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D'Hendecourt, L.B.; Jourdain de Muizon, M.

Astron. Astrophys. 223, L5–L8 (1989)

ASTRONOMY AND ASTROPHYSICS

Letter to the Editor

The discovery of interstellar carbon dioxide

L.B. d'Hendecourt[1] **and M. Jourdain de Muizon**[2,3]

[1] Groupe de Physique des Solides, Université de Paris 7, Tour 23, 4 Place Jussieu, F–75251 Paris Cedex 05, France
[2] Sterrewacht Leiden, Postbus 9513, NL–2300 RA Leiden, The Netherlands
[3] Observatoire de Paris, Section de Meudon, F–92190 Meudon, France

Received July 25; accepted August 18, 1989

Summary. The LRS instrument on board IRAS has provided good quality low resolution spectra of thousands of relatively bright and point like infrared sources. We have detected in the LRS spectra of 3 such sources a strong absorption feature at 15.2 μm the position of which coincides with the absorption expected from the ν_2 bending mode of the CO_2 molecule. This band appears together with a strong and very broad absorption band centered at 13.5 μm and which is attributed to the librational mode of the water molecule in ice. Laboratory data involving mixtures of H_2O and CO_2 ices provide a fit to the observed bands and allow us to determine the quantity of these molecules along the line of sight to these objects. The CO_2 molecule is thus detected for the first time in the interstellar medium and its abundance is shown to be roughly equal to that of solid CO.

Key words: Infrared radiation – spectroscopy – Interstellar medium: dust, molecules, H II regions, molecular clouds

1. Introduction

The presence of molecular mantles made of volatile ices such as H_2O, NH_3, CO and various hydrocarbons is well established from numerous spectroscopic observations of astronomical sources, generally protostars, deeply embedded in molecular clouds (Willner et al., 1982; Lacy et al, 1984). Vibrational transitions of simple molecules and chemical subgroups of more complex ones fall in the 2–20 μm region (Allamandola, 1984) and laboratory simulations provide numerous data to identify simple molecules such as CO and H_2O. Observed positions and widths of the astronomical lines are usually well reproduced in the laboratory and column densities of the observed molecules on the line-of-sight can be reliably estimated (d'Hendecourt and Allamandola, 1986; Sandford and Allamandola, 1988).

Water ice has been first identified through its OH streching vibration, which, due to hydrogen bonding, forms a very intense and broad absorption band at 3.07 μm (Léger et al., 1979). The bending mode of the H_2O molecule is observed around 6 μm from airborne observations (Tielens et al., 1984) and the librational mode (hindered rotation) has been tentatively observed with great difficulties in the spectra of some OH/IR stars (Gillett and Soifer, 1976; Roche and Aitken, 1984, Muizon et al., 1986). Other molecules such as CO, NH_3, and more complex species have also been identified thanks to laboratory simulations. In particular, the CO molecule in the solid icy form has been detected in many sources (Lacy et al., 1984; Geballe, 1986) and it has been shown that its concentration relative to H_2O lies between 1 and 20%.

Among the molecules easily produced in the laboratory by UV photolysis of ices, CO_2 is the most conspicuous and the easiest to identify in the infrared. CO_2 ice provides two strong absorption bands located respectively at 4.27 μm (O=C=O asymmetrical stretch) and 15.2 μm (bending mode). Unfortunately, these two bands cannot be observed from the ground or from an airplane because of the large scale height of atmospheric CO_2, so that models of interstellar ices generally exclude CO_2 ice for lack of observations. The CO_2 bending mode is a relatively strong and narrow feature that appears in photolysed laboratory ices. In this paper we report its detection towards several protostars.

2. Observations and results

We have searched for the solid CO_2 band at 15.2 μm by exploring the IRAS database of Low Resolution Spectra (LRS). The LRS instrument onboard IRAS was a slitless spectrometer, covering the wavelength interval 7.8 to 22.5 μm, in two wavelength channels, 7.8–13 μm and 11.5–22.5 μm, being recorded simultaneously, with a resolution varying inside each band from about 10 to 60 (IRAS Explanatory Supplement, 1988). The wavelength scale is accurate within 0.1 μm. We have examined the LRS spectra of numerous known or newly discovered compact H II regions and embedded protostellar objects, with special attention given to all sources in which H_2O or CO ices had already been observed. We found an absorption band at 15–15.2 μm in several LRS sources. We choose to present here only the three sources having the strongest bands. These are: AFGL 961 (IRAS 06319+0415) in the Rosette Nebula, AFGL 989 (IRAS 06384+0932) in the Cone Nebula and AFGL 890 (IRAS 06084–0611). AFGL 961 and 989 are both included in the sample of "Infrared spectra of protostars" by Willner et al. (1982). These early low resolution spectra showed that both sources have a strong absorption band at 3 μm due to water-ice and a less pronounced silicate absorption at 10 μm. Medium resolution spectra in the 4.5–4.8 μm region by Geballe (1986) clearly show a strong absorption feature at

Send offprint requests to: L.B. d'Hendecourt

4.67 μm in these two sources. This band corresponds to the C≡O stretching vibration of carbon monoxide (Lacy et al., 1984). As for AFGL 890, no spectroscopic observations earlier than IRAS are available.

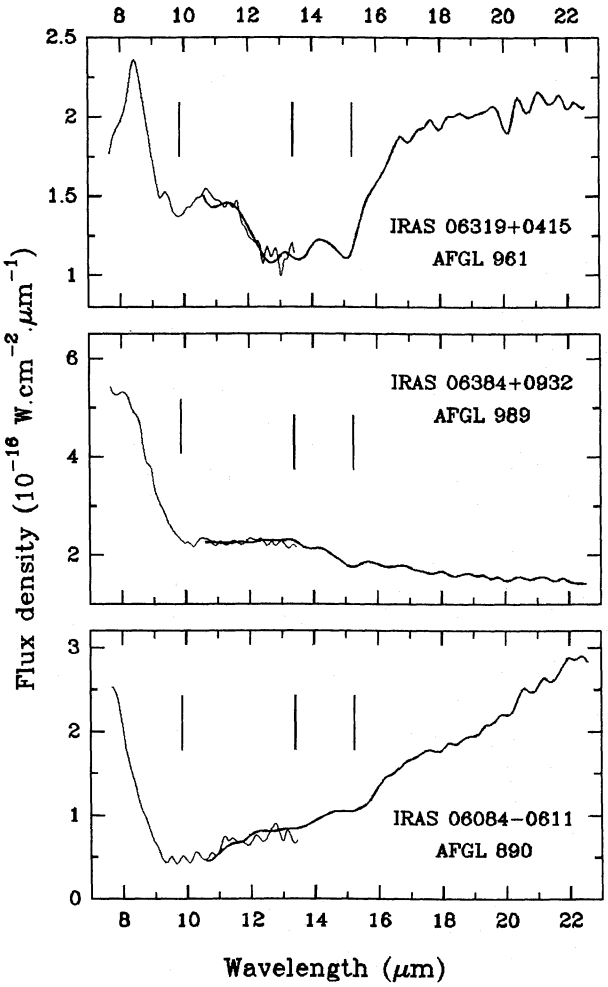

Fig. 1. IRAS–LRS spectra of the three sources. The thin line is band 1 of the LRS and the thick line is band 2. The various absorption bands discussed in the text (silicates, 10 μm; H_2O, 13.5 μm; CO_2, 15.2 μm) are indicated by the vertical lines.

The average LRS spectra of the three sources are presented in Figure 1. The 15.2 μm absorption band is prominent in the three objects, although it lies on the edge of a very broad absorption centred at about 13.5 μm which is due to the libration mode of water-ice (Cox, 1989). The profile of this water-ice band is itself distorted on its short wavelength edge because of the presence of the broad 10 μm silicate absorption band. The reality of the 15.2 μm absorption feature is confirmed because it is clearly present in all the individual LRS spectra of these sources.

3. Analysis of the spectra

3.1. Removal of the silicate absorption band

Infrared spectra towards embedded protostars, as well as OH/IR stars, obtained from ground-based observatories or with the LRS instrument show prominent absorption bands located at 9.7 and around 18 μm which are attributed to SiO stretching and bending modes in some kind of silicates (Gillett et al., 1975; Volk and Kwok, 1987). To interpret the observed spectra displayed in Figure 1, we have used another LRS spectrum in which the silicate absorption band does not show an apparent strong absorption feature longwards of 11 μm. For this purpose, the spectrum of S 140 has been normalised in optical depth ($\mathrm{Ln}(I/I_0)$) to the spectrum of each of our three sources. The normalisation point is taken at the maximum optical depth in the silcate band at 9.75 μm. For S 140, the baseline is determined by joining a straight line between the points at 7.5 and 14 μm and another one between 14 and 23 μm. According to data on amorphous silicates, the extinction (i.e. the absorption) of amorphous silicate smokes is close to 0 around 14 μm (Day, 1979) and this justifies this procedure. For our three AFGL sources accurate baseline subtraction is difficult because the true value of the continuum is not well known. We have subtracted the baseline as a straight line between 7.5 and 23 μm.

The residual absorption spectra are shown for the 3 sources in Figure 2. The residual absorption consists in a very broad ($\Delta\lambda \approx 4\,\mu$m) feature centred at approximately 13.5 μm and a sharper absorption band at 15.2 μm.

3.2. Laboratory signature of a mixture of H_2O–CO_2 ice

A mixture of water ice and carbon dioxide shows various absorption bands which are discussed extensively in the literature (d'Hendecourt and Allamandola, 1986; Sandford et al., 1988; Sandford and Allamandola, 1988). In the 10–20 μm region, the H_2O librational mode (hindered rotation) is very sensitive to the exact nature of the ice (Hagen et al, 1983; d'Hendecourt and Allamandola, 1986; see also Cox, 1989). For the purpose of this paper, the results of the experiments described in d'Hendecourt et al. (1986) have been used. A mixture of H_2O:CO:NH_3:CH_4 (6:2:1:1) was deposited under vacuum on a cold (10 K) window and photolysed with an UV lamp to simulate the interstellar radiation field. Infrared spectra of the deposited film are taken before and after photolysis. During the photolysis, as much as 10% of the initial CO is converted to CO_2 and the strong stretching band of CO_2 at 4.23 μm dominates the spectrum together with the bending mode at 15.2 μm. This last band is the only prominent one which appears between 10 and 20 μm.

Using such laboratory spectra, we obtain a fit to the residual absorption in AFGL 961 which is displayed in Figure 3. The fit presented in Figure 3 is strongly convincing and a similarly excellent fit is obtained for AFGL 890. The laboratory band position and width for the H_2O librational mode fall within 5% of the observed values. For CO_2, the band position is reproduced within 1%. Such an accuracy is very good for solid state features which are very sensitive to various effects such as mixing with different molecules, temperature of deposition and other thermal annealing effects. Note that for CO_2, the width of the band is larger in the astronomical spectrum (resolution of 30 cm^{-1}) because the laboratory spectrum was obtained at a much higher resolution (1 cm^{-1}). Moreover, in the laboratory sample, the

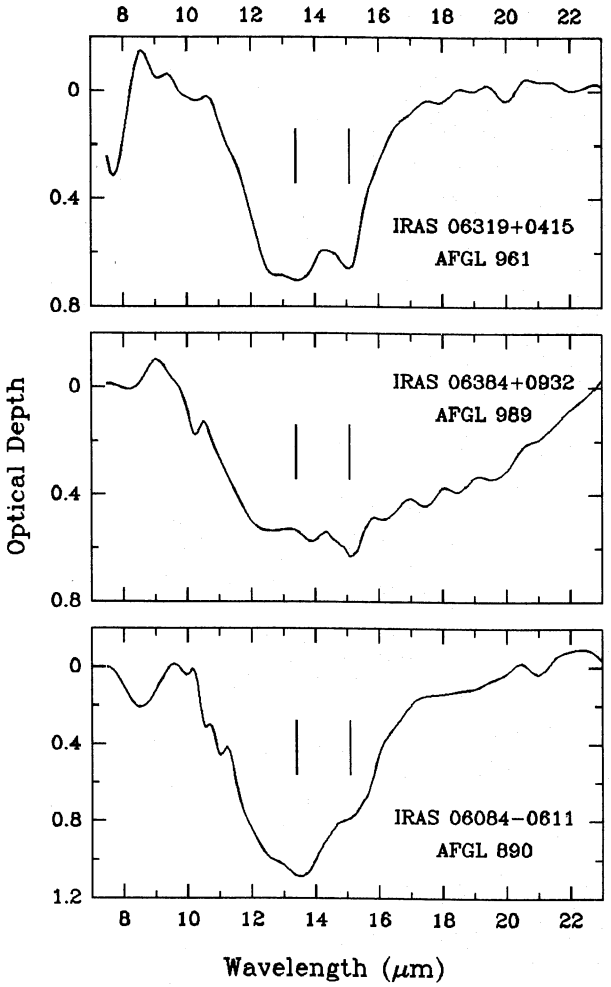

Fig. 2. Residual spectra of the three sources, obtained after removal of the silicate absorption. The only major features left in these spectra are those of H_2O ice (13.5 μm) and CO_2 ice (15.2 μm).

precise proportion of CO_2 and H_2O is not necessarily the same as in the source and we have not attempted to fit the relative strengths of the CO_2 and H_2O bands. As for AFGL 989, the residual absorption band is broader; this is an effect of improper baseline subtraction, the colour temperature in this source being somewhat lower than in S 140.

3.3. Column density determinations

As described in d'Hendecourt and Allamandola (1986), the number of adsorbed species along the line of sight can be accurately determined if the integrated absorbance A_m of the given species is known. From laboratory simulations, A_m is measured for many molecules as well as for mixtures. The characteristics of the laboratory bands are given in Table 1.

Finally, we derive the number of molecules along the line-of-sight towards these three objects. For the H_2O band, the resolution of the LRS instrument is good enough to resolve the band and Eq.1 applies. In doing so, following Russell and Thompson (1957), a correction is made on the observed optical depth and width of the CO_2 band to account for the resolution

Table 1. Laboratory parameters of the bands

	H_2O 13.5 μm	CO_2 15.2 μm
$\Delta\nu$ [cm^{-1}] (a)	255	18
ν_c [cm^{-1}] (a)	770	656
A_m [cm.mol.$^{-1}$]	2.6×10^{-17} (b)	4.1×10^{-17} (c)

(a) From d'Hendecourt et al. (1986); (b) From d'Hendecourt and Allamandola (1986); (c) From Sandford et al. (1988).

Table 2. Column densities

[mol.cm^{-2}]	AFGL 961	AFGL 989	AFGL 890
N_{CO_2}	2.0×10^{17}	9.3×10^{16}	9.5×10^{16}
N_{CO} (a)	3.5×10^{17}	3.5×10^{17}	–
N_{H_2O} (b)	6.6×10^{18}	6.1×10^{18}	8.8×10^{18}

(a) From Geballe (1986); (b) These numbers are derived from the 13 μm band in the LRS spectra.

of the LRS. The resulting CO_2 column densities for the three sources are given in Table 2, together with the CO column densities from Geballe (1986) when available.

4. Discussion

4.1. The 13.5 μm water ice band

The analysis of this band in the source AFGL 961 is reported by Cox (1989). In the laboratory, the exact position of this band depends on the temperature of deposition and, to some extent, on the mixing of H_2O with other molecules. It shifts from 11.5 μm for an ice deposited at 77 K (Léger at al., 1979) to 13.3–13.6 μm in freshly deposited water mixture at 10 K (Hagen et al., 1983; d'Hendecourt and Allamandola, 1986). The quality of the fit obtained in Figure 3 shows that the ice observed in these sources has been slowly accreted on very cold grains ($\sim$ 10 K), as it is expected in molecular clouds. For AFGL 961, the column density of water deduced from the 13.5 μm band (Table 2) corresponds to about 2×10^{-4} g.cm^{-2}, a quantity which is similar to the one obtained by Cohen (1976) in this object from the measurement of the 3.07 μm water ice band.

4.2. The 15.2 μm band of CO_2

This band is identified as being due to the bending mode of the CO_2 molecule embedded in ice and the fit obtained in Figure 3 strengthens this identification. The presence of CO_2 in an interstellar ice mantle is indeed not a surprise and was previously proposed in various models of grain chemistry (d'Hendecourt et al., 1985, 1986) and shown to be readily produced by irradiation of realistic grain mantle analogs. In AFGL 961 and 989, for which frozen CO data are available, the CO/CO_2 ratio is between 2 and 3. From gas phase models, the CO_2 abundance is always quite low, 10^{-5} to 10^{-4} times the CO abundance (Prasad and Huntress, 1980; Mitchell et al., 1978). The presence of solid CO_2 in such abundances implies that the formation of CO_2 is thus essentially a grain process.

In AFGL 961, the number of solid CO and CO_2 molecules represents about 10% of the content of water ice. Such a number is noticeably less than the amount predicted by d'Hendecourt

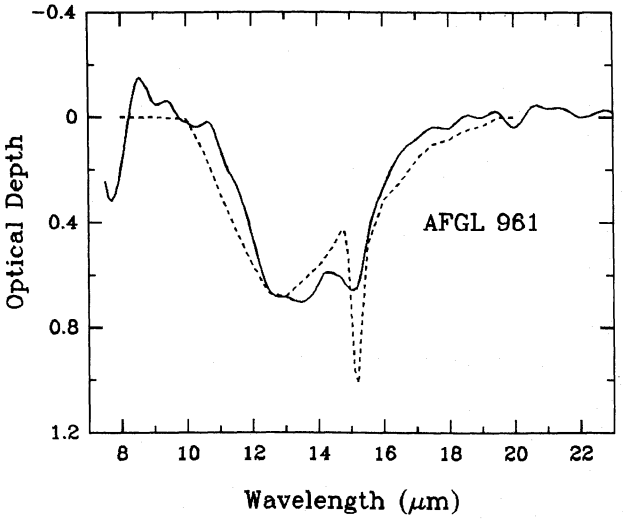

Fig. 3. Comparison of the residual spectrum of AFGL 961 (continuous line) with a laboratory spectrum of a mixture of H_2O and CO_2 ices (dashed line). The laboratory spectrum is normalised at 13 μm to the residual spectrum of AFGL 961.

et al. (1985) in a model describing the interaction between gas and grain phases in molecular clouds. In this model, the release of molecules from mantles to the gas phase is independent of the molecules. A selective release of molecules with low binding energies (e.g. CO) would decrease the abundance of these molecules relative to species having a high binding energy (e.g. H_2O).

Finally, because grain mantles are most probably releasing their ice mantles to the gas phase to prevent complete accretion of volatile species (d'Hendecourt et al., 1982; Léger et al., 1985), large amounts of CO_2 should be released in the gas phase where, reacting with H_3^+, they should produce the HCO_2^+ ion (Herbst et al., 1977). Large quantities of HCO_2^+, exceeding theoretical predictions by two orders of magnitude, have been detected towards the Galactic Centre sources Sgr A and Sgr B2 (Minh et al., 1988) and the release of CO_2 from grain mantles appears to be a natural explanation for this observed high abundance of HCO_2^+. More detailed calculations to test this hypothesis have to be performed but because the amount of solid CO_2 to be released from ices is known with a reasonable accuracy for the first time, we have a direct means to quantitatively evaluate the feed-back of the grain chemistry to the gas phase in molecular clouds.

We expect, in the spectrum of these objects, a strong absorption band at 4.27 μm (2340 cm^{-1}) with an approximate width of 0.03 μm (12 cm^{-1}). For example, in AFGL 961, the optical depth of such a band, if resolved, would be about 2, making it the most intense solid state infrared feature observable in the interstellar medium besides H_2O.

5. Conclusion

We have discovered the CO_2 molecule in three sources. This molecule constitutes a significant part of the volatile molecular mantles frozen on interstellar grains. In the solid phase, 25 to 30% of the accreting CO appears transformed to CO_2, probably as a result of photochemistry induced by the UV radiation on the mantles. The presence of the strong absorption band of water ice at 13.5 μm and the fit of a laboratory spectrum to the observed astronomical spectra suggest that the CO_2 is mixed with water ice as well as CO and that such a situation is qualitatively well reproduced by laboratory simulations. Release of grain mantles to the gas phase will provide large amounts of CO_2 that may be detected via the HCO_2^+ ion. Thus a possible test of the effect of grain chemistry on the gas phase in molecular clouds is proposed.

Finally, although the LRS instrument onboard IRAS provides only low resolution data, it is remarkable that, because of the width of solid state features, such spectra yield the first detection of an abundant important interstellar molecule. No doubt that the better spectral resolution and larger wavelength coverage available with ISO (the Infrared Space Observatory) will provide rich insight into the grain chemistry and its relation to the gas phase.

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