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# Formation of long-lived $CD_n^{2+}$ and $CH_n^{2+}$ dications

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**Abstract.** A systematic study of the formation of $CD_n^{2+}$ and $CH_n^{2+}$ dications in fast charge-stripping collisions with Ar atoms was conducted. The experimental method was based on the detection of the D (or H) fragments of the molecular ion of interest, and thus reducing the effect of the fraction of molecular ions containing the $^{13}C$ isotope and other beam impurities. We observed long-lived $CD_2^{2+}$, $CD_4^{2+}$, and $CD_5^{2+}$ dications. In the same process neither long-lived $CD^{2+}$ nor $CD_3^{2+}$ were observed. The mean lifetime of $CD_2^{2+}$ was determined to be $4.0\ {}^{1.3}_{1.1}$ $\mu$s, and those of $CD_4^{2+}$ and $CD_5^{2+}$ were longer than 2.1 and 3.3 $\mu$s, respectively. The production cross sections of $CD_n^{2+}$ from different $CD_m^+$ beams were measured. Long-lived $CD_2^{2+}$ was formed from all $CD_m^+$ beams ($m \geqslant 2$) and also directly from the rf ion source. In contrast, $CD_4^{2+}$ and $CD_5^{2+}$ were formed only from $CD_4^+$ and $CD_5^+$, respectively.

## 1. Introduction

Long-lived $CH_n^{2+}$ dications have been the subject of experimental and theoretical work since their first discovery in the early 1980s (Ast *et al* 1981, Proctor *et al* 1981 and Rabrenovic *et al* 1983b). These molecular ions were formed, for example, in charge-stripping collisions at keV energies, $CH_n^+ + T \rightarrow CH_n^{2+} + T + e^-$, where T is an atom or molecule (see, for example, Ast *et al* 1981, Proctor *et al* 1981, Rabrenovic *et al* 1983a, b, Raheja *et al* 1986, Mathur *et al* 1986, Mathur and Badrinathan 1987, Mathur 1988, Hamdan *et al* 1988, Hamdan and Brenton 1988). Direct formation from the neutral methane molecule in ion sources is not commonly seen, a fact which was attributed to the poor overlap between the geometry of the dication and the neutral molecule. Better overlap between the doubly and singly charged molecular ions makes the formation of the dications in charge-stripping collisions possible. If the formation of $CH_n^{2+}$ depends strongly on the overlap between the initial and final nuclear wavefunction, as suggested, one would expect the rate of the reaction $CH_m^+ + T \rightarrow CH_n^{2+} + T + e^-$ ($m \geqslant n$) to depend on the choice of the parent molecule. We measured the rate of formation of $CD_n^{2+}$ and $CH_n^{2+}$ from $CD_m^+$ ($m = 1$–5) and $CH_m^+$ ($m = 1$–4) molecular ion beams, respectively, colliding with Ar atoms at 850 keV.

The improved understanding of the structure and properties of the $CH_n^{2+}$ dications was strongly affected by theoretical studies (see, for example, Pople *et al* 1982, Siegbahn 1982, Heil *et al* 1983, Wetmore *et al* 1984, Koch *et al* 1987, Hamdan *et al* 1988, Wetzel *et al* 1993, Gu *et al* 1998). It has been suggested, for example, that $CH_4^{2+}$ has a planar geometry, and

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that explains why it is not formed by direct double ionization of $CH_4$. Another example is the electronic ground state of $CH^{2+}$ for which the calculated potential energy curve has a local well too shallow to support a long-lived state. One experimental complexity for such studies is the possible mixing of $^{12}CH_n^+$ and $^{13}CH_{n-1}^+$ beams (Wetmore *et al* 1984, Koch *et al* 1987, Mathur 1988). We present in the following section an experimental method designed to distinguish between $^{12}CH_n^{2+}$ and $^{13}CH_{n-1}^{2+}$ by dissociating these dications and separating $H_n$ from $H_{n-1}$ events.

It is important to note that our experimental knowledge about $CH_n^{2+}$ dications originates not only from the collisional studies discussed above, but also from photoionization (Dujardin *et al* 1985), Auger spectroscopy (Spohr 1970), double charge transfer in slow $H^+ + CH_4$ collisions (Fournier *et al* 1985) and other methods. Note that some of these methods are limited to $CH_4$ because only $CH_4$ is easily available in the gas phase.

Mean lifetimes of the observed $CH_n^{2+}$ dications were estimated from their time of flight between formation and detection by Ast *et al* (1981), Mathur *et al* (1986) and Hamdan *et al* (1988a), for example. We have also performed direct measurements of the unimolecular dissociation rate of all the $CH_n^{2+}$ dications formed in fast charge-stripping collisions. To increase the chance for detection of the long-lived dications of interest in this work we have also used $CD_m^+$ beams. If these dications decay by tunnelling through a potential energy barrier, then it is expected that a $CD_n^{2+}$ would have a longer lifetime than the associated $CH_n^{2+}$ because of their larger reduced mass.

## 2. Experimental

The $CD_n^{2+}$ dications were produced by charge stripping $CD_m^+$ ($n \leqslant m \leqslant 5$) in fast collisions with Ar atoms. The $CD_m^+$ molecular ions, created in the rf ion source of the Technion 1 MV Van de Graaff accelerator, were accelerated to 850 keV and then directed by a 15° analysing magnet toward the target cell where the charge-stripping reactions took place. A velocity selector (Wien filter) was used before the target cell to direct only ions through and further clean the beam from contaminants having a different velocity than the $CD_m^+$ beam. We have used both $CD_m^+$ and $CH_m^+$ beams in order to avoid certain beam impurities which can produce a signature similar to $CD_n^{2+}$ or $CH_n^{2+}$ formation. The experimental methods and apparatus used to determine the existence of the long-lived $CH_n^{2+}$ dications and measure their decay rate have been previously described in detail (see Ben-Itzhak *et al* 1993a, b, Gertner *et al* 1994, Rosner *et al* 1997), and thus will only be briefly outlined here. The technique used to distinguish $^{12}CH_n^{2+}$ from $^{13}CH_{n-1}^{2+}$ is discussed in more detail.

To form the long-lived $CD_n^{2+}$ dications, a beam of $CD_m^+$ was charge-stripped by collisions with Ar atoms in a differentially pumped target cell, where the pressure was typically 0.1–10 mTorr. The pressure in the rest of the system was kept below $10^{-6}$ Torr. The reaction products emerging from the target cell were separated by their energy to charge ratio using an electrostatic parallel plate deflector. A voltage of about 10 kV directed the doubly charged $CD_n^{2+}$ ions toward a photo-diode detector located 948 mm downstream from the target cell at a deflection angle of about 5°, which was set using a rotatable arm (see figure 1 in Gertner *et al* (1994)). Another similar detector, placed on the beam axis, was used for normalization by monitoring the neutral D (or H) fragments. The detectors used produce a signal proportional to the energy of the detected particle. One experimental advantage of using $CD_m^+$ over $CH_m^+$ beams is the better resolution between neighbouring $n$D than $n$H peaks ($n$H denotes the simultaneous hit of $n$ H fragments) in the energy spectrum, as well as better separation of the D peak from the electronic noise. This is because the energy of the fragments is proportional to their mass

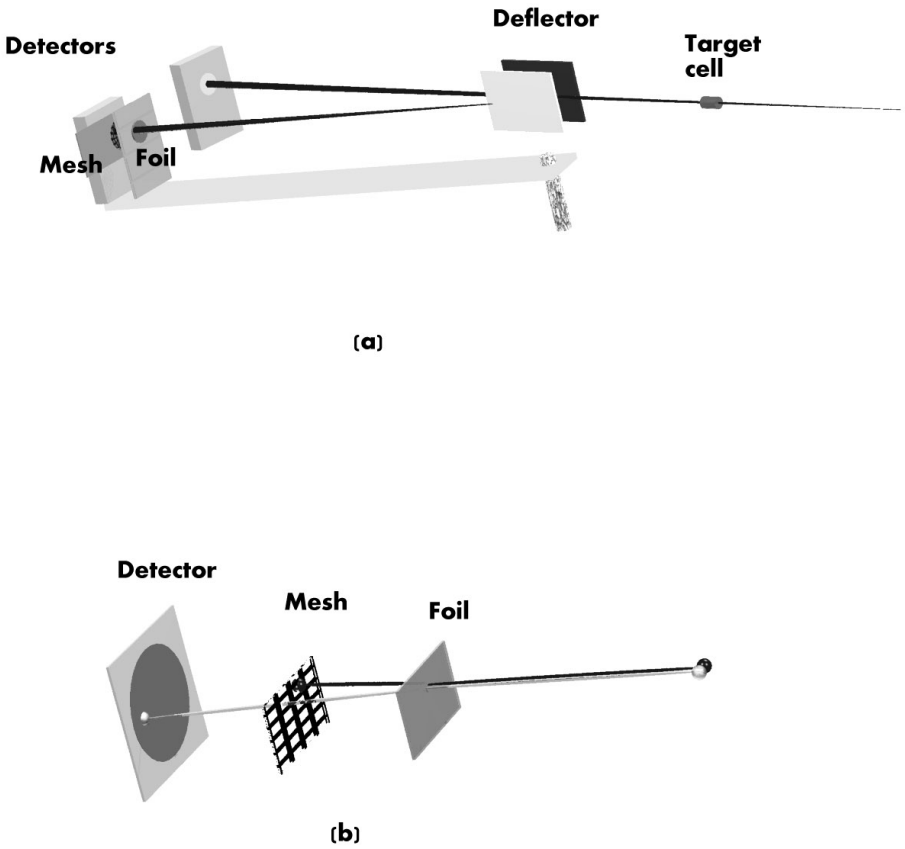


**Figure 1.** A schematic view of the experimental setup. (*a*) The detector used for normalization to the neutral H or D yield is on the right. The second detector is used to detect the ions. A mesh and/or a foil can be placed in front of it. (*b*) A blow up showing the foil and mesh in action, i.e. dissociating a molecule in the foil and stopping one fragment by the mesh while detecting the other fragment.

fraction. For example, a D fragment of $CD_2^{2+}$ has 106 keV while a H fragment from $CH_2^{2+}$ has only 61 keV. This energy separation becomes worse with increasing number of hydrogen atoms in the dication under study.

The dications of interest are separated from the other ions by their trajectory, as shown in figure 1. It is important to note that a $^{13}CH_{n-1}^{2+}$ will follow the same trajectory and produce the same signal as a $^{12}CH_n^{2+}$, an issue which has caused debates about data interpretation in previous measurements (see, for example, Koch *et al* 1987, Mathur 1988). To overcome this difficulty we placed a thin carbon foil ($\sim$10 $\mu$g cm$^{-2}$) after a narrow slit (1 mm wide) through which only $CH_n^{2+}$ ions could pass. The thin foil causes the dissociation of all molecular ions and the signal associated with the detection of $n$H serves as a signature of $^{12}CH_n^{2+}$ formation, clearly eliminating the impact of the $^{13}$C isotope on the measurement. This also eliminates confusion with any atomic impurity in the beam, and was used by Ben-Itzhak *et al* (1990), for example, to distinguish $Ne_2^{2+}$ from $Ar^{2+}$. The acceptance angle of the detector was larger than the angular spread of the dissociation fragments in order to increase the detection efficiency. However, this somewhat complicates the experimental method because the detection of all the

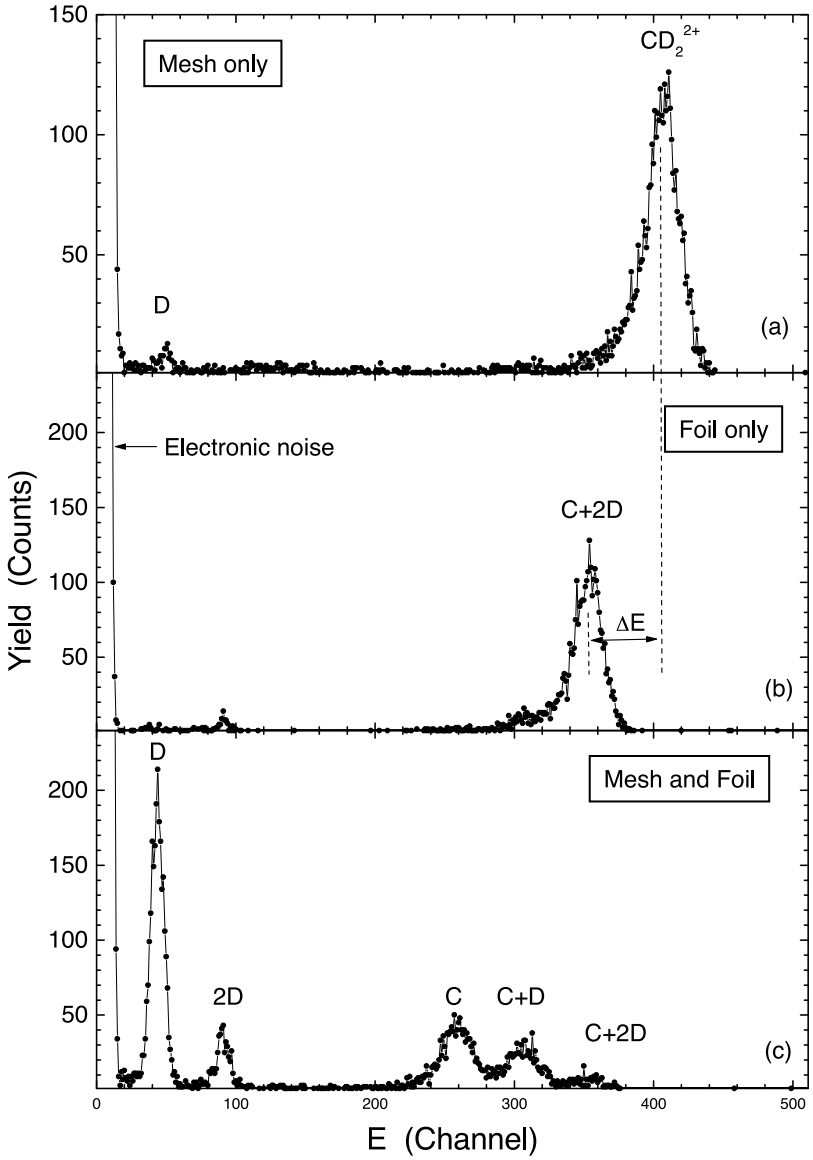


**Figure 2.** A typical energy spectrum of the molecular ions and fragments emerging from the target cell with the detector placed on the $CD_2^{2+}$ trajectory. Detector 'covered' with (*a*) mesh only, (*b*) foil only, (*c*) mesh and foil (see text). Note that the 'full energy' peak is shifted by the energy loss, $\Delta E$, when the molecular ions pass through the thin carbon foil.

fragments of the same molecular ion produce a signal proportional to the sum of their energies. Thus, in order to distinguish the $n$H channel there is a need to discriminate against multiple hits. This is accomplished by placing a 30% transmission mesh in front of the detector (see figure 1). The thin foil can be moved out of the way such that the yield of H or D fragments from the unimolecular dissociation in flight toward the detector can be measured.

The $CD_2^{2+}$ dications are used, hereafter, as an example of the experimental procedures. The spectra observed by the energy sensitive detector (PIN diode), when the deflection voltage

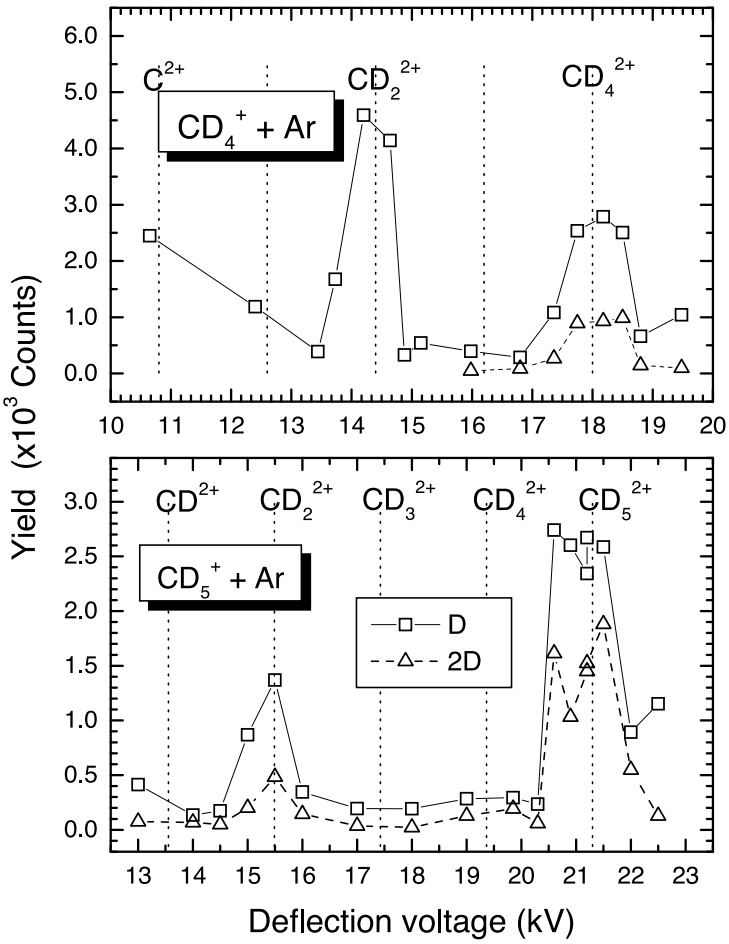


**Figure 3.** The yield of D and 2D fragments of $CD_n^{2+}$, produced from $CD_4^+$ and $CD_5^+$ beams, as a function of the deflection voltage.

is set so that the $CD^{2+}$ impinge on it, are presented in figure 2. When a mesh is placed in front of the detector (upper figure), the full energy peak mainly represents the $CD^{2+}$ dications. The small D peak at lower energies is due to the molecular ions dissociated between the analyser and the detector. In the middle figure the measurement with only a thin foil placed very close in front of the detector is shown (i.e. without the mesh). In this case, only fragments reach the detector. A 'full energy' peak labelled 'C + 2D', appears at a somewhat lower energy, due to the energy loss in the foil (see $\Delta E$ in figure 2(*b*)). 'Full energy' events still exist because all the fragments hit the detector simultaneously and their energy signals are added. In the lowest figure, the energy spectrum obtained with both the mesh and foil is shown. Due to the introduction of the mesh some of the fragments do not reach the detector and the D and 2D peaks become pronounced.

The yields of D and 2D, identified by their energy signal shown in figure 2(*c*), are measured as a function of the deflection voltage (see, for example, figure 3 where the scans for $CD_4^+$ and $CD_5^+$ beams are shown). Both yields peak where the $CD_2^{2+}$ is expected to hit the detector after passing through the thin foil. The ratio between the D and 2D peaks is in agreement with

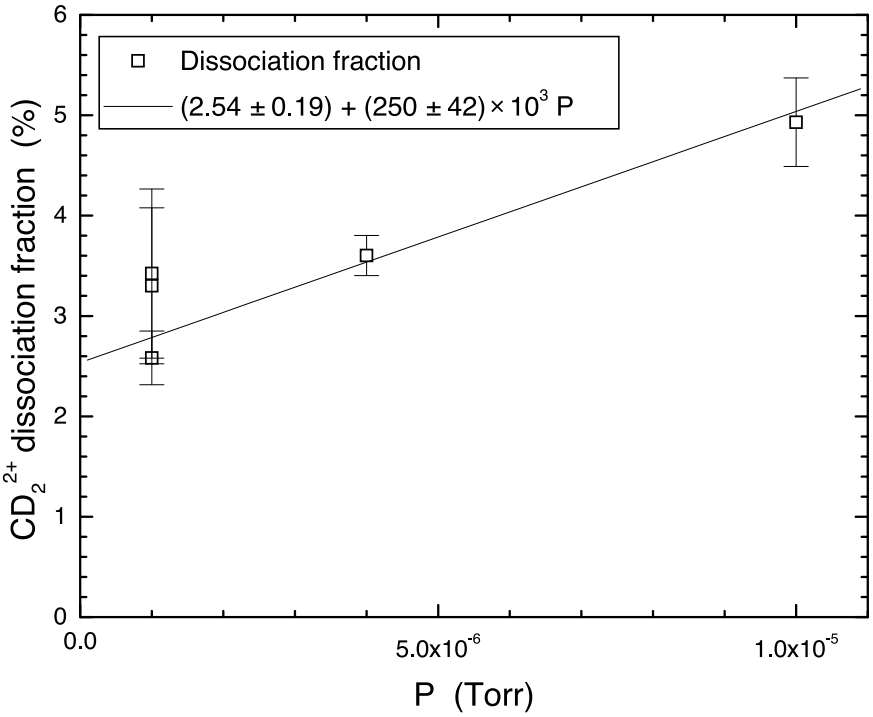


**Figure 4.** The yield of D fragments of $CD_2^{2+}$, produced from a $CD_2^+$ beam, as a function of the pressure after the deflector.

that expected due to the mesh transmission, i.e. $\frac{N(2D)}{N(D)} = \frac{T}{2(1-T)}$, where $T$ is the transmission of the mesh. This is a clear indication that long-lived $^{12}CD_2^{2+}$ dications are formed in fast $^{12}CD_2^+$ + Ar collisions. However, one could be concerned that the $^{12}CD_2^+$ beam might have a $^{12}CD_3^+$ fragment of an accelerated $^{12}CD_4^+$ ion having 765 keV, and thus have a similar rigidity as the main $^{12}CD_2^+$ beam. These two beams cannot be resolved by our 15° analysing magnet. If $^{12}CD_n^{2+}$ ($n = 1$–3) dications are produced from this impurity beam they will also have $n$D fragments and might affect the measurement. Fortunately, $^{12}CD_n^{2+}$ dications produced from the 765 keV $^{12}CD_3^+$ impurity beam have significantly different energy to charge ratios, and thus are easily separated from the $^{12}CD_2^{2+}$ dications by the electrostatic deflector.

Once the long-lived $^{12}CD_2^{2+}$ dications were identified we determined their production cross section from a common measurement of their yield as a function of the Ar pressure in the target cell (see figure 4). Note that the measured yield of D fragments has to be divided by their transmission through the mesh, $2T(1-T)^2$ (one D fragment out of three fragments), to get the $^{12}CD_2^{2+}$ yield. Furthermore, the yield of neutral D fragments relative to the main $^{12}CD_2^+$ beam was measured also as a function of target pressure, because the neutral D fragments were used for normalization. The production cross sections, thus determined, from all $CD_m^+$ precursors are presented in table 1.

The observed $^{12}CD_2^{2+}$ dications are clearly long lived as their flight time from the target cell to the deflector exit was about 150 ns. However, it is of great interest to determine their mean lifetime with much higher precision than just a rough estimate based on flight time through the apparatus. First, the doubly charged molecular ions are dissociated by a thin foil and their energy spectrum, shown in figure 2(*c*), indicates no significant fraction of any ions other than

**Table 1.** Cross sections for $CD_2^{2+}$ production in $CD_m^+$ + Ar ($m \geqslant 2$) collisions at 850 keV ($\sigma_{m2}$ in units of $10^{-18}$ cm$^2$).

| $m$ | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| $\sigma_{m2}$ | $12.6 \pm 1.0$ | $1.76 \pm 0.15$ | $6.15 \pm 0.61$ | $3.55 \pm 0.50$ |
| $\sigma_{m2}/P_m^2$ [a] | $12.6 \pm 1.0$ | $0.59 \pm 0.05$ | $1.0 \pm 0.1$ | $0.36 \pm 0.05$ |

[a] $P_m^2$ is the number of combinations of $CD_2$ out of $CD_m$ (see text).

the expected $^{12}CD_2^{2+}$ dications, i.e. only D, 2D, C, C + D, and C + 2D peaks are observed, and their ratios are as expected for the mesh transmission (see, e.g., Berkner *et al* (1971, 1973), Morgan *et al* (1971), Heber *et al* (1985), Gertner *et al* (1994), Rosner *et al* (1997), for details about the mesh method).

We have used a method similar to the mesh method, described in detail in a previous publication by Gertner *et al* (1994), to measure the effective mean lifetime. Briefly, this method is based on the measurement of the number of D fragments from unimolecular dissociation between the deflector exit and the detector, $N[CD^+ + D^+]$, i.e. a measurement of the D fragment yield with the detector covered with the mesh. This is then compared with the total yield of $^{12}CD_n^{2+}$, $N_0(CD_2^{2+})$, dissociated or not, given by the number of 'full energy' counts in the energy spectrum measured without the mesh. Both these measurements are properly normalized to the yield of neutral D fragments. Assuming a single exponential decay the mean lifetime is given by

$$\tau = \frac{-x/v}{\ln\left[1 - \frac{N[CD^+ + D^+]}{N_0(CD_2^{2+})}\right]}, \tag{1}$$

where $x = 496$ mm is the distance between the deflector exit and the mesh, $v$ is the beam velocity, and the ratio $\frac{N[CD^+ + D^+]}{N_0(CD_2^{2+})}$ is given by

$$\frac{N[CD^+ + D^+]}{N_0(CD_2^{2+})} = \frac{N(D)/T(1-T)}{N(FE)}. \tag{2}$$

In the equation above $N(D)$ and $N(FE)$ are the number of D fragments and full energy counts measured with and without the mesh, respectively, and $T$ is the mesh transmission. Note that unimolecular dissociation of $CD_n^{2+}$ might produce $D_n^+$ in addition to $D^+$ fragments; however, our measurements indicate that the single $D^+$ fragment is the favoured dissociation channel, as was also noted, for example, by Rabrenovic *et al* (1983a). In the method described above it is assumed that the yield of fragments measured without the foil is due solely to unimolecular dissociation. However, under the existing experimental conditions, i.e. residual gas pressure of about $10^{-6}$ Torr, some dissociation is induced by collisions with remnant gas atoms or molecules. To separate the unimolecular dissociation from the collision induced dissociation (CID) the yield of the D fragments as a function of the pressure between the deflector exit and the detector was measured, as shown in figure 4. The value of $N(D)$ extrapolated to zero pressure is the true number of unimolecular dissociation events, which is then used as $N(D)$ in equation (2). The unimolecular dissociation rate of the other $CD_n^{2+}$ dications (i.e. $n = 4, 5$) was lower than the CID rate. In these cases only a lower limit for the mean lifetime was determined.

## 3. Results and discussion

We measured the charge-stripping processes $CD_m^+ + Ar \rightarrow CD_n^{2+}$ ($m = 1$–5) and $CH_m^+ + Ar \rightarrow CH_n^{2+}$ ($m = 1$–4) at 850 keV, where $m \geqslant n$ in both cases. For each collision system we

scanned the deflection voltage looking for the relative production rate of all possible $CD_n^{2+}$ or $CH_n^{2+}$ dications. The yield of D and also 2D fragments of $CD_4^{2+}$ and $CD_5^{2+}$ as a function of the deflection voltage are shown in figure 3. The dissociation of the $CD_n^{2+}$ dications was induced by the thin foil placed in front of the detector, as discussed in the previous section. A quick glance at the figure shows that $CD_4^{2+}$ and $CD_5^{2+}$ are formed only by stripping $CD_4^+$ and $CD_5^+$, respectively, while $CD_2^{2+}$ is formed by the charge stripping of both. The latter was formed from any $CD_m^+$ ($m = 2$–5). It can also be seen that $CD^{2+}$ and $CD_3^{2+}$ are not observed in these collisions. Next, we discuss some specific issues related to each of the $CD_n^{2+}$ dications ($n = 1$–5) and later we address some common issues. The results for $CH_n^{2+}$ are similar to those of the respective $CD_n^{2+}$ presented below.

### *3.1. $CD^{2+}$*

The $CH^{2+}$ molecular ion has been observed in charge-stripping collisions of a few keV $CH^+$ beams (see, for example, Ast *et al* 1981, Proctor *et al* 1981, Mathur *et al* 1986, Mathur and Badrinathan 1987, Mathur 1988, Hamdan *et al* 1988a, b), and its lifetime was estimated to be about 3 $\mu$s from the typical flight time between its formation and detection. Since the first observation the identity of the long-lived state of $CH^{2+}$ has been debated. Furthermore, some have questioned if such long-lived states do exist (see, for example, Koch *et al* 1987, Wetzel *et al* 1993). As this controversial issue is not the topic of this study we will refer those interested to a few recent publications where it is discussed in detail by Gu *et al* (1998) and Ben-Itzhak *et al* (1999a).

We have found no long-lived $CD^{2+}$ (or $CH^{2+}$) dications in any of the fast charge-stripping reactions $CD_m^+ + Ar$ (or $CH_m^+ + Ar$). In some cases the count rate of full energy signals peaked at the voltage associated with this dication, for example, $^{14}N^{2+}$ and $^{13}C^{2+}$ for $CD^+$ and $CH^+$ beams, respectively. However, in all these cases there was no peak of D or H fragments when the foil was used to induce dissociation. This indicates the importance of forcing molecular dissociation to create a well-defined signature for formation of 'exotic' long-lived molecular ions. It is suggested by theory that the $A\,^2\Sigma^+$ state of $CH^{2+}$ is metastable with some long-lived vibrational states (see Gu *et al* 1998, Ben-Itzhak *et al* 1999a). However, the bond length of this state is predicted to be about 6 au, i.e. much longer than that of all the $CH_m^+$ parent ions. This makes the overlap between the initial and final nuclear wavefunctions negligible and it is not surprising that this state is not populated in the fast charge-stripping collisions reported here, for which the transitions are too fast to allow nuclear rearrangement.

### *3.2. $CD_2^{2+}$*

The $CH_2^{2+}$ dication is the most likely $CH_n^{2+}$ dication to be produced in charge-stripping collisions, as can be seen from the cross sections measured by Proctor *et al* (1981). The cross section for $CH_2^+ + N_2 \rightarrow CH_2^{2+}$ at 5 keV is the largest of all charge-stripping reactions of the form $CH_m^+ + N_2 \rightarrow CH_m^{2+}$ by more than an order of magnitude. Furthermore, it is comparable to the $C^+ + N_2 \rightarrow C^{2+}$ suggesting that $CH_2^{2+}$ is very stable and easy to form. More detailed translation energy loss spectrometry studies of $CH_2^+ + T \rightarrow CH_2^{2+}$ at keV collision energies were performed by Ast *et al* (1981) and Mathur *et al* (1986). Rabrenovic *et al* (1983b) have shown that $CH_2^{2+}$ is a possible dissociation product of unstable $CH_4^{2+}$ formed in similar charge-stripping collisions. A theoretical study of the potential surface of $CH_2^{2+}$ conducted by Pople *et al* (1982) indicates that the potential minimum is very deep and has a high activation barrier for deprotonation. Thus, they predicted that $CH_2^{2+}$ will have long-lived states.

We observed the formation of long-lived $CD_2^{2+}$ and $CH_2^{2+}$ from all parent $CD_m^+$ ($m = 2$–

5) and $CH_m^+$ ions ($m = 2$–4), respectively. The cross sections for $CD_2^{2+}$ formation from the different parent ions are presented in table 1. It can be seen that it is most likely to form $CD_2^{2+}$ from the $CD_2^+$ parent only when electron stripping is needed without additional bond breaking. The trend of decreasing cross sections with increasing precursor size is not uniform and more detailed calculations are needed to explain why it is least likely to form the $CD_2^{2+}$ from the $CD_3^+$ molecular ion. Note that the number of ways to form a $CD_2^{2+}$ increases rapidly with the number of D atoms of the parent molecular ions. We have divided the production cross section $\sigma_{m2}$ by the number of possible ways to form $CD_2^{2+}$ from each parent molecular ion in the last line of table 1. It can be seen that this ratio decreases even more rapidly with the size of the parent molecular ion, i.e. with the number of bonds breaking. However, it is still less likely to form $CD_2^{2+}$ from $CD_3^+$ than from $CD_4^+$.

The mean lifetime of $CD_2^{2+}$ was determined to be $4.0 \pm^{1.3}_{1.1}$ $\mu$s from a direct measurement using the mesh method described in the previous section (see also Gertner *et al* 1994). Furthermore, the fact that no C fragments are seen in the energy spectrum measured with the mesh only, shown in figure 2(*a*), suggests that unimolecular dissociation of $CD_2^{2+}$ results mainly in $D^+ + CD^+$. The CID cross section of $CD_2^{2+}$ in air was determined to be $(2 \pm 1) \times 10^{-15}$ cm$^2$. This cross section has a similar magnitude as that of other dications, like $NeAr^{2+}$ and $HeAr^{2+}$, at a similar collision energy (see Ben-Itzhak *et al* 1993a, 1999b).

Given that this molecular ion possesses such a long mean lifetime we searched for metastable $^{12}CH_2^{2+}$ dications directly from the accelerator ion source. These doubly charged ions were accelerated to 1700 keV and survived all the way to the detector, i.e a flight time of about 3 $\mu$s. The $^{12}CH_2^{2+}$ dications were distinguished from $^{14}N^{2+}$ using the foil and mesh method as explained in the experimental section. The fact that $CH_2^{2+}$ dications can be formed by double ionization of $CH_4$ or by single ionization (charge stripping) of all $CH_m^+$ ($m = 2$–5) indicates that they are very stable against unimolecular dissociation.

### *3.3. $CD_3^{2+}$*

Previous reports about long-lived $CH_3^{2+}$ dications are conflicting. Ast *et al* (1981) reported a clear peak, which they identified as $CH_3^{2+}$ dications, in the energy loss spectrum following a slow (5 keV) $CH_3^+ + N_2 \rightarrow CH_3^{2+}$ charge-stripping reaction. In contrast, Mathur *et al* (1986) reported no such peak in similar measurements at energies ranging from 1 to 5 keV. Proctor *et al* (1981) repeated the measurements of Ast *et al* (1981) with negative results. It is not clear what the source of this discrepancy between the experimental results is, and we are not aware of any additional experimental observation of the $CH_3^{2+}$ dication. A theoretical study of the potential surface of $CH_3^{2+}$ conducted by Pople *et al* (1982) suggests that the potential minimum is very shallow and that this dication will dissociate rapidly into $CH_2^+ + H^+$.

We have found no long-lived $CD_3^{2+}$ (or $CH_3^{2+}$) dications in any of the fast charge-stripping reactions $CD_m^+ + Ar$ where $m = 3$–5 (or $CH_m^+ + Ar$ where $m = 3$–4), as can be seen from figure 3. Our result is consistent with the theoretical prediction of Pople *et al* (1982) and the experimental work of Proctor *et al* (1981) and Mathur *et al* (1986).

### *3.4. $CD_4^{2+}$*

Many studies of the double ionization energy of methane have been conducted using a variety of experimental methods like Auger spectroscopy by Spohr *et al* (1970), double charge transfer by Fournier *et al* (1985), photoion–photoion coincidence by Dujardin *et al* (1985), and charge stripping by Ast *et al* (1981), Proctor *et al* (1981), Rabrenovic *et al* (1983b), Raheja *et al* (1986) and Mathur *et al* (1986). The results of these measurements are discussed by Mathur

*et al* (1986). The mean lifetime of the $CH_4^{2+}$ dication was estimated to be larger than 1 $\mu$s from the fact that its flight time from formation to the detector is about 3 $\mu$s in a few measurements by Ast *et al* (1981), Rabrenovic *et al* (1983b) and Raheja *et al* (1986). The stability of $CH_4^{2+}$ dications was attributed by Pople *et al* (1982) to the deep minimum in the calculated potential energy surface and the high activation barrier for deprotonation. However, the decay rate (i.e. the mean lifetime) of this metastable dication was not calculated, to the best of our knowledge. It was shown by Rabrenovic *et al* (1983b) that these metastable dications decay preferentially by the $CH_4^{2+} \rightarrow CH_3^+ + H^+$ reaction, which is the lowest dissociation channel according to the calculations of Siegbahn (1982). The unstable $CH_4^{2+}$ dications formed in charge-stripping collisions, on the other hand, dissociate mainly without charge separation into $CH_2^{2+}$ or $C^{2+}$ (see Proctor *et al* 1981, Rabrenovic *et al* 1983b). Transient $CH_4^{2+}$ dications formed directly from neutral methane by double photo-ionization dissociate mainly into $CH_4^{2+} \rightarrow CH_3^+ + H^+$ (50%), $CH_2^+ + H^+ + H$ (30%), $CH^+ + H^+ + 2H$ (7%), and $CH_2^+ + H_2^+$ (13%) (see Fournier *et al* 1985). Fast proton impact ionization of methane results in similar dissociation channels for the transient $CH_4^{2+}$ dications (see Ben-Itzhak *et al* 1993c).

We observed the formation of long-lived $^{12}CD_4^{2+}$ dications in fast charge-stripping collisions of $^{12}CD_4^+$, i.e. $^{12}CD_4^+ + Ar \rightarrow {}^{12}CD_4^{2+}$, with similar results for $^{12}CH_4^{2+}$. In contrast, no long-lived $^{12}CD_4^{2+}$ dications were observed from the charge stripping of $^{12}CD_5^+$, i.e. $^{12}CD_5^+ + Ar \not\rightarrow {}^{12}CD_4^{2+}$. This is most likely due to the large difference between their geometries. The cross section for the $^{12}CD_4^+ + Ar \rightarrow {}^{12}CD_4^{2+}$ reactions was found to be $\sigma_{44} = (2.40 \pm 0.16) \times 10^{-18}$ cm$^2$. The mean lifetime of the $^{12}CD_4^{2+}$ dications was found to be longer than 2.1 $\mu$s.

### *3.5. $CD_5^{2+}$*

The $CH_5^{2+}$ dication can be formed in charge-stripping collisions from a beam of protonated methane, i.e. $CH_5^+ + Ar \rightarrow CH_5^{2+}$. Protonated methane is formed in ion sources under high pressure conditions as shown, for example, by Mathur *et al* (1986). Proctor *et al* (1981) measured the cross section for this reaction (at 5 keV) to be about 20 times smaller than the same process in which $CH_2^{2+}$ is produced. However, it is not clear if the smaller production rate is due to dication stability or the Franck–Condon factors being smaller. Mathur *et al* (1986) measured the energy loss in this reaction but the lack of a measured value for single ionization for the $CH_5$ radical prevented the evaluation of the second ionization potential from their measurement. Theoretical treatment of this dication is even more scarce.

We were unable to get a clean enough beam of $CH_5^+$ to perform a charge stripping experiment because of the large $OH^+$ impurity beam. An additional problem was the poor energy resolution between the different $n$H peaks and the fact that the single H peak was partly lost below the electronic noise because for $CH_5^+$ each H had only 50 keV before passing through the carbon foil. As a result, in this case we studied only the $CD_5^+$ beam.

It can be clearly seen from figure 3 that $^{12}CD_5^{2+}$ dications are formed in $^{12}CD_5^+ + Ar$ collisions. The cross section for charge stripping at 850 keV was determined to be $\sigma_{55} = (7.26 \pm 0.19) \times 10^{-18}$ cm$^2$. The mean lifetime was determined to be longer than 3.3 $\mu$s. There is clearly a need for theoretical work on this dication in order to evaluate the experimental results reported so far by Proctor *et al* (1981), Mathur *et al* (1986) and this work, and even more importantly to guide future experimental work.

In general, the production cross sections of $CD_m^{2+}$ by pure charge stripping of the respective $CD_m^+$ molecular ions are shown in table 2. All these charge-stripping cross sections are of a similar order of magnitude. Producing the smaller $CD_2^{2+}$ is more likely as one would expect.

**Table 2.** Cross sections for $CD_m^{2+}$ production in $CD_m^+$ + Ar collisions at 850 keV ($\sigma_{mm}$ in units of $10^{-18}$ cm$^2$).

| $m$ | 2 | 4 | 5 |
|---|---|---|---|
| $\sigma_{mm}$ | $12.6 \pm 1.0$ | $2.40 \pm 0.16$ | $7.26 \pm 0.19$ |
| $\sigma_{mm}/\sigma_{22}$ | 1 | $0.19 \pm 0.02$ | $0.57 \pm 0.05$ |
| $\sigma_{mm}/\sigma_{22}$ [a] | 1 | $\frac{1}{40}$ | $\frac{1}{20}$ |

[a] Relative charge-stripping cross sections at 5 keV from Proctor *et al* (1981).

However, it is somewhat surprising that it is easier to form a long-lived $CD_5^{2+}$ than $CD_4^{2+}$, a fact which calls for further theoretical treatment. The charge-stripping cross sections relative to the $^{12}CD_2^+ + Ar \rightarrow {}^{12}CD_2^{2+}$ cross section are also shown in table 2 where they are compared with the values measured by Proctor *et al* (1981) for similar collisions at 5 keV. In both measurements charge stripping of $CD_4^+$ is the least likely, but the differences at the high collision energies are much smaller than at lower energies.

The mean lifetimes determined for $CD_2^{2+}$, $CD_4^{2+}$ and $CD_5^{2+}$ (for the last two only lower limits) are in good qualitative agreement with the predictions of Pople *et al* (1982). There is similar agreement between their prediction that $CH^{2+}$ and $CH_3^{2+}$ are unstable and the fact that they are not observed in our measurements. One may expect that more detailed knowledge will be gained from the measurement of the mean lifetime of $CD_2^{2+}$, however, to accomplish that one has to determine what the decaying state is. Given that $CD_2^{2+}$ is observed to decay into $D^+ + CD^+$ as predicted for its electronic ground state by Pople *et al* (1982), it is very likely that this is the electronic state formed, and for which the mean lifetime was measured. Mean lifetimes are also expected to depend strongly on the vibrational state of the metastable molecular ion. Typically in our experiments the singly charged parent molecular ion, $CD_2^+$ for example, is formed in the ion source in its ground electronic state with a Maxwell–Boltzmann vibrational energy distribution of a few thousand degrees. The transitions from these initial states to the $CD_2^{2+}$ metastable states are vertical during the fast charge-stripping collisions and they can be estimated by calculating the Franck–Condon factors. Therefore, calculations of the vibrational wavefunctions of the parent and daughter molecular ions are needed to associate the measured mean lifetime with a specific vibrational state. Furthermore, the decay rates of the different vibrational states need to be calculated.

## 4. Summary

We have conducted a systematic study of the formation of long-lived $CD_n^{2+}$ and $CH_n^{2+}$ dications in fast (850 keV) charge-stripping collisions with Ar atoms. No $CD^{2+}$ and $CD_3^{2+}$ or the respective $CH_n^{2+}$ were observed in any of the charge-stripping reactions. On the other hand, we observed the formation of long-lived $CD_2^{2+}$ from all parent molecular ions having enough D atoms. However, it is more likely to form this dication in charge stripping of $CD_2^+$ ($CH_2^+$) than from molecular ions which also require bond breaking. Long-lived $CD_4^{2+}$ ($CH_4^{2+}$) and $CD_5^{2+}$ were produced only from their respective $CD_4^+$ ($CH_4^+$) and $CD_5^+$ singly charged molecular ions. All the charge-stripping cross sections with no bond breaking were found to be more similar to each other than at 5 keV collision energies, where large differences were observed. The mean lifetime of the $CD_2^{2+}$ was measured to be $4.0 \pm^{1.3}_{1.1}$ $\mu$s. Similar measurements for $CD_4^{2+}$ and $CD_5^{2+}$ yielded only lower limits for their mean lifetimes of 2.1 and 3.3 $\mu$s, respectively.

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