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Internal energy effects in the reactivity of CO_2^{2+} doubly charged molecular ions with CO_2 and CO

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Dedicated to Professor Helmut Schwarz on the occasion of his 60th birthday in appreciation of his manifold contributions to mass spectrometry and ion chemistry.

Abstract

Reactivity of the dication CO_2^{2+} in dependence on its internal energy was studied in collision with CO_2 and CO. The dication was obtained by photoionization of the CO_2 molecule by synchrotron radiation and the guided beam apparatus CERISES was used in these studies. Spontaneous dissociation of CO_2^{2+} to CO^+ and O^+ was observed without any target gas in the reaction cell. With CO_2 or CO as a target gas, CO^+ and O^+ fragment ions were formed as products of dissociative charge transfer, while the contribution of collision-induced dissociation of the reactant CO_2^{2+} to their formation was found negligible. The CO^+ yield showed a considerable dependence on the internal energy of the reactant dication CO_2^{2+}: the branching ratio CO^+/O^+ increased gradually with photon energy between 38.7 and 39.4 eV. We interpret this observation as being due to the increase in the instantaneous distances at the extrema of vibrational motion of the dication with increasing internal energy. This modifies the Franck-Condon factors in the charge transfer process and leads to a preferential population of the vibrationally excited states of the product cation CO_2^+(C) known to lead exclusively to the dissociation products $CO^+ + O$. An indirect mechanism that requires the coupling of the first excited (a) state of the dication with the higher vibrational states of the CO_2^{2+} (X) state is proposed to explain the threshold behaviour observed in our results.

Keywords: Dication; Ion–molecule reactions; Photoionization; CO_2^{2+}; Vacuum ultraviolet

1. Introduction

The last two decades registered a growing interest for small molecular multiply charged ions. At first glance, the presence of two positive charges on a molecular assembly questions its stability [1]. In fact, in many cases, molecular dications have rather long lifetimes due to the characteristics of their potential energy surface [2–5] (e.g., 4 s for the X state of CO_2^{2+}). The existence of doubly charged molecular ions as metastable chemical species allows the manifestation of their particular and new chemical behaviour. In most

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cases their structure is different from the neutral precursor one, hence, the multiple ionisation can be considered as an intermediate step towards the synthesis of new stable chemical compounds.

The existence of stable multiply charged ions represented a puzzle for the scientific community and it required the criticism of well-established chemical concepts. In 1967, for example, it has been necessary to invoke the development of a "new bonding concept" [6] to completely justify the structure and the stability of the multiply charged carbocations.

Starting from these fundamental chemical physics aspects, the interest for multiply charged ions started to propagate. Their long lifetimes revealed them as fundamental components of the laboratory and astrophysical plasmas. More recently, their key role in the chemistry and the composition of the planetary ionospheres [7] has been suggested. In perspective their very high energy content makes them a possible source of energy that can be released on the molecular size scale.

The reactivity of the multiply charged ions has been the subject of many investigations. The common knowledge is that, as would be expected, a long-range charge transfer process dominates [8–10], even if minor bond-forming reactive channels have already been observed both in crossed beam and guided beam experiments [8,9,11–13]. Unfortunately, in all cases there was no selection of the internal energy of the reacting multiply charged ion, even if it is clear that the understanding of elementary reaction mechanisms would take advantage from a precise definition of the reacting ion state as it has been the case for monocation–molecule reactions [14]. Nonetheless, to our knowledge, the effect of internal energy on the reactivity of multiply charged ions has been investigated only in the case of fragmentation studies [15–18].

Hereafter, we report the outcomes of an internal energy dependent experiment in the case of the reactivity of CO_2^{2+} dications with CO_2 and CO neutral molecules, where ions are produced in states of increasing internal energy via photoionisation by synchrotron radiation. Though some minor bond-forming channels were detected and will be described in a forthcoming paper, this paper is focused on the major product ions resulting from the charge transfer between the CO_2^{2+} dication and the neutral molecule M.

The first observation of the CO_2 doubly charged ion was reported in 1964 [19]. Since that time, the system has received a great attention both from the experimental or the theoretical point of view. The potential of double ionisation has been measured via different experimental techniques [16,20,21] and is known to be around 37.4 eV. Millie et al. [20] carried out the first calculation of the dication potential energy surfaces. More recently, Hograve [22] and Hochlaf et al. [23] calculated the characteristics of the potential energy surfaces (PES). In particular, Hochlaf et al. [23] generated a detailed description of the PES for the first three electronic states of CO_2^{2+} ($X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$). This study showed that all states have a linear geometry and a barrier towards direct dissociation. However, compared to the neutral CO_2, the PES wells are significantly flatter in all directions and the equilibrium distances of the doubly charged ion are slightly longer than for the neutral molecule. For the fundamental state, they found an equilibrium C–O distance of 1.207 Å (instead of 1.154 Å in the neutral) and a barrier towards dissociation that reaches its maximum height of 1.3 eV at 1.99 Å. The threshold for the unimolecular dissociation process: CO_2^{2+} ($X^3\Sigma_g^-$) $\rightarrow O^+(^3S) + CO + (X^2\Sigma^+)$ has been determined experimentally to lie between 1.4 ± 0.5 eV [20] and 1.6 ± 0.3 eV [16] above the appearance energy of the dication. This is in agreement with the calculated barrier height for the dissociation of the ground state of the dication (1.3 eV). The first excited $a^1\Delta_g$ state is shown to have an equilibrium C–O distance of 1.214 Å and to lie at 1.35 eV above the dication X state, a value which is in agreement with the value of 1.3 ± 0.1 eV measured in a double electron coincidence experiment by Hall et al. [21].

The reactivity of the carbon dioxide dication has already been studied in the past [7–9,13]. As expected, the charge transfer process dominates [7,8], but the cross-section for bond forming channels have been observed in particular for the reaction of CO_2^{2+}

with D_2 and HD [8,9,13]. Up to now, no evidence of bond-forming channels has been found in the reactions of CO_2^{2+} with "heavy" neutral partners.

2. Experimental

The CERISES apparatus has been previously described in detail [24]. However, since these studies take advantage of an important upgrade, i.e., the insertion of a quadrupolar mass filter, we will describe this new feature more precisely. CERISES (acronym for "Collision Et Réaction d'Ions Sélectionnés par Electrons de Seuil") is divided into three differentially pumped sections, which correspond to a source, a reaction and an ion detection region.

In the source region, the parent ions involved in the reaction are produced by photoionisation of the neutral precursor (CO_2) with the monochromatized synchrotron radiation coming out from a conventional bending-magnet beamline. The vacuum ultra-violet (VUV) photon energies are scanned by tuning the SA31 beamline monochromator [25] from 30 to 45 eV, in order to populate non-dissociative states of the molecular dication, and study the evolution of their reactivity. The entrance and exit slits of the monochromator were, at all times, opened to their maximal value of 1 and 2 mm for the entrance and exit slits, respectively. This is providing with a high flux, at the expense of the resolution, that was still better than 100 meV in the 40 eV energy range. In order to remove the second and higher order radiation from the refracted beam, a 1000-Å thick aluminium filter was intersecting the VUV beam between the exit slit of the monochromator and the experiment. As aluminium strongly absorbs photons having energies above 72 eV, the filter provides with pure first order light between 36 and 72 eV.

CERISES has been recently upgraded to MS/MS capabilities by implementing a quadrupole/octopole/quadrupole arrangement. This configuration now allows investigating uni- as well as bi-molecular reactions occurring in the octopole for mass-selected ions. Stable dications are always produced in the source together with single ionisation products, as well as dissociative double ionisation products. Therefore, when studying the reactivity of dications, it is mandatory to be able to select ions according to their mass to charge ratio in order to isolate them from the mixture that emerges from the source. After their production by photoionisation, all ions are extracted from the source by a small field of 1V/cm, and injected through a stack of electrodes into the newly inserted quadrupolar mass filter. The mass filter is a 350 mm long Nermag-type filter, with rods of 12 mm diameter and is equipped with 30 mm long prefilter elements. The nominal mass range of this apparatus goes from 5 to 1000 Da. A mean dc potential between 2 and 3 V accelerates ions into the filter. At the exit of the device, a three-element einzel lens is refocusing the ions into a first radio frequency octopolar ion guide towards the reaction cell. As far as time scales are concerned, the parent dications produced in the source need about 40 μs to reach the end of the first quadrupole.

The reaction of the dication with the neutral molecule (here CO or CO_2) takes place within the end of the first octopolar ion guide in a 4 cm long scattering cell filled with the neutral target gas at a pressure between 1 and 2×10^{-4} Torr, that is kept constant during the course of the experiments. The pressure is chosen as to never induce more than 10% reactivity of the parent ion beam, in order to work in a single collision regime.

The kinetic energy of the parent ions when they react with the target molecule is defined by the dc potential on the first octopole relative to the potential at which the reactant ions are created in the source. It can be varied between 0.3 and 20 eV in the laboratory frame with a typical distribution width of 0.25 eV FWHM (these values have to be doubled when dealing with dications). Experiments described here have been done at a constant collision energy of the dication of 20 eV in the laboratory frame.

The product ions are captured by the radio frequency guiding field inside the first octopole and extracted by a small dc potential (0.7 V) into a second octopole ion guide. This part of the set-up was

developed to study the reactions of monocations with molecules, and the amplitude of the radio frequency guiding field was optimised for this purpose [24]. However, since the reactivity of dications leads to the production of two ions with identical charges, ions produced by dication reactions or fragmentations usually exhibit much larger kinetic energy release distributions. For instance, it has been shown that in the case of CO_2^{2+}, the natural fragmentation of the molecular ion can lead to the production of O^+ ions with as much as 3 eV kinetic energy [9,17]. This kinetic energy is beyond the collection efficiency of our guiding field, and it leads to a non-negligible loss of those ions, especially when they are emitted perpendicularly to the axis of the experiment. We estimated that 50% of the O^+ ions are lost in the present configuration. A more powerful radio-frequency source is under development to palliate this effect. At the exit of the second ion guide, product and parent ions are injected and mass selected into a second quadrupolar mass filter, and are finally detected by a multichannel plate detector.

Neutral gas samples used in the source or in the cell were all of analytical purity quality, and by recording their mass spectra, we checked the absence of any contaminant before measurements. In order to separate the products of reaction coming either from the parent dication or from the neutral target, we used a sample of isotopically labelled $^{13}CO_2$, from Eurisotop Company, that has purity better than 98%. The major contaminant in that sample is $^{12}CO_2$.

3. Results and discussion

3.1. Spontaneous dissociation of the CO_2^{2+} ion

In Fig. 1 we report the photon energy dependence of the ion yields for CO_2^{2+}, O^+ and CO^+ without gas in the reaction cell. The data sets are not corrected for the photon intensity, but are comparable to each other. In these conditions we are measuring the appearance energy for the CO_2 double photoionisation and the energy threshold for its spontaneous unimolecular fragmentation inside the ion guide:

$$CO_2^{2+}(X^3\Sigma_g^-) \rightarrow O^+(^4S) + CO + (^2\Sigma^+)$$

For the double ionisation process, we find a threshold of 37.4 ± 0.1 eV, in good agreement with values reported in the literature [16,20,21]. For the dissociation channel, we find its threshold at about 38.7 ± 0.15 eV, also in good agreement with the values reported in the literature for direct dissociation [16,20]. Hence, according to the height of the barrier calculated by Hochlaf et al. [23], the fundamental state of CO_2^{2+} should fragment into CO^+ and O^+ above 38.7 eV.

CO^+ and O^+ signals shown in Fig. 1 are due to metastable dissociation of the dication. However, one can observe that the intensities for the two channels are not equal. As already mentioned, this is due to a kinetic energy dependent discrimination, which reduces the O^+ detection, as it is the lighter ion that bears most of the kinetic energy release. The CO^+/O^+ ratio is shown as an inset in the lower part of Fig. 1, and it appears to be constant and equal to 2 soon after threshold. This is the signature of a kinetic energy release distribution, which stays constant in the whole investigated internal energy range.

3.2. Dication internal energy

As the photon energy is varied, one produces a population of photoions that exhibits a gradual change of its internal energy distribution. In these measurements, the internal energy of the dications was not determined by means of the threshold photoelectron–photoion coincidence (TPEPICO) technique, usually used with CERISES [24]. Hence, to get a full description of the dication internal energy, one would have to collect in coincidence the two threshold electrons and the dication as well as its reaction products [26]. This is unreachable with our collection efficiency. However, some internal energy selection of the reactant is naturally occurring due to the metastable lifetime of the dications. Hence, as explained in the introduction, molecular dications are metastable versus dissociation into $O^+ + CO^+$ and, in our set-up, only unfragmented ions can emerge from the first quadrupolar mass filter.

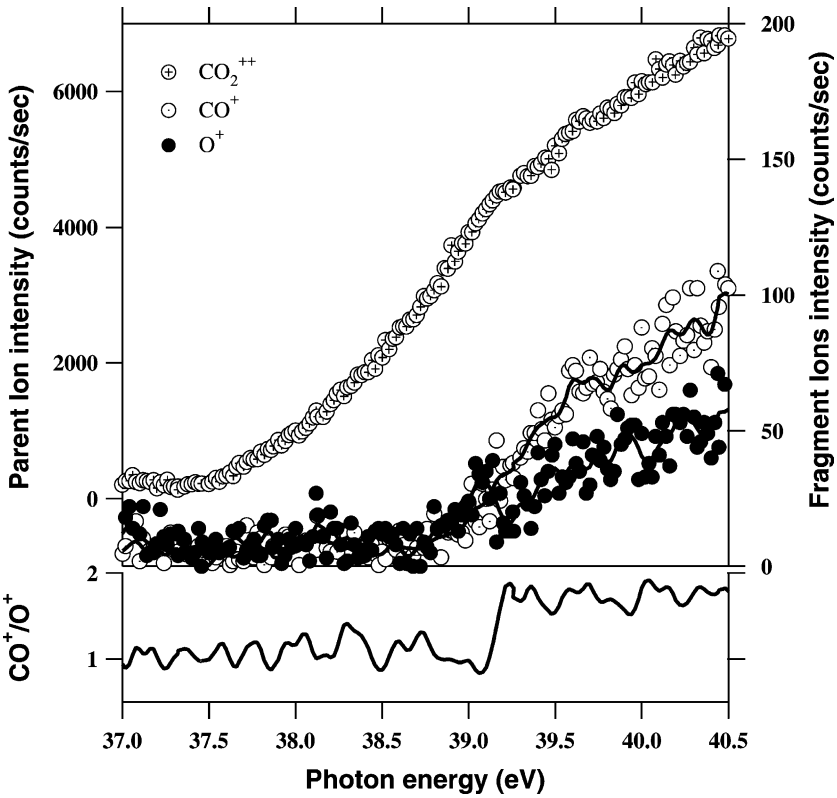

Fig. 1. Excitation spectrum of the CO_2^{2+} as a function of photon energy, without gas in the scattering cell. O^+ and CO^+ signals result from the spontaneous dissociation of the parent ion, occurring in the ion guides. The inset in the lower part of the figure represents intensity ratio CO^+/O^+ as a function of photon energy.

This implies that only species having natural lifetimes long enough to reach the end of the filter without fragmentation will be able to react. It puts a serious constraint on the internal energy that one can expect to find in the molecular dication. Mathur et al. [5] carried out an experimental measurement of the dication decay in a heavy ion storage ring. They observed a decay curve dominated by a 4s component. However, as a rule of thumb, one can consider that the more internal energy the dication contains, the shorter its lifetime will be. Experiments performed in the microsecond timescale gave different lifetime observations [2–4] and this is probably due to the different time windows of the experimental set-ups [4]. Recently, a study of the dissociation dynamics of CO_2^{2+} in coincidence with two threshold electrons [27,28] has shown that when looking at metastability in the microsecond time range, CO_2^{2+} is metastable between 38.8 and 40.4 eV. Authors of these works ascribe this metastability to spin forbidden conversion from excited singlet states to the ground triplet state and not to tunnelling through the barrier of the ground state. However, the relative intensity of parent ions, which survive in these internal energy and time ranges is negligible compared to the one due to direct dissociation. As a consequence, we consider that the reacting CO_2^{2+} beam mainly contains dications in their ground electronic state.

3.3. $CO_2^{2+} + CO_2$ and $CO_2^{2+} + CO$ reactions

Two typical mass spectra corresponding to the $^{13}CO_2^{2+} + {}^{12}CO$ and $^{12}CO_2^{2+} + {}^{13}CO_2$ reactions

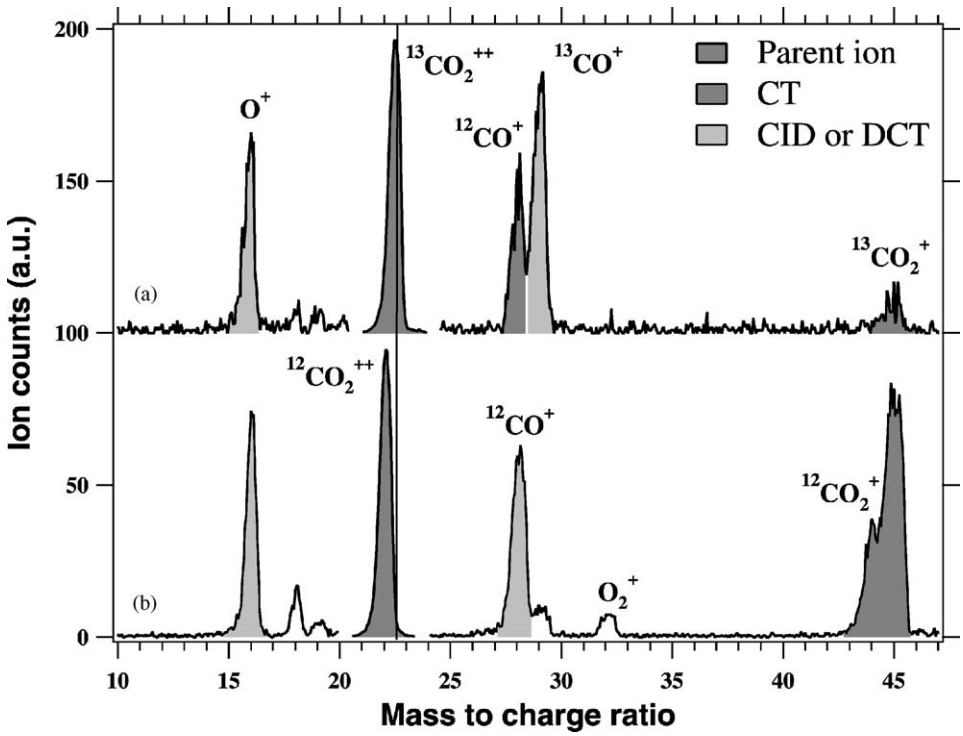

Fig. 2. Mass spectra corresponding to the reactions $^{13}CO_2^{2+} + {}^{12}CO$ (a) and $^{12}CO_2^{2+} + {}^{13}CO_2$ (b). Both mass spectra were recorded at the photon energy of 45 eV, and for a collision energy of 20 eV in the laboratory frame. The peak corresponding to parent ion was scaled down to the same size as product ions intensity.

are shown in Fig. 2a and b, respectively. Both mass spectra were recorded at 45 eV photon energy, where the dication production presents a maximum, providing with good signal to noise ratio for the reactive channels. Apart from the intense parent dication peak, four major peaks are visible in the mass spectra. Two peaks correspond to the non-dissociative charge transfer: $^{12}CO_2^+$ and $^{13}CO_2^+$ in (a), and $^{13}CO_2^+$ and $^{12}CO^+$ in (b). The other two peaks, $^{12}CO^+$ and O^+ in (a), and $^{13}CO^+$ and O^+ in (b), can result either from a collision-induced dissociation (CID) of the parent dication, or from a dissociative charge transfer (DCT).

To summarize, the major reaction channels are:

$$CO_2^{2+} + M \rightarrow O^+ + CO^+ + M \quad \text{(CID)}$$

$$CO_2^{2+} + M \rightarrow O^+ + CO + M^+ \quad \text{(DCT)}$$

$$CO_2^{2+} + M \rightarrow O + CO^+ + M^+ \quad \text{(DCT)}$$

$$CO_2^{2+} + M \rightarrow CO_2^+ + M^+ \quad \text{(CT)}$$

We will now show that it is possible to exclude the CID as a major source of the CO^+ and O^+ fragments. In Fig. 3, we report the photon energy dependence of the ion yields for CO_2^{2+}, O^+ and CO^+ when the CO neutral target is introduced in the reaction cell. The dication yield is unchanged compared to Fig. 1, but the two fragment ions are now appearing at the same energy as the double ionisation. This confirms our interpretations that fragment ions observed in Fig. 1 are due to spontaneous dissociation, and not to dissociation resulting from collision with residual gas. Moreover, when comparing the intensity of the two channels, it is clear that it is no more exhibiting the 2:1 CO^+/O^+ ratio that was observed for spontaneous

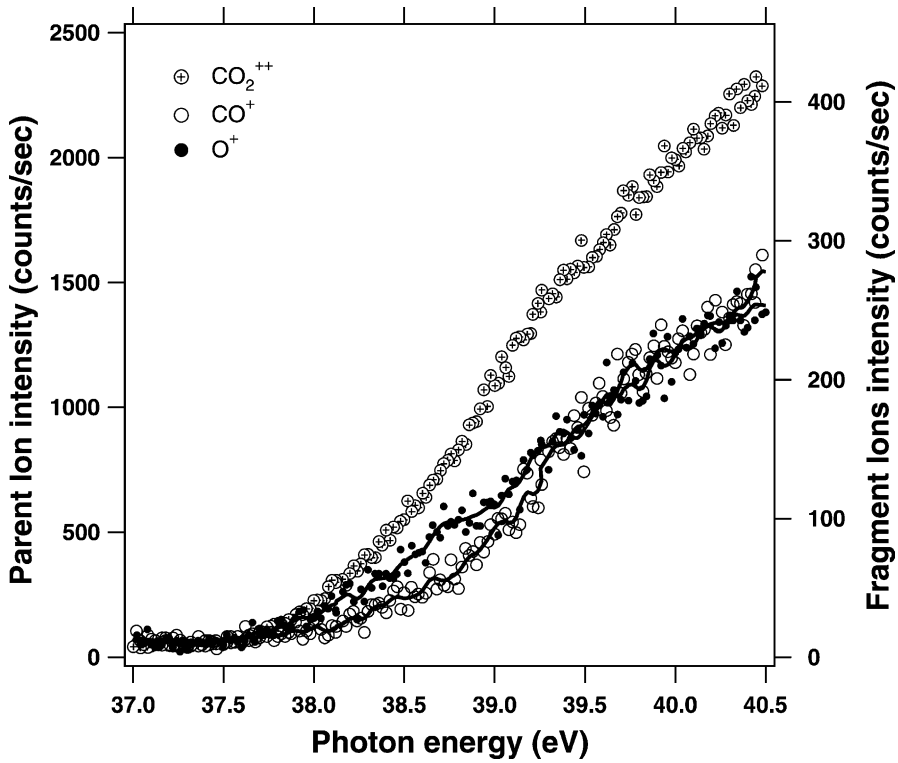

Fig. 3. Excitation spectrum of $^{13}CO_2^{2+}$, O^+ and $^{13}CO^+$ when a neutral gas (^{12}CO) is introduced into the scattering cell.

dissociation. The ratio is now closer to 1. This considerable change in the relative intensity is the key information to rule out the CID. Hence, if CID was to occur, the Coulomb repulsion would affect the transmission of both fragment ions in the way observed for the spontaneous dissociation of the dication. Therefore, a similar ratio, close to 2 should be observed. Instead, when DCT is involved, the Coulomb repulsion is now occurring between the CO_2^{+*} and the M^+ partner, and it is in a subsequent step that the O^+ or CO^+ fragments are released with much less difference in their kinetic energy distributions. We can therefore neglect the CID process in our description, as well as the strong discrimination in the detection of light fragments that was due to a large kinetic energy release. This result confirms the possible major role of DCT in CO^+ formation that was pointed out on the base of energetic considerations in the reaction of $CO_2^{2+} + D_2$ [9].

3.4. Internal energy effect on the CO_2^{2+} reactivity

In Fig. 4, we plotted the ratio between dissociative charge transfer products as a function of photon energy for each reaction; i.e., (a) $^{13}CO^+/O^+$ for the $^{13}CO_2^{2+} + {}^{12}CO$ reaction and (b) $^{12}CO^+/O^+$ for the $^{12}CO_2^{2+} + {}^{13}CO_2$ reaction. The data sets have been corrected for the contribution of the spontaneous dissociation of the parent ion. The large oscillations below 37.7 eV are artefacts due to the division procedure applied to poor signal to noise data sets. However, an increase is clearly seen from 38.7 up to 39.4 eV. This global trend is very similar for both neutral targets, and is also visible in Fig. 3.

As the collection efficiency of the ionic products does not depend on the photon energy, the change of the CO^+/O^+ ratio indicates that we are in presence of a photon energy effect in the relative CO^+ and O^+ production. Following the previous discussion, the

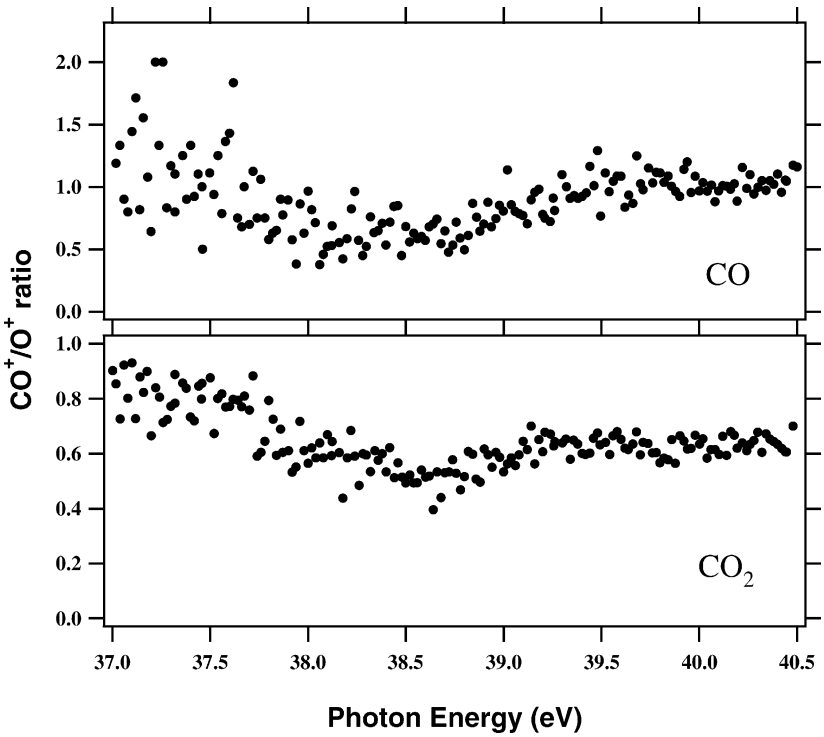

Fig. 4. Photon energy dependence of the ratio between the products resulting from dissociative charge transfer: (a) $^{13}CO^+/O^+$ for the reaction $^{13}CO_2{}^{2+} + {}^{12}CO$ and (b) $^{12}CO^+/O^+$ for the reaction $^{12}CO_2{}^{2+} + {}^{13}CO_2$.

explanation of this evolution has to be searched in the fragmentation mechanism of $CO_2{}^+$ ions produced by charge transfer. Moreover, the independence of the general trend on the neutral partner suggests that the key of the process is the internal energy content of the $CO_2{}^{2+}$ dication itself, that reflects into the fragmentation of $CO_2{}^+$ formed by charge transfer.

The dissociation of the $CO_2{}^+$ produced by the ionisation of neutral CO_2 has been extensively studied [29–34]. The monocation has four bound electronic states ($X\,^2\Pi_g$, $A\,^2\Pi_u$, $B\,^2\Sigma_u{}^+$, $C\,^2\Sigma_g{}^+$). The first three do not lead to direct dissociation since their respective continuum cannot be reached by a vertical transition from the CO_2 ground state (Franck-Condon gap). On the contrary, the C state, known to lie 19.39 eV above the neutral X state, can either dissociate into.

$$CO_2{}^+(C^2\Sigma_g{}^+) \rightarrow CO(^1\Sigma^+) + O^+(^4S), \quad 19.07\,eV \tag{1}$$

$$CO_2{}^+(C^2\Sigma_g{}^+) \rightarrow CO^+(^2\Sigma^+) + O(^3P), \quad 19.47\,eV \tag{2}$$

The branching ratio between the two channels is depending on the $CO_2{}^+$ internal energy content. Due to the energetics, the ground vibrational state dissociates only via process (1). But above this limit, i.e., as soon as some vibrational energy is conferred to $CO_2{}^+$ ($C\,^2\Sigma_g{}^+$), the dissociation follows almost exclusively the process (2). The dissociative path has been investigated theoretically by Praet et al. [29] and by Bombach et al. [30]. The mechanism proposed for reaction (1) requires an intersystem crossing that is rate limiting as it can only be achieved through the bending of $CO_2{}^+$, while the reaction (2) does not. This explains that when both channels are populated competitively, channel (2) becomes exclusively populated. Recently, Morin et al. [35] confirmed this interpretation as they showed that the preparation of $CO_2{}^+$ in a bent geometry through excitation of a transient core excited state enhanced

considerably the O^+ ion yield after population of the C state. From these considerations, one can conclude that, if the C state is populated with small internal energy, it will lead to O^+, but as soon as it is excited, it will lead to CO^+ formation. In our results, we effectively observe an increase of the relative intensity of the CO^+ channel when increasing the photon energy. This excludes an interpretation of our results based on the bending of the molecular structure of the dication.

The $CO_2{}^+$ C state has a geometry that is very similar to the neutral X state one (this reflects itself in the almost exclusive transition $CO_2{}^+$ C(0, 0, 0) ← CO_2 X(0, 0, 0) in the photoelectron spectrum of CO_2) and the fundamental state of the dication exhibits slightly elongated C–O distances (1.207 Å instead of 1.154 Å in the neutral). If the charge transfer from the ground vibrational state of the dication produces the C state of $CO_2{}^+$, one can consider that due to the Franck-Condon factors only the lowest state will be populated. This should therefore lead to a preferential dissociation into $O^+ + CO$ and would explain the low CO^+/O^+ ratio observed close to the double ionisation threshold. Instead, when considering the very large internuclear distances that can be reached close to the barrier of the dication X state (up to 1.99 Å), if charge transfer to the C state occurs in this geometry, it will most probably lead to the population of highly excited vibrational states, and to subsequent dissociation into $CO^+ + O$. This interpretation, based on the idea that was introduced by Herman [36] in the case of CO^{2+} charge transfer, would qualitatively explain our results.

However, this interpretation should lead to a gradual and smooth change of the CO^+/O^+ ratio from the double ionisation threshold energy, while we observe in Fig. 4, a clear threshold effect around 38.7 eV. Moreover, Hochlaf et al. [23] calculated the Franck-Condon factors for the direct formation of the dication by photoionisation, and showed that there is a Franck-Condon gap above 38 eV in the X state of the dication. The population of highly excited states of the dication has therefore to be searched for indirect processes. We mentioned before the work of Slattery et al. [27,28] who showed that there is a coupling between the electronically excited singlet states of the dication and the triplet ground state of the dication. By studying metastable fragmentations, they provide experimental evidence that this forbidden coupling is taking place in the microsecond timescale. As 38.7 eV corresponds to the experimental [21] as well as theoretical [23] threshold of the first electronic singlet excited state ($a^1\Delta_g$), we propose an indirect mechanism that involves, as a first step, the formation of the first electronic excited state ($a^1\Delta_g$) of the dication. The second step, occurring during the 40 μs necessary to reach the reaction cell, is the internal conversion by forbidden coupling to highly excited vibrational states of the $X^3\Sigma_g{}^-$ state of the dication. The subsequent charge transfer to the C state of the monocation should then induce the increased production of CO^+. Let us mention that the direct charge transfer from the first excited state of the dication is not expected to lead to a preferential production of CO^+, as the equilibrium distance of this state [23] (1.214 Å) is similar to the one of the dication ground state. It can therefore also be ruled out to interpret our results.

4. Conclusions

By analysing the fragment ion yield with and without reactant gas, it is shown that the O^+ and CO^+ fragment ions result essentially from dissociative charge transfer of the primary $CO_2{}^{2+}$ dication, while CID of the dication is negligible. Moreover, the CO^+ ion yield exhibits a peculiar dependency with the internal energy of the dication. Measurements show an increase of the CO^+/O^+ branching ratio for energies corresponding to the population of the first electronic excited state of the molecular dication. We propose to rationalize this result as being related to the evolution of the instantaneous distances at the extrema of vibrational motion of the dication when increasing its internal energy. The increase of internal energy would then lead to a preferential population of vibrationally excited levels of the $CO_2{}^+$ C state, which are known to exclusively lead to dissociation into $CO^+ + O$. An indirect mechanism that requires the coupling of the first excited (a) state of the dication with the higher vibrational states of the

CO_2^{2+} (X) state is proposed to explain the threshold behaviour observed in our results.

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