Gas-phase CO\textsubscript{2} toward massive protostars\textsuperscript{*}

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Abstract. We present infrared spectra of gas-phase CO\textsubscript{2} around 15\,\mu m toward 14 deeply embedded massive protostars obtained with the Short Wavelength Spectrometer on board the Infrared Space Observatory. Gas-phase CO\textsubscript{2} has been detected toward 8 of the sources. The excitation temperature and the gas/solid ratio increase with the temperature of the warm gas. Detailed radiative transfer models show that a jump in the abundance of two orders of magnitude is present in the envelope of AFGL 2591 at $T > 300$ K. No such jump is seen toward the colder source NGC 7538 IRS9. Together, these data indicate that gas-phase CO\textsubscript{2} shows the same evolutionary trends as CO\textsubscript{2} ice and other species, such as HCN, C\textsubscript{2}H\textsubscript{2}, H\textsubscript{2}O, and CH\textsubscript{3}OH. The gas-phase CO\textsubscript{2} abundance toward cold sources can be explained by gas-phase chemistry and possible freeze-out in the outer envelope. Different chemical scenarios are proposed to explain the gas-phase CO\textsubscript{2} abundance of $1–2 \times 10^{-6}$ for $T > 300$ K and of $\sim 10^{-8}$ for $T < 300$ K toward AFGL 2591. The best explanation for the low abundance in the warm exterior is provided by destruction of CO\textsubscript{2} caused by the passage of a shock in the past, combined with freeze-out in the coldest part at $T < 100$ K. The high abundance in the interior at temperatures where all oxygen should be driven into H\textsubscript{2}O is unexpected, but may be explained either by production of OH through X-ray ionization leading to the formation of abundant gas-phase CO\textsubscript{2}, or by incomplete destruction of evaporated CO\textsubscript{2} for $T > 300$ K.

Key words. stars: formation – ISM: abundances – ISM: molecules – infrared: ISM – ISM: lines and bands – molecular processes

1. Introduction

Carbon dioxide is predicted to be among the more abundant carbon- and oxygen-bearing gas-phase species in massive star-forming regions (e.g. Charnley 1997). However, the lack of a permanent dipole moment restricts observations of this molecule to infrared wavelengths. Due to its ubiquitous presence in the Earth’s atmosphere, it was not until the launch of the Infrared Space Observatory (ISO) that a systematic search for CO\textsubscript{2} toward star-forming regions could be performed. Van Dishoeck et al. (1996) made the first search for gas-phase CO\textsubscript{2} absorption toward a few deeply embedded massive protostars. Since then, ISO has detected gas-phase CO\textsubscript{2} toward many astronomical objects, including other massive protostars (Dartois et al. 1998; van Dishoeck 1998), planetary atmospheres, and Asymptotic Giant Branch stars (e.g. Lellouch et al. 2002; Justtanont et al. 1998; Cami et al. 2000).

Van Dishoeck et al. (1996) derive tentative gas-phase CO\textsubscript{2} abundances of $\sim 10^{-7}$ averaged over the line of sight. Somewhat higher abundances of a few times $10^{-7}$ are found in the direction of Orion-IRc2/BN, whereas more than an order of magnitude lower abundances are found toward the shocked regions Peak 1 and 2 (Boonman et al. 2003). Envelope models by Doty et al. (2002) predict abundances of a few times $10^{-8}$ for temperatures $\leq 100$ K and a few times $10^{-7}–10^{-6}$ for $T \sim 100–300$ K. Hot core models by Charnley (1997) also predict abundances of $10^{-7}–10^{-6}$ for $T \sim 200–300$ K. On the other hand, Charnley & Kaufman (2000) show that shocks containing a high H/H\textsubscript{2} ratio can destroy CO\textsubscript{2}, giving a possible explanation for the lower abundances found for the Orion shocked regions. Similarly, low gas-phase CO\textsubscript{2} abundances of $\sim 10^{-8}$ are predicted by gas-grain chemistry in the post-shock gas for dark-cloud type environments (Charnley et al. 2001).

In addition to gas-phase CO\textsubscript{2}, abundant CO\textsubscript{2} ice has been seen toward intermediate- to high-mass star-forming regions (de Graauw et al. 1996; D’Hendecourt et al. 1996; Gerakines et al. 1999; Nummelin et al. 2001). Abundances up to $10^{-5}$ have been found, much higher than the gas-phase CO\textsubscript{2} abundances. The ice abundances are highest for the coldest sources, implying that grain-mantle evaporation is important for the

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chemistry in warmer sources (van Dishoeck 1998). One of the main questions is whether abundances of gas-phase CO$_2$ as high as $\sim 10^{-5}$ are observed in any star-forming region.

In this paper, observations of the $v_2$ ro-vibrational band of gas-phase CO$_2$ around 15 μm toward 14 embedded massive young stars are presented. All sources in our sample have luminosities between $\sim 10^4$–$10^5$ $L_\odot$ and do have complementary ISO data on ices and other gas-phase molecules (e.g. Lahuis & van Dishoeck 2000; Gerakines et al. 1999; Keane et al. 2001b). The observations and reduction of the data are summarized in Sect. 2. Section 3 describes the analysis, using pure absorption models to derive abundances and gas/solid ratios. Radiative transfer effects are taken into account in Sect. 4 and the results are discussed in Sect. 5. Finally, the conclusions are presented in Sect. 6.

### 2. Observations and reduction

The $v_2$ ro-vibrational band of gas-phase CO$_2$ around 15 μm has been observed with the Short Wavelength Spectrometer (SWS) in the AOT6 grating mode toward all sources. The spectra have been reduced using the ISO-SWS Interactive Analysis System SIA using the ISO Off-line Processing (OLP version 10) software modules and calibration files. In addition, the instrumental fringes have been removed by a combination of an optimized spectral response calibration and robust sine wave fitting (Lahuis & van Dishoeck 2000). The spectra have been rebinned to an effective spectral resolution of

![Fig. 1. ISO-SWS spectrum of AFGL 2136 between 14.5 and 16 μm. The dashed line shows the adopted continuum, the solid line a good fitting ice mixture of polar + annealed ice (H$_2$O:CO:CO$_2$ = 100:3:20+ H$_2$O:CH$_3$OH:CO$_2$ = 1:1:1 respectively) to the observed CO$_2$ ice band (Gerakines et al. 1999).](image-url)

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Table 1. Observed sources and their properties.

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$^a$ For sources where multiple IDs are listed, the spectra presented in this paper are a combination of all of these.

$^b$ Continuum flux at $\sim 15$ μm in the ISO-SWS aperture, obtained by extrapolating the continuum flux in the 14.5–14.8 μm region.

$^c$ The first reference refers to the luminosity, the second to the distance.

Normalised ISO-SWS spectra in the region of the gas-phase CO$_2$ $\nu_2$ bending mode for all sources. The solid CO$_2$ feature has been removed (see text). The $\nu_2$ ro-vibrational band of gas-phase CO$_2$ has been detected toward the sources AFGL 2136, AFGL 2591, AFGL 4176, MonR2 IRS3, NGC 7538 IRS1, NGC 7538 IRS9, W 33 A, and W 3 IRS5. The spectra of AFGL 2136, AFGL 2591, AFGL 4176, and NGC 7538 IRS9 have been analysed previously by van Dishoeck et al. (1996). The reduced spectra presented here are however of much higher quality. Both the instrument calibration and the reduction routines within the ISO-SWS pipeline as well as the SWS Interactive Analysis have improved significantly since 1996. In addition for AFGL 2136, AFGL 2591, and AFGL 4176, the spectra of multiple independent observations of the same source have been combined, leading to an additional increase in the final S/N ratio.

An example of the resulting spectra is shown in Fig. 1 together with a fit to the CO$_2$ ice band, using an ice mixture similar to that found by Gerakines et al. (1999). Although the laboratory ice fit follows the solid-state feature quite well, it shows some small deficiencies, which could be due to the presence of other solid-state features that are not accounted for in the...
Fig. 3. The strength of the CO$_2$ (02$^2$0) ← (01$^1$0) hotband (thick line) compared to the fundamental (01$^1$0) ← (00$^0$0) band (thin line) for different excitation temperatures, using $b = 3$ km s$^{-1}$ and $N = 1 \times 10^{16}$ cm$^{-2}$.

ice fit. Therefore the final spectra have been divided by a manual fit to the CO$_2$ ice band, resulting in the normalised spectra presented in Fig. 2. Different fits to the continuum have been made to investigate their effect on the shape and depth of the gas-phase CO$_2$ band and these have been taken into account in the analysis of the spectra.

3. Analysis

3.1. Homogeneous pure absorption models

The modeling of the spectra has been performed by computing synthetic spectra using the method described in Lahuis & van Dishoeck (2000). In this method, the source is assumed to be a homogeneous sphere with a single temperature $T_{ex}$ and column density $N$. Here it is assumed that only absorption takes place and that emission can be neglected. The effects of adopting a non-homogeneous source and including emission are discussed in Sect. 4. The models are not sensitive to the CO$_2$ line width as long as the lines are not saturated, which becomes important only for $b \lesssim 1$ km s$^{-1}$. A mean Doppler $b$-value of 3 km s$^{-1}$ is adopted (see also Boonman et al. 2003), but values up to $b = 10$ km s$^{-1}$ have been explored. Similar values are used in the modeling of other observed ro-vibrational absorption lines in the same wavelength region toward these sources (e.g. Lahuis & van Dishoeck 2000; Keane et al. 2001a). For comparison, Mitchell et al. (1990) derive line widths of $b \sim 4$–7 km s$^{-1}$ from high-resolution observations of the CO ro-vibrational band around 4.7 $\mu$m. The resulting synthetic spectra have been convolved to the nominal spectral resolution of the ISO-SWS spectra for comparison with the data.

The molecular line data have been taken from the HITRAN 2000 database (http://www.hitran.com). The model includes the fundamental (01$^1$0) ← (00$^0$0) band at 14.983 $\mu$m, the hotbands (02$^2$0) ← (01$^1$0) and (02$^2$0) ← (01$^1$0) at 14.976 and 16.18 $\mu$m respectively, and the (10$^0$0) ← (01$^1$0) band at 13.87 $\mu$m. The (02$^2$0) ← (01$^1$0) and (10$^0$0) ← (01$^1$0) bands are not detected. The (02$^2$0) ← (01$^1$0) hotband coincides with the fundamental $Q$-branch, making it difficult to detect. Figure 3 shows the shape and strength of the CO$_2$ fundamental and the (02$^2$0) ← (01$^1$0) hotband for different excitation temperatures. This shows that for $T_{ex} \gtrsim 300$ K the (02$^2$0) ← (01$^1$0) hotband starts to play a role. This hotband was not included in the previous modeling of the CO$_2$ spectra by van Dishoeck et al. (1996).

The best fit to the data has been determined using the reduced $\chi^2$-method. Since the $P$-branches of the C$_2$H$_2$ $\nu_5$ and HCN $\nu_2$ ro-vibrational bands extend into the region of the CO$_2$ $\nu_2$ band, these bands are included in the modeling, using the best fit parameters from Lahuis & van Dishoeck (2000). For all sources, their contribution is less than the noise level, but they are included for consistency. The best fitting model parameters are listed in Table 2 for all sources. The uncertainty in the excitation temperature includes errors due to different continuum fits.
The results show that warm CO$_2$ gas at $T \gtrsim 200$ K is detected toward half of the sources and suggest that for the hottest sources, AFGL 2591, AFGL 2136, and AFGL 4176, also the $(02^20) \leftarrow (01^10)$ hotband contributes. The gas-phase $^{13}$CO$_2$ band near 15.4 μm is not detected in our sources.

A good fitting CO$_2$ model is presented in Fig. 4. Figure 5 shows an example of $x_{\nu 2}$ contours for the source AFGL 2136. It illustrates that the column density of the gas-phase CO$_2$ is well constrained, but that the excitation temperature shows a larger spread.

Comparison of our results for AFGL 2136 to those by Sandford et al. (2001) shows a lower excitation temperature than their $T_{\text{ex}}$ of 580 K. Also, their column density in the 580 K gas is more than an order of magnitude higher than that found here. This discrepancy is likely caused by the low signal-to-noise in the spectrum presented by Sandford et al. (2001), which is also hampered by the presence of instrumental fringes. These fringes are carefully removed in our spectra. In addition, our AFGL 2136 spectrum shows the detection of a few $P$- and $R$-branch lines (Fig. 4), which poses an extra constraint on the excitation temperature and column density. The fact that the CO$_2$ ice fit shown in Fig. 1 does not match the observed continuum very well between 14.6 and 14.8 μm introduces an uncertainty of ~100 K in the excitation temperature, which is accounted for in the results in Table 2. Therefore, the newly reduced spectra presented here allow a more reliable estimate of the excitation temperature and column density of the CO$_2$ $\nu_2$ ro-vibrational band.

Figure 6 presents a comparison of the CO$_2$ excitation temperature $T_{\text{ex}}$(CO$_2$) and that of C$_2$H$_2$, a good tracer of the warm gas (Lahuis & van Dishoeck 2000). Only those sources are shown for which both excitation temperatures are determined. The cross denotes typical error bars for $T_{\text{ex}} \gtrsim 200$ K.

3.2. Abundances

The CO$_2$ column densities have been converted into abundances, using the total H$_2$ column densities (cold + warm...
3.3. Gas/solid ratios

Gas/solid ratios can be determined by combining the derived gas-phase CO$_2$ column densities with those for CO$_2$ ice for the same sources from Gerakines et al. (1999) (see Fig. 7). This ratio increases with temperature, consistent with the location of CO$_2$ in the warm inner part of the envelope, above the evaporation temperature (Fig. 8). However, the increase is less strong and the ratios are lower than for H$_2$O, although pure CO$_2$ ice is more volatile than H$_2$O (Fig. 8; Boonman & van Dishoeck 2003). This is probably due to the fact that toward our sources CO$_2$ ice is mostly embedded in a H$_2$O ice matrix and that its column density is only 10–23% of that of H$_2$O ice (Gerakines et al. 1999). In addition, gas-phase H$_2$O abundances of up to $\sim 10^{-4}$ are easily formed above $T > 230$–300 K, thus rapidly increasing the H$_2$O gas/solid ratio (Charnley 1997).

4. Radiative transfer effects

4.1. Filling in by emission

In this section, the effect of possible emission along the line of sight on the derived CO$_2$ column densities and abundances is investigated. To this purpose a similar excitation model as that described in Boonman et al. (2003) has been set up. This excitation model includes energy levels for CO$_2$ up to $J = 40$ in both the $v_2 = 0$ and 1 vibrational states. The level populations are calculated adopting a Boltzmann distribution using $T_{ex}$ from Table 2. As a central radiation source, a blackbody with $T = 300$ to 600 K has been explored.

Adopting a homogeneous source as before, but including both absorption and emission along the line of sight, shows that the CO$_2$ column densities needed to match the observations are up to $\sim 30\%$ higher than those listed in Table 2 as long as the excitation temperature is less than $\sim 250$–300 K. This is within the listed error bars. The emission only becomes important for $T_{ex} \gtrsim 250$–300 K, i.e. for the sources W 3 IRS5, AFGL 2136, AFGL 4176, NGC 7538 IRS1, and AFGL 2591 (see also Boonman et al. 2003). For these sources, the CO$_2$ column density that best matches the observations can be up to a factor of $\sim 3$ higher than that derived from the pure absorption models (Table 2). Note that this model does not include other radiative transfer effects, such as infrared pumping, nor does it include temperature and density gradients, so that the derived CO$_2$ abundances within this model are not very accurate.

4.2. Temperature and density gradients: Jump models

Van der Tak et al. (2000b) show that a density and temperature gradient is present in their sample of deeply embedded massive young stars, which is a sub-set of the sample studied here. Since radiative transfer effects are expected to be largest for the warmer sources, AFGL 2591 is taken as a test case. Adopting the physical model for AFGL 2591 derived by van der Tak et al. (2000b), the level populations and radiative transfer are calculated with the Monte Carlo code of Hogerheijde & van der Tak (2000) on a grid of concentric shells, assuming spherical geometry. The calculations include energy levels up to $J = 40$ in both the $v_2 = 0$ and $v_2 = 1$ states, the same as in the excitation model described in Sect. 4.1. The collisional rate coefficients used are taken from Allen et al. (1980). Radiative excitation through the 15 $\mu$m band due to warm dust mixed with the gas is included, using grain opacities from Ossenkopf & Henning (1994) and assuming $T_{dust} = T_{gas}$. No external radiation field apart from the 2.73 K cosmic background radiation was applied. The resulting level populations are used in the excitation model described above to calculate a synthetic model spectrum including both emission and absorption along the line of sight. As a central radiation source a blackbody at $T > T_{dust}$ in the innermost shell is chosen. The resulting model spectrum is then compared with the observed absorption spectrum.
For AFGL 2591 it is found that a constant CO2 abundance $x(\text{CO}_2) = n(\text{CO}_2)/n(\text{H}_2)$ throughout the envelope produces a synthetic spectrum with a $Q$-branch that is too narrow compared to the observations (Fig. 9). This indicates that the constant abundance model is dominated by absorption from gas at $T < 300$ K. Therefore a model with a jump in the abundance at $T = 300$ K has been tried. It is found that a model spectrum with a CO2 abundance of $\sim 1 - 2 \times 10^{-6}$ for $T > 300$ K and $10^{-8}$ for $T < 300$ K can reasonably explain the observed spectrum (Fig. 9). Applying a jump at lower temperatures, e.g. $T = 200$ K or $T = 100$ K produces a $Q$-branch that is too narrow. This indicates that the observed $Q$-branch represents warm CO2 gas from the inner part of the molecular envelope at $T \geq 300$ K, in agreement with that inferred from the pure absorption models. It also shows that the CO2 abundance in the outer envelope is much lower, about two orders of magnitude. Similar jumps in the abundance have been seen for other molecules toward AFGL 2591, such as HCN, H$_2$O, and SO$_2$ (Boonman et al. 2001; Boonman & van Dishoeck 2003; Keane et al. 2001a; van der Tak et al. 2003).

Similarly one of the colder sources, NGC 7538 IRS9, is modeled for comparison using the physical model derived by van der Tak et al. (2000b). It is found that a constant CO2 abundance of $\sim 7 \times 10^{-8}$ can reproduce the observed spectrum. A model with a jump in the abundance at $T = 100$ K and $x(\text{CO}_2) = 2 \times 10^{-7}$ for $T > 100$ K and $x(\text{CO}_2) = 1 \times 10^{-9}$ for $T < 100$ K gives a similarly good fit in terms of $\chi^2$. This indicates that for NGC 7538 IRS9 no evidence for a jump in the abundance at temperatures $T \geq 300$ K is found. The result that a jump in the abundance at $T = 100$ K fits the observed spectrum equally well as the constant abundance model may suggest that most of the CO2 is frozen-out onto the grains below this temperature.

The corresponding CO2 column densities for the best fit models for AFGL 2591 and NGC 7538 IRS9 are a factor of $\sim 1.5 - 2$ higher than those listed in Table 2 respectively. On the other hand, the abundance toward NGC 7538 IRS9 is somewhat lower than that derived from the pure absorption models (Table 2).

The above results indicate that a jump in the CO2 abundance is present for the warmer, more evolved sources, but that no such jump is seen toward the colder objects. This suggests that also for AFGL 2136, AFGL 4176, and NGC 7538 IRS1 a jump in the CO2 abundance is present.

Observations of the intermediate-mass protostars AFGL 490 and AFGL 7009S show CO2 abundances of a few $10^{-7}$, similar to those derived from the pure absorption models in Sect. 3.2 (Schreyer et al. 2002; Dartois et al. 1998). These CO2 abundances do not show a clear trend with temperature (Fig. 7). However the results from the detailed radiative transfer models indicate much higher CO2 abundances in the warm inner part of the envelope for the more evolved sources. Combined with the somewhat lower CO2 abundance toward the cold source NGC 7538 IRS9, this suggests that the CO2 abundance increases with temperature and evolutionary state.

5. Discussion

5.1. CO2 as an evolutionary tracer

In Sect. 3 it is shown that $T_{\text{ex}}(\text{CO}_2)$ increases with $T_{\text{ex}}(\text{C}_2\text{H}_2)$, indicating that it is a tracer of the warm gas. The gas/solid ratio also increases with the temperature of the warm gas and the CO2 ice abundance decreases (Figs. 7 and 8). The higher ratios for the warmer sources suggest that they are in a later evolutionary stage than the sources with low gas/solid ratios, with the higher temperatures due to dispersion of a larger fraction of the molecular envelope (van der Tak et al. 2000b; van Dishoeck & van der Tak 2000).

Although the abundances derived from the pure absorption models do not show a clear trend with temperature, the results from the jump models in Sect. 4.2 suggest that the CO2 abundance increases with temperature. In addition, the same sources with a high CO2 excitation temperature and correspondingly a
higher gas/solid ratio also show evidence for thermal processing of $^{13}$CO$_2$ and CO$_2$ ice (Boogert et al. 2000; Gerakines et al. 1999). Together, this shows that CO$_2$ can be used as an evolutionary tracer.

5.2. Chemistry in cold sources: NGC 7538 IRS9

Envelope models by Doty et al. (2002) predict gas-phase CO$_2$ abundances of $\sim 10^{-6}$ at $T \lesssim 300$ K for $t \sim 3 \times 10^8$–$10^9$ yrs. This indicates that pure gas-phase chemistry can explain the observed abundances toward the colder sources, such as NGC 7538 IRS9, that show no evidence for a jump in the abundance for $T \gtrsim 300$ K (Sect. 4.2).

In the colder sources, the high CO$_2$ ice abundances and low gas/solid ratios indicate that a large fraction of the envelope still contains cold material. This suggests that the observed gas-phase CO$_2$ absorption is dominated by the colder outer envelope where evaporation has not yet taken place. However, these sources may still hide a small region in the inner envelope containing hot, abundant gas-phase CO$_2$, which cannot be detected with the present observations, e.g. due to continuum optical depth effects.

5.3. Chemistry in warm sources: AFGL 2591

5.3.1. Comparison to hot core and shock models

The high inferred gas-phase CO$_2$ abundance in the inner envelope of AFGL 2591 for $T > 300$ K but lack of a jump at $T \sim 100$ K in Sect. 4.2 is unexpected. Such a jump is observed for simple ice constituents such as H$_2$O and CH$_3$OH in hot core-type objects (e.g. van der Tak et al. 2000a; Maret et al. 2002), which is due to evaporation of H$_2$O-rich ices around $T \sim 90$–110 K (Fraser et al. 2001). Since most of the CO$_2$ ice is embedded in H$_2$O ice, it will evaporate around the same temperature (Fig. 10). The high gas/solid ratio and low CO$_2$ ice abundance of $1.7 \times 10^{-6}$ (Gerakines et al. 1999) toward AFGL 2591 indicate that evaporation of CO$_2$ ice does occur (see also Fig. 7, right panel). The lack of a jump around 100 K then indicates that CO$_2$ must be rapidly destroyed in the gas phase after evaporation in the $T \sim 100$–300 K zone. At $T > 300$ K, either the CO$_2$ is only partially destroyed or it has quickly reformed in the gas-phase.

Second, the CO$_2$ solid-state abundances toward the cold sources with little or no ice evaporation are an order of magnitude higher than the gas-phase CO$_2$ abundance in the inner hot envelope of AFGL 2591 (Fig. 7). This suggests that CO$_2$ is originally formed on grain surfaces, and not simply due to freeze-out of CO$_2$ gas. The discrepancy between the observed gas-phase and solid-state CO$_2$ abundances provides further evidence for rapid destruction of CO$_2$ in the gas phase after evaporation from the grains. Charnley & Kaufman (2000) propose that shocks can be responsible for this.

A study of the Orion shocked regions Peak 1 and 2 shows gas-phase CO$_2$ abundances of $\sim 3 \times 10^{-6}$, which are best explained by destruction of the CO$_2$ in a shock containing a high H/H$_2$ ratio of $\sim 0.01$, and subsequent reformation in the gas-phase (Boonman et al. 2003). A similar abundance of $\sim 10^{-8}$ is found in the envelope of AFGL 2591 for $T < 300$ K in Sect. 4.2. This suggests that the outflow may have (partially) destroyed the CO$_2$ in the envelope of AFGL 2591 in the past, and that it has not yet been reformed. However, such a shock model cannot explain the high abundance in the inner envelope at $T > 300$ K, unless destruction is much less efficient in the densest inner part due to e.g. a lower H/H$_2$ ratio.

Doty et al. (2002) propose that a heating event can also destroy CO$_2$ through the reaction CO$_2$ + H$_2$ $\rightarrow$ CO + H$_2$O. Recent calculations by Talbi & Herbst (2002) however show that this reaction is not likely to play a dominant role in the interstellar medium.

The primary formation route of CO$_2$ in the gas-phase is through the reaction CO + OH $\rightarrow$ CO$_2$ + H which proceeds rapidly at $T \gtrsim 100$ K (Charnley 1997). Above $T \sim 230$–300 K most of the OH is driven into H$_2$O, thus reducing the formation of CO$_2$ through gas-phase reactions. This formation route predicts gas-phase CO$_2$ abundances of $\sim 10^{-6}$ at $T = 100$ K to a few $\times 10^{-7}$ at $T = 300$ K (Charnley 1997). This is much lower than the inferred CO$_2$ abundance of $1$–$2 \times 10^{-6}$ for $T > 300$ K toward AFGL 2591. On the other hand, gas-phase CO$_2$ can also be formed through the reaction of CO + H$_2$O, but this reaction has an energy barrier of $\sim 5.2 \times 10^4$ K, preventing production of significant CO$_2$ in the molecular envelope.

5.3.2. Comparison to UV, cosmic- and X-ray models

Alternatively, the UV flux from the protostar may be high enough in the inner envelope to produce OH through direct photodissociation of H$_2$O. This could maintain sufficient OH in the gas-phase to form abundant gas-phase CO$_2$ in the interior at $T \gtrsim 300$ K. However, photodissociation is estimated to play a role only up to $r \sim 10^4$ cm from the central source, much smaller than the inner radius of the physical model used.

![Fig. 10. Gas-phase CO$_2$ abundances in the envelope of AFGL 2591 for chemical ages of $3 \times 10^3$, $3 \times 10^4$, $3 \times 10^5$, and $3 \times 10^6$ yrs (after Doty et al. 2002). a) Gas-phase chemistry including evaporation of CO$_2$ ice for $T \sim 100$ K. The initial CO$_2$ abundance of $3 \times 10^{-5}$ for $T \gtrsim 100$ K and the cosmic ray ionization rate of $\zeta_{CR} = 5.6 \times 10^{-17}$ s$^{-1}$ from Doty et al. (2002) have been adopted. b) Gas-phase chemistry adopting $n$(CO$_2$)/$n$(H$_2$) = 0 initially, $\zeta_{CR} \sim 10^{-20}$ s$^{-1}$ for $T < 200$ K, and an ionization rate of $\zeta = 2 \times 10^{-16}$ s$^{-1}$ for $T > 200$ K.]
in Sect. 4.2. Doty et al. (2002) suggest that cosmic-ray or X-ray ionization can also produce significant OH, which is then channelled into CO_2. Using the chemical model from Doty et al. (2002) for AFGL 2591 and adopting a zero initial gas-phase CO_2 abundance corresponding to the destruction of CO_2 by a shock, indeed predicts enhanced CO_2 abundances of ~10^{-6}–10^{-5} in the interior for T > 200 K if a high ionization rate of 2 × 10^{-16} s^{-1} is adopted (Fig. 10). This illustrates that a high ionization rate in the inner envelope can produce a jump in the CO_2 abundance at temperatures larger than 100 K as found for AFGL 2591. This model adopts an artificially low cosmic-ray ionization rate of ζ_{CR} ∼ 10^{-20} s^{-1} in the outer envelope, predicting gas-phase CO_2 abundances of ~10^{-6} for T ≤ 200 K, consistent with that found in Sect. 4.2. Adopting ζ_{CR} = 5.6 × 10^{-17} s^{-1} as derived by van der Tak & van Dishoeck (2000) from HCO^+ observations results in much higher abundances of ~10^{-6}–10^{-5} for T ∼ 100–200 K and ~10^{-7} for T < 100 K, somewhat higher than that found for AFGL 2591. However, freeze-out of CO_2 onto the grains is likely to play a role for T < 100 K, which is not included in the model.

Doty et al. (2002) note that the ionization rate needs to be at least on the order of ζ = 5.6 × 10^{-17} s^{-1} in the interior, in order to account for the high gas-phase HCN abundances for T ∼ 300 K. This is consistent with our proposed chemical scenario of a high ionization rate in the inner envelope, explaining the jump in the CO_2 abundance for T ∼ 300 K. Although the production of CO_2 through X-ray ionization involves destruction of gas-phase H_2O and CO, the predicted enhanced CO_2 abundances in Fig. 10 are ≤10% of those predicted for H_2O and CO. In addition, abundant gas-phase H_2O and CO are observed in the warm inner envelope from infrared absorption (e.g. Boonman et al. 2000; Mitchell et al. 1990), suggesting that these molecules are not significantly affected by X-rays. Since the cosmic-ray ionization rate is expected to be roughly constant or potentially decreases inward within the molecular envelope, the enhanced ionization rate in the warm interior seems more likely caused by X-rays from the young star than cosmic rays from outside the molecular envelope. Using the photoionization cross section from Wims et al. (2000), it is estimated that X-rays of a few keV can affect the chemistry up to radii at which T ∼ 400 K in the envelopes of massive protostars. Recently, X-ray emission within this energy range has been detected toward MonR2 IRS3, one of our warm sources, further suggesting that X-ray ionization may be important for the CO_2 chemistry in the inner envelope of massive young stars (Preibisch et al. 2002; Kohno et al. 2002).

5.3.3. Comparison to dynamical models

Another possibility is that gas-phase CO_2 in the interior results from ice evaporation at T ∼ 100 K in the past, and is subsequently heated as the protostar evolves to higher temperatures at the same point in the envelope, without being destroyed. However, material initially at T < 100 K will consequently be heated to T > 100 K, where ice evaporation occurs almost instantaneously (Fraser et al. 2001). This predicts gas-phase CO_2 abundances of ~10^{-6}–10^{-5} between 100 and 300 K, contrary to the inferred abundance of ~10^{-8}.

A second scenario to consider would be the dynamical transport of gas-phase CO_2 formed between 100 and 300 K inward to the T > 300 K region, e.g. through infall motions. In this case, however, the CO_2-ice containing material at T < 100 K would be transported inward to the T = 100–300 K region. At this point, the CO_2 ice would evaporate immediately, thus maintaining a large gas-phase CO_2 abundance for T = 100–300 K.

At present, a combination of the destruction of CO_2 by a past shock in the outflow, and either a high X-ray ionization rate in the interior which rapidly reforms gas-phase CO_2 for T > 300 K or incomplete destruction of evaporated CO_2 for T > 300 K, seems the most likely explanation for the inferred jump in the gas-phase CO_2 abundance for T > 300 K toward AFGL 2591. As noted by Doty et al. (2002), more experimental work on the chemistry of gas-phase CO_2 is needed to obtain a better knowledge of the formation and/or destruction pathways of gas-phase CO_2 in the envelopes of massive protostars.

6. Conclusions

The main conclusions of this work are:

- The CO_2 excitation temperature correlates well with that of C_2H_2, a good tracer of the warm gas.
- Overall abundances of a few ×10^{-7} are inferred from the pure absorption models, showing little trend with temperature. However, a jump in the CO_2 abundance for T ∼ 300 K of about two orders of magnitude is seen toward AFGL 2591, but not toward NGC 7538 IRS9. This suggests that only the warmer, more evolved sources show a jump in the CO_2 abundance.
- The results from the detailed radiative transfer models including a temperature and density gradient indicate that the CO_2 abundance increases with temperature and evolutionary state. Together with the increasing gas/solid ratio and CO_2 excitation temperature, this makes gas-phase CO_2 a useful evolutionary tracer for massive protostars.
- The inferred gas-phase CO_2 abundance toward NGC 7538 IRS9 can be explained by quiescent gas-phase chemistry in the cold outer envelope with possible freeze-out.
- The high observed gas-phase CO_2 abundance for T > 300 K in combination with the low abundance of ~10^{-8} for T < 300 K toward AFGL 2591 cannot be explained by grain-mantle evaporation or gas-phase chemistry. The low abundance for T ∼ 100–300 K is best explained by destruction of CO_2 through the passage of a shock in the past. The high abundance in the interior is best explained by either enhanced formation of OH through X-ray ionization, producing abundant CO_3 through its reaction with CO, or incomplete destruction of evaporated CO_2 for T > 300 K.
- The fact that the highest inferred gas-phase CO_2 abundance is still a factor of ~10 lower than the observed CO_2 ice abundances in cold sources where the ice has not yet
evaporated, suggests that CO$_2$ is originally formed on grain surfaces rather than by freeze-out of CO$_2$ gas.

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