J. Phys. Chem. A **2009,** *113,* 14755–14759

Double Photoionization of CO_2 Molecules in the 34−50 eV Energy Range[†]

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Received: May 26, 2009; Revised Manuscript Received: June 24, 2009

The double photoionization of CO_2 molecules has been studied in the 34−50 eV photon energy range, by the use of synchrotron radiation and detecting electron−ion and electron−ion−ion coincidences. Three processes have been observed: (i) the formation of the CO_2^{2+} molecular dication, (ii) the production of a metastable $(CO_2^{2+})^*$ that dissociates, with an apparent lifetime of 3.1 μs, giving rise to CO^+ and O^+ ions, and (iii) the dissociation leading to the same products, but occurring with a lifetime shorter than 0.05 μs. The relative dependence on the photon energy of the cross section for such processes has been measured. While for the production of the molecular dication a threshold is observed, in agreement with the vertical threshold for double ionization of CO_2, for the dissociative processes the threshold appears to be lower than that value, indicating the presence of an indirect dissociation, probably leading to the formation of CO^+ together with a neutral autoionizing oxygen atom.

I. Introduction

The first experimental evidence of the CO_2^{2+} dication formation by electron impact ionization has been reported in 1961.[1] Since that observation, the double ionization of CO_2 has been studied in several laboratories by the use of different techniques, including the photoionization. The large interest in such processes is due to the involvement of CO_2 in several atmospheric phenomena of the Earth and of other planets. As an example, the importance of the CO_2^{2+} dication and its dissociation in the atmosphere of Mars, where CO_2 is the main component, has been recently shown.[2]

In the case of electron impact and photoionization, two mechanisms can in general be invoked for the formation of a molecular dication. One occurs through the deposition of enough energy in a core orbital to cause the removal of one inner shell electron. Subsequently, an electronic relaxation of the formed ion causes the ejection of another electron from a valence orbital. This is the so-called Auger ionization process,[3] which is currently studied for many molecules in the gas phase including CO_2.[4] Alternatively, the double ionization of a molecule can occur by removing two valence electrons with a single photon, at an energy around the double ionization threshold. Such a process is governed by electron−electron correlation and provides important information about the structure and dynamics of the CO_2^{2+} molecular dication.[5] For these ionization studies one can use photons coming from a lamp or tunable synchrotron radiation coupled with a monochromator.[6]

Like most of molecular dications, CO_2^{2+} is unstable and, when it is formed just above the double ionization threshold energy, can dissociate to give CO^+ and O^+. This dissociation reaction has been studied employing a variety of techniques: electron impact ionization mass spectrometry,[7,8] double charge exchange,[9] and photoionization mass spectrometry.[10−17] In some cases, also coincidence detection techniques have been applied.[5,11−13,15−19] Such studies have shown that the dissociation reaction

$$CO_2^{2+} \rightarrow CO^+ + O^+$$

can involve several electronic states of the molecular dication and occurs according to different kinetic schemes:[5] the threshold energy for double ionization of CO_2 is 37.3 eV, very fast dissociations, with lifetime shorter than ~0.05 μs, occur predominantly when the ionization energy is larger than 41 eV, while between 37.3 and 41 eV also dissociation through metastable $(CO_2^{2+})^*$ states is also involved.[5]

In the present paper we report on the double photoionization of CO_2, in the 34−50 eV photon energy range, by the use of synchrotron radiation and detecting electron−ion and electron−ion−ion coincidences. The use of the synchrotron as a light source provides the possibility to select the energy of the photons, keeping a high intensity of the signal. Therefore, with the present results we expect to improve the information about the energetics and the dynamics of the double photoionization of CO_2. The experimental setup is practically the same as we have already used recently for studying the double photoionization of N_2O molecules.[20,21] The results for CO_2 allow us to obtain the photon energy dependence of the cross sections for

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[†] Part of the "Vincenzo Aquilanti Festschrift".

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10.1021/jp9048988

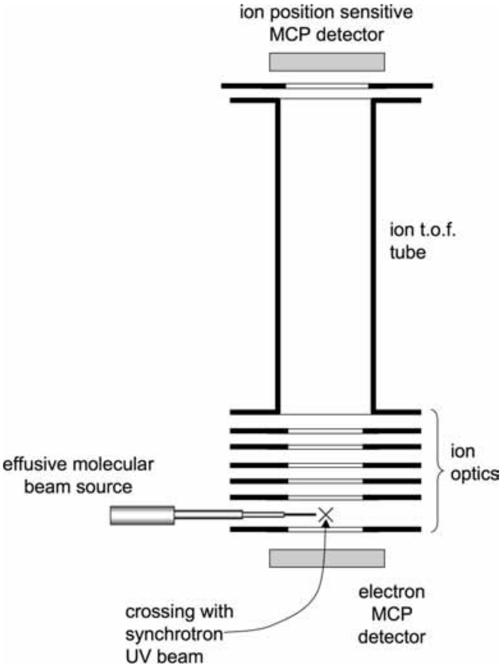

Figure 1. Outline of the experimental setup used for the double photoionization study of CO_2 molecules with synchrotron radiation.

the three processes open in the energy range that has been investigated: the molecular dication CO_2^{2+} formation, the fast dissociation, and the dissociation through the formation of a metastable $(CO_2^{2+})^*$ state. An analysis of the coincidence plots led also to the determination of the lifetimes for the metastable state.

II. Experimental Section

The experiment has been performed at the ELETTRA Synchrotron Light Laboratory using the ARPES end station at the Gasphase Beamline. Details about the beamline and the end station have been already reported elsewhere,[22] while the apparatus used in the present experiment has been described previously.[20,21] Only a few features relevant to the present investigation are described here.

Figure 1 shows a sketch of the experimental setup. The energy selected synchrotron photon beam crosses an effusive molecular beam of CO_2, and the product ions are then detected in coincidence with photoelectrons. The monochromator uses a 400 lines/mm spherical grating in first diffraction order. The entrance and exit slits of the monochromator have been adjusted in order to have a photon energy resolution between 2.0 and 1.5 meV in the investigated 34−50 eV range. In order to avoid spurious ionization effects, due to photons of higher order energy, a magnesium film filter was used. The CO_2 molecular beam and the light beam cross at right angles. The gas inlet source is supplied with a gaseous mixture of CO_2 and helium, and this allows us to normalize all ion signals, at each photon energy, to the total ion yield of helium at that energy.

The ion extraction and detection system has been assembled following the model described by Lavollèe.[23] Such a time-of-flight (TOF) device, with an ion position sensitive detector, is particularly designed in order to measure the spatial momentum components of the dissociation ionic products. However, for the experiment described here, the position information has been not used and only total ion arrival times to the microchannel plate (MCP) detector have been considered for electron−ion and electron−ion−ion coincidences. Practically, mass spectra were recorded using photoelectrons as starting pulses, and then ions were counted as a function of the delay times measured by the time-to-digital-converter array connected with the multianode. All experiment components are controlled by a computer that also records experimental data. The incident photon flux and the gas pressure have been monitored and stored in separate acquisition channels. Ion yields have been then corrected for pressure and photon flux changes while varying the photon energy.

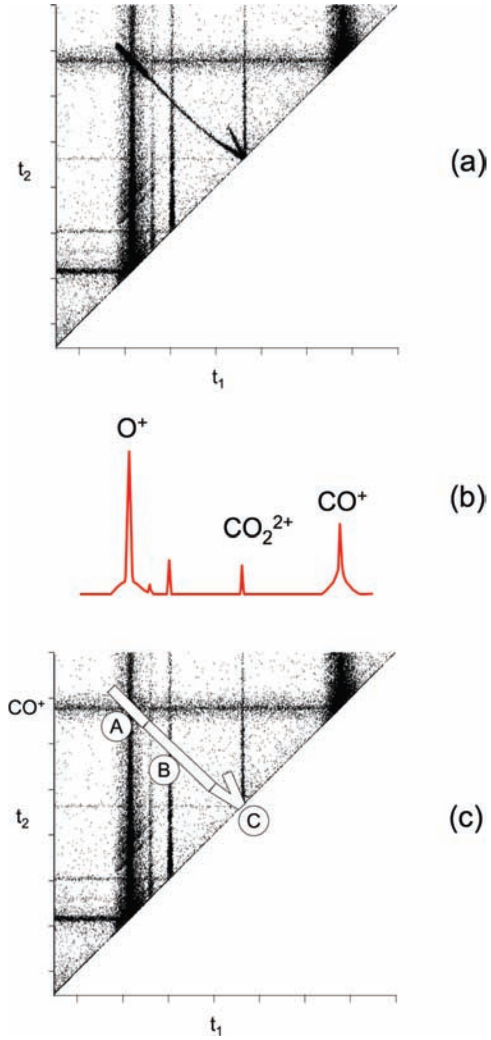

Figure 2. Spectra of coincidences for the double photoionization of CO_2 at a photon energy of 44 eV: (a) plot of the delay times t_1 and t_2 (see text); (b) mass spectrum of the product ions at the same photon energy; (c) the plot reported above, where the different areas for the analysis of the lifetime of metastable $(CO_2^{2+})^*$ dication are indicated.

The carbon dioxide is supplied to the needle beam source from a commercial cylinder filled with about 10 atm at room temperature. The gas has a 99.99% nominal purity and has been used without any further treatment. An adjustable leak valve along the input gas pipe line is used in order to control the gas flow, which is monitored by checking the pressure in the main vacuum chamber.

III. Data Analysis

A typical coincidence plot is reported in Figure 2a. Plots of this type are obtained in the following way. Each single or double photoionization event produces one or two photoelectrons that are detected almost immediately by the MCP located just above the scattering volume (see Figure 1). The electron pulses are the start for the TOF measurement, and when an ion arrives to the ion detector with a delay time t_1, the detection logic system records also a possible second ion with a delay time t_2. Therefore, the dots in the plot are related to couples of t_1 and t_2 delay times with respect to the detection of a photoelectron. The analysis of coincidence plots like that one of Figure 2a is very useful since it provides many details about the double ionization processes.[24] The distribution of t_1 delay times only, reported in Figure 2b, provides the mass spectrum of product ions. Moreover, the dots within the "A" area of Figure 2c are CO^+/O^+ coincidences produced by a fast dissociation occurring when the molecular dication precursor is still within the reaction volume or immediately close. In other words, the dications leading to these "A" coincidences dissociate with a lifetime shorter than ~0.05 μs. The dots within the "B" area are coincidences related to dissociations occurring with lifetimes longer than ~0.05 μs and the reaction occurs when the metastable $(CO_2^{2+})^*$ dication is still in the region indicated as "ion optics" in Figure 1, where a gradient of electric field is present. The dissociation events occurring when the metastable $(CO_2^{2+})^*$ is flying along the ion TOF tube (see Figure 1) fall within the "C" area that is V shaped. Such a shape is a consequence of the fact that the drift tube is field free and ions produced by a dissociation can be ejected, with a characteristic KER distribution, in all directions with respect of the center of mass. Therefore the two arms of the V are characterized by different slopes, m_1/m_2 or m_2/m_1.[24]

The intensity of the CO_2^{2+} peak, in the mass spectrum of Figure 2b, as a function of the photon energy, normalized for the photon flux, give us the relative cross section for the molecular dication formation. On the other hand, counting the true coincidences in area "A" provides the cross section for the "direct dissociation", while counting the true coincidences in the areas "B" and "C" provides the cross section for the formation of the metastable $(CO_2^{2+})^*$. The relative cross sections so obtained are reported in Figure 3.

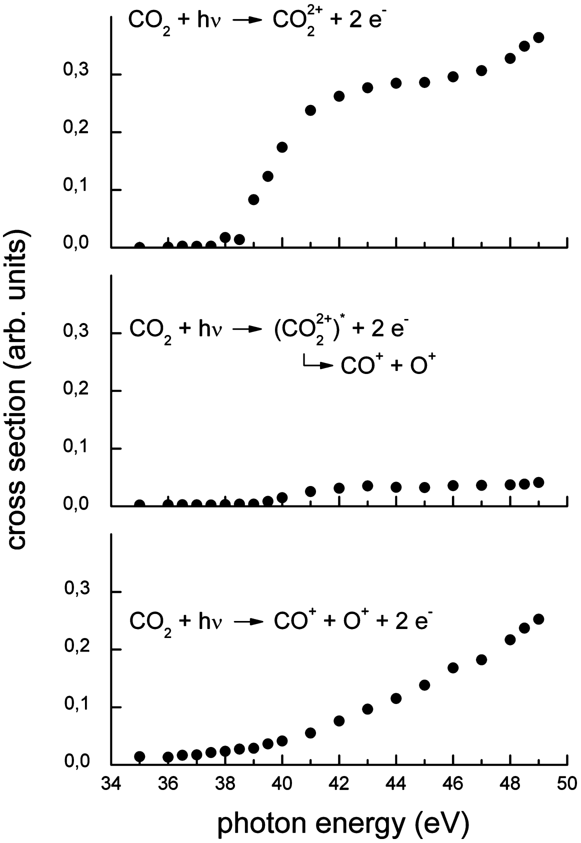

Figure 3. Photon energy dependence of the cross section for the three photoionization processes observed in the 34−50 eV energy range.

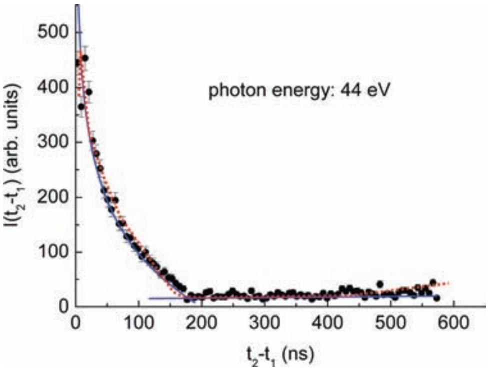

Figure 4. Density of coincidences between one photoelectron and two photoions, within the areas B and C of Figure 2, as a function of the time difference $t_2 - t_1$, for a photon energy of 44 eV. The dotted line represents a Monte Carlo simulation with $\tau = 3.1$ μs and KER = 4 eV, while the continuous lines are the results obtained by the use of the formulas in ref 24 with the same value of τ.

Another important result is the distribution of the dot density along the areas "B" and "C". Field and Eland[24] have shown that such a density distribution is correlated with the lifetime, τ, of the metastable dication. Those authors derived some simple mathematical expressions for the density of coincidences I, as a function of the time difference $(t_2 - t_1)$, in the areas "B" and "C". Following their analysis, in the area "B" the density distribution is given by

$$I(t_2 - t_1) = A_1 \exp\left[-\left(\frac{m_1 + m_2}{m_1 - m_2}\right)\frac{t_2 - t_1}{2\tau}\right]$$

while in the are area "C" the density distribution is given by

$$I(t_2 - t_1) = A_2\left\{\ln\left[\frac{(t_2 - t_1)_{\max}}{(t_2 - t_1)}\right] + \frac{t_0}{\tau}\left[1 - \frac{(t_2 - t_1)}{(t_2 - t_1)_{\max}}\right] + \frac{t_0^{\,2}}{2.2!\tau^2}\left[1 - \frac{(t_2 - t_1)^2}{(t_2 - t_1)_{\max}^{\,2}}\right]\right\}$$

where t_0 is the flight time of the ion in the field free drift tube. However, in order to obtain the lifetime of the metastable $(CO_2^{2+})^*$ and of other molecular dications, Field and Eland[24] preferred the use of a Monte Carlo trajectory simulation. For the analysis of the present data we have used both methods. A computer routine has been written in order to evaluate the t_1 and t_2 distribution once the kinetic energy released (KER) by the two ionic fragments and the dissociation lifetime, τ, of the metastable dication have been fixed. In such a routine, the remaining parameters, namely, the location of the ionization center within the beam crossing zone, the thermal velocity of the molecule, and the direction of the two ionic fragments, have been pseudorandomly chosen. Then a simulation of the experimental $I(t_2 - t_1)$ dependence has been performed adjusting KER and τ and evaluating the standard deviation as a reliability level of the simulation. To give an example, a typical $I(t_2 - t_1)$, for the photon energy of 44 eV, is reported in the Figure 4, where the dots are the experimental results and the dotted line is obtained with a simulation with 10^6 trajectories. In order to give

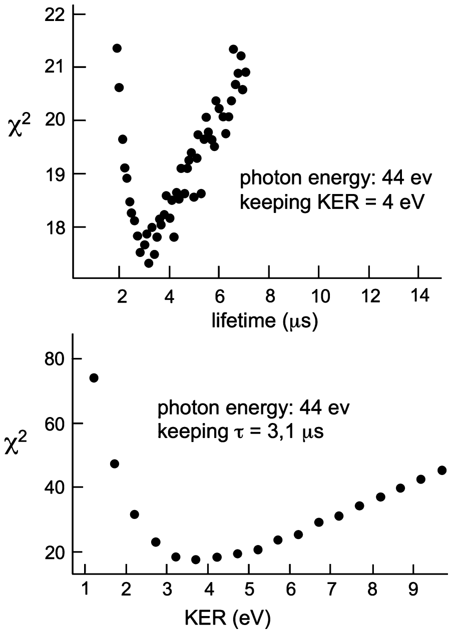

Figure 5. The dependence of the square of the standard deviation, χ^2, on the lifetime and KER during the best fit analysis of data of Figure 4.

an idea of the sensitivity of the method, in Figure 5 we reported the square of the standard deviation, χ^2, as a function of the lifetime τ, when KER = 4 eV, and as a function of the KER, for $\tau = 3.1$ μs. Extending such an analysis to other photon energies, we have obtained similar results and therefore we can conclude that the lifetime of the metastable $(CO_2^{2+})^*$ dication, in the photon energy range between 40 and 48 eV, is $\tau = 3.1 \pm 0.9$ μs, with a KER of 4 ± 1 eV. Very similar results have been obtained also by the fit of the density distributions with the formulas by Field and Eland reported above (continuous lines in Figure 4). However we have to note that the analysis with the Monte Carlo simulation is more practical and it seems also more reliable. In fact, with the above formulas, one has to analyze separately the "B" and "C" areas, since the normalization factors A_1 and A_2 are different. With the trajectory simulation one obtains a dependence that can fit simultaneously the distributions in both areas.

IV. Discussion

The threshold for the double photoionization of CO_2 molecules has been reported to be 37.34 ± 0.01 eV.[5] Looking at the cross sections for the molecular dication formation (upper panel of Figure 3) it appears that the present results are in good agreement with that previous determination. However, when considering the $CO^+ + O^+$ formation (lowest panel), the situation seems to be a little more complicated. Previous measurements have provided various results: Dujardin and Winkoun[12] reported 37.9 ± 0.4 eV, Millié et al.[13] gave 39.7 ± 0.5 eV, Masuoka[15] found 39.2 ± 0.3 eV, while Franceschi et al.[25] provided a value of 38.7 ± 0.15 eV. All these results are above the threshold for the molecular dication formation. It has to be noted that the thermodynamic threshold for $CO^+ + O^+$ formation, starting from CO_2, is 33.15 eV[26] and therefore the maximum KER is expected to be ~4 eV. However, recently Slattery et al.[5] found a rather lower threshold value of 35.56 ± 0.10 eV. Our measurement appears to be in good agreement with that recent determination. Slattery et al.[5] explain such a behavior by assuming, for photon energies below the threshold, an indirect dissociative double photoionization mechanism that involves an autoionizing state of the oxygen atom:

$$CO_2 + h\nu \rightarrow (CO_2^{+})^* e^- \rightarrow CO^+ + O^* + e^- \rightarrow CO^+ + O^+ + 2e^-$$

where $(CO_2^{+})^*$ represents an excited state of singly charged carbon dioxide. In other words, the photon produces an excited molecular cation that dissociates leading to an autoionizing oxygen atom. Later on this atom ejects a second electron. An indirect ionization, below the vertical threshold for the second ionization, has been also recently observed for the double photoionization of N_2O molecules.[20,21]

Our cross sections are on a relative scale, nevertheless, the relative trends are in agreement with the energy dependence of the branching ratios reported by Slattery et al.,[5] except at higher photon energy (see middle panel in Figure 3), where the former authors reported a very low production of the metastable dication.[5]

From the analysis of the spectra of coincidences, measured in the range of photon energies from 40 to 48 eV, we have obtained a lifetime $\tau = 3.1 \pm 0.9$ μs for the metastable dissociation

$$(CO_2^{2+})^* \rightarrow CO^+ + O^+$$

This should be an indication that, at least in such a range, the metastable dication is produced through a vertical Franck–Condon transition. Looking at the lifetime values available in the literature for this system, one finds several different results, spread in a wide range: Tsai and Eland[10] have reported a value of 21.6 μs, Newton and Sciamanna[27] found a value of 3.3 μs, while Field and Eland obtained a value of 0.9 μs. Slattery et al.[5] noted that these results are correlated with the experimental time observation windows, that are characteristic of the specific setup used for each measurement. For the three cases mentioned above, such time windows are respectively 5–50, 3–9, and 0.01–2.2 μs. Consequently, Slattery et al.[5] suggest that in double photoionization of CO_2 all states that are within the energy available are populated according to their Franck–Condon factors and that the measured lifetime is an average value in the time window characteristic of the experimental setup. According to this suggestion, which appears to be very reasonable, the lifetime value obtained by us must be considered as an average over the observation time window of our experimental setup, that is 0.05–2.6 μs.

V. Conclusions

Combining the results of the present experiment with those reported previously, it is possible to assess some of the characteristics of the double photoionization of CO_2. The present results confirm that the molecular dication, CO_2^{2+}, is produced with a threshold energy of 37.3 eV, in good agreement with the previous determination.[5] Metastable $(CO_2^{2+})^*$ dications, at lower concentration, are also formed, but it is necessary to point out that these species are to be considered unstable only within the time scale of observation of our apparatus which ranges from 0.05 to 2.6 μs. Taking into account previous determinations of lifetime for this ion, it is important to note that the double photoionization produces dication states populated according to the whole available energy and the Franck–Condon factors. Therefore, the lifetime determined in each experiment is to be considered as a mean value affected by the average over the time range of the observation.

The dissociative double photoionization, namely, those events leading to CO^+ and O^+ in a time shorter than ~0.05 μs, exhibits a cross section that increases with the photon energy, becoming, at about 50 eV, comparable with that for CO_2^{2+} formation. Moreover, this process appears with an energy threshold lower than that exhibited by the molecular dication formation, confirming the recent results by Slattery et al.,[5] although in contradiction with previous experiments.[12,13,15,25] This observation could be an indication of the presence, below the threshold, of a possible indirect ionization process, where an excited molecular monocation $(CO_2^+)^*$ is formed and then dissociates with the formation of an autoionizing oxygen atom.

It must be emphasized that the dissociative double ionization, leading to the formation of CO^+ and O^+ ions with very short lifetime (<0.05 μs), is one of the main ionization channels. For such fast processes it has been shown that the coupling of ion imaging technique with electron−ion−ion coincidence[23] can give very detailed information, as recently reported for the N_2O double photoionization case.[21] We would like to apply such a type of study also to the CO_2 case, and we have already started work in this direction.

Acknowledgment. The authors are grateful to J. H. Eland and T. A. Field for useful suggestions. Financial contributions from the MUR (Ministero dell'Università e della Ricerca) are gratefully acknowledged. F.V. and F.P. gratefully acknowledge a travel support by the "Sincrotrone Trieste S.C.p.A."

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JP9048988