in the perturbed eigenenergies E_j, the radiation from an atom represented by (A6) to all possible final states Φ_f is given by

$$I_k(t) \propto \sum_q \sum_f |\langle\Phi_f|X_q|\Psi_k\rangle|^2, \tag{A7}$$

where $\langle\Phi_f|X_q|\Psi_k\rangle$ is the usual electric dipole matrix element for a radiative transition, and X_q is the component of X along polarization direction q. Substituting for Ψ_k from (A6) gives

$$I_k(t) \propto \sum_q \sum_f \Big|\sum_i a_{ik}\langle\Phi_f|X_q|\phi_i\rangle\Big|^2 e^{-\Gamma_k t/\hbar}. \tag{A8}$$

To simplify calculations, we assume that the phases of the mixing coefficients a_{ik} are random and neglect the sum over interference terms in (A8). This assumption is based on the fact that the transit times of the incident ions across the uniform extent of the electron beam are of the order of 10 nsec, and the interaction can occur anywhere within this time domain, which is comparable to the mean lifetimes against radiative decay. The expression for the total radiated intensity then becomes

$$I_k(t) \propto \sum_i |a_{ik}|^2 \sum_f \sum_q |\langle\Phi_f|X_q|\phi_i\rangle|^2 e^{-\Gamma_k t/\hbar}. \tag{A9}$$

We assume that the lower states Φ_f are not perturbed by the fields, which is justified by the fact that the electric field strengths needed for equivalent mixing vary roughly as n^{-5} (a factor of 4 larger for $n_f = 3$, 32 for $n_f = 2$). We then can write

$$\sum_q |\langle\Phi_f|X_q|\phi_i\rangle|^2 \propto A_{if}, \tag{A10}$$

where A_{if} is the Einstein transition probability for electric-dipole transitions between unperturbed states ϕ_i and Φ_f.

The width Γ_k of perturbed state ψ_k is determined by the relative admixture of basis functions in its wave function,

$$\Gamma_k = \sum_i |a_{ik}|^2\gamma_i, \quad \gamma_i = \hbar\sum_f A_{if}, \tag{A11}$$

where γ_i represents the width of unperturbed basis state ϕ_i. Combining Eqs. (A9)–(A11), we obtain an expression for the total radiated intensity from an ensemble of atoms produced in perturbed state ψ_k,

$$I_k(t) \propto \Gamma_k e^{-\Gamma_k t/\hbar}. \tag{A12}$$

The fraction b_k of D ($n=4$) atoms in the kth perturbed state which decay by giving off Balmer-β radiation is

$$b_k = \sum_{f(n=2)}\left(\sum_i |a_{ik}|^2 A_{if}\right) \Big/ \sum_{f(n=3,2,1)}\left(\sum_i |a_{ik}|^2 A_{if}\right). \tag{A13}$$

Making the assumption that an excited D ($n=4$) atom produced by dissociative recombination has

an equal probability of occupying any of the 32 perturbed eigenstates $\Psi_k(\vec{r}, t)$ results in the following expression for the total intensity of Balmer-β radiation from such an ensemble of atoms:

$$I_\beta(t) \propto \sum_k b_k \Gamma_k e^{-\Gamma_k t/\hbar} . \tag{A14}$$

The fraction $b(485.9)$ of the ensemble which radiates Balmer-β is given by

$$b(485.9) = \frac{1}{32} \sum_k b_k . \tag{A15}$$

For convenience, we represent the sum over exponential decay terms in (A 14) approximately by the single exponential $e^{-t/\tau}$, with the lifetime τ given by

$$\tau^{-1} = \sum_k b_k \Gamma_k \Big/ \hbar \sum_k b_k , \tag{A16}$$

and substitute the value of τ obtained from this expression into Eqs. (6)–(8) to correct the observed photon count rates. The error introduced by the use of this approximation is less than 2%.

The values listed in part (a) of Table I for the branch ratio $b(485.9)$ and lifetime τ were calculated using Eqs. (A15) and (A16) and correspond to the assumption that all perturbed states have an equal probability of being populated by the dissociative-recombination process. Part (b) of Table I contains results obtained when only the perturbed $4s(m_j = \pm\frac{1}{2})$ states are assumed to be populated by the interaction. In this case the sums over k in Eqs. (A15) and (A16) were restricted to two terms representing the perturbed 4s states, and the factor $\frac{1}{32}$ in Eq. (A15) was replaced by $\frac{1}{2}$.

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