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Long lived CH^{2+} and CD^{2+} dications

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Abstract

A search for long lived CH^{2+} and CD^{2+} dications formed in fast charge stripping collisions of CH^+ and CD^+ on Ar was conducted. An experimental method based on the detection of the H (or D) fragments of the dication was developed, in order to eliminate possible confusion with $^{13}C^{2+}$ for the first and $^{14}N^{2+}$ for the latter. The flight time of these dications through the apparatus is about 70 ns, well below the 3 μs time associated with earlier observations of CH^{2+}. Our measurements indicate that no long lived states of either of these dications are formed in fast charge stripping collisions. However, this result does not exclude the possibility that long lived states, like the excited $A\ ^2\Sigma^+$ metastable state, are populated in slow charge stripping collisions. (Int J Mass Spectrom 192 (1999) 157–163) © 1999 Elsevier Science B.V.

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1. Introduction

Long lived CH^{2+} dications were first observed in mass spectra following slow charge stripping collisions during the early 1980's [1,2]. These collisions between a few kiloelectron volts CH^+ molecular ions and a target atom or molecule produced a signal at $m/q = 6.5$, which was associated with the formation of long lived CH^{2+} dications. The lifetime of these ions was estimated from the typical flight time through the apparatus to be about 3 μs [1,3–6]. Since their discovery these dications have been the subject of an ongoing controversy about their existence as long lived states due to both experimental and theoretical work. For example, structure calculations of Pople et al. [7] suggested that CH^{2+} has a repulsive ground state and thus should dissociate immediately after the charge stripping reaction. However, some later calculations indicated a shallow minimum in the potential energy curve (PEC) of the electronic ground state [5,8–11], and others still showed that this state is repulsive [12,13]. In addition to the question of whether or not the electronic ground state of CH^{2+} can sustain a long lived state, there were some doubts about the validity of the observation itself. Measurements similar in nature to those where CH^{2+} was observed [1,3–6], but using a much higher resolving power, thus separating $^{13}C^+$ from $^{12}CH^+$, showed no long lived CH^{2+} [12]. From the latter measurements and their ab initio calculations, which showed a repulsive ground state, Koch et al. [12] concluded that the earlier measurements led to the erroneous conclu-

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sion that metastable CH^{2+} was detected. Distinguishing $^{12}CH^{2+}$ from $^{13}C^{2+}$ and some other experimental problems were discussed and excluded by Wetmore et al. [8] and further arguments were given later by Mathur [14]. This question is still unsettled and has attracted more recent work. An attempt to create CH^{2+} directly by electron impact ionization in an ECR ion source by Wetzel et al. [11] failed. Furthermore, their structure calculations indicated that there are no low lying bound or quasibound states of CH^{2+}. In contrast very recent structure calculations by Gu et al. [13] showed that the excited $A\ ^2\Sigma^+$ state may sustain vibrational states. Furthermore, the estimated decay rate of this state to the dissociating ground state is very slow, thus suggesting that this might be the long lived state observed previously. However, one should note that this excited state has an equilibrium internuclear distance of about 6 a.u., i.e. much longer than that of the parent CH^+ in its ground state. Thus, for long lived CH^{2+} to be formed in charge stripping collisions either the transition is far from being vertical or the CH^+ is in a state with a long bond length prior to the collision.

To try to settle the issue of a long lived state of CH^{2+}, we have performed measurements of charge stripping of CH^+ in thin Ar gas. We have used faster beams so that the flight time through our apparatus is about 70 ns, thus allowing measurements of metastable CH^{2+} dications having lifetimes somewhat smaller than 70 ns. The same experiment was conducted using a CD^+ beam to reduce the uncertainty caused by the large $^{13}C^+$ (~1% natural abundance relative to ^{12}C) contaminant in the $^{12}CH^+$ beam. Even more important, if these dications decay by tunneling through a potential energy barrier, CD^{2+} is expected to have a much longer lifetime than CH^{2+} due to its larger reduced mass. To eliminate the possible accidental identification of $^{13}C^{2+}$ or $^{14}N^{2+}$ with $^{12}CH^{2+}$ and CD^{2+}, respectively, we have used the signal of H or D fragments of these dications as an indication for their formation, as explained in the following section. In addition we calculated all the vibrational resonances sustained in the excited $A\ ^2\Sigma^+$ metastable state, and found that some have lifetimes longer than a few microseconds.

2. Experimental

The CH^+ molecular ions, produced from methane gas 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° analyzing 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 charged ions through and further clean the beam from contaminants having a different velocity than the CH^+ beam. The experimental methods and apparatus, used to determine if long lived CH^{2+} dications were created, were similar to those used in previous experiments (see, e.g. [15–18]) and will only be briefly outlined here. The new technique used to distinguish CH^{2+} from $^{13}C^{2+}$ is discussed in more detail.

To form the long lived CH^{2+} dications, a beam of CH^+ was charge stripped by a thin target of Ar gas in a differentially pumped target cell, with a typical target pressure of 0.1–10 mTorr. Under these conditions 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 10 kV directed the doubly charged ions, $^{12}C^{2+}$, $^{13}C^{2+}$, and the $^{12}CH^{2+}$ dications of interest, through a 4 mm collimator toward a photodiode detector located 530 mm downstream from the exit of the deflector. This detector was moved using a rotatable arm (see Fig. 1 from [16]) to scan the range of deflection angles of interest. Another similar detector, placed on the beam axis, was used for normalization by monitoring the yield of neutral H fragments. The detectors used produce a signal proportional to the energy of the particle detected, as shown in Fig. 1. It is important to note that a $^{13}C^{2+}$ will follow the same trajectory and produce the same signal as a $^{12}CH^{2+}$, an issue that caused debate about data interpretation in previous measurements (see, e.g. [12,14]). To overcome this difficulty the dications had to pass through a thin carbon foil (10 μg/cm^2) positioned on the trajectory of each doubly charged ion, as shown in Fig. 2. Molecular ions passing through a thin foil dissociate

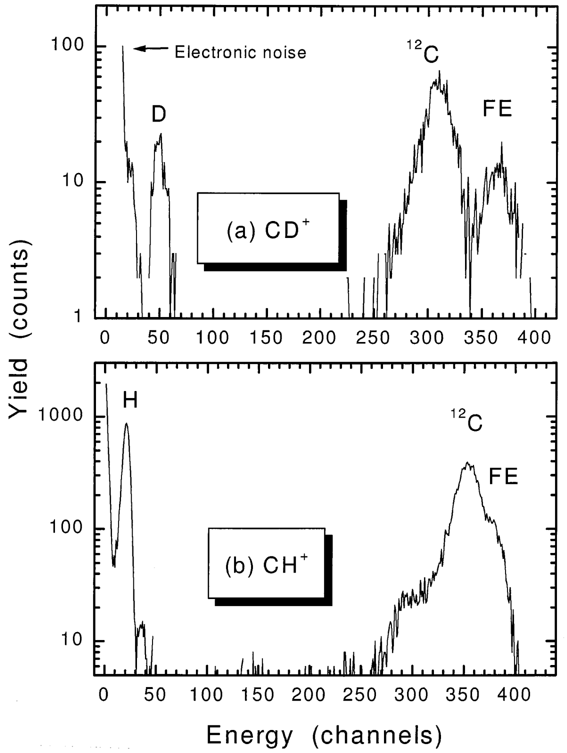

Fig. 1. A typical energy spectrum of the fragments emerging from the thin carbon foil placed on the trajectories of (a) CD^+ and (b) CH^+.

and the signal associated with the detection of the H fragments is an unambiguous signature of CH^{2+} formation, clearly eliminating the impact of the ^{13}C isotope on the measurement. The acceptance angle of the detector was larger than the angular spread of the dissociation fragments to insure high detection efficiency. However, this somewhat complicates the method because simultaneous hits of all the fragments of the same molecular ion produce a signal proportional to the sum of their energies. Thus, in order to distinguish the H fragments from the others there is a need to discriminate against multiple hits. This is accomplished by placing a 30% transmission mesh in front of the detector (see Fig. 2).

The measured normalized yields of H, ^{12}C and full-energy signals associated with ^{13}C or simultaneous hits of the H and ^{12}C fragments of $^{12}CH^{2+}$, are shown in Fig. 3 as a function of the deflection angle.

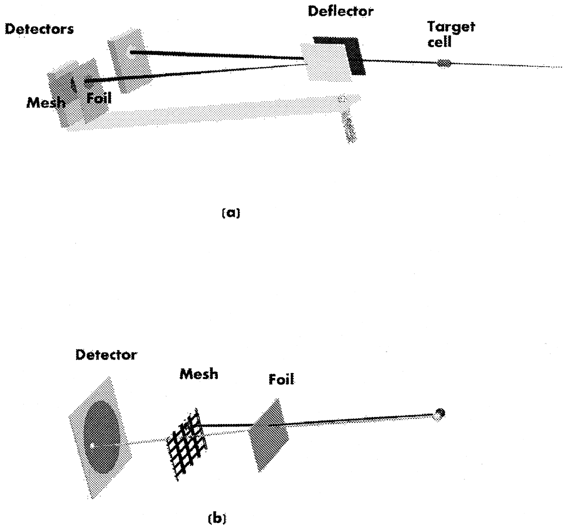

Fig. 2. (a) A schematic view of the experimental setup. (b) The foil and mesh used in front of the detector to distinguish between the fragments of the molecular ion. In the real mesh the hits are separated by many unit cells [16,18].

The $^{12}C^{2+}$ and the full-energy signals peak at the expected deflection angles and their relative intensity is about 2.8 ± 0.4%. This fraction cannot be compared to the natural ^{13}C abundance, because it depends also on the ratio of C^+ to CH^+ ions produced in the ion source. This just demonstrates why the

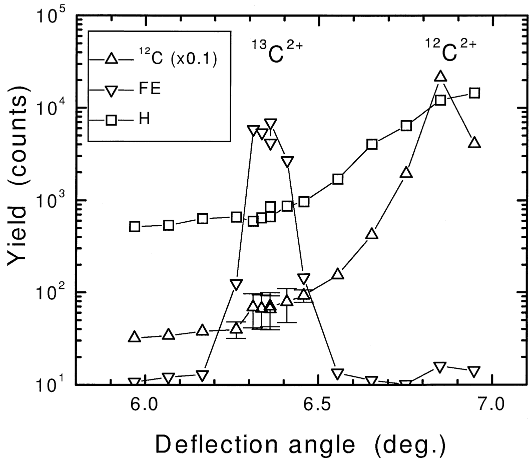

Fig. 3. The normalized yields of H, ^{12}C, and full-energy events for CH^+ beam, as a function of the deflection angle, $V_{def} = 15$ kV.

measurement without the foil cannot provide clear evidence about CH^{2+} production in the collisions under study. In contrast, the normalized yield of H fragments, shown also in Fig. 3, does not peak at the deflection angle associated with the $^{12}CH^{2+}$ trajectory, thus indicating clearly that long lived $^{12}CH^{2+}$ dications are not produced in the collisions under study. The background yield of H fragments at all deflection angles is due to collision induced dissociation of CH^{+}. Note that the yield of H fragments peaks close to the deflection angle associated with $^{12}C^{2+}$. This is due to an impurity beam of CH_2^+ having 793.3 keV (these are fragments of fully accelerated CH_3^+ molecular ions), which has a rigidity similar to that of the 850 keV CH^+ beam. Charge stripping of the lower energy CH_2^+ produces CH_2^{2+} molecular ions which are deflected along a similar trajectory as $^{12}C^{2+}$ from the main CH^+ beam because of the similarity of the energy to charge ratio, 396.6 and 392, respectively. The possible impact of this beam impurity on the low energy charge stripping measurements of CH^{2+} was discussed by Wetmore et al. [8].

We have repeated the measurements using a CD^+ beam produced from CD_4 for several reasons. Most importantly, CD^{2+} dications are expected to be more stable than CH^{2+} if they decay by tunneling through a potential energy barrier, as mentioned in sec. 1. In addition there are a few experimental advantages for studying CD^{2+} over CH^{2+}. (1) The $^{13}C^+$ isotope is not present in the $^{12}CD^+$ beam; however, some $^{14}N^+$ impurity beam might be present. Typically, the $^{13}C^+$ contaminant is higher because of the high natural abundance of this carbon isotope. (2) None of the accelerated CD_n^+ molecular ions or fragments has the same rigidity as the $^{12}CD^+$ beam. (3) The D fragment, having 121.4 keV, is better resolved from the electronic noise in the energy spectrum, shown in Fig. 1, than the H fragment, which has only 65.4 keV.

The CD^{2+} experiment was carried out following procedures similar to those discussed above for the CH^{2+} dication except that the deflection voltage was scanned and the detector was kept at a fixed angle. The normalized yields of D, ^{12}C, and full-energy signals are shown in Fig. 4 as a function of the deflection voltage. Only $^{14}N^{2+}$ ions contributed to the full-energy signals. This was verified by the same foil-mesh method. One can see that the $^{14}N^{2+}$ impurity is much smaller than the $^{13}C^{2+}$ impurity in the CH^{2+} experiment. If formed, CD^{2+} should peak at the same deflection voltage as the $^{14}N^{2+}$ impurity. The D fragments show no peak where the $^{12}CD^{2+}$ ions are expected, clearly indicating that no long lived CD^{2+} dications are produced in the collisions under study.

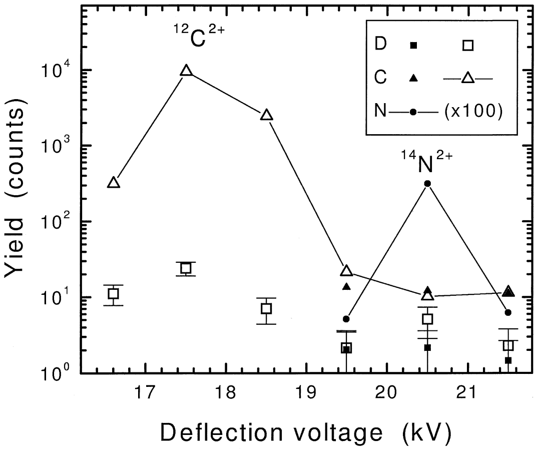

Fig. 4. The normalized yields of D, ^{12}C, and full-energy events for CD^+ beam, as a function of the deflection voltage, $\alpha_{def} = 9°$. Full symbols denote a measurement with higher beam current.

3. Results and discussion

The main experimental result presented here is that neither long lived CH^{2+} nor CD^{2+} dications were detected in the fast charge stripping collisions under study, i.e. $CH^+ + Ar$ (and $CD^+ + Ar$) at 850 keV. This seems to be in contradiction with previous observations of long lived CH^{2+} dications in charge stripping collisions at a few kiloelectron volts [1–6,14]. In particular, one notes that the fast beams used in our experiment enabled the detection of dications with mean lifetimes as short as 50 ns, much shorter than the 3 μs lifetime estimated from the lower energy experiment. However, one has to be more cautious with negative results. The fact that no CH^{2+} or CD^{2+} dications were detected in this study

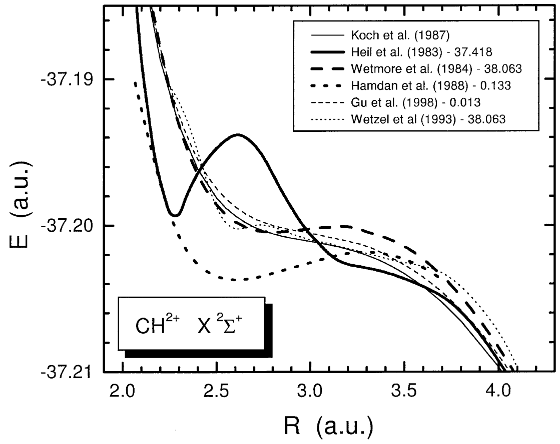

Fig. 5. Potential energy curves for the electronic ground state of CH^{2+} at large *R*. Note that the thick curves have a local minimum while the thin ones are purely repulsive.

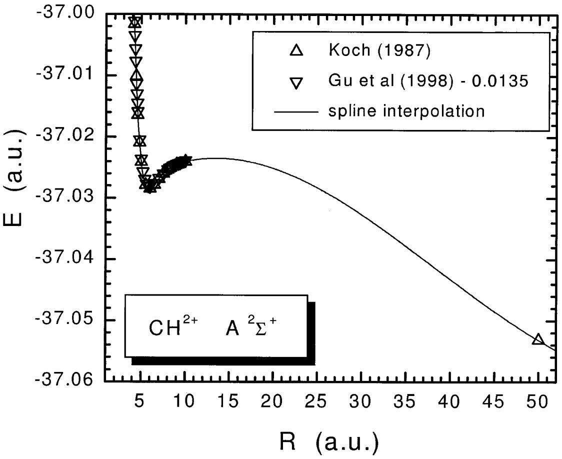

Fig. 6. Potential energy curves for the excited $A\ ^2\Sigma^+$ state of CH^{2+}. The solid line is a spline fit to the calculated values represented by symbols (the value at $R = 100$ a.u. was included).

can indicate either that they do not have long lived states or that such states are not populated in the fast charge stripping collisions under study. To further investigate the possible existence of long lived CH^{2+} previous structure calculations are presented and tunneling rate calculations have been conducted.

The electronic ground state of the CH^{2+} dications was the one associated with the observations of its long lived states in slow charge stripping collisions mainly because of the nice agreement between the measured transition energy and the energy difference between the ground states of the parent CH^+ and the daughter CH^{2+} (see, e.g. discussion in [8]). Also their electronic ground state have similar bond lengths, which allows a good overlap between the initial and final nuclear wave functions. However, this state cannot support a long lived state. Some calculations, including the most recent ones, indicate that the ground state potential energy curve is repulsive in spite of the shoulder around 3 a.u., caused by an avoided crossing [7,11–13]. Other calculations suggest a shallow local minimum caused by the same avoided crossing [5,8,9], as shown in Fig. 5. We have searched for resonances and their widths (i.e. quasi-bound vibrational states) for all the potential energy curves showing a potential well in Fig. 5 [5,8,9]. We have used the high precision phase-amplitude method [19] to calculate the location and width ($1/\tau$) of each resonance for zero angular momentum. No resonances exist for $^{12}CH^{2+}$ in any of these potentials. The more massive $^{12}CD^{2+}$ has a resonance only in the potential energy curve calculated by Hamdan et al. [5]. However, this state decays too rapidly ($\tau = 1.4 \times 10^{-13}$ s) by tunneling through the potential energy barrier to be the one observed in the slow charge stripping experiments. We thus conclude that the electronic ground state of CH^{2+} could not be the one observed in the slow charge stripping collisions.

Next, we consider low lying excited states of CH^{2+}, in particular, the first excited state of the $^2\Sigma^+$ symmetry. It can be seen that this state, $A\ ^2\Sigma^+$, has a local minimum according to the calculations by Gu et al. [13] and Koch et al. [12], shown in Fig. 6. These calculations are in agreement with most previous calculations [8,9] except the calculations by Wetzel et al. [11] which suggest that all states of CH^{2+} are repulsive. Gu et al. [13] also calculated the resonance widths of the $v = 0$ and 1 vibrational states bound to the $A\ ^2\Sigma^+$ state to be 4.6×10^{-13} and 4.6×10^{-12} a.u., respectively, for the $A\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ transition. This indicates that the decay of the excited $A\ ^2\Sigma^+$ state to the electronic ground state is very unlikely. They therefore suggested that this state might be the long lived state of CH^{2+} observed previously in slow

Table 1
Resonance energies, widths, and mean lifetimes of (a) CH^{2+} and (b) CD^{2+}, for $l = 0$; only a lower limit was computed for vibrational states having $\tau > 3.1 \times 10^{15}$ s because of numerical reasons

v	E_v (a.u.)	Γ_v (a.u.)	τ_v (s)
(a) $^{12}CH^{2+}$			
0	$-37.027\,641$	$<7.85 \times 10^{-33}$	$>3.1 \times 10^{15}$
1	$-37.026\,135$	$<7.85 \times 10^{-33}$	$>3.1 \times 10^{15}$
2	$-37.024\,979$	4.42×10^{-22}	5.5×10^{4}
3	$-37.024\,210$	2.25×10^{-13}	1.1×10^{-4}
4	$-37.023\,727$	1.01×10^{-7}	2.4×10^{-10}
(b) $^{12}CD^{2+}$			
0	$-37.027\,865$	$<7.85 \times 10^{-33}$	$>3.1 \times 10^{15}$
1	$-37.026\,695$	$<7.85 \times 10^{-33}$	$>3.1 \times 10^{15}$
2	$-37.025\,702$	$<7.85 \times 10^{-33}$	$>3.1 \times 10^{15}$
3	$-37.024\,917$	1.28×10^{-27}	1.9×10^{10}
4	$-37.024\,335$	1.28×10^{-18}	18.9
5	$-37.023\,921$	5.77×10^{-12}	4.2×10^{-6}
6	$-37.023\,631$	2.31×10^{-7}	1.0×10^{-10}

charge stripping collisions. According to Koch et al. [12] the $A\ ^2\Sigma^+$ state is metastable and the vibrational resonances can decay by tunneling through the potential energy barrier in addition to the electronic transition to the ground state. We have calculated all vibrational resonances and their widths for the $A\ ^2\Sigma^+$ state of $^{12}CH^{2+}$ and $^{12}CD^{2+}$ using the phase amplitude method [19]. The spline fit to the tabulated potential energy curve calculated by Koch et al. [12], also shown in Fig. 6, was used for these calculations. Four of the vibrational resonances of $^{12}CH^{2+}$ shown in Table 1 have mean lifetimes ($\tau = 1/\Gamma$) longer than the 3 μs lifetime estimated for the observed long lived CH^{2+}. These long lifetimes are a result of the very large width (~18 a.u.) of the shallow potential energy barrier and the large reduced mass of these dications. The $v = 0$ vibrational state, for example, can decay by electronic transitions to the ground state and by tunneling, for which the rates are 4.6×10^{-13} and $<7.8 \times 10^{-33}$ a.u., respectively. Thus, the tunneling rate is negligible and the mean lifetime of this state is about $\tau_0 = 53\ \mu$s. It is important to note that this tabulated potential energy curve is sparse at large internuclear distances, and as a result the calculated mean lifetimes might change somewhat because of deviations of the spline fit curve from the "exact" potential energy curve. Better values for these resonances could be calculated if the potential energy curve would be computed at a few additional values of R. However, we expect that the low vibrational resonances will still have long lifetimes for tunneling. This clearly indicates that CH^{2+} has long lived states, and that the negative result of our experimental search is just an indication that this state cannot be populated in fast charge stripping collisions, for which the collision time is about 10^{-16} s. The transition rate between the parent CH^+ ions, assuming that they are in their electronic ground state ($R_0 = 2.1$ a.u.), and the excited $A\ ^2\Sigma^+$ state of $^{12}CH^{2+}$ ($R_0 = 6$ *a.u.*, see Fig. 6) is expected to be very small because of the very poor overlap between the initial and final vibrational wave functions.

Now, even though theory suggests the existence of a long lived state of CH^{2+}, some questions still remain concerning the observation of long lived $^{12}CH^{2+}$ in slow charge stripping collisions. (1) The $A\ ^2\Sigma^+$ state is about 4.7 eV higher than the $X\ ^2\Sigma^+$ ground state of CH^{2+}, thus the agreement between the measured transition energy and the energy difference between the CH^+ ground state and the CH^{2+} $A\ ^2\Sigma^+$ state is not as good as with the ground state of the latter. One might try to overcome this problem by suggesting that the initial state is either highly excited vibrationally or it is a metastable state of CH^+. Mathur and Badrinathan [4] argued that the latter is less likely for their ion source. Given that the potential well of the electronic ground state of CH^+ is only about 3 eV deep, even the highest excited vibrational state will leave a difference larger than 1 eV. (2) The charge stripping collisions where CH^{2+} was observed are much slower than those reported here, about 3 keV as compared to 850 keV. This increases the collision time by more than an order of magnitude, and changes of R during the collision might be more likely. However, the collision time for 3 keV projectile energy is $\sim 1.5 \times 10^{-15}$ s, still short enough for one to consider the transition as vertical. Thus, it is not clear why the cross section for $CH^{2+}(A\ ^2\Sigma^+)$ production should be much larger for the slow collisions than that for the fast collisions.

Further experimental work is needed as the production of long lived CH^{2+} will still cause debate. For example, studies of charge stripping of a few kiloelectron volts CD^+ should be conducted, because many experimental problems are removed (like ^{13}C isotope and the impurity beam of CH_2^+ fragments of CH_3^+ at $\frac{14}{15}$ of the beam energy). Another possibility are studies in which one probes the molecular nature of the observed CH^{2+} by dissociating it after the analyzer, either by using a thin foil as suggested here or a thin gas target as discussed briefly by Hamdan et al. [6].

To summarize, long lived CH^{2+} and CD^{2+} dications were not observed in fast charge stripping collisions of 850 keV CH^+ and CD^+ on Ar. Calculations of the locations and widths of the vibrational resonances bound to the $A\ ^2\Sigma^+$ excited state of this dication indicate that long lived states exist. Similar calculations show that the $X\ ^2\Sigma^+$ electronic ground state cannot sustain any long lived state ($\tau > 1\ \mu s$). The fact that the long lived $A\ ^2\Sigma^+$ state was not detected in our measurements is attributed to the poor overlap between the initial and final vibrational wave functions, which makes the transition probabilities in the $CH^+ + Ar \rightarrow CH^{2+}$ reaction, too small to be detected. The question of how the $A\ ^2\Sigma^+$ state of CH^{2+} can be populated in slow (a few kiloelectron volts) charge stripping collisions, where the observation of long lived CH^{2+} has been reported, still awaits explanation.

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