Measurement of the Ultrashort Bond Length in He$_2^{++}$

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Coulomb-explosion experiments have been carried out on both the dihelium cation He$_2^+$ and the corresponding doubly charged molecule He$_2^{++}$ yielding bond-length distributions for each species. These measurements provide the first experimental evidence for the bond length of He$_2^{++}$. The most probable value of the measured bond-length distribution is 0.75 ± 0.02 Å. We also determine the lifetime to be longer than 5 μsec. This demonstrates the suitability of the Coulomb-explosion method to the study of structures of short-lived, highly reactive, rare, or otherwise exotic molecules.

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The rotational and vibrational spectra of diatomic molecules provide us with a rich source of information about bonding in such systems.[1] In the case of ionic molecules, however, spectroscopic measurements have proven to be far more difficult. This is a consequence of the extremely high reactivity of such molecular ions. Nevertheless, great strides have been made in recent years and there is now a growing body of knowledge on simple singly charged molecules.[2] For multiply charged molecules, however, there is little detailed experimental information available, aside from proof of existence in mass-spectrometric analyses. For the case of doubly charged diatomics, only a few molecules [such as N$_2^{++}$ (Ref. 3) and NO^{++} (Ref. 4)] have been studied. This scarcity of experimental data is in contrast to the importance such species play in combustion dynamics, high-temperature plasmas, and interstellar clouds.

The method of Coulomb-explosion imaging has been demonstrated in recent years to be a particularly powerful method to study many-body dynamics in polyatomic molecules.[5] In this Letter, we report the first such experiments with a multiply charged molecule. Using this method, the three-dimensional images of nuclei within individual molecules are recorded with unit efficiency for all molecules within a fast beam. As such, this technique is especially suited to studying rare, short-lived, and highly reactive species such as highly charged molecules, which are difficult to produce and contain in large densities.

Helium is chemically the least reactive of all of the elements, yet a variety of small helium-containing molecules are known to exist as long-lived or even stable species.[1] These include HeH$^+$, He$_2$, He$_2^+$, and He$_2^{++}$. Although not very common in the laboratory, because of the abundance of helium in stellar atmospheres and in interstellar clouds, many of these molecules are considered to be of astrophysical interest.[6]

Among these, He$_2^{++}$ is perhaps the simplest, but least known. As the isoelectronic analog of the neutral H$_2$ molecule, the doubly charged dihelium molecule provides an unusual example of the most basic electron-pair bond.

He$_2^{++}$ was first studied theoretically in 1933 by Pauling.[7] Using $1s$ hydrogenlike single-electron functions and an effective nuclear charge, his variational treatment showed that while the internuclear potential between two He$^+$ ions is repulsive at large separations, the exchange and electron-nuclear attraction integrals overcome the nuclear repulsion at intermediate distances. The resulting potential well has a minimum at 0.75 Å, with a 1.4-eV barrier at 1.1 Å, and supports four vibrational levels. Since that time, several workers have improved upon Pauling's treatment[8] and it now appears that with a predicted bond length of 0.70 Å, it will prove to be the smallest molecular system. This equilibrium distance is amazingly close to the 0.74- and 0.77-Å bond lengths in the isoelectronic H$_2$ and HeH$^+$ molecules, respectively.

While there is no spectroscopic information available from experiment, He$_2^{++}$ has recently been observed by charge stripping of He$_2^+$ with a double-focusing mass spectrometer.[9] While that experiment demonstrated the existence of this species as a long-lived molecule, there has been no confirmation of its predicted bond length. In order to test this prediction, we have measured the bond-length distribution within He$_2^{++}$ by Coulomb-explosion imaging.

Singly charged ^{3}He^{4}He$^+$ ions were produced in a radio-frequency discharge in the terminal of the Argonne Dynamitron and accelerated to 2 MeV. After emerging from the accelerator, the ions were magnetically analyzed through an 8° bend by magnet $M1$ (see Fig. 1). These ions were then further bent through 25° by a second magnet ($M2$). To produce the doubly charged species, a 10-cm-long gas cell was introduced between the two magnets and filled with N$_2$ at a pressure of ~ 0.1 Torr. The magnet $M2$ was then returned to select the secondary ^{3}He^{4}He^{++} beam. As pointed out in Ref. 9, this method of collisional charge changing proved necessary because the small predicted bond length of He$_2^{++}$ implies unfavorable Franck-Condon factors for direct production in the ion source. The isotopic form ^{3}He^{4}He^{++} was used to avoid confusion of He$_2^{++}$ with atomic He$^+$ ions.
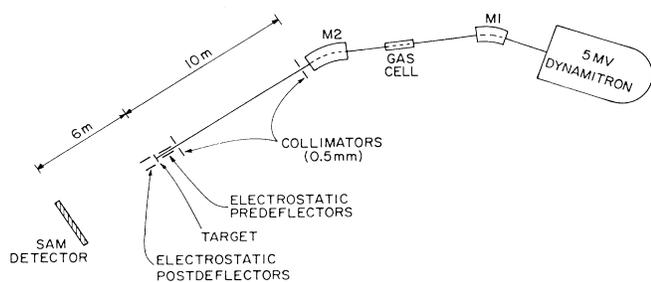
FIG. 1. Schematic diagram of the experimental apparatus described in text.

FIG. 2. Contour plots of the spatial distribution of helium nuclei on the surface of the SAM detector following Coulomb explosions of (a) ^{3}He^{4}He$^+$ and (b) ^{3}He^{4}He^{++} molecules. Because of the electrostatic deflection, the ^{3}He^{++} and ^{4}He^{++} distributions are separated in the X direction. The contour levels are $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, and $\frac{1}{32}$ of the peak intensity. The size of these distributions reflects the differences in the mean bond lengths of these molecules (see text).

After magnetic selection, the beam was collimated to ± 0.09 mrad over a 10-m path length. Upon entering the scattering chamber, the beam was electrostatically "predeflected" horizontally by 40 mrad and passed through a thin ($\sim$100-Å) Formvar film. Because of the high velocity of the ion beam (and the high density of this solid film), the projectile electrons are all stripped shortly ($\sim 10^{-16}$ sec) after entering the solid.[10] This leaves two bare helium nuclei that rapidly separate in a violent dissociation process which has been termed a "Coulomb explosion."[11] The characteristic vibrational ($\sim 10^{-14}$-sec) and rotational ($\sim 10^{-12}$-sec) periods of the initially bound molecules are long compared to the stripping time. Thus, for each molecule in the beam, the final velocities of the dissociation fragments are essentially determined by the spatial geometry of the nuclei at the instant that the molecule enters the stripping foil.[5]

After emerging from the stripper foil, the dissociation fragments were charge and mass separated by a "post-deflection" electric field region in the direction opposed to the predeflection. This combination of predeflection and post deflection serves to limit the dissociation region to within a few millimeters of the target, thus eliminating contamination of the results by dissociation fragments in the beam (produced by collisions with residual-gas atoms or spontaneous decay). Thus, only the molecules that survive the flight time (1.5 μsec) are measured. By observing the relative intensities of predissociation fragments, we have estimated the lifetime of He$_2^{++}$ to be longer than 5 μsec.

Following the post deflection, the Coulomb-explosion fragment ions continue through a field-free flight path ($\sim$6 m). The ^{3}He^{++} and ^{4}He^{++} ions, confined to electrostatically separated "cones" (see Fig. 1), then strike a segmented-anode multiwire proportional chamber (SAM). This SAM detector, which will be described in detail elsewhere,[12] measures the two-dimensional positions ($\sim$1-mm resolution) and relative arrival times ($\sim$400-psec resolution) for both nuclei in each molecule. The two-dimensional spatial distribution of the explosion fragments on the surface of the detector are shown in Fig. 2 for both ^{3}He^{4}He^{++} and ^{3}He^{4}He$^+$. These data

represent the results for about 10^5 molecules. There are two high-density regions seen for each molecular ion. One is the zone of ^{3}He^{++} fragments and the other is of the ^{4}He^{++} fragments. For each individual molecule incident on the stripping foil, both fragment nuclei are observed at the detector. After compensating for the difference in deflections for the two masses, the corrected ^{3}He-^{4}He distance on the face of the detector is a measure of the transverse component of their relative velocity. The longitudinal component is measured by the difference in the time of arrival of the ions. Thus the total kinetic energy in the center of mass of the two nuclei can be deduced for each individual molecule in the beam. Except for a negligible vibrational kinetic energy, this asymptotic center-of-mass energy is equal to the initial potential energy ($4e^2/r$) immediately after the electron stripping (where r is the instantaneous internuclear separation). Hence, as will be discussed later, we have derived the complete distribution of bond lengths in the original molecules from these data. Even without such detailed analyses, the raw data shown in Fig. 2 can be quite revealing. For instance, the diameters of the fragment ion "cones" are quite different for the two molecules studied. This implies a smaller mean bond length for the He$_2^{++}$ molecule for the singly charged species.

Before discussing the physical significance of these results, two technical points should be mentioned. Because of the influence of the stripping medium used to initiate the Coulomb explosion, the actual dissociation potential

while in the solid generally deviates from the purely Coulombic interaction assumed here. However, because of the high velocity of these ions and the ultrathin stripping films used[13] in these experiments, such effects have been minimized. Of these effects, the most serious are small-angle multiple scattering of the projectile nuclei while in the target, and the electron polarization "wake" produced in the solid medium.[14] We have measured the Formvar stripping foil thickness to be 1.3 $\mu g/cm^2$ (Ref. 15) and estimate the effect of multiple scattering to be ~1 mrad.[16] This results in an overall uncertainty of 0.02 Å in the bond length of each individual projectile molecule. Second, we have selected a subset of the data in order to avoid the necessity of correcting for the "wake."[17] The principal effect of the wake is a reorientation of the internuclear vector, with only a small influence on the internuclear separation, for molecules aligned near the beam direction. To minimize possible errors caused by these effects, we have ignored molecules in which the direction of the relative velocity of the fragment ions in the projectile frame is within 36° of the beam direction.

Figure 3(a) shows the results of converting the measured center-of-mass kinetic energies of the Coulomb dissociations into distributions of bond lengths as described earlier. It should be compared with the theoretical potential curves [Fig. 3(b)]. The He_2^+ has been studied both experimentally[18] and theoretically.[8] The results of our measurement of the bond-length distribution of He_2^+ are in good agreement with the potential curve. We find the most probable bond length to be 1.10 Å and the distribution of the bond lengths is confined to the allowed region of the potential well. This is consistent with the expectation that many vibrational states will be populated in the collisions producing He_2^+ in the ion source.

The data on the $^3He^4He^{++}$ bond length serve as the first confirmation of the potential-energy calculation of this, the simplest, doubly charged molecule. For our sample of molecules, we find the most probable bond length to be 0.75 Å. This value and the shape of the bond-length distribution are consistent with the calculated potential curve. The measurements of the distributions for the two molecular ions were performed under exactly the same experimental conditions, the only difference being the insertion of the gas cell and the retuning of magnet $M2$. The overlap of the two radial distributions [Fig. 3(a)] is quite small. Because the flight time from the gas cell to the foil stripper is ~2 μsec, the vibrational-state population of He_2^{++} ions reaching the target should be free of the highest-lying predissociative states (those with lifetimes shorter than the flight time) which are favored by Franck-Condon excitation. This component of the beam dissociates before the stripper and is purged by the electrostatic deflectors. Nevertheless, because of the larger bond lengths of the broad He_2^+ distribution, the Franck-Condon factors do not
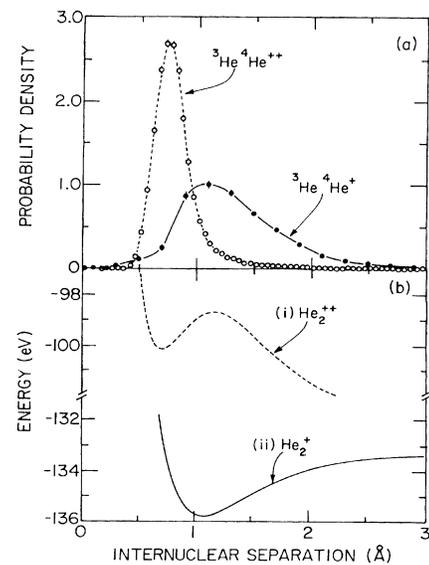
FIG. 3. (a) Measured distributions of bond lengths for $^3He^4He^+$ (filled circles) and $^3He^4He^{++}$ (open circles). The curves are drawn to guide the eye. (b) Theoretical potential curves for these molecules (see Ref. 8).

favor population of the ground vibrational state of the smaller doubly charged molecule. We presumably populate several of the lowest-lying levels and thus the value of the most probable bond length measured here should be interpreted as an upper limit for the equilibrium bond length, rather than representative of the ground state. Because of this contribution of excited states, and our neglect of small deviations from the pure Coulomb dissociation, our results overestimate the equilibrium bond length by ~0.05 Å.

This experiment has demonstrated clearly that the Coulomb-explosion imaging method is suitable for the measurement of the structure of doubly ionized molecules, which are difficult to measure by more conventional methods. This is also a demonstration of its capability to determine the structure of species with quite short lifetimes. The He_2^{++} system is simple enough that the present state of theoretical calculations is adequately accurate for interpreting these experiments. It is reassuring that the Coulomb-explosion results are consistent with the calculations. For more complex cases the situation is not yet as clear and more experimental work is needed for testing the theoretical predictions.

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