Very Slow Spontaneous Dissociation of CO^{2+} Observed by Means of a Heavy Ion Storage Ring

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Long lived (0.8 ms, 6 ms, and > 3.8 s) states in CO^{2+} have been observed for the first time by monitoring beams of 75–300 keV ions in the ion storage ring ASTRID. It is the first experimental evidence that a doubly charged molecule can be stable on a time scale of seconds. The results are theoretically interpreted by means of a multichannel Schrödinger analysis based on *ab initio* computations of potential energy curves and off-diagonal spin-orbit couplings. This analysis indicates that $^3\Pi(v=0)$ accounts for the long lived component. The two decay components in the ms range probably derive from higher excited states in CO^{2+}.

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Small molecules carrying two positive charges (dications) have received considerable interest in recent years [1–4]. A conspicuous feature of these species is that all vibrational levels are embedded in a dissociation continuum and hence are bound to decay, sooner or later, by spontaneous (unimolecular) decomposition; in fact, reliable ps–μs lifetimes towards dissociation have been measured for some dications [3,4]. Although theoretical calculations suggest that dications can be very long lived, experimental evidence is lacking. Despite substantial experimental and theoretical efforts, it has turned out to be very difficult, except in a few cases, to obtain detailed information on dicationic structures and dissociation dynamics. Doubly charged carbon monoxide, CO^{2+}, has been known since 1932, when it was first observed in a mass spectrometer. More than almost any other doubly charged molecule, CO^{2+} has been a constant source of confusion and it has been difficult for experimentalists and theorists alike to converge to a coherent picture [1,5]. One reason for this is that in experiments carried out so far, it has only been possible to follow CO^{2+} on a time scale of μs. This is a sufficiently long time for establishing the occurrence of the unimolecular process $CO^{2+} \rightarrow C^{+} + O^{+}$ [6–9]. However, the precursor state for this process and the mechanism leading to the fragmentation have been much debated [1,5–17], and it is as yet unclear whether CO^{2+} contains levels that are stable on mass spectrometer instrumental time scale [6–8].

Here we report the results of a new type of experiment for doubly charged molecules which allows the dissociation of CO^{2+} to be observed for several seconds. In order to interpret the results, spin-orbit couplings between low-lying states in CO^{2+} have been calculated by multiconfiguration linear response theory. There are many *ab initio* calculations of potential curves of CO^{2+} available in the literature [5,10,14–16,18], however, invariably performed with basis sets of, by present day standards, rather modest sizes. Thus, the potential curves of some of the lowest states in CO^{2+} were recalculated with a much larger basis set than has been used before.

The present experiment was carried out on the Aarhus Storage Ring in Denmark (ASTRID). The ring, which has been discussed by Møller [19], is 40 m in circumference and has two 45° bending magnets in each of the four corners. Ions were injected into the ring from a 200-kV accelerator. The CO^{2+} beam was produced from electron-impact ionization of CO in a plasma-type ion source [20]. The CO gas consisted of 99% ^{13}C and 88% ^{16}O, and our data were taken with $^{13}C^{16}O^{2+}$ (and in a few cases also with $^{13}C^{18}O^{2+}$) molecular ions to avoid beams of $^{14}N^{+}$ and $^{14}N_2{}^{2+}$ in the ring. The beam current of $^{13}C^{16}O^{2+}$ was typically 20 nA. After being injected into the ring, the beam intensity was measured as a function of time by monitoring the production of neutral particles occurring from rest gas collisions (see below) by means of a neutral-particle dsetector installed in a chamber behind one of the bending magnets in the ring. Two different detectors were available: an 8-mm-diam open electron multiplier and a 25-mm-diam tandem channel-plate detector. The average pressure in the ring was $\sim 3\times10^{-11}$ mbar and the rest gas was dominated by H_2.

Measurements of lifetimes in the range of ~ 50 μs to fractions of seconds are possible at the ring by recording the count rate of neutral particles as a function of time after injection. The lower limit is set by the revolution time in the ring, and the upper limit is dictated by the destruction time due to collisions with the rest gas which is typically several seconds. Storage times of selected atomic and molecular negative ions have been determined by this method [21]. Later, several lifetimes of metastable low-lying energy levels of negative atomic ions have been studied by this technique at ASTRID [22–24].

A stable CO^{2+} molecule may undergo collisional-

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induced fragmentation via charge exchange with the rest gas (R) and produce a neutral atom that may be counted in the particle detector:

$$\begin{aligned} CO^{2+}+R &\rightarrow C^0+O^++R^+ \\ &\rightarrow O^0+C^++R^+ . \end{aligned} \tag{1}$$

It is clear that the instant production of neutral particles is proportional to the stored beam intensity for a fixed energy of the stored beam since the density of rest gas atoms is constant in time. The beam of CO^{2+} may also undergo spontaneous dissociation:

$$CO^{2+}\rightarrow C^++O^+ . \tag{2}$$

Thus, for each electronic state (i) of the CO^{2+} beam we may write the change in the number of stored particles as

$$dN^i(t)=-N^i(t)k_c^i\,dt-N^i(t)k_d^i\,dt , \tag{3}$$

where the first term accounts for the losses due to rest gas collisions and the second represents all possible spontaneous (collisionless) dissociation channels. From Eq. (3) we get for the total number of CO^{2+} ions

$$N(t)=\sum_i N^i(t)=\sum_i N_0^i e^{-t(k_c^i+k_d^i)} , \tag{4}$$

where $N_0^i=N^i$ $(t=0)$. If $i=0$ is a "stable" state ($k_d^0\ll k_c^0$) and $i=1,2,\ldots$ are some fast decaying states ($k_d^i\gg k_c^i$) we get

$$N(t)=N_0^0 e^{-t/\tau_0}+\sum_i N_0^i e^{-t/\tau_i} , \tag{5}$$

where $\tau_0=1/k_c^0$ and $\tau_i=1/k_d^i$. This expression constitutes the basis for the fit to the obtained data.

The decay of the CO^{2+} beam was studied at 75, 150, and 300 keV. On a long time scale (10 s), the observed intensity of the stored beam exhibited an exponential decay with a characteristic time of 3.8 s at 75 keV, 2.2 s at 150 keV, and 2.6 s at 300 keV storage energy. We ascribe this to collisional-induced fragmentation (τ_0) and calculate the destruction cross section to be $\sim 10^{-15}$ cm^2.

A fast decrease of the beam intensity was observed in the short time interval up to ~20–30 ms, as shown in Fig. 1 (note that the ion revolution time at 300 keV is only ~28 μs, so each data point represents an average over many revolutions). In some of the atomic systems studied earlier at ASTRID [22,24], the lifetimes depended on the magnetic-dipole field (B) in the ring via the Zeeman effect that mixes magnetic substates of the different fine-structure levels. With CO^{2+} we found two fast decay times $\tau_1=6\pm 2$ ms and $\tau_2=0.8\pm 0.2$ ms independent of the beam energy ($\propto B^2$), as tested at 75, 150, and 300 keV injection energy. From fits to the data with all three exponential functions, the relative population of the three states (N_0^0:N_0^1:N_0^2) was found to be $1{:}1\times 10^{-3}{:}0.3\times 10^{-3}$ at 300 keV.

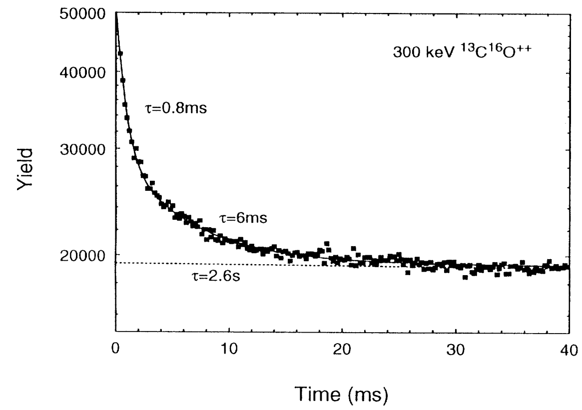

FIG. 1. The yield of neutral particles at the detector as a function of time after injection for storage of 300 keV $^{13}C^{16}O^{2+}$. The full curve is the best fit obtained with a sum of three exponential functions, one of which was fixed at a decay time of 2.6 s (dashed line). 2.6 s was obtained from a separate fit to a 5 s wide time spectrum.

The potential curves for the $^1\Sigma^+$, $^3\Pi$, $^1\Pi$, and $^3\Sigma^-$ states were calculated with the same approach as used in [5], i.e., with complete active space self-consistent field (CAS SCF) and multireference configuration interaction (MRCI) methods [25,26]. The calculation in [5] was improved by using a larger basis set and a much larger CI expansion. Briefly, the basis sets given in Ref. [27] were expanded to [8s5p3d1f] for both carbon and oxygen by adding diffuse d functions with exponents 0.071 and 0.15 and f functions with exponents 0.8 and 1.313 for carbon and oxygen, respectively. The 3σ-6σ and 1π-2π active orbital were optimized in CAS SCF calculations for each state separately. For the MRCI calculations no selection scheme was adopted, i.e., all 492 ($^1\Sigma^+$), 592 ($^3\Pi$), 432 ($^1\Pi$), and 584 ($^3\Sigma^-$) configurations generated by the CAS procedure were used as reference states. The calculated potential curves are shown in Fig. 2.

The spin-orbit couplings among the lowest dicationic states $^1\Sigma^+$, $^3\Pi$, and $^3\Sigma^-$ were obtained as residues of

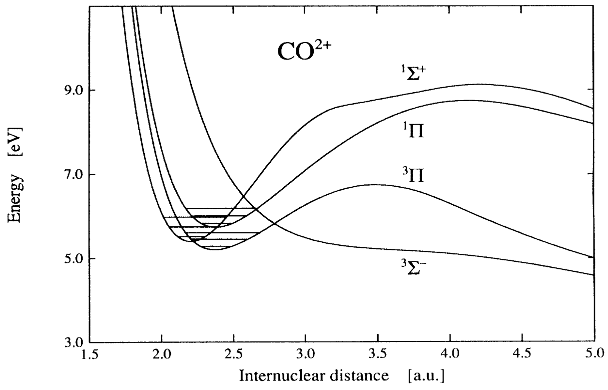

FIG. 2. Potential curves for the lowest electronic states of CO^{2+} from the present MRCI calculations. The energy scale refers to the dissociation limit $C^+(^2P)+O^+(^4S)$.

linear response functions of multiconfigurational self-consistent field (MCSCF) states [28]. The solution to the multiconfiguration linear response (MCLR) eigenvalue equation,

$$(E-\omega_k)X_k=0\,, \tag{6}$$

gives the excitation energy ω_k for state k with respect to an MCSCF reference state. E is the MCSCF Hessian, S is a metric matrix, and the solution vector X_k is a representation of the excited state. The coupling constants are given by

$$\langle 0|H_{\text{s.o.}}|k\rangle=H^{[1]}_{\text{s.o.}}X_k\,, \tag{7}$$

where $\langle 0|$ is the MCSCF reference state and $H^{[1]}_{\text{s.o.}}$ is a row vector containing the spin-orbit operator with the structure of an MCSCF gradient. Reference wave functions were of complete or restricted active space type and optimized for extended basis sets. The results presented in Fig. 3 were converged to within a few percent with respect to sizes of active space and basis set. It follows from Fig. 3 that both the $^1\Sigma^+$ and $^3\Pi$ states interact with the $^3\Sigma^-$ state via the spin-orbit operator. Thus, the lower vibrational levels in the $^1\Sigma^+$ and $^3\Pi$ states are more likely to spontaneously dissociate by radiationless transitions to the repulsive $^3\Sigma^-$ state (electronic predissociation [29]) rather than by tunneling through the potential barriers (tunneling predissociation [29]).

The rates for electronic predissociation of vibrational levels of the $^1\Sigma^+$ and $^3\Pi$ states are obtained from the solution of the exterior complex dilated multichannel Schrödinger equation describing the nuclear motion. This approach makes no assumptions regarding the coupling strengths between the different electronic states [29]. The finite element method [30] was used in order to solve the coupled differential equations. The potential curves for the $^1\Sigma^+$, $^3\Pi$, and $^3\Sigma^-$ states were taken from the MRCI calculations. The calculations show that the $^3\Pi$ state decays directly to the $^3\Sigma^-$ state, however, much slower than predicted earlier [5] (see Table I). The lowest vibrational level decays on a time scale of tens of milliseconds, $v=1$ has a lifetime of less than 1 μs, and higher vibrational levels are even much more short lived. According to the calculations, only $v=0$ is sufficiently long lived to be stored in the storage ring. The low vibrational levels of the $^1\Sigma^+$ state interacts only weakly with the $^3\Sigma^-$ state, and, provided that there was no $^1\Sigma^+$-$^3\Pi$ interaction, the $v=0$ level would be very long lived. However, the $^1\Sigma^+$-$^3\Pi$ spin-orbit interaction opens a decay route for $^1\Sigma^+$ to the $^3\Sigma^-$ state *via* the $^3\Pi$ state, a process known as indirect predissociation [29]; this shortens the lifetime for $^1\Sigma^+(v=0)$ to around 2 μs. Excited vibrational levels in $^1\Sigma^+$ are according to the calculations too short lived to survive even extraction from the ion source. The lifetime of $\sim$20 ms predicted for $^3\Pi(v=0)$ is of course very sensitive to the location of the crossing with the $^3\Sigma^-$ state. With an upward shift of the $^3\Sigma^-$ potential by 30 meV it increases by a factor of 10 and for a shift of $\sim$70 meV it is comparable to the ion storage time. In view of the difficulties for theory to accurately predict potential curves for dications [4], an error of 70 meV does not seem unrealistic. The $^1\Sigma^+(v=0)$ lifetime is less sensitive since it derives from an indirect process, and is still of the order of 10 μs even after a shift of 70 meV. The lifetime of the $^1\Sigma^+(v=0)$ state is too short lived to be measured in the present experiment. It is likely to be the precursor state of the unimolecular decay observed in several mass spectrometry experiments [6-9], and the calculated lifetime is in rather good agreement with the 9 μs estimated in Ref. [7]. It could finally be noted that the interpretation given here is opposite to the one given in Ref. [5], where the $^1\Sigma^+$-$^3\Pi$ interaction was disregarded and the predissociation rates were estimated on the basis of a perturbation approach (Fermi-Wentzel golden rule [29]). Normally it is considered that a treatment as given here, i.e., an exact solution of the coupled equations, is only needed for strong predissociations. It is the peculiar situation which occurs in dications, with even the lowest energy levels affected by a continuum, that necessitates a more sophisticated treatment.

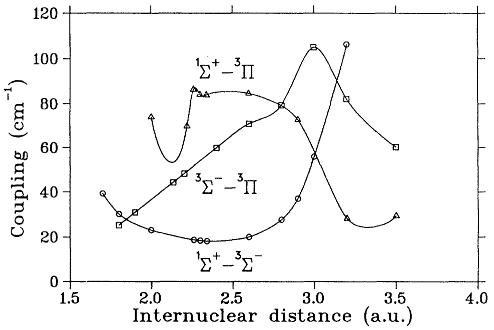

FIG. 3. Spin-orbit couplings between $^1\Sigma^+$-$^3\Pi$, $^1\Sigma^+$-$^3\Sigma^-$, and $^3\Pi$-$^3\Sigma^-$ states in cm^{-1}.

TABLE I. Spontaneous dissociation lifetimes for CO^{2+}.

Lifetimes		State
Experiment	Theory[b]	
...	1.3 ns	$^1\Sigma^+(v=1)$
...	0.3 μs	$^3\Pi(v=1)$
9 μs[a]	2.0 μs	$^1\Sigma^+(v=0)$
0.8 ms	...	2 $^1\Sigma^+$?
6 ms	...	2 $^1\Sigma^+$?
> 3.8 s	20 ms	$^3\Pi(v=0)$

[a] Time-of-flight mass spectrometer with ^{12}CO^{2+} [7].

[b] The theoretical results were obtained with the potentials given in Fig. 2.

It remains to account for the slow (0.8 and 6 ms) decay of CO^{2+} observed for the first time in the present work. The fractional population of the levels that give rise to these decays is very small, which makes it difficult to associate these processes with any of the $^1\Sigma^+$, $^3\Pi$, or $^1\Pi$ states. Under the conditions prevailing in the ion source it is reasonable to expect vertical transitions from CO ($X\,^1\Sigma^+$, $v=0$) to various states of CO^{2+} [31]. This means that it would be extremely difficult to account for fractional populations of the order of 0.1% or less [N_0^1 and N_0^2 in Eq. (5)] on the basis of Franck-Condon factor calculations (see, e.g., [5]). A more likely explanation is that the ms components in the stored beam come from more highly excited states. A possible candidate is the $2\,^1\Sigma^+$ state [5], which has a double minimum. It is known that the first minimum is easily populated by vertical transitions from ground state CO [17] and that the vibrational levels in the first minimum are short lived with respect to tunneling into the second minimum. From the second minimum, which has a broad potential barrier, tunneling may give rise to the observed slow decay. No detailed calculations of the process have been made and the interpretation must be regarded as tentative.

In summary, we have conclusively and unambiguously demonstrated by means of ion storage ring technology that a doubly charged molecule, in this case CO^{2+}, can be stable on a time scale of seconds. In addition, spontaneous dissociations on the time scale of ms have been observed. Theoretical calculations based on new potential curves and off-diagonal spin-orbit couplings suggest that $^3\Pi(v=0)$ accounts for the long lived component in the stored CO^{2+} beam. The ms decay probably arises from higher excited states.

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