

We continued our collaborative studies of long lived doubly charged molecular ions, such as HeNe$^{2+}$, HeAr$^{2+}$, He$_2$$^{2+}$, CH$_n$$^{2+}$ and CO$^{2+}$. These molecular ions are formed by charge stripping a few hundred keV singly charged molecular ion beam (from the Van de Graaff accelerator at the Technion, Israel) in a thin gas target. Usually, the doubly charged ions are formed in transient states, which promptly decay. If a measurable fraction of these doubly charged molecular ions decay within their flight time to the detector, then their decay rate can be measured using the experimental methods we reported previously [1-3]. Each new molecular ion studied has different constraints, requiring further development of the basic experimental techniques. In addition we developed a new technique, which provides a simultaneous measurement of the decay rate and the kinetic energy release upon dissociation [4]. This additional information can be used to determine the decay mechanism and the states for which the decay rate is measured.

Measured mean lifetimes are a stringent test of the potential energy curves and the decay process. This is due to the strong dependence of the decay rates on the energy of the barrier in the case of tunneling or the coupling and overlap between the states for predissociation [4].

We have recently reported first experimental evidence for the existence of long-lived $^3$He$^{40}$Ar$^{2+}$ molecular ions. A new experimental method was used to verify that the measured ion is not $^{43}$Ca$^{2+}$ or $^{40}$ArH$_3$$^{2+}$ [Publication #109]. The mean lifetime was determined to be longer than 40 µs [Publication #67], much longer than any doubly charged rare gas dimer we measured previously. Calculations of the vibrational state population and the mean lifetimes of the four lowest electronic states indicate that all of them are very long lived and they may be populated in HeAr$^+$ + Ar $\rightarrow$ HeAr$^{2+}$ charge stripping collisions.

The long-lived HeNe$^{2+}$ molecular ion, when discovered, was somewhat of a mystery with regard to the electronic state in which it had been detected [5]. Previous calculations of the
lowest potential energy curves indicated that the electronic ground state is unbound [6]. Elaborate multi-reference configuration interaction (MRCI) calculations of Heinemann and Koch [Publication #11], in contrast, indicate that the electronic ground state can support a single vibrational state, as shown in Fig. 1. This state, however, decays too rapidly to be detected (τ~11 ps). Many excited electronic states have also been calculated and the dipole decay rates of the vibrational resonances have been computed. Some of the decay rates are in agreement with the measured values not only for the most abundant $^4\text{He}^{20}\text{Ne}^{2+}$ isotope but also for two other isotopes we have measured. In Fig. 2 we show the possible long lived electronic states. The measured mean lifetimes of the different isotopes do not differ much from each other as expected for decay by dipole transitions (for further details see Publication #11).

![Figure 1](image1.png)

**Figure 1.** The calculated $X\,^1\Sigma^+$ ground state potential energy curve of HeNe$^{2+}$. Solid line – our work [Publication #11]; dashed line – Ref. [6].

![Figure 2](image2.png)

**Figure 2.** The possible vertical transitions from the $^3\text{He}^{22}\text{Ne}^+$ ground state to the $d\,^3\Pi$, $C\,^1\Pi$, $D\,^1\Sigma^+$, and $E\,^1\Sigma^+$ states of $^3\text{He}^{22}\text{Ne}^{2+}$, which have mean lifetimes in agreement with experiment.

The existence of long-lived CH$^{2+}$ molecular ions has been the topic of many heated debates since the first report of their existence and mean lifetime (τ~3 µs) [7]. Some theorists predicted a repulsive ground state for this molecular ion while others claimed it has a shallow minimum (see [8,9], for example). We have searched for resonances in all available ground state potentials shown in Fig. 3, using the phase-amplitude method [Publication #81], and found none for CH$^{2+}$ [Publication #86]. According to our tunneling rate calculations and the dipole decay
Rate calculations of Gu et al. [10] the excited $A^{2}\Sigma^{+}$ state, shown in Fig. 4, supports long lived states ($\tau \sim 50 \mu s$ for the $v=0$ state, for example).

![Figure 3](image_url1). Potential energy curves for the $X^{2}\Sigma^{+}$ electronic ground state of CH$_2^{+}$. Note that the thick curves have a local minimum while the thin ones are purely repulsive.

![Figure 4](image_url2). 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 [9,10] (the value computed at $R=100$ a.u. was included in the fit).

In addition to the debate about the identity of the long-lived state of CH$_2^{+}$ there was a “clash” between experimentalists about the validity of the experimental observation. Some argued that the measured doubly charged ion was $^{13}$C$_2^{2+}$ [9] while others explained why that cannot be the case [11]. To overcome this experimental problem we measured the H fragments produced by a thin foil placed in front of the detector, as shown in Fig. 5 (see Publication #109 for experimental details). The yield of H fragments does not peak where the CH$_2^{+}$ molecular ions are expected, as shown in Fig. 6, indicating that such long-lived molecular ions are not formed in the charge stripping reactions we studied [Publication #86]. The $^{13}$C does appear as expected. Therefore, one has to be careful to distinguish between it and the CH$_2^{+}$ experimentally. Note that the $A^{2}\Sigma^{+}$ state is not likely to be populated in a vertical transition because of its large equilibrium internuclear distance, $R_0$. 
Using the same experimental methods [Publication #109] we explored the formation and stability of all CD$_n^{2+}$ (n=1-5) and CH$_n^{2+}$ (n=1-4) molecular ions [Publication #70]. In particular, we were interested in their formation from different CD$_m^+$ and CH$_m^+$ parent ions, respectively, and the impact of that on the mean lifetime and production cross section. CD$_2^{2+}$ molecular ions were formed from all parent ions with $m \geq 2$ but the production cross section depended on $m$. CD$_4^{2+}$ and CD$_5^{2+}$ were formed only from their respective singly charged parent. In the same charge stripping reactions neither CD$_2^{2+}$ nor CD$_3^{2+}$ were observed. The mean lifetime of CD$_2^{2+}$ was determined to be $4.0 \pm 1.3 \mu$s, while the mean lifetimes of CD$_4^{2+}$ and CD$_5^{2+}$ were determined to be longer than 2.1 and 3.3 $\mu$s, respectively.

Using experimental methods similar to those used in the measurements described above [1-3] we measured a mean lifetime of $300 \pm 40$ ns for $^3$He$^4$He$^{2+}$ [12], as reported in our previous progress report. Belkacem *et al.* [13] reported mean lifetimes longer than a few $\mu$s for this molecular ion, an observation associated with the vibrational ground state [14]. This molecular ion has a metastable electronic ground state, and thus is expected to decay by tunneling through the potential energy barrier. While the theoretically predicted mean lifetime for the $v=2$ state, $\tau \sim 16$ ns [15-18], is the closest to our measured value, it is off by almost a factor of 20. One
would expect that the potential energy curve of this 2-electron molecular ion would be known well enough such that agreement between theory and experiment is better. Using the phase shift method [15] to calculate the decay rate by tunneling of this molecular ion we have shown that a distribution of highly excited rotational states, peaked around \( l=14 \) for \( v=1 \) (or \( l=22 \) for \( v=0 \)), is in agreement with the measurement. It was suggested that this population of rotational states is a result of the production mechanism of \(^3\text{He}^4\text{He}^+\) in the rf ion source [12].

The suggestion that \(^2\text{He}_2^+\) dimers are preferentially formed with high angular momentum is of great importance for those who are interested in ion chemistry. However, it is based on the assumption that we measured the decay by tunneling of the electronic ground state and that the potential energy curve is precise. The first assumption, in particular, can lead to false conclusions, as we have seen in the Ne\(\text{Ar}^{2+}\) case [19], and thus it is important to verify which quantum state is decaying. To address this issue we calculated the potential energy curves and decay rates of many excited states of this molecular ion. Furthermore, we have developed a new experimental method, which enables the simultaneous determination of the mean lifetime and kinetic energy release (KER) upon dissociation. This method is based on 3D imaging of the dissociating fragments using a CCD camera and a split anode photo multiplier tube coupled to a microchannel plate detector with a phosphor anode, as shown in Fig. 7. The first gives precise position information (\( \delta x \sim 30 \mu\text{m} \)) while the second provides a precise measurement of the time difference between the two fragments (\( \delta t \sim 0.31 \text{ ns} \)).

**Figure 7.** A schematic view of the 3D imaging experimental setup.
Molecular ions dissociating by tunneling or predissociation are expected to have very narrow KER distributions, practically delta functions. Decay by dipole transitions, in contrast, results in wider KER distributions, as shown schematically in Fig. 8. This additional information, therefore, can help distinguish between decay mechanisms. Furthermore, if the resolution is sufficient, the quantum state of the dissociating molecular ions may be determined.

To test the new method we have recently measured the decay rate of $^{12}$C$^{16}$O$^{2+}$ [20]. We chose this molecular ion because one of its states has a decay rate [21,22] for which our method has high sensitivity. Furthermore, the excitation energy [21] and KER [22] of this state, as well as others, were also reported. The CO$^{2+}$ molecular ion decays mainly by predissociation [23]. We have measured the lifetimes of a few vibrational states of $^{12}$C$^{16}$O$^{2+}$ to better precision than previous measurements, which are superior in determining the energy of the decaying states [21,22]. Explicitly, $\tau=670\pm50$ and $\tau=26\pm5$ ns were measured for the states with KER values of 5.713 and 5.841 eV, respectively. The measured mean lifetimes and kinetic energy releases are consistent with previous measurements [21,22]. We also computed the mean lifetimes and KER of a few low-lying states, using the potential energy curves reported by Andersen et al., [23].

The state associated with 5.713 eV KER has a mean lifetime 3 orders of magnitude shorter than the measured value [20], thus calling for better theoretical treatment of the CO$^{2+}$ structure and decay.

We then used this new method to measure the mean lifetime and KER of long-lived $^3$He$^4$He$^{2+}$ molecular ions. Our recent results $\tau=164\pm20$ ns and a KER of $9.8\pm0.2$ eV are consistent with the previous mean lifetime measurement within the experimental uncertainty. The accuracy of the mean lifetime measurement has improved dramatically mainly because we

**Figure 8.** Schematic potential energy curves of a typical AB$^{2+}$ molecular ion. Curve (1) supports metastable states while (2) and (3) are repulsive. The decay mechanisms are denoted on the figure as (a) predissociation, (b) tunneling, and (c) dipole transition to a dissociating state.
solely measured dissociating molecules [24]. More importantly, the measured KER sets limits on the possible dissociating states as shown in Fig. 9. A distribution of states peaked around $v=1$ and $l=14,15$ is in nice agreement with the data. In contrast, a distribution of states peaked around $v=0$ and $l=22$, which was in reasonable agreement with our first measurements, does not now agree. Furthermore, from the inset it can be seen that a single state is not in agreement with the measurement.

**Figure 9.** Calculated and measured mean lifetimes and KER values of many rovibrational states of $^3\text{He}^4\text{He}^{2+}$.

To verify that no other decay process may contribute we have calculated many excited states of the $^3\text{He}^4\text{He}^{2+}$ molecular ion and found one state, the $a^1\Sigma^+$ state, which can decay by dipole transitions. The computed mean lifetimes and KER of this excited state, however, are not in agreement with the data [24]. Following the elaborate experimental and theoretical work, we can state that the original suggestion associating the measured mean lifetimes with highly excited rotational states is verified. This high angular momentum has to originate from the formation mechanism of the parent $^3\text{He}^4\text{He}^+$ molecular ion, because the angular momentum does not change significantly in fast charge stripping collisions. Further studies of the collisions forming the $^3\text{He}^4\text{He}^+$ in the plasma are called for. In order to determine if these high angular momentum states were measured just because they matched the range of high experimental sensitivity or because He$_2^+$ formation really peaks at high $l$ values, we have started similar measurements of
the homonuclear $^4\text{He}_2^{2+}$ dimers. For this isotope low $l$-states as well as high $l$-states are within the high sensitivity range of our experimental technique (see proposal A.3.7).

**References**