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Ion irradiation of ices: astrochemical and astrobiological applications

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Abstract. We present some recent results obtained by an ongoing research that aims into the experimental study of the effects induced by fast ions in solids, in particular frozen gases. The technique used to analyze the effects of irradiation has been "in situ" infrared spectroscopy.
Here we discuss the formation of carbon chain oxides (e.g. C_3O_2) after ion irradiation of frozen CO. A detailed study of the IR spectroscopic properties of solid frozen formamide is presented along with the modifications induced by ion irradiation. The results are relevant to explain the presence of molecules in the circumstellar environment of a newly born star. Those molecules could be produced by energetic processing of dust and released to the gas phase after warming up.

Key words. Astrochemistry- Astrobiology - methods: laboratory - Interstellar dust- Planets and satellites- techniques: spectroscopic

1. Introduction

Solids in space are made of refractories (mostly silicates and carbons) and ices that are continuously subjected to energetic processing. Among these ion irradiation plays, in some instances, a relevant role. The study of the induced effects and their relevance in astrophysical environments has been based on laboratory simulations of relevant targets irradiated by fast charged particles under physical conditions that mimic the astrophysical ones.

Fast ions penetrating matter release their energy to the target material. As a consequence many molecular bonds are broken along the ion-track and, in a very short time (one picosec or less), radical and molecular fragments recombine giving rise to a rearrangement in the chemical structure. Thus, in addition to the alteration of the chemical and lattice structure of the target material, new molecular species (not present before irradiation) may be formed. Our group has been involved for 25 years in the experimental study of the effects induced by fast ions in solids, in particular frozen gases. The techniques used to analyze the effects of irradiation are Infrared, Raman and UV-Vis-NIR spectroscopy (e.g., Strazzulla et al. 2001).

When occasionally (e.g. in the circumstellar environment of a newly born star) dust is warmed up, those newly formed molecules are released into the gas phase. Some of them are so complex to produce an organic refractory

Send offprint requests to: G. Strazzulla residue. The competition between the sketched route for the molecular synthesis and the gas-phase chemistry is one of the "hot" arguments of the astro-chemistry or even of the astro-biology when the synthesized species are thought to play a role in the (pre)-biological evolution.

Here some results recently obtained from laboratory experiments are summarized, in particular:

- the synthesis of carbon chain oxides after ion irradiation of frozen CO
- a quantitative study of the IR spectroscopic properties of low T solid formamide, a molecule particularly relevant to astrobiology, before and after ion irradiation.

2. Experimental apparatus

The experimental results reported in this paper have been obtained using in situ infrared (IR) spectroscopy (e.g., Strazzulla et al. 2001) performed in a stainless steel vacuum (better than 10^{-7} mbar) chamber facing an FTIR spectrometer. Inside the chamber an IR transparent substrate (usually crystalline silicon) is in thermal contact with a cold finger (10-300 K). A needle valve allows to admit pre-prepared gases (here CO) or vapour present in a flask containing a liquid substance (here formamide) into the chamber, where they freeze on the substrate. The vacuum chamber is interfaced with an ion implanter (200 kV; Danfysik) from which ions with energy up to 200 keV (400 keV for double ionizations) can be obtained. The substrate holder forms an angle of 45^o both with the ion beam and with the IR beam, so that spectra can be easily taken in situ, even during irradiation, without tilting the sample. For this purpose the IR spectrometer is positioned (by a moveable optical bench) such that the IR beam is transmitted, through a hole in the sample holder, by the substrate. Spectra shown in the following are ratioed to the background spectrum and have been obtained with a resolution of 1 cm^{-1}.

In this work we used 200 keV H^+ ions. In order to avoid macroscopic heating of the targets the current density was maintained low enough (from 100 nA cm^{-2} to a few μA cm^{-2}). The ion fluence in ions cm^{-2} is measured by a charge integrator and monitored during irradiation.

200 keV H^+ ions penetrate about 2 μm in CO or in formamide, calculated using the TRIM program (Transport of Ions in Matter; e.g., Ziegler 1977; Ziegler et al. 1996). The thickness of deposited layers was always thinner than the penetration depth of incoming ions. As usual we express the irradiation dose in eV/16amu (for details see Strazzulla et al. 2001).

3. The synthesis of carbon chain oxides

Laboratory experiments have shown that carbon chain oxides (e.g. CCO, C_3O, C_3O_2, C_4O, C_5O_2, C_7O_2) are formed after ion irradiation and UV photolysis of CO-rich ice mixtures (e.g., Strazzulla et al. 1997; Gerakines & Moore 2001; Trottier & Brooks 2004; Loeffler et al. 2005) along with carbon dioxide (CO_2) which is the most abundant species formed. Figure 1 shows the spectrum of pure carbon monoxide in the 2500-1900 cm^{-1} spectral range at 16 K before and after ion irradiation with 200 keV H^+. The highest ion fluence was 1.5×10^{15} ions cm^{-2}. It is evident that after irradiation several new absorption features are present which indicate the formation of molecular species not present in the original ice sample. In Figure 1 the intense CO band at about 2139 cm^{-1} and the CO_2 band at about 2343 cm^{-1} are out of scale. Main carbon chain oxides bands formed after irradiation are also labeled. After irradiation the sample has been warmed up and spectra have been taken at different temperatures (Figure 2). It is evident that all features decreases in intensity indicating subliamtion of the molecules present in the icy sample.

In dense molecular clouds during the collapse phase high CO depletion is observed and it is believed that gas phase CO freeze out on dust grains forming CO-rich icy grain mantles. It is generally accepted that icy grain mantles suffer from cosmic ion and UV irradiation during the collapse phase and up to the sublimation phase caused by the new formed protostellar object. When sublimation takes place

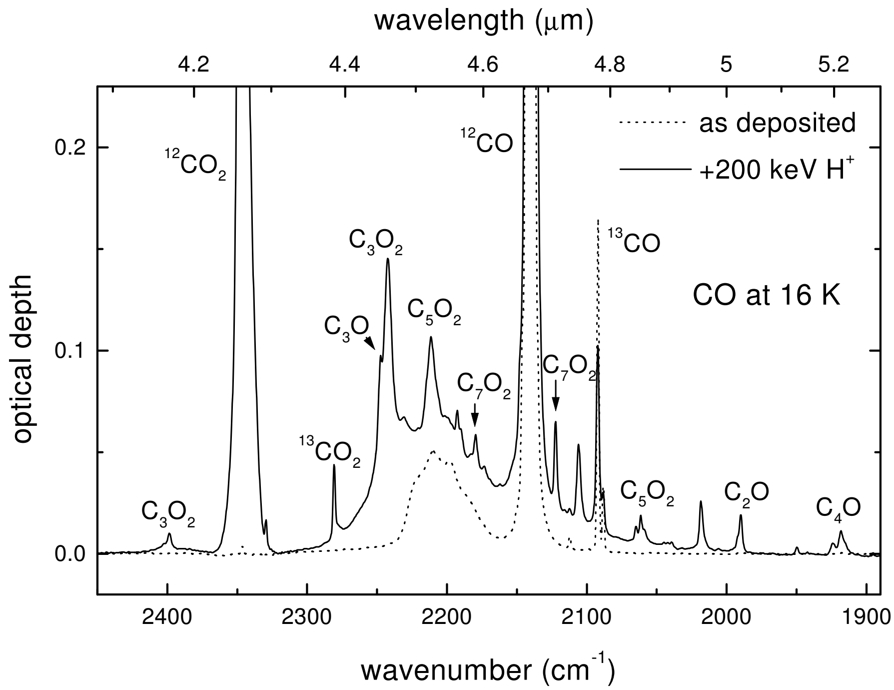

Fig. 1. IR transmittance spectrum (2500-1870 cm^{-1}; 4.00-5.35 μm), in optical depth scale, of carbon monoxide as deposited at 16 K on a KBr substrate before and after irradiation with 200 keV H$^+$ ions.

volatile species, such as CO, are released back to the gas phase along with all other molecular species formed during irradiation of icy mantles. Detection of gas phase CCO and C_3O in the cold, dark cloud TMC-1 has been reported (Matthews et al. 1984; Brown et al. 1985; Ohishi et al. 1991; Kaifu et al. 2004) and it has been estimated that fractional abundance of CCO values about 6×10^{-11} and that of C_3O values about 1.4×10^{-10}. Furthermore it has been shown that carbon chain oxides could be formed after ion-molecule gas phase reactions. A quantitative analysis of laboratory experiments here presented has shown that an amount of CCO and C_3O compatible with that observed towards the TMC-1 cloud can in fact be formed after ion irradiation of CO icy mantles. Based on these laboratory results we suggest that carbon chain oxides observed in dense molecular clouds can be formed in the solid phase after irradiation of CO ice mantles and can be released to the gas phase after sublimation of volatile mantles (Trigilio et al. 2007).

4. Formamide

The role of formamide ($HCONH_2$)as prebiotic precursor for the synthesis of nucleic acids bases has been shown under a variety of conditions (e.g. Saladino et al. 2003, 2004, 2005). It has been observed as a gas phase molecule in different environments: in interstellar medium (Millar 2004), in the long period comet C/1995 O1 Hale-Bopp (Bockele-Morvan 2000) and, tentatively, in young stellar object W33A (Schutte et al. 1999) and NGC 7538 IRS9 (Raunier et al 2004).

In a recent paper Brucato et al. (2006) measured the absorbances of the major IR bands of frozen formamide and the results of

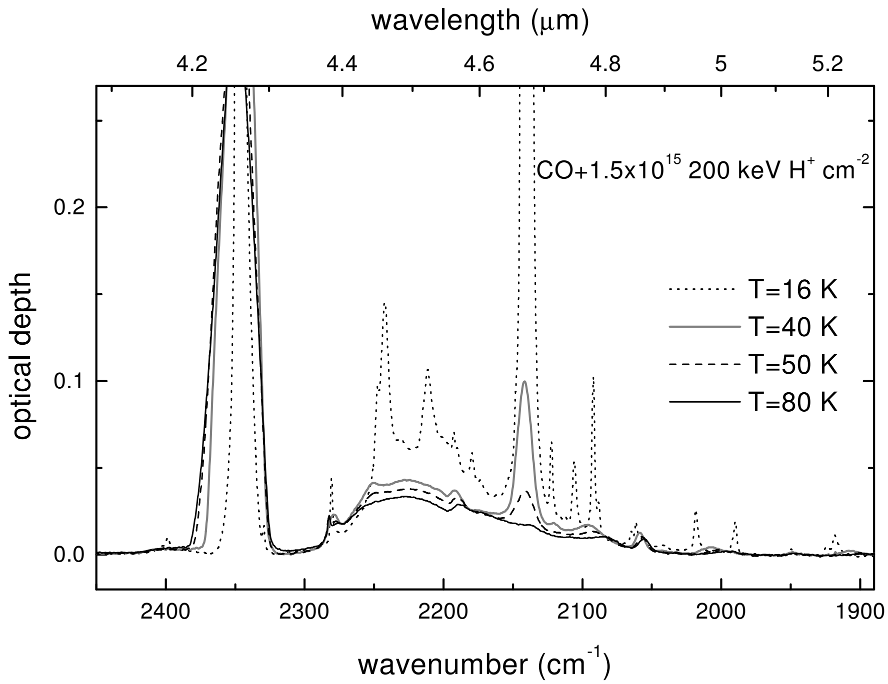

Fig. 2. IR transmittance spectra (2500-1870 cm^{-1}; 4.00-5.35 μm), in optical depth scale, of carbon monoxide irradiated at 16 K with 200 keV H^+ ions and after warm-up at 40, 50 and 80 K.

200 keV H^+ ion irradiation experiments. New molecules have been synthesized and identified in the spectra.

Figure 3 shows two spectra of ($HCONH_2$) before and after irradiation with 200 keV H^+ ions (12 eV/16 amu) at 20 K in the 2500-1250 cm^{-1} range. The peak positions of fundamental vibrational modes of formamide and their assignments are reported in Table 1 along with the measured integrated absorbances.

From figure 3 it is clear the presence, after ion irradiation, of new bands whose peak positions and identification is reported in Table 2. In the 2430-1800 cm^{-1} spectral region CO and CO_2 are easily identified. The band observed at 2260 cm^{-1} testifies for the synthesis of isocyanic acid (HNCO). The weak band at 2083 cm^{-1} is due to cyanate anion CN^-. The presence of the SiH stretching band is due to the fraction of protons that cross entirely the ice sample and implant into the silicon substrate. Another intense band, located at 2165 cm^{-1} is commonly assigned to cyanate anion OCN^- (Grim and Greenberg 1987, Hudson et al. 2001, Broekhuizen et al. 2004). The ammonium cyanate complex $NH_4^+OCN^-$ is evidenced by the wide band at 1478 cm^{-1} which is ascribed to NH_4^+ (Raunier et al. 2004).

It is important to note that the species produced after irradiation are mostly the same of those produced in a large number of irradiation experiments conducted by different groups on different icy mixtures containing simple H, O, C, and N bearing molecules.

Irradiated samples have been occasionally warmed up from 20 K to room T (about 1 K/min). This induces a differential evaporation of species having different volatilities. In Figure 4 the IR spectra of formamide as deposited, after irradiation at a dose of 24 eV/16amu at 20 K, and after warming up at 125 K and 220 K are shown. Spectra have been arbitrarily shifted for clarity. It is evident that the volatile species are desorbed while the bands

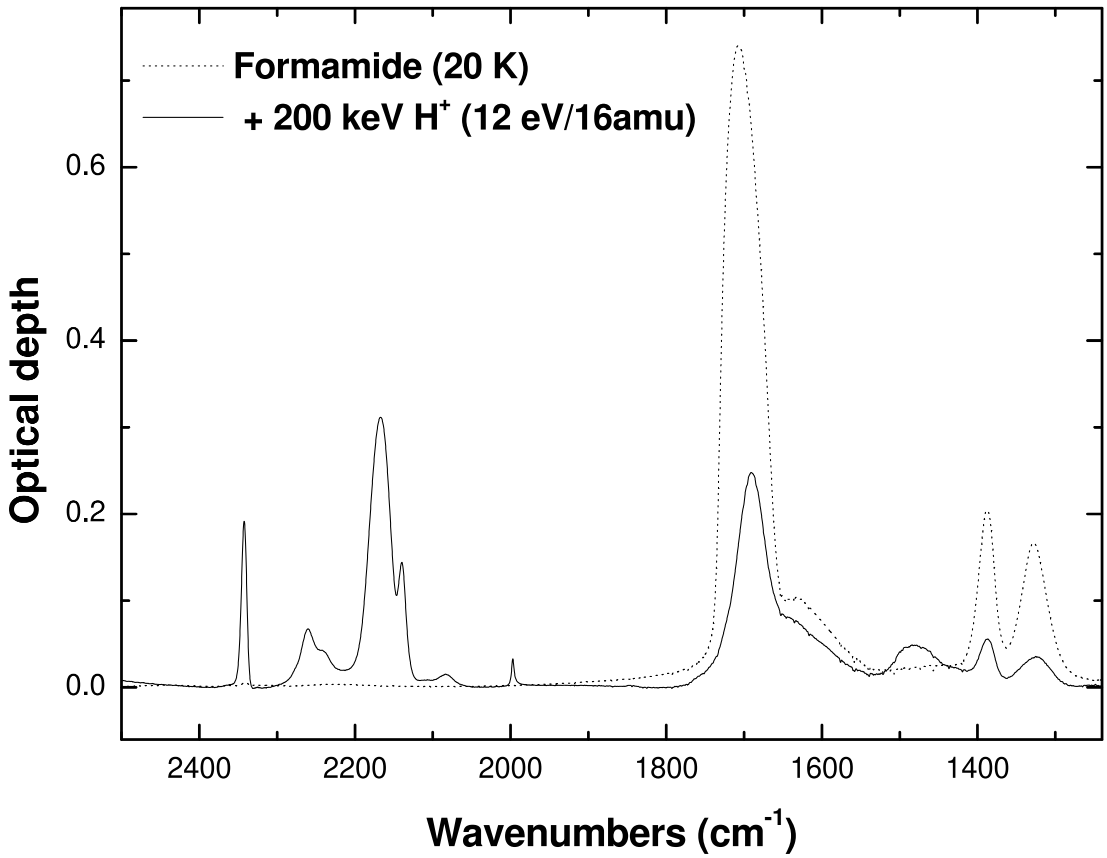

Fig. 3. IR transmittance spectra (2500-1250 cm^{-1}; 4.00-8.00 μm), in optical depth scale, of formamide as deposited at 20 K on a silicon substrate (dot line) and after irradiation at a dose of 12 eV/16amu with 200 keV H^+ ions (full line).

Table 1. Peak position, vibration assignments and integrated absorbances of frozen (20 K) amorphous formamide.

Peak position			Integrated absorbance
cm^{-1}	μm	Assignment	($\times 10^{-17}$cm mol^{-1})
1708	5.85	ν_4 CO stretch	6.54 (ν_4+ν_5)
1631	6.13	ν_5 in plane NH_2 sc.	
1388	7.2	ν_6 in plane CH sc.	0.68
1328	7.53	ν_7 CN stretch	0.85

of ammonium cyanate are left over. Spectral profile of $NH_4^+OCN^-$ is in agreement with that measured by reaction at 10 K of co-deposited NH_3 and HNCO (Raunier et al. 2004). During

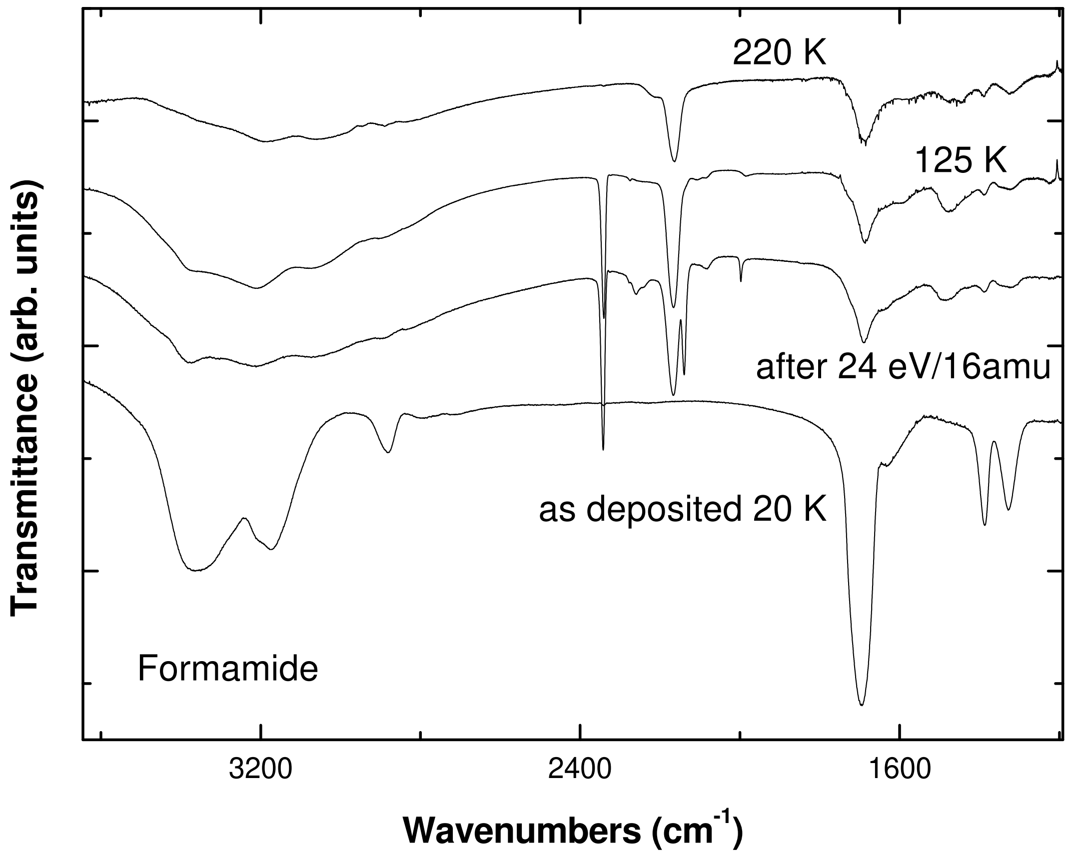

Fig. 4. Comparison of the spectra of (from the bottom to the top): formamide as depositedat 20 K, after irradiation at a dose of 24 eV/16amu, and after warming up at 125 K and 220 K. Spectra have been arbitrarily shifted for sake of clarity.

warming up the increased mobility of those molecules may favor their reaction into ammonium cyanate. Further features observed in the Figure 4 at 220 K correspond to crystalline formamide (Brucato et al. 2006).

The results here presented might have relevant astrophysical application. The reported measurements of integrated absorbances allows to measure the abundance of formamide synthesized in laboratory experiments or observed in the solid phase in astrophysical environments. By the way formamide has been synthesized by UV photolysis and proton irradiation of HCN containing ices (Gerakines et al. 2004) or by UV irradiation of HNCO ice (Raunier et al. 2004) and H_2O, CO, NH_3 ice mixtures (Demyk et al. 1998, Broekhuizen et al. 2004) but it was not possible to have a precise determination of the amount of synthesized formamide just because of the lack of measured integrated absorbances.

If the detection of solid formamide in protostellar sources (Raunier et al. 2004) is confirmed, the experimental results on ion pro-

Table 2. Peak positions, vibration modes and molecule assignments of newly formed IR bands after irradiation of formamide at 20 K with 200 keV H^+ ions.

Peak position			
cm^{-1}	μm	Vibration	Assignment
2342	4.27	C=O stretch	CO_2
2260	4.42	$N{=}C{=}O_{asym.}$ stretch	HNCO
2238	4.47	N=N stretch	N_2O
2165	4.62	$N{=}C{=}O_{asym.}$ stretch	OCN^-
2140	4.67	C≡O stretch	CO
2083	4.80	C≡N stretch	CN^-
1997	5.01	Si-H stretch	SiH
1478	6.77	$N\text{-}H_{sym.}$ bending	NH_4^+

cessing of formamide ice have to be considered when astronomical and laboratory spectra are compared. In fact the flux of low energy cosmic rays irradiating grains in the interstellar medium is enough to produce the effects that have been simulated in the laboratory.

5. Conclusion

We have presented some experimental results obtained after ion irradiation of frozen CO (in particular the synthesis of carbon chain oxides) and formamide (in particular the synthesis of ammonium cyanate).

Cosmic ion irradiation of solids in circumstellar environments of young stars or in the dense interstellar medium has been simulated. After irradiation, warming up the target causes the sublimation of volatile molecules. This simulates the thermal processing suffered by the dust near a forming star.

The results suggest that if the delivery on the early Earth by comets, meteorites and IDPs of organic compounds favored the origin of life, then we have to deal with the search of plausible pathways for the synthesis of biomolecules in space at low temperature. Ion and photon processing of ices containing H, C, N, and O shows a specificity in driving the chemistry in space that requires to be investigated in details.

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References

Bockelée–Morvan, D., Lis, D. C., Wink, J. E., & al. 2000, A&A 353, 1101.

Brown R.D., Godfrey P.D., Cragg D.M., et al., 1985, 297, 302.

Brucato J.R., Baratta, G.A., Strazzulla G., 2006, A&A, 455, 395.

van Broekhuizen, F.A., Keane, J. V., & Schutte W. A. 2004, A&A 441, 249.

Demyk, K., E. Dartois, L. d'Hendecourt, & al., 1998, A&A 339, 553.

Gerakines P.A., & Moore M.H., 2001, Icarus, 154, 372.

Gerakines, P.A., Moore, M. H., & Hudson, R.L. 2004, Icarus, 170, 202.

Grim, R. J. A., & J. M. Greenberg 1987, ApJ, 321, L91.

Hudson, R. L., M. H. Moore, & Gerakines, P. A. 2001, 550, 1140.

Kaifu N., Ohishi M., Kawaguchi K., &, 2004, Publ. Astron. Soc. Japan, 56, 69.

Loeffler M.J., Baratta G.A., Palumbo M.E., Strazzulla G., & Baragiola R., 2005, A&A, 435, 587.

Matthews H.E., Irvine W.M., Friberg P., Brown R.D., & Godfrey P.D., 1984, Nature, 310, 125.

Millar, T.J. 2004, Organic molecules in the interstellar medium. In Astrobiology: future perspectives, ed. P. Ehrenfreund, W. Irvine, T. Owen, L. Becker, J. Blank, J.R. Brucato, L. Colangeli, S. Derenne, A. Dutrey, D. Despois, A. Lazcano, F. Robert, Kluwer Academic Publisher vol. 305, 17.

Ohishi M., Suzuki H., Ishikawa S., & al., 1991, ApJ, 380, L39.
Raunier, S., Chiavassa, T., Duvernay, F., Borget, F.,m Aycard, J.P., Dartois, E., & d'Hendecourt, L. 2004, A&A 416,165.
Saladino, R., Ciambecchini, U., Crestini, C., Costanzo, G., Negri, R., & Di Mauro E. 2003, ChemBiochem 4, 514.
Saladino, R., Crestini, C., Costanzo, G., & Di Mauro, E. 2004, Cour. Org. Chem. 8, 1425.
Saladino, R., Crestini, C., Neri, V., Brucato, J.R., Colangeli, L., Ciciriello, F., Di Mauro, E., & Costanzo, G. 2005, ChemBioChem 6, 1368.
Schutte, W.A., Boogert, A.C.A., Tielens, A.G.G.M., Whittet, D.C.B., Gerakines, P.A., Chiar, J.E., Ehrenfreund, P., Greenberg, J.M., van Dishoeck, E.F., & de Graauw, Th. 1999, A&A 343, 966.
Strazzulla G., Brucato J.R., Palumbo M.E., & Satorre M.A., 1997, A&A, 321, 618.
Strazzulla, G., Baratta, G. A., & Palumbo, M. E. 2001, Spectrochim. Acta A, 57, 825.
Trigilio C., Palumbo M.E., Siringo C., & Leto P., 2007, ApSS, in press.
Trottier A., & Brooks R.L., 2004, ApJ, 612, 1214.
Ziegler, J. F. 1977, The Stopping and Range of Ions in Matter. V. 2–6. Pergamon Press, New York.
Ziegler, J. F., J. P. Biersack, & U. Littmark 1996, The Stopping and Range of Ions in Solids, Pergamon Press, New York.