Dissociative double photoionization of CO2 molecules in the 36–49 eV energy range: angular and energy distribution of ion products

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Dissociative double photoionization of CO2, producing CO+ and O+ ions, has been studied in the 36–49 eV energy range using synchrotron radiation and ion–ion coincidence imaging detection. At low energy, the reaction appears to occur by an indirect mechanism through the formation of CO+ and an autoionizing state of the oxygen atom. In this energy range the reaction leads to an isotropic distribution of products with respect to the polarization vector of the light. When the photon energy increases, the distribution of products becomes anisotropic, with the two ions preferentially emitted along the direction of the light polarization vector. This implies that the molecule photoionizes when oriented parallel to that direction and also that the CO2+ dication just formed dissociates in a time shorter than its typical rotational period. At low photon energy, the CO+ and O+ product ions separate predominantly with a total kinetic energy between 3 and 4 eV. This mechanism becomes gradually less important when the photon energy increases and, at 49 eV, a process where the two products separate with a kinetic energy between 5 and 6 eV is dominant.

I. Introduction

The first observation of the CO2+ dication, formed by electron impact ionization of carbon dioxide was reported in 1961. Since that experiment, the double ionization of CO2 has been studied in several laboratories. These kinds of processes are of great interest because of the involvement of CO2 in several atmospheric phenomena of the Earth and of other planets and in plasma environments. In Mars’ atmosphere, where CO2 is the main component, the importance of the CO2+ dication and its dissociation has been recently demonstrated.

Like most of molecular dications, CO2+ is unstable and, when it is formed just above the double ionization threshold energy, can dissociate to give CO+ and O+. Such a dissociative reaction has been investigated with a variety of techniques like electron impact ionization mass spectrometry, double charge exchange, and photoionization mass spectrometry. In some cases, coincidence detection techniques have been applied.

We have recently reported some results on the double photoionization of carbon dioxide, in the 34–50 eV photon energy range, by the use of the synchrotron radiation. Those results, together with other experimental data that recently appeared in the literature, allow us to assert that the molecular CO2+ dication is unstable and dissociates to give rise to CO+ and O+ ions,

\[
\text{CO}_2 + h\nu \rightarrow \text{CO}^+ + \text{O}^+ + 2\text{e}^-, \quad (1)
\]

with a wide range of lifetimes. Although the vertical threshold for the formation of the molecular CO2+ dication is 37.3 eV, it has been found that the reaction (1) starts at around 35.6 eV, indicating the presence, in this lower energy range, of an indirect mechanism leading to the production of the CO+ ion together with an autoionizing state of the oxygen atom. However, many features of the possible mechanisms promoting the reaction (1) are still not well characterized.

It is well known that the measurement of the angular and energy distribution of products, with respect to the polarization vector of the ionizing light, is a powerful tool for understanding details of the photodissociative microscopic process. Such measurements provide the angular distribution of formed ions, usually given as \(I(\theta)\sin \theta\),

\[
I(\theta) \sin \theta = \frac{\sigma_{\text{tot}}}{4\pi} \left[ 1 + \frac{\beta}{2} (3 \cos^2 \theta - 1) \right] \sin \theta,
\]

where \(I(\theta)\) and \(\sigma_{\text{tot}}\) are the differential and the total cross section of the process, respectively, while \(\theta\) is the angle between the velocity vector of the fragment ion and the light polarization direction. The anisotropy parameter \(\beta\) runs between -1, for the orientation of the dissociating molecule perpendicular to the electric field vector (e.g. \(\Sigma\) to \(\Pi\) transition), up to a value of 2 for the parallel transition (e.g. \(\Sigma\) state to \(\Sigma\) state). An isotropic distribution of fragment ions is characterized by \(\beta = 0\).
Measurements of $\beta$ for the dissociative double ionization of CO$_2$ have been performed by Masuoka and coworkers$^{16,17}$ in the photon energy range from 41 to 100 eV, exploiting synchrotron radiation coupled with time of flight analysis of the dissociation products, and a photoion–photoion coincidence detection. Some other studies have been also carried out at higher photon energies, where core orbitals of the target molecules are involved.$^{23,24}$ However, detailed information on the possible mechanisms promoting reaction (1) in proximity to the threshold, and on their evolution with rising photon energy is still lacking. In particular detailed experimental characterization of the $\beta$ parameter for double photoionization at the threshold provides unique information on the mechanisms in terms of molecular orbitals. In recent years, the high potential for coupling photoion–photoion coincidence with imaging techniques has been shown.$^{24,25}$ For photon energies around the double ionization threshold, this technique has provided valuable information about the N$_2$O system, where the angular distribution has been found rather anisotropic, with the $\beta$ parameter ranging from $\beta = 0$ at low energies up to $\beta = 1.5$ and $\beta = 1.6$ for the dissociation leading to N$^+ +$ NO$^+$ and to N$_2$$^+$ + O$^+$, respectively.$^{25}$ Recently Pesic et al. studied the photodissociation of CO$_2$, at a photon energy of 308 eV, exciting C(1s) core orbital electrons.$^{24}$

In this paper we report the angular and energy distribution of ion products for reaction (1) in the 36–49 eV photon energy range. The experiments have been carried out using synchrotron radiation and a time of flight mass spectrometer equipped with a position sensitive ion detector. The data has been analyzed in order to obtain, as a function of the photon energy, the anisotropy parameter $\beta$ and the kinetic energy released (KER) in the ion products. Preliminarily, it is important to point out a substantial difference between the dissociative process as studied in our previous paper$^{20}$ and the one investigated and discussed here. In Fig. 1 we show a typical coincidence map as obtained in our previous work$^{20}$ for a photon with energy 44 eV. The relative cross sections for CO$_2^{2+}$ dication formation reported in that paper come from the analysis of the photon energy dependence of the relevant peak in the mass spectrum. The relative cross sections for the “instantaneous” CO$^+$ + O$^+$ dissociation result from the analysis of the coincidence CO$^+$ /O$^+$ spot in the map, while those for the metastable (CO$_2^{2+}$)$^m$ formation were obtained from the analysis of the trace of coincidence points connecting the CO$^+$ /O$^+$ spot with the CO$_2^{2+}$ dication position. The word “instantaneous” used above is related to the typical ion flight times in the measured spectra. Thus we can define dissociations occurring within $\sim$50 ps of the photoionization event as “instantaneous”.$^{20}$ In the present work we have studied in detail such “instantaneous” dissociations with the ion imaging technique.

II. Experimental

The experiment has been carried out at the synchrotron light laboratory ELETTRA (Trieste, Italy) by the use of the ARCES end station of the Gasphase Beamline. Details about the beamline and the end station have been already reported elsewhere,$^{27}$ while the apparatus used in the present experiment has been specified previously.$^{20,25,26}$ Only some features relevant for the present investigation are described here.

Fig. 2 shows schematically the experimental set up. The energy selected synchrotron light 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$^{-1}$ spherical grating in first diffraction order. The entrance and exit slits of the monochromator have been adjusted in order to give a photon energy resolution between 1.5 and 2 meV in the investigated 36–49 eV range. In order to avoid spurious effects, due to ionization by photons of higher energy, a magnesium film filter was placed in the synchrotron radiation beam. The molecular and the light beams cross at right angles.

The ion extraction and detection system has been assembled following the design described by Lavollée.$^{28}$ Such a time-of-flight spectrometer, with an ion position sensitive detector, is particularly designed in order to measure the spatial momentum components of the ionic dissociation products. The electron detector, located just below the interaction volume (see Fig. 2), consists of a stack of three micro-channel plates followed by a copper anode. The ion detector also consists of a stack of three-micro channel plates located at the end of the drift tube. The signals are read by an array of anodes arranged in 32 rows and 32 columns.$^{28}$ Such an arrangement allows the detection of the position of the ion arriving on the detector plate. In the experiment the photoelectron signals are used as start pulses, and then ions are counted as a function of their arrival time and position on the detector. The delay times are measured by an array of time-to-digital converters connected with the multi anode. Therefore, the obtained images are resolved in time,
allowing an easy transformation to angle and energy distributions. All experiment components are controlled by a computer that also records experimental data.

The incident photon flux and gas pressure have been monitored and stored in separate acquisition channels. Ion yields have then been corrected for pressure and photon flux changes while varying the photon energy.

Carbon dioxide is supplied to the needle beam source from a commercial cylinder at 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.

In order to test the efficiency and the performance of the experimental set up, we have measured the angular distribution of CO\(^+\) and O\(^+\) product ions in the double photoionization of CO\(_2\) at 308 eV. The results compare well with those available in the literature\(^{23,24}\) recorded with a similar experimental set up. In particular, we have obtained an anisotropy parameter \(b = 0.5\), in good agreement with that obtained by Pesic \(et\ al.\)^{24} The data in the 36–49 eV photon energy range were recorded using the same experimental conditions.

Fig. 3 shows a typical 3D representation of the angular distribution of products at photon energy of 49 eV.

III. Results and data analysis

The angular distributions of product ions of reaction (1) are reported in Fig. 4 as \(I(\theta)\sin \theta\) (see eqn (2)). Like in the 3D distribution of Fig. 3, the data have been again collected for CO\(^+\) and O\(^+\) in coincidence, normalized and summed. They have been used to determine the value of the anisotropy parameter \(b\), giving \(b = 0\) at 36 eV, with an increase to \(b = 1.1\) at 39 eV and finally a decrease to \(b = 0.7\) at 41 eV and \(b = 0.6\) for the last two energies, 44 and 49 eV.

The kinetic energy distribution of the two product ions, as obtained from the analysis of the ion images, is reported in Fig. 5 as a function of the photon energy. The energy distributions at 36 eV are not very clear because of the low intensity of the signal, as can be also argued from the large scatter of the data in the angular distribution at 36 eV (see Fig. 4), due to the low cross section at this energy.\(^{20}\)

For the other energies the distributions are much better defined and the total kinetic energy released can be more meaningfully plotted as shown in Fig. 6. Looking at such distributions it is evident that, in the photon energy range here...
considered, they mostly arise from the contribution of two components, indicating the presence of two mechanisms for the reaction (1). We have analyzed these distributions by fitting them with simple Gaussian functions, as shown by the dotted lines in the Figure. This analysis allowed us to obtain the mean total kinetic energy released as a function of the photon energy, for each one of the two mechanisms, the one dominant at the lowest energy (labelled A), and the other dominant at the higher energies (labelled B). The kinetic energy released for the two mechanisms is plotted in Fig. 7.

In a more rigorous and quantitative treatment, in place of simple Gaussian functions for such an analysis, one should use Gaussian functions convoluted with exponential decays to account for the lifetime of the dissociating oxygen atom autoionizing state and the interatomic distance distribution of the two ions during the Coulomb explosion. However, we do not have any detailed information about such lifetimes and therefore we cannot carry out a more rigorous analysis. Nevertheless, we made some rough attempts by using reasonable lifetime values and the results still confirm the occurrence of a double mechanism, one dominating at low photon energies and the second one emerging at higher energies.

IV. Discussion

The anisotropy parameter $\beta$ not only describes the asymmetry of the angular distribution of product ions for reaction (1), but also allows definition of the anisotropy in the dissociative double photoionization cross section. Specifically, with respect to the light polarization direction, the parallel cross section, $\sigma_\parallel$, is related to the perpendicular one, $\sigma_\perp$, by the equation

$$\frac{\sigma_\perp}{\sigma_\parallel} = \frac{2 - \beta}{1 + \beta}. \quad (3)$$

In the photon energy range investigated in this experiment, we have found that the ratio ranges from a minimum of 0.4 up to 0.9. This means that the parallel cross section is always larger than the perpendicular one, except at 36 eV photon energy, where the ratio is 2. In that case the ionization is isotropic and the product ions are distributed in all directions with a spherically symmetric probability. It has to be noted that such a low energy is below the vertical threshold for double photoionization of 37.34 eV, but above the thermodynamic level of ground state products $\text{CO}^+ + \text{O}^+$ that lies at 33.15 eV. Despite of the low cross section the isotropy of the distribution appears clear from the Fig. 4. One can explain the presence of reaction products at this low energy by assuming an indirect mechanism, as suggested by Slattery et al. and also supported by our recent results. Although the isotropy appears well evident, the low intensity does not allow to extract a meaningful energy distribution of product ions. At higher energies, the ionization cross section
increases and therefore the signal becomes more intense, making obtaining anisotropy parameters $\beta$ easier. Our values of $\beta$ appear to be in agreement with the early values obtained by Masuoka.17

In a recent study, we have found that the N$_2$O molecule behaves in a similar way when doubly ionized at about the same photoenergy range:25 at very low energy, the $\beta$ parameter is zero, that is the reaction occurs isotropically with respect to the light polarization direction, but when the photon energy increases the $\beta$ parameter increases up to 1.5. Therefore for N$_2$O the angular distribution of ion products for both N$^+$ + NO$^+$ and N$_2$^+ + O$^+$ channels is more anisotropic with respect to the CO$_2$ case and the parallel cross section is larger than the perpendicular one. An anisotropic distribution of products indicates the fulfilment of two requirements: the double photoionization occurs if the molecule is appropriately oriented, with respect to the polarization vector, when it absorbs the photon and ejects two electrons. Moreover, the dissociation must take a time shorter than the typical rotational period of the formed dication.25

The kinetic energy distributions of CO$^+$ and O$^+$ products provide further interesting information about the reaction (1). As already discussed in the previous section, the simple analysis of the total kinetic energy distributions in terms of Gaussian functions indicates, in the photon energy range between 39 and 49 eV, the presence of two mechanisms, one producing ions with a total kinetic energy between 3 and 4 eV and a second one with energy between 5 and 6 eV (see Fig. 6). These energy features are of interest for trying to understand the role of states involved in the dissociation process. Some low lying electronic energy levels of the CO$_2$$^{2+}$ dication have been reported by Slattery et al.4 on the basis of the threshold of the photoelectron coincidence spectrum. In Fig. 8 these states are shown with an energy scale that starts from the ground state of the neutral CO$_2$ molecule and are compared with the electronic energy levels for the dissociation products. Hochlaf et al.29 calculated the potential energy curves along the collinear CO$^+$–O$^+$ separation coordinate, keeping the C–O distance fixed at the equilibrium one in the ground state CO$_2$$^{2+}$ dication, that is 1.22 Å. The calculation has shown that all electronic states of the dissociation products are connected with those of the molecular dication through potential barriers. In particular, the ground state CO$_2$$^{2+}$(X$^3$Σ$^g$) dication is connected, along the collinear CO$^+$–O$^+$ separation coordinate, with the ground state ion products, CO$^+$(X$^2$Σ$^g$) and O$^+$(^4$S$0), through a barrier that is about 1.4 eV above the bottom of the potential well. For the electronic states immediately above, the potential barriers, correlating with the ion products, are even higher.29

Looking at the energy levels in Fig. 8, taking into account some information from the calculation by Hochlaf et al.29 and the results of the present analysis, some considerations can be drawn about the reaction (1). As we have already discussed, below the vertical threshold of 37.34 eV, the dissociation occurs through the formation of a CO$^+$ ion and an autoionizing state oxygen atom that ionizes later on:

$$\text{CO}_2 + h\nu \rightarrow \text{CO}^+ + \text{O}^* + e^- \rightarrow \text{CO}^+ + \text{O}^+ + 2e^-.$$  \hspace{1cm} (4)

In the case when the double photoionization happens at the energies around the vertical threshold and the dissociation leads to CO$^+$ and O$^+$ in their ground electronic and vibro-rotational states (33.15 eV$^+$), then one expects an energy release of the product ions of 4.2 eV. Values of the kinetic energy released lower than 4.2 eV should indicate the involvement of some excited internal modes of the final
diatom. This seems to be the case of the mechanism A mentioned in the previous section.

The second mechanism, labeled as B, which dominates in the higher energy range and leads to a kinetic energy release larger of about 2 eV, with respect to the other mechanism A (see Fig. 6 and 7), must be due to the population of an electronically or vibro-rotationally (or both) excited state of the CO$_2$ dication, and possibly leading to an excited electronic state of ion products. However, on the basis of the sequence of dication states determined by Slattery et al. and considering the calculations by Hochlaf et al. it is difficult to assign the involved electronic states unequivocally in this second mechanism, B.

Moreover, under the assumption of a simple Coulombic repulsion responsible for the kinetic energy release of product ions, the two characteristic energies for the two mechanisms correspond to two average distances where the two ions start separating. These distances are at around 4.5 Å for mechanism A and around 2.5 Å for mechanism B. At such distances one expects a transition from the internal rearrangement of the dication to the opening of the Coulomb explosion channel.

It is also interesting to compare the kinetic energy release obtained in the present paper with the one reported by Masuoka et al. in the 40–100 eV photon energy range. Looking at that paper it appears that the authors obtained the kinetic energy release in the CO$^+$ + O$^+$ dissociation by analysing the shape of the time-of-flight peaks of CO$^+$ and O$^+$ detected in coincidence. Therefore, that data should be comparable with our “instantaneous” dissociation channel. By using a curve fitting procedure Masuoka et al. have obtained an average kinetic energy release ranging from about 5 to 6 eV in the 40–50 eV photon energy, in reasonable agreement with our results. However, the higher resolution achievable in our ion-imaging measurements allowed us to also observe an additional mechanism at lower energy (mechanism A), not evident in the earlier work.

Finally, the recent electron impact experiment reported by King and Price also provided further values of the kinetic energy release due to the competition of several dissociation mechanisms. However, in that paper the authors obtained the released kinetic energy distribution from the analysis of the metastable trace in the coincidence maps. For an excitation energy of 50 eV they found an average value of 4.4 ± 0.4 eV. Such a value must be compared not with the present results, referring to an “instantaneous” channel, but with the value of 4 ± 1 eV that we have reported in our previous paper, obtained from a trajectory calculation analysis of the metastable trace in the coincidence maps.

V. Conclusions

The results here reported demonstrate some important aspects of the dissociative double photoionization of CO$_2$ in the 36–49 eV energy range. At low energy, the reaction occurs by an indirect mechanism, that is through the formation of CO$^+$ and an autoionizing oxygen atom state. In this energy range the reaction occurs with an isotropic distribution of products with respect to the polarization vector of the light. When the photon energy increases, the distribution of products becomes anisotropic, with the two ions preferentially emitted along the direction of the light polarization vector. This implies that the molecule photoionizes when oriented parallel to that direction, and also that the CO$_2$ dication just formed dissociates in a time shorter than its typical rotational period.

At low photon energy, the CO$^+$ and O$^+$ product ions are separating predominantly with a total kinetic energy between 3 and 4 eV. However, such a mechanism becomes gradually less important when the photon energy increases and at 49 eV a different mechanism, where the two product ions are separating with a kinetic energy between 5 and 6 eV, is dominating.

The present paper demonstrates the high potential of the experimental technique used: the coupling of ion–ion coincidence with ion imaging. The angular distribution of the ionic products with respect to the light polarization vector and their kinetic energy distribution reveals important new information about the dynamics of the dissociative reactions of type (1).

It has to be stressed that, recently, a large variety of experimental data became available for the double photoionization of CO$_2$ in the vacuum ultraviolet region. This data provided many and complementary details about the dynamics of the ionization process and the following dissociative channels. It would be desirable to obtain a unified description of the potential energy surfaces of this systems at a level of accuracy achievable with current computational techniques, together with accurate dynamic calculations.

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