

Sensitivity of Coulomb-explosion images to the shapes of molecular potentials: The case of He_2^{2+}

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A quantitative analysis of the results of a recent Coulomb-explosion experiment with He_2^{2+} is described. Using the adiabatic potential curve predicted for the $^1\Sigma_g^+$ ground state of this relatively simple dication, a Monte Carlo simulation of the Coulomb-explosion process was performed. The results show that such methods can faithfully reproduce the experimental results when accurate potential-energy surfaces are available. The implications for more complex systems are discussed.

Most of our knowledge of the structures of free molecules comes from indirect observations that focus on properties (for example, energy or mass spectra) that depend on structure. In recent years, an alternative method of studying molecular structures has been developed.¹ In contrast to spectroscopic studies, the new technique of Coulomb-explosion imaging (CEI) yields geometrical images of individual molecules. CEI takes advantage of the large (and rapid) Coulomb repulsion of the nuclei within molecules which are suddenly stripped of their electrons. The first experiments with this new technique have already revealed structural images of several important species, such as, C_2H_3^+ ,² CH_4^+ ,³ NH_4^+ ,¹ and He_2^{2+} ,⁴ among others.

Of these, He_2^{2+} is the simplest system studied to date. He_2^{2+} was first explored theoretically in 1933 by Pauling.⁵ Since that time, several workers have improved upon Pauling's treatment and the modern theoretical potentials agree quite well with each other.⁶ The first experimental observation of this molecular ion was made only recently by charge stripping of He_2^+ and subsequent analysis in a double-focusing mass spectrometer.⁷ Following that discovery, the bond length distribution was measured by CEI,⁴ and the most probable bond length was found to be 0.75 ± 0.02 Å in very good agreement with the theoretical predictions. It is the aim of this Brief Report to make a more complete quantitative comparison between the CEI data⁴ and theory. Through such a comparison, we demonstrate the sensitivity of the CEI data to the detailed shape of the potential energy surface.

The experiment as been described previously,⁴ but a few major points which are important to the present analysis will be reiterated here. Singly charged $^3\text{He}^4\text{He}^+$ 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. They then passed through a 10-cm-long gas cell (filled with N_2 at a pressure of ~ 0.1 Torr) producing $^3\text{He}^4\text{He}^{2+}$ ions which were directed toward the target by means of a second analyzing magnet. Before hitting the solid target, the beam was electrostatically "predeflected" to clean it of predissociation fragments. The molecules surviving the flight time between

the gas cell and the predeflector (~ 1.5 μs) then struck the target which was located 3.6 cm downstream of the exit of the deflector. Because of the high velocity of the ion beam, the projectile electrons are all stripped shortly ($\sim 10^{-16}$ s) after entering the solid target (~ 100 Å Formvar). This leaves two bare helium nuclei that rapidly separate, a process called "Coulomb explosion." These bare helium fragments were "postdeflected," by a second electrostatic field following the target, toward the segmented anode multiparticle (SAM) detector. This SAM detector, which has been described elsewhere,⁸ measures the three-dimensional velocities for both nuclei in each molecule. Thus, the total kinetic energy in the center of mass of the two nuclei can be deduced for each individual molecule in the beam. This kinetic energy distribution, which is shown in Fig. 1, is representative of the initial bond-length distribution of the molecules in the beam.⁹ It has already been shown that the most probable value extracted from the data is consistent with the calculated potential curve. It is our purpose in this Brief Report to show that the shape of this distribution is in quantitative agreement with the theoretical potential as well.

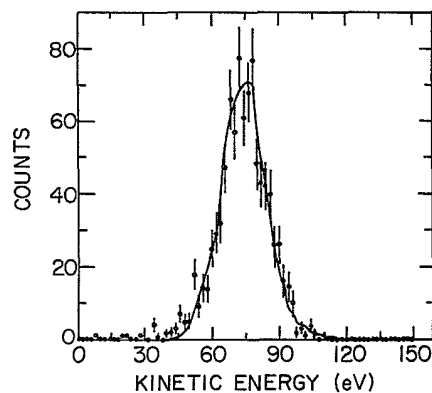


FIG. 1. Kinetic-energy distribution in the center of mass of $^3\text{He}^4\text{He}^{2+}$. The points with error bars are the experimental results and the solid line is the result of the simulation, as described in the text.

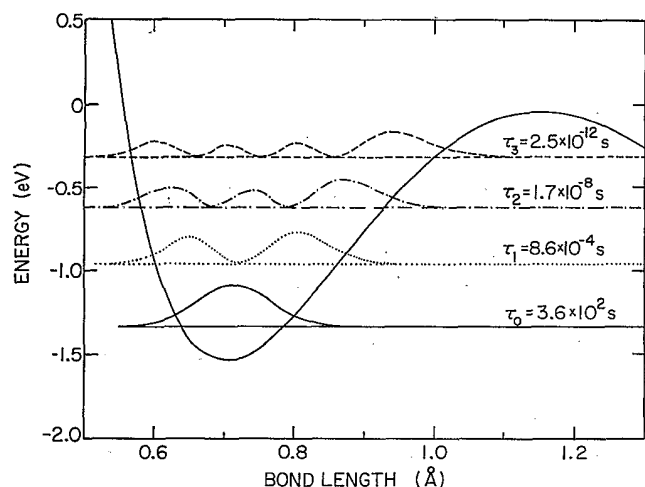


FIG. 2. Theoretical $X^1\Sigma_g^+$ potential curve of ${}^3\text{He}{}^4\text{He}^{2+}$ taken from Yagisawa, Sato, and Watanabe (Ref. 6). The four vibrational states and the squares of the corresponding wave functions are indicated. The predicted lifetimes (Ref. 12) are given for each level.

Before discussing the details of the method, three important 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 slightly from a purely Coulombic interaction. Another effect to consider is the small-angle multiple scattering of the projectile nuclei while in the target, which can produce a broadening of the final velocity distributions. Finally, in order to improve the accuracy of the kinetic-energy distribution far from equilibrium, we have taken experimental cuts in the data aimed at eliminating any possible source of low-probability spurious events which could affect the tails of the distribution. This has the consequence of reducing the statistical accuracy of the data, but has a minor influence on the overall shape of the spectrum.

In order to compare the experimental result with the potential curve, we simulated the Coulomb explosion process using a Monte Carlo technique which has been described elsewhere.^{10,11} The simulation includes the effect of correlation of multiple scattering with the Coulomb repulsion and uses a realistic screened potential to describe the repulsion between the two nuclei while the molecule is in the solid. The initial distribution for the internuclear distances was given by the square of the wave functions calculated by solving the Schrödinger equation for the four different vibrational states using the potential curve calculated by Yagisawa, Sato, and Watanabe⁶ (see Fig. 2). For each state, a final kinetic-energy distribution was simulated by means of 3000 trajectories. These simulated distributions are shown in Fig. 3. Note that small energies correspond to larger initial internuclear separations. These final distributions were combined, using multiple linear regression, to best fit the experimental distribution. As can be seen in Fig. 1, the simulation and the data agree. A good indication of the quality of the result is given by the different weights ex-

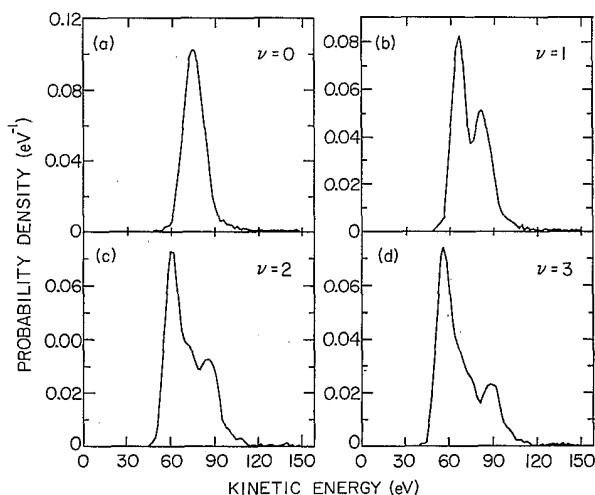


FIG. 3. Simulated final kinetic-energy distributions in the center of mass for the four vibrational states. Each distribution is calculated starting from the corresponding wave function (squared) of ${}^3\text{He}{}^4\text{He}^{2+}$ and simulating the trajectories of 3000 molecules from that ensemble. (a), (b), (c), and (d) correspond to $\nu=0, 1, 2,$ and $3,$ respectively.

tracted for each vibrational state: $C_0=0.57\pm 0.08$, $C_1=0.27\pm 0.07$, $C_2=0.06\pm 0.06$, and $C_3=0.10\pm 0.03$ (the indices represent the vibrational quantum number). The fact that the two last coefficients are negligible can be understood in terms of the lifetimes of the two highest vibrational states. Because of the difference in bond length between He_2^+ and He_2^{2+} , direct ionization of the singly-charged di-helium would predominantly populate the uppermost levels of the doubly-charged molecular ion. However, since the lifetimes^{12,13} of these two states (see Fig. 2) are both substantially shorter than the flight time between the gas cell and the predeflector ($\sim 1.5\mu\text{s}$), those states should be dissociated before reaching the target as can be inferred from the small values of C_2 and C_3 in the fitting result.

These data demonstrate that for the case of a relatively simple diatomic molecular ion, Coulomb-explosion data can be quite sensitive to the detailed shape of the vibrational potential. The lifetimes of the upper states depend sensitively on the shape of the potential barrier and any contribution of these levels would have been apparent in the low-energy region of the measured kinetic energy distribution (see Fig. 3). Similar work has also been carried out on more complex triatomic and polyatomic systems^{14,15} indicating the sensitivity of these measurements to the detailed shapes of molecular potentials. The precision of such studies could be greatly improved by extending these measurements to higher beam energies and consequently reducing the contributions of multiple scattering. It is now clear that using CEI, new insights on the geometrical distributions of nuclei within molecules can be explored.

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