Kinetic-energy release in the dissociative capture-ionization of CO molecules by 97-MeV Ar^{14+} ions

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The dissociation of CO^{Q+} molecular ions ($Q=4$ to 9) produced in multiply ionizing collisions accompanied by the transfer of an electron to the projectile has been studied using time-of-flight techniques. Analysis of the coincident-ion-pair flight-time-difference distributions yielded average values of the kinetic-energy releases for the various dissociation reactions. These values were found to be as much as a factor of 2 greater than the kinetic-energy releases expected for dissociation along Coulombic potential curves. The average kinetic-energy release observed for a given ion pair with charges q_1 and q_2 are nearly equal to the point-charge Coulomb potential energies for an ion pair with charges q_1+1 and q_2+1, suggesting that the parent molecular ion is formed with two electrons, on average, in highly excited states that do not contribute to the screening of the nuclei.

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I. INTRODUCTION

Several recent investigations have examined the kinetic energy released in the dissociative ionization of CO molecules by fast (MeV/u) ions generated by particle accelerators [1–3]. Interest in this topic derives from the fact that such collisions are capable of removing many electrons from a molecule on a time scale of 10^{-17} s. Thus it has been possible to study details of the dissociation pathways for CO^{Q+} molecular ions having Q as high as 7 by this technique. Since the average impact parameters involved in ionizing collisions with fast ions are large, the energy transferred to the nuclei of the molecule is negligible and, hence, the energy liberated in the dissociation process is directly reflected in the final velocities of the dissociation products. Experimentally the kinetic-energy release (KER) for a given dissociation reaction may be deduced by analyzing the time-of-flight (TOF) difference distribution for the corresponding product ion pair.

Determination of the distribution of KER from TOF difference data alone is complicated by the fact that many states may be populated in the collision. In addition to this, the initial orientation of the molecular ion is not known, and hence numerous simulations of ion-pair trajectories must be performed to transform a time-difference distribution into a kinetic-energy distribution [1,3]. While the KER distribution provides the most complete information regarding the molecular states contributing to a dissociation reaction, the average or most probable KER values (which may be more easily determined) are frequently used to characterize the prominent dissociation channels. The results presented in Refs. [1] and [3] have shown that the KER distributions for the dissociative ionization of CO by 2.4-MeV/u Ar^{14+} and

1-MeV/u F^{4+} ions are characterized by broad peaks with long, high-energy tails. The KER maxima are approximately centered around the Coulomb potential energies calculated for point-charge ions separated by the ground-state equilibrium bond distance, but because of the high-energy tails the average KER values are systematically higher than the Coulomb energies. On the other hand, Mathur *et al.* [2] measured the kinetic energies of C and O ions from the dissociative ionization of CO by 5.1-MeV/u F^{8+} ions, and concluded that the maximum ion kinetic energies were lower than those expected for dissociation along purely Coulombic potential curves. This finding appears to contradict the results of the other two studies. However, its validity is somewhat questionable because the measured single-ion kinetic-energy distributions contained contributions from several different dissociation reactions. In a study of ionization and dissociation of N_2 and CO in collisions with low-energy Ar ions (0.5–0.8 keV/u), Vancura and Kostroun [4] found that the TOF peak positions of the dissociation product ions were consistent with kinetic energies equal to the Coulomb energies.

The KER in dissociative multiphoton ionization of diatomic molecules by lasers also has been under active investigation [5–9]. The multiphoton ionization process is capable of accessing many of the same charge states that are produced in ion-molecule collisions. One important difference in the two excitation methods is the time scale for ionization, which is more than 10^2 and 10^5 times longer with femtosecond and picosecond lasers, respectively, than with fast ion collisions. When picosecond lasers are employed, dissociation occurs during the laser pulse. In contrast to the large KER observed in ion-molecule collisions, it has been found that the KER from multiphoton dissociative ionization of diatomic molecules with picosecond lasers is typically only about 45% of the Coulomb potential energy for $Q<4$ [9]. True Coulomb explosions, in which the full Coulomb potential energy is liberated, have only been observed for molecular ions of I_2 excited with intense laser pulses of 30–80-fs duration [10].

The present work was undertaken for the purpose of extending the investigation of KER in ion-molecule collision-

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induced dissociation processes to higher charge states by focusing on collisions in which multiple ionization of the target is accompanied by the transfer of an electron to the projectile. These so called capture-ionization (CI) collisions occur at much smaller impact parameters, on average, than collisions in which the projectile charge remains unchanged. Imposing the requirement that the projectile must capture an electron greatly accentuates the probabilities for multielectron removal from a target atom or molecule relative to those for single or double ionization [11,12].

II. EXPERIMENTAL METHOD

A beam of 97-MeV Ar^{4+} ions was extracted from the Texas A&M K500 superconducting cyclotron and sent through a 180-$\mu g/cm^2$ Al stripper foil into an analyzing magnet, which was used to select the Ar^{14+} ion-beam fraction. The Ar^{14+}-ion beam was collimated to a diameter of 1 mm and directed through a differentially pumped gas cell system (described in Ref. [1]). Ions produced by collisions inside the cell were accelerated through a 4.8-mm-diameter exit aperture into a TOF spectrometer by an electric field (700 V/cm) directed transverse to the beam direction. The TOF spectrometer employed a second acceleration stage (1042 V/cm), a 5-cm-diameter flight tube 15-cm in length, and an ion detector consisting of two 40-mm-diameter microchannel plates in a chevron configuration. A projectile charge analyzer, composed of a vertical bending magnet and a one-dimensional position-sensitive microchannel plate detector system, was located downstream from the gas cell. For each accepted event, three parameters were recorded in coincidence; the TOF of the first dissociation product ion to reach the detector, the flight time difference between the first ion and its dissociation partner, and the position signal from the charge analyzer (which identified the exit charge of the projectile). The three-parameter data were acquired on a MICROVAX II computer and recorded on magnetic tape event by event.

The target gas pressure was maintained at 1 mTorr by means of a capacitance manometer and an automatic valve. This pressure was low enough to ensure that double-collisions events were negligible. In order to increase the beam intensity so that the detection rate for CI collisions could be optimized without damaging the projectile detector in the charge analyzer, a mask was used to prevent projectiles with exit charges ⩾14+ from hitting the detector. Calibration of the TOF $(m/q)^{1/2}$ scale (where m and q, respectively, are the detected ion's mass and charge) was accomplished by measuring TOF spectra for an Ar target gas. The time scales were calibrated using an ORTEC model 462 time calibrator. Details of the electronic system are the same as described in Ref. [1], with the addition of logic units necessary to process the projectile position signals.

III. RESULTS AND DISCUSSION

Coincidence first-ion TOF spectra are displayed in Fig. 1 for (a) ionization collisions in which the projectile charge remained unchanged, and (b) CI collisions in which the charge of the projectile decreased by one unit. It is readily apparent that the higher charge states are greatly accentuated
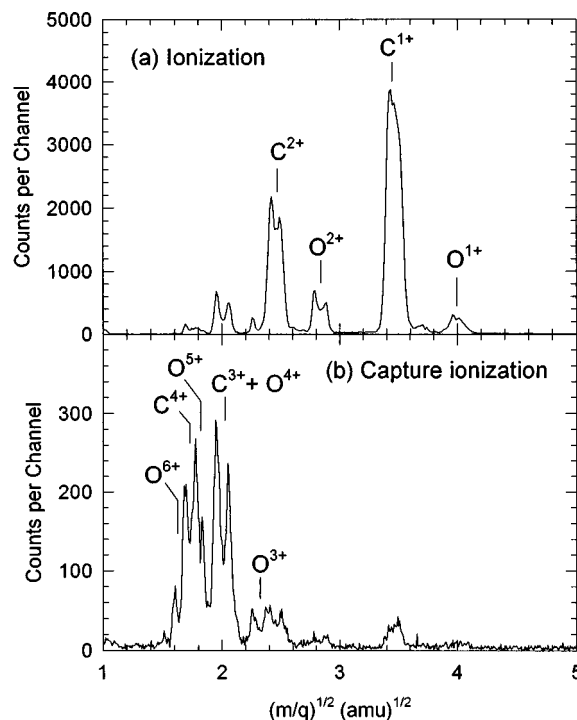

FIG. 1. First-ion coincidence TOF spectrum of CO dissociation products from (a) dissociative ionization collisions of 97-MeV Ar^{14+}, and (b) dissociative capture-ionization collisions of 97-MeV Ar^{14+}.

in the CI spectrum. The calibration TOF spectrum obtained for the CI of Ar displayed a bell-shaped charge distribution which peaked at Ar^{8+}. In the case of CO, however, the most probable molecular ion produced in CI collisions was found to be CO^{7+}. The average recoil energy imparted to the CO molecules is estimated to be in the range of 0.1–0.4 eV [13]. In view of the fact that the KER's are extracted from *differences* in the TOF's of the two dissociation product ions, it is safe to assume the effect of this small recoil energy is entirely negligible.

A two-dimensional array of first-ion TOF versus ion-pair TOF differences was constructed from the three parameter data by selecting only those events recorded in coincidence with the detection of a charge 13+ Ar projectile. Events associated with each dissociation reaction appeared as an "island" in this two-dimensional array (see Fig. 1 in Ref. [14]). Projection of these event islands onto the time difference axis then yielded the individual time-difference distributions. Time-difference distributions obtained for several of the dissociation reactions are shown in Fig. 2.

Two different methods were used to determine the average KER's from the time-difference distributions. The first method employed the matrix transformation procedure described in Refs. [1] and [15] to obtain the KER distributions, from which the average KER's were computed. The second method was based upon an analysis of the time-difference distribution widths similar to that described by Ben-Itzhak, Ginther, and Carnes [16]. The average KER's obtained by these two methods generally agreed to within 10%, and so they were averaged to obtain the final average KER's listed in column 2 of Table I. Also presented in Table I, column 3, are the average KER's for ionization collisions in which the
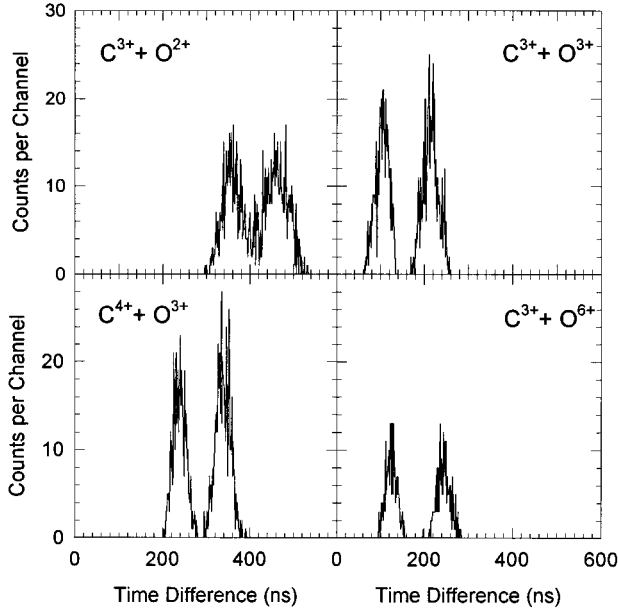
FIG. 2. Flight time difference distributions for several ion pairs from the dissociation of multicharged CO molecular ions.
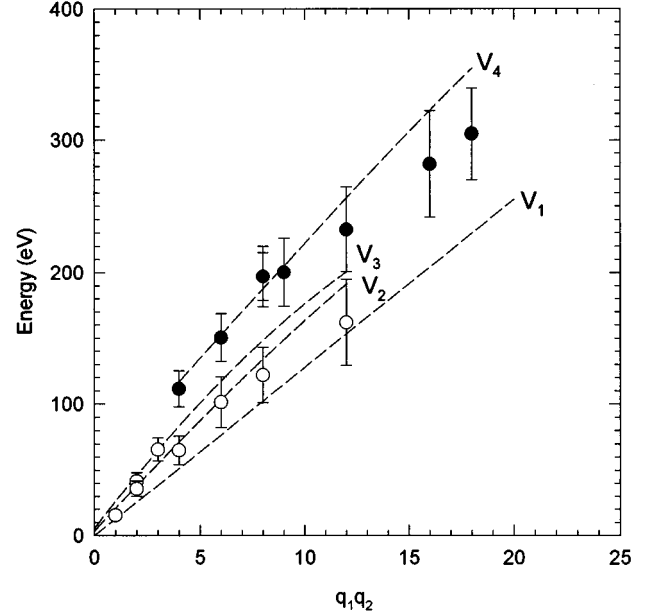

FIG. 3. Average KER values as a function of ion-pair charge product for ionization collisions (open circles) and capture-ionization collisions (filled circles). The dashed curve labeled V_1 delineates the point-charge Coulomb potential energy. The dashed curves labeled V_2, V_3, and V_4 are defined in the text.

projectile charge remained unchanged. These values, which are not significantly different from those given previously [1], were determined in the same way as those for CI. Using the KER distributions given in Ref. [3], it was possible to compute the average KER's for several reactions from the dissociative ionization of CO by 1-MeV/u F^{4+} ions. The agreement between these values and those obtained in the present study is found to be quite good.

A graph of the average KER values plotted versus the product of the ion-pair charges ($q_1 q_2$) is shown in Fig. 3. The dashed line labeled V_1 delineates the point-charge Coulomb potential energy $q_1 q_2 / R_e$, where R_e is the ground-state equilibrium bond length. As noted previously [1], the average KER's for ionization collisions systematically exceed the Coulomb energies (by 35% on average). It is evident from

TABLE I. Average KER values for dissociative ionization and capture-ionization of CO molecules by 97-MeV Ar^{14+}.

Dissociation reaction	Average KER for capture ionization (eV)	Average KER for ionization (eV)
$CO^{2+} \rightarrow C^{1+} + O^{1+}$		15.4±3.0 (15.3)[a]
$CO^{3+} \rightarrow C^{2+} + O^{1+}$		35.8±5.8 (33.1)[a]
$CO^{3+} \rightarrow C^{1+} + O^{2+}$		41.5±6.5 (36.7)[a]
$CO^{4+} \rightarrow C^{3+} + O^{1+}$		65.7±8.8
$CO^{4+} \rightarrow C^{2+} + O^{2+}$	112±14	65 ±11 (62.5)[a]
$CO^{5+} \rightarrow C^{3+} + O^{2+}$	150±18	101 ±19
$CO^{6+} \rightarrow C^{2+} + O^{4+}$	197±18	
$CO^{6+} \rightarrow C^{4+} + O^{2+}$	197±23	122 ±21
$CO^{6+} \rightarrow C^{3+} + O^{3+}$	200±26	
$CO^{7+} \rightarrow C^{4+} + O^{3+}$	233±32	162 ±33
$CO^{8+} \rightarrow C^{4+} + O^{4+}$	282±40	
$CO^{9+} \rightarrow C^{3+} + O^{6+}$	305±35	

[a]Average KER values for 1-MeV/u F^{4+} collisions computed from the KER distributions given in Ref. [3].

Fig. 3 that the situation is much more dramatic for capture-ionization collisions. In this case, all of the experimental average KER values are far larger than the Coulomb energies (some by as much as a factor of 2).

In the absence of detailed theoretical information about the potential-energy curves for multicharged CO molecules, interpretation of these results is limited to rather qualitative speculation. To begin with, it should be recognized that the dissociative potential curves for a multicharged diatomic molecule can accommodate a wide range of KER's. Low-lying molecular states characterized by high electron densities between the two nuclei will generally give KER values less than the point-charge Coulomb potential energy, while highly excited states with greatly reduced nuclear screening can give KER's that are larger than the Coulomb energy. The present results therefore indicate that most of the molecular states populated in dissociative capture-ionization collisions must be highly repulsive. Classically, this means that the two ions are not fully screened by the electrons that remain after the collision. Clearly, in the limit of totally stripped dissociation product ions (for which $q_1 q_2 = 48$), the KER must converge to the point-charge Coulomb potential energy. In fact, both sets of data in Fig. 3 do appear to be approaching the Coulomb energy curve at the highest values of $q_1 q_2$.

Ben-Itzhak et al. [3] made the interesting observation that structural features appearing in their KER distributions for a given ion pair with charges (q_1, q_2) corresponded in energy to the Coulomb potential energies for apparent ion charges $q_1 + 1$ and/or $q_2 + 1$. They suggested that these features were due to the dissociation of CO molecular ions containing an electron in such a highly excited state (e.g., a molecular ion Rydberg state) that its contribution to the screening of the nuclei was negligible. Subsequent dissociation of this molecular ion would therefore yield a KER of either

$(q_1+1)q_2/R_e$ or $q_1(q_2+1)/R_e$. These potential energies are delineated by the dashed curves labeled V_2 and V_3, respectively, in Fig. 3. It is apparent that most of the experimental average KER values for the ionization collisions fall very close to the V_2 and V_3 curves. Pursuing this idea further, the Coulomb potential energies for *two* highly excited electrons, $(q_1+1)(q_2+1)/R_e$, have been delineated [for the observed (q_1,q_2) combinations] by the dashed curve labeled V_4 in Fig. 3. It may be seen that this curve falls tantalizingly close to most of the experimental average KER values for the capture ionization collisions.

IV. CONCLUSIONS

Coincidence TOF spectra of CO dissociation products resulting from dissociative capture ionization collisions by 97-MeV Ar^{14+} ions, in which multiple ionization of the CO molecule is accompanied by the transfer of an electron to the projectile, have revealed that substantial yields of C^{3+}, C^{4+}, O^{4+}, O^{5+}, and O^{6+} ions are produced. The average KER values for dissociative capture-ionization were found to be much larger than those observed for dissociative ionization, which, in turn, are apparently larger than those observed in dissociative multiphoton ionization. Both ion-molecule collision processes gave average KER values that were greater than the point-charge Coulomb potential energies for the detected ion-pair charges (q_1,q_2). Those for ionization collisions were close to the Coulomb potential energies for ion-pair charges (q_1+1,q_2) or (q_1,q_2+1), while those for capture-ionization collisions were close to the Coulomb potential energies for ion-pair charges (q_1+1,q_2+1). These observations tend to suggest that, on average, one electron is raised to a highly excited molecular orbital in the ionization collisions, while two electrons (on average) are excited in the smaller impact parameter, more violent, capture-ionization collisions.

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