SPITZER INFRARED SPECTROGRAPHER OBSERVATIONS OF CLASS I/II OBJECTS IN TAURUS: COMPOSITION AND THERMAL HISTORY OF THE CIRCUMSTELLAR ICES

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ABSTRACT

We present observations of Taurus–Auriga Class I/II protostars obtained with the Spitzer InfraRed Spectrograph. Detailed spectral fits to the 6 and 15.2 micron ice features are made, using publicly available laboratory data, to constrain the molecular composition, abundances, and levels of thermal processing along the lines of sight. We provide an inventory of the molecular environments observed, which have an average composition dominated by water–ice with 12% CO2 (abundance relative to H2O), 2%–9% CH3OH, 14% NH3, ∼3% CH4, 2%–9% H2CO, <0.6% HCOOH, and <0.5% SO2. We find CO2/H2O ratios nearly equivalent to those observed in cold clouds and lines of sight toward the galactic center. The unidentified 6.8 micron profiles vary from source to source, and it is shown to be likely that even combinations of the most common candidates (NH2+ and CH3OH) are inadequate to explain the feature fully. We discuss correlations among SED spectral indices, abundance ratios, and thermally processed ice fractions and their implications for CO2 formation and evolution. Comparison of our spectral fits with cold molecular cloud sight lines indicates abundant pre-stellar ice environments made even richer by the radiative effects of protostars. Our results add additional constraints and a finer level of detail to current full-scale models of protostellar and protoplanetary systems.

Key words: astrochemistry – infrared: ISM – ISM: abundances – ISM: molecules – stars: pre-main sequence

1. INTRODUCTION

The chemical and thermal evolution of protostellar environments affects the spectral appearance of ices observed in the sequential stages of pre-main-sequence evolution (e.g., Willner et al. 1982; Gerakines et al. 1999; van Dishoeck 2006). The presence of the ice absorption features is often easily recognized, with the most common ones in the mid-infrared wavelength range found at 6.0, 6.8, and 15.2 μm, but the exact feature shapes depend strongly on the composition of the ice as determined by the initial condensation and subsequent thermal processing and UV irradiation. Mixing ices can cause wavelength shifts in the resonances of the individual components within the ice matrix (e.g., Ehrenfreund et al. 1999; Palumbo & Baratta 2000; Oberg et al. 2007), and differences in the lattice structure caused by either radiation damage or thermal processing are spectroscopically identifiable (e.g., Hagen et al. 1981; Moore & Hudson 1992; Maldon et al. 1998; Kouchi & Kuroda 1990).

The initial reservoir of star formation material, the diffuse interstellar medium (ISM), is extremely ice-poor (e.g., Gillett et al. 1975; Whittet et al. 1997). It is not dense enough to shield its dust grains, upon which ices condense (e.g., Tielens & Allamandola 1987), from incident destructive photons. Only when cold molecular clouds of high density (nH > 104 cm−3) are formed can interstellar ices survive and be observed. In the Taurus molecular cloud, for example, a well-known seat of starbirth, ices are observed toward background stars even in quiescent regions unaffected by the newly formed stars (e.g., Bergin et al. 2005; Knez et al. 2005; Whittet et al. 2007). These studies reveal absorptions attributable to H2O, CO, and CO2, as well as some less-constrained absorptions (e.g., the still unidentified band at 6.8 μm) due to presumably more complex species. The ice bands observed toward these field stars are smooth, indicating amorphous and unprocessed compounds, and low upper limits can be placed on some species created by UV radiation (e.g., “XCN;” Gibb et al. 2004). These observations support the theory that molecular cloud ice chemistry is dominated by efficient cold grain–surface reactions. The presence of larger complex molecules (such as HCOOH, which can be formed at low temperatures; Keane 2001) demonstrates the potential complexity of these reactions and indicates that protostars are born into a pre-enriched chemical environment.

Surveys of deeply embedded young stellar objects (YSOs) reveal a limited range of thermal processing, indicative of differences in YSO environment and temperature (e.g., Gerakines et al. 1999; Gibb et al. 2004). Studies of less-extinguished protostars (Class I in the classification of Lada 1987) show evidence of enhanced complex molecule formation (H2CO, XCN, OCS, PAHs (polycyclic aromatic hydrocarbons)), ice crystallization, further thermal annealing, and ice matrix segregation (see e.g., Alexander et al. 2003; Keane et al. 2001; Ehrenfreund et al. 1998; Watson et al. 2004; Gibb et al. 2004; Boogert et al. 2004).

Finally, the least embedded Class II objects have seemingly accreted or dissipated most of their cold natal envelopes and have heated the outer layers of their dust disks above the sublimation temperature of astrophysical ices. These objects tend to show silicate dust emission, PAH emissions, and weak or nonexistent ice signatures (e.g., Forrest et al. 2004; Furlan et al. 2006), though some Class II edge-on systems have ice absorptions arising from the cold disk midplane (e.g., Pontoppidan et al. 2005; Furlan et al. 2008).

Differences in the chemical and physical structure exist between YSOs with masses either above or below a few M⊙.
(van Dishoeck 2003). Some of these dissimilarities may be attributed to observational biases (low-mass YSOs are generally closer and can be better resolved), but others are likely to be dependent on the intrinsic nature of the object (e.g., the role of shocks, core temperature, and infall timescales). For example, low-mass YSO studies claim higher abundances of CO$_2$ relative to H$_2$O (Boogert et al. 2004; Pontoppidan et al. 2008) and amorphous silicate dust (Watson et al. 2004), than surveys of more massive YSOs. This paper focuses on the relatively underexplored categories of low-mass Class I protostars and Class I/II transition objects (henceforth both groups will be collectively referred to as Class I/II objects) with ice absorptions by analyzing mid-infrared spectroscopy of 16 Taurus–Auriga YSOs (<1–3 Myr old; White & Ghez 2001), observed with the InfraRed Spectrograph (IRS; Houck et al. 2004) on board the Spitzer Space Telescope (SST; Werner et al. 2004). Our sample overlaps slightly with that of the extensive recent work by the e2d team (e.g., Boogert et al. 2008; Pontoppidan et al. 2008; Öberg et al. 2008), and we indicate differences in our approach and findings throughout this paper. This study helps complete our view of the ice evolutionary sequence from cold molecular clouds through warmer environments with protoplanetary disks. These low-mass, possibly early solar analogs are essential pieces to the puzzle of solar system formation.

Section 2 contains a short description of the sample, observations, and data reduction. In Section 3, we describe how the ice features are identified, isolated, and analyzed, and in Section 4, we look at trends seen in the feature optical depths. In Section 5, we derive the composition of the carriers of the primary ice absorptions and evaluate candidates for some of the less constrained features. In Section 6, we discuss composition and spatial distribution of the ices and place our observations in the context of pre-main-sequence evolution.

2. OBSERVATIONS

2.1. Target Sample Description

The Taurus–Auriga dark cloud is a nearby ($d \sim 140$ pc; Bertout et al. 1999), low-density ($n_s \sim 1–10$ pc$^{-3}$; Gomez et al. 1993) star-forming region containing predominantly young, low-mass protostars. It provides an opportunity to study closely low-mass Class I protostars. It provides an opportunity to study closely low-mass Class I protostars and Class II transition objects (henceforth both groups will be collectively referred to as Class I/II objects) with ice absorptions by analyzing mid-infrared spectroscopy of 16 Taurus–Auriga YSOs (<1–3 Myr old; White & Ghez 2001), observed with the InfraRed Spectrograph (IRS; Houck et al. 2004) on board the Spitzer Space Telescope (SST; Werner et al. 2004). Our sample overlaps slightly with that of the extensive recent work by the e2d team (e.g., Boogert et al. 2008; Pontoppidan et al. 2008; Öberg et al. 2008), and we indicate differences in our approach and findings throughout this paper. This study helps complete our view of the ice evolutionary sequence from cold molecular clouds through warmer environments with protoplanetary disks. These low-mass, possibly early solar analogs are essential pieces to the puzzle of solar system formation.

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2.2. Observational Procedure and Data Reduction

Our sample was observed with Spitzer’s IRS as part of the IRS Disks project (PI: J. Houck & D. Watson; PID 2) during guaranteed time awarded to the IRS instrument team (2004 February-March). All of our targets were observed using the full 5–37 μm wavelength coverage, combining either the Short Low and Low Long (SL, LL; 5.2–14 μm, 14–38 μm; /λ/Δλ ∼ 90) modules on the IRS, or the SL with the Short High and Long High (SH, LH; 10–19 μm, 19–37 μm; /λ/Δλ ∼ 600) modules, depending on the expected flux levels.

Most (12) of the objects were observed using a small spectral map (3 × 2) rather than a single pointing; this strategy avoids the need for pointing peak-ups and allows, in principle, for a better reconstruction of the spectrum in cases of small mispointings. The three-step sequence was carried out in the dispersion direction, with the steps separated by three quarters (for the SL module) or one-half (for the other modules) of the slit width. The two-step sequence corresponds to the normal IRS nod distance of one-third of the slit length. The other four objects were observed in the IRS staring mode, using only the two nods along the slit. Observational details of all our Class I/II targets are listed in Table 1.

We analyzed data from pipeline version S13, using the SMART package (Higdon et al. 2004). The standard IRS Disks reduction procedures, as well as any spectra requiring special treatment, are described in Furlan et al. (2006, 2008).

The uncertainty in each wavelength bin is taken to be half of the nod difference in flux level, except where this value is smaller than 1% of the flux. In those cases, the uncertainties are taken to be 1% of the flux in order to prevent underestimation. We estimate an absolute spectrophotometric accuracy of 5%–10%.

For the field stars, we used the previously published data for Elias 16 (Bergin et al. 2005) and Elias 13 and CK 2 (Knez et al. 2005), without re-reducing the data.

2.3. IRS Spectra Description

In Figure 1, we show the IRS spectra of the 16 Class I/II stars in our sample. The YSO mid-infrared spectra are dominated by broad solid state resonances, particularly those at 6.0, 6.8,
Figure 1. Our sample IRS spectra. The lower-left object has been marked with the locations and primary carriers of the most prominent absorption features. Note that the 9.7 μm silicate feature may also appear partly or wholly in emission.

3. METHODS

3.1. Isolating the IR Features and Determining Optical Depths

3.1.1. YSO Spectra

The optical depth, τ, and shape of the individual absorption features under consideration are extracted from the astronomical spectra using a mathematical continuum fit. We make a cubic spline fit to the ∼5–20 μm continuum of each spectrum using the following relatively feature-free regions: blueward of the 6 μm H2O feature; between the unidentified 6.8 μm feature and the onset of the 9.7 μm silicate band; and redward of the CO2 feature, while ensuring that none of the 9.7, and 15.2 μm. Additional, but less pronounced, features are visible in some spectra at 7.7 μm and as a broad band centered at 18 μm. Silicates are responsible for the broad 9.7 and 18 μm features, which can occur in either absorption (e.g., L1551 IRS 5), emission (e.g., IRAS 04108+2803A), or both.

The 6.0 μm feature is primarily due to the O–H bending mode of water ice, while the 6.8 μm feature remains largely unidentified, with CH3OH and NH4+ (among others) as suggested carriers. The 7.7 μm absorption is generally attributed to solid CH4, and the 15.2 μm band is due to the O–C–O bending mode of solid CO2. A complete inventory of absorption features identified in our spectra is contained in Table 2.

Spectra for W3(OH) and the Class 0 objects (Figure 2) contain many of the same features.
Table 2
Absorption Features Identified in Our YSO Spectra

| Wavelength (μm) | Carrier(s)         | Mode                           | A (10^{-17} cm molec^{-1}) | Reference |
|-----------------|--------------------|--------------------------------|----------------------------|-----------|
| Ice Features    |                    |                                |                            |           |
| 5.81            | H₂CO               | C=O stretching                 | 0.96                       | 1         |
| 5.85            | HCOOH              | C=O stretching                 | 6.7                        | 2         |
| 6.0             | H₂O                | H–O–H bending                  | 1.2–1.3^a                  | 3         |
| 6.8             | CH₃OH?, NH₃, organics | O–H bending, C–H deforming     | ...                        | 4         |
| 7.58            | SO₂                | S–O stretching                 | 3.4                        | 4         |
| 7.7             | CH₄                | C–H deforming                  | 0.73                       | 4         |
| 15.2            | CO₂                | O–C–O bending                  | 1.5^b                      | 3         |
| Other Features  |                    |                                |                            |           |
| 9.7             | Silicates          | Si–O stretching                | ...                        | 5         |
| 14.97           | CO₂                | gas-phase ν₂ bend             | ...                        |           |
| 18–20           | Silicates          | O–Si–O bending                 | ...                        |           |

Notes. ^a A depends on temperature; range represents 10–120 K. ^b A for H₂O:CO₂ mix; see Section 3.3.

References (1) Schutte et al. (1993), (2) Maréchal (1987), (3) Gerakines et al. (1995), (4) Boogert et al. (1997), (5) van Dishoeck et al. (1996).

Figure 2. IRS spectra of the Class 0 protostars CepE-MM (in Cepheus) and L1448 LRS 2 (in Perseus), and the line of sight to W3(OH) through the W3 molecular cloud. The 9.7 μm silicate absorption feature in CepE-MM is saturated.

feature wings are included in the continuum. We calculate the optical depth in the spectral features using \( F_\lambda = F_\lambda_{cont}e^{-\tau_\lambda} \).

Because the 9.7 μm silicate feature is highly complex, and detailed modeling of the silicate mineralogy is beyond the scope of this paper, accurate extraction of ice features blended with the 9.7 μm silicate complex (e.g., those of CH₃OH, NH₃, and H₂O) is impractical. However, the 11–13 μm H₂O libration band and the 18 μm absorption feature in particularly silicate-rich spectra are much broader and shallower than the 15.2 μm ice absorption they overlap, so we can treat these shapes as pseudocontinua in order to isolate the CO₂ ice absorption.

Additional steps are needed to extract small features in the 7–8 μm range. The wide variation in 6.8 μm and silicate absorption profile wings requires that each spectrum be treated individually. For objects not affected by the silicate feature blueward of 8 μm, a straight-line continuum (~7.1–8 μm) is imposed to
isolate any features. For objects affected by both the 6.8 and the 9.7 μm features, two straight-line continua are imposed: one from ~7.1–7.5 μm and one from ~7.5–8 μm (Figure 3).

3.1.2. Laboratory Spectra

We use laboratory data from the Leiden University ice analog databases\(^6\) (Gerakines et al. 1993, 1996; Ehrenfreund et al. 1996, 1999; van Broekhuizen et al. 2006) to identify the composition and apparent temperatures of the ices seen in our targets. In order to provide a direct comparison between the feature optical depths measured in the laboratory and those observed in the astronomical spectra, we removed a straight-line continuum from the laboratory data. For the wavelength ranges of interest, optical depths calculated using a straight-line continuum differ, on average, by less than half of a percent from those calculated using a more complicated cubic spline one. The wavelengths of the baseline ends are generally equal to the continuum points used in the astronomical spectra’s spline fitting, with an occasional slight shift to ensure feature wings are excluded from the continuum. In Figure 4, we show the range of abundances contained in the Leiden databases’ nonirradiated H₂O:CH₃OH:CO₂ mixtures (\(T = 10 – 185\) K, all circles); note that this plot does not represent the fraction of the database comprising other molecules (e.g., CH₄ and H₂O) or UV-irradiated mixtures.

The temperatures given in this paper, except where otherwise noted, refer to laboratory conditions. Interstellar temperature barriers for crystallization, sublimation, and other physical processes are lower than their laboratory counterparts, due to the lower pressure and longer interaction timescales in interstellar space (e.g., Boogert et al. 2000). Assumptions about particle shapes have not been applied to the laboratory spectra used in this broad analysis, and such corrections would in any case be inappropriate for the annealed inhomogeneous mixtures used (Gerakines et al. 1999).

3.2. Spectral Fitting

To confirm the validity of using laboratory spectra to model circumstellar material, we estimate the total extinction \(A_V\) along the line of sight toward our YSOs using \(A_V /\tau_{SI} \sim 17\) (Rieke & Lebofsky 1985). We find \(A_V \sim 3–34\) for our total sample—and \(A_V \sim 6–34\) for those objects without clear signs of dust emission contaminating the absorption feature—compared with the average extinction of \(A_V \sim 1–5\) toward Taurus association stars (Myers et al. 1983). In addition, recent work has shown that in dense regions, this relation with a given \(\tau_{SI}\) substantially underestimates \(A_V\) (Whittet et al. 1988; Chiar et al. 2007), so the total circumstellar extinction is likely to be even higher.

Thus, we assume that the foreground absorption toward the Taurus region is relatively low and that the spectral ice features result from material in the circumstellar environment. In contrast with a least components type of analysis (e.g., Boogert et al. 2008; Pontoppidan et al. 2008), we determine the ice composition and column densities of the circumstellar ice by fitting linear combinations of laboratory data to the observed IRS spectra. With the laboratory data described in Section 3.1.2, detailed spectral fitting is performed on the 6.0 and 15.2 μm features using a standard \(\chi^2\)-minimization technique. The equation solved is

\[
\tau(\lambda) = \sum a_i \tau_{lab,i}(\lambda),
\]

where the scale factors \(a_i\) of each component are the free parameters in the fit. To compare goodness of fit among various combinations, we use \(\chi^2\), the reduced \(\chi^2\) parameter. This is defined as \(\chi^2 = \chi^2/(n-m)\), where \(n\) is the number of spectral data points, and \(m\) is the number of free parameters in the fit. Traditional statistics require \(\chi^2\sim 1\) for an acceptable fit, but our values are often significantly larger or smaller. Artificially small \(\chi^2\) values can be caused by uncertainty overestimation or by poor signal to noise. Large values may be a result of uncertainty underestimation, unknown uncertainties in the laboratory spectra, or the existence of components not included in the fits. Therefore, \(\chi^2\) comparisons may be made to determine the best laboratory fit to a single spectrum; however, comparisons of goodness of fit among different YSO spectra are not necessarily valid. Quantities derived using a fitted spectral feature (e.g., processed fractions, column densities) are calculated using an average of all fits for that feature with a \(\chi^2\) within 20% of the minimum.

3.3. Column Densities

To calculate column densities along the lines of sight to the YSOs, we use the relation (e.g., Alexander et al. 2003)

\[
N(\text{cm}^{-2}) = \sum \frac{\tau_{i} \Delta \lambda}{\lambda_{\text{peak}} A}.
\]
where $\Delta \lambda$ is the wavelength bin size, $\lambda_{\text{peak}}$ is the wavelength of the feature’s peak optical depth, and $A$ (cm mole$^{-1}$) is the band strength as determined in the laboratory.

### 3.4. SED Spectral Index

To provide better resolution in evolutionary status than the simple Lada (1987) classification, we use the spectral index $\alpha$ (e.g., Kenyon & Hartmann 1995):

$$\alpha \equiv \frac{d \log F_{\lambda}}{d \log \lambda} = \frac{\log \lambda F_{\lambda_2} - \log \lambda F_{\lambda_1}}{\log \lambda_2 - \log \lambda_1},$$

(3)

where we choose $\lambda_1$ and $\lambda_2$ to lie within well-calibrated and nearly featureless parts of the spectrum but as much separated as possible (i.e., $\lambda_1 = 7$ $\mu$m and $\lambda_2 = 30$ $\mu$m; Table 3). The slope of this section of the spectrum depends upon a variety of factors, including the disk radius, total envelope density, outflow cavity opening angle, and inclination angle. With the exception of the inclination angle, all of these factors depend upon the total dust column density in such a way that more dust produces a steeper SED slope, and models demonstrate that inclination angle effects are generally less significant than these other factors (Furlan et al. 2008). Thus small values for the spectral index $\alpha$ indicate a relatively blue or exposed stellar object, but with increasing $\alpha$ the spectrum becomes redder, indicating the YSO is more heavily embedded in dust.

### 4. OPTICAL DEPTH TRENDS

In Figure 5, we show correlations in the optical depths of the three strongest absorptions attributed to ices (at 6.0, 6.8, and 15.2 $\mu$m) in our YSO sample. Clearly, the 6.0 and 6.8 $\mu$m features are very closely correlated, with linear Pearson correlation coefficient $r = 0.96$ (Figure 5(a)). The peak ratio is $\tau_{6.8}/\tau_{6.0} \sim 0.96 \pm 0.03$, and the straight-line fit passes within 0.01 of the origin. Since the 6.0 $\mu$m band is primarily attributed to the bending mode of H$_2$O, this correlation indicates that the carrier(s) of the 6.8 $\mu$m band forms and evolves in a similar, polar environment.

There is a looser correlation between the 6.0 $\mu$m and the 15.2 $\mu$m optical depths in our YSOs ($r = 0.7$, Figure 5(b)), resulting in a wider ratio range $\tau_{6.0}/\tau_{15.2} \sim 0.43$–1.65. When the same ratios are calculated for the laboratory spectra, though the spread is even wider (0.01–3.6), only a small fraction fall within the range defined by the YSOs (Figure 4, filled circles); the 15.2 $\mu$m CO$_2$ feature is generally much stronger than the 6.0 $\mu$m water–ice feature, independent of temperature. Mixtures dominated by H$_2$O provide most of the closest matches. In addition, there are two lab mixtures of nearly 1:1 H$_2$O:CH$_3$OH:CO$_2$ abundances (center of Figure 4) which have $\tau_{6.0}/\tau_{15.2}$ ratios comparable to the YSO ones but only after they have been heated to high temperatures ($T \gtrsim 125$ K), nearing the ice sublimation points. The Leiden database has a scarcity of water-rich, CO$_2$-poor (<20%) H$_2$O:CH$_3$OH:CO$_2$ mixtures in the temperature range 10–180 K, though based on this comparison, these compositions appear to be astronomically relevant. Because of the undersampling of compositions in this range, we are not able to constrain the ice composition well from the $\tau_{6.0}/\tau_{15.2}$ ratio alone.

Despite being closely correlated with $\tau_{6.0}$, the 6.8 $\mu$m peak optical depth is even less correlated with the 15.2 $\mu$m depths ($r = 0.56$, Figure 5(c)). This indicates that much of the inherent scatter in the $\tau_{6.8}/\tau_{6.0}$ ratio is due to variations in the 6.8 $\mu$m feature among different lines of sight.

### 5. SPECTRAL FEATURE ANALYSES

In order to set more accurate constraints on the ice properties than feature-strength analysis provides, we perform spectral fitting and detailed analysis of the most prominent features.

#### 5.1. The 6.0 $\mu$m Feature

Each YSO spectrum is fitted over the wavelength range 5.4–6.3 $\mu$m using the method described in Section 3.2 and the component set listed in Table 4. An example result is shown in Figure 6, and the total sample residuals, after subtraction of the 6 $\mu$m components, are shown in Figure 8 later in the text. Due to overlap with the unidentified 6.8 $\mu$m feature, the range beyond 6.3 $\mu$m was excluded in order to avoid imposing an artificial structure on any fit residuals. These fits focus on identifying the constituents of the 6.0 $\mu$m feature–H$_2$O, H$_2$CO, HCOOH, and NH$_3$, as described in the following subsections. This suite of species is similar to that employed by Boogert et al. (2008) to explain their extracted component set C1–5.

Either noise or saturation of the absorption bands in the background star/Class 0 sample prevents detailed spectral fitting of the 6 $\mu$m features, so we scaled a pure H$_2$O (10 K) spectrum to match the peak optical depth at 6.0 $\mu$m in order to calculate N(H$_2$O; See Table 8 later in the text). The shape of the 6 $\mu$m W3 spectrum is too irregular to be reasonably fit with a solid H$_2$O lab spectrum in this manner.

#### 5.1.1. H$_2$O

Water is the least volatile and most abundant of the ices typically found along protostellar lines of sight. The mid-infrared spectrum offers three strong features of water ice: narrow ones at 3.1 and 6.0 $\mu$m, and a broad ($\sim 11–20$ $\mu$m) feature peaking at 13 $\mu$m. To turn these profiles into water–ice column density is somewhat problematic in each case. The 3.1 $\mu$m ice feature is generally regarded as the cleanest measure of H$_2$O ice column density (e.g., Tielens et al. 1984). However, inconvenient gaps in the spectrum transmitted by Earth’s atmosphere make it difficult to determine the continuum on the short wavelength side of this feature in ground-based observations,
which would be the source of most of the comparisons we could make to our data. In addition, rather significant extinction and scattering near 3 μm are inevitably associated with protostars and can affect the profile of the water–ice feature. Furthermore, this may lead to the bulk of the 3 μm background continuum taking a significantly different path through the protostellar envelope than that which gives rise to the longer wavelength features. The latter effect would be rather more serious in systems viewed closer to edge-on, such as IRAS 04169+2702 and DG Tau B.

Extinction at 6 μm is similar to that at 13 μm, and both are significantly smaller than that at 3 μm (extinction in magnitudes smaller by factors of ~2–3; Mathis 1990; Indebetouw et al. 2005). Thus, the optical paths sampled at 6 and 13 μm, and the ice column densities derived, should be similar and may be more characteristic of the line of sight to the embedded protostar than is the case at 3 μm. In observed spectra, the 6 μm feature is the easiest of the three to analyze, as there are fewer problems in determination of the continuum. However, the depth and profile of the 6 μm feature are possibly influenced by absorption from species other than water ice, as shown, for example, by Boogert et al. (2008). The 13 μm water–ice libration feature is broad and overlaps many other absorptions, including the loosely constrained 9.7 μm silicate feature, so its optical depth and feature shape are hard to measure precisely.

Taking account of all of these difficulties, we choose to measure water–ice column density with the 6 μm feature, and

### Table 4

| Composition     | Temperature (K) | Radiation* |
|-----------------|-----------------|------------|
| Pure H$_2$O     | 10              | ...        |
| Pure H$_2$O     | 30              | ...        |
| Pure H$_2$O     | 50              | ...        |
| Pure H$_2$O     | 120             | ...        |
| Pure H$_2$CO    | 10              | ...        |
| Pure HCOOH      | 10              | ...        |
| H$_2$O:CH$_4$ b 1:0.33 | 50     | 1 hr       |
| H$_2$O:NH$_3$  b 1:0.2 | 10          | 1 hr       |

Notes. *The equivalent of 10$^{15}$ cm$^{-2}$ s$^{-1}$ photons (E$_γ$ > 6 eV) for the noted length of time.

References All spectra from Leiden University’s Sackler Laboratory ice analog databases.

Figure 5. Relationships between feature peak optical depths for our low-mass YSOs. Panel (a) shows $\tau_{6,8\mu m}$ vs $\tau_{6,0\mu m}$, panel (b) shows $\tau_{15,2\mu m}$ vs $\tau_{6,0\mu m}$, and panel (c) shows $\tau_{15,2\mu m}$ vs $\tau_{6,8\mu m}$. The dashed lines indicate the best linear fit.
check against the possibility of substantial “contamination” from other species using the 13 \mu m feature. To calculate the H$_2$O column density, we use the 6.0 \mu m feature fit results along with Equation (2) (summed over from other species using the 13 \mu m check against the possibility of substantial “contamination”)

Figure 6. 6 \mu m feature of IRAS 04016+2610, fit by a combination of pure H$_2$O at 10 K and 50 K (dots and short dashes), pure H$_2$CO at 10 K (dot-dash), pure HCOOH at 10 K (dash-triple dots), and H$_2$O:NH$_3$ 10:2 at 10 K (long dashes). The solid line is the sum. The 6.8 \mu m feature is deliberately excluded from the fit.

Evident in Figure 7 is a good correlation between the 13 \mu m and 6 \mu m water signatures, with Pearson’s $r = 0.74$. That the correlation is tight indicates that, if an additional ice component is significant at 6 \mu m, its abundance relative to water ice must be essentially constant.

5.1.2. H$_2$CO and HCOOH

Many of the objects in our sample have additional absorptions centered around $\sim$5.8 \mu m that can be well fit by a combination of H$_2$CO (formaldehyde) and HCOOH (formic acid) ices. Solid H$_2$CO is observed in many protostellar systems (e.g., Keane et al. 2001; Gibb et al. 2004) and plays an important role in the production of complex organic molecules (Schutte et al. 1993). H$_2$CO is difficult to detect independently in YSO Spitzer spectra; its 3.47 \mu m C–H stretch feature is beyond the wavelength range of the IRS, and its weaker 6.68 \mu m C = O stretch feature is blended with the 6.8 \mu m absorption, itself not well understood. The H$_2$CO column densities (Table 5) are derived using the observed integrated optical depth of the 5.8 \mu m feature (as determined from the spectral fits) and a band strength of $A_{H_2CO} = 9.6 \times 10^{-18}$ cm molec$^{-1}$ (Schutte et al. 1993).

Solid and gas-phase HCOOH has been detected in both low- and high-mass star-forming regions (e.g., Cazaux et al. 2003; Schutte et al. 1999; Bottinelli et al. 2004; Remijan et al. 2004; Keane et al. 2001). Within the IRS wavelength range, there are solid-state HCOOH absorptions at 5.8 and 7.2 \mu m, and several in the 8–11 \mu m range (Bisschop et al. 2007). The latter ones are blended with the 9.7 \mu m silicate complex, but the 7.2 \mu m band, though intrinsically $\sim$4 times weaker than the 5.8 \mu m
resonance, is detectable and indeed is tentatively identified in 6 of our 16 objects (Section 5.3). We have derived HCOOH column densities (Table 5) by integrating the observed optical depth of the 5.8 μm feature (as determined from the spectral fits) and using a band strength of $A_{\text{HCOOH}} = 6.7 \times 10^{-12}$ cm molec$^{-1}$ (Maréchal 1987).

5.1.3. NH$_3$

Solid NH$_3$ (ammonia) has mid-infrared features at 6.15 μm and 9.3 μm (e.g., Sandford & Allmandola 1993), blended with the 6 μm water–ice and 9.7 μm silicate features, respectively. The effect on the 6 μm H$_2$O feature is negligible until the NH$_3$ concentration reaches ~9% (Keane et al. 2001). At higher concentrations, an excess appears around 6.15 μm on the red side of the 6 μm band in laboratory spectra, which fits well the broad 6 μm feature observed in many of our YSO spectra. Analyses of the 9 μm inversion mode resonance by Lacy et al. (1998) and Gibb et al. (2000) indicate that circumprotostellar NH$_3$ exists primarily in an H$_2$O-dominated matrix. Therefore, an H$_2$O:NH$_3$ (1:0.2) mixture, rather than pure NH$_3$, is used in the spectral fits. Because no satisfactory band strength measurements for NH$_3$ in such a mixture exist, the upper limit NH$_3$ column densities (Table 5) are estimated by using the band strength of pure water ice for the H$_2$O:NH$_3$ mixture and extrapolating the column density of NH$_3$ based on its fractional abundance in the final fit.

5.1.4. PAHs

After contributions due to H$_2$O, H$_2$CO, HCOOH, and NH$_3$ are subtracted, small residuals in the 6.1–6.4 μm range, varying in strength, shape, and peak position, are observed in 11 of the sample’s 16 YSOs (Figure 8). PAH absorption has been suggested as a candidate for the 6.2–6.3 μm feature observed in many massive protostars (Schutte et al. 1996). Using the average interstellar PAH spectrum compiled by Hony et al. (2001) as a reference, we examined the peak position and widths of the YSO residuals. Of the objects within our sample with excess absorptions peaking between 6.2 and 6.3 μm, only three (IRAS 04361+2540, DG Tau B, and HL Tau) have an excess with a width similar to that seen in the PAH spectrum, and none of these three match the PAH feature in shape and peak position. Though the PAH relative band strengths often depend upon the molecular environment and ionization level, the broad 7.5–9 μm complex and the 6.2 μm feature are consistently observed at comparable strength in astronomical environments (Hony et al. 2001), yet we find no correlation in the YSO spectra between the 6.2 μm and 7.7 μm optical depths—the ratios are scattered between 0 and 7.5. Moreover, the prominent but narrow PAH peak at 11.3 μm (consistently ~1.4× as strong as the 6.2 μm peak; Chan et al. 2000; Hony et al. 2001) and the lesser ones at 12.7, 13.5, and 14.3 μm are not observed in the YSO data. Thus, in agreement with Keane et al. (2001), we find it unlikely that PAHs contribute significantly around 6.2–6.3 μm.

5.2. The 6.8 μm Feature

Though the 6.8 μm interstellar absorption band was discovered nearly 30 years ago (Puget et al. 1979), its identification remains ambiguous and inconclusive. Species ranging from hydrocarbons to alcohols to carbon dust have been proposed to contribute to the feature in a variety of sources (see Keane et al. 2001). Here, we focus on CH$_3$OH and NH$^+_3$—the candidate carriers most commonly accepted as explaining at least part of the absorption (e.g., Boogert & Ehrenfreund 2004).

5.2.1. CH$_3$OH

The position of the 6.8 μm feature coincides with the C–H deformation mode of alcohols, and of these, methanol is the most

| Object          | $N$(H$_2$O)$^{a}$ | $N$(CO$_2$)$^{b}$ | $N$(H$_2$CO)$^{c}$ | $N$(HCOOH)$^{d}$ | $N$(NH$_3$)$^{e}$ | $N$(SO$_2$)$^{f}$ | $N$(CH$_3$)$^{g}$ | $N$(CH$_3$OH)$^{h}$ |
|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| IRAS 04016+2610 | 5.91 ± 0.2       | 17.4 ± 1.4       | 1.9              | 1.8              | <12.1            | <0.1             | 0.4              | 8.3 ± 1.4        |
| IRAS 04108+2803A| 2.90 ± 0.3       | 9.5 ± 2.4        | 0.3              | 0.6              | <9.0             | 1.7 ± 1.1        | 8.0 ± 2.6        | 6.3 ± 1.5        |
| IRAS 04108+2803B| 4.44 ± 0.2       | 11.1 ± 1.5       | 2.2              | 0.8              | <9.0             | <0.7            | 5.6 ± 1.2        | 6.3 ± 1.5        |
| IRAS 04154+2823  | 1.07 ± 0.2       | 19.3 ± 7.9       | 0.1              | 0.0              | <28.4            | <0.5            | 23.2 ± 9.1       | 6.3 ± 1.5        |
| IRAS 04169+2702  | 4.33 ± 0.2       | 10.1 ± 1.5       | 2.4              | 1.0              | <9.0             | <0.5            | 3.9 ± 1.2        | 6.3 ± 1.5        |
| IRAS 04181+2654A | 3.63 ± 0.2       | 11.4 ± 1.8       | 3.6              | 0.2              | <9.0             | <0.1            | 3.1 ± 1.4        | 6.3 ± 1.5        |
| IRAS 04181+2654B | 4.18 ± 0.4       | 15.6 ± 2.3       | 7.1              | 0.7              | <25.6            | <0.3            | 4.5 ± 2.0        | 6.3 ± 1.5        |
| IRAS 04239+2436  | 4.44 ± 0.2       | 12.6 ± 1.5       | 2.4              | 0.0              | <12.5            | 0.6 ± 0.2        | <0.5            | 3.8 ± 1.5        |
| IRAS 04295+2251  | 2.82 ± 0.3       | 9.4 ± 2.3        | 1.7              | 0.4              | <15.3            | <1.0            | 2.4 ± 1.8        | 6.3 ± 1.5        |
| IRAS 04361+2547  | 7.38 ± 0.3       | 4.9 ± 1.5        | 0.0              | 0.9              | <9.0             | <0.1            | 4.3 ± 0.7        | 6.3 ± 1.5        |
| IRAS 04365+2535  | 5.31 ± 0.2       | 15.2 ± 1.6       | 1.8              | 0.5              | <13.0            | <0.1            | 0.8 ± 0.7        | 8.5 ± 1.6        |
| IRAS 04381+2540  | 7.92 ± 0.2       | 11.8 ± 0.8       | 0.8              | 0.5              | <9.2             | 0.2 ± 0.1        | 0.3 ± 0.3        | 6.3 ± 1.5        |
| DG Tau B         | 5.65 ± 0.6       | 7.5 ± 1.5        | 0.0              | 0.5              | <17.7            | 1.2 ± 0.6        | <0.4            | 3.5 ± 1.5        |
| HL Tau           | 1.91 ± 0.2       | 7.3 ± 2.8        | 5.9              | 0.7              | <11.0            | 1.0 ± 0.5        | <1.2            | 4.0 ± 2.8        |
| IC 2087IR        | 2.13 ± 0.2       | 19.5 ± 4.5       | 0.8              | 0.1              | <26.7            | <0.2            | 1.8 ± 2.2        | 8.7 ± 4.5        |
| L1551IR S5       | 10.90 ± 0.2      | 8.0 ± 1.3        | 0.0              | 0.0              | <9.0             | <0.0            | 1.7 ± 0.4        | 3.2 ± 1.3        |

Notes. The first column gives the object name, and the second through ninth columns give the column densities of H$_2$O, CO$_2$, H$_2$CO, HCOOH, NH$_3$, SO$_2$, CH$_4$, and CH$_3$OH. NH$_3$(CO) and N(HCOOH) have typical absolute uncertainties of ~10%.

$^a$Uncertainties listed are statistical, and derived from the residual differences between the data and our models. There are potential systematic errors as well, as described in Section 5.1.1.

$^b$Using band strength of H$_2$O:CO$_2$ mixture; see Section 6.1.

$^c$Based on 5.8 μm feature alone.

$^d$CH$_3$OH intermixed with CO$_2$, from high-resolution 15.2 μm feature fits.

$^e$A feature was detected in the SO$_2$ wavelength range but with an overly narrow width; value given is an upper limit.

Table 5

Derived Solid-state Molecular Abundances in Our YSO Sample
likely to be found in interstellar abundance. Theoretical models of ice processes predict the creation of solid methanol through the sequential hydrogenation of CO ice, that has been accreted from the gas phase onto dust grains (Tielens & Charnley 1997). The presence of methanol ice in interstellar and protostellar environments is observationally supported by detection of its own resonances—e.g., the C–H stretching mode at 3.54 \( \mu \text{m} \) (Grim et al. 1991) and the C–O stretch at 9.8 \( \mu \text{m} \) (Gibb et al. 2000)—as well as by signatures of its interactions with other molecules (especially CO\(_2\); e.g., Ehrenfreund et al. 1998).

Our sample spectra do not contain the near-infrared wavelengths of CH\(_3\)OH's multiple stretching modes, and the 9.8 \( \mu \text{m} \) resonance is blended with the silicate absorption. However, constraints on the CH\(_3\)OH abundance can be derived using the 15.2 \( \mu \text{m} \) CO\(_2\) band, as the interaction of CH\(_3\)OH with CO\(_2\) changes the feature shape near 15.4 \( \mu \text{m} \) (Sections 5.4 and 6.1). The relative strength of the 15.4 \( \mu \text{m} \) shoulder implies that at most 50% of the 6.8 \( \mu \text{m} \) feature is due to CH\(_3\)OH in a CO\(_2\) matrix, although CH\(_3\)OH unmixed with CO\(_2\) could be present to provide additional absorption at 6.8 \( \mu \text{m} \). Since CH\(_3\)OH is thought to form in a hydrogenated environment, the assignment of at least part of the 6.8 \( \mu \text{m} \) absorption to this molecule is then supported by the close correlation of the 6.0 \( \mu \text{m} \) and 6.8 \( \mu \text{m} \) optical depths (Section 4).

5.2.2. NH\(_4^+\) The NH\(_4^+\) ion was proposed as the carrier of the 6.8 \( \mu \text{m} \) band by Grim et al. (1989), and since then, this proposal has achieved varying levels of success (e.g Schutte et al. 1996; Keane et al. 2001; Schutte & Khanna 2003). The ion can be produced in the laboratory by the acid-base reaction HNCO + NH\(_3\) \( \rightarrow \) OCN\(^-\) + NH\(_4^+\) (Keane 1997) or in UV-irradiated H\(_2\)O:CO:NH\(_3\) mixtures (as in Figure 8).

NH\(_4^+\) has expected counter-ion features at 4.62 \( \mu \text{m} \) (OCN\(^-\)) and 6.3 \( \mu \text{m} \) and 7.41 \( \mu \text{m} \) (HCOO\(^-\), produced by photolysis). The 4.62 \( \mu \text{m} \) feature does not fall within the IRS wavelength coverage, and the 7.41 \( \mu \text{m} \) signature is too weak to be conclusively identified in our data. However, some of our sample objects do have a small excess absorption near 6.3 \( \mu \text{m} \).
(Section 5.1.4), which is unlikely to be attributable to PAHs. It may instead be due to HCOO$^-$, indicating photolysis and subsequent warming of a polar ice containing NH$_3$. We use the ratios of the laboratory 6.3 $\mu$m (HCOO$^-$) and 6.8 $\mu$m (NH$_3^+$) peaks ($\tau_{6.8}/\tau_{6.3} \sim 1.7$ after the H$_2$O feature is removed), along with the equivalent widths of the YSO and laboratory features, to estimate the NH$_3^+$ contribution to the 6.8 $\mu$m feature. Using this method, we find that, within our sample, 6%-58% of the 6.8 $\mu$m feature can be attributed to NH$_3^+$ (HL Tau is an outlier whose particularly large 6.3 $\mu$m excess indicates $\lesssim$91% of its 6.8 $\mu$m feature may be due to NH$_3^+$ using this method).

5.2.3. Fits and Summary

Figure 8 shows a comparison of the 6.8 $\mu$m features, after subtraction of the 6 $\mu$m contributors, with a variety of 6.8 $\mu$m candidate laboratory spectra, all rebinned to the resolution of the observations. The bottom two lab spectra (Labs B and C) have CH$_3$OH/H$_2$O abundance ratios of 100 and 0.1, and the gray vertical lines indicate the peak positions of these mixtures. The relative amount of methanol present affects the peak substructure. While in some cases, the YSO peak positions and relative strengths closely resemble the laboratory data (e.g., IC 2087 IR and IRAS 04239+2436), in others there is no correlation at all (e.g., IRAS 04169+2702). The abundance of CH$_3$OH (relative to H$_2$O) has been found to vary by almost an order of magnitude among different protostellar lines of sight (e.g. Pontoppidan et al. 2003; Gibb et al. 2004), which may partly explain the observed variety of peak substructures.

The top laboratory spectrum in Figure 8 (Lab A) is an H$_2$O:CO:NH$_3$ deposit, irradiated to create NH$_3^+$ and subsequently warmed from 10 K to 165 K. The irradiated spectrum at 10 K peaks 0.1 $\mu$m blueward of our sample’s bluest feature; in order to align with any of the observed profiles, the irradiated mixture must be heated to near the H$_2$O sublimation temperature, as the sublimation appears to cause the redward peak shift (Schutte et al. 1996). Moreover, the width of the NH$_3^+$ feature is too narrow ($\sim$0.25 $\mu$m) to account for the entire 6.8 $\mu$m feature widths observed toward each YSO (average $\sim$0.4 $\mu$m). Even if multiple NH$_3^+$ laboratory spectra at various temperatures are combined in order to reproduce the observed feature width, the resultant peak position remains too blue to match the YSO data.

Noting that many of the YSO 6.8 $\mu$m features share characteristics with the profiles of both CH$_3$OH (triple peaks, 7 $\mu$m shoulder) and NH$_3^+$ (asymmetric peak near 6.75 $\mu$m), we attempted fitting them with a combination of the laboratory components. While no remarkably good fits were achieved, there emerged a general trend that equal contributions from NH$_3^+$ and from CH$_3$OH in a water-dominated matrix, with varying amounts of nearly pure CH$_3$OH intermixed, came closest to reproducing many of the YSO feature width-to-depth ratios (i.e., mixtures of irradiated NH$_3$, CH$_3$OH/H$_2$O$\sim$0.1, and CH$_3$OH/H$_2$O$\sim$100 in the approximate ratios from 1:1:0 to 1:1:1). However, the overall 6.8 $\mu$m astronomical feature shapes could not be well matched in terms of either peak alignment or subpeak relative strengths.

Based on this work, we conclude that we cannot rule out NH$_3^+$ and CH$_3$OH as contributors each of at most $\sim$50% to the 6.8 $\mu$m band, but we emphasize that even the 50/50 combinations do not reproduce the overall feature shapes. Studies of this feature performed with higher-resolution ISO–SWS observations (e.g., Keane et al. 2001; Schutte et al. 1996) find a similar variety of structure and peak positions, confirming that it may be difficult or physically impossible to adequately explain the feature using the same set of components for all sight lines.

5.3. The 7–8 $\mu$m Range

Because of the uncertainties due to the low resolution and low signal-to-noise ratio of the 7–8 $\mu$m optical depth spectrum, as well as the inherent narrowness of the 7–8 $\mu$m features, we did not attempt to fit the shape of the spectral features with laboratory profiles but rather focused on detection of the 7.25 $\mu$m HCOOH, $\sim$7.6 $\mu$m SO$_2$, and 7.7 $\mu$m CH$_4$ features.

5.3.1. HCOOH

The 7.25 $\mu$m HCOOH band is intrinsically $\sim$4 times weaker than the 5.85 $\mu$m one (Bisschop et al. 2007). Based on the amount of HCOOH in the fitted spectra in Section 5.1, the expected 7.25 $\mu$m optical depths in the YSO spectra are $\lesssim$0.02. Indeed, we do observe small features at 7.25 $\mu$m in six of our 16 objects. It should be noted, however, that the strength of these do not correlate with the HCOOH column densities derived from the spectral fits and the stronger 5.85 $\mu$m feature ($r = 0.06$); there are also other species with weak signatures very close to this wavelength (e.g., HCOO$^-$ and HCONH$_2$; Schutte et al. 1999). As the optical depth profiles here are neither strong nor resolved enough to conclusively distinguish among these species’ signatures, these HCOOH detections must remain tentative.

5.3.2. CH$_4$ and SO$_2$

In 13 of our 16 objects, we observe a feature near 7.7 $\mu$m, where the ($v_3$) C–H deformation mode of CH$_4$ is expected. Laboratory studies have shown that this resonance’s position and width are strongly dependent on the molecular environment, becoming blueshifted (as far as 7.64 $\mu$m) and broadened when mixed with a variety of other ices, including H$_2$O, CO, CH$_3$OH, and CO$_2$ (Boogert et al. 1997). In addition, there is the possibility of blending with the nearby SO$_2$ feature, whose 7.58 $\mu$m S–O stretching band has been shown to vary its peak position from 7.45 to 7.62 $\mu$m, depending on the temperature and the molecular environment (Boogert et al. 1997).

In order to disentangle absorption due to SO$_2$ and CH$_4$, we fit each YSO’s 7.45–8 $\mu$m wavelength range with two Gaussian curves, allowing the peak of one (representing SO$_2$) to shift between 7.45 $\mu$m and 7.62 $\mu$m and constraining the other peak (CH$_4$) to 7.62 $\mu$m or larger. A Gaussian approximation was chosen because both the SO$_2$ and CH$_4$ profiles are too narrow, compared with the IRS resolution, to evaluate any substructure.

In many cases, a single Gaussian was sufficient, indicating a single, distinct feature of either SO$_2$ or CH$_4$, depending on peak position. Of our 16 YSOs, seven show only a 7.7 $\mu$m feature with little or no asymmetrical excess, three only have a distinct feature peaking within the SO$_2$ range, four show both distinct features, and two show a broad absorption with additional peaks within the SO$_2$ range (i.e., fit by overlapping Gaussians). Using the range of laboratory feature FWHMs measured by Boogert et al. (1997), we find that in four of the nine objects with either distinct features or a Gaussian fit in the 7.45–7.62 $\mu$m range, the feature width is too narrow ($\Delta \nu \lesssim 0.06$ $\mu$m) to be attributed to solid SO$_2$. These may be due to random noise creating an apparent peak or to CH$_4$ gas lines found between $\sim$7.4 $\mu$m and 8 $\mu$m. SO$_2$ also has gas lines in this region, but these are very weak (Boogert et al. 1997). For the five remaining features, we use Equation (2) with a band strength $A_{SO_2} = 3.4 \times 10^{-17}$ cm mol$^{-1}$ (Khanna...
et al. 1988) to determine the SO$_2$ column density; for the other objects, an upper limit to n(SO$_2$) is determined (Table 5).

Of the 13 objects with a distinct 7.7 $\mu$m CH$_4$ feature or Gaussian fit, seven have FWHMs comparable to those observed in laboratory mixtures (Boogert et al. 1997), particularly in those mixtures where CH$_4$ and either H$_2$O, CH$_3$OH, or NH$_3$ exist in roughly equal abundance. The remaining six objects have wider features, which may be explained by variations in temperature or ice mantle composition along the line of sight. To determine the column density of CH$_4$ toward each YSO, we use Equation (2) with a band strength $A_{\text{CH}_4} = 7.3 \times 10^{-18}$ cm molecule$^{-1}$ (pure CH$_4$; discussion in Boogert et al. 1997) and integrate the optical depth between 7.6 $\mu$m and 7.9 $\mu$m. Upper limit estimates for the three nondetections are provided by the noise in the spectrum (Table 5).

5.4. The 15.2 $\mu$m Feature

A double-peaked structure in the 15.2 $\mu$m feature, often observed in systems with an exposed source of heating and radiation (such as Class I/II objects), is associated with the dual peaks of the degenerate $\nu_2$ bending mode in pure CO$_2$ ice. This structure becomes less pronounced or disappears altogether when the apolar CO$_2$ molecules are embedded in an H$_2$O-rich polar matrix (e.g., Ehrenfreund et al. 1999). Thus, the presence of a double-peaked feature indicates that thermal processing has occurred, segregating the CO$_2$ from the polar matrix. The broad shoulder on the red side of the absorption, centered around 15.4 $\mu$m, has been attributed to CO$_2$ interactions with other molecules, particularly CH$_3$OH, and the strength and shape of the shoulder depend on both temperature and relative abundances (e.g., Dartois et al. 1999). Theoretical studies suggest that solid CO$_2$ is formed by oxidation of CO ice (e.g., Tielens & Hagen 1982; Ruffle & Herbst 2001), so the co-existence and interaction with solid CH$_3$OH (also formed from CO; Tielens & Charnley 1997) are not unexpected.

In the fits, made for the high-resolution spectra between 14.7 $\mu$m and 16 $\mu$m, we include cold (10 K–30 K) deposits of H$_2$O:CO$_2$, pure CO$_2$, and an irradiated deposit of CO:H$_2$O, as well as warmer (>100 K) mixtures of H$_2$O:CH$_3$OH:CO$_2$ (Table 6). The cold mixtures containing H$_2$O are used to estimate the contribution from nonprocessed material along the line of sight. The warmer H$_2$O:CH$_3$OH:CO$_2$ spectra represent ices which have been warmed and have undergone the chemical and physical changes, including segregation of the CO$_2$, resulting from that processing. The pure CO$_2$ component, though measured at 10 K, does not greatly differ in shape until sublimation at ~80 K and is here used as a measure of segregated, highly processed ice.

Our fitting components differ from the recent work by Pontoppidan et al. (2008), which is focused almost exclusively on detailed methanol-free CO:CO$_2$:H$_2$O mixtures. Certainly these combinations can produce good fits to the CO$_2$ ice feature. However, in the following, we will adhere to the conventional approach involving a warm CH$_3$OH ice component, since we find that in most cases this produces better fits to our spectra than methanol-free mixtures, and it takes into account the strong evidence of solid methanol in many protostellar environments (e.g., Pontoppidan et al. 2003; Gibb et al. 2004). It is worth noting that, since good fits are obtained by both classes of models, neither method should be thought to provide a unique solution to the ice-composition analysis.

Using a single-component fit, we find that a nearly equal-parts mixture of H$_2$O:CH$_3$OH:CO$_2$ at temperatures of >100 K provides the lowest $\chi^2$ fit to the observed YSO 15.2 $\mu$m absorption bands, in accordance with previous results for more massive protostars (e.g., Ehrenfreund et al. 1999; Gerakines et al. 1999). Where present, the dual peak positions align, and the approximate strength of the 15.4 $\mu$m shoulder is replicated. The fit improves, however, by an average of ~50% of $\chi^2$, when we allow multiple components (Figure 9). The combination of these additional components reproduces the relative peak strengths, the inter-peak dip depth, and the shape of the 15.4 $\mu$m shoulder without requiring a specific single temperature.

Our multicomponent fits indicate that for our YSO sample, a smaller amount of CH$_3$OH (~14%) at lower temperatures is sufficient to account for the observed 15.4 $\mu$m shoulder, and equal parts H$_2$O, CO$_2$, and CH$_3$OH are reflected at high temperatures (higher than those identified by, e.g., Ehrenfreund et al. 1999), when the CO$_2$ has at least partly migrated out of the matrix. Laboratory mixtures at these higher temperatures that also contain the smaller fractions of CH$_3$OH have an asymmetrical dual peak that is not observed in the YSO spectra; mixtures with H$_2$O, CH$_3$OH, and CO$_2$ in a 1:1:1 ratio at lower temperatures show a stronger shoulder at 15.4 $\mu$m.
Figure 10. Model of the absorption around 10 \( \mu m \) in IRAS 04016+2610. Shown are the observed data (points), the GCS 3 silicate profile (long dashes; Kemper et al. 2004), pure water–ice at 10 K (dash-triple dots), and the two methanol-bearing mixtures described in Section 5.4 and listed in Table 6 (short dashes and dot dashes), scaled per this object’s 15.2 \( \mu m \) fit. The remnant peak at 9 \( \mu m \) is likely NH\(_3\) ice. The model and observation are consistent with one another in the relevant wavelength range.

Figure 11. Comparison of fits to the Serpens background star CK 2 (top) and Taurus background star Elias 16 (bottom). The left panels are repeats of the fits by Knez et al. (2005), where the dotted line is a laboratory spectrum of H\(_2\)O:CO\(_2\) 10:1 at 10 K, the dashed line is H\(_2\)O:CO\(_2\) 1:1 at 10 K, and the dash-dot line is CO:N\(_2\):CO\(_2\) 10:5:2 at 30 K. The mismatch on the red wing is caused by the forced continuum at \( \sim \)16.5 \( \mu m \), which ignores the extent of some of the ice feature wings as measured in the laboratory. In the right panels, the dash-dot line is the same, but the H\(_2\)O:CO\(_2\) 10:1 spectrum has been replaced with H\(_2\)O:CH\(_3\)OH:CO\(_2\) 9:2:1 at 30 K (long dashes) and the H\(_2\)O:CO\(_2\) 1:1 with H\(_2\)O:CH\(_3\)OH:CO\(_2\) 0.9:0.3:1 at 30 K (dash-triple dot).

Methanol-bearing ice mixtures have distinctive absorptions elsewhere in the mid-infrared spectrum, notably at 6.8 \( \mu m \) and 9.8 \( \mu m \). The former feature is discussed above (Section 5.2). The latter unfortunately lies in the very bottom of the silicate absorption feature. In the mixtures that best fit the 15.2 \( \mu m \) ice feature, the 9.8 \( \mu m \) feature is either very weak or not particularly sharp. Thus, it is difficult to separate possible 9.8 \( \mu m \) methanol ice absorption from small silicate-feature profile variation. In general, a combination of absorption from the ice mixture that best fits the 15.2 \( \mu m \) feature, and from interstellar silicate grains (toward GCS 3; Kemper et al. 2004), can be made to fit the spectrum, as illustrated in Figure 10. However, this result depends sensitively on the fit of the continuum and the silicate absorption profile, which as noted above is not very well defined for these types of environments. We found no meaningful, quantitative constraints on a putative CH\(_3\)OH ice component from the 9.8 \( \mu m \) feature.

The 15.2 \( \mu m \) features in the molecular cloud sight lines have previously been fitted with predominantly cold, polar H\(_2\)O:CO\(_2\) mixtures (Bergin et al. 2005; Knez et al. 2005). We find that the \( \chi^2 \) of the fits can be matched or reduced by including components containing methanol—specifically, the cold counterparts of the H\(_2\)O:CH\(_3\)OH:CO\(_2\) components used in our Class I/II fits described above (Figure 11). The percentage of polar ice found (\( \sim \)75%–80%) is comparable to that identified by Bergin et al. (2005) and Knez et al. (2005), and the abundance ratios N(CO\(_2\))/N(H\(_2\)O) from those studies are preserved.

We have calculated the total CO\(_2\) column density (Table 5) observed along each embedded object and molecular cloud line of sight using Equation (2). The exact band strengths of some of the laboratory mixtures used in the 15.2 \( \mu m \) fits are undetermined. The fitting results indicate that the vast majority of the CO\(_2\) ice resides alongside H\(_2\)O ice, so we use a band strength of 1.5 \( \times \)10\(^{-17}\) cm mole\(^{-1}\) for the 15.2 \( \mu m \) absorption from a H\(_2\)O:CO\(_2\) 1:1 ice (Gerakines et al. 1995). The observed optical depth spectra were integrated between 14.7 \( \mu m \) and 16 \( \mu m \). We use the relative contributions
of each fitting component to estimate the column density of solid CO₂ in each stage of thermal processing (Table 7): radiation-only (10K–30 K, “cold”), some thermal heating (“warm”), and CO₂ segregation. We have also estimated the column density of solid CH₃OH embedded in CO₂ using the the CH₃OH abundance and relative contribution of each laboratory fit component (Table 5).

6. DISCUSSION

6.1. Ice Composition: Abundances With Respect to H₂O

6.1.1. CO₂ Column Density

The column densities observed in our sample of Class I/II YSOs yield N(CO₂)/N(H₂O) ~0.12±(0.04) (Table 5, Figure 12), which is consistent with the values previously derived for many different lines of sight, averaging N(CO₂)/N(H₂O) ~0.17±(0.03) (Gerakines et al. 1999; Nummelin et al. 2001; Gibb et al. 2004; Knez et al. 2005; Alexander et al. 2003), but significantly lower than the value of N(CO₂)/N(H₂O) ~0.3, with large scatter, reported by Boogert et al. (2004) and Pontoppidan et al. (2008). Our study is unique in the sense that we use the band strength A₁₅₅₁₀ of an H₂O:CO₂ mixture. If we instead use the band strength for pure CO₂, we find N(CO₂)/N(H₂O) ~0.16±(0.04), nearly equivalent to the results of the majority of previous studies, which include high- and low-mass YSOs, background field stars sampling molecular clouds, and galactic center sight lines sampling diffuse interstellar material and molecular clouds.

The dashed line in Figure 4 identifies the locus of compositions with CO₂/H₂O = 0.12, which are clearly under-represented in the heated samples from the Leiden University database. Good profile fits can only be achieved by combining ice mixtures, and this gap in composition space may explain some of the difficulties experienced in fitting 6 μm features. Further laboratory exploration of the water-rich mixtures around the observed ratio with CO₂ may help to improve constraints on the column density of H₂O ice based on the 6 μm feature.

6.1.2. Evolutionary Trends in CO₂

When considering the Class I/II sample in conjunction with the Class 0 objects, we find N(H₂O) to be well correlated (N(CO₂) less so) with the spectral index α, where more embedded sources (higher α) show higher column densities, as is expected (Figure 13; left 2 panels). The ratio N(CO₂)/N(H₂O) increases as the objects evolve toward lower α-values (Figure 13; the right panel).

The sublimation temperature of solid H₂O is ~40 K higher than that of pure CO₂ ice (Gerakines et al. 1995). Thus, with increased exposure to thermal radiation, N(CO₂)/N(H₂O) is expected to go down, seemingly contradicting our observations. Although CO₂ molecules embedded in a polar matrix may become “trapped” and able to survive to temperatures nearing the sublimation limit of H₂O, the thermal destruction of H₂O before CO₂ is unlikely.

An explanation of the high column density of CO₂ in more exposed environments may be found in the formation of additional CO₂ in Class I/II objects. Photodissociation of H₂O leads to the production of radicals (e.g., OH) which can react to form CO₂ on the grain surface (e.g., CO+OH→CO₂; Allamandola et al. 1988). Some other reaction pathways to form CO₂ in molecular clouds and star-forming regions have activation barriers which become less obstructive in warmer, more exposed environments (e.g, Ruffle & Herbst 2001; van Dishoeck & Blake 1998). Indeed, in UV-irradiated H₂O:CH₃OH:CO₂ laboratory samples, CO₂ eventually reaches a constant abundance level due to an equilibrium between destruction and formation (Ehrenfreund et al. 1999), while the abundance of H₂O further decreases due to photodissociation.

The values measured toward the background stars Elias 16, Elias 13, and CK 2 cannot be extrapolated from this trend. The N(CO₂)/N(H₂O) ratios for these lines of sight (Table 8) are not lower than the ratios observed toward the YSOs. This discrepancy may be due to the fact that the interstellar lines of sight probe a variety of environments and compositional structure, while protostellar sight lines are dominated by the circumstellar material. Possibly, the lower temperatures in interstellar regions stifle CO₂ formation mechanisms with activation barriers, while areas of increased density favor H₂O production.

6.1.3. HCOOH

Apart from one outlier at N(H₂O) ~1.1 ×10¹⁹ cm⁻² (L1551 IRS 5), the column densities of HCOOH and H₂O are strongly related (r = 0.61, Figure 14). This supports laboratory
Figure 13. Relationships between the SED spectral index ($\alpha$; 7–30 $\mu$m) and $N$(CO$_2$), $N$(H$_2$O), and $N$(CO$_2$)/$N$(H$_2$O). The filled circles represent our Class I/II data, and the open circles represent the Class 0 objects.

experiments demonstrating that the most likely formation environments of solid HCOOH are those that also produce H$_2$O ice, through either radiative processing or cold-surface reactions (Bisschop et al. 2007). We find $N$(HCOOH)/$N$(H$_2$O) $\sim$0%–2%, with an average of 0.6%, well within the $\lesssim$5% abundance ratio observed in lines of sight toward massive and low-mass protostars (Bisschop et al. 2007; Boogert et al. 2008).

6.1.4. CH$_3$OH

The observed $N$(CH$_3$OH)/$N$(H$_2$O) ratios in our sample do not show a clear trend (Figure 14). It is known that the $N$(CH$_3$OH)/$N$(H$_2$O) abundance varies greatly from source to source (e.g. Boogert & Ehrenfreund 2004), and it may be better to analyze the CH$_3$OH abundance with respect to CO$_2$.

CH$_3$OH can be detected in the spectrum in three places. When it is intermixed with CO$_2$, a shoulder at 15.4 $\mu$m due to CH$_3$OH can be observed in the 15.2 $\mu$m feature; and CH$_3$OH also shows 6.8 and 9.8 $\mu$m bands (the latter is blended in the 9.7 $\mu$m silicate complex). In Figure 15, we show the ratio of the optical depth at 15.4 $\mu$m (vertical axis) and 6.8 $\mu$m (horizontal axis), both with respect to the optical depth at 15.2 $\mu$m. Filled circles represent the astronomical measurements, while the plus signs indicate the ratios measured in the laboratory spectra. The laboratory spectra show a correlation between the two features, whose exact position depends on the temperature. The 15.4/15.2 $\mu$m $\tau$ ratios observed in the astronomical data are within the range measured in the laboratory, but the corresponding 6.8 $\mu$m optical depths are significantly greater than the laboratory values. This could be understood if only a small fraction of the CH$_3$OH along the line of sight is embedded in a CO$_2$ matrix or if there are significant contributions to the 6.8 $\mu$m feature from other components.

Using the laboratory fits to the 15.2 $\mu$m complex in the high-spectral-resolution data, we estimate the column density of solid CH$_3$OH intermixed with CO$_2$ as 30%–56% with respect to CO$_2$, corresponding to $N$(CH$_3$OH)$_{total}$/N(H$_2$O) $\sim$2%–9% (Table 5). Assuming that $\lesssim$50% of the 6.8 $\mu$m feature is due to CH$_3$OH (Section 5.2.3), we estimate $N$(CH$_3$OH)$_{total}$/N(H$_2$O) $\lesssim$5%–17%. There are two outlying values, for IRAS 04108+2803A and IRAS 04181+2654B, at 32% and 28%. Although we do not place high confidence in these as absolute values because of the 6.8 $\mu$m uncertainties, they are consistent with the detection of solid CH$_3$OH with abundances (relative to H$_2$O) up to $\sim$25% toward low-mass YSOs (as well as the overall scatter in abundance; Pontoppidan et al. 2003; Boogert et al. 2008). Thus, our data support the presence of a significant CO$_2$-poor H$_2$O:CH$_3$OH ice component.

6.1.5. CH$_4$

We observe a range of $N$(CH$_4$)/$N$(H$_2$O) ratios from $\sim$0.3% to 8% in our sample (Figure 16), with an average of 2.6% and a single outlier (IRAS 04154+2823A) at 23%. Our measurements largely overlap with the ratios of $\sim$0.5%–4% reported in the literature (e.g., Boogert et al. 1996; Gibb et al. 2004), though
ratios up to 13% are reported by Öberg et al. (2008). The higher values in our sample (>4%, dashed line in Figure 16) may be partially ascribed to additional absorptions unresolvable at the SL-module resolution, such as gas-phase CH₄ lines (Boogert et al. 1997), or to matrix-dependent variations in band strength. Hudgins et al. (1993) found that the band strength for the 7.7 μm CH₄ feature may vary by as much as a factor of 2.8 between H₂O-rich and CO-rich matrices. We use the value for pure CH₄, which lies approximately midway between the two extremes.

Laboratory studies of solid CH₄ indicate that it can be formed by a variety of processes—including UV photolysis of CH₃OH ices (Allamandola et al. 1988) and grain–surface hydrogenation of carbon (Tielens & Hagen 1982)—and that the resulting absorption profile has characteristics unique to its formation pathway and embedding matrix (Boogert et al. 1997). Unfortunately, the low signal-to-noise ratio of the CH₄ measurements prevents a detailed analysis of the spectral profiles; however, the broad range of peak positions and widths implies that the CH₄ embedding matrices vary across the sample.

6.2. Segregation of CO₂ Ice

In the colder parts (<20 K) of a star-forming region, well removed from the hot cores and embedded protostars or buried in dense clumps, apolar CO₂ ice is formed embedded in a polar H₂O matrix (e.g., Boogert & Ehrenfreund 2004). The 15.2 μm CO₂ resonance will appear to be broad and single-peaked. As these ices are heated, as for instance happens in the circumstellar environments of YSOs, the CO₂ can migrate out of the polar matrix and aggregate, either as a surface layer or in bulk apolar clumps within the matrix (e.g., Sandford & Allamandola 1990; Ehrenfreund et al. 1999). The spectral appearance of the CO₂ resonance changes, and a double-peaked structure, with peaks at 15.1 and 15.25 μm, becomes apparent rather rapidly (Figure 17). The migration process also destabilizes the CO₂:CH₃OH interactions and reduces the 15.4 μm shoulder. Due to the apparent spectral difference between segregated CO₂ ice and CO₂ ice embedded in an H₂O:CH₃OH matrix, it is possible to determine the relative mass contained in both of these phases.

In Figure 18, we show the variation in the CO₂ 15.2 μm absorption feature in our sample, along with laboratory spectra of CO₂ fully embedded in the matrix (top; 10 K) and fully segregated CO₂ (bottom; 130 K). The dashed lines indicate the positions of the double-peaked segregated CO₂ and the shoulder at 15.4 μm due to embedded CO₂ interacting with CH₃OH. We show only the Class I/II objects for which high-resolution spectra are available, as the double-peaked structure is not resolved in the low-resolution spectra. Several of the spectra clearly show the double-peaked structure, while all deviate from the smooth, unprocessed Taurus cloud profiles as published by Whittet et al. (2007); Bergin et al. (2005); Knez et al. (2005). Indeed, from the multi-component fits described in Section 5.4, we find evidence in all of our low-mass YSO spectra for moderate-temperature thermal processing (<100 K; CO₂ warmed but not segregated), in agreement with Boogert et al. (2004) but in contrast with Nummelin et al. (2001). However, unlike Boogert et al. (2004), we also find evidence for high-temperature processing—five of the nine objects (IRAS 04016+2610, IRAS 04239+2436, IRAS 04365+2535, DG Tau B, and IC 2087 IR) have 15.2 μm profiles entirely dominated by warmed ices in which a significant fraction (∼20%–40%) of the CO₂ has segregated from the polar formation matrix.

From the multi-component fits, we can derive the mass distribution of CO₂ ice over the phases (cold, warm, segregated). The phase transitions correspond to laboratory temperatures, which in turn translate to (lower) astrophysical temperatures.
The onset of CO₂ segregation occurs at a temperature near 105 K in the laboratory (Figure 17), which corresponds to an astrophysical temperature of ∼65 K (e.g., Boogert et al. 2000). The CO₂ evaporation temperature depends on the relative abundance of other species, particularly H₂O, but the mixtures with the most physically likely abundances (i.e., CO₂/H₂O < 1) show an average sublimation temperature of ∼150 K, or 80 K in astrophysical environments. Thus, the segregated column densities of Table 7 represent CO₂ ice at circumstellar or 80 K in astrophysical environments. Thus, the segregated fraction does not show a clear trend with total dust opacity.

### 6.2.1. Segregation of CO₂ Ice in Molecular Clouds and W3(OH)

All three interstellar cloud sight lines show single-peaked 15.2 μm profiles with very little substructure; CK 2 and Elias 16 are remarkably similar in shape (Figure 11), despite indications that ice mantles in Serpens may be fundamentally different from those in Taurus (e.g., Eiroa & Hodapp 1989; Whittet et al. 2007). These results give support for the cold-grain origin of at least some of the CH₃OH observed toward protostars; the presence of the unidentified 6.8 μm band in background star sight lines (in particular CK 2 and Elias 16; Knez et al. 2005) is consistent with the assignment of CH₃OH as a carrier.

Interestingly, the spectrum of W3(OH), which has the reddest SED of our entire sample, shows a clearly double-peaked CO₂ feature, indicating pure CO₂ along the line of sight, which could have been formed by thermal segregation (Figure 20). The segregation fraction is ∼26%, comparable to the Class I/II average of ∼30%. Given the difference in segregation with the pure molecular cloud lines of sight, the most likely explanation is that this line of sight samples not only the cold foreground W3 cloud but also the warmer, thermally processed CO₂ ices around the massive protostars in the W3(OH) region. The strong similarity of the 15.2 μm absorption profile toward W3(OH) to those of the low-mass Taurus objects is curious, as the line of sight toward W3(OH) is highly diverse, containing an ultra-compact HII region, strong outflows, and H₂O/OH maser emissions (Turner & Welch 1984; Alcolea et al. 1993; Argon et al. 2003). Future spectroscopic observations with higher angular resolution will resolve the spatial structure and provide useful information on the complexity of the early stages of CO₂ heating in embedded objects.

### 7. Conclusions

We have analyzed the mid-infrared molecular ice features in 16 Class I/II low-mass YSOs using Spitzer IRS observations. Using detailed comparisons to laboratory ice analog spectra, we find the ice mantle compositions to be dominated by H₂O and CO₂ ice but with significant abundances of additional species such as CH₃OH, H₂CO, HCOOH, NH₃, CH₄, and SO₂ (∼10% each).

Detailed spectral fits to the 6 μm feature reveal that ≥80% of the band can be attributed to H₂O, with additional absorptions near 5.85 μm identified as HCOOH and H₂CO. Some of the observed spectra have a broader 6 μm peak that can be well-fit by H₂O:NH₃ ices, providing evidence for the presence of solid NH₃. On the long-wavelength wing of the 6 μm feature, small absorption remnants are observed, varying in strength, shape, and peak position among the sources. We show that these are highly unlikely to be the result of PAH absorption, due to the absence of other expected PAH features at 7.5–9 μm and 11–14 μm.

We have examined the unidentified 6.8 μm feature and discussed its assignment to solid CH₃OH and NH₄⁺, the two most common candidates. While no high-quality spectral fits could be achieved using these two components, we find that on average the observed YSO features could be approximately fit by equal contributions from NH₄⁺ and from a CH₃OH/H₂O~0.1 mixture,
Figure 17. “Dip-to-peak” ratio as a measure of the amount of CO$_2$ segregation. (a) Demonstrates how the values were measured for each laboratory ice spectrum, using pure CO$_2$ as an example. (b) The relative dip strength as a function of laboratory ice temperature, showing the rapid onset of the process near $\sim 105$ K. Much of the scatter in (b) is due to the dependence of CO$_2$ segregation temperature on the exact composition of the matrix in which it is embedded. The large asterisks in the upper left represent pure CO$_2$ ice.

Figure 18. High-resolution 15 $\mu$m Class I/II profiles visually ordered by “peakiness,” normalized to 1, and vertically offset for clarity. The dotted lines at 15.1 $\mu$m and 15.25 $\mu$m mark the peak positions of pure CO$_2$, and the one at 15.4 $\mu$m indicates the CH$_3$OH:CO$_2$-complex shoulder. The top and bottom spectra are laboratory mixtures as indicated.
with varying amounts of nearly pure CH$_3$OH intermixed. However, we find a wide variety of feature shapes in our sample, indicating that the interstellar component(s) producing this band vary greatly from object to object, and a single simple carrier or set of carriers may be inadequate to explain the feature.

In the 7–8 μm range, we are able to isolate and identify features attributed to CH$_4$, SO$_2$, and (tentatively) HCOOH ices. The high CH$_4$ ice abundances derived from these, along with the variety of feature shapes and peak positions within the sample, suggest variations in line-of-sight molecular environment or possible absorption contamination by unresolvable gas-phase CH$_4$ lines. The solid SO$_2$ and CH$_4$ band profiles are very sensitive to molecular environment and temperature, and additional high-resolution studies of this wavelength range will yield further information on molecular ice interactions and abundance structures along the line of sight.

The 15.2 μm solid CO$_2$ bending mode feature is well-reproduced by multi-component laboratory fits comprising ice analogs (H$_2$O, CH$_3$OH, CO, CO$_2$) in various stages of radiative and thermal processing. Using the relative contribution of the components to each high-resolution feature profile, we find that all of the YSO ice environments have undergone at least some thermal heating, and 5 of the 9 have profiles entirely dominated by processed ices in which a significant fraction (~20%–40%) of the CO$_2$ has segregated from the polar formation matrix.

The molecular ice abundance ratios, particularly $N$(CO$_2$)/$N$(H$_2$O), are consistent with the values observed in a wide variety of sight lines, but within the sample, we observe a negative correlation between this ratio and the mid-infrared SED spectral index. This evidence describes a more complicated polar CO$_2$ environment than indicated by previous studies. Comparison of the SED spectral index with the ice temperatures derived from the 15.2 μm fits confirms the presence of cold ices in more deeply embedded objects and warmer, annealed ices in more evolved ones.

Comparison with molecular cloud sight lines show that our fits are consistent with a scenario in which H$_2$O-rich grain mantles with CO$_2$ and CH$_3$OH relative abundances of $\sim 20$ and $\lesssim 10\%$, respectively, as well as traces of other species, form in the cold molecular clouds and are subsequently heated by young protostars. This thermal processing sublimes the most volatile species while inducing molecular interactions and migrations that become spectroscopically detectable. The wide range of both molecular abundances and thermal processing levels observed within our sample indicates that young stars have a strong effect on their surrounding environments.

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