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# Absolute total cross section measurements of the collision-induced dissociation of $CO^+$

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## Abstract

Absolute total cross sections for the dissociation of the $CO^+$ beam to $C^+$ and $O^+$ [$CO^+ + H_2$ (or $N_2$, $SF_6$) → $C^+$ (or C) + O (or $O^+$)] in the energy range from 1.0 to 9.0 keV were measured. We found values of the order from $10^{-19}$ to $10^{-17}$ cm$^2$ for the dissociation to channel $C^+ + O$ with all targets used herein. While for the dissociation through channel $C + O^+$ the absolute total cross section show overall decreases of at least one order of magnitude. The measurements reported here are not found in the literature and the increasing availability of the data on these systems may stimulate work in this direction.

*Keywords:* $CO^+$; Absolute total cross section; Collision-induced dissociation

## 1. Introduction

In any collisional interaction between ions and neutral molecules, the perturbation of the projectile ion with the neutral target molecule leads to the collisional excitation of the former. If the vertical excitation energy is much larger than the dissociation energy of projectile ions, then projectile ion could result in its fragmentation. Collision-induced dissociation (CID) can be used to study different fundamentals aspects. CID has been a widely used ion-molecule collision technique for structure determination and fragment pathway analysis, has also been useful in identifying the electronic states of the dissociation products, as well as to measure cross section of dissociation process [1–8].

Collision of fast molecular ions with target atoms or molecules is a subject of fundamental interest as well as of importance for fields such as astronomy, chemical reactions, and most importantly plasma injection heating. In collisions of molecular ions with target atoms, several competing reactions are involved such as dissociation, ionization, and electron capture. The importance of each of these reactions is dependent upon the initial state of the molecular ions as well as on the collisional energy.

Carbon monoxide is the second most abundant molecule in the universe after molecular hydrogen, and is present in wide variety of astrophysical environments. Therefore, it is important the investigations about $CO^+$ ion for the knowledge of physical and chemical processes taking place in the atmospheres of planets. However, singly charged carbon monoxide has been less observed in those environments [2]. Studies about collision-induced dissociation of $CO^+$ ion are scarce; however, the studies about photoionization as well as dissociative recombination and excitation of $CO^+$ ion are very abundant [9–15].

Studies about ion-molecule and ion-atom with $CO^+$ are scarce, however several experiments related with the interaction between $CO^+$ ion with atoms and simples molecules have been reported [16–23]. These investigations have allowed obtaining fundamental information about its electronic structure. The first work about the collision of $CO^+$ with molecules appeared in 1957 [16]. In this work, Melton and Wells studied the induced-collision dissociation of $CO^+$ with $H_2$, $D_2$, $N_2$ and CO. They measured the relative cross section for dissociation of $CO^+$ with respect to dissociation with He from 1 to 5 keV projectile energy.

Dowek et al. [6] studied the $He^+$–CO and He–CO collision to know different electronic states of CO and $CO^+$. Their results

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show a Rydberg series from 11 to 14 eV in the CO. They also could identify the excited states $A^2\Pi$, $B^2\Sigma^+$, $C^2\Sigma^+$, $D^2\Pi$ y $F^2\Sigma^+$ of $CO^+$. Krishnamurthi et al. [23] used the $CO^+$–$H_2$ collision to study the excitation to states $B^2\Sigma^+$, $C^2\Sigma^+$ and $D^2\Pi$, with energies of projectile of 1.8 keV. Dentamaro and Katayama [24] studied the transition between $A^2\Pi(v=0)$ and $B^2\Sigma^+(v=0)$ states of $CO^+$ using CID. Moran et al. [24] measured the threshold of dissociation of CO to $C^+$ and O using CID form 0.65 to 3.2 keV, their results show a threshold of dissociation at $19.5 \pm 1.0$ eV. Lu et al. [5] studied $CO^+ + CO$ reaction and found the appearance potential of $C^+$ at $2.5 \pm 0.1$ eV. The fragmentation of $CO^+$ has been also studied using multicharged heavy impact ion [25–27].

In this work, we have measured the absolute total cross section of the dissociation of $CO^+$ to $C^+ + O$ and $C + O^+$ in collision with $H_2$, $N_2$ and $SF_6$, in the range from 1 to 9 keV and 5 to 9 keV, respectively.

## 2. Experimental

The present apparatus is practically the same used previously [28–30]. A schematic diagram of the experimental apparatus is shown in Fig. 1. The $CO^+$ beam was electrostatically accelerated, momentum analyzed by means of a magnetic mass spectrometer, and passed through a series of collimators before entering the gas cell. The dissociation cross sections were measured by passing the $CO^+$ beam through the gas cell. The beam interacted with the gas in the cell and is dissociated to $C^+$ and O or C and $O^+$. The dissociation products entered the detection chamber and were mass/charge separated by an electric field produced by the appropriate voltage applied to a pair of plates. This field diverted the charged fragments 12° from the path of the undeflected beam direction. On one side, a parallel-plate electrostatic analyzer was located 20 cm away from the edge of the plates and oriented at 45° between the charged fragment direction and the field. A channel electron multiplier (CEM) was positioned at the exit of the analyzer. A rectangular slit of 0.3 mm width and 10 mm long was placed in front of the CEM, and a collimator of 2.8 mm diameter at the entrance of the energy analyzer provided the energy analysis of the charged fragments by sweeping the applied voltage between the plates of the analyzer. These conditions result in an energy resolution ($\Delta E/E$) of 0.04. In this work, the parallel-plate analyzer was not used. On the opposite side from the undeflected beam direction, a CEM with a 0.9-cm-diameter active area was located to register the total fragment count rate. A retractable Faraday cup was placed at the exit of the target cell to measure the total current of the ions beam. The detectors and the analyzer were shielded to prevent unwanted events. This setup allows the measurement of the laboratory energy distribution of the charged fragments, the current intensity of the initial ion beam, and the total intensity of the fragments, all necessary for the measurement of the absolute total cross sections. Due to the energy liberated in the dissociation process, and to ensure the detection of all particles, the cross sections were measured under different conditions. The diameter of the entrance aperture of the collision cell was reduced from 1 to 0.45 mm, and the distance from the exit aperture to the detectors was decreased by 10 cm; no significant change in the measurements for the total cross sections was found. The data from which the cross sections were calculated were obtained under "single collision condition" by the well known expression:

$$F_j = \alpha \sigma_{ij} P \tag{1}$$

where $F_j$ is the ratio of the intensity of the fragment $j$ to the intensity of the initial beam with single charge $i$, $\sigma_{ij}$ the cross section for the dissociation to the fragment $j$, where $i$ is the charge state of the beam particle before interaction, $j$ the fragment after the interaction, $P$ the gas cell pressure, and $\alpha$ is given by the expression:

$$\alpha = \frac{N_L l}{RT} \tag{2}$$

where $N_L$ is the Loschmidt's number, $R$ the gas constant, $T$ the absolute temperature, and $l$ is the effective length of the gas cell.

The interaction cell contained the molecular gas targets ($H_2$, $N_2$ or $SF_6$) at a constant pressure of less than 0.2 mTorr, thereby guaranteeing single collision conditions.

## 3. Results and discussion

When CO is ionized, $CO^+$ is formed, and in collisions with target, the $CO^+$ may undergo the following processes:

$$CO^+ + X_2 \rightarrow C^+ + O^0 + X_2 \tag{3}$$

$$CO^+ + X_2 \rightarrow C^0 + O^+ + X_2 \tag{4}$$

$$CO^+ + X_2 \rightarrow C^0 + O^0 + X_2{}^+ \tag{5}$$

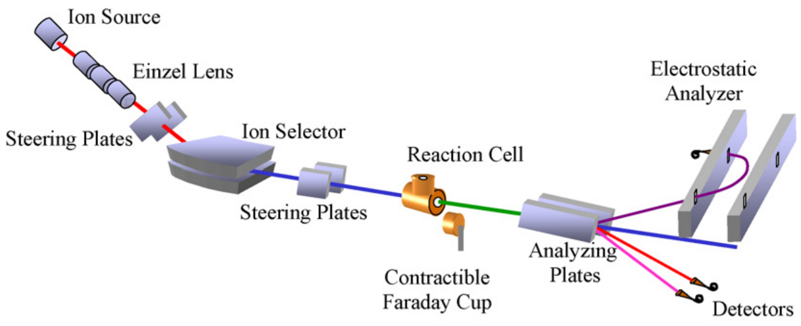

Fig. 1. Experimental apparatus.

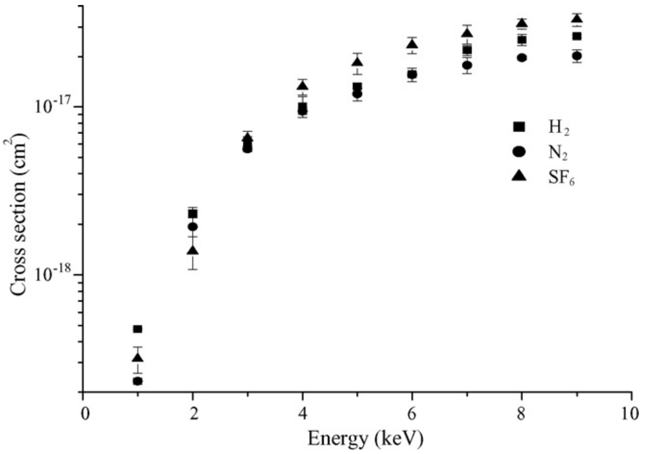

Fig. 2. Absolute total cross section for the dissociation of $CO^+$ through $C^+ + O$ channel, in collision with $H_2$ (■), $N_2$ (●) and $SF_6$ (▲).

and

$$CO^+ + X_2 \rightarrow C^+ + O^+ + X_2 + e \tag{6}$$

However, the main dissociation paths of $CO^+$ leading to the production of ionic fragments are the channels (1) and (2).

The $CO^+$ ions were produced, accelerated, focused, and allowed to pass through a set of collimators into the target cell that was maintained at a constant pressure. Both parent ions as well as fragments resulting from the dissociative excitation in collision with the target were registered on one of the open channeltrons by setting the required voltage on the electrostatic deflection plates. These measurements were conducted at different distances between the electrostatic deflection plates and the detector. Following that, the distance was chosen to be 14 cm, in which the total collection of both ions was achieved.

The cross sections were determined by the standard method based on the measurement of the growth of the intensity of the fragments as a function of the target pressure in the reaction cell. We applied the first- and second-order approximations for the solution of the coupled differential equations that describe the growth of the intensity of each fragment as a function of the pressure. The difference between both values being less than 3%. Then the cross sections were determined from the linear regression of the growth of the intensity of each fragment as a function of pressure.

Fig. 2 shows the absolute total cross section of the dissociation of $CO^+$ to $C^+$ and O in collision with $H_2$, $N_2$ and $SF_6$, with the error bars representing the reproducibility of the data. The values of the cross section, over the energy range under study, are very similar to the different targets (Table 1). Fig. 3 shows the absolute total cross section of the dissociation through the channel $C + O^+$, in collision with $H_2$ and $N_2$. It was not possible to measure the cross section at projectile energies lesser than 5 keV with our experimental system. At low projectile energies, <5 keV, it is not possible distinguish between the signals of the fragments and the noise. With $SF_6$ target only was possible to measure the cross section at 8 and 9 keV projectile energies, the results were of $5.37 \pm 0.064 \times 10^{-18}$ and $7.56 \pm 0.29 \times 10^{-18}$ cm$^2$, respectively (Table 2). Considering the targets used in this work (molecular system), we assumed that during the collision, part of the kinetic energy of the $CO^+$ is transferred into internal excitation energy of the target as well as projectile, yielding $X_2^*$ and $CO^{+*}$ in dissociative or metastable states lying at different energies above the $C^+ + O$ or $C + O^+$ dissociative limits. The quantum structure of the target determines the value of energy transferred into the projectile.

Table 1
Absolute Total cross sections for the formation of $C^+$ ions coming from the collision of $CO^+$ ion on $H_2$, $N_2$ and $SF_6$

| Energy (keV) | $\sigma$ ($\times 10^{-17}$ cm$^2$) | | |
|---|---|---|---|
| | $H_2$ | $N_2$ | $SF_6$ |
| 1 | 0.03 | 0.02 | 0.05 |
| 2 | 0.14 | 0.19 | 0.23 |
| 3 | 0.62 | 0.56 | 0.61 |
| 4 | 1.32 | 0.94 | 1.01 |
| 5 | 1.83 | 1.20 | 1.33 |
| 6 | 2.34 | 0.11 | 1.57 |
| 7 | 2.72 | 1.77 | 2.17 |
| 8 | 3.13 | 1.96 | 2.52 |
| 9 | 3.06 | 2.02 | 2.64 |

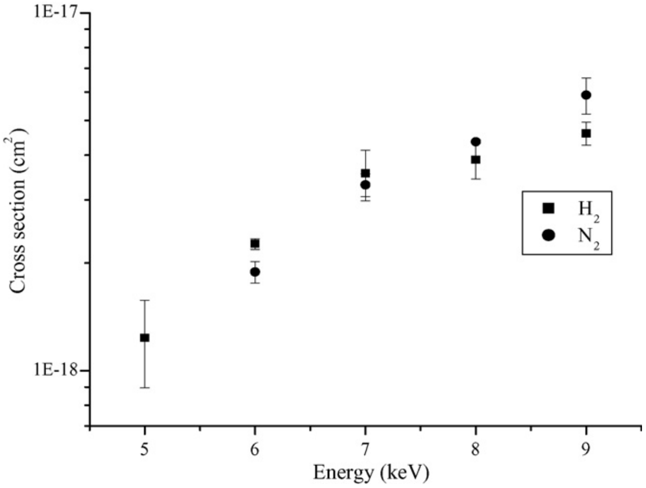

Fig. 3. The absolute total cross section of the dissociation of $CO^+$ through $C + O^+$ channel in collision with $H_2$ (■), and $N_2$ (●).

On the other hand, the channel $C + O^+$ is reached at 10.5 eV according Ref. [23] and we assumed that at projectile energies lesser than 5 keV it is not possible obtain the necessary energy transfer. Fig. 4 shows some of the states of $CO^+$, which

Table 2
Absolute total cross sections for the formation of $O^+$ ions coming from the collision of $CO^+$ ion on $H_2$, $N_2$ and $SF_6$

| Energy (keV) | $\sigma$ ($\times 10^{-17}$ cm$^2$) | | |
|---|---|---|---|
| | $H_2$ | $N_2$ | $SF_6$ |
| 5 | 1.24 | – | – |
| 6 | 2.26 | 1.89 | – |
| 7 | 3.56 | 3.30 | – |
| 8 | 3.89 | 4.36 | 0.54 |
| 9 | 4.60 | 5.90 | 0.76 |

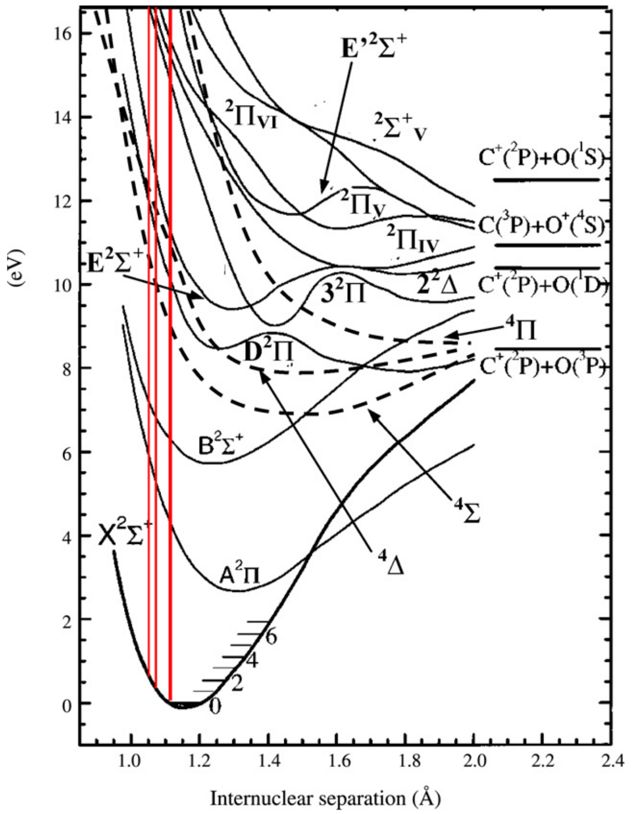

Fig. 4. Potential energy curves of $CO^+$ [23].

could be excited in the collision process. It is reasonable, therefore, to suppose that at low kinetic projectile energies the $CO^+$ highly excited states are not populated ($^2\Pi_{IV}$, $^2\Pi_V$, $^2\Pi_{VI}$, $^2\Sigma^+_V$ and $E'^2\Sigma$), therefore, is less likely to open the channel $C + O^+$. Finally, we assumed that when the collision occur with a complex target (complex quantum structure) it is possible that the energy is transferred into the target in place of into the projectile. Therefore, we have not observed $O^+$ fragments at projectile kinetic energies lesser than 8 keV when used $SF_6$ as target.

## 4. Conclusions

Absolute total cross sections for the dissociation of the $CO^+$ beam to $C^+ + O$ and $C + O^+$ in the energy range from 1.0 to 9.0 keV has been measured. Absolute total cross section for the dissociation of $CO^+$ through the channel $C + O^+$ is preferred. However, the type molecular target has a strong influence in the dissociation of $CO^+$.

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## References

[1] V.R. Bhardwaj, et al., Phys. Rev. A 58 (1998) 2834.
[2] S. Rosen, et al., Phys. Rev. A 57 (1998) 4462.
[3] V. Sidis, J. Phys. Chem. 93 (1989) 8128.
[4] F.A. Gianturco, S. Kumar, Z. Phys. D 37 (1996) 155.
[5] W. Lu, P. Tosi, D. Bassi, J. Chem. Phys. 111 (1999) 8852.
[6] D. Dowek, et al., Phys. Rev. A 28 (1983) 2838.
[7] P. Lablanquie, et al., Phys. Rev. A 40 (1989) 5673.
[8] R.G. Cooks, J. Mass Spectrom. 30 (1995) 1215.
[9] K. Furuya, A. Matsuo, T. Ogawa, J. Phys. B: At. Mol. Opt. Phys. 35 (2002) 3077.
[10] C.M. Marian, et al., Chem. Phys. 130 (1989) 361.
[11] T. Masouka y, E. Nakamura, Phys. Rev. A 48 (1993) 4379.
[12] K. Wang y, V. Mckoy, J. Phys. Chem. 99 (1995) 1643.
[13] W. Kong, y.W. Hepburn, J. Chem. Phys. 99 (1995) 1637.
[14] M. Evans y, C.Y. Ng, Chem. Phys. 111 (1999) 8879.
[15] Z. Bembenek, et al., J. Mol. Spectros. 165 (1994) 205.
[16] C.E. Melton, G.F. Wells, J. Chem. Phys. 27 (1957) 5.
[17] M. Kimura, J. Gu, G. Hirsch, R.J. Buenker, Phys. Rev. A 61 (2000) 032708-1.
[18] M.E. Rudd, R.D. DuBois, L.H. Toburen, C.A. Ratcliffe, T.V. Goffe, Phys. Rev. A 28 (1983) 3244.
[19] M.B. Shah, H.B. Gilbody, J. Phys. B 23 (1990) 1491.
[20] R. Browning, H.B. Gilbody, J. Phys. B 1 (1968) 1149.
[21] R.S. Gao, L.K. Johnson, C.L. Hakes, K.A. Smith, R.F. Stebbings, Phys. Rev. A 41 (1990) 5929.
[22] C.P. Safvan, et al., Phys. Rev. A 60 (1999) R3361.
[23] V. Krishnamurthi, et al., Phys. Rev. A 44 (1991) 5460.
[24] T.F. Moran, J.B. Wilcox, L.E. Abbey, J. Chem. Phys. 68 (1978) 261.
[25] N.M. Kabachnik, et al., Phys. Rev. A 57 (1998) 990.
[26] T. Matsuo, et al., Phys. Rev. A 60 (1999) 3000.
[27] C. Caraby, et al., Eur. Phys. J. D. 2 (1998) 53.
[28] F.B. Yousif, et al., Int. J. Mass Spectrosc. Ion Process. 171 (1997) 127.
[29] G. Hinojosa, et al., J. Phys. B: At. Mol. Opt. Phys. 32 (1999) 915.
[30] I. Alvarez, et al., J. Phys. B: At. Mol. Opt. Phys. 33 (2000) 9.