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Dissociative recombination of the CO^{2+} dication

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Dissociative recombination of a doubly charged molecular ion CO^{2+} has been studied, using a heavy-ion storage ring. There are two final channels of this reaction ($C + O^+$ and $O + C^+$) that were found to be of about equal strength up to an energy of about 2 eV. The total recombination cross section (yielding C or O) is found to be $\sigma = [2.2/E(\text{eV})] \times 10^{-16}$ cm^2 for $E \leqslant 1$ eV, where E is the electron energy. This indicates that the recombination is of the direct type with a curve crossing between the initial state and some repulsive curve of the singly charged ion. Within an accuracy of a factor of 2 we obtain a total recombination rate coefficient $\alpha = 0.9 \times 10^{-7}$ cm^3 s^{-1} at $T = 300$ K that is comparable to that of CO^+. [S1050-2947(99)51011-1]

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Almost all multiply charged diatomic molecular cations are unstable towards dissociation because their vibrational levels are embedded in the dissociative continuum, and as a consequence they are in general difficult to study both from an experimental and a theoretical point of view. Some molecular dications have lifetimes of less than a microsecond [1,2], but other ions have much longer lifetimes [3], mostly due to large barriers against dissociation. In the particular case of the dication CO^{2+}, it has been shown at the ASTRID heavy-ion storage ring that the vibrational ground state of this dication has a lifetime of at least 3.8 s [3,4]. This is long enough to perform advanced experimental studies in a storage ring that require time for injection, acceleration, and data accumulation. The long storage time allows for internal rovibrational cooling of the molecular ions and hence provides a well-defined initial state of the molecular ion.

Carbon monoxide is the second most abundant molecule in the universe, H_2 being the most abundant, and its presence has been detected in many astrophysical objects including planetary and cometary atmospheres. In regions where energetic photons ionize or dissociate H_2, singly charged CO^+ ions may survive because of the lack of a fast reaction with H_2 to yield HCO^+ [5]. It might be speculated whether CO^{2+} may be created in such regions, perhaps near an O star. The CO^+ and CO^{2+} ions may be destroyed by dissociative recombination with free electrons, and for CO^+ this process has been studied extensively (for recent references see [6,7]). The recombination of CO^{2+} with free electrons has not, to our knowledge, been studied before.

The CO^{2+} molecular ion holds a special position among diatomic dications. It was observed already in 1932 by mass spectroscopy [8], and has to date been investigated using a plethora of experimental and theoretical techniques; for example, Auger spectroscopy [9], double charge-transfer spectroscopy [10], photofragment spectroscopy [11], translational energy spectroscopy [12], threshold photoelectron coincidence spectroscopy [13], and lifetime measurements using storage rings [4]. To determine the importance and consequences of doubly charged molecular cations in plasmas one needs to know the molecular structure of the dications, which has been studied to some extent. Moreover, the reactivity of the dications, which is the subject of the present Rapid Communication, must be known.

The dissociative recombination (DR) reaction of CO^{2+} may be written as

$$CO^{2+} + e^- + E \rightarrow \begin{cases} C^+(\alpha) + O^0(\beta) + E_{\text{release}} \\ C^0(\alpha') + O^+(\beta') + E'_{\text{release}}, \end{cases} \tag{1}$$

where E is the kinetic energy of the electron in the center-of-mass frame, α and β are the electronic states of the resulting atoms/ions, and E_{release} is the kinetic-energy release carried away by the fragments in the form of kinetic energy.

The energy gain upon recombination with electrons is considerably higher for dications than for singly charged ions. For recombination of heavy molecular ions like the polycyclic aromatic hydrocarbons, this may result in fragmentation of the dications, whereas the singly charged ions may be able to emit the excess energy as radiation [14]. To our knowledge, recombination of doubly charged *molecular* cations has not been studied before, either in afterglow experiments or by merged-beams techniques. The recombination of multiply charged *atomic* ions with electrons has been studied extensively over the last decade mainly because of its importance in fusion plasmas and hot astrophysical plasmas (see, e.g., Ref. [15]).

Until now, the study of the DR processes has been limited to singly charged molecular ions. This has been due to the difficulty in producing, storing, and manipulating multiply charged molecular ions. With singly charged diatomic molecular ions DR leads to the production of two neutral atoms, and much effort has been devoted to determining the electronic states of the atoms and the cross section of the DR process [16]. In the case of molecular ions with more than two atoms, the focus has been on determining the chemical composition of the neutral fragments as well as the DR cross section [17]. With the CO^{2+} dication we have in the present work obtained the total DR cross section as a function of energy and the branching ratio for the two final channels of Eq. (1).

It is believed that only the vibrational ground state of the $^3\Pi$ state has a lifetime long enough to survive several seconds of storage in the ring, although other CO^{2+} states lie near this state [4]. After the capture of the electron, highly excited states of the CO^+ molecular ion are formed, and in this context it is interesting to note that bound Rydberg states

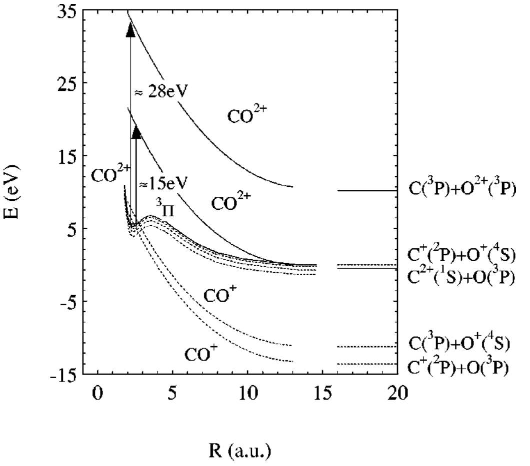

FIG. 1. The $X\,^3\Pi$ potential-energy curve of CO^{2+} and the asymptotic atomic energy limits are shown. Some curves of CO^+ (dashed) and CO^{2+} (full) as well as some Rydberg states belonging to the dication ground state are drawn from an artist's point of view. The energy scale refers to the dissociation limit $C^+(^2P)+O^+(^4S)$.

of the ion CO^+ [18] have been reported to exist. To calculate the DR cross section and the branching ratio of Eq. (1), knowledge of such states and couplings between the states is required to study the dynamical evolution of the molecular system after the initial electron capture to the final channels of the DR reaction. In the present case of the CO^{2+} dication, the initial state is already in the dissociative continuum, something not encountered in singly charged systems. The fact that the dissociation takes place along potential-energy curves of a charged molecule is also different from the systems studied so far. In Fig. 1 we show schematically some potential-energy curves and the atomic limits.

The measurement was carried out using ASTRID, the Aarhus Storage Ring Denmark [19]. The experimental technique has been described in detail elsewhere [20]. Briefly, $^{13}C^{16}O^{2+}$ ions were produced in an electron-impact ion source and injected into the storage ring at an energy of 300 keV (the isotopic substitution ensured that there was no N^+ or $N_2{}^{2+}$ contamination in the beam). The ions were then accelerated to 5.9 MeV in approximately 2.5 s, which allowed most of the electronically and vibrationally excited species formed in the ion source to decay. Previous measurements [4] on the lifetimes of CO^{2+} indicate that the short-lived components in the beam decay in milliseconds. This fast beam was then merged with an electron beam provided by the electron cooler in one of the arms of the storage ring. The electron cooler provides a magnetically confined, adiabatically expanded electron beam with laboratory energies in the range 40–2000 eV. An electron energy of 111.7 eV results in a zero center-of-mass energy for the CO^{2+} ion at 5.9 MeV. Other center-of-mass energies were obtained by changing the energy of the electrons.

When CO^{2+} recombines with an electron the following dissociative recombination pathways are possible:

$$CO^{2+}+e^-\rightarrow C^+ + O(18.9\text{ eV})$$

$$\rightarrow C+O^+(16.6\text{ eV}),$$

where we have assumed all fragments to be in the ground state (the listed energies are hence an upper limit of the kinetic energy gained by the fragment ions/neutral ions). The dissociative excitation (DE) channel,

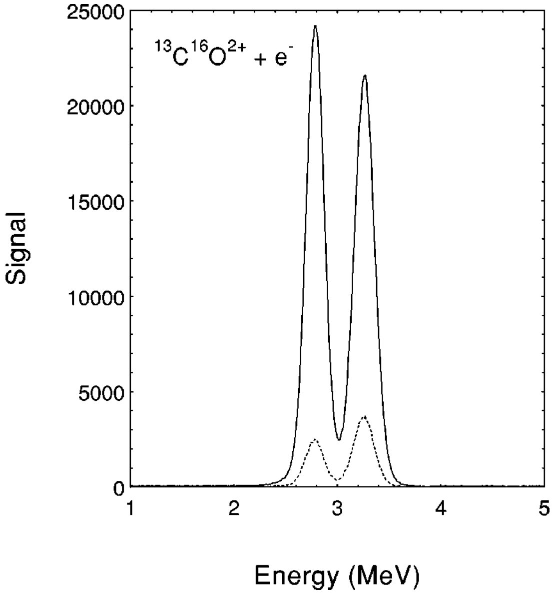

FIG. 2. Pulse height spectrum of neutral C and O particles detected by the solid-state detector. The full curve is recorded with electrons on at $E=0$ (in the ion rest frame), and the dashed curve is recorded without electrons.

$$CO^{2+}+e^-\rightarrow C^{2+}+O+e^-(5.8\text{ eV}),$$

is open at all energies. However, synchrotron experiments [21] have shown that C^{2+} is not produced at energies below $\simeq 15$ eV (see Fig. 1), and we argue below that this channel plays a minor role at low energy. The channel

$$CO^{2+}+e^-\rightarrow C+O^{2+}+e^-(-4.9\text{ eV})$$

is endothermic and opens when the electron energy is greater than the indicated value. Synchrotron experiments [21] have shown that O^{2+} is produced at energies only above $\simeq 28$ eV, and the channel is not expected to be significant at low energy. Finally, electron-impact dissociation may take place at any energy,

$$CO^{2+}+e^-\rightarrow C^+ + O^+ + e^-(5.3\text{ eV}),$$

but the charged fragments are not recorded in the present setup (their trajectories lie too close to the parent ion beam within the bending magnets) and the presence of this channel can only cause depletion of the recombination channels.

The neutral particles formed by the above processes passed undeflected through the bending magnet of the storage ring and were detected by a large (4×6 cm^2) solid-state detector. The advantages of using the combination of high-energy beams and a solid-state detector are the almost unit detection efficiency and the fact that the C and O atoms hitting the detector give rise to pulses of different heights. As can be seen from Fig. 2 the C and O atoms can be resolved — they carry kinetic energy in proportion to their mass.

The C and O yields were measured as a function of the electron energy, and the so-called rate coefficient [22] for their formation was determined from

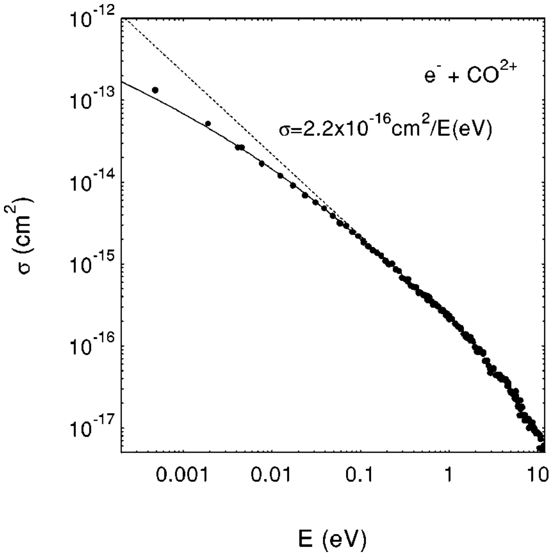

FIG. 3. Absolute cross sections ($\sigma = \langle v\sigma \rangle / v$) for the formation of either C or O. The dashed curve shows a 1/E dependence. Due to the finite energy resolution a deviation from 1/E occurs at low energy as calculated by the solid curve, which has $kT_\perp = 22$ meV and $kT_\parallel = 0.5$ meV. The relative errors of the measurement are comparable to the spot sizes, but the absolute values are accurate to within a factor of 2, due to the uncertainty in ion current measurement.

$$\langle v\sigma \rangle (\mathrm{cm}^3/\mathrm{s}) = \frac{N_s - N_b}{N_i} \times \frac{v_i}{l n_e \epsilon}, \qquad (2)$$

where N_s is the number of C or O atoms detected with the electron beam present, N_b is the neutral ions produced in the absence of the electron beam (from background gas collisions), N_i is the number of ions passing through the target area (electron cooler) (all measured for some fixed time interval δt), v_i is the ion velocity, l is the length of the electron cooler, n_e is the electron density, and ϵ is the detector efficiency.

For the measurement of absolute cross sections, the ion current was too low to be measured directly by the current transformer in ASTRID. The ion current was therefore estimated by monitoring the signal on a calibrated set of electrostatic pickup plates. This gives a source of error in the overall absolute scale that we estimate to be a factor of 2 at most.

Figure 3 shows the absolute DR cross section for CO^{2+} (the sum of C and O production). The solid line is a 1/E fit to the data taking into consideration the experimental electron-energy resolution (a longitudinal energy spread of 0.5 meV and a transverse energy spread corresponding to a factor of 4.5 adiabatic expansion of 22 meV [22]). The 1/E dependence at low energy suggests a direct mechanism for the recombination process [23]. Thus, we expect repulsive CO^+ curves to cross the initial CO^{2+} $^3\Pi$ curve near the local minimum (see Fig. 1). In fact, high-resolution photoelectron spectroscopy experiments [18] indicate the existence of a dissociative CO^+ state at ~3.2 eV above the X $^3\Pi$ $v=0$ level. At larger center-of-mass energies, the deviation from the 1/E dependence suggests the occurrence of different mechanisms/channels. We discuss these possibilities below.

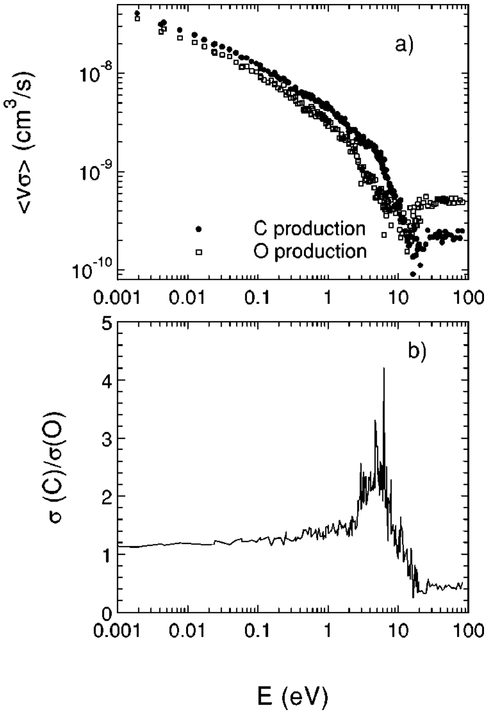

FIG. 4. (a) Rate coefficients for the formation of C and O. (b) The ratio of C and O formation as a function of the energy.

It has not been possible to isolate the dissociative excitation channel (final $C^{2+} + O$) that is energetically open at any electron energy, since both fragments could not be detected simultaneously. The observed (1/E) energy dependence of the neutral production cross section indicates that DE is not important at low energies (since in general, DE would increase with increasing electron energy). Further, the almost equal production of C and O suggests that the open channel leading to C^{2+} and O does not play a significant role at low energies. In essence, at low energy, neutral atoms (C and O) are believed to be due to DR only.

Figure 4(a) shows the rate coefficients as a function of the center-of-mass energy for the formation of neutral C and O. The formation of C is energetically favored and the C production rate is consistently slightly larger than the O production rate at low energy. After ~2 eV the O production rate starts falling off rapidly, whereas the cross section for the C channel exhibits a shoulder. This gives the peak in the ratio of C to O production as shown in Fig. 4(b). At even higher energies the relative O production picks up again. Although theoretical knowledge is insufficient at present to explain the dynamics in detail, we may point out the following:

The doubly charged diatomics differ from the usually studied singly charged ions in that the ions are metastable and have a local minimum in their initial potential-energy curve. The barrier height for the CO^{2+} $^3\Pi$ state is about 1.5 eV (see Ref. [4]). This is the region in which the C production is particularly favored over the O production [yielding the peak in Fig. 4(b)]. This might indicate that some unknown mechanism removes flux from the $C^+ + O$ channel and perhaps into the C + O^+ channel.

Photodissociation studies of Masuoka and Nakamura [21] indicate that the vertical distance between the CO^{2+} ground state and repulsive curves leading to $C^{2+} + O$ and $O^{2+} + C$ is

~15 eV and ~28 eV, respectively (see Fig. 1). We attribute the increase in the neutral C and O production at high energy [see Fig. 4(a)] to dissociative excitation to such repulsive curves:

$$\mathrm{CO}^{2+}+e^- \rightarrow \mathrm{C}^{2+}+\mathrm{O}+e^-$$
$$\rightarrow \mathrm{C}+\mathrm{O}^{2+}+e^-.$$

From the measured cross section [$2.2\times10^{-16}\ \mathrm{cm}^2/E(\mathrm{eV})$] we obtain a DR rate coefficient $\alpha=0.9\times10^{-7}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$ at $T=300$ K, which is comparable to that of CO^+ [7]. Thus in the case of CO the dication is not destroyed faster than the cation by DR.

In summary, we have made a study of dissociative recombination with a doubly charged molecular ion, CO^{2+}. The storage ring technique yields both total cross sections and branching ratios. The total DR rate at $T=300$ K is about the same as for CO^+. Below ~2 eV we observe an almost equal production of C and O from DR. The $1/E$ dependence of the cross section suggests that a direct mechanism is responsible for the DR process at low energy. Our results call for further theoretical work on highly excited CO^+ states and an investigation of the dynamics and influence of dissociative barriers on dissociative recombination.

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