Near-Coulombic behavior in the dissociative ionization of CO_2 due to impact by Ar^{8+}

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The Coulomb explosion of CO_2 in collisions with Ar^{8+} ions of 120 keV has been examined experimentally using a position sensitive detector with a triple coincidence technique. The technique has allowed the full characterization of the structure of the exploding molecule. Purely Coulombic fragment energies fit the experimental results well, across the range of fragment energies. Modifications to the molecular geometry are observed, in the form of widening of the zero point bend distribution and sequential processes are found to be unimportant in the dissociation process. [S1050-2947(99)05805-9]

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In the collision of a highly charged ion (HCI) with a triatomic molecule, the molecule may be multiply, ionized and then fragment into atomic ions which possess high kinetic energies. For example,

$$X^{8+} + CO_2 \rightarrow {CO_2}^{L+} \rightarrow O^{M+} + C^{N+} + O^{K+},$$

where $L = M + N + K$. Such a reaction is normally referred to as a Coulomb explosion, although the total energy released has always been somewhat lower than for a purely Coulombic process [1]. The simplest technique used to identify and measure the kinetic energy of the fragment ions is time-of-flight (TOF) mass spectrometry [2,3]. In the study of the analogous process of laser induced Coulomb explosions, techniques such as covariance mapping [4] have used TOF to derive information about which ions are produced in the same event, for example, ${CO_2}^{3+} \rightarrow O^+ + C^+ + O^+$, the (1,1,1) channel. However, when a triatomic molecule even a slight bend Coulomb explodes, the fragments move in a plane and not in one dimension, therefore only the projection of momentum along the detector axis can be measured. This means that the structure of the exploding molecule cannot be unambiguously determined. Recent experiments [1,5,6] have made a major advance by using TOF in conjunction with position sensitive detection, to characterize completely the motion all three positive ion fragments produced in a Coulomb explosion event, in three dimensions (x, y, t). In the present experiment this technique has been employed to study the Coulomb explosion of CO_2 induced by collisions with Ar^{8+} of 120 keV.

The present experimental setup is similar to that described earlier [7] and so will only be briefly summarized here. In the present experiment, a beam of Ar^{8+} ions from an ECR ion source [8] is accelerated to an energy of 120 keV, collimated by a 2 mm aperture and crosses a target gas beam of CO_2 introduced through a multicapillary plate. The product ions are collected by an extraction field of 450 V/cm, applied perpendicularly to the incident ion beam and the target gas beam. Ejected electrons accelerated in the opposite direction to the fragment ions, pass through a 1 mm hole and an array of capillaries, before being detected by a channel electron multiplier. These electrons give rise to prompt electronic pulses, which provide the trigger for an oscilloscope. The product ions drift in a TOF region which is terminated by a pair of microchannel plates 40 mm in diameter. The signal from the microchannel plates is collected by a ''backgammon'' type anode [9,10]. The four output signals from the anode are amplified by fast preamplifiers (Ortec: 142 B) and the time profile of each signal is recorded by one channel of a fast digital storage oscilloscope (Tektronix: DSA602A). The signal from the oscilloscope is sent to a PC by a GPIB interface and the x-y position is determined from the relative heights of the pulses recorded on each channel.

In Fig. 1, a triple coincidence map for CO_2 shows the islands belonging to the different fragmentation channels. The three ions detected in a dissociation event, for example, ${CO_2}^{5+} \rightarrow O^{2+} + C^+ + O^{2+}$, which will be referred to as (2,1,2), give six points in the map. That is, $O^{2+}_{\text{forward}} + C^+$ island has a corresponding point in the $O^{2+}_{\text{backward}} + C^+$ and the $O^{2+}_{\text{forward}} + O^{2+}_{\text{backward}}$ island, and the mirror image is also shown in the map. The apparent scatter in the data is somewhat misleading, as the plot considers only the projection of velocity along the spectrometer axis, by considering each event individually using positional as well as timing information greater precision is achieved. That is, $O^{2+}_{\text{forward}} + C^+$ island has

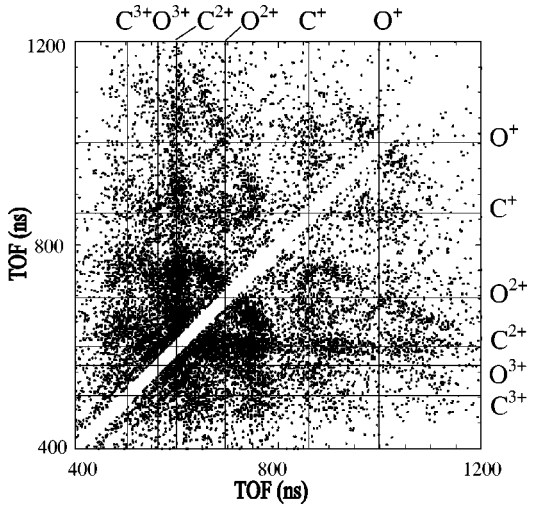

FIG. 1. Triple coincidence map for CO_2. One Coulomb explosion event, in which three positive ion fragments are produced, gives six points on the map (see text).

TABLE I. Signal strength for various dissociation channels.

Channel	Signal strength %
1,1,1	5.5
1,2,1	3.0
2,1,1	6.5
2,2,1	25.2
2,1,2	8.8
2,2,2	51

a corresponding point in the $O^{2+}_{\text{backward}}+C^{+}$ and the $O^{2+}_{\text{forward}}+O^{2+}_{\text{backward}}$ island, and the mirror image is also shown in the map. Table I shows the relative strengths of the observed channels. Theses strengths may not represent the partial cross sections of the channels, as they are dependent on the probability of the production of ejected electrons which trigger the experiment. The higher channels are likely to give rise to the ejection of more Auger electrons and lead to preferential detection. However, the relative symmetry of the channels this is another is important.

For the dissociation of CO_2^{4+} and CO_2^{5+}, the asymmetric channels (2,1,1, and 2,2,1) are stronger than the symmetric channels (1,2,1, and 2,1,2). This is consistent with the fact that the statistical weight for the asymmetric channels is double that for the symmetric ones. However, the more asymmetric channel (3,1,1) is not observed, even though it would lead to the same number of electrons captured as the (2,2,1) channel and therefore the same Auger electron ejection probability. Similar patterns have been observed between the (2,2) and (3,1) channels in N_2 for slow collision with Ar^{8+} [11]. In the analogous process of infrared laser induced field ionization, the tendency to produce symmetric channels has been noted for some time [12]. The process has been ascribed to the many reverses of the electric field direction, which gives rise to equal probabilities for the release of an electron at both ends of the molecule.

In HCI impact, the electric field due to the ion does not reverse its direction and so such an equalization of probability can not take place. In laser induced Coulomb explosion [2,13–15], the ac electric field is applied for typically 50 fs, whereas in the present experiment the dc field is applied for the order of only one femtosecond. It appears therefore, that one femtosecond is enough time for the electron cloud of the molecule to redistribute, before dissociation takes place. The observations of the laser experiments can therefore, be explained by this intrinsic molecular process, without the need to invoke field reversal.

The nuclear geometry of the exploding molecule can be observed, the identified channels, by reconstructing the O-C-O angle θ from the trajectories of the fragment ions. A comparison of θ for the (2,2,2), (2,2,1), and (2,1,1), channels is shown in Figs. 2(a), 2(b), and 2(c) together with a calculation of the bend distribution in the ground state neutral molecule undergoing zero point motion [16]. Although statistics become poorer for the (2,1,1) channel it is noticeable that the bend distribution widens as the channel decreases. A similar tendency was observed in HCI induced dissociation of H_2O [5,6]. An explanation for this tendency is simply that

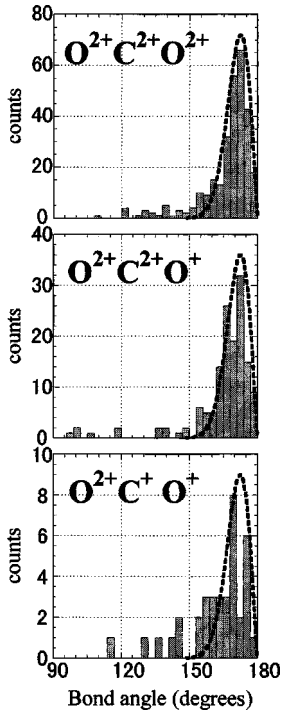

FIG. 2. Histogram of O-C-O angle (θ) reconstructed from fragment velocities for (a) (2,2,2) channel, (b) (2,2,1) channel, (c) (2,1,1) channel. The probability function for θ corresponding to the zero point motion of the neutral molecule is depicted by the dashed lines.

for the higher channels the repulsion between the ions is greater, causing dissociation to occur rapidly. For the lower channels however, some relaxation of the molecule, leading to nuclear rearrangement can take place during the dissociation process. Enhancement to the bend angle of CO_2 has been reported in the laser induced Coulomb explosion of CO_2 from the ground vibrational state [14,17] and from a distribution of excited vibrational levels [13]. A distribution of bends peaked at 180° and extending to 140° was found to be a good fit to data derived from initially ground state molecules [17]. Although this is a small widening of the ground state distribution, it also implies that straightening has taken place. Straightening has not occurred in the present HCI impact experiment, implying that this process is associated with molecular stretching, alignment reorientation, which takes place in a laser field.

Figures 3(a) and 3(b) show plots of the fragment velocities as a function of the measured bond angle for the (2,2,2) and (2,2,1) channels, respectively, also shown are classical trajectory calculations of the velocities due to a purely Coulomb potential. The fragment velocities show a dependence on the measured bond angle, which is in good agreement with the pure Coulomb theory. For O^{6+} collisions with H_2O at 92.4 keV [1,5,6] the calculated ion interaction potentials gave a good fit to the experimentally measured fragment ion energies, but this was around 10% lower than the pure Coulomb value. The present results may be closer to pure Coulomb explosions than in the case of H_2O because a different HCI has been used, this is currently under investigation.

In laser induced Coulomb explosion experiments on CO_2 [13,14,17], the fragment ion kinetic energies have been

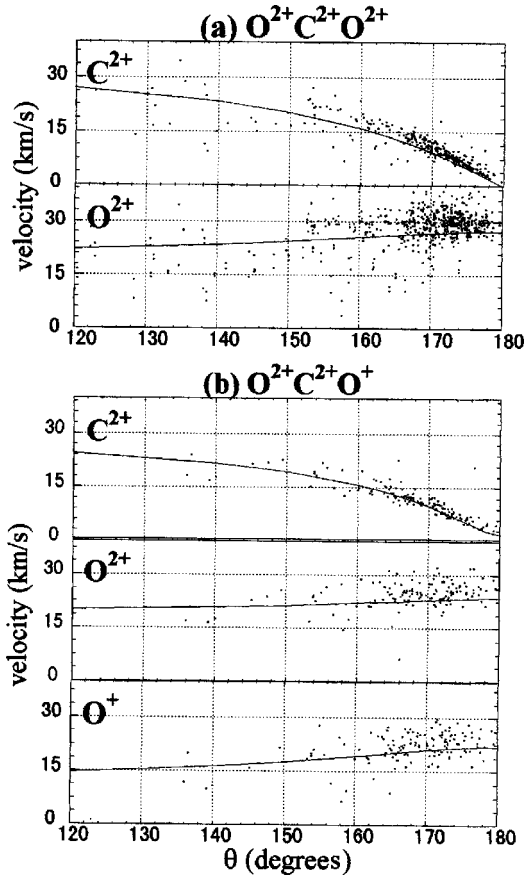

FIG. 3. Plots of fragment velocities against θ for (a) (2,2,2) channel and (b) (2,2,1) channel. Solid lines are simulated values obtained by assuming the pure Coulomb explosion.

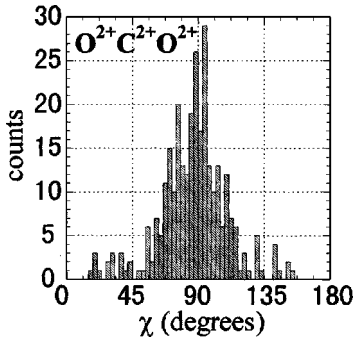

FIG. 4. Histogram of the angle χ for the (2,2,2) channel, the inset shows graphically the case of a simultaneous dissociation where the velocity vector of the carbon ion V_c is at right angles to the velocity vector $V_{of}-V_{ob}$ where V_{of} and V_{ob} are the velocity vectors of the forward and backward oxygen ions, respectively.

shown to be roughly half of the pure Coulomb energy. This can be explained by the importance of a critical internuclear distance at which the ionization rate increases by orders of magnitude [18]. As the electric field reaches a maximum in no less than 50 fs, the molecule has time to ionize, and begin to dissociate before the peak field is reached, allowing the critical internuclear distance to come into effect. The present results indicate that the effect of the critical distance can be overcome, in a laser experiment, if the laser pulse duration is close to 1 fs. Near Coulomb fragment energies should then be observed.

The small spread of the carbon velocities in Fig. 3 is a good indicator of the simultaneity of the fragmentation process, but this has been confirmed by considering the velocity vector between the two oxygen ions and the velocity vector of the carbon ion [5]. If the charge states of the oxygen ions are equal then an angle χ between the velocity vectors will be 90° the two C-O bonds break simultaneously. Figure 4 shows a plot of signal strength against χ for the (2,2,2) channel. The distribution is strongly peaked at 90° indicating that the dissociation process is to a high degree nonsequential, this is also found to be true for the other symmetric channels. Asymmetric channels do not peak at 90°, but do peak at angles consistent with a nonsequential process.

These results which relate the molecular structure to its fragmentation pattern and the final fragment velocities, can help to explain observations made of the fragmentation of CO_2 in collisions with Si^{8+} of 100 keV [3]. In that work only the energy distributions of the fragment ions were measured, and so it was necessary to deduce dissociation paths. The kinetic energies measured peaked at between 0 and 0.5 eV and extended to 5 eV for C^+ and peaked at 2 eV extending to 10 eV in the case of C^{2+}. The tails of the distributions were thought by the authors to be too long to be explained by bending of the molecule, and so two speculative sequential processes were suggested to account for them. Although the energy distributions measured in the Si^{8+} collision experiment were not channel resolved we can compare them with the results from the plots of fragment velocity against bond angle, such as are shown in Fig. 3. At the most probable angle, 173°, the kinetic energy of the C^+ ions, from the (1,1,1) channel is 0.5 eV and the kinetic energy of the C^{2+} ions from the (2,2,2) channel is 2 eV, both are similar to Si^{8+} collision results of 0–0.5 and 2 eV, respectively. The kinetic energy of the C^+ ions at 150°, the tail of the Coulomb distribution is around 6 eV and the kinetic energy of the C^{2+} ion it is around 25 eV, compared to the values of 5.3 and 10 eV, respectively, for the Si^{8+} impact case. In conclusion the entire range of kinetic energies observed in the Si^{8+} collision experiment can be accounted for by the distribution of possible bends in the CO_2 molecule. There is consequently no need to invoke nonsequential processes. Furthermore nonsequential processes are shown to be unimportant by the use of the present technique: First Fig. 4 shows χ to be strongly peaked at 90° indicating that the C-O bonds are broken simultaneously. Secondly the carbon ion energies, in Fig. 3, depend on the measured CO_2 bond angle, in close accordance with the pure Coulomb calculations.

The power of the triple coincidence technique in conjunction with a PSD, to unambiguously identify the dissociation channels, their resulting fragment velocities and the underlying molecular geometry is quite striking. The dissociative ionization of CO_2 in collisions with Ar^{8+} at 120 keV has been shown to give rise to symmetric channels and result in simultaneous breaking of the C-O bonds as being well characterized by the Coulomb explosion model. Although this closeness to the pure Coulomb model is not understood at present, investigation of the fragmentation dependence on target species and projectile energy is presently underway.

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