

# Is it possible to detect frozen O<sub>2</sub> and N<sub>2</sub> on interstellar grains?

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**Abstract.** We continue to study the effects of ion irradiation on frozen ices with a view to their astrophysical relevance. The technique used to evidence molecular alteration is “in situ” infrared (IR) spectroscopy. Here, we present results obtained irradiating by 3–60 keV helium and argon ions, frozen CO, and mixtures CO:O<sub>2</sub> and CO:N<sub>2</sub>. The relevance of these studies for astrophysical applications is related to the fact that IR bands of frozen O<sub>2</sub> and N<sub>2</sub> are difficult to be observed. We investigate if their presence on ice mantles of interstellar grains could be evidenced through the changes in the CO profile or the presence of new species formed by energetic processing. The results indicate that the CO band at around 2140 cm<sup>-1</sup> is only slightly modified by the simple mixing with the two non-polar species and, more deeply, by ion irradiation of the mixtures. Carbon dioxide (CO<sub>2</sub>) is the major species produced by irradiation. In CO:O<sub>2</sub> mixtures ozone (O<sub>3</sub>) is produced at a large rate. Also carbon suboxides are formed by ion irradiation of CO and CO:N<sub>2</sub> mixtures, the profile of their bands is different in the two cases and can be used as tracer of the presence of N<sub>2</sub> in icy mantles.

**Key words:** ISM: dust – ISM: molecules – infrared: interstellar: lines

## 1. Introduction

IR spectra of several stellar objects show an absorption feature at about 2140 cm<sup>-1</sup> which is attributed to solid (frozen) CO in interstellar and/or circumstellar grain mantles. These objects are both young stars still embedded in their placental cloud and field stars located behind a dark cloud. In most cases it is possible to separate two independent absorption components (Lacy et al. 1984; Whittet et al. 1989; Tielens et al. 1991; Chiar et al. 1994, 1995), namely a narrow ( $\Delta\tilde{\nu} = 3 - 9$  cm<sup>-1</sup>) feature at about 2140 cm<sup>-1</sup> and a broader ( $\Delta\tilde{\nu} \sim 10$  cm<sup>-1</sup>) and generally weaker feature at about 2136 cm<sup>-1</sup>.

The narrow feature has been attributed to solid CO mixed in with non-polar molecules such as CO<sub>2</sub>, N<sub>2</sub> or O<sub>2</sub> and the

broad feature to solid CO mixed in with polar molecules such as H<sub>2</sub>O. Furthermore attempts have been made to fit the narrow component with relatively pure CO matrices (Tielens et al. 1991).

Palumbo & Strazzulla (1993) presented a model to account for observations of both field and embedded stars. Toward field stars the broad component is well fitted with CO produced by ion irradiation of H<sub>2</sub>O:CH<sub>3</sub>OH ices (10 K) while the narrow component with irradiated (10 K) pure CO. Note that after ion irradiation of pure CO, the abundance of CO becomes, at a dose of the order of 12 eV/16amu, of the order of 30%, most of it being converted into CO<sub>2</sub> and suboxides. Thus it is possible to compare the shape of the CO band, as measured in the laboratory after irradiation, with the one observed in astrophysical sources. In other words it is not necessary to do particle shape calculations (Tielens et al. 1991; Palumbo & Strazzulla 1993). Toward embedded stars the observed band is well fitted by the same mixture but with the population responsible for the broad component, heated to about 67 K. As noted by Palumbo & Strazzulla (1993) such a temperature has to be considered as an average. Around these stars a radiation field increases the grain temperature: near the star all icy mantles sublimate; at a certain distance only the H<sub>2</sub>O-dominated mantles can survive; at greater distance grains are unperturbed as those observed towards field stars.

Chiar et al. (1995) have compared recent observations of IR sources in the Taurus Dark Cloud with laboratory spectra. They find that for embedded sources a good fit of the broad component is obtained with CO produced after ion irradiation of a H<sub>2</sub>O:CH<sub>3</sub>OH mixture.

All of the above models are compatible with two different scenarios: in the first one H<sub>2</sub>O-rich mantles form e.g. during the contraction of the cloud when the gas density is lower and when CO-poor layers are expected to accrete. When the density gets higher ( $n_0 \geq 10^4$  cm<sup>-3</sup>) CO-rich mantles would accrete on the top of the previous mantles. On the other hand, two different grain populations could exist: the first one with CO-rich (possibly mixed with non polar species) mantles in the inner and denser portion of the cloud; the second population, with H<sub>2</sub>O-dominated mantles, would prevail in the outer portion of

the cloud. Whatever is the case we can expect that on the CO-rich grains (or layers) even O<sub>2</sub> and N<sub>2</sub> can accrete. Then it is interesting to study spectral properties of their mixtures and the alteration induced by ion irradiation.

In a recent work Bergin et al. (1995) studied the gas-phase chemistry in dense interstellar clouds including grain surface molecular depletion and desorption. Among their finding it is interesting, for the present paper, that for all relevant astronomical timescales ( $t \geq 10^4$  yrs) and for dust temperatures less than 20 K, CO is the main constituent of ice mantles. Molecular oxygen assumes a comparable abundance only deep in the cloud and after a time of about  $10^6$  yrs. Molecular nitrogen and water ice have, at most, an abundance of 0.1 with respect to CO.

In this paper we present results obtained irradiating CO, CO:O<sub>2</sub> and CO:N<sub>2</sub> frozen mixtures with helium and argon ions at energies from 3 to 60 keV. The relevance of these studies for astrophysical applications is related to the fact that IR bands of frozen O<sub>2</sub> and N<sub>2</sub> are difficult to be observed. Thus their presence on ice mantles of interstellar grains could be evidenced observing the modifications induced (even upon irradiation) on the IR bands of species such as CO also present in the ice and/or due to the presence of new species formed by energetic processing. It is important to note that a direct observation of homonuclear, and then infrared inactive molecules, is possible. In fact, Ehrenfreund et al. (1992) have shown that in a solid matrix the transition of O<sub>2</sub> molecules gets weakly infrared active, due to the perturbation of the surrounding species. Furthermore Sandford et al. (1993) have attributed an observed weak absorption feature near  $4141 \text{ cm}^{-1}$  in the spectrum of WL5, to solid molecular hydrogen.

## 2. Experimental

A description of the experimental apparatus used to obtain “in situ” IR spectra of irradiated and unirradiated frozen gases has been given elsewhere (Strazzulla & Baratta 1991). A scattering chamber is faced to a FTIR Perkin-Elmer (mod. 1710) spectrophotometer ( $4400\text{--}400 \text{ cm}^{-1} = 2.27\text{--}25 \mu\text{m}$ ) through KBr windows. Vacuum conditions are better than  $10^{-7}$  mbar. Frosts are accreted onto a silicon crystal (111) substratum, put in contact with a cold finger (10–300 K), by admitting the chosen gas (or mixture) into the chamber, through a needle valve. All of the spectra shown in the next sections are ratioed to a background spectrum of the silicon wafer and have been obtained with a resolution of  $2 \text{ cm}^{-1}$ . The substratum plane forms an angle of 45 degrees with the IR beam and the ion beam so that, before, during and after irradiation, spectra can be obtained without tilting the sample.

Ion beams are obtained from an ion gun (3 kV) or from an ion implanter (30 kV). From this latter double ionized Ar beams with energy up to 60 keV can also be obtained.

Impinging ions deposit energy into the target both by ionizations and excitations of irradiated molecules (electronic energy loss) and by elastic collisions with bombarded nuclei (nuclear energy loss). The electronic ( $S_e$ ) and nuclear ( $S_n$ ) stopping powers (energy loss per unit path length) of some of the used ions

**Table 1.** Properties of used ions.

	$S_n$	$S_e$	$S_{tot}$	Range
	eV $\text{cm}^2/10^{15}$ CO molecules			$10^{17}$ CO molecules/ $\text{cm}^2$
3 keV He <sup>+</sup>	5.8	4.7	10.5	2.5
60 keV Ar <sup>++</sup>	151	52	203	3

are reported in Table 1, together with the ion range (penetration depth).

Experiments with He<sup>+</sup> have been performed depositing species at a known rate (previously calibrated, see Palumbo & Strazzulla 1993) and irradiating at the same time. The deposited energy (eV/16amu) has been calculated from the knowledge of the deposition rate and the used ion current.

Experiments with Ar<sup>++</sup> have been performed depositing thin layers (column density of about  $10^{17}$  molecule/ $\text{cm}^2$ ) and then irradiating them with the beam passing through the target (see Table 1). The deposited energy (eV/16amu) has been calculated from the knowledge of the stopping power of the used ions and from the measurement of the amount of impinging ions (ion current  $\times$  irradiation time).

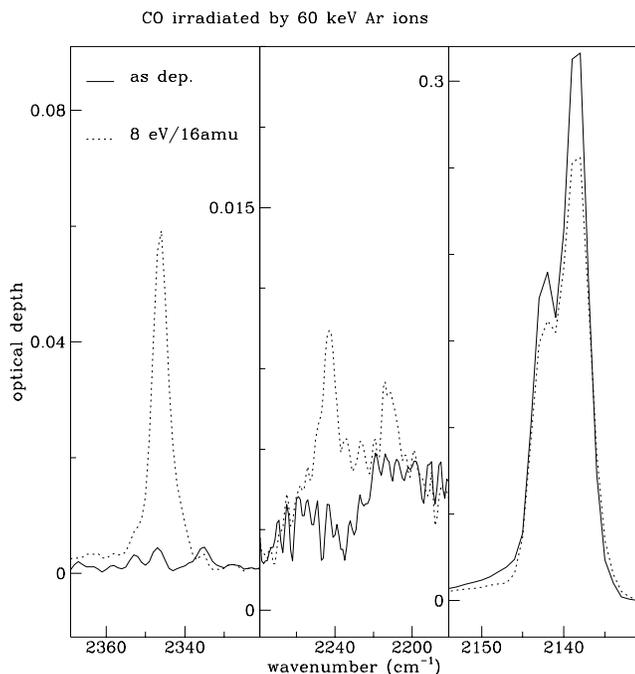
Doses are given in eV/16amu because this is a convenient way to compare the results of experiments performed with species of different molecular weight and for mixtures.

Ion currents in the range of 100’s of nano to a few  $\mu\text{ampere cm}^{-2}$  have been used in order to avoid a macroscopic heating of the target.

## 3. Results

### 3.1. Pure CO

Pure and irradiated CO ice has been already studied by our group (Palumbo & Strazzulla 1993). Here we summarize the results and present new data. Pure CO ice at 10 K shows an absorption feature at about  $2138 \text{ cm}^{-1}$  due to the fundamental vibrational mode C $\equiv$ O, with FWHM  $\sim 4 \text{ cm}^{-1}$  measured on an optical depth scale and an inclination angle of 45 degrees (see Table 2). Spectra of pure CO ice have been compared with those of CO irradiated with 3 keV He<sup>+</sup> ions (Palumbo & Strazzulla 1993). Peak position of as-deposited CO is different from that  $2140 \text{ cm}^{-1}$  reported in Palumbo & Strazzulla (1993). FWHM is larger than the value ( $2.5 \text{ cm}^{-1}$ ) by Sandford et al. (1988). Recent work still in progress and aimed to measure the optical constants of ices (Baratta et al., in preparation) has made clear the cause of these differences: because of the relevant variations in the real part of the refractive index across the band, the shape of the band is strongly dependent on the inclination angle between the IR beam and the target. At 45 degrees the FWHM is  $4 \text{ cm}^{-1}$  at 0 degrees (i.e. the IR beam perpendicular to the plane of the substratum) it is lower. Note however that, for mixtures containing less than about 30 percent of CO, or after irradiation



**Fig. 1.** IR spectra, in three spectral ranges, of pure CO before (solid line) and after irradiation with 60 keV Ar<sup>++</sup> (8 eV/16amu; dashed line). The formation of new bands at about 2340 cm<sup>-1</sup> (CO<sub>2</sub>) and a double structure at 2214 and 2242 cm<sup>-1</sup> (suboxides) is evident after irradiation.

of pure CO, the optical properties of the target change and the differences due to the inclination angle are negligible. In fact peak positions and FWHM of CO:O<sub>2</sub> (1:1) mixtures reported in Table 2 are identical, within the limitation of the different spectral resolutions, to those observed at zero degrees (Ehrenfreund, private communication).

In Fig. 1 we show the spectra, due to pure CO as deposited and after irradiation with 60 keV Ar<sup>++</sup> (8 eV/16amu). The formation, after irradiation, of new bands at about 2340 cm<sup>-1</sup> and a double structure at 2214 and 2242 cm<sup>-1</sup> is observed after irradiation. The former is easily attributed to the O=C=O asymmetric stretch in CO<sub>2</sub> (we observe also the band due to the O=C=O bend at around 660 cm<sup>-1</sup>). We attribute the other two bands to carbon suboxides (C<sub>3</sub>O<sub>2</sub>, and/or C<sub>3</sub>O, and/or C<sub>2</sub>O). Bands at 2242 and 1989 cm<sup>-1</sup> have been observed in ion-irradiated H<sub>2</sub>O:CO ice mixtures (Moore et al. 1991) and attributed to C<sub>3</sub>O<sub>2</sub> and C<sub>2</sub>O respectively. A band at 2237 cm<sup>-1</sup> has been observed after irradiation of H<sub>2</sub>O:CO<sub>2</sub> ice mixtures (Moore & Khanna 1991; Brucato et al. 1996) and attributed to C<sub>3</sub>O<sub>2</sub> (Moore et al. 1991). Gerakines et al. (1996) observed bands at 2243 and 2248 cm<sup>-1</sup> (as well as the bands due to carbon dioxide) after UV irradiation of CO, CO<sub>2</sub> and H<sub>2</sub>CO. Gerakines et al. (1996) attributed these bands to C<sub>3</sub>O and C<sub>3</sub>O<sub>2</sub> respectively. Thus we are not able to identify the specific carbon suboxide. The formation of a refractory, (polymer-like i.e. constituted by sub-units but not by a single monomer) carbon suboxide, has been detected, by mass spectrometry and elemental analysis, in ion irradiated

CO along with volatile species such as CO<sub>2</sub> and O<sub>2</sub> (Haring 1984; Chrisey et al. 1985).

We have calculated an upper limit for the production of suboxides (from the band at 2142 cm<sup>-1</sup> attributed to C<sub>3</sub>O<sub>2</sub>). The lowest dose we used (1.8 eV/16amu), for 60 keV Ar<sup>++</sup> irradiation, corresponds to an ion flux of  $\approx 1.5 \times 10^{13}$  ions/cm<sup>2</sup> and sputtering effects are negligible (Johnson 1990, Fig. 3.21). We then assume that all of the carbon atoms (from CO) that do not form carbon dioxide, form the suboxide. In this way we evaluate the integrated absorbance of the C<sub>3</sub>O<sub>2</sub> band and find a value of  $\approx 5 \times 10^{-17}$  cm/molecule.

It is interesting to note that except for the experiment at the lowest dose the sum of carbon atoms from CO, CO<sub>2</sub> and suboxides, is lower than the amount of initial carbon, and becomes lower and lower as the irradiation dose increases. Similarly to what has been found for experiments with hydrocarbons (Strazzulla & Baratta 1992) where a progressive dehydrogenation (or, equivalently, carbonization) has been suggested, and for experiments with glycine (Foti et al. 1991) where a progressive loss of oxygen, nitrogen and hydrogen (or, equivalently, carbonization) has been inferred, we suggest that, in the present case, a loss of oxygen produces a progressive carbonization of the synthesized suboxides. Stopping the experiment at a given dose we get materials with a different degree of oxidation.

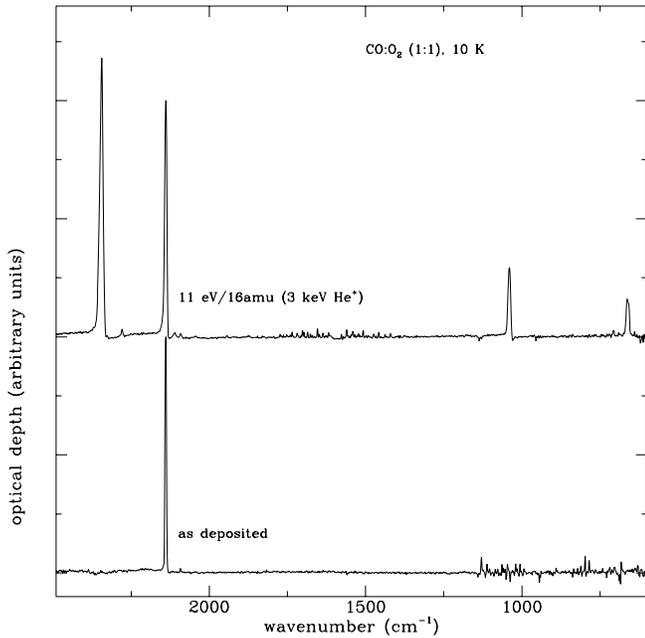
### 3.2. CO:O<sub>2</sub> (1:1) and CO:N<sub>2</sub> (1:1) mixtures

In Fig. 2 we show the spectra, normalized to the CO peak, due to a CO:O<sub>2</sub> (1:1) mixture as deposited (10 K) and after irradiation with 3 keV He<sup>+</sup> (11 eV/16amu). Also in this case the formation of new bands at about 2340 and 660 cm<sup>-1</sup> is evident, which are easily attributed to CO<sub>2</sub>. An intense band at 1039 cm<sup>-1</sup> and a weaker one at 706 cm<sup>-1</sup> are due to ozone (Diem & Lee 1982). The formation of ozone from the photolysis of molecular oxygen has already been reported (Grim & d'Hendecourt 1986). The bands around 2230 cm<sup>-1</sup>, which we attribute to suboxides, are lacking. This is better seen in Fig. 3 where we show the spectra, due to CO:O<sub>2</sub> (1:1) as deposited and after irradiation with 60 keV Ar<sup>++</sup> ions (10 eV/16amu). The explanation of the lack of the band due to suboxides is that, after the rupture of the C≡O bond, the carbon atom has a high probability to bond with molecular oxygen, producing carbon dioxide at a higher rate as it is made clear from the comparison between Figs. 1 and 3.

Fig. 4 shows the spectra due to a CO:N<sub>2</sub> (1:1) mixture as deposited (10 K) and after irradiation with 60 keV Ar<sup>++</sup> ions (13 eV/16amu). In this case a new band at about 2340 cm<sup>-1</sup>, attributed to CO<sub>2</sub>, and a broad structure at about 2250 cm<sup>-1</sup> are found after irradiation. Although we continue to attribute this latter feature to carbon suboxides, its shape, peak position and intensity is different from that obtained after irradiation of pure CO (see Sect. 3.3).

### 3.3. Summary of experimental results

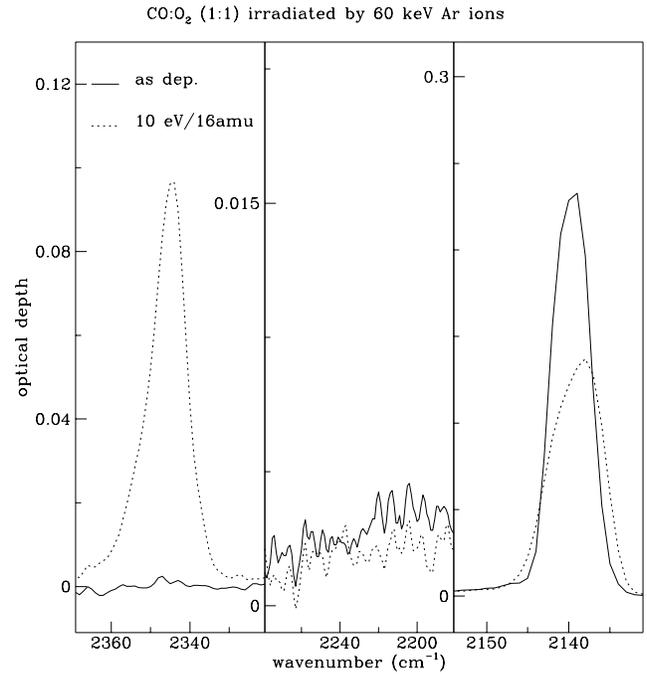
In Table 2 we summarize the results reporting, for each of the irradiated target, peak position and FWHM of CO, CO<sub>2</sub>, O<sub>3</sub> and



**Fig. 2.** IR spectra, in the spectral range 2400–550  $\text{cm}^{-1}$ , of a CO:O<sub>2</sub> (1:1) mixture before and after irradiation with 3 keV He<sup>+</sup> (11 eV/16amu). Spectra are normalized at the maximum of the CO feature.

suboxide bands. CO peak position does not change much with mixture and irradiation dose; FWHM increases with dose, except when CO is mixed with nitrogen. CO<sub>2</sub> peak position ranges between 2343 and 2346  $\text{cm}^{-1}$ , its FWHM between 4 and 22  $\text{cm}^{-1}$ . It broadens with increasing irradiation dose. As mentioned above the main distinctive feature among the different studied targets are changes in the CO and CO<sub>2</sub> profiles and the presence of suboxides. Suboxides are absent when molecular oxygen is in the mixture and have a different peak positions and FWHM in pure CO and in the mixture with nitrogen. Because the same spectral region is typical of cyano compounds we suspect, although we have not an evident proof, that also some nitrogen is bonded in the newly formed material.

In Fig. 5 we report the percentages of the major produced species, with respect to the initially deposited CO, as a function of irradiation dose. Data refer to irradiation of pure CO, and of 1:1 mixtures of CO with N<sub>2</sub> and O<sub>2</sub>. The values have been obtained by using the absorbances as given by Gerakines et al. (1996) for all species but for the suboxide. For this latter we used the value estimated above. As mentioned above, except for the experiment at the lowest doses the sum of carbon atoms from CO, CO<sub>2</sub> and suboxides, is lower than the amount of initial carbon, and becomes lower and lower as the irradiation dose increases. Most of the material goes to form a carbon-rich residue. The results on CO reported in Fig. 5 can be compared with those obtained by Gerakines et al. (1996) after UV irradiation. Those authors report that after 1 hr of UV irradiation, corresponding to the maximum dose suffered by ice mantles in IS clouds, almost all of the CO is still there. This means that



**Fig. 3.** IR spectra, in three spectral ranges, of a mixture CO:O<sub>2</sub> (1:1) before (solid line) and after irradiation with 60 keV Ar<sup>++</sup> (10 eV/16amu; dashed line). A new band at about 2340  $\text{cm}^{-1}$  (CO<sub>2</sub>) is formed after irradiation, but no suboxides.

CO is virtually unaltered by UV irradiation. Ion bombardment alters it much more efficiently.

#### 4. Astrophysical applications

In this section we discuss the possible applications of the experimental results to the physics of ices in dense interstellar clouds and, in particular, on the possibility to infer the presence of molecular oxygen and nitrogen from IR observations in the 2400–2100  $\text{cm}^{-1}$  region. This region should be fully covered by ISO observations and could provide a lot of new information whose interpretation will need laboratory experimental results as those reported here.

##### 4.1. Ion doses in interstellar clouds

It has been evaluated that icy grain mantles in dense clouds, suffer ion irradiation for  $10^5 - 10^8$  years. The former estimate refers to the case of grain mantles which evaporate immediately after formation while the latter estimate refers to the limit case of icy grain mantles (or at least a part of them) which survive for all the dust lifetime (Palumbo & Strazzulla 1993). A reasonable estimate for the cosmic proton flux is  $J(E=1 \text{ MeV})=3 \text{ cm}^{-2} \text{ sec}^{-1}$  (Jenniskens et al. 1993). The specific energy loss of a 1 MeV proton in a typical grain containing heavy atoms (C, N, O, Si) is  $S \simeq 5 \times 10^{-15} \text{ eV cm}^2/\text{atom}$ . Thus after a time of  $3 \times 10^{12} - 3 \times 10^{15} \text{ sec}$  the energy deposited on a grain (dose) is given by  $S \times J \times \text{time}$  and values 0.05–50 eV/atom (C, N,

**Table 2.** Spectral properties of CO, CO<sub>2</sub>, O<sub>3</sub> and suboxide in as deposited targets and after irradiation by 60 keV Ar<sup>++</sup> ions at the given doses.

ice composition	CO		CO <sub>2</sub>		O <sub>3</sub>		Suboxide	
	peak cm <sup>-1</sup>	FWHM cm <sup>-1</sup>	peak cm <sup>-1</sup>	FWHM cm <sup>-1</sup>	peak cm <sup>-1</sup>	FWHM cm <sup>-1</sup>	peak cm <sup>-1</sup>	FWHM
CO	2138	4	–	–	–	–	–	–
+ 2 eV/16amu	2138	5	2346	4	–	–	2214, 2242	10
+ 8 eV/16amu	2138	4	2346	5	–	–	2214, 2242	10
+ 12 eV/16amu (a)	2139	7	2346	7	–	–	2213, 2244	10
+ 21 eV/16amu (a)	2139	8	2347	9	–	–	2211, 2242	10
+ 43 eV/16amu	2138	8	2345	15	–	–	–	–
+ 71 eV/16amu	2138	8	2345	17	–	–	–	–
CO:O <sub>2</sub> 1:1	2139	5	–	–	–	–	–	–
+ 4 eV/16amu	2138	7	2345	6	1040	8	–	–
+ 10 eV/16amu	2138	8	2344	10	1040	8	–	–
+ 11 eV/16amu (b)	2139	8	2344	12	1040	10	–	–
+ 23 eV/16amu	2138	8	2344	16	1040	10	–	–
+ 59 eV/16amu	2139	8	2343	22	–	–	–	–
CO:N <sub>2</sub> 1:1	2139	4	–	–	–	–	–	–
+ 1 eV/16amu	2139	4	2347	5	–	–	2247	broad
+ 5 eV/16amu	2139	4	2346	6	–	–	2235, 2247, 2263	≥ 40
+ 13 eV/16amu	2139	4	2346	8	–	–	2235, 2247, 2263	≥ 40
+ 26 eV/16amu	2139	5	2346	9	–	–	2234, 2247, 2262	≥ 40
+ 66 eV/16amu	2139	5	2343	14	–	–	2235, 2247, 2259	≥ 40
CO <sub>2</sub>	–	–	2343	12	–	–	–	–

(a) 3 keV He<sup>+</sup> (Palumbo & Strazzulla 1993); (b) 3 keV He<sup>+</sup>.

O, Si). That is the dose range in which most of our experiments have been performed.

Both UV and cosmic ray irradiation may cause surface processing of interstellar grains. The comparison between the two processes is not the purpose of this paper, however we note that either both processes produce the same effects, which then are to be summed up, or the effects discussed here are due only to cosmic rays.

#### 4.2. The CO band

Peak position of the CO band remains almost unaffected both from the mixing with molecular nitrogen and oxygen and from ion irradiation. As irradiation proceeds the FWHM increases from 4 to 8 cm<sup>-1</sup> but in the case of a mixture with nitrogen the FWHM increases only from 4 to 5 cm<sup>-1</sup>.

From the profile of the CO band in dense molecular clouds a narrow ( $\Delta\tilde{\nu} = 3 - 9$  cm<sup>-1</sup>) feature attributed to a grain population dominated by CO mantles can be identified that might be mixed with non polar species and, possibly, subjected to energetic processing.

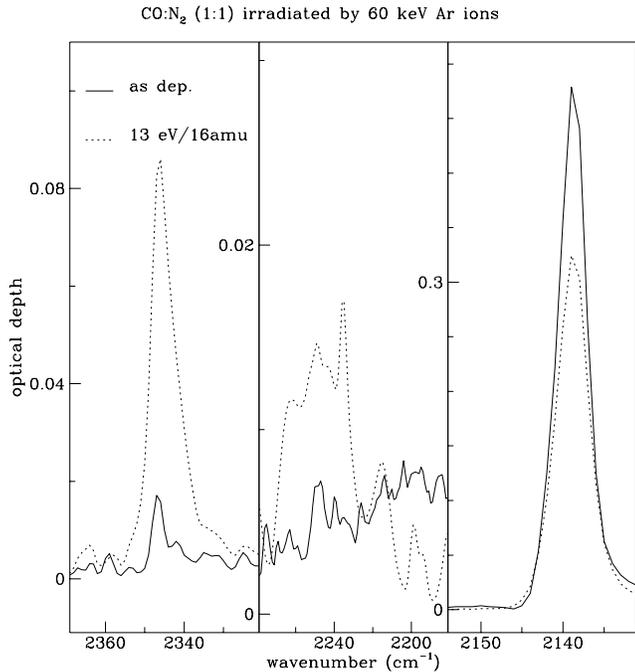
On the basis of our experiments we can say that, in the case of the lowest observed FWHM (3-5 cm<sup>-1</sup>), we should be observing unprocessed ice mantles or processed ice mantles only if CO is mixed with molecular nitrogen.

#### 4.3. The CO<sub>2</sub> band

Carbon dioxide is not predicted to have appreciable abundance in the gas phase in dense clouds so that its condensation on interstellar grains can be neglected while its presence may be due to surface processing such as UV and cosmic ray irradiation (Whittet & Walker 1991; Palumbo & Strazzulla 1993) or to reaction between O and CO on grain surfaces (Tielens & Allamandola 1987). CO<sub>2</sub> has in fact been observed, by IRAS, along the line of sight of three protostellar objects (d'Hendecourt & de Muizon 1989).

Laboratory data testify the formation of CO<sub>2</sub> after irradiation of frozen CO (pure and mixtures with O<sub>2</sub> and N<sub>2</sub>), CH<sub>3</sub>OH, H<sub>2</sub>O:CH<sub>3</sub>OH mixtures (Palumbo 1996). Thus CO<sub>2</sub> can be expected to be produced in the different grain populations.

We believe that peak position of the band that might be observed at around 2340 cm<sup>-1</sup> cannot be used for discriminating between different models of its formation. Large FWHM (15-20 cm<sup>-1</sup>) are expected for carbon dioxide formed by energetic processing of CO rich mantles. Also in this case however, the presence of nitrogen mixed with CO could give rise, by ion irradiation, to a band with a relatively narrow FWHM (5-10 cm<sup>-1</sup>). However it is important to note that the CO<sub>2</sub> band is broad when produced both by ion (Palumbo 1996) and UV irradiation of polar ice mixtures. It can be very narrow ( $\simeq 4$  cm<sup>-1</sup>) when pure CO or a CO:O<sub>2</sub> mixture containing little water are UV-irradiated (Ehrenfreund, private communication). Thus any



**Fig. 4.** IR spectra, in three spectral ranges, of a mixture CO:N<sub>2</sub> (1:1) before (solid line) and after irradiation with 60 keV Ar<sup>++</sup> (13 eV/16amu; dashed line). A new band at about 2340 cm<sup>-1</sup> (CO<sub>2</sub>) and a structured feature at around 2260 cm<sup>-1</sup> (suboxides) appear after irradiation.

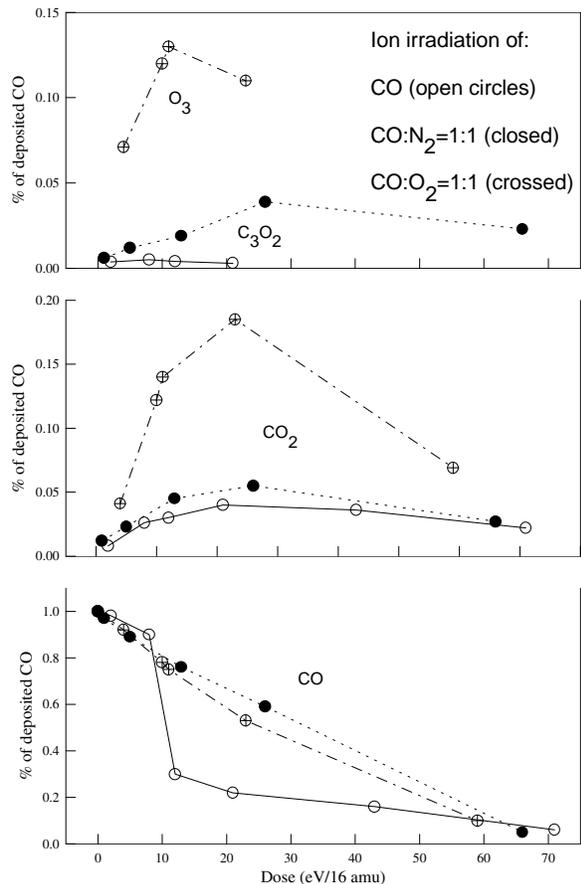
conclusion based only on the shape of the band has to be taken with caution.

Further information should be obtained from the measurement of the CO/CO<sub>2</sub> ratio in astronomical spectra and its comparison with laboratory data.

#### 4.4. Search for carbon suboxides

The experimental finding that bands attributed to suboxides are absent in an irradiated CO:O<sub>2</sub> mixture and have a different peak positions and FWHM in pure CO and in a CO:N<sub>2</sub> mixture can be used to trace the irradiation history of nonpolar species on icy mantles in which CO, probably directly condensed from the gas phase, is an abundant species. We have evaluated the integrated absorbance of the most intense band attributed to suboxides and find that their detection is possible. This can be also seen from Figs. 1 and 4, where a value on the order of 30 is measured for the ratio of the optical depths of CO/suboxides. In astronomical spectra the optical depth of the CO bands varies in a wide range and assumes, in some sources values greater than 1 (e.g. Tielens et al. 1991). As an example in NGC 7538 IRS 9 an optical depth of 2.6 has been measured. In that source an optical depth in the order of 0.09 is expected for the suboxide band.

Suboxides (C<sub>2</sub>O and C<sub>3</sub>O) have been detected, in the gas phase, in dark clouds at abundances of about 10<sup>-5</sup>-10<sup>-6</sup> relative to CO (Ohishi et al. 1991). Gerakines et al. (1996), based on results of photoprocessing of pure CO, suggest that the desorption from icy grains mantles could be an important source



**Fig. 5.** The percentages of the major produced species, with respect to the initially deposited CO, are reported vs irradiation dose. Data refer to irradiation of pure CO, and of 1:1 mixtures of CO with N<sub>2</sub> and O<sub>2</sub>. Lines have been drawn only to guide the eye.

for the observed gas phase abundance. In any case it seems unlikely that condensation from the gas phase could explain their presence on icy mantles. Thus their detection in the solid phase could imply a formation via energetic processing.

On the basis of our results we should be able to infer the presence of molecular oxygen and/or nitrogen on icy mantles. The detection of bands due to suboxides would discriminate, from their peak position and shape, between mantles dominated by CO and mantles in which molecular nitrogen is an important constituent. The absence of suboxides and the detection of ozone would indicate a dominance of molecular oxygen. However the detection of the most intense ozone band at around 1040 cm<sup>-1</sup> is difficult due to the strong silicate absorption band. Moreover a direct observation of molecular oxygen, as suggested by Ehrenfreund et al. (1992), could be also possible.

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