Dissociative photo-multiple-ionisation of CO and CO$_2$

B Bapat$^1$, Vandana Sharma$^1$, I A Prajapati$^1$, K P Subramanian$^1$, R K Singh$^2$ and G S Lodha$^3$

$^1$Physical Research Laboratory, Ahmedabad 380009, India
$^2$Institute for Plasma Research, Gandhinagar 382428, India
$^3$Raja Ramanna Centre for Advanced Technology, Indore 452013, India
E-mail: bapat@prl.res.in

Abstract. In a photoelectron–photoion coincidence experiment on CO and CO$_2$, we have observed the formation and fragmentation of singly to triply charged CO$_2$ and singly to quadruply charged CO at various energies. Doubly charged cations of both molecules are found to have unstable as well as stable states. Cations with higher charge are found to dissociate promptly. The energy dependence of the relative partial cross-sections in the energy range 125–310 eV are presented.

1. Introduction

Photoionisation of atoms and molecules provides us rich data on electronic processes in them. Likewise, photodissociation of molecules provides a means of probing the ro-vibrational and electronic excitation of molecules. With the availability of synchrotron radiation, the study of dissociative photoionisation of molecules under soft x-ray bombardment has become feasible.

Photoionisation is widely regarded as a versatile tool for studies aiming to unravel the electronic structure, primarily due to its energy and angular momentum selectivity and the weak nature of the perturbation. Electron correlation in the target can be effectively probed by this method, as is evidenced by studies on few-electron systems. Since the photon interacts with electrons through a one-body operator, the experimental observation of multiple excitation and ionisation suggests that many-body effects (i.e. electron correlation) plays a strong role in photoionisation and related processes. The work on He [1] or H$_2$ [2] are excellent examples in this context. Photoionisation of CO [3, 4] and CO$_2$ [5, 6] has been studied by several workers in the past and various issues such as thresholds, dissociation channels and kinetic energy release have been addressed. However, there is no clear understanding of the mechanisms of formation of multiply charged molecular ions which are precursors to dissociation. In this contribution we present the results of multiple ionisation and subsequent dissociation of CO and CO$_2$ using radiation in the energy range 125–310 eV from the Indus-1 synchrotron.

2. Experimental Details

The Indus-1 synchrotron is a 450 MeV second generation storage ring, with radiation flux peaking at 202 eV (6.1 nm). The experimental station consists of a time-of-flight mass spectrometer of Wiley-McLaren type, with two linear extraction stages. Photoelectrons and photoions generated in an interaction volume of 2 mm$^3$ formed by the overlap of an effusive gas beam with the photon beam. The interaction volume is maintained close to ground potential. The extraction field,
the photon beam and the molecular beam were mutually orthogonal, with the extraction field parallel to the photon polarisation axis. Photoions and photoelectrons were extracted in opposite directions by an electric field of strength 300 V cm\(^{-1}\) over a 10 mm length, followed by a second extraction stage of strength 580 V cm\(^{-1}\) over a length of 6 mm. Following the acceleration, the ions drift through a field-free region of length 63 mm and are detected by a 40 mm diameter channelplate. The channelplate was biased at \(-4\) kV to increase the detection efficiency of the ions. Flight time of ions was measured by an electron–ion coincidence. The electron detector was a channeltron of diameter 12 mm with a 3 mm aperture, placed 16 mm from the ion source. Signals from the detector were amplified, subjected to constant fraction discrimination, and fed to the inputs of a time-to-digital convertor (TDC; Lecroy MTD133). The TDC is capable of recording up to four signals in the stop channel for every start signal. Thus, a four-fold ion coincidence could be observed using this data acquisition system. The timings of the hits w.r.t. the start pulse were written to a computer disk as a single event. The event list could be sorted and analysed after the experimental run.

3. Results
TOF spectra were recorded at a few energies in the range 125-310 eV. Not all energies were covered for both targets. No attempt was made to observe resonances in the dissociative ionisation cross-sections as a function of energy due to the limited photon energy resolution.

Figure 1 shows the TOF spectra of dissociative ionisation products of CO and CO\(_2\) at 250 eV. In both cases the doubly charged molecular ion was seen, but higher charge states of the molecular ion were not. This indicates instability of the highly charged CO\(_2\) and CO. To determine the highest charge states generated in this experiment, we look into the coincidence maps of the fragments. These are shown in Figure 2. The spectra show that the highest states are 4+ in case of CO and 3+ in the case of CO\(_2\). The break-up channels for the two molecules are shown in Table 1.

The observation of CO\(_3^+\), and its subsequent three-body dissociation has been reported

![Figure 1](image_url). Time-of-flight spectra of ions arising from dissociative photoionisation of CO [left] and CO\(_2\) [right], respectively. Both spectra were obtained at 250 eV photon energy.
**Figure 2.** Ion pair coincidence spectra arising from dissociative photoionisation of CO [left] and CO$_2$ [right], respectively. Both spectra were obtained at 250 eV photon energy. Note that the highest charge state of the dissociation precursor is CO$^{4+}$ and CO$_2$$^{3+}$ respectively.

**Table 1.** Dissociation channels for CO and CO$_2$ under photon impact. Precursors deduced from the observed ion–ion coincidences are also shown. Partial cross-sections relative to the undissociated parent are shown here for 250 eV photon energy.

| molecule | precursor | channel | cross-sec. ratio |
|----------|-----------|---------|-----------------|
| CO       | CO$^+$    | undissociated | 1.00          |
| CO$^+$   | C + O$^+$ |         | 1.61           |
| CO$^+$   | C$^+$ + O |         | 0.164          |
| CO$_2$$^+$| C$^+$ + O$^+$ |         | 0.394          |
| CO$_2$$^+$| C$^+$ + O$^+$ |         | 0.637          |
| CO$_2$$^+$| C$^+$ + O$_2$$^+$ |         | 0.023          |
| CO$_3$$^+$| C$^+$ + O$^+$ |         | 0.09           |
| CO$_3$$^+$| C$^+$ + O$_2$$^+$ |         | 0.007          |
| CO$_4$$^+$| C$^+$ + O$_2$$^+$ |         | 0.52           |
| CO$_2$   | CO$^+$    | undissociated | 1.00          |
| CO$_2$$^+$| O + CO$^+$ |         | 1.01           |
| CO$_2$$^+$| O$^+$ + neutrals |         | 4.30           |
| CO$_2$$^+$| C$^+$ + neutrals |         | 2.44           |
| CO$_2$$^+$| CO$^+$ + O$^+$ |         | 0.75           |
| CO$_2$$^+$| C + O$^+$ + O$^+$ |         | 0.31           |
| CO$_2$$^+$| C$^+$ + O$^+$ + O$^+$ |         | 0.02           |
| CO$_2$$^+$| C$^+$ + O$_2$$^+$ + O$^+$ |         | 0.03           |
| CO$_2$$^+$| C + O$^2$$^+$ + O$^+$ |         | 0.02           |
| CO$_2$$^+$| C$^+$ + O$^+$ + O$^+$ |         | 0.08           |
Figure 3. Probability of formation of various ion fragments by dissociative ionisation of CO and CO$_2$, relative to the formation of a parent molecular ion (CO$^+$ and CO$_2^+$ respectively), as a function of photon energy. Note the similarity in the energy dependence for all fragments of both species. The error in determination of the ratios is approximately 10% for dissociation of singly charged precursors, and goes up to about 20% for the highest precursor charg states.

elsewhere [8]. Here we focus on the energy dependence of the formation of various fragments as a function of photon energy. To this end, the areas of the ion peaks in the simple TOF spectra and the areas of the islands in the ion pair coincidence TOF spectra were obtained, and normalised to the area of the parent ion peak. This eliminates the dependence of the yield of various ions on the target gas density and photon flux. The normalised yields (or relative partial cross-sections) are shown in Figure 3.

The kinetic energy released during dissociation can be calculated for two-body break-ups by a simple expression based on the width of the $(t_1,t_2)$ coincidence distribution. An alternate representation of the coincidence distribution is to plot coincidence counts as a function of the difference between the flight times of the coincident ions, $t_1 - t_2$. Lablanquie [9] have shown how the width of the difference distribution, $w$ is related to the KER, when a dication fragments into two singly charged fragments. We extend the method to the case of unequal charge sharing. If a molecule $M$ breaks-up into fragments of mass $m_1, m_2$ and charge $q_1, q_2$, the time of flight of the two ions are given by

$$t_i = t_i^0 - \frac{p_i}{q_i E} \ (i = 1, 2),$$

where $t_i^0$ are the flight times of zero KE ions, $p_i$ are the momenta of arbitrary ions, and $E$ is the electric field in the ion creation region. Noting that that for two-body dissociation $\vec{p}_1 = -\vec{p}_2 \ (\equiv \vec{p})$, we get
Table 2. Kinetic energy released in two-body dissociation channels observed in the present work, as a function of photon energy. Values are in eV.

| Parent Channel | 125 eV | 150 eV | 200 eV | 250 eV | 295 eV |
|----------------|--------|--------|--------|--------|--------|
| CO$_2$ CO$^+$+O$^+$ | 30.6   | –      | 25.4   | 27.1   | 27.1   |
| CO C$^+$+O$^+$ | –      | 22.6   | 22.6   | 28.6   | 24.5   |
| C$_2^+$+O$^+$ | –      | 43.6   | 30.7   | 43.6   | 30.7   |
| C$^+$+O$_2^+$ | –      | 43.6   | 54.7   | 47.2   | 36.9   |
| C$_2^+$+O$_2^+$ | –      | –      | 40.9   | 45.4   | –      |

\[ t_1 - t_2 = [t_1^0 - t_2^0] - \frac{p}{E} \left( \frac{1}{q_1} + \frac{1}{q_2} \right), \]  

(2)

The width \( w \) of the \( t_1 - t_2 \) distribution is twice the maximum difference in the flight times:

\[ w = \frac{2p}{QE}. \]  

(3)

where \( Q = q_1q_2/(q_1 + q_2) \) is the reduced charge and \( M \) is the reduced mass of the ion pair. If \( U \) is the kinetic energy released, we obtain

\[ w = \frac{2(2MU)^{1/2}}{QE}. \]  

(4)

This expression was used to derive the KER in all two-body break-ups from the observed widths of the coincidence maps. The values obtained are shown in Table 2. In the present experiment the time-difference resolution is 10 ns.

4. Conclusions

We find three features in the cross-sections that are similar for both targets. The first of these is the broad rise in the fragment cross-sections as one approaches the C-K-shell energy (284 eV), and a rapid drop in the cross-sections thereafter. The second feature is that the highest charge states are only seen at energies just below the C-K-shell energy, for both molecules. The third feature is that the KER in two-body dissociation does not show a clear trend with photon energy. Considering the moderate accuracy of the measurement, it could be considered largely independent of the photon energy for all dissociation channels. The most surprising feature is the observation of very high charge states. At the photon energies for which the highest charge states of molecular ions are observed, the \( K \) shells of the atoms constituting the molecules are not excited. None of the atoms have occupied \( M \) shells, thereby precluding Auger processes. Therefore, only autoionisation and shake-off can be considered responsible for the observed multiple ionisation. Spectroscopy of the ejected electrons might shed more light on the mechanisms.
Acknowledgement
We are grateful to R V Nandedkar, A K Sinha and Indus-1 support staff for generous assistance during the beamtime.

References
[1] Briggs J S and Schmidt V 2000 J. Phys. B: At. Mol. Opt. Phys. 33 R1-R48
[2] Dujardin G, Besnard M J, Hellner L, and Malinovitch Y 1987 Phys. Rev. A 35 5012
[3] Masuoka Toshio and Nakamura Eiken 1993 Phys. Rev. A 48 4379
[4] Hosaka K, Adachi J, Golovin A V, Takahashi M, Teramoto T, Watanabe N, Jahnke T, Weber Th, Schffler M, Schmidt L, Osipov T, Jagutzki O, Landers A L, Prior M H, Schmidt-Böcking H, Dörner R, Yagishita A, Semenov S K, Cherepkov N A 2006 Phys. Rev. A 73, 022716
[5] Berg L E, Karawajczyk A and Stromholm C 1994 J. Phys. B 27 2971
[6] Masuoka T, Nakamura E, and Hiraya A 1996 J. Chem. Phys. 104 6200
[7] Masuoka Toshio 1994 Phys. Rev. A 50 2298
[8] Singh R K, Lodha G S, Sharma Vandana, Prajapati I A, Subramanian K P and Bapat B 2006 Phys. Rev. A 74 022708
[9] Lablanquie P, Nenner I, Millie P, Morin P, J. H. D. Eland J H D, Hubin-Franskin M J and Delwiche J 1995 J. Chem. Phys. 82 2951