

# Carbon dioxide-methanol intermolecular complexes in interstellar grain mantles<sup>\*</sup>

E. Dartois<sup>1,2</sup>, K. Demyk<sup>2</sup>, L. d'Hendecourt<sup>2</sup>, and P. Ehrenfreund<sup>3</sup>

<sup>1</sup> Institut de Radioastronomie Millimétrique, 300 rue de la piscine, 38406 Saint Martin d'Hères, France

<sup>2</sup> Institut d'Astrophysique Spatiale, Bât. 121, Université Paris XI, 91405 Orsay Cedex, France

<sup>3</sup> Leiden Observatory, P.O. Box 9513, 2300 RA Leiden, The Netherlands

Received 24 March 1999 / Accepted 18 August 1999

**Abstract.** We present new laboratory data to interpret the Infrared Space Observatory (ISO) spectra of protostellar objects, and particularly RAFGL7009S. Our experimental results show that solid methanol and carbon dioxide exhibit specific intermolecular interactions. We propose the formation of a Lewis acid-base complex between carbon dioxide and methanol molecules to explain specific substructure of the 15.2  $\mu\text{m}$  CO<sub>2</sub> bending mode observed in different objects.

The various CO<sub>2</sub> bending mode patterns observed in many lines of sight can be interpreted as a combination of both this complex formation and the temperature evolution of the ices. The temperature induced segregation of ice mantles containing CO<sub>2</sub> can be monitored by the <sup>13</sup>CO<sub>2</sub> stretching mode shift toward the pure CO<sub>2</sub> ice position. The large width observed for this mode towards interstellar sources partly results from the different temperatures sampled along the line of sight.

Given the amount of methanol involved in RAFGL7009S, on the basis of ground based observations, we derive that about half of the so called “6.85  $\mu\text{m}$ ” band and a quarter of the 4.9  $\mu\text{m}$  bands can be accounted for by the deformation modes and 2 $\nu_8$  transitions of CH<sub>3</sub>OH.

**Key words:** ISM: abundances – ISM: individual objects: RAFGL 7009S – infrared: ISM: lines and bands

## 1. Introduction

The CO<sub>2</sub> bending mode, as observed with the ISO satellite, presents a pattern that significantly varies from one line of sight to another and can exhibit two to three distinct components at  $\sim 15.1$ ,  $\sim 15.25$  and  $\sim 15.4$   $\mu\text{m}$  (see de Graauw et al. 1996 and Fig. 1). These features were at first associated with possible absorption arising from other molecules present in the ice mantles, such as formic acid, whose  $\nu_9$  mode falls not far from the carbon dioxide bending mode. This particular hypothesis

can be rejected due to the absence, in the full spectrum, of the other formic acid modes, at least in strength compatible with the 15.2  $\mu\text{m}$  mode, such as a CO stretch around 1700  $\text{cm}^{-1}$ . Another hypothesis one may consider is the grain size and shape effects that could influence light absorption and scattering. For example, it is well known that scattering is responsible for the long wavelength wing of the water ice stretching mode at 3  $\mu\text{m}$  (Rouan & Leger 1984). Very specific grain shapes (e.g. needles) would cause an asymmetry in some bands, and in extreme cases give rise to apparent new features (Bohren & Huffman 1983). It is however difficult to imagine a strong effect arising at 15.2  $\mu\text{m}$ , a wavelength well above typical interstellar grain radii, when the CO<sub>2</sub> stretching mode as well as other solid state molecular absorptions in the infrared seem little affected (e.g. CH<sub>4</sub>, Dartois et al. 1998).

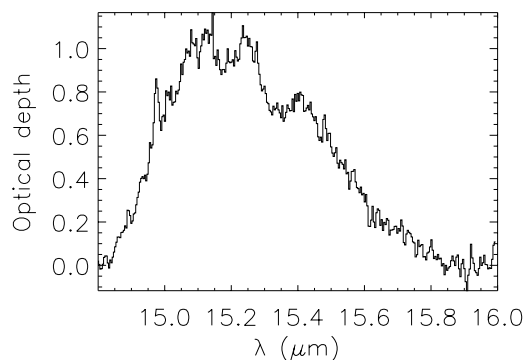
Recently, fairly good fits to the astronomical CO<sub>2</sub> bending mode data has been obtained with the spectra of CO<sub>2</sub>-CH<sub>3</sub>OH ice mixtures (Ehrenfreund et al. 1998), showing that interactions between the molecules in the ice represent an alternative way to justify the peculiar line shapes observed. Irradiated ice mixtures have also been investigated in that way (Palumbo et al. 1998).

In a different region of the spectrum, the “6.85  $\mu\text{m}$ ” band is a prominent feature in the line of sight to various protostellar sources, becoming almost as strong as the 6  $\mu\text{m}$  water bending mode in some of them (Willner et al. 1982). Its identification remains however unclear. The “6.85  $\mu\text{m}$ ” band has been attributed to various molecules including CH<sub>3</sub>OH and NH<sub>4</sub><sup>+</sup> based on its spectral position and experiments (Tielens et al. 1984, Grim & Greenberg 1987, Schutte & Greenberg 1997, Demyk et al. 1998). In addition, CH<sub>3</sub>OH may represent a significant fraction of ice mantles, as derived from observations of modes at shorter wavelength (e.g. 3.53  $\mu\text{m}$ , Allamandola et al. 1992) or through comparisons between the shape of the CH<sub>3</sub> deformation modes in the mid infrared region ( $\sim 1400$   $\text{cm}^{-1}$ , Schutte et al. 1996) and laboratory results.

We show hereafter that a physical link exists between carbon dioxide and methanol: a complex involving these two molecules can form and the intermolecular interactions influence the carbon dioxide bending mode line shape. Furthermore, ground based observations using UKIRT have shown that methanol is particularly abundant towards RAFGL7009S and W 33A (Dar-

Send offprint requests to: E. Dartois (dartois@iram.fr)

<sup>\*</sup> Based on observations with ISO, an ESA project with instruments funded by ESA Member States (especially the PI countries: France, Germany, the Netherlands and the United Kingdom) and with the participation of ISAS and NASA



**Fig. 1.** Peculiar substructure observed in the solid CO<sub>2</sub> bending mode absorption band toward RAFGL7009S. The sharp feature at 14.98 μm is the gas phase CO<sub>2</sub> counterpart (Dartois et al. 1998).

tois et al. 1999). From our experiments we demonstrate that this last molecule forms an electron donor-acceptor complex with carbon dioxide.

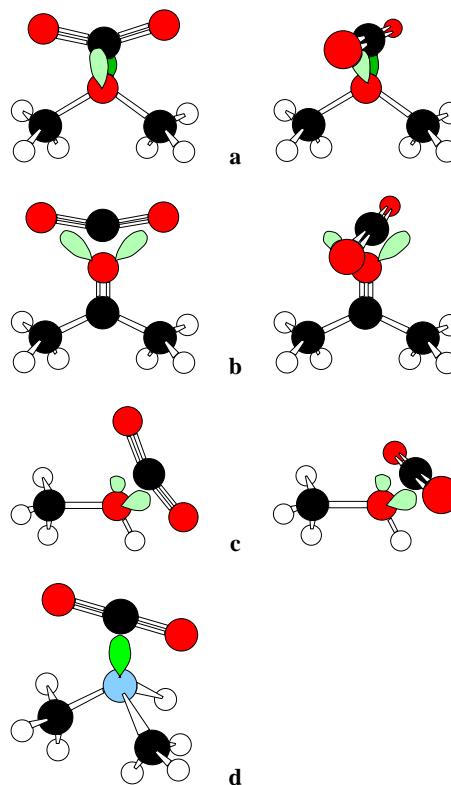
In this paper, we assess in the first part experimentally the process responsible for these changes in the CO<sub>2</sub> spectra and in the second part we develop the astrophysical implications.

## 2. Observations and results

The spectra of RAFGL7009S and S140 were recorded with the SWS instrument onboard ISO during the 124<sup>th</sup> and 177<sup>th</sup> revolutions of the satellite. The SWS01 and SWS06 spectra obtained are part of the SOLSTA and MMDUSTY programs. The data have been rebinned to a resolving power of 500 to 2000 depending on the AOT and wavelength range. The reality of the features was estimated separating the upward and downward scans to compare them, a “true feature” being present in both scans. An overview of the ISO-SWS spectrum of RAFGL7009S between 2.5 and 18 μm has been presented in d’Hendecourt et al. (1996), where ice features, most of them reproduced in the laboratory, are described. We present in Fig. 1, a close up on the CO<sub>2</sub> bending mode region at 15.2 μm, which is the main purpose of this paper.

## 3. Molecular interactions

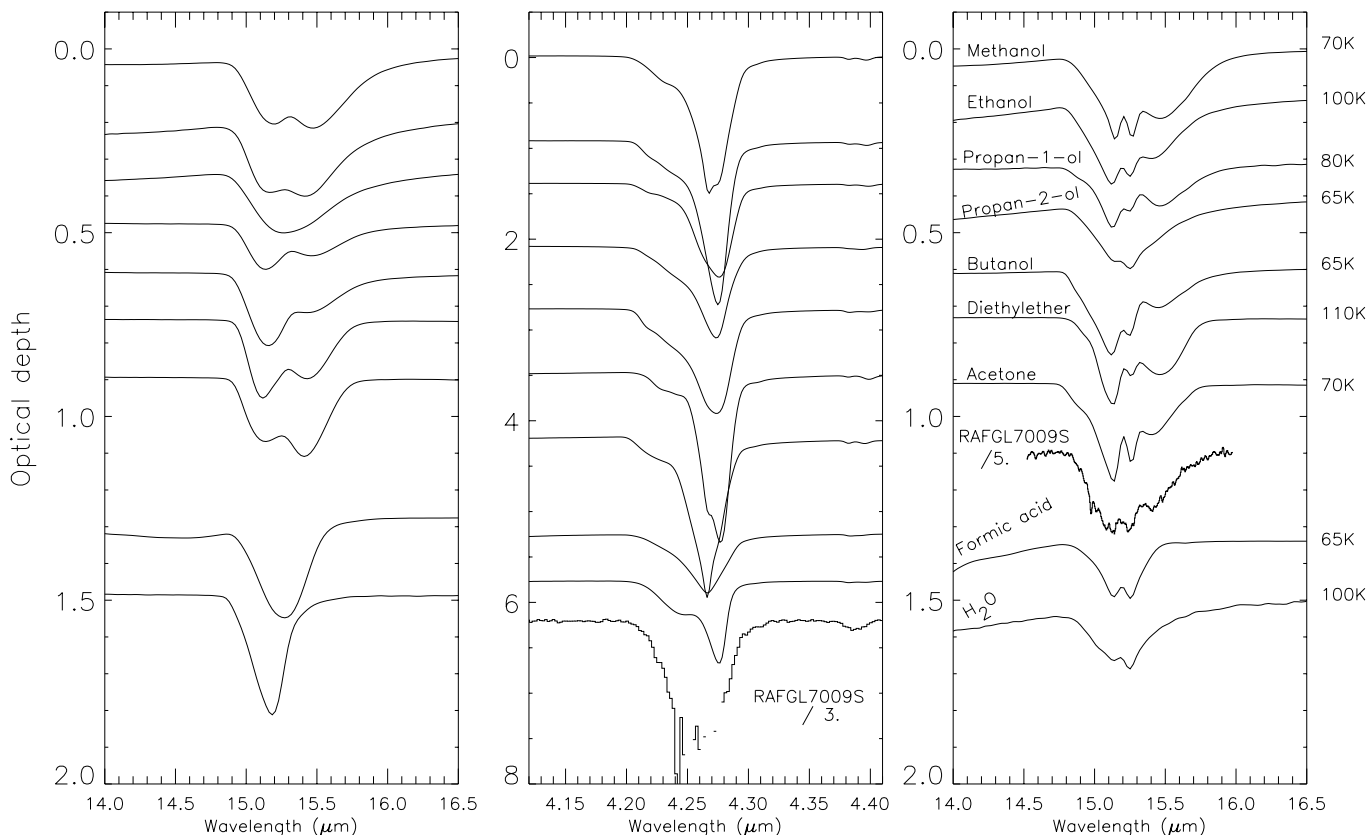
Carbon dioxide is well studied in chemistry as a solvent to synthesise or separate components in a mixture of chemicals. The complexes formed by this molecule are the subject of numerous theoretical and experimental studies. Molecular interactions are revealed through the behavior of the various bands of a molecule. In particular, infrared spectroscopy is a powerful tool to probe molecular interactions. Experiments in the microwave and radio spectral regions as well as *ab initio* calculations (Jamróz et al. 1995) and infrared spectroscopy (Kazarian et al. 1996) have shown that CO<sub>2</sub> could act as a Lewis acid if mixed with water, amines or amides. Long before, experiments had inferred the specific interactions of CO<sub>2</sub> with methanol (Hemmaplardh & King 1972), ethanol (Gupta et al. 1973) butan-1-ol and diethylether (Massoudi & King, 1973) among other solvents.



**Fig. 2a–d.** Schematic representation of the possible complex geometries between the CO<sub>2</sub> and, from top to bottom, the dimethylether **A**, acetone **B**, methanol **C** and dimethylamine **D**. The CO<sub>2</sub> molecule interacting is deformed and the degeneracy of the  $\nu_2$  bending mode is removed. Atoms are represented as follows: white circle (hydrogen), black filled circle (carbon), grey anthracite (oxygen), light grey (nitrogen). The lobes on oxygen and nitrogen atoms represent the lone electron pairs.

The acidity of the carbon dioxide molecule comes from the carbon atom being bound to two oxygen atoms. It then loses part of its electronic density to the benefit of the oxygen atoms. Molecules possessing at least a lone electron pair can thus interact with this molecule forming an Electron-Donor Acceptor complex (EDA). This interaction influences the strength of the intramolecular bonds. In the CO<sub>2</sub> case, the oxygen atoms are repelled whereas the interaction takes place through the carbon atom, modifying the bond angles. This interaction has strong effects on the infrared spectrum. The degeneracy of the CO<sub>2</sub>  $\nu_2$  bending mode is broken and two distinct modes appear. *Ab initio* calculations (Jamróz et al. 1995) attribute the higher frequency mode to the out-of-plane vibration (the bent CO<sub>2</sub> defines a plane, see Fig. 2), the other one being the in-plane mode. They also show that the atom giving the electrons lies in the same plane as the deformed molecule. The stabilisation energy of the complex formed is calculated to be of the order of 20 to 40 kJ/mole (Handbook of Physics and Chemistry), representing 10 to 20% of the formation enthalpy of H<sub>2</sub>O. It is thus a relatively strong coupling.

Observable consequences on an infrared spectrum are the splitting of the CO<sub>2</sub> bending mode, and the appearance of a weak



**Fig. 3.** Spectra of CO<sub>2</sub>:X—1:1 mixtures where X represents different molecules possessing sp<sup>2</sup> or sp<sup>3</sup> hybridized oxygen atoms. On the left is shown the  $\nu_2$  bending mode of carbon dioxide at 4 K just after deposition. The two right panels summarize spectra of the stretching and bending mode of CO<sub>2</sub> at the temperature at which the  $\nu_2$  mode shows a three peaks substructure similar to the one seen in space. The noisy spectrum is the one observed by ISO towards RAFGL7009S and separate the mixtures where the band substructures are seen from the ones that don't match (see text for explanations). One notes that while the bending mode of CO<sub>2</sub> is affected by the complex formation, the stretching mode remains unsplit but alters and develops a high frequency wing in the high temperature ranges.

new mode. This last one should arise in the 1300–1600 cm<sup>-1</sup> region of the spectrum, corresponding to the symmetric stretching vibration (Shimanouchi 1972) which becomes slightly active when the molecule is bent. The antisymmetric mode  $\nu_3$  is in principle less affected by the interaction as the CO<sub>2</sub> molecule tends to position itself at right angle to the axis defined by the Lewis acid bonds. It will therefore perturb much more the bending than the stretching mode.

## 4. EDA complex formation

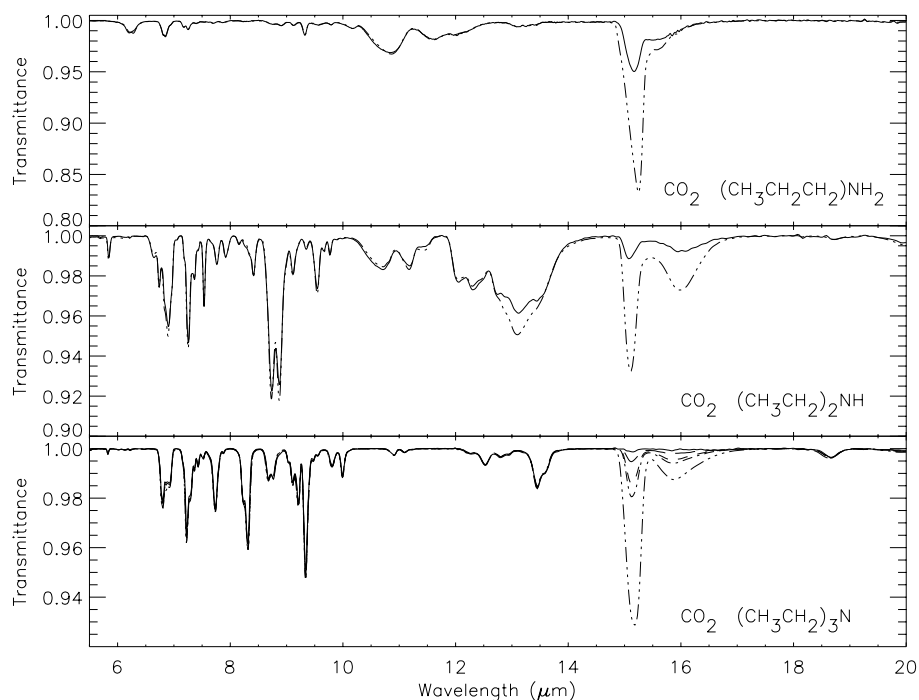
### 4.1. Study of complex formation in the laboratory

To test the donor-acceptor complex hypothesis discussed above, we have performed many experiments at the IAS. The experiments we performed use the classical techniques of matrix spectroscopy. Gas mixtures are slowly deposited onto a cold (4–100 K) substrate transparent to infrared wavelengths (CsI window). Infrared spectra are recorded with an IFS66v Bruker Fourier Transform Spectrometer (FTS). Details of such experiments can be found elsewhere (e.g. Allamandola 1987).

We chose to prepare ice samples containing in roughly equal proportions CO<sub>2</sub> and another molecule with lone electron

pair(s). To interact with CO<sub>2</sub>, we first chose molecules that could be abundant in interstellar space such as H<sub>2</sub>O, HCOOH, NH<sub>3</sub>. As methanol seems to be a good candidate to reproduce the astronomical spectrum (Ehrenfreund et al. 1998), we then decided to perform the same analysis with molecules from the alcohol group: CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, C<sub>3</sub>H<sub>7</sub>OH (2 isomers, propan-1-ol and propan-2-ol), C<sub>4</sub>H<sub>9</sub>OH (butan-1-ol). In a subsequent step, to ensure ourselves that the process was not specific to the alcohol group molecules, but to lone electron pairs, we also use C<sub>3</sub>H<sub>6</sub>O (acetone) and C<sub>4</sub>H<sub>12</sub>O (diethylether). In the last experiments, to fully investigate our EDA hypothesis based on interactions with lone electron pair(s), we find necessary to choose other molecules with another kind of atom presenting free electron doublet(s), here the nitrogen atom. Our choice was made on (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N (triethylamine, tertiary amine), (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH (diethylamine, secondary amine) and (C<sub>3</sub>H<sub>7</sub>)NH<sub>2</sub> (propylamine, primary amine) for experimental reasons (a vapor pressure of a few tens of a millibar at ambient temperature is preferable to obtain significant mixing ratios with the CO<sub>2</sub> molecule).

Selected results from these experiments are shown in Fig. 3 (oxygen containing molecules) and Fig. 4 (amines). We clearly see in these figures the three component splitting of the CO<sub>2</sub>



**Fig. 4.** Spectra of CO<sub>2</sub>-amine mixtures deposited at 4 K in which the CO<sub>2</sub>-amine ratio has progressively been increased (giving rise to the different curves in each sub-panel). The resultant spectra have been normalised to some well known amine lines. This allows to show the growth of two lines at  $\sim 15.2 \mu\text{m}$  and  $\sim 16 \mu\text{m}$ , attributed by us to the carbon dioxide perturbed bending mode transitions. The second band around  $16 \mu\text{m}$  is attributed to a complex formation (see text) through the interaction between the free doublet from the nitrogen atom and the carbon atom in the CO<sub>2</sub> molecule.

bending mode when CO<sub>2</sub> is mixed with methanol, ethanol, propanol, butanol, diethylether and acetone. In the stretching mode region, the shape of the band is not altered too much as can be seen on Fig. 3 (middle panel), even when the substructure appears in the  $15.2 \mu\text{m}$  band.

The temperature at which the bending mode shows a triple substructure is roughly related to the strength of the interaction between the acid and the base and the evaporation temperature of the less volatile species but stay for the molecules shown in this panel from 65 to 110 K.

The mixtures that do not exhibit the triple substructure can nevertheless show a double peaked structure at a temperature near the CO<sub>2</sub> evaporation one (Fig. 3. and Sandford & Allamandola, 1990). This structure is then not related to the complex formation but to the particular CO<sub>2</sub> crystalline interactions when a layer of pure CO<sub>2</sub> forms by migration of this molecule on top of the mantle. This stage can be very rapid as it is because we approach the CO<sub>2</sub> evaporation temperature.

When the experiments are performed with molecules from the alcohol group, the interaction is always present but with the propan-2-ol the effect is less pronounced. This is certainly due to the steric environment of this molecule compared to the propan-1-ol, which reduces the process. This picture agrees with our general ideas on the complex formation.

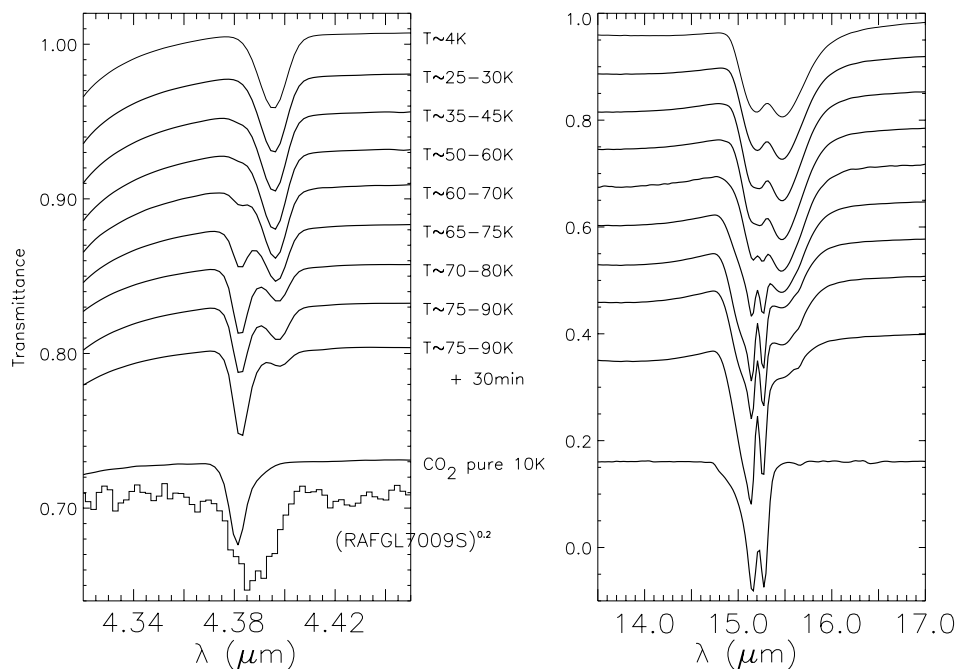
Experiments with H<sub>2</sub>O, NH<sub>3</sub> and formic acid did not lead to the same observations although these molecules also possess lone electron pairs. In these cases, the complex formation is probably inhibited by the possibility of such molecules to form strong hydrogen bonds. This is confirmed by other experiments dedicated to the H<sub>2</sub>O-CO<sub>2</sub> complex formation in a nitrogen matrix. It has been shown (Fredin et al. 1975) that a 1:1 complex of the EDA type effectively forms when these molecules are di-

luted in a nitrogen matrix. The C<sub>2</sub> axis of the water molecule is then perpendicular to the axis of the CO<sub>2</sub> one, the oxygen atom pointing toward the carbon atom of carbon dioxide (Jonsson et al. 1975). The same occurs for NH<sub>3</sub> that forms a geometrically similar complex, the C<sub>3</sub> axis perpendicular to the axis of the CO<sub>2</sub> molecule (Fredin & Nelander 1976). When these molecules are codeposited in an ice mixture, the hydrogen bonding interaction will dominate the ice structure, hindering the complex formation.

In the last step of our study, we mix the CO<sub>2</sub> with molecules containing a nitrogen atom. These molecules are *not astrophysically relevant but help to constrain the CO<sub>2</sub> EDA complex hypothesis* as the same interactions should occur with the nitrogen atom lone pair. Their infrared spectra are very complex as they have many atoms. To distinguish transitions associated with CO<sub>2</sub> from those of the amines we have proceeded by depositions increasing each time the carbon dioxide to amine ratio (Fig. 4). After normalisation on the bands already known to pertain to the amines, we expect, at first approximation, to see the CO<sub>2</sub> related bands grow. The small deviations in the amine bands normalisation come from slight phase change as the carbon dioxide concentration changes. As can be seen on Fig. 4, an additional band appears at  $\sim 15.5\text{--}16 \mu\text{m}$ . We again interpret this bending mode splitting in terms of the complex formation.

#### 4.2. EDA complex formation and CO<sub>2</sub> segregation

The CO<sub>2</sub>-X complex formation (where X is a Lewis base) is able to break (in two) the degeneracy of the CO<sub>2</sub> bending mode at low temperature (Fig. 3) but a warm-up of the ices is necessary to reproduce more precisely the interstellar observations (three subpeaks). During the annealing of the sample, an additional



**Fig. 5.** Spectral evolution of an ice mixture composed of equal proportions of CO<sub>2</sub> and CH<sub>3</sub>OH during a warm-up sequence. The <sup>13</sup>CO<sub>2</sub> stretching mode region (left panel) as well as the corresponding <sup>12</sup>CO<sub>2</sub> bending mode region (right panel) are shown. The lower spectrum is a pure CO<sub>2</sub> ice spectrum at 10 K shown for comparison. The histogram spectrum represents the isotope absorption region in the line of sight of the astronomical source RAFGL7009S.

structure appears in the bending mode in the subpeak initially at 15.2  $\mu\text{m}$ , becoming more and more alike the astronomical spectra of embedded objects.

Of particular interest is then to look at the isotope absorptions to constrain the mechanism responsible for this as it is much less abundant and therefore diluted in the ice matrix. Thus, it behaves in the same way as the first isotope concerning the complex interactions but does not agglomerate, therefore being more appropriate to reveal the effects experienced during the warm-up. Fig. 5 presents the warm up of the methanol-CO<sub>2</sub> ice experiment.

The temperatures indicated in the right part of the left panel are indicative of the range of temperature in which the spectra were recorded to ensure a good signal to noise ratio. The temperature was increased in steps of about one hour between each spectrum, except for the last two spectra that showed a rapid variation. Because we approach the CO<sub>2</sub> sublimation temperature, in the ice matrix the carbon dioxide molecule can then almost freely migrate to the surface whereas for the spectra at lower temperature, there is no evolution at the laboratory timescale (a day). This reflects the fact that the activation energies for the processes are exponentially dependent.

In space, we expect to obtain the same behavior, but at lower temperatures due to the much longer timescale of evolution implied. The exact temperature will also vary with the presence of other less volatile constituent in the mantle like water (which is expected from our fit with equal proportions of water, methanol and carbon dioxide, Fig. 6.) and the fact that in space the ambient pressure is much lower than the one encountered in the laboratory, even in the so called “dense cores”.

The <sup>13</sup>CO<sub>2</sub> stretching mode absorption, located at 4.395  $\mu\text{m}$  just after deposition is progressively transferred into another component at 4.38  $\mu\text{m}$ , revealing the rearrangement of the ice

mantle as the sample is annealed. In the main isotope (<sup>12</sup>CO<sub>2</sub>) bending mode region, the initial two broad features goes through a three-peak structure. The bending mode feature evolution is entirely correlated to the <sup>13</sup>CO<sub>2</sub> stretching mode progressive shift and ends in a two sharp peak feature at high temperature (T~70–80 K). Below the warm-up sequence (Fig. 5) is plotted a pure CO<sub>2</sub> sample deposited and recorded at 10 K. Comparing the warm spectra to the pure CO<sub>2</sub> spectrum, there is evidence that during warm-up some CO<sub>2</sub> migrates into the matrix. It then aggregates either at the surface or in the bulk to form a pure carbon dioxide mantle or crystallites. The isotope absorption feature around 4.39  $\mu\text{m}$  is then a sensitive and practical probe of the temperature evolution of this ice.

The broadness of the <sup>13</sup>CO<sub>2</sub> profile observed toward RAFGL7009S could then be a combination of the different line absorption positions of the isotope stretching mode but require a small contribution by another mixture like a CO<sub>2</sub>:H<sub>2</sub>O 1:1 to fill the gap at 4.385  $\mu\text{m}$ . Given the profile observed at 15.2  $\mu\text{m}$  (where we would not observe the triple substructure with such a mixture), as well as the fits on methanol transitions obtained in the short wavelength part of the spectrum (Dartois et al. 1999), this should not be the major contribution.

The observation of asymmetric profiles in various protostars would be the proof of the complex formation and provide a second temperature constrain as the dependence can be measured in the laboratory.

As a conclusion, we have shown that CO<sub>2</sub> interacts with some Lewis bases to form an EDA complex. The complex formation is betrayed by the splitting of the CO<sub>2</sub>  $\nu_2$  bending mode. Warm-up of the resulting ice can provide additional structure in the band as a combination of both the complex and some pure CO<sub>2</sub> ice segregation.

## 5. Astrophysical implications

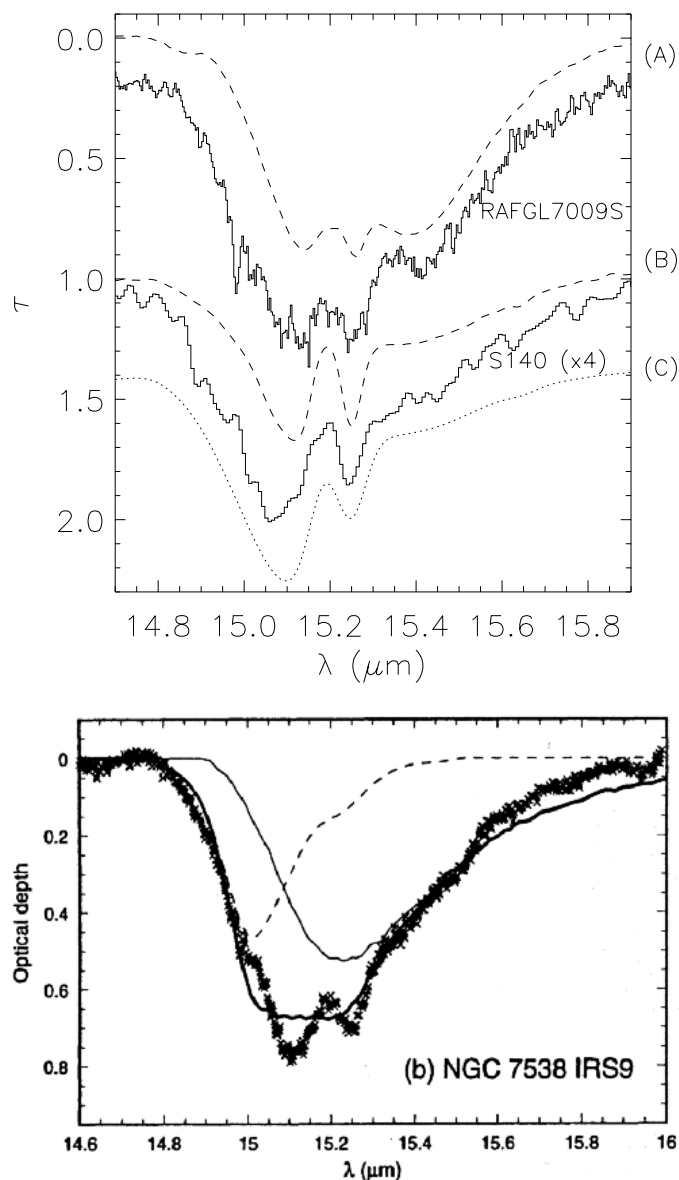
### 5.1. Interstellar candidate: CH<sub>3</sub>OH

Of all the molecules used to constrain the possible physical process occurring in ices containing CO<sub>2</sub>, only a few are astrophysically relevant, and the best candidate is certainly methanol. This molecule has indeed been detected with high abundances in RAFGL7009S and W 33A through methanol very specific combination modes (Dartois et al. 1999). In space, the ice mantles are generally water dominated and we have performed experiments with carbon dioxide, methanol and water. In these experiments, various proportions of these three molecules mixed in the same ice matrix have been used. The bending mode of CO<sub>2</sub> can only split if the water content in the mixture does not exceed too much the methanol content because as shown above, hydrogen bonding inhibits the complex formation and thus the splitting of the mode. We thus show not only that methanol must be abundant to satisfy the stoichiometric properties of the complex formation but also that the phase in which this complex forms is physically segregated from the bulk of the water ice (Ehrenfreund et al. 1998). This effect might be a line of sight effect (sampling different grains at various temperature spatially uncorrelated) or could be due to the mantles forming an onion-like structure, both hypotheses being indistinguishable without spatial information.

### 5.2. Temperature diagnostics

The comparison between experiments and interstellar CO<sub>2</sub> profiles is instructive. The differences observed from source to source reveal the thermal evolution of the ice. By their own nature, the protostellar envelopes display a temperature evolution both in time (due to the embedded star evolution itself) and radius (the flux constancy in radiative transfer imply the temperature must decrease with radius if there is no emitting source apart from the central star). The resultant spectra we observe towards different lines of sight are then affected by both. We know from the laboratory experiments that to a spectrum corresponds an evolutionary step, and we can obtain a more complete overview of the degree of evolution by comparing different ice modes as now the complete spectra are available with ISO. Only with such a complete scan of the possible observable transitions can we infer the degree of evolution of the sources. This experimental knowledge is one additional clue to infer the age of the condensations, and we can say that given sources are more evolved than others. However, saying that it is due to a more massive star, heating more efficiently the dust, or that it is due to a longer exposition of dust to a moderate radiation requires information from other observations or modes.

Let us focus on RAFGL7009S, NGC7538 IRS9 and S140 sources. S140 is a source located in the L1024 dark cloud, in a massive star forming region. In S140, ices are at a high temperature, certainly at a very late stage of their evolution, as solid CO is absent from the spectrum and the water bending mode located around 6  $\mu$ m is beginning to show some crystallisation. Ices in RAFGL7009S are at an earlier temperature stage (d'Hendecourt



**Fig. 6.** Upper panel: spectra of the sources RAFGL7009S and S140 in the CO<sub>2</sub> bending mode region. The long-dashed fits proposed are laboratory spectra of H<sub>2</sub>O:CO<sub>2</sub>:CH<sub>3</sub>OH (1.3:1:1) mixtures, deposited at 10 K, and warmed up. The temperature reached when the spectra are recorded are 80–90 K (A) and a combination of 110 and 120 K spectra (B). The short-dashed fit (C) is a H<sub>2</sub>O:CO<sub>2</sub>:CH<sub>3</sub>CH<sub>2</sub>OH (1:2:0.5) mixture, deposited at 10 K and warmed up at about 110 K. This last experiment is presented to show the non-uniqueness of the interpretation if based only on this band. Lower panel: for comparison we show the SWS06 spectrum of NGC7538 IRS9 as obtained by de Graauw et al. (1996). See text for discussion.

et al. 1996). Comparison of their respective spectra with laboratory data shows that a good agreement is obtained for an ice temperature of about 110–120 K for S140 (Fig. 6), higher than the one needed to reproduce RAFGL7009S spectrum (about 80–90 K). Note that in space this temperature is likely to be slightly lower as the time scale for the evolution of the ice is much longer than in the laboratory. NGC7538 IRS9 (Fig. 6,

lower panel) represents a case similar to S140. However, the complete spectrum of this source reveals the presence of more volatile ices than in S140, like CO (Whittet et al. 1996) which means that ices reside in a less evolved environment.

The NGC7538 IRS9 spectrum presented in Fig. 6, together with the S140 one, is one of the two characteristic CO<sub>2</sub> bending mode profiles first showed in de Graauw et al. (1996). It is dominated by a two peaks substructure. The other “class” of line profiles is represented by RAFGL7009S and GL2136 (three peaks), this last source being also reported in de Graauw et al. (1996). These spectra, together with our interpretation, clearly show that we probe the sources at various evolution stages. However, if we compare the solid phase to the CO<sub>2</sub> gas component, the evolutionary scheme is more difficult to establish. In NGC7538 IRS9, the carbon dioxide gas to solid ratio is around 0.01 whereas for GL2136 it is 0.02 (van Dishoeck et al. 1996). The water gas to solid ratio is less than 0.04 for NGC7538 IRS9, about 0.4 in GL2136 and the gas component is much hotter in this last source. Taking only this into account, GL2136 appears hotter than NGC7538 IRS9, in which many molecules are still in the ice mantles (van Dishoeck & Helmich 1996). The solid CO<sub>2</sub> bending mode region reveals something less straightforward as the substructures observed in GL2136 are associated, in the laboratory, with a less thermally evolved complex between CO<sub>2</sub> and CH<sub>3</sub>OH than what we derive for NGC7538 IRS9. Even if we now understand the physical parameters which allow the interpretation of the spectra, it shows that we lack in such cases additional spatial information to know precisely to what extent the region where the gas is observed is related to the solid phase location in the clouds.

In addition to the CO<sub>2</sub> bending mode line profile, a high resolution monitoring of the CO<sub>2</sub> second isotope stretching mode can provide useful clues about the evolutionary stage of interstellar ices as previously discussed. Both modes behaviours and line shapes are good indicators of the degree of evolution of the sources. It can be understood as a sort of “third dimension” in the ice study. Indeed, if we can relate the profiles to given temperatures or physical state in the laboratory, we can infer the temperature at which the ices have been raised.

### 5.3. Uniqueness of the candidate

We chose to show the ethanol-CO<sub>2</sub> mixture spectrum in Fig. 6 as well as the methanol-CO<sub>2</sub> one in comparison to S140 to demonstrate that the effects of molecular interactions lead to infrared spectra whose interpretation may not be unique. To identify the astrophysical candidate, one must spectroscopically look at the full range of the infrared spectra provided by ISO to observe potential other molecular modes, or look at specific transitions from observations in ground based atmospheric windows, like we did for RAFGL7009S. *Indeed, in our experiments the ethanol mixture provides a very good fit to the spectrum of the source but methanol is definitively the right interstellar candidate.*

## 6. The methanol impact on the overall spectrum

The interactions described above have led us to observe RAFGL7009S from the ground. The measurements of the methanol combination modes allows to precisely determine its column density ( $3.3\text{--}3.8 \times 10^{18} \text{ cm}^{-2}$ , Dartois et al. 1999). As a moderately complex molecule, methanol possesses numerous transitions (Fig. 7). We can then predict and compare the relative importance of the other modes in the ISO-SWS01 spectrum.

In particular, we address now the question of the assignment of the 6.85  $\mu\text{m}$  band. We can evaluate methanol contribution to this band. To do this we invert the equation generally used to infer the molecules column densities in a given line of sight:

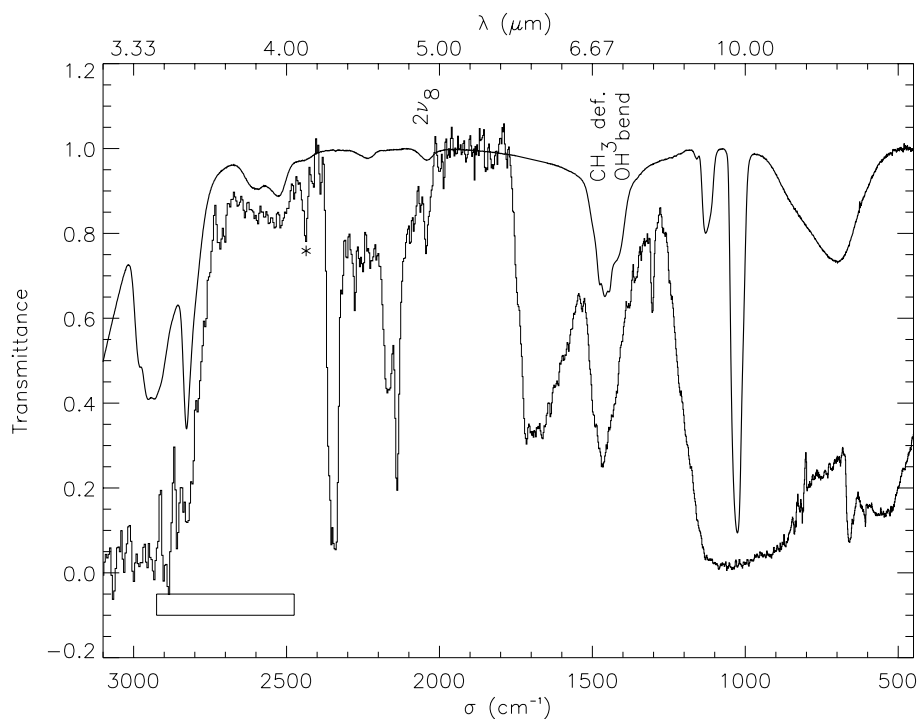
$$\int \tau(\bar{\nu}) d\bar{\nu} = A \times N$$

where  $\bar{\nu}$  is the wavenumber,  $\tau(\bar{\nu}) = \ln(\frac{I_0}{I})$ ,  $A$  is the integrated absorption cross section (cm/molecule) of the considered transition and  $N$  is the column density ( $\text{cm}^{-2}$ ). The methanol CH<sub>3</sub> deformation and OH bending modes (6.85  $\mu\text{m}$ ) have an integrated absorption cross section comprised between 1.1 and  $1.2 \times 10^{-17} \text{ cm molec}^{-1}$  in the case of the ice mixtures used for the comparison at short wavelength (Dartois et al. 1999). We then obtain for the broad 6.85  $\mu\text{m}$  band a predicted integrated absorbance given by:

$$\int \tau(\bar{\nu}) d\bar{\nu} = (1.1\text{--}1.2) \times 10^{-17} \times (3.3\text{--}3.8) \times 10^{18}$$

which leads to a value of 36–46  $\text{cm}^{-1}$ . The measurement of the 6.85  $\mu\text{m}$  band integrated absorbance on the astrophysical spectrum gives  $95 \pm 15 \text{ cm}^{-1}$ . Methanol can then provide 32% to 56% of this band (the uncertainty coming from both the continuum evaluation and integrated absorption cross section), and part of it could be carried by another ice constituent. Up to 10% could be accounted for by the OCN<sup>-</sup> counterion, i.e. NH<sub>4</sub><sup>+</sup>, (Demyk et al. 1998) but still 30% to 60% of the band remains unaccounted for.

The 2 $\nu_8$  methanol overtone falls at 2040  $\text{cm}^{-1}$  (4.9  $\mu\text{m}$ ), at the place of a band attributed to OCS (Geballe et al. 1985, Palumbo et al. 1995). The integrated absorbance of this line in the astrophysical spectrum is  $4 \pm 1 \text{ cm}^{-1}$ . We can now evaluate the integrated absorbance ratio between the 6.85  $\mu\text{m}$  and 4.9  $\mu\text{m}$  bands in the laboratory spectrum of pure methanol deposited at 10 K, which leads to 0.025. The integrated absorption cross section for this overtone is then  $2.7\text{--}3.0 \times 10^{-19} \text{ cm molec}^{-1}$ . We use this value and the column density toward RAFGL7009S, derived from the short wavelength modes of methanol to evaluate the contribution of this overtone to the 4.9  $\mu\text{m}$  mode: 0.9–1.2  $\text{cm}^{-1}$ . Comparing this to the ISO observations, one fourth to one third of the band can be attributed to methanol and the rest to another molecule such as OCS. The bandwidth of the 2 $\nu_8$  methanol feature explains rather well the peculiar shape of the interstellar 4.9  $\mu\text{m}$  band whose base is wide and center relatively narrower. The base is certainly due to the methanol overtone. Palumbo et al. (1995, 1997) did obtain a better fit to their spectrum in this wavelength region with mixtures containing both methanol and carbonyl sulfide (OCS).



**Fig. 7.** Pure methanol ice spectrum deposited at 10 K and transmittance spectrum extracted from the source RAFGL7009S. The laboratory spectrum is normalised to the abundance of methanol derived from ground based observations. The astronomical spectrum region highlighted by the rectangle correspond to the one covered by the observations performed at UKIRT (Dartois et al. 1999)

## 7. Conclusion

The study of the 15.2  $\mu\text{m}$  CO<sub>2</sub> bending mode profile in RAFGL7009S as well as in other objects reveals that, in the ice mantles, intermolecular interactions are responsible for the peculiar line shape observed. We have been able to constrain the interaction on the basis of experiments and show that it originates from the interaction between a Lewis base and acid. This study leads to the detection of the formation of interstellar intermolecular complexes between the carbon dioxide and methanol molecules present in roughly similar abundances in the grain mantles. The CO<sub>2</sub> bending mode line shape traces this physical interaction in the ice mantle, but is not sufficient in itself to uniquely identify the interacting molecule. If we limit ourselves to the good agreement between the two spectra in Fig. 6, we may expect that ethanol is rather abundant in ice mantles. This is not the case, regarding the entire infrared spectrum. Additional constraints on the possible candidates (cosmic abundance, laboratory investigations and specific modes vibrations expected from the candidate in other infrared regions) are needed to claim for a definitive identification. Methanol is this candidate.

The CO<sub>2</sub> profiles observed in various lines of sight show evidence for both complex formation and thermochemical evolution of the ice. A sensitive probe of this evolution is given in the laboratory by the <sup>13</sup>CO<sub>2</sub> isotope stretching mode line shape which indicates the degree of segregation in ices. The profile analysis in all the known sources and their comparison is another step to understand ice evolution around young stellar objects.

The inferred candidate interacting with CO<sub>2</sub> (i.e. CH<sub>3</sub>OH) allows to explain the global spectrum of RAFGL7009S.

Methanol is responsible for about 30 to 60% of the so-called “6.85  $\mu\text{m}$ ” band and partly contributes to one fourth to one third of the feature at 4.9  $\mu\text{m}$  attributed to OCS.

It seems paradoxical that the “6.85  $\mu\text{m}$ ” band in this source, that we detected since the very first ISO observations, was not attributed to methanol. Infrared vibrational spectroscopy of unknown solids often offers a limited diagnostics because blending of lines coming from different candidates may lead to non-unique assessment of the spectra. This is a serious limitation in the analysis of the profiles of infrared bands using only very narrow wavelength regions. However, a careful interpretation of laboratory experiments can help to overcome this difficulty, as we have shown in this paper with the fine tuning interpretation of the complex and blended “6.85  $\mu\text{m}$ ” bands.

## References

- Allamandola L.J., 1987, *J. Mol. Str.* 157, 255
- Allamandola L.J., Sandford S.A., Tielens A.G.G.M., Herbst T.M., 1992, *ApJ* 399, 134
- Bohren C.F., Huffman D.R., 1983, In: *Absorption and scattering of light by small particles*. John Wiley, New York
- Dartois E., D’Hendecourt L., Boulanger F., et al., 1998, *A&A* 331, 651
- Dartois E., Schutte W., Geballe T.R., et al., 1999, *A&A* 342, 32
- Demyk K., Dartois E., d’Hendecourt L., et al., 1998, *A&A* 339, 553
- Van Dishoeck E.F., Helmich F.P., 1996, *A&A* 315, L177
- Van Dishoeck E.F., Helmich F.P., De Graauw T., et al., 1996, *A&A* 315, L349
- Ehrenfreund P., Dartois E., Demyk K., d’Hendecourt L., 1998, *A&A* 339, L17
- Fredin L., Nelander B., 1976, *Chem. Phys.* 15, 473
- Fredin L., Nelander B., Ribbegard G., 1975, *Chemica Scripta* 7, 11
- Geballe, T.R., Baas, F., Greenberg, J.M., Schutte, W., 1985, *A&A* 146, L6



- De Graauw T., Whittet D.C.B., Gerakines P.A., et al., 1996, A&A 315, L345
- Grim R.J.A., Greenberg J.M., 1987, ApJ 321, 91
- Gupta S.K., Leslie R.D., King A.D., 1973, J. of Phys. Chem. 77, 2011
- d'Hendecourt L., Jourdain De Muizon M., Dartois E., et al., 1996, A&A 315, L365
- Hemmaplardh B., King A.D., 1972, J. of Phys. Chem. 76, 2170
- Jamróz M.H., Dowbrowolski J.C., Bajdor K., Borowiak M.A., 1995, J. Mol. Struct. 349, 9
- Jonsson B., Karlstrom G., Wennerstrom H., 1975, Chem. Phys. Letters 30, 58
- Kazarian S.G., Vincent M.F., Bright F.V., Liotta C.L., Eckert C.A., 1996, J. Am. Chem. Soc. 118, 1729
- Massoudi R., King A.D., 1973, J. of Phys. Chem. 77, 2016
- Palumbo M.E., Tielens A.G.G.M., Tokunaga A.T., 1995, ApJ 449, 674
- Palumbo M.E., Geballe T.R., Tielens A.G.G.M., 1997, ApJ 479, 839
- Palumbo M.E., Baratta G.A., Brucato J.R., et al., 1998 A&A 334, 247
- Rouan D., Leger A., 1984, A&A 132, L1
- Sandford S.A., Allamandola L.J., 1990, ApJ 355, 357
- Schutte W.A., Greenberg J.M., 1997, A&A 317, 43
- Schutte W.A., Tielens A.G.G.M., Whittet D.C.B., et al., 1996, A&A 315, L333
- Shimanouchi T., 1972, Tables of molecular vibrational frequencies. Nat. Bur. Stand
- Tielens A.G.G.M., Allamandola L.J., Bregman J., et al., 1984, ApJ 287, 697
- Whittet D.C.B., Schutte W.A., Tielens A.G.G.M., et al., 1996, A&A 315, L357
- Willner S.P., Gillett F.C., Herter T.L., et al., 1982, A&A 253, 174