First Observation of Four-Body Breakup in Electron Recombination: $C_2D_5{}^+$

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We report the first observation of four-body breakup in electron dissociative recombination of a molecular ion: $C_2D_5{}^+$. In an ion storage ring experiment, the branching ratio for the process $C_2D_5{}^+ + e^- \rightarrow C_2D_2 + D + D + D$ was determined to be 13%. This means that three covalent chemical bonds are broken as a result of the action of a single electron. This is the first time a four-body breakup of chemical bonds has been observed in a low-energy binary reaction.

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Dissociative recombination (DR) is the process wherein a molecular ion captures a free electron and then disposes the reaction energy by dissociating into neutral atoms and/or molecules. This complex process plays a significant role in determining the chemical composition of many natural and laboratory-produced plasmas, including plasma-enhanced combustion, as it is the dominant neutralization mechanism for plasmas in which the gas temperature is a few thousand degrees or less and the electron temperature is lower than a few eV (i.e., $T_e <$ 30 000 K) [1]. Chemical kinetic models used in the fields of astrophysics, atmospheric science, combustion, and plasma processing are sensitive to the choice of DR energy-dependent rate constants or cross sections as well as reaction product distributions, which are used as input in such models.

A variety of experimental techniques have been utilized to measure DR kinetics, including merged beam, shock-heated and flowing afterglow, ion trap, IR spectroscopic techniques, and more recently ion storage rings. The field has been recently reviewed by Larsson [1] and by Mitchell [2]. Until the application of ion storage ring techniques, determining complete product branching ratios proved to be extremely difficult for all but the simplest of molecular DR reactions. Ion storage rings offer particular advantages for measuring branching ratios, owing to the high luminosity obtained with a circulating ion beam and the high energy at which the ions are stored.

The experimental difficulties were compounded by the lack of any satisfactory theoretical treatment for predicting the product distributions of DR for polyatomic ions. Calculating the DR product branching ratios for polyatomic ions from first principles has proven to be exceedingly challenging, due to the difficulty of treating molecular dissociation of such a highly excited species along a multidimensional potential. The mechanisms of DR have recently been reviewed by Guberman [3,4]. One often cited argument put forth by Bates [5,6] suggested the most favored dissociative channels would be those necessitating the fewest rearrangements of valence bonds.

This conventional wisdom was shattered when the first DR measurements of polyatomic ions were reported from the ion storage rings [7]. A richer, and more violent, chemical process was revealed, one exhibiting a larger number of product channels, more strong-bond dissociations, and more fragmentation into three neutral products (the so called "three-body dissociation products"). The growing number of storage ring DR measurements continues to show surprising results. Here we report results for the recombination of electrons with $C_2D_5{}^+$, showing the first evidence for a four-body dissociation product channel in an electron-molecular cation recombination reaction. The geometric structure of $C_2D_5{}^+$ is shown in Fig. 1.

Measurements were made at the CRYRING heavy ion storage ring located at the Manne Siegbahn Laboratory in Stockholm, Sweden. The facility and the experimental procedure have been described previously in detail [8]. The dissociative recombination neutral reaction products were detected by means of an ion-implanted surface barrier detector, and the branching ratios were obtained by means of the transmission grid technique [9]. The

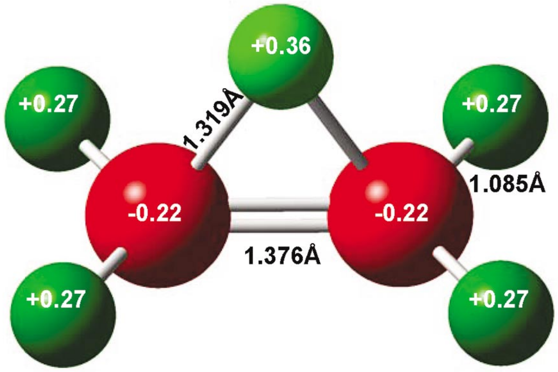

FIG. 1 (color). Geometric structure of $C_2D_5{}^+$ calculated with GAUSSIAN03 [23] at the B3LYP/$6-311++G(3df,2p)$ level of theory. The shades represent charge on each atom (also given numerically), obtained from a natural population analysis.

energy-dependent DR cross section for $C_2D_5{}^+$ is very large 7.5×10^{-13} cm^2 at 1 meV with no apparent resonances over the entire energy range studied, i.e., 1–100 meV. The DR cross section decreases with increasing collision energy as $E^{-1.11}$. For ions of the form $C_2H_n{}^+$, where $n = 1$–5, the magnitude of the cross section depends only weakly on n [9,10]. The thermal rate coefficients, determined by convoluting the DR cross sections over a Maxwellian temperature distribution, are represented by $\alpha(T_e) = [(2.8 \pm 0.5) \times 10^{-7}] \times (T/300)^{-(0.79\pm0.03)}$ cm^3 s^{-1}. The energy dependence is slightly larger than that expected for the direct mechanism of DR, indicating that part of the DR is due to the indirect mechanism [3], which implies that some electrons are captured into predissociating Rydberg states instead of directly into a dissociating neutral state.

The product branching ratios were obtained by inserting a grid with a well-defined transmission probability in front of the detector [7,9,10]. Particles blocked by the grid were not detected, so peaks in the pulse-height spectrum represent a mass spectrum consisting of the undissassociated neutral molecule and all possible neutral fragments. Assignment of the peaks to different masses is straightforward and unambiguous, and the intensities of the peaks can be associated with contributions from all the possible dissociation channels through a set of linear equations. Branching fraction experiments were done only at nominally zero collision energy, which in practice means collision energies of 1 meV or smaller, as determined by the energy spread in the electron beam.

At zero collision energy, ten possible exothermic dissociation channels exist for the reaction of $C_2D_5{}^+$ with an electron:

$$C_2D_5{}^+ + e^- \rightarrow C_2D_4 + D + 6.55\ \text{eV} \tag{1}$$

$$\rightarrow C_2D_3 + 2D + 1.81\ \text{eV} \tag{2}$$

$$\rightarrow C_2D_3 + D_2 + 6.32\ \text{eV} \tag{3}$$

$$\rightarrow C_2D_2 + 3D + 0.33\ \text{eV} \tag{4}$$

$$\rightarrow C_2D_2 + D_2 + D + 4.85\ \text{eV} \tag{5}$$

$$\rightarrow CD_3 + CD_2 + 3.84\ \text{eV} \tag{6}$$

$$\rightarrow CD_4 + CD + 2.7\ \text{eV} \tag{7}$$

$$\rightarrow C_2D + 2D_2 + 8.50\ \text{eV} \tag{8}$$

$$\rightarrow C_2D + D_2 + 2D + 3.98\ \text{eV} \tag{9}$$

$$\rightarrow CD_3 + C + D_2 + 0.45\ \text{eV} \tag{10}$$

The indicated kinetic energy release is a maximum value, which assumes all products are formed in their ground state [11].

From the energy spectrum of $C_2D_5{}^+$ dissociative recombination fragment products shown in Fig. 2, it is immediately apparent that the branching ratios for channels (8) and (9) are zero since contributions from these channels would result in the formation of a C_2D fragment at 26 amu, which is not observed. Similarly, the absence of signal at 12 amu indicates channel (10) is also closed. A system of linear equations describing the contributions of the remaining seven channels to the different mass peaks is solved in order to obtain the product branching ratios. Such an analysis indicates channel (3) is also closed, and channel (7) cannot be definitely distinguished from zero, having a determined branching ratio of 0.01 ± 0.01. Branching ratios for the remaining five channels are shown in Table I.

A general conclusion from the statistical phase-space theory of Herbst [12,13] is that although polyatomic ion-electron reactions can produce an assortment of neutral

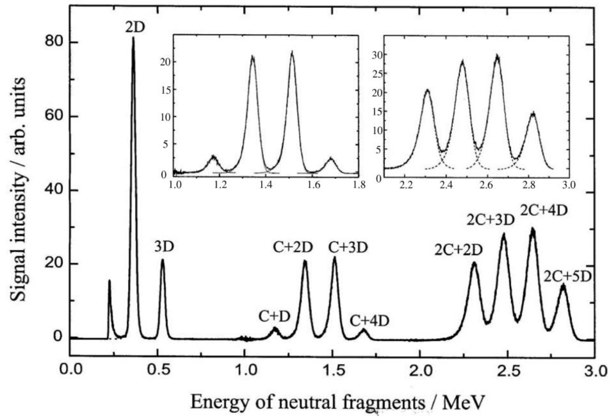

FIG. 2. All neutral fragments originating from one recombination event reached the detector at approximately the same time (i.e., all had essentially the same velocity), and each fragment impinged on the detector with an energy proportional to its kinetic energy and, hence, its mass. Pulse-height spectrum for the $C_2D_5{}^+ + e^-$ recombination reaction with a grid ($T = 0.297$) in front of the detector. The solid line refers to to the experimental data, whereas the dashed line depicts the fit. The inserts show the Gaussian fits (dashed lines) of the two groups of peaks corresponding to the C + nD and 2C + nD signals, where the 2C + 5D signal occurs at the full beam energy of 2.8 MeV. The background signal from collision induced dissociations with the ambient gas has been subtracted. This background signal was determined when the electron beam was switched off. The branching ratios were measured at 1 meV center of mass collision energy. Since the peaks are slightly assymmetric each of the peaks was fitted to a sum of two Gaussian functions of which the distance between them was constant for each group of overlapping peaks. This ensured a fit that is virtually undistinguishable from the data.

species, the reaction pathways involving only minimal disruption of the molecular ion as a result of electron attack and subsequent bond breakage—for example, loss of a single hydrogen atom or molecule—is always a prominent if not the dominant channel. A previous consideration of $C_2D_5{}^+$ dissociative recombination by Bates [6] concluded that the primary dissociation channels would likely be (1) and (6), with much smaller contributions from (2)–(4) or (5).

As indicated in Table I, the channels involving minimal disruption of the molecular ion and/or removal of only a single valance bound atom/fragment are in fact observed; however, they are clearly not the dominant channels. Channel (1), which corresponds to rupture of the carbon-deuterium bond to form C_2D_4 and a deuterium atom, and channel (6), which represents direct cleavage of the carbon-carbon bond, both have relatively small branching fractions of 0.12 and 0.17, respectively. Direct cleavage of single valance bonds, as suggested by Herbst and by Bates, accounts for less than 30% of the overall reactivity.

The $C_2D_5{}^+$ recombination reaction shows a propensity to undergo multibody fragmentation by the loss of additional deuterium species; dissociation of two carbon-deuterium bonds upon recombination accounts for 27% of the overall reactivity, while dissociation of three such bonds represents the largest reactivity component with a branching percentage of over 40%. While storage rings have uncovered more three-body dissociation pathways than had previously been anticipated, the observation of a four-body product channel for dissociation of a molecular species is still very surprising.

Formation of neutral products via channel (4) requires nearly all the reaction exothermicity to be directed into internal energy of the $C_2D_5{}^*$ species and not into translational energy. The present data do not allow a distinction to be made between a concerted expulsion of two or three deuterium atoms and a sequential dissociation mechanism for forming the products of channels (2) and (4). [Channel (1) is sufficiently exoergic to form a C_2D_4 neutral with a large amount of internal energy, allowing for possible subsequent dissociations of one or even two deuterium atoms.] A previous report on the dynamics of H_2O^+ recombination demonstrated that the three-body product channel, forming $2H + O$, occurs via a single-step dissociation without a well-defined $H_2{}^*$ or OH^* intermediate [14]. For a more complicated polyatomic such as $C_2D_5{}^+$, it is not possible to conduct the position/time sensitive kinetic energy release measurements required to differentiate the dissociation mechanism, since the molecular neutral fragments can be formed in any rovibrational state up to the dissociation limit. In approximately 30% of the reactions, the initial dissociation, whether concerted or sequential results in net loss of D_2, as shown in channel (5). The large fraction of events leading to the formation of D_2 is also unusual [7,9,10,15].

TABLE I. Branching ratios at one meV collision energy for the different channels of the $C_2D_5{}^+ + e^-$ recombination reaction. The errors given in parenthesis stem from the errors obtained by fitting the peaks in the mass spectrum and the error from the experimental determination of $N_a L_\alpha$.

Product channel	Branching ratio
(1) $C_2D_4 + D + 6.55$ eV	0.12 (0.03)
(2) $C_2D_3 + 2D + 1.81$ eV	0.27 (0.04)
(4)$C_2D_2 + 3D + 0.33$ eV	0.13 (0.03)
(5)$C_2D_2 + D_2 + D + 4.85$ eV	0.29 (0.03)
(6)$CD_3 + CD_2 + 3.84$ eV	0.17 (0.01)

Four-body fragmentation has previously been studied in some detail in for example dissociative photoionization of D_2 [16] and electron-impact double-ionization of He [17], where the four-body fragmentation occurs as a consequence of electron-electron correlation, and in photodetachment of the cluster ion $O_8{}^-$ [18], where four oxygen molecules results from the removal of the loosely bound electron. Neither of these cases are comparable with the present observation of the formation of four neutral products, and hence the breaking of three chemical bonds, by the recombination of $C_2D_5{}^+$ with an electron.

The measurements reported here for the dissociative recombination of $C_2D_5{}^+$ are expected to play an important role in both plasma-enhanced combustion and astrophysical chemical kinetics models. Plasma-enhanced combustion is the deliberate introduction of plasma or ionic species into a combustion environment in order to enhance ignition. Chemical kinetic modeling has shown the enhancing effect of the ionic species to be highly sensitive to the number of radical fragments produced during dissociative recombination, the model's ionic termination step [19]. Since $C_2H_5{}^+$ is one of the more abundant ions present in plasma-enhanced combustion environments, the large degree of fragmentation observed upon DR will undoubtedly have a significant impact on the kinetic modeling results. Astrophysical models have recently started to incorporate three-body product channels for DR reactions, based on general conclusions from the initial storage ring measurements. For $C_2D_5{}^+$, the initial model of Herbst and coworkers [20] included reaction channels representing loss of either one D-atom or one D_2 molecule with equal probability, whereas more recent models use losses of one, two, three, and even four deuterium atoms with branching ratios of 0.2, 0.2, 0.4, and 0.2, respectively [21,22]. Only two- and three-body product channels were considered ($D_2 + D$ and $2D_2$, for example, not 3D).

As noted previously, the complexity of the DR process makes it difficult to develop a general theory capable of predicting branching ratios for the DR of polyatomic molecular ions. In discussing the various mechanisms that drive dissociative recombination, Guberman illustrates how very small interactions can play a large role in the DR of diatomic and triatomic ions and how the DR of polyatomic ions is even more complicated due to the additional degrees of freedom[3,4]. Clearly, a better theoretical understanding of the fragmentation mechanism is needed. The current storage ring measurement of the $C_2D_5{}^+$ recombination reaction reveals competition between carbon-carbon and carbon-deuterium bond dissociation and also reveals breakup into two, three, and four-body products from reaction channels with excess exothermicity ranging from 0.33–6.7 eV, and as such appears to be an excellent data set for theoretical consideration.

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