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SWS observations of solid CO_2 in molecular clouds*

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Abstract. We report absorption features of solid CO_2 stretching and bending modes in several lines of sight, including embedded young stellar objects and the Galactic Center source Sgr A*. The overall CO_2 abundance in ices is $\sim 15\%$ relative to H_2O. Profile shapes are consistent with the presence of grain mantles with distinct polar (H_2O-rich) and nonpolar (CO or CO_2-rich) layers. In addition to the normal isotopic form, we report detection of the stretching mode of $^{13}CO_2$; the $^{12}C/^{13}C$ ratio is consistent with terrestrial and interstellar values.

Key words: ISM: molecules – dust, extinction – infrared: interstellar: lines – stars: pre-main sequence – Galaxy: center

1. Introduction

A key problem in astrophysics is to understand the cosmic evolution of carbon, from its creation by nucleosynthesis in post-main-sequence stars to its inclusion in living systems on the surface of the Earth. Between these extremes, dust grains provide a repository for condensed carbon in interstellar clouds and protoplanetary disks. In molecular clouds, refractory carbon and silicate grains acquire icy mantles, composed primarily of H_2O, but also containing carbon-bearing species such as CH_4, CH_3OH and CO (Whittet 1993). The relative abundance of CH- and CO-bonded carbon in the ices is an important (but currently poorly constrained) parameter; this will affect chemical evolution when the ices are subject to irradiation and warm-up with the onset of star formation.

Ground-based observations showed that CO is a ubiquitous constituent of grain mantles in cold, dense regions of molecular clouds (Chiar et al. 1995 and references therein). Its abundance may range up to $\sim 50\%$ of the H_2O abundance. The presence of CO on grains naturally led to the prediction that CO_2 might also be present, as CO_2 forms readily in laboratory ice analogues containing CO when subject to energetic processing such as ultraviolet irradiation or particle bombardment (e.g. d'Hendecourt et al. 1986; Sandford et al. 1988). Profiles of the 4.67 μm CO feature in the spectra of several young stellar objects (YSOs) are best fit by laboratory mixtures of CO and CO_2 (Chiar et al. 1995), suggesting that energetic production of CO_2 is, indeed, occurring in the vicinities of these embedded stars.

Direct spectroscopic detection of interstellar CO_2 was previously hindered by the presence of CO_2 absorption in the Earth's atmosphere. Both the strong stretching-mode resonance at 4.27 μm (2340 cm^{-1}) and the bending-mode resonance at 15.2 μm (660 cm^{-1}) require a satellite platform for detection. Observations of the bending mode with the low resolution spectrometer of the Infrared Astronomical Satellite have been reported (d'Hendecourt & Jourdain de Muizon 1989), but this instrument had insufficient spectral resolution to provide a very sensitive diagnostic. Following the launch of the Infrared Space Observatory (ISO; Kessler et al. 1996) it is possible to observe

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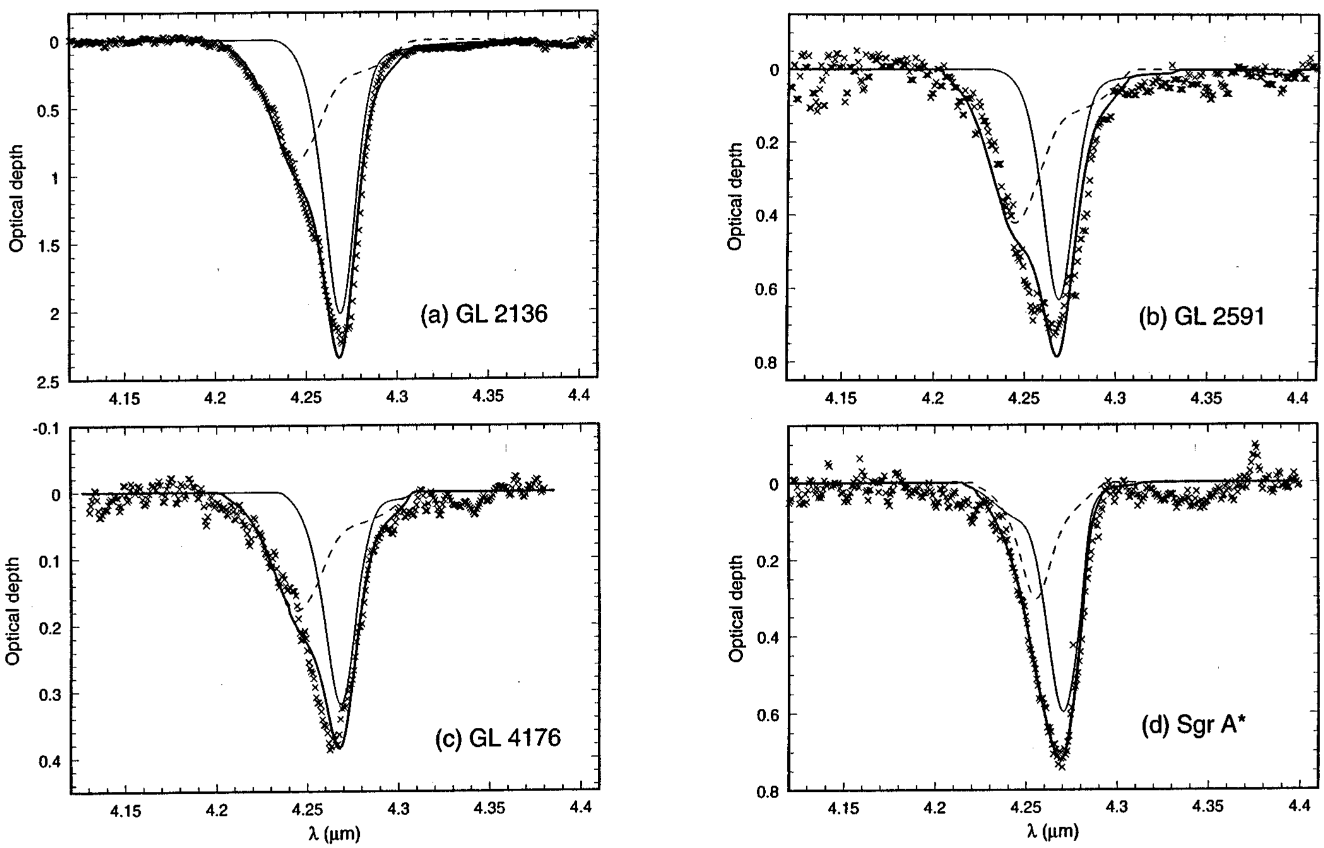

Fig. 1. Optical depth spectra of the $^{12}CO_2$ stretching mode feature in (a) GL 2136, (b) GL 2591, (c) GL 4176 and (d) Sgr A*. Observational data are represented by '×' symbols. Best-fitting models based on laboratory data (thick lines) are also shown; polar and nonpolar components of the models are plotted separately as continuous and dashed lines, respectively.

both vibrational modes at appropriate resolving power. This Letter reports first detection of CO_2 in molecular clouds observed by ISO; an accompanying paper (van Dishoeck et al. 1996) reports a search for gas phase CO_2 in four of the five sources included here.

2. Observations

The ISO short wavelength spectrometer (SWS; de Graauw et al. 1996) was used to obtain spectra in the regions of the CO_2 stretching and bending modes (4.1–4.4 μm and 14–16 μm, respectively). Four of the infrared sources included in this study, GL 2136, GL 2591, GL 4176 and NGC 7538 IRS9, are thought to be YSOs embedded in molecular clouds. For comparison, we also discuss SWS data for the Galactic Center source Sgr A*, reported by Lutz et al. (1996): although often used as a probe of dust in the diffuse ISM, the presence of absorption by CO_2 and H_2O ices implies the presence of molecular material in this line of sight. The four YSOs were observed in SWS grating mode AOT06, giving a mean resolving power $\lambda/\Delta\lambda \sim 2000$. Sgr A* was observed in mode AOT01 (full grating scan, speed 4), yielding resolution a factor ~ 2 lower. The instrument, its calibration, and data reduction techniques are described in detail elsewhere in this volume.

3. Results and discussion

The stretching mode is detected in all five sources. The bending mode is seen in GL 2136, NGC 7538 IRS9 and Sgr A* (but is too weak in Sgr A* for detailed profile analysis). Only upper limits could be set on bending modes in GL 2591 and GL 4176. Optical depth spectra are shown in Fig. 1 (stretching mode) and Fig. 2 (bending mode), together with fits described below. Note that the stretching mode in NGC 7538 IRS9 (not shown) is saturated. Optical depths were calculated by fitting local continua through adjacent regions of the flux spectra (4.10–4.18 and 4.32–4.37 μm for the stretch mode; 14.6–14.8 and 15.8–16.0 μm for the bend mode). Positions, widths (FWHM) and peak optical depths are listed in Table 1. Weak absorptions at 4.39 μm due to the $^{13}CO_2$ stretching mode were also detected in GL 2136 ($\tau_{\rm max} \approx 0.04$) and NGC 7538 IRS9 ($\tau_{\rm max} \approx 0.1$). The $^{12}CO_2/^{13}CO_2$ ratio is $\sim$ 40–70, comparable with terrestrial and interstellar $^{12}C/^{13}C$ ratios.

Gas phase absorption lines may cause fine structure in the solid state profiles. In the case of the stretch mode, the P and R branches of the ro-vibrational spectrum of gaseous CO_2 cannot be easily distinguished from the solid state feature (van Dishoeck et al. 1996). In the case of the bend mode, the unresolved Q branch causes excess absorption near 14.98 μm in the

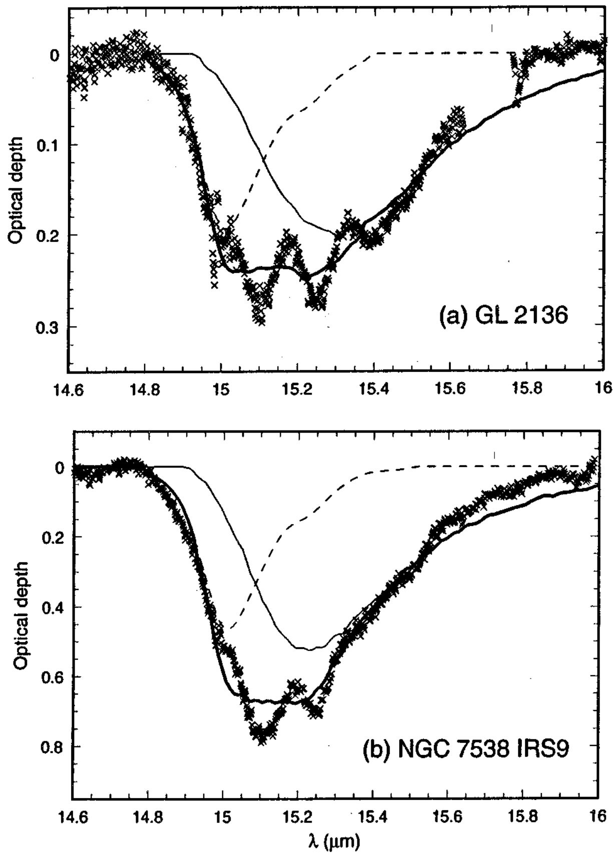

Fig. 2. Optical depth spectra of the $^{12}CO_2$ bending modes in (a) GL 2136 and (b) NGC 7538 IRS9. Lines and symbols have the same meaning as in Fig. 1. Note that the model spectra do not attempt to fit narrow substructure in the profiles.

Table 1. Positions, widths and optical depths of the observed $^{12}CO_2$ features. For the bending mode, the positions of the subpeaks are given in GL 2136 and NGC 7538 IRS9. Units for ν_0 and $\Delta\nu$ are cm^{-1}. A colon indicates an uncertain value.

Source	Stretching mode			Bending mode		
	ν_0	$\Delta\nu$	τ_{max}	ν_0	$\Delta\nu$	τ_{max}
GL 2136	2342.2	19.3	2.14	655.9 662.4	24.5	0.28
GL 2591	2344.8	25.8	0.71	—	—	<0.1
GL 4176	2345.3	19.7	0.37	—	—	<0.1
N 7538 IRS9	2345:	>20	>3	655.8 662.0	19.7	0.78
Sgr A*	2342.5	17.2	0.72	656.2	19:	0.07

Table 2. Solid state column densities of $^{12}CO_2$ from our results, together with values for H_2O and CO from the literature. All values are in units of 10^{17} cm^{-2}.

Source	$N(CO_2)$	$N(H_2O)$	N(CO)	Reference
GL 2136	6.1	50	1.8	1, 2
GL 2591	2.7	17	<0.5	3, 4
GL 4176	1.2	9	<0.5	5
N 7538 IRS9	12	80	10	2, 6
Sgr A*	1.5	12	$\lesssim$1.5	7

References: 1. Schutte et al. (1996a); 2. Tielens et al. (1991); 3. Smith et al. (1989); 4. Lacy et al. (1984); 5. Ehrenfreund et al. (in preparation); 6. Schutte et al. (1996b); 7. McFadzean et al. (1989).

short-wavelength wing of the solid state feature: this structure is clearly seen in GL 2136 and NGC 7538 IRS9 (Fig. 2). Estimated gas phase CO_2 column densities are only a few percent of the solid state CO_2 column densities (van Dishoeck et al. 1996).

Solid state CO_2 column densities (Table 2) were calculated from the formula $N = \int \tau(\nu)d\nu/A$, where A is the band strength. The integration is carried out over the entire profile of the observed feature. A is only weakly dependent on the composition of the matrix containing the CO_2 (Gerakines et al. 1995), thus we effectively measure $N(CO_2)$ summed over all possible matrices. Also listed in Table 2 are results for H_2O and CO in ices, estimated from data in the literature. Note that N(CO) towards Sgr A* is based on a tentative detection in IRS12 contrasted with non-detections in IRS3 and IRS7 (McFadzean et al. 1989); all three sources lie in the SWS beam.

The five objects in our sample have $N(CO_2)/N(H_2O)$ ratios in the range 0.12–0.16. It is interesting that the Galactic Center source, presumably obscured by foreground clouds, yields essentially the same result as the embedded YSOs. The relative CO abundance is lower, varying between 0.13 (NGC 7538 IRS9) and < 0.03 (GL 2591). No objects in the present study have solid CO abundances approaching the highest values seen in some dark clouds (Chiar et al. 1995). Together, CO and CO_2 account for a substantial fraction of the inventory of detected molecules in interstellar ices. This may be contrasted with the rather low abundance of CH bonded carbon in known species such as CH_3OH (5–10%) and CH_4 ($\sim$ 1%) (Whittet 1993; Boogert et al. 1996). Our current inventory is no doubt far from complete.

Laboratory spectra for various ice mixtures containing CO and CO_2 at 10–80 K (Ehrenfreund et al. 1996) were used to fit the observed CO_2 profiles. Model spectra were calculated using Mie theory for power-law size distributions of spherical particles in the small particle limit. The fitting routine selects the best fitting mixture or combination of mixtures by χ^2 minimization from a suite of 47 calculated spectra. The method is the same as previously used to fit ground-based solid CO spectra (Chiar et al. 1995). Results are summarized in Table 3 and plotted with the observed spectra in Figs. 1 and 2. Best fits were obtained in every case by combining a polar mixture (dominated by H_2O) with a nonpolar mixture (dominated by CO_2) at temperatures 10–30 K, consistent with studies of solid CO. However, it is generally the nonpolar ices that contribute greatest optical depth in the CO feature, whereas polar ices dominate the CO_2 features. Hence, the distribution of CO and CO_2 between polar and nonpolar ices must be different. This is expected if CO in the more volatile nonpolar ices is partially desorbed in conditions that promote

Table 3. Summary of best-fitting laboratory mixtures.

Source	Mixtures	T (K)	τ_{max}
	Stretching mode:		
GL 2136	H_2O:CO_2:CO = 100:8:8	30	2.02
	H_2O:CO_2 = 1:10	10	0.89
GL 2591	H_2O:CO_2:CO = 100:8:8	30	0.63
	H_2O:CO_2 = 1:10	10	0.42
GL 4176	H_2O:CO_2:CO = 100:5:10	10	0.32
	H_2O:CO_2 = 1:10	10	0.18
Sgr A*	H_2O:CO_2:CO = 100:8:8	30	0.60
	CO:CO_2 = 100:50	10	0.30
	Bending mode:		
GL 2136	H_2O:CO_2:CO = 100:5:10	10	0.20
	H_2O:CO_2 = 1:10	10	0.19
N 7538 IRS9	H_2O:CO_2 = 100:20	10	0.53
	H_2O:CO_2 = 1:10	10	0.46

CO_2 formation, whereas CO in the polar ices is converted more efficiently into CO_2.

The bending modes in GL 2136 and NGC 7538 IRS9 show considerable structure, with subpeaks at 15.10 and 15.25 μm and a shoulder at 15.4–15.6 μm (Fig. 2). We interpret this structure in terms of a broad ($\sim 0.5\,\mu$m) underlying component, peaking around $\sim 15.2\,\mu$m, with separate narrow component(s) responsible for the subpeaks. The broad component is well fit by essentially the same combination of polar and nonpolar mixtures that fit the stretching mode (Table 3). The subpeaks might arise in a minor phase (containing $< 15\%$ of the total CO_2) which is indistinguishable in the stretching region. Two classes of model might explain them. First, bulk spectra of *pure* CO_2 show splitting of the bending mode (this vibration is doubly degenerate and splits when the axial symmetry is broken). However, particle shape influences the positions of the subpeaks (Ehrenfreund et al. 1996), and good fits to the observed positions are only obtained for a very restrictive set of parameters (oblate or prolate spheroids with axial ratios 0.1 ± 0.05). Alternatively, the narrow subpeaks might reflect the presence of traces of CO_2 in an environment which allows multiple trapping sites: e.g., a CO:O_2:CO_2 = 100:50:8 mixture shows subpeaks at 15.12 and 15.19 μm, near those in the interstellar spectra. However, the subpeaks are very sensitive to matrix conditions and concentrations (see Fig. 3 of Ehrenfreund et al. 1996). Thus, both explanations for the substructure require very special conditions, either in grain population or in mantle composition. It is clear that, in principle, much information on interstellar ices is contained within these features.

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