Eur. Phys. J. D **2**, 53–56 (1998)

THE EUROPEAN PHYSICAL JOURNAL D

Fragmentation of CO^+ molecular ion through dissociative excited states produced by swift multicharged heavy ion impact on CO molecules[⋆]

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Received: 16 October 1997 / Received in final form: 6 February 1998 / Accepted: 23 February 1998

Abstract. CO^+ molecular ion excitation induced by 6.7 MeV/amu Xe^{44+} ion impact was studied using recoil ion momentum spectroscopy. The Kinetic Energy Release (KER) distribution clearly shows the population of CO^{+*} highly excited states. Excellent agreement is observed when comparing this distribution to previous low lying states calculation. Surprisingly high KER components were present in our spectra with values as high as 29 eV. The simple Coulomb model is obviously unable to explain the measured fragmentation energies for the process $CO^{+*} \rightarrow C^+ + O$, involving a neutral fragment.

PACS. 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states (including lifetimes, state mixing, etc.) – 39.90.+d Other instrumentation and techniques for atomic and molecular physics – 33.15.Fm Bond strengths, dissociation energies

After many years devoted to the study of fast multiply charged ion-atom collisions, it is worth noting the growing interest toward molecular targets [1-6]. The understanding of the interaction processes, which differ from the ion-atom simple case, on one hand, and the relaxation of the transferred energy to the molecule, on the other hand, are the aspects which have attracted the attention of the scarce experiments performed up to now. This understanding is of major importance for other fields such as radiation damage in polymers and biological material. Furthermore the multiple ionisation efficiency of multiply charged ions gives access to the study of the stability and the spectroscopy of transient highly charged molecular ions. Indeed, it has been shown that ion impact, compared to photo-ionisation, populates higher excited states of the target [2, 7].

Since highly charged and excited molecular ions mainly dissociate, the total kinetic energy of the fragments or Kinetic Energy Release (KER) measurements are mostly performed. In the case of ion (or photon)-atom collisions, the success of the Recoil Ion Momentum Spectroscopy (RIMS) has led to refined information on multiple ionisation [8, 9], photo ionisation [10, 11] or electron capture [12, 13] processes. Our goal is to improve the KER measurement resolution applying this technique in the field of ion-molecule collisions. Only two experiments using this technique have been previously reported [5, 14].

We present results concerning the collision between Xe^{44+} (6.7 MeV/amu) ions and CO molecules. For this swift projectile the main process to occur is ionisation. Furthermore, due to the high projectile charge, the multiple ionisation is far to be negligible. The experiment was performed at the GANIL facility. The apparatus was designed for ion-atom collisions and has been described in details elsewhere [8]. Briefly, the CO target is provided by a supersonic gas jet which avoids the thermal energy spread limiting the momentum resolution. The collision region is surrounded by an uniform electric field which extracts the recoil ions and projects them on a microchannel plate detector .The spectrometer fulfils the time focusing condition [15] (Fig. 1).

The multiple ionisation KER distributions were determined experimentally from the two fragments time of flight measured in coincidence, using the same procedure as described in [2]: an iterative matrix transformation converts the time difference between the two fragments into total KER distributions through an ion trajectory simulation inside the spectrometer. This simulation gives also access to the spectrometer collection and detection efficiencies. These measurements together with the CO^{q+} charge state distributions (up to CO^{9+}) and all the fragmentation channels will be presented in a forthcoming paper [16] in which the data analysis method will be described in more details. The ratio between multiple and single ionisation experimentally obtained is 0.35. Only 27% of the single ionisation leads to fragmentation ($CO^{+*} \rightarrow C^+ + O$: 14.5%; $CO^{+*} \rightarrow C + O^+$: 12.5%).

[⋆] Experiment performed at GANIL facility, Caen, France

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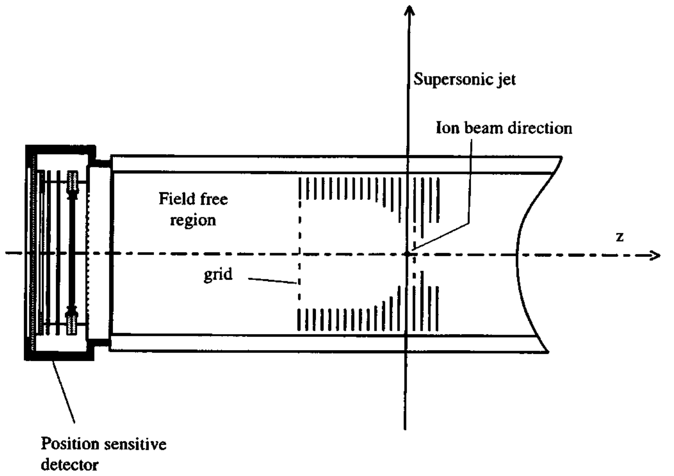

Fig. 1. Experimental set-up.

In a first step, we concentrate on the dissociative single ionisation of CO *via* CO^{+*} highly excited states. These states have already been studied by different techniques [17, 18]. Their energy were deduced indirectly from the shape of time of flight peaks, using Photo-Electron Photo-Ion Coincidences (PEPICO) [18]. We propose a direct measurement of the KER distributions through the full momentum vector determination of the fragments.

This is achieved using a position sensitive detector (PSD). The time of flight and the ion impact position on the detector are recorded after conventional fast pulse handling techniques and simple algebra give the three components of the recoil ion momentum vector. Due to the limited area of the PSD (Ø = 40 mm) and to the high kinetic energy of the fragments (compared to the recoil ion energies currently observed in ion-atom collisions [8]), the collection efficiency has to be evaluated carefully. We have carried out a Monte-Carlo simulation of fragment ion trajectories in our apparatus, assuming an isotropic dissociation, in order to estimate this collection efficiency. Figure 2 shows the C^+ fragment momentum distributions measured at different extraction electric field values together with our simulated efficiency which depends on the kinetic energy of the fragment. As the extracting field is increased, the collection efficiency cut off is shifted toward higher KER values. We checked that these distributions corrected for the efficiency lead to identical curves for each of the extracting field values.

The sum of these three measurements is given in Figure 3 and represents the total momentum distribution of the C^+ fragment. Up to now, no condition has been imposed on the second fragment charge state. Since our interest is for the dissociative single ionisation, we have to subtract the contribution of multiple ionisation channels which lead to a C^+ fragment:

$$\text{Single ionisation } CO^{+*} \rightarrow C^+ + O$$
$$\text{Multiple ionisation } CO^{q+} \rightarrow C^+ + O^{(q-1)+}.$$

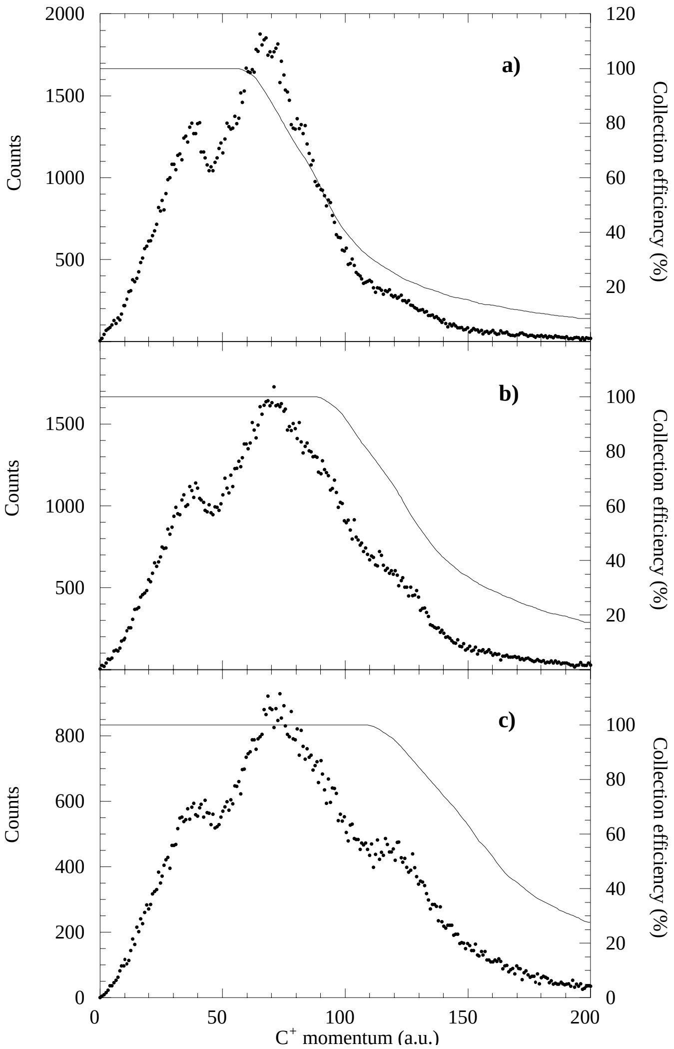

Fig. 2. Uncorrected C^+ momentum distributions measured with different extracting electric field values (a: 135 V/cm; b: 270 V/cm; c: 405 V/cm). The full line represents the simulated collection efficiency as a function of the C^+ momentum.

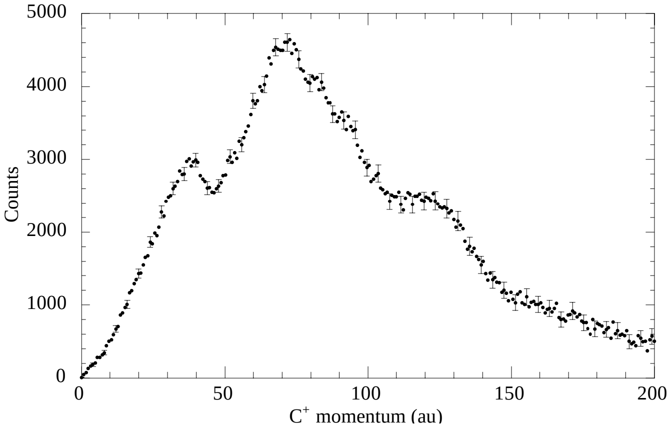

Fig. 3. Total C^+ momentum distribution corrected for the collection efficiency.

Table 1. KER and momentum values from the potential energy curves of various excited states of CO^+ molecular ion calculated by Krishnamurthi *et al.* [19].

CO^+ state	Energy ^{a} (eV)	Total KER (eV)	C^+ KER (eV)	C^+ momentum (a.u.)
$^4\Delta$	22.11	0.4	0.23	19.1
$2\ ^2\Pi$	23.27	1.58	0.9	37.9
$E\ ^2\Sigma$	25.3 ^{b}	3.61	2.06	57.3
$^4\Pi$	26.48	4.79	2.74	66.1
$3\ ^2\Pi$	28.07	6.38	3.65	76.3

^{a} Excitation energies with respect to the total energy of the zeroth vibrationnal level of neutral CO ground state ($X\ ^1\Sigma^+$) (−113.0937 hartrees).
^{b} Taken from [18].

Table 2. Proportions, C^+ KER and momentum of the different CO^+ excited states populated during the collision. The names of the closest calculated states are given to the five lower excited states observed. The four higher excited states are named α, β, γ and δ.

CO^+ state	Proportion (%)	C^+ KER (eV)	C^+ momentum (a.u.)
$^4\Delta$	9.2	0.27	20.7
$2\ ^2\Pi$	21.1	0.86	37.0
$E\ ^2\Sigma$	14.7	1.95	55.8
$^4\Pi$	13.2	2.8	66.8
$3\ ^2\Pi$	15.6	3.6	75.9
α	11.9	5.4	92.7
β	6.1	8.8	118.6
γ	4.3	11.4	134.8
δ	2.8	16.5	161.9

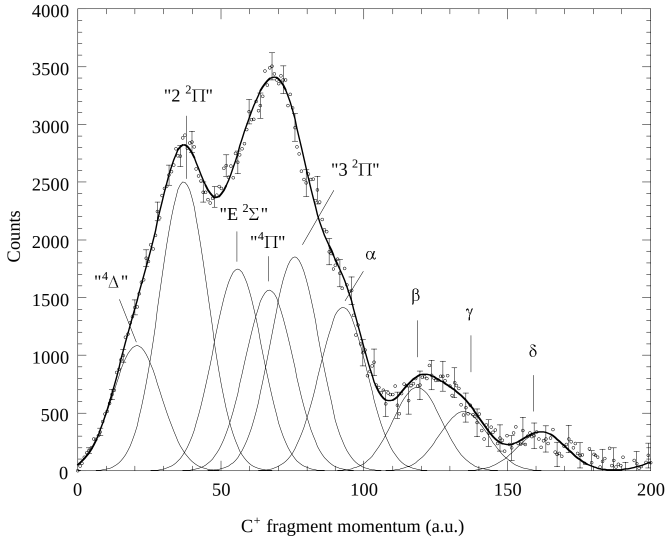

Fig. 4. C^+ momentum distribution corresponding to the ($CO^{+*} \rightarrow C^+ + O$) fragmentation channel.

The resulting C^+ momentum distribution coming from the channel ($CO^{+*} \rightarrow C^+ + O$) is presented in Figure 4. The main structures already clearly appear on this momentum spectrum but a de-convolution is still to be performed to get the contribution of all the populated states. Our momentum resolution is due to the finite width of the CO gas jet which is between 1 and 2 mm. The position resolution is then fixed and thus the resolution for two momentum components. For a 405 V/cm extracting field, the momentum resolution is around 8 a.u. for C^+ fragments (corresponding to a C^+ KER resolution of 0.2 eV at a KER value of 0.23 eV and of 0.8 eV at 3.65 eV). Therefore, as the instrumental broadening function, we used gaussian curves with a fixed width equal to the apparatus resolution [12]. In the fitting procedure, we used the line positions calculated using all electron, ab initio, molecular- orbital method [19] as starting values (Tab. 1). These lines were sufficient to reproduce the low KER part of the spectrum. But in order to match the whole spectrum, four additionnal states had to be introduced whose position was given by the fit (named α, β, γ and δ).

A remarkable agreement (Tab. 2) is observed between the five lower KER components and those expected from the calculation of [19]. Nevertheless, it is clear that higher excited states should be invoked to understand the C^+ momentum spectrum (Fig. 4). The α (5.4 eV), β (8.8 eV) and γ (11.4 eV) lines are very close to the higher components found experimentally in [18] (6 eV, 8.5 eV and 10.5 eV respectively). The δ (16.5 eV) component is observed for the first time. This excited state, which was never calculated, still need to be identified.

Previous results concerning multiple ionisation of CO [2, 7, 20], disagree when comparing their measured average KER values with the point charge Coulomb model. This model is obviously too simple to treat the molecular ion fragmentation since many excited states are populated during the ionisation process and branches into a complex set of dissociation channels. This statement is corroborated by the results we present concerning the ($CO^+ \rightarrow C^+ + O$) channel for which the Coulomb model cannot be invoked. Nevertheless, we measure excited states associated to total KER values as high as 29 eV.

The proportion and the corresponding momentum of each state are given in Table 2. Even if the Π states seem to be preferentially populated (at least 50% of the total), it is difficult to state on a strong "selection rule" for the excitation-ionisation process in multiply charged ion-molecule collisions.

As a conclusion, the agreement between the experimentally measured KER distribution and the components deduced from the theoretical calculation of [19] is excellent. Highly excited states are populated and need to be identified. Further calculations should be performed. But this observation seems to confirm the efficiency of fast multiply charged ions to populate high excited states of the molecular ions produced during the collision. We show that the recoil ion momentum spectroscopy can be applied to molecular fragmentation to provide a direct momentum measurement and an enhanced energy resolution. This resolution can be further improved by inserting an electrostatic lens within the extraction region. We reached a factor 4 enhancement of the resolution in an ion-atom collision experiment recently performed [21]. One should keep in mind that this technique measures the fragment momentum vector meaning that angular and KER distributions are accessible at the same time and, since it is a coincident measurement, for each fragmentation channel (even those involving a neutral fragment), leading to a new insight of the molecular fragmentation dynamics.

We thank Daniel Lelièvre for his skillful technical support before and during the experiment. The authors are indebted to François Frémont for his critical reading of the manuscript.

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