Photon Stimulated Ion Desorption of Condensed CO_2 at $\sim$ 85 K Studied by Synchrotron Radiation

Gunar V. S. Mota, Daniel E. Weibel[†], and Geovane S. Araújo, and Maria Luiza M. Rocco
Instituto de Química, Universidade Federal do Rio de Janeiro,
Cidade Universitária, Ilha do Fundão, 21949-900 Rio de Janeiro-RJ, Brazil
[†] *INMETRO, AV. Nossa Senhora das Graças, 50, Xerém,*
Duque de Caxias, 25250-020, Rio de Janeiro-RJ, Brazil

Photon stimulated ion desorption (PSID) from condensed carbon dioxide has been studied for photon excitation energies ranging from 93 to 193 eV. PSID studies have been performed at the Brazilian synchrotron light source (LNLS), Campinas, during a multi-bunch operation mode of the storage ring. The results showed that after photon excitation several ions desorbed from the CO_2 films: C^+, O^+, CO^+ and O_2^+. PSID experiments showed that ion desorption was enhanced only at the Si resonance excitations. When the thickness of the CO_2 was $\sim$ 500 L or higher, almost no desorption yield was observed. The study of the dependence of the relative partial ion yield on the photon excitation showed that the X-ray induced Electron Stimulated Desorption (XESD) mechanism has to be invoked to explain the origin of the desorbed ions in the energy region studied.

Keywords: Photon stimulated ion desorption (PSID); Condensed carbon dioxide; Synchrotron radiation; X-ray induced Electron Stimulated Desorption (XESD)

I. INTRODUCTION

The study of desorption processes by photon and electron impact of adsorbed molecules has become a very active field in recent years due to its relevance in a number of different areas, such as polymerization, microelectronic, photobiology, interstellar chemistry, etc. Thus, an increasing number of studies related with the so-called DIET (Desorption Induced by Electronic Transitions) processes have been reported [1]. Specifically, the interaction of CO_2 with metal surfaces and CO_2 multilayers has received much attention due to the possibility if its use as an inexpensive reactant in methanation reactions [2]. In the case of interstellar chemistry, the suggested presence of pure CO_2 ice on Mars could modify the prediction of the loss of its atmosphere due to solar wind-induced sputtering. These photon and electron driven reactions of CO_2 ice were also used to explain the presence of formaldehyde in Mars atmosphere, formed by complex reactions involving CO_2 and H_2O [3]. Anashin V. *et al.* [4] studied the photodesorption process of cryosorbed CO_2 molecules with synchrotron radiation. The substrate was a stainless steel plate and the excitation energy was about 280 eV. The obtained results showed that the photodesorption yield of CO_2 molecules increases with coverage and that the desorption process for condensed CO_2 involves mostly cracking of CO_2 molecules into CO and O. In addition, the desorption rate is constant and independent of the surface coverage.

Within this broad range of interests, there are also many recent studies which try to understand the basic mechanisms of metastable and ion desorption from solid CO_2 using electrons, lasers and synchrotron radiation (SR) as excitation sources. In this paper, an investigation of photon stimulated ion desorption (PSID) of condensed CO_2 on Si(100) substrate has been performed with the purpose of getting insight into the mechanisms of ion desorption from pure solid CO_2.

In the present study we carried out PSID studies of thick CO_2 films in the energy range from 93 to 193 eV. The obtained results can be explained mainly by the X-ray induced electron stimulated desorption mechanism (XESD).

II. EXPERIMENTAL

Ionic desorption experiments were performed at the TGM (Toroidal Grating Monochromator) beam line of the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil, which covers a photon energy range from 12 to 310 eV. The photon flux was up to 10^{13} photons/s and the photon spot size was about 2 x 0.5 mm^2. The angle of the SR, operating in the multi-bunch mode, with respect to the surface normal was 60 degrees [5]. The results presented here correspond only to the energy range between 93 and 193 eV (2p and 2s Si excitations). The experiments were carried out in an ultra-high vacuum system (base pressure $\sim$5 x 10^{-9}Torr), equipped with a ceratron multiplier as detector and a liquid N_2 cryostat for sample cooling. The samples were prepared by exposing the Si (100) substrate at $\sim$85 K to several hundred L of CO_2 (1 L = 1 x 10^{-6} Torr.s). The sample holder was attached to a couple of 5 mm Cu rods (OFHC) connected directly to the bottom of the cryostat. The temperature was monitored using a K-type thermocouple attached to the back of the Si substrate. The Si substrate was set at about 1 cm from the bottom of the liquid N_2 reservoir to obtain the lowest temperature possible.

The time-of-flight technique (ToF) was used for the identification of the ions desorbed after photon excitation. The ions were extracted by a pulsed potential of + 480 V, with 1 μs pulse width and a recurring cycle of 10 kHz. The distance between the substrate surface and the entrance of the detector was 11.5 cm. The output signal of the detector was processed as usual by pulse counting and recorded by a TDC (time-to-digital converter) with a maximum resolution of 1ns/channel. Fig. 1 shows a schematic diagram of the experimental set up used for the PSID studies at LNLS.

The mass assignment was done by using a similar procedure described in detail elsewhere [6,7]. Briefly, the ion flight
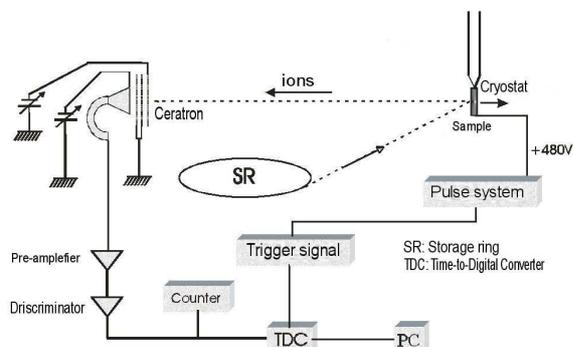
FIG. 1: Schematic diagram of the experimental set up used in PSID studies of condensed CO_2 on Si(100) at LNLS.

FIG. 2: Dependence of XAS spectra of condensed CO_2 at the 2p and 2s excitation energies for different CO_2 film thicknesses.

time was simulated with the program SIMION 3D 6.0 and then the entire spectrum was calibrated according to the two-point calibration equation of the type:

$$ToF = A(m)^{1/2} + B$$

where ToF is the flight time of a given ion, m the mass for single charged ions, and A and B empirical constants that have to be calculated by measuring the flight time of at least two known masses.

The photoabsorption spectrum was recorded by measuring the Relative Partial Electron Yield (RPEY) simultaneously with a photon flux monitor (Au grid). The final data was normalized by this flux spectrum to correct for fluctuations in beam intensity. The energy calibration was performed by using the value for the $L_{2,3}$ transition of silicon [8].

III.   RESULTS AND DISCUSSION

Fig. 2 shows the dependence of the XAS (X-ray absorption spectroscopy) spectra of solid CO_2 recorded at the Si *L*-edge (2s and 2p). The photon energy covers from 93 up to 193 eV. The coverage ranges from 0 to 1100 Langmuir. The spectrum shows two main absorption peaks which are related to the *L* absorption edge of Si(100) (2p and 2s excitations). Figure 2 shows also that the intensity of the absorption lines corresponding to Si 2p and 2s excitations decreases when the number of layers of CO_2 increases. At 500 L, the features associated with the Si substrate almost disappear. Figure 3 shows a typical ToF spectrum of condensed CO_2 at the Si 2p excitation energy (101 eV). As can be seen in Fig. 3, several ions desorbed after photon excitation. The presence of H^+ can not be observed in the ToF spectrum due to the noise produced by the pulsed extraction potential (intense signal to the left of Fig. 3). H^+ has a calculated ToF lower than 1 μs and therefore its signal overlaps with the intense signal of the extraction pulse.

In order to gain insight into the ionic desorption process from condensed CO_2, we have measured ToF spectra at different photon energies around the Si *L*-edge. The photon energy dependence of the relative partial ion yield (RPIY) from
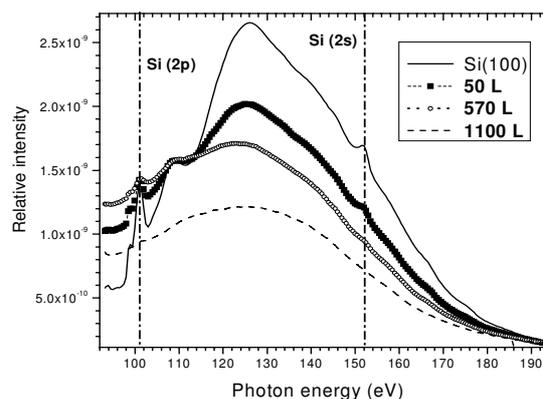
condensed CO_2 on the excitation energy is shown in Figure 4. The RPIY was calculated with respect to the total ion yield (TIY) in the range 93 – 193 eV. The TIY is the sum of all ion yields measured between 93 and 193 eV. As can be seen in Fig. 4, outside the silicon resonant excitation region almost no desorption can be observed. Therefore, this RPIY is a measurement of the contribution to the ion desorption yield from secondary electrons originated after photon excitation.
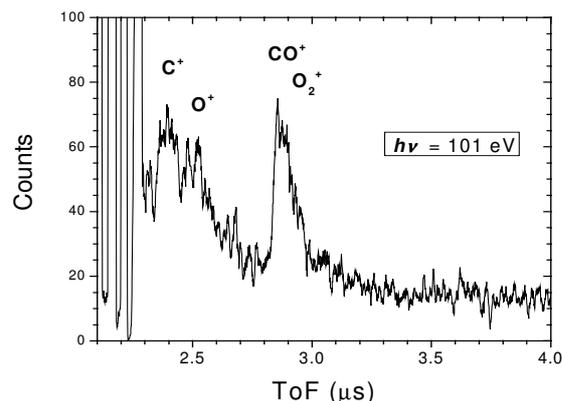

FIG. 3: Typical ToF spectrum of ions emitted from the surface of solid CO_2 (thickness ~200 L). The intensity signal observed before 2.25 μs was generated by the pulsed extraction potential applied to the substrate.

In the PSID model of Knotek and Feibelman [9,10], the multiple holes formed in the valence orbitals are created via intra-atomic or inter-atomic Auger transitions following core-level excitation of adsorbate molecules. This is the well known Auger Stimulated Ion Desorption (ASID) mechanism that was studied extensively for molecules adsorbed or condensed on surfaces [11-13] as well as polymers [14-18]. In addition to such a direct process another (indirect) process, X-ray induced electron stimulated desorption (XESD) [19,20] is an important mechanism for desorption of species from a surface when no direct excitation of the top monolayers is produced. In the XESD mechanism, desorption of surface
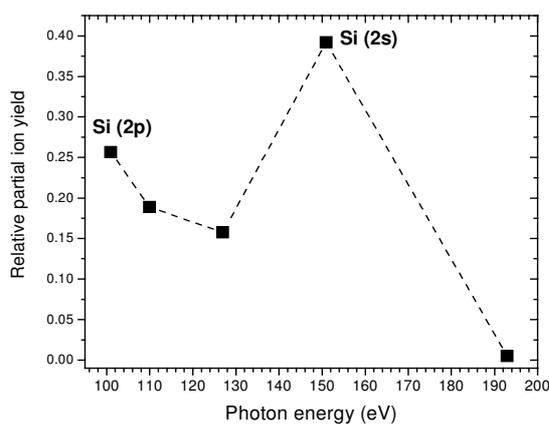
FIG. 4: Relative partial ion yield for condensed CO_2 (film thickness ~200 L) at the silicon *L*-edge excitation energies.

species is caused by outgoing energetic Auger and photoelectrons, most of which will originate in the bulk. The fragmentation and desorption process by XESD may go via single and multiple valence excitations and ionizations. Chen *et al.* [21] have studied the relative contribution of each desorption channel (AES vs. XESD) to the total desorption yield and have obtained important information about the desorption mechanisms of $CHCl_3$ adsorbed on Si(100) at the silicon 2p-edge. Recently, PSID results at the silicon and chlorine 1s-edges from condensed chloroform on Si(100) [22] also pointed out to the importance of the XESD process. The results presented in Fig. 4 showed that the ionic desorption from condensed CO_2 occurs mainly at the energies corresponding to the exci-

tation of the Si substrate (2p, 2s).

Therefore, the results presented in Fig. 4 can be well explained in terms of the indirect desorption process, the XESD mechanism, i.e., desorption of surface species induced by outgoing energetic photoelectrons and Auger eletrons, most of which originated in the bulk. Photoelectron and Auger yields are higher at the Si excitation energies and therefore an increase of the RPIY is accordingly observed at these photon energies.

IV. CONCLUSIONS

PSID studies of condensed CO_2 films were reported using synchrotron radiation ranging from 93 to 193 eV. The results showed that C^+, O^+, CO^+ and O_2^+ were the main fragments desorbed after photon excitation. The observed relative ion yields can be interpreted taking into account the XESD mechanism. The RPIY is higher at 2p and 2s excitation energies of Si, where the yield of secondary photoelectrons and Auger electrons is maximum.

Acknowledgement

[1] See *Desorption Induced by Electronic Transition, DIET* , Burns A. R., Stechel E. B. and Jennison D. R. (eds), Springer Series in Surface Science, Springer-Verlag: Berlin, Heidelberg, 1993 and following editions.

[2] K. H. Ernst, D. Schlatterbeck, and K. Christmann, Phys. Chem. Chem. Phys. **1**, 4105 (1999).

[3] L. Siller et al., J. Chem. Phys. **118**, 8898 (2003).

[4] V. Anashin et al., Nucl. Instr. And Meth. In Phys. Res. A **405**, 258 (1998).

[5] M. L. M. Rocco, G. S. Faraudo, F. C. Pontes, and G. G. B. de Souza, Polymer Degradation and Stability **88**, 213 (2005).

[6] M. L. M. Rocco, D. E. Weibel, L. S. Roman, and L. Micaroni, Surface Science **560**, 45 (2004).

[7] D. E. Weibel, M. L. M. Rocco, F. C. Pontes, M. Ferreira, and G. G. B. de Souza, Polymer Degradation and Stability **91**, 712 (2006).

[8] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. **39**, 125 (1967).

[9] M. L. Knotek and P. J. Feibelman, Physical Review Letters **40** (14), 964-967 (1978).

[10] M. L. Knotek and P. J. Feibelman, Surface Science **90** (1), 78-90 (1979).

[11] C. Keller, M. Stichler, G. Comelli, F. Esch, S. Lizzit, D. Menzel, and W. Wurth, J. Electr. Spectrosc. Relat. Phenom. **93**, 135 (1998).

[12] T. Sekiguchi, H. Ikeura-Sekiguchi, and Y. Baba, Surf. Sci. **454**, 363 (2000).

[13] Y. Baba, Low Temp. Phys. **29**, 228 (2003).

[14] N. Ueno and K. Tanaka, Jpn. J. Appl. Phys. Part 1, **36**, 7605 (1997).

[15] E. Ikenaga, K. Kudara, K. Kusaba, K. Isari, S. A. Sardar, S. Wada, K. Mase, T. Sekitani, and K. Tanaka, J. Electr. Spectrosc. Relat. Phenom. **114**, 585 (2001).

[16] S. Wada, R. Sumii, K. Isari, S. Waki, E. O. Sako, T. Sekiguchi, T. Sekitani, and K. Tanaka, Surf. Sci. **528,** 242 (2003).

[17] M. L. M. Rocco, G. S. Faraudo, F. C. Pontes, R. R. Pinho, M. Ferreira, and G. G. B. de Souza, Chemical Physics Letters **393,** 213 (2004).

[18] M. L. M. Rocco, G. S. Faraudo, R. R. Pinho, M. Ferreira, F. C. Pontes, and G. G. B. de Souza, J. Electr. Spectrosc. Relat. Phenom. **141**, 1 (2004).

[19] D. E. Ramaker, T. E. Madey, R. L. Kurtz, and H. Sambe, Phys. Rev. B **38**, 2099 (1988).

[20] D. Purdie, C. A. Muryn, N. S. Prakash, P. L. Wincott, G. Thornton, and D. S. L. Law, Surf. Sci. **251**, 546 (1991).

[21] J. M. Chen, S. C. Yang, and Y. C. Liu, Surf. Sci. **391,** 278 (1997).

[22] M. L. M. Rocco, G. V. Mota, and R. R. Pinho, J. Electr. Spectrosc. Relat. Phenom. **151**, 135 (2006).