Electron-impact dissociative excitation of CD_n^+ $(n=2-5)$: Detection of light fragment ions D^+ and D_2^+

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Absolute cross sections are reported for the electron-impact dissociative excitation of the deuterated hydrocarbon ions CD_n^+ $(n=2-5)$ from threshold to 70 eV using a crossed beams technique. The method focuses on detecting and measuring light dissociation-product ions from a heavy target. The ion targets are typical of those formed in the discharge ion source, and some may be in excited electronic and/or vibrational states. A common feature of the studied targets was a dominant D^+ formation cross section with almost the same absolute value of 2×10^{-16} cm^2 for all n from 25 to 70 eV. The present measurements are compared with the available data, and for D^+ from CD_2^+ and CD_5^+ the data agree well with recent results obtained with the storage-ring technique. [S1050-2947(98)01207-4]

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I. INTRODUCTION

Simple hydrocarbon molecular ions are important constituents in planetary and commentary atmospheres [1]; they are present in some plasma processing [2]; and they are important as impurities present in edge plasmas of fusion reactors [3]. Electron-impact dissociative excitation, ionization, and recombination of simple hydrocarbons are all important collision processes that must be considered and included in modeling of these plasmas. Only a limited number of measurements on molecular ions have been carried out [4], if one does not include activity in the field of dissociative recombination [5]. The lack of data for dissociative excitation (DE) is even more extreme when the light fragment ions (H^+, H_2^+) are detected as the dissociation products from hydrocarbon ions. One reason for this is that the excess kinetic energy released in the DE is predominantly carried away by light dissociation fragments, making it difficult to collect and detect all of them [6].

We have previously reported [6] DE cross sections for obtaining D^+ from CD^+ and described in some detail the technique for the measurements. As a continuation of our work on electron-impact dissociation, with emphasis on light fragment ion detection, we present absolute cross sections for D^+ and D_2^+ from CD_n^+ $(n=2-5)$. Depending on the interaction energy, different dissociative processes are contributing more or less to the formation of D^+, and they are represented by

$$e+CD_n^+\rightarrow D^+ + \text{products} + e,$$

$$e+CD_n^+\rightarrow D^+ + \text{products} + 2e, \qquad (1)$$

and

$$e+CD_n^+\rightarrow D^+ + \text{products}.$$

These processes are, respectively, called dissociative excitation, which could be direct or resonant (RDE), dissociative ionization (DI), and resonant ion pair formation (RIP); their cross sections are herein denoted by σ_{DE}, σ_{DI}, and σ_{RIP}.

The present absolute cross section results are compared with the data from storage ring experiments [7,8] and with the cross sections deduced by Ehrhardt and Langer [9] in their survey for controlled fusion.

II. EXPERIMENTAL METHOD

As noted above, the JILA crossed beams apparatus, which was adapted for light fragment ion detection, and the experimental procedure employed to obtain absolute cross sections have been described in detail in a previous publication [6]. Briefly, ions are extracted from a dc discharge ion source [10], accelerated to 7000 eV energy, mass selected by a 60° sector magnet, and directed into a collision chamber, where a magnetically confined electron beam [11] intersects the ion beam at 90°. Source conditions were empirically optimized (mixture of CD_4 and He) for maximum source stability and ion beam intensity. The target ions produced in this way could be in vibrationally and/or electronically excited states; it was not possible to control or calculate the state distributions. A major problem that accompanies colliding beams experiments is the presence of rather large fragment counting rates due to breakup of target ions on both ambient gas particles and surfaces. It is necessary to perform systematic checks to eliminate spurious false signals and to chop the electron beam (in our experiment at 1000 Hz) in order to separate the true signal produced in the electron-ion collisions from background events.

Fragment ions resulting from the dissociation of the target ions may gain several electron volts of kinetic energy from the dissociation, and as a consequence they will have a larger angular spread than the primary beam and will have a broad energy spread as well [6]. In order to assure full collection of fragment ions, extensive ion trajectory modeling using

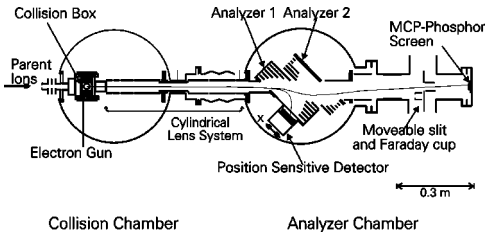

FIG. 1. Crossed electron-ion beams interaction and fragment ion analysis apparatus.

SIMION [12] was carried out for the postinteraction ion optics and detector chamber. The postcollision part of the experimental setup is shown schematically in Fig. 1. Immediately after the collision region, both target and fragment ions experience strong acceleration (by typically 5–7 keV) in the first part of the cylindrical lens system designed to collect, accelerate, and transport the fragment ions of interest into the analyzer chamber. The analyzer chamber contains two 45° electrostatic analyzers, a position sensitive detector (PSD), and a set of horizontal deflectors. The first analyzer separates studied fragment ions from the other product ions and from the parent beam. At the same time, the selected ions are deflected onto the PSD that consists of a pair of microchannel plates with sensitive diameter of 40 mm and a resistive anode. Counts from the PSD are registered according to the x-y positions and time gates in two separate histogram memories so that signal counts can be obtained for all x-y positions. The width of the light fragment ion distribution in the y direction (vertical) is relatively narrow, while in the x direction (direction of PSD movement) it is broader; and for some fragments, especially ones from the heavier studied targets, it can become so great that significantly less than 100% of fragments are detected at that PSD location. To overcome the possibility of signal loss, translation of the PSD to different locations in the x direction is necessary, and a procedure for summing up the signal at different x values must be applied. The PSD is mounted on a linear motion feedthrough with linear travel of 50 mm, and motion is achieved by micrometer adjustment so that reproducible and accurate settings are possible, thus making such a summation procedure reliable. The parent ion beam in large measure retains its initial collimation and with the help of a second 45° electrostatic analyzer and horizontal deflectors that follow, it is redirected toward the electrically isolated small collection chamber, where the ion current is measured.

The dissociation cross section σ at each energy E is determined [6] from the signal count rate R of studied fragment ions; beam currents I_e and I_i and velocities v_e and v_i of electrons and ions, respectively; elementary charge e; form factor F (which takes the spatial overlap of the two beams into account); and detection efficiency ε for collection and detection of the studied ''signal'' ions through the relationship [13]

$$\sigma(E)=\frac{Re^2}{I_eI_i}\frac{v_ev_i}{(v_e^2+v_i^2)^{1/2}}\frac{F}{\varepsilon}. \tag{2}$$

The detection efficiency of the PSD was measured for all fragment ions in separate experiments. For this, beams of a few femptoamperes of either D^+ or $D_2{}^+$ at the appropriate energy were directed alternatively onto the PSD or into a Faraday cup with a vibrating reed electrometer attached. The electron energy scale was calibrated by measuring the cross section for single ionization of N^+ ions, linearly extrapolating it to zero, and ascribing the intercept as the spectroscopic threshold energy [14]. A scanning slit probe located in the center of the collision volume can be rotated to measure spatial profiles of either the electron or the ion beam.

III. RESULTS AND DISCUSSION

The measured absolute cross sections for D^+ fragment production following electron impact on $CD_n{}^+$ $(n=1-5)$ are shown in Figs. 2 and 3. Our previous results [6] for CD^+ are presented in Fig. 2(a) for comparison. The deuterated targets are chosen because the energy and angular spread of D^+ fragment ions are smaller than those of H^+ ions (from $CH_n{}^+$). Relative uncertainties [15], dominated by fluctuation in the form factor, statistical scatter of the data, and uncertainties in the procedure of summing up the signal at different PSD positions are shown at one standard deviation (1σ) level as the bars with the points. The combined absolute uncertainty U at the 1σ level includes systematic uncertainties, which do not affect the relative shape of the data. These are added in quadrature to the relative uncertainties to obtain the total uncertainty, estimated to be 14% at the 1σ level for points near the maximum cross section.

The cross sections for obtaining $D_2{}^+$ fragments from DE of $CD_n{}^+$ $(n=3-5)$ were also measured and they are shown in Fig. 4. They are found to be about an order of magnitude smaller than the cross sections for obtaining D^+ from the same targets. In the early stage of our experiment, we had experimental difficulties that brought us to improperly assign the fragment ions from $CD_2{}^+$ [17]. Our present measurements detecting $D_2{}^+$ from $CD_2{}^+$ show that the cross section is too small to be measured with the present technique.

The main observations may be summarized as follows. (1) Remarkably, the cross sections for obtaining D^+ from $CD_n{}^+$ are effectively identical in value $(2\times10^{-16}\ \mathrm{cm}^2)$ independent of n once the initial rise from threshold is past, continuing to 70 eV, the highest electron energy at which the measurements are done. (2) The cross section for formation of D^+ from a given target dominates that for formation of $D_2{}^+$ by approximately an order of magnitude.

For $n=2$ and 5, measurements have also been performed [7,8] on $CH_n{}^+$ using a storage ring and detecting the complementary neutral to H^+ (CH and CH_4). For comparison, the DE results of Semaniak *et al.* [8] on $CH_5{}^+$ are shown along with the present results for $CD_5{}^+$ in Fig. 3. This comparison is possible because both ions, $CH_5{}^+$ and $CD_5{}^+$, have the same electronic structure. The results are in perfect agreement in the energy range between the threshold and 23 eV, above which they diverge from each other. This is explained by the different techniques used to measure DE. In the present experiment fragment ions, D^+, are detected and the cross section displayed in Fig. 3 is the composite [see Eq. (1)]

$$\sigma_{\mathrm{tot}}=\sigma_{\mathrm{DE}}+\sigma_{\mathrm{DI}}+\sigma_{\mathrm{RDE}}+\sigma_{\mathrm{RIP}}. \tag{3}$$

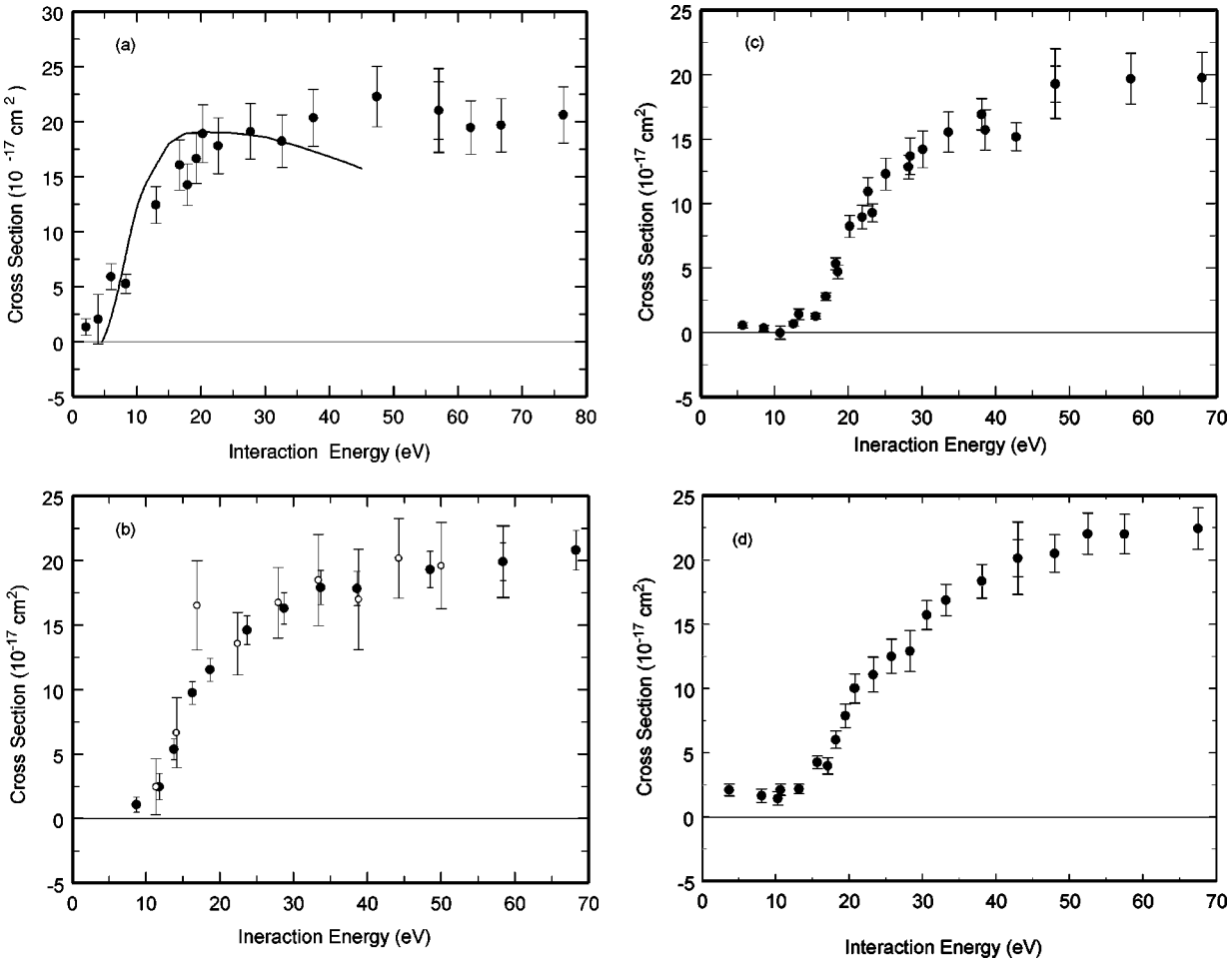

FIG. 2. Absolute cross section vs interaction energy for electrons bombarding CD_n^+ producing D^+. Solid points represent average experimental values, and the bars display relative uncertainties at 1σ level, while the absolute uncertainty at 1σ level is shown at one energy by the outer bar. (a) CD^+ target ions; solid points are from Ref. [6] and the solid curve illustrates the data (C/CD^+) measured in a storage-ring experiment, Ref. [16]. The difference past 30 eV is ascribed to DI (see discussion in Ref. [6] and for CD_5^+). (b) CD_2^+ target ions. Open circles show the data (CH/CH_2^+) measured in the storage-ring experiment, Ref. [7]. Their estimated total uncertainty at the 1σ level is approximately 25% and is shown as the bars at each point. (c) CD_3^+ target ions. (d) CD_4^+ target ions.

The recent storage-ring measurement [8] detected neutral CH_4, and did not register fragments from DI or RIP, so the quantity measured was $\sigma_{DE}+\sigma_{RDE}$. Hence, subtracting the measured cross sections from each other yields $\sigma_{DI}+\sigma_{RIP}$. To perform the subtraction the storage-ring data past 23 eV were first fitted to the functional form $(A/E)\ln E+B$. In Fig. 3 the difference is shown as a solid line and it is hypothesized that this represents σ_{DI}, since for energies above 23 eV, σ_{RIP} should be negligible. Of course, this result must be considered with extreme caution because the internal excitation energies of the ion targets may be different in the two experiments, being ''hot'' in the present experiment and ''cold'' in the storage-ring work.

For $n=2$, the cross sections measured here are identical (see Fig. 3) to those measured with the storage ring [7], indicating no detectable dissociative ionization that yields D^+. At one energy, 17 eV, the ring measurement diverges, but there are no supporting nearby points, so we speculate that this is probably just a simple statistical ''outlyer.''

It is difficult to make definitive statements about the appearance potentials of D^+ from various ions. Sample calculated proton affinities [18] for C, CH, CH_2, CH_3, and CH_4 are, respectively, 5.4, 7.2, 8.2, 5.2, and 5.0 eV. As far as we know, there is no information about repulsive surfaces to which transitions are made to yield the product observed. Since, if one assumes Frank-Condon transitions, the appearance potentials would be the proton affinities plus some unknown energies to reach the repulsive surfaces, no comparisons can be made with expected and observed appearance energies. This is coupled with the fact that the target ions may be internally excited. This latter point is obviated for three cases (CD^+, CD_2^+, and CD_5^+), since, as discussed above, the results agree over the threshold region with storage-ring measurements where the ions have time to relax to the ground electronic and vibrational levels.

We note that in the absence of any measurements on DE of hydrocarbon ions, and driven by the need for such data to model the edge plasmas of fusion devices, Ehrhardt and Langer [9] in 1987 deduced the DE cross sections based on the results for dissociation of neutral hydrocarbon molecules. They also assumed that dissociation is dominated by removal of a single light particle and that the probability of removing each hydrogen from a given hydrocarbon is equal. Our measured cross sections for D^+ from CD_n^+ ($n=2-4$) confirm

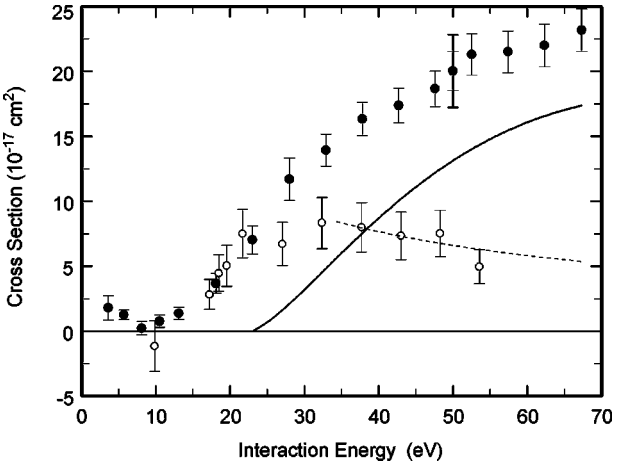

FIG. 3. Absolute cross section vs interaction energy for electrons bombarding CD_5^+ producing D^+. Solid points and bars are as defined in Fig. 2. Open circles show the data (CH_4/CH_5^+) measured in a storage-ring experiment, Ref. [8], and the bars are as defined in Fig. 2(b). The dashed curve is an extension of the ring data, Ref. [8], to higher energies (see text). The solid line is an estimate of the dissociative ionization cross section σ_{DI} (see text), determined by subtracting the storage-ring data from the present data for interaction energies above 23 eV.

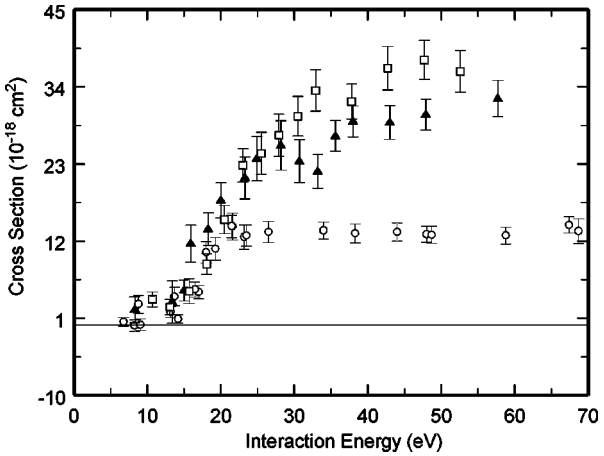

FIG. 4. Absolute cross section measurement for D_2^+ fragments from CD_n^+: ○, CD_3^+; ▲, CD_4^+; □, CD_5^+. Points represent average experimental values, and the bars represent relative uncertainties at the 1σ level.

their deduction that the cross sections have almost the same value independent of n, but their deduced values are three times lower than our measured ones. Deviating from the pattern of sameness, their deduced cross section for H^+ from CH^+ is six times smaller than our measured one.

IV. CONCLUSION

Measurements have been performed and are reported here for electron-impact dissociative excitation of CD_n^+ ions ($n=2-5$) over an energy range 2–70 eV. The total expanded uncertainty in the results is about 20%. Two facts are highlighted. (1) The cross sections for obtaining D^+ from all studied targets are almost the same (2×10^{-16} cm^2) once the initial rise from the threshold is past. We have no models or suggested explanations for this behavior. (2) The most prominent channel, among the studied ones, is the one in which D^+ is formed. The present measurements are compared with those obtained for CD^+ [16], CH_2^+ [7], and CH_5^+ [8] using a storage-ring technique, and the cross sections are found to be identical (CD_2^+) or identical within uncertainties over that part of the energy range where they are expected to be the same (CD^+ [6], CD_5^+). Outside this energy range, the results have been subtracted from each other to obtain an estimate of the dissociative ionization cross section for CD^+ [6] and CD_5^+. The cross section for the dissociation channel where D_2^+ fragment ions are formed is much weaker and it becomes progressively weaker going from D_2^+/CD_5^+ toward the lighter target ions. The employed technique is for measuring light fragment ions in electron-impact dissociative excitation of small heteronuclear ions and it produces data complementary to those becoming available from ion storage rings, in that the method presented here addresses target ions characteristic of a plasma environment.

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