

Infrared spectra of CO₂ in H₂O:CH₃OH:CO₂ icy mixtures

M.E. Palumbo and G.A. Baratta

Osservatorio Astrofisico di Catania, Via S. Sofia 78, 95123 Catania, Italy

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Abstract. We have studied by laboratory infrared spectroscopy the profile of the CO₂ absorption bands in different H₂O:CH₃OH:CO₂ mixtures. Icy mixtures have been accreted on a substrate at 12.5 K inclined of 45 degrees with respect to the infrared beam of the spectrometer. Spectra have been taken with the electric vector of the infrared beam parallel (P polarized) and perpendicular (S polarized) to the plane of incidence. The samples have been warmed up and spectra have been taken at different temperatures. We confirm CO₂ segregation after warm-up. Furthermore we find that when segregation occurs the profile of CO₂ bands are different in the two different polarization cases. As shown by Baratta et al. (2000) this means that these laboratory spectra cannot be directly compared to the astronomical spectra.

Key words: methods: laboratory – ISM: molecules – ISM: dust, extinction – infrared: ISM: lines and bands

1. Introduction

Laboratory experiments and theoretical calculations had predicted and ISO observations have confirmed the presence of solid carbon dioxide (CO₂) in icy grain mantles in dense molecular clouds. It has been estimated that the solid CO₂ abundance is ~10–23% with respect to water ice (e.g., Gerakines et al. 1999).

The profile of the band due to the CO₂ bending mode (at 15.1 μm) observed towards several embedded objects (e.g., de Graauw et al. 1996; Ehrenfreund et al. 1997a; Gerakines et al. 1999) is characterized by a considerable structure with sub-peaks. Preliminary comparisons of laboratory spectra of icy mixtures containing CO₂ with ISO spectra (de Graauw et al. 1996) have shown that it is not possible to find a single laboratory spectrum which fits the CO₂ observed bands and it has been suggested that the observed features are due to the sum of at least two independent components, namely CO₂ mixed in polar and non polar matrices. Alternatively, Strazzulla et al. (1998) have considered solid CO₂ produced after ion irradiation of ice

mixtures containing C-bearing and O-bearing species. In particular they have fitted the bending mode of solid CO₂ observed towards the embedded source NGC7538 IRS1 with laboratory spectra of CO₂ produced by ion irradiation of CO at 10 K and warmed-up to 40 K and CO₂ produced in a H₂O:CH₃OH mixture. These mixtures are consistent with those used to fit the profile of the CO band at about 2140 cm⁻¹ (4.67 μm; Palumbo & Strazzulla 1993; Teixeira et al. 1998). Recently, Ehrenfreund et al. (1998, 1999), Gerakines et al. (1999) and Boogert et al. (2000) have analysed a large sample of high resolution ISO spectra. They have compared the profile of the stretching and bending mode of solid CO₂ and the stretching mode of ¹³CO₂ with several laboratory spectra of CO₂-containing icy mixtures. Based on these comparisons it has been suggested that an ice mixture of H₂O, CO₂ and CH₃OH in similar proportions is present on grains close to massive protostars and that thermal processing which induces ice segregation is responsible of the observed features.

Here we present the results of a new experimental study of the profile of the CO₂ bands at about 2340 cm⁻¹ (4.27 μm; ¹²CO₂ asymmetric stretching mode), 2280 cm⁻¹ (4.38 μm; ¹³CO₂ asymmetric stretching mode), 660 cm⁻¹ (15.1 μm; ¹²CO₂ bending mode) in different H₂O:CH₃OH:CO₂ ice mixtures. Icy samples have been deposited at 12.5 K and spectra have been taken with the electric vector of the infrared beam parallel (P polarized) and perpendicular (S polarized) to the plane of incidence. The samples have also been warmed up and spectra taken at different temperatures.

2. Experimental set-up

The infrared spectra here shown have been taken in the 4400–500 cm⁻¹ (2.27–20 μm) range with either a Perkin-Elmer (model 1710) or a Bruker Equinox 55 FTIR spectrometer. A stainless steel vacuum chamber (shown in Fig. 1) faces the spectrometer through KBr windows. Gases are accreted by a gas inlet on a silicon (or KBr) substrate inclined of 45 degrees with respect to the infrared (IR) beam of the spectrometer. The substrate is put in thermal contact with a closed-cycle helium cryostat whose temperature can be varied in the 10–300 K range. For each sample, at all the examined temperatures, two spectra with the electric vector of the infrared beam parallel (P polarized) and

Send offprint requests to: M.E. Palumbo
(mepalumbo@alpha4.ct.astro.it)

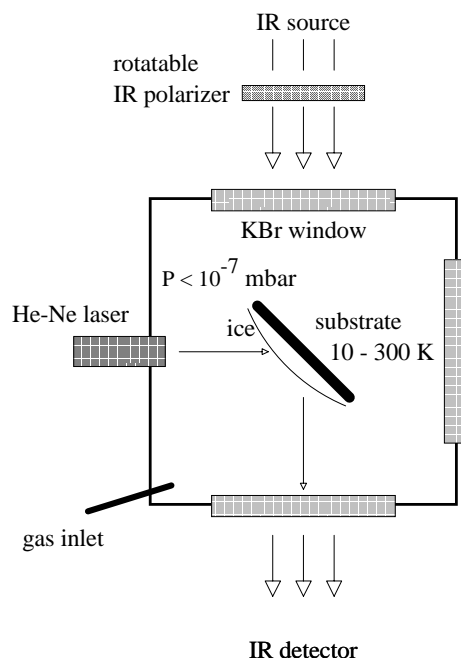


Fig. 1. Schematic view of the experimental set-up

perpendicular (S polarized) to the plane of incidence have been taken where the polarization of the infrared radiation is changed by rotating a polarizer placed in the path of the infrared beam (Fig. 1). All the spectra for a given polarization are ratioed to the corresponding spectrum of the background acquired before deposition. Unless when differently specified, spectra have been taken at a resolution of 1 cm^{-1} and sampling of 0.25 cm^{-1} . For a detailed description of the experimental procedure the reader is referred to Baratta & Palumbo (1998).

3. Experimental results

We have studied the profile of the absorption bands due to solid CO₂ in different H₂O:CH₃OH:CO₂ ice mixtures as deposited at 12.5 K and after warm-up. Detailed studies of the CO₂ bands profile in thin film icy mixtures have been recently published (Sandford & Allamandola 1990; Ehrenfreund et al. 1999; Dartois et al. 1999; Boogert et al. 2000). All these studies have been carried out with the substrate plane perpendicular to the infrared beam of the spectrometer (normal incidence). Here we present spectra taken with the sample inclined of 45 degrees with respect to the IR beam of the spectrometer and in both P and S polarizations. It has been shown (Baratta et al. 2000) that spectra taken in S polarized light are equivalent to those taken at normal incidence. Baratta & Palumbo (1998) have shown that when the spectrum is taken at oblique incidence in two different polarizations it is possible to clearly evaluate the contribution of reflection in the profile of the bands. Indeed reflection gives rise to additional features in the spectrum. Furthermore it has been shown that some instances exist for which the IR band absorption profiles of thin films at oblique incidence depend on the polarization of the IR beam of the spectrometer (e.g., Berreman 1963; Jones & Swanson 1991; Baratta et al. 2000). For

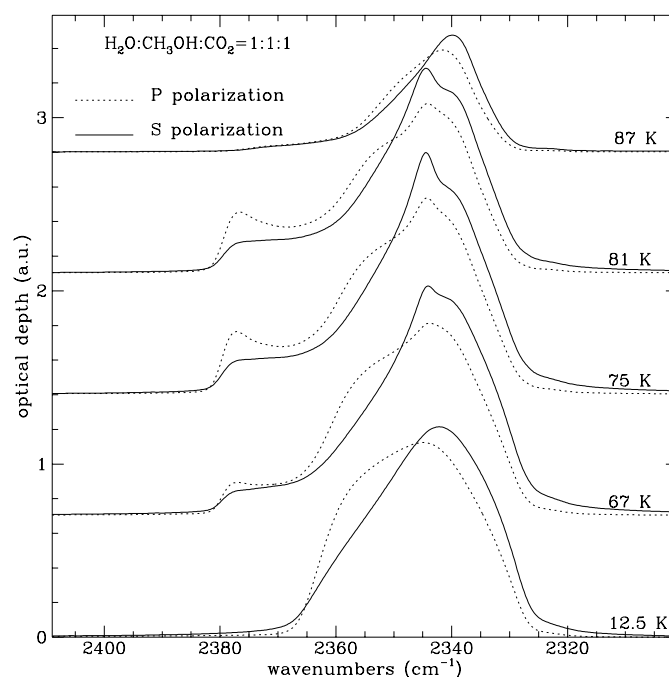


Fig. 2. Infrared spectra of the CO₂ stretching mode in a H₂O:CH₃OH:CO₂=1:1:1 mixture taken in P (dotted lines) and S (solid lines) polarized light at 12.5 K and after warm-up. Spectra have been shifted upward by 0.7 in the optical depth scale, for clarity.

example, this is the case for the fundamental vibration modes of solid CO, CO₂, and CH₄ (e.g., Parker & Eggers 1966; Zomfoten 1978; Jones & Swanson 1991; Baratta & Palumbo 1998) and, in general, depends on the optical constants (n , k). When this occurs laboratory spectra are no longer representative of small particles extinction cross sections.

3.1. The ¹²CO₂ asymmetric stretching mode

Fig. 2 shows the profile of the CO₂ stretching mode in a H₂O:CH₃OH:CO₂=1:1:1 mixture at different temperatures in both P and S polarizations. It is evident that the profiles at the same temperature in the two polarizations are different. After warm-up the profiles are modified due to CO₂ segregation (e.g., Ehrenfreund et al. 1999). In the S polarization case peak position shifts from 2342 cm^{-1} (at 12.5 K) to 2344 cm^{-1} (at 80 K) and a shoulder appears at 2340 cm^{-1} . In the P polarization an additional feature appears at 2376 cm^{-1} . This latter feature is real, however it is not due to absorption (k) but to the increased reflectivity corresponding to the region across the absorption band where $n < 1$ (e.g., Osberg & Horning 1952; Baratta & Palumbo 1998). Similar results have been obtained for the mixtures H₂O:CH₃OH:CO₂=2:1:1 and 10:1:2 as well as for the mixtures H₂O:CO₂=1:1 and CH₃OH:CO₂=1:1.

Fig. 3 shows the profile of the CO₂ stretching mode in a H₂O:CH₃OH:CO₂=10:5:1 mixture at different temperatures in both P and S polarizations. In this case the profiles in the two different polarizations at any temperature are very similar indicating that when CO₂ is diluted in the mixture the effects due

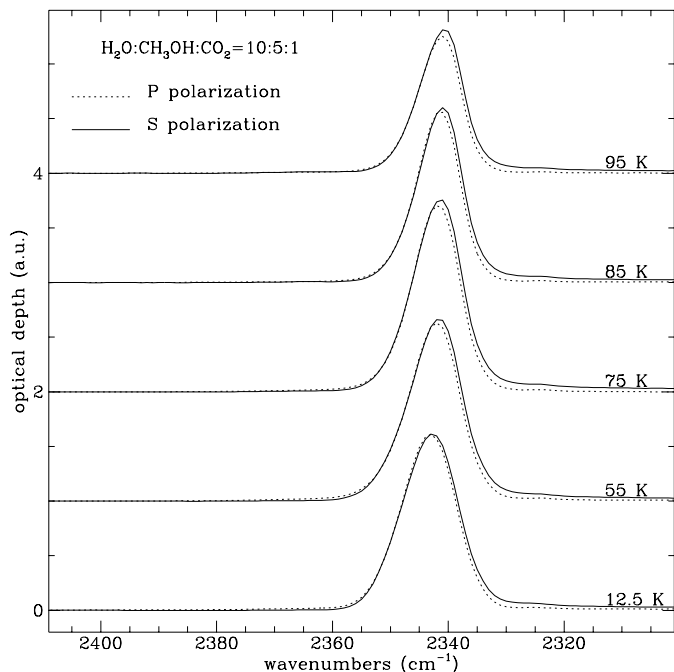


Fig. 3. Infrared spectra of the CO₂ stretching mode in a H₂O:CH₃OH:CO₂=10:5:1 mixture taken in both P (dotted lines) and S (solid lines) polarized light at 12.5 K and after warm-up. Spectra have been taken at a resolution of 2 cm⁻¹ and sampling of 1 cm⁻¹. Spectra have been shifted upward by 1 in the optical depth scale, for clarity.

to the reflectivity are negligible. Furthermore no modification of the profile occurs after warm-up (to 95 K) except than a slight shift in peak position showing that no CO₂ segregation occurs in diluted CO₂ mixtures. After warm-up to higher temperature (~120 K, not shown) a shoulder appears at about 2346 cm⁻¹. This blue shift indicates the formation of clathrate hydrates in the H₂O:CH₃OH=10:5 mixture where the small amount of CO₂ acts as a sensitive local probe (Blake et al. 1991).

3.2. The ¹³CO₂ asymmetric stretching mode

Fig. 4 shows the profile of the ¹³CO₂ stretching mode in a H₂O:CH₃OH:CO₂=1:1:1 mixture at different temperatures in both P and S polarizations. In this case the profiles in the two different polarizations at any temperature are very similar. However the profiles are modified after warm-up. In particular peak position shifts from 2277 cm⁻¹ (at 12.5 K) to 2275 cm⁻¹ (at 80 K) and a narrow feature appears at 2282 cm⁻¹. This feature is present in both polarizations indicating that it is due to absorption (*k*). Indeed it is due to CO₂ segregation in the icy mixture (Boogert et al. 2000). Similar results have been obtained for the mixtures H₂O:CH₃OH:CO₂=2:1:1 and 10:1:2. We have also studied the profile of the ¹³CO₂ stretching mode in a H₂O:CH₃OH:CO₂=10:5:1 mixture at different temperatures in P and S polarizations. Again the profiles in the two polarizations at any temperature are the same. Furthermore, after warm-up peak position shifts from 2278 cm⁻¹ (12.5 K) to 2275 cm⁻¹ (95 K) while no other features appear.

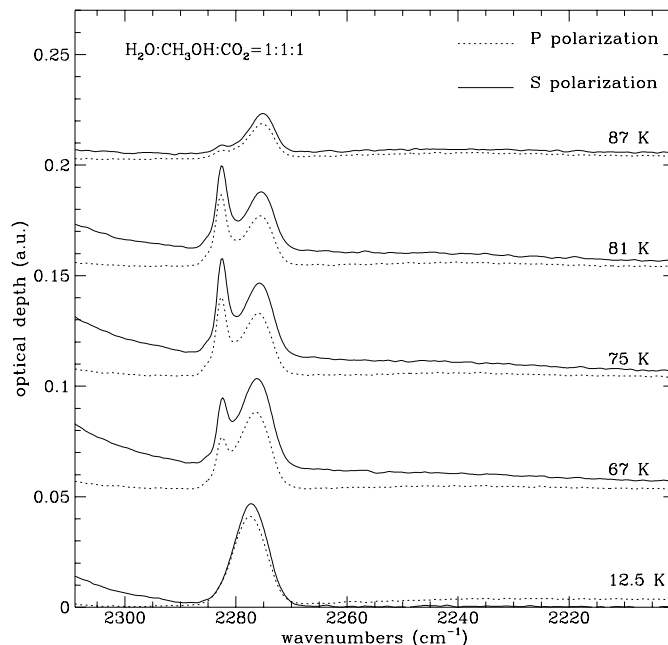


Fig. 4. Infrared spectra of the ¹³CO₂ stretching mode in a H₂O:CH₃OH:CO₂=1:1:1 mixture taken in P (dotted lines) and S (solid lines) polarized light at 12.5 K and after warm-up. Spectra have been shifted upward by 0.05 in the optical depth scale, for clarity.

3.3. The ¹²CO₂ bending mode

Fig. 5 shows the profile of the bending mode in a H₂O:CH₃OH:CO₂=1:1:1 ice mixture at different temperatures in the spectra taken in the two polarizations (S and P). It is evident that spectra in the two polarizations are different. After warm-up above 60 K CO₂ segregation occurs and the profile of the band changes. A double peak appears at 660 cm⁻¹ and 655 cm⁻¹. This is characteristic of pure or annealed CO₂ (Sandford & Allamandola 1990; Ehrenfreund et al. 1997b). The shoulder at 649 cm⁻¹ already present at 12.5 K, is attributed to a Lewis acid-base complex between carbon dioxide and methanol molecules (Dartois et al. 1999). Furthermore the P polarized spectra exhibit a feature at 675 cm⁻¹ that is not present in the S polarized spectra. Similarly to the feature at 2376 cm⁻¹, this feature is real, however it is not due to absorption (*k*) but to the increased reflectivity corresponding to the region across the absorption band where *n* < 1. Similar results have been obtained for the mixtures H₂O:CH₃OH:CO₂=2:1:1 and 10:1:2 as well as for the mixtures H₂O:CO₂=1:1 and CH₃OH:CO₂=1:1. Again in a H₂O:CH₃OH:CO₂=10:5:1 ice mixture the profile of the bending mode at different temperatures in the spectra taken in the two polarizations are the same and no evident modifications occur after warm-up in the 65–85 K range.

4. Discussion

We have presented the results of a study of the profile of the CO₂ bands in H₂O:CH₃OH:CO₂ ice mixtures as deposited at 12.5 K and after warm-up. Mixtures studied are H₂O:CH₃OH:CO₂=1:1:1, 2:1:1, 10:1:2 and 10:5:1,

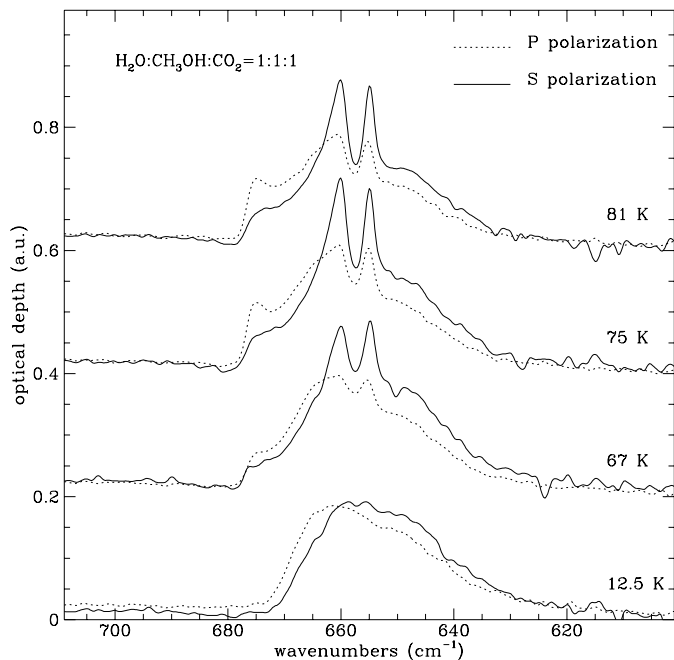


Fig. 5. Comparison between the profiles of the CO₂ bending mode in a H₂O:CH₃OH:CO₂=1:1:1 mixture taken in the two polarizations (P and S) at 12.5 K and after warm-up. Spectra have been shifted upward by 0.2 in the optical depth scale, for clarity.

H₂O:CO₂=1:1 and CH₃OH:CO₂=1:1. In all cases the profile of the studied bands (i.e., ¹²CO₂ asymmetric stretching mode, ¹³CO₂ asymmetric stretching mode and ¹²CO₂ bending mode) shows a clear modification after warm-up. This modification of the profile indicates a change in the structure of the ice which is referred to as segregation (Blake et al. 1991; Ehrenfreund et al. 1999; Dartois et al. 1999; Boogert et al. 2000). In the case of the 10:5:1 mixture, that is when CO₂ is a minor component in the mixture, no CO₂ ice segregation takes place (Blake et al. 1991). We have estimated that CO₂ segregation occurs after warm-up when the relative abundance of CO₂ is greater than about 10%. Spectra shown indicate that CO₂ ice segregation occurs in the 65–85 K range. In fact at about 85 K the features associated with segregation disappear and most of CO₂ sublimates (see also Sandford & Allamandola 1990; Dartois et al. 1999). Sublimation of CO₂ occurs at higher temperature in the 10:5:1 mixture where no CO₂ segregation is observed. In the CH₃OH:CO₂=1:1 mixture CO₂ segregation starts at about 65 K however CO₂ is not released at 85 K but remains trapped in the ice as a segregate up to the crystallization temperature of methanol.

In this work infrared spectra have been taken in two different polarizations (P and S) and it has been shown that in the case of ¹²CO₂ stretching and bending modes when ice segregation takes place, spectra in the two polarizations are different. Furthermore features at 2375 and 675 cm⁻¹ appear in the two spectral regions in the P polarization case. It has been shown (Baratta et al. 2000) that these features are absent in spectra taken at normal incidence. Furthermore Baratta & Palumbo (1998) have shown that these features are real. In fact for a number of molecular

solids as thin films the difference between the spectra taken at normal and oblique incidence is used for the determination of transverse and longitudinal optical mode frequencies (e.g., Jones & Swanson 1991; Ovchinnikov & Wight 1994).

In molecular clouds, ices form as mantles on grains. Also in the case of the interaction of light with small particles, features similar to those observed in laboratory spectra appear (whose position however depends on particle shape). In this case these additional features are due to absorption although they have the same origin (i.e., $k^2 - n^2$ value across the band) as those observed for thin films in laboratory (e.g., Ehrenfreund et al. 1997b; Baratta et al. 2000). Indeed laboratory experiments have shown that an absorption feature at about 2375 cm⁻¹ is present in the IR spectra of CO₂ clusters (Fleyfel & Devlin 1989; Dissekamp & Ewing 1993).

Baratta et al. (2000) have shown that when IR laboratory spectra of thin films depend on the incidence angle or at oblique incidence on the polarization of the IR beam of the spectrometer, then laboratory spectra are not representative of small particle extinction cross sections. If this is the case laboratory spectra of thin films cannot be directly compared to the astronomical spectra. Thus the comparison between laboratory spectra of segregated CO₂ with ISO spectra (e.g., Ehrenfreund et al. 1998, 1999; Gerakines et al. 1999; Dartois et al. 1999) gives questionable results. For a meaningful comparison optical constants of the segregated ice should be known. However as shown by Baratta & Palumbo (1998) the measurement of reliable optical constants of icy mixtures is not straightforward. Of course the conclusions here drawn do not exclude that thermal processing and annealing take place in icy mantles but simply that the comparison with laboratory spectra cannot prove it and in particular no information on icy mixture and temperature of grain mantles can be derived from these comparisons.

This conclusion does not apply to the ¹³CO₂ stretching profile which in fact is the same in P and S polarization and hence laboratory spectra can be directly compared to astronomical ones. However for this absorption feature heating of the ice has the same effect on the band profile as increasing the H₂O/CO₂ and CH₃OH/CO₂ mixing ratio (Boogert et al. 2000). Thus the ¹³CO₂ stretching mode is poorly suited to determine an accurate H₂O:CH₃OH:CO₂ mixing ratio or the precise temperature of the mixture.

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References

- Baratta G.A., Palumbo M.E., 1998, *J. Opt. Soc. Am. A* 15, 3076
- Baratta G.A., Palumbo M.E., Strazzulla G., 2000, *A&A* 357, 1045
- Berreman D.W., 1963, *Physical Rev.* 130, 2193
- Blake D., Allamandola L.J., Sandford S.A., Hudgins D., Freund F., 1991, *Science* 254, 548
- Boogert A.C.A., Ehrenfreund P., Gerakines P., et al., 2000, *A&A* 353, 349

- Dartois E., Demyk K., d'Hendecourt L., Ehrenfreund P., 1999, A&A 351, 1066
- de Graauw Th., Whittet D.C.B., Gerakines P., et al., 1996, A&A 315, L345
- Disselkamp R., Ewing G.E., 1993, J. Chem. Phys. 99, 2439
- Ehrenfreund P., d'Hendecourt L., Dartois E., et al., 1997a, Icarus 130, 1
- Ehrenfreund P., Boogert A.C.A., Gerakines P.A., Tielens, A.G.G.M., van Dishoeck, E.F., 1997b, A&A 328, 649
- Ehrenfreund P., Dartois E., Demyk, K., d'Hendecourt L., 1998, A&A 339, L17
- Ehrenfreund P., Kerkhof O., Schutte W.A., et al., 1999, A&A 350, 240
- Fleyfel F., Devlin J.P., 1989, J. Phys. Chem. 93, 7292
- Gerakines P.A., Whittet D.C.B., Ehrenfreund P., et al., 1999, ApJ 522, 357
- Jones L.H., Swanson B.I., 1991, J. Phys. Chem. 95, 2701
- Osberg W.E., Horning D.F., 1952, J. Chem. Phys. 20, 1345
- Ovchinnikov M.A., Wight C.A., 1994, J. Chem. Phys. 100, 972
- Palumbo M.E., Strazzulla G., 1993, A&A 269, 568
- Parker M.A., Eggers Jr. D.F., 1966, J. Chem. Phys. 45, 4354
- Sandford S.A., Allamandola L.J., 1990, ApJ 355, 357
- Strazzulla G., Nisini B., Leto G., Palumbo M.E., Saraceno P. 1998, A&A 334, 1056
- Teixeira T.C., Emerson J.P., Palumbo M.E., 1998, A&A 330, 711
- Zumofen G., 1978, J. Chem. Phys. 68, 3747