New Method for the Study of Dissociation Dynamics of State-Selected Doubly Charged Ions: Application to CO^{2+}

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A new technique is described which is capable of observing the stability of specific states of doubly charged molecular ions with vibrational level resolution. The method is based on the process of double photoionization using synchrotron radiation. Pairs of threshold electrons identify the initial state, and the resulting ions are characterized by their times of flight. Lifetimes have been measured for specific levels of CO^{2+} and confirm, except for the very lowest levels, the intrinsic instability of this species on the μs time scale. [S0031-9007(98)07388-8]

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Doubly charged molecular ions or dications are intrinsically unstable species owing to the Coulomb repulsion between the nuclei which, in most diatomic molecules, leads to potential curves whose bound parts, where they occur, lie well above their dissociation limit. Nevertheless, doubly charged molecular ions have been observed in mass spectrometers for over 60 years, indicating lifetimes of at least microseconds. The advent of ion storage rings has extended our knowledge on their stability and, in the case of CO^{2+}, Andersen *et al.* [1] demonstrated that this dication can exist in a state that has a lifetime in excess of several seconds. This dication was also shown to exist in two other states with lifetimes in the ms range. The spectroscopy of molecular dications has progressed markedly with the development of a new photoelectron spectroscopic technique, threshold photoelectrons coincidence (TPEsCO) spectroscopy [2]. In this technique double ionization thresholds are localized by the detection of pairs of near-zero energy electrons or threshold electrons. Vibrational structure of CO^{2+} was resolved in this way with a resolution of 80 meV allowing the double ionization potential to be determined with unprecedented accuracy and vibrational series to be identified [3]. Improved resolution of vibrational structure in CO^{2+} was obtained by Lundqvist *et al.* [4] using Doppler free kinetic energy release spectroscopy which depends on the inherent instability of dications. Here the C^+ and O^+ fragment ions are detected in coincidence and their kinetic energy determined from the measurement of their time of flight (TOF). In order to be detected as a well-resolved peak in this technique, the dications must dissociate in less than 0.1 μs. In the case of CO^{2+}, this technique revealed all the features observed in the TPEsCO spectrum as well-resolved peaks except for the very lowest levels, indicating that, except for a handful of levels, CO^{2+} states have lifetimes of less than 0.1 μs. In this Letter we present a new technique that prepares dication in well-defined vibrational states and studies their dissociation dynamics. By means of this technique we have been able to propose an assignment for the states responsible for the storage ring observations of Andersen *et al.* [1] and identify others with lifetimes in the μs range.

The experimental method is based on TPEsCO spectroscopy combined with ion time-of-flight spectroscopy and coincidence techniques. Synchrotron radiation is used to doubly ionize the molecule of interest, and a particular state of the dication is prepared by adjusting the photon energy to be that of the state threshold. In this situation the photoionization process results in two threshold electrons and the formation of the state is then identified by the coincident detection of the electron pair. This coincidence signal then triggers a voltage pulse which sweeps the ions into a TOF spectrometer where their mass and energy are measured. Thus, for a diatomic molecule, this experiment involves the coincident detection of two threshold electrons and one or two ions, depending on whether the dication fragments or not.

The experiments were performed on beamline SA31 at the Super ACO storage ring in Orsay, France. This beamline is equipped with a plane grating and operates with a resolution of about 35 meV in the 40 eV region. During the observations an aluminum filter was inserted to remove higher order photons. A schematic diagram of the instrument is presented in Fig. 1. The light beam crosses at right angles the target gas beam effusing from a hypodermic needle. The interaction region is set 10 mm from the entrance of the electron spectrometer and 5 mm from that of the ion TOF spectrometer. The photoelectrons are detected in an electron spectrometer based on a 45 mm radius 90° cylindrical electrostatic analyzer which is operated in the threshold mode using the penetrating field technique [5]. Here, the field from an extraction electrode, set at 300 V, penetrates into the interaction region through a grounded shield electrode to create a shallow potential depression that guides threshold electrons into the optics assembly. Electrons with energies above a few meV escape

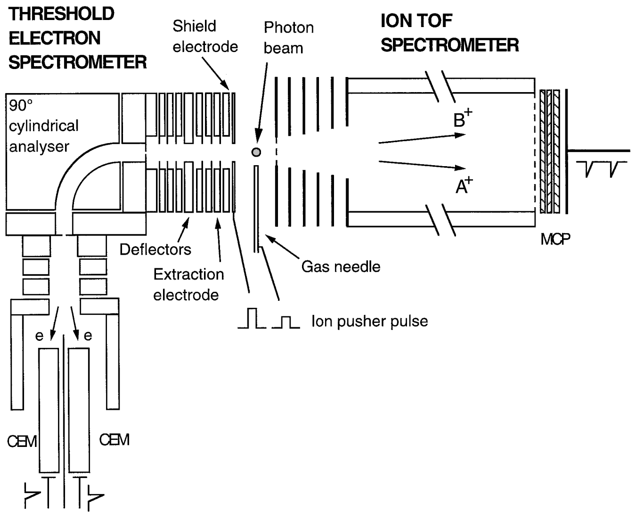

FIG. 1. Schematic diagram of the instrument. The TOF tube is 12 cm long and the mean radius of the 90° cylindrical electrostatic analyzer is 45 mm. The ions are detected on microchannel plates (MCP) and electrons are detected by ceramic channel electron multipliers (CEM) with 5 × 15 mm rectangular apertures separated by a thin shield plate to prevent cross talk.

from the depression and are not collected. This technique combines high efficiency, as threshold electrons are collected over 4π sr, as well as high resolution (meV range). The threshold electrons are detected on two channel electron multipliers (CEM), set side by side, with the input optics adjusted such that the electron intensity is divided equally between them. Double ionization events are detected as coincidences in the signals of the CEM's occurring during a 10 ns time window.

The ions are analyzed in an improved Wiley-McLaren-type two-field TOF spectrometer constructed following the design principles described by Eland [6]. The drift tube is 12 cm long and is typically operated at a potential of -1 kV. This corresponds to a pusher pulse of 300 V (2 μs long) on the shield electrode and 100 V on the gas needle. Under these conditions the flight time of CO^{2+} is of the order of 2 μs compared with about 0.15 μs for electrons in the threshold electron spectrometer. A further 0.15 μs is required by the electronics to apply the pusher pulse, making a dead time of about 0.3 μs between the double ionization event and the application of the sweep field in the interaction zone. During this time the C^+ and O^+ ions with typical kinetic energies from dissociation of 3 eV travel about 3 mm which is insufficient to affect their collection efficiency. The detection efficiency for ions was determined to be 25% compared to 45% for electrons. In this configuration, lifetimes of CO dications in the range 0.1 to 10 μs can be measured.

The vibrational structure of CO^{2+} obtained with improved photon beam resolution using the TPEsCO method has recently been reanalyzed and reassigned [7]. This spectrum is shown in Fig. 2 along with the state assignments. The main result of the reassignment is to locate the $^1\Sigma^+$ $v = 0$ level one vibrational quantum lower, just 26 meV above the $X^3\Pi$ $v = 1$ level, compared to the initial assignment of Dawber *et al.* [3]. These new assignments and energies are now in very good agreement with those obtained theoretically by Larsson *et al.* [8]. The full line in Fig. 2 corresponds to a Gaussian fit and is the sum of the component states that were each fitted as a progression by adjusting the molecular constants. A feature of threshold electron (single or pair) spectra is that the intensity envelopes of the vibrational progressions are not smooth. This is a consequence of autoionization processes that predominate in the near threshold region.

The stability of vibrational states such as those shown in Fig. 2 was studied by setting the photon energy at the threshold energy of a specific level and recording the corresponding flight times of the resulting ions in coincidence with electron pairs as described above. Typical TOF spectra for selected levels are displayed in Fig. 3 and represent coincidences between three particles, two electrons and one ion. These spectra can contain a sharp peak corresponding to CO^{2+} ions that survive to the detector and two broad, roughly rectangular peaks from C^+ and O^+ fragment ions. The width of these peaks is a direct indication of the kinetic energy released in the dissociation process and their profile is related to the angular distribution of the fragments, a rectangular form indicating an isotropic distribution. CO^{2+} ions that dissociate during the flight to the detector yield fragment ions that are recorded at times between the sharp and broad peaks. The ion TOF

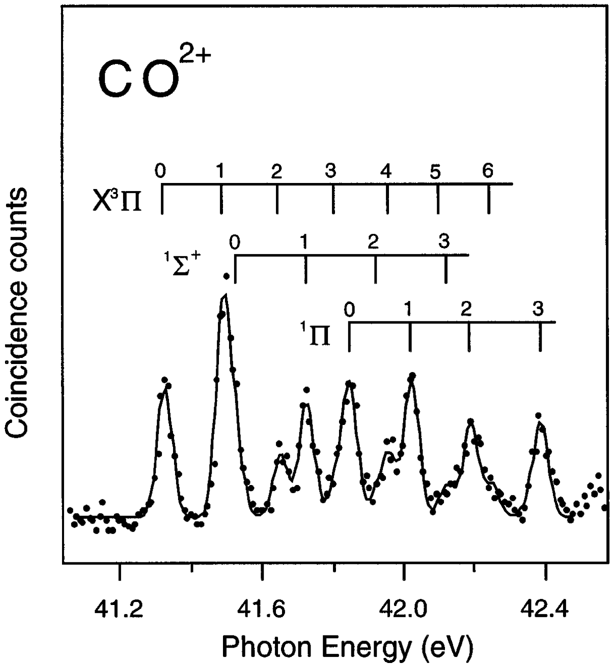

FIG. 2. TPEsCO spectrum of CO showing vibrational levels of the lowest three states of the CO dication. The full line represents a Gaussian fit to the data.

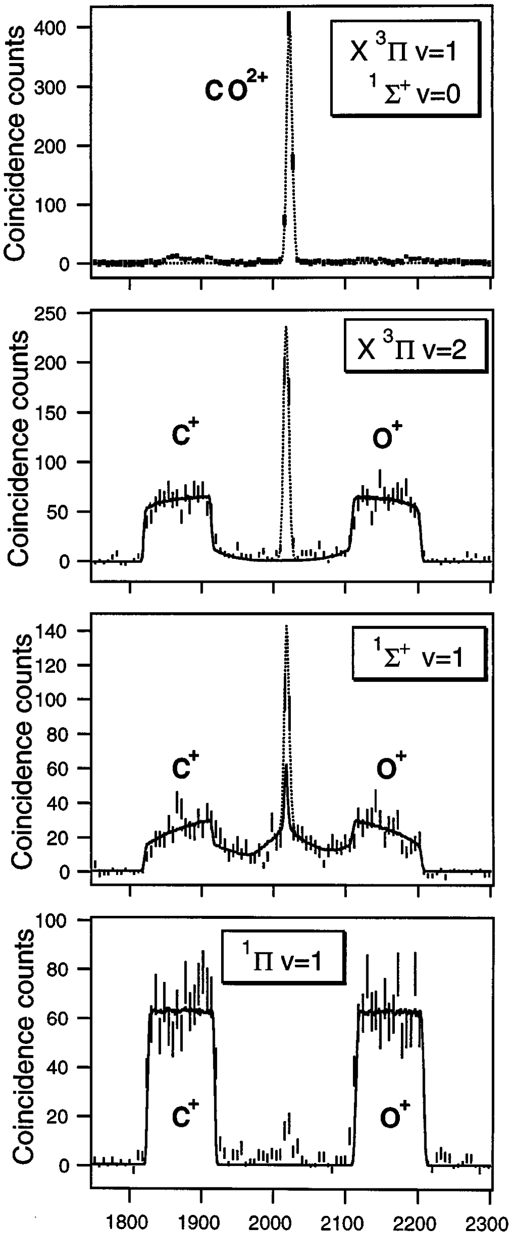

FIG. 3. TOF spectra of the ions resulting from formation of the indicated levels of CO^{2+} and corresponding to coincidences between three particles, two electrons and one ion. The full lines are simulated spectra from which the lifetime of the levels can be obtained. The CO^{2+} peak in the spectrum of the $X^3\Pi$ $v = 2$ level is contributed by the tail of the lower lying $X^3\Pi$ $v = 1$ and $^1\Sigma^+$ $v = 0$ levels (see text). Note that doubly charged species are more efficiently detected than singly charged ones. The TOF spectra were obtained in typically 5–8 hours.

spectra of Fig. 3 have been corrected for random coincidences which were evaluated by triggering the pusher pulse with a signal generator. The correction procedure can be verified by plotting the flight times of the C^+ and O^+ ion coincidences. Such a plot for the $^1\Pi$ $v = 1$ level is shown in Fig. 4 and now represents coincidences between four particles, two electrons and two ions. In such a plot, true coincidences appear around a line of slope -1 with a spread dependent on the thermal motion of the molecules in the target beam. The intensities here should then be coherent with the intensities in the TOF spectra such as those of Fig. 3 once the ion detection efficiency (25%) for the second ion is taken into account.

If the lifetime is much longer than the time of flight (2 μs), then a single peak corresponding to CO^{2+} is recorded and this is so for the second peak of Fig. 2 composed of a superposition of the $X^3\Pi$ $v = 1$ and $^1\Sigma^+$ $v = 0$ levels as can be seen in the top plate of Fig. 3. On the other hand, if the lifetime is much shorter than the TOF then only the C^+ and O^+ ions appear in the spectrum as for the $^1\Pi$ $v = 1$ level. In the intermediate situation where the lifetime is of the same order as the TOF both the parent ion and its fragments appear in the spectrum, and this is the case, in this study, for the $X^3\Pi$ $v = 2$, $^1\Sigma^+$ $v = 1$, and $^1\Pi$ $v = 0$ levels. In these situations the lifetime can then be estimated by modeling the ion TOF distributions. The present simulation is based on the Monte Carlo method and contains the instrumental geometry, potential configuration, kinetic energy release, angular distribution (isotropic), thermal motion of target molecules as well as the time delay in the pusher pulse electronics. The simulations corresponding to lifetimes of 700 and 200 ns for the $^1\Sigma^+$ $v = 1$,and $X^3\Pi$ $v = 2$ level, respectively, are shown as full lines in Fig. 3. A lifetime of 200 ns was also determined for the $^1\Pi$ $v = 0$ level (not shown). The central CO^{2+} peak, not accounted for in the simulation, is contributed by the wing of the intense peak of the $X^3\Pi$ $v = 1$ and $^1\Sigma^+$ $v = 0$ levels. Incompletely resolved neighboring levels can contribute to the TOF spectra, particularly those lying at energies immediately below and must be taken into account when analyzing the data.

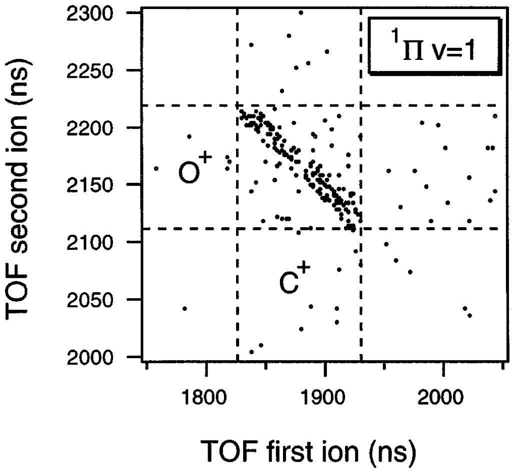

FIG. 4. TOF spectrum of C^+ and O^+ ions resulting from dissociation of the $^1\Pi$ $v = 1$ state and corresponding to coincidences between four particles, two electrons and two ions.

TABLE I. Lifetimes and energies of the lowest vibrational levels of CO^{2+}.

State	Vibrational level	Energy (eV)[a]	Lifetime This work (μs)	Lifetime Others
$X^3\Pi$	0	41.325	>10	>3.8 s[b]
	1	41.489	>10	0.8 ms[b]
	2	41.650	0.2 ± 0.1	<0.1 μs[c]
	3	41.813	<0.1	<0.1 μs[c]
	4	41.960		<0.1 μs[c]
$^1\Sigma^+$	0	41.525	>10	6 ms[b]
	1	41.725	$0.7^{+0.2}_{-0.1}$	0.6 μs[c]
	2	41.925		<0.1 μs[c]
$^1\Pi$	0	41.846	$0.2^{+0.15}_{-0.2}$	<0.1 μs[c]
	1	42.020	<0.1	<0.1 μs[c]
	2	42.185		<0.1 μs[c]

[a]Ref. [7]; [b]Ref. [1]; [c]Ref. [4].

Threshold electron analyzers are characterized by asymmetric transmission functions with a tail of "hot" electrons whose magnitude depends on the experimental parameters. In the present experiments, to enhance the signal intensity, the threshold analyzer resolution was slightly lower than that which produced the spectrum of Fig. 2, and there is a slight overlap between the $X^3\Pi$ $v = 1$ and $v = 2$ states. It must also be kept in mind that the relative intensity of the CO^{2+} peak is probably enhanced in the TOF spectra because of the more efficient detection of this ion due to the higher charge and kinetic energy with which it impinges on the detector.

CO^{2+} lifetimes corresponding to the observations of Andersen *et al.* [1] and Lundqvist *et al.* [4] along with the present results are reported in Table I. The level numbering of the $^1\Sigma^+$ state of Lundqvist *et al.* [4], based on that of Dawber *et al.* [3], has been increased by one following the results of Hochlaf *et al.* [7]. In their storage ring experiments, Andersen *et al.* [1] observed CO^{2+} ions with three long lifetimes (>3.8 s, 6 ms, 0.8 ms). The longest lived state was assigned to $X^3\Pi$ $v = 0$, but neither of the other two lifetimes was attributed to any of the $^3\Pi$, $^1\Sigma^+$, or $^1\Pi$ states. It was considered, first, assuming Franck-Condon transitions dominate in the ion source, that the relative populations of these states would be much higher than those observed and, second, based on their calculations, that these states were too strongly predissociated by the repulsive $^3\Sigma^-$ state [1]. Instead, levels of the $2^1\Sigma^+$ state lying almost 4 eV above the ground state were proposed. However, this latter state was observed both in this work and in that of Lundqvist *et al.* [4] to have a short lifetime, below 0.1 μs. Here the $X^3\Pi$ $v = 1$ and the $^1\Sigma^+$ $v = 0$ levels (20% of peak in Fig. 2) were observed to have lifetimes in excess of 10 μs; consequently, we tentatively assign the 0.8 ms and 6 ms lifetimes to these states, respectively. The longer lifetime is assigned to $^1\Sigma^+$ $v = 0$ as in the present observations $^1\Sigma^+$ $v = 1$ was found to be longer lived than $^3\Pi$ $v = 2$; thus, it is reasonable to assume that $^1\Sigma^+$ $v = 0$ lives longer than $X^3\Pi$ $v = 1$. This same conclusion was also reached in the theoretical calculations of Andersen *et al.* [1]. As can be seen in the table, the lifetimes observed here are in good agreement with those determined by Lundqvist *et al.* [4] except for the $X^3\Pi$ $v = 2$ and $^1\Pi$ $v = 1$ levels where we observe lifetimes longer than 0.1 μs.

The stability of CO^{2+} is now the most well documented of any dication. In fact, it has only one quasistable level, the $v = 0$ level of the $X^3\Pi$ ground state with a lifetime >3.8 s [1]. The lifetime of higher levels decreases dramatically as their energy increases and, 0.4 eV above the ground state, no level with a lifetime greater than 0.1 μs appears to exist. However, this rapid decrease does not have a simple dependence on energy as the lifetime of the $^1\Sigma^+$ $v = 0$ level was found to be longer than that of the $X^3\Pi$ $v = 2$ level lying immediately below it. Nevertheless, some 30 discrete levels have been observed in the CO^{2+} spectrum with energies up to 4.5 eV above the ground state with a width determined by the instrumental resolution (<40 meV), indicating lifetimes of at least 2×10^{-14} s. In fact, theory indicates that the lifetime of all the discrete vibrational levels known [3,4] for CO^{2+} is determined by the coupling to a single dissociative state, the $^3\Sigma^-$ state, and thus all dissociate to ground state $C^+(^2P)$ and $O^+(^4S)$ fragments as was observed.

Herein, the characteristics of a new experimental technique have been demonstrated whereby, for the first time, the stability of specific vibrational states of doubly charged molecular ions can be studied. In principle, the penetrating field method is capable of resolutions down to the meV range. In the future, with the appropriate light source, such resolution will furnish more detailed information on diatomic dications and open up the rich and complex field of polyatomic dication structure dynamics.

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