



# Carbonates and ices in the $z = 0.89$ galaxy-absorber towards PKS 1830–211 and within star-forming regions of the Milky Way

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## ABSTRACT

A pair of 6.0 and 6.9  $\mu\text{m}$  absorption features are frequently observed in Milky Way (MW) molecular-clouds and YSOs; they also occur in the  $z = 0.886$  rest-frame of a molecule-rich spiral galaxy obscuring blazar PKS 1830–211. I calibrate  $\chi^2$ -fitting methods, which match observations with two or three laboratory spectra. The 6.0- $\mu\text{m}$  component is dominated by  $\text{H}_2\text{O}$  ice, as expected. Included MW sources were selected using opacity criteria which limit the range of explored  $\text{H}_2\text{O}$ -ice column densities to  $1.6\text{--}2.4 \times 10^{18}$  molecules  $\text{cm}^{-2}$ , while the  $\text{H}_2\text{O}$ -ice density in the galaxy absorber is  $(2.7 \pm 0.5) \times 10^{18}$  molecules  $\text{cm}^{-2}$ .  $\text{CH}_3\text{OH}$  ice and / or small ( $< 0.1\text{-}\mu\text{m}$ -sized) Ca- and Mg-bearing carbonates contribute at 6.9  $\mu\text{m}$ . The 41 per cent  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  molecular ratio in the PKS 1830–211 absorber is significantly higher than in the molecular cloud towards Taurus-Elias 16 ( $< 7.5$  per cent) and similar to the highest value in MW YSOs (35 per cent in AFGL 989). Fitted carbonate ( $-\text{CO}_3$ ): $\text{H}_2\text{O}$  ratios in the galaxy absorber of 0.091 per cent are low in comparison to most of the ratios detected in the MW sample (0.2 per cent–0.4 per cent;  $\sim 0$  per cent in AFGL 989). Inorganic carbonates could explain the increased oxygen depletion at the diffuse-medium-to-molecular-cloud transition, which Jones and Ysard associated with unobserved organic carbonates or materials with a C:O ratio of 1:3.

**Key words:** Galaxy: abundances – Infrared: ISM – stars: pre-main-sequence – quasars: individual: PKS 1830–211 – solid state: refractory – solid state: volatile.

## 1 INTRODUCTION

In 1977 Puetter et al. (1978) observed Milky Way (MW) protostars OMC 2-IRS3, GL 989, GL 2591, GL 2884, and NGC 7538 with the Kuiper Airborne Observatory (KAO) and found absorption features near 6.0 and 6.9  $\mu\text{m}$  in addition to the known 3.0  $\mu\text{m}$  ‘ice’ and 9.7  $\mu\text{m}$  ‘silicate’ features. Puetter et al. (1979) subsequently observed massive star-forming region W51–IRS2 and suggested that the water of hydration in silicates could carry the 6.0- $\mu\text{m}$  band, carbonates could carry the 6.9- $\mu\text{m}$  feature and that hydrocarbons could be additional components. May 1978 KAO observations of W33A (Soifer et al. 1979) provided the best early data set. Some 45 yr after discovery, the bulk of the 6.0- $\mu\text{m}$  band is associated with  $\text{H}_2\text{O}$  ice and the origins of the 6.9- $\mu\text{m}$  band are ‘enigmatic’ with at least two components (e.g. Boogert et al. 2008). This ‘W’-shaped feature (Aller et al. 2012) is also seen in the  $z = 0.886$  face-on spiral galaxy lens obscuring blazar PKS 1830–211 (Winn et al. 2002).

The goals of this work are to determine the primary dust component(s) responsible for the 6.9- $\mu\text{m}$  band. I compare results in the different MW and galaxy-absorber sightlines because differences in the dust components are a consequence of chemical and physical variations in their host environments. I use the smallest number of laboratory spectra in order to allow the statistics of the fits (reduced-chisquared values,  $\chi_r^2$ ), to distinguish between models. In cases

where the modelling is inconclusive, I constrain the results with information from other observations. Contributing dust components are:  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  ices, carbonates (calcite, dolomite, or magnesite), SiC,  $\text{OCN}^-$ , and  $\text{CO}_2$  ice. For the remainder of this paper the reader should assume that  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_3\text{OH}$  are ices unless stated otherwise.

Typical infrared absorption bands in MW star-forming environments are described in Section 2. MW source selection criteria are explained in Section 3 and their characteristics are described in Section 4.  $\text{H}_2\text{O}$ , methanol ( $\text{CH}_3\text{OH}$ ), and carbonate models of the 6–8- $\mu\text{m}$  spectra are outlined in Section 5; the laboratory data are listed in Section 5.1 and Table 1, and the fit parameters are in Table 2. 20- $\mu\text{m}$ -sized SiC grains are added to the 6–8- $\mu\text{m}$ -model of Mon R2 IRS 3 in Section 5.4. Abundances of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , carbonates, and SiC are derived in Section 6. In Section 7, shorter-wavelength bands at 4.3 and 4.6  $\mu\text{m}$  in the PKS 1830–211 spectrum are associated with  $\text{CO}_2$  and  $\text{OCN}^-$ , respectively. The quantitative results are summarized in Section 8 and the observational and theoretical consequences of a population of carbonate dust discussed in Section 9. The conclusions are in Section 10.

## 2 INFRARED ABSORPTION BANDS IN MW MOLECULAR-CLOUDS AND YSOS

3–12  $\mu\text{m}$  spectra of YSOs and sightlines through molecular clouds towards background stars within the MW contain several features

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**Table 1.** Laboratory data: peak wavelength,  $\lambda_{pk}$ ; sample thickness (grain size),  $d$ ; mass density ( $\rho$ ); mass absorption coefficient,  $\kappa_{pk}$  at the peak wavelength; peak width,  $\Delta_\nu$ ; integrated band strength,  $A_i$ ; and the frequency range for the  $A_i$  calculation.  $\kappa_{pk}$  and  $A_i$  are derived in Appendices B1 and B3, respectively.

Absorber	$\lambda_{pk}$ $\mu\text{m}$	$d^a$ $\mu\text{m}$	$\rho$ $\text{g cm}^{-3}$	$\kappa_{pk}$ $\text{cm}^2 \text{g}^{-1}$	$\Delta_\nu^b$ $\text{cm}^{-1}$	$A_i$ $\text{cm molecule}^{-1}$	$\nu_1 - \nu_2$ $\text{cm}^{-1}$	References <sup>c</sup>
6–7 $\mu\text{m}$ components								
<b>Ices</b>								
H <sub>2</sub> O	6.05	0.41	0.94	1700	144	$1.1 \times 10^{-17}$	1100–1900	1, 6
CH <sub>3</sub> OH	6.85	0.56	0.64	3000	115	$1.1 \times 10^{-17}$	1200–1800	1, 7
<b>Carbonates</b>								
Dolomite, CaMg(CO <sub>3</sub> ) <sub>2</sub>	6.87	0.15	2.86	33 000	120	$1.94 \times 10^{-15d}$	1200–1700	2
Magnesite, MgCO <sub>3</sub> <sup>e</sup>	6.87	0.15	2.98	27 000	120	$1.53 \times 10^{-15}$	1200–1700	2
Calcite, CaCO <sub>3</sub>	6.97	0.11	2.72	49 000	125	$3.24 \times 10^{-15}$	1100–1640	2
Calcite, nCaCO <sub>3</sub> <sup>f</sup>	6.97	~0.04	2.72	63 000	96	$3.21 \times 10^{-15}$	1100–1640	2
<b>Silicon carbide overtone spectrum</b>								
bSiC <sup>g</sup>	6.48	22	3.2	210	55	$2.4 \times 10^{-18h}$	1460–1585	3
4–5 $\mu\text{m}$ components								
<b>Ice</b>								
$\nu_3$ CO <sub>2</sub>	4.27		1.68	34 000	18	$7.6 \times 10^{-17i}$	–	4, 8
<b>Organic residue</b>								
OCN <sup>-</sup>	4.61				~30 <sup>j</sup>	$1.3 \times 10^{-16k}$	–	5

<sup>a</sup>Sample thickness,  $d$ , is used as a proxy for grain length in refractory components (see Appendix B2 for justification). The nominal volume is  $d^3$ .

<sup>b</sup>fwhm

<sup>c</sup>References: spectrum and film thickness from 1—Hudgins et al. (1993), 2—Bowey & Hofmeister (2022), 3—Hofmeister et al. (2009); spectrum from 4—van Broekhuizen et al. (2006), and 5—Brucato, Baratta & Strazzulla (2006). References for ice mass densities,  $\rho$ : 6—H<sub>2</sub>O at 20 K—Dohnálek et al. (2003); 7—CH<sub>3</sub>OH at 20 K—Luna et al. (2018); and 8—CO<sub>2</sub> at 80 K Mangan et al. (2017). Refractory measurements and densities were obtained at room temperature.

<sup>d</sup>To follow chemical convention, the formula has two CO<sub>3</sub> groups because Fe and Mg are interchangeable in the same lattice positions. Quoted band strength is the value per CO<sub>3</sub> group to match the other carbonates.

<sup>e</sup>Magnesite provided a good fit to data for Sakurai’s Object (Bowey & Hofmeister 2022), the integrated cross-section and fwhm is included for completeness.

<sup>f</sup>The prefixed n in the chemical formula is to distinguish the very thin film.

<sup>g</sup>Overtone bands in 6H Alfa/Aesar sample orientated *E*⊥*c*; Sakurai’s Object was better fitted with a different sample (a 25- $\mu\text{m}$ -thick  $\beta$  SiC wafer).

<sup>h</sup>Blended with peak at 6.17  $\mu\text{m}$ .

<sup>i</sup>Pure CO<sub>2</sub> band strength Gerakines et al. (1995).

<sup>j</sup>Estimated from Brucato et al. (2006) data.

<sup>k</sup>van Broekhuizen, Keane & Schutte (2004), accuracy  $\pm 20$  per cent.

between the 3.0- $\mu\text{m}$  H<sub>2</sub>O ‘ice’ and 9.7- $\mu\text{m}$  ‘silicate’ bands. They include:

## 2.1 Bands between 3 and 5 $\mu\text{m}$

Absorption bands near 3.25, 3.44, and 3.47  $\mu\text{m}$  are not a part of this study because they do not appear in the PKS 1830–211 galaxy-absorber spectrum; they have recently been modelled with PAHs and hydrogenated PAHs co-condensed with H<sub>2</sub>O ice (Chiar et al. 2021). While the 3.25- $\mu\text{m}$  band is normally associated with PAHs the 3.47- $\mu\text{m}$  band is typically attributed to nano-diamonds (e.g. Allamandola et al. 1992). Bands at 3.54 and 3.95 are used to obtain CH<sub>3</sub>OH abundances (e.g. Gibb et al. 2004). Two, normally prominent, narrow absorption bands at 4.27  $\mu\text{m}$  (fwhm  $\approx 0.03$   $\mu\text{m}$ ) and 4.61  $\mu\text{m}$  (fwhm  $\approx 0.06$   $\mu\text{m}$ ) are assigned to the C=O stretch in pure CO<sub>2</sub> or mixed CO<sub>2</sub> bearing ices, and a CN stretch in OCN<sup>-</sup> or XCN, respectively (e.g. Gibb et al. 2004; Brucato et al. 2006).

## 2.2 The 6.0- $\mu\text{m}$ H<sub>2</sub>O and carbonaceous band

The non-Gaussian 6.0  $\mu\text{m}$  (fwhm  $\approx 0.5$   $\mu\text{m}$ ) band associated with H<sub>2</sub>O ice is thought to contain additional contributions from carbonaceous materials. Possible contributors include: Organic Refractory Material (ORM; Gibb & Whittet 2002), a 5.85- $\mu\text{m}$  C=O (carbonyl) band which occurs in Hydrogenated Amorphous Carbon (HAC) formed in an oxygen-bearing atmosphere (Grishko & Duley 2002),

and formic acid (HCOOH) as well as formate (HCOO<sup>-</sup>) ion, which might contribute at 6.33  $\mu\text{m}$  (see Boogert et al. 2008).

## 2.3 An ‘enigmatic’ band near 6.9 $\mu\text{m}$

### 2.3.1 CH<sub>3</sub>OH ice

CH<sub>3</sub>OH (e.g. Gibb et al. 2004) is a reasonable match to the  $\sim 0.4$ - $\mu\text{m}$  wide 6.9  $\mu\text{m}$  band in many environments but the inferred abundance is frequently higher than estimates derived from the CH<sub>3</sub>OH bands at 3.54 and 3.95  $\mu\text{m}$ . In addition, the peak-wavelength of the astronomical band shifts between sources whilst the CH<sub>3</sub>OH peak does not, so two components are thought to contribute (Keane et al. 2001; Boogert et al. 2008, 2011).

### 2.3.2 Aromatic and aliphatic candidates

Combinations of Polycyclic aromatic hydrocarbons (PAHs) have been found too narrow to fit the features in star-forming regions (Chiar et al. 2021; Mattioda et al. 2020). However, a narrower 6.9  $\mu\text{m}$  absorption feature in the ISO spectrum of the line of sight towards Sgr A\* (the MW Galactic Centre), which includes molecular-cloud and diffuse medium dust, is associated with asymmetric CH deformation modes in diffuse-medium aliphatic hydrocarbons (Chiar et al. 2000) because it is insufficiently broad to match CH<sub>3</sub>OH. This narrower

feature has also been identified in the ice-free diffuse medium sightline towards Cyg OB2 no.12 (Hensley & Draine 2020).

### 2.3.3 Oxygen-rich candidates—silicates and carbonates

Inorganic carbonates (of mineralogical formula  $X\text{-CO}_3$ , where X is usually a combination including Mg, Ca, or Fe) were early candidates for the 6.9- $\mu\text{m}$  band (Sandford & Walker 1985) due to the occurrence of a strong band (arising from an asymmetric stretch within the  $\text{CO}_3^{2-}$  ion; see White 1974) near to this wavelength. However, Keane et al. (2001) excluded them from consideration because the 0.6- $\mu\text{m}$  wide carbonate bands in existing laboratory spectra were broader than the astronomical features. Bowey & Hofmeister (2005) found a match with the overtone spectrum of a crystalline silicate from the melilite ( $\text{Ca}_2\text{Mg}(\text{Si},\text{Al})_2\text{O}_7$ ) group, but laboratory measurements of a set of melilites (Bowey & Hofmeister 2022) were used to prove that the ‘melilite’ band was produced by minor (<0.1 per cent by mass) contamination of the sample with carbonate powder.<sup>1</sup> With the initial purpose of correcting the ‘melilite’ spectra, Bowey & Hofmeister (2022) obtained spectra of very thin  $\sim 0.04\text{--}0.15\text{-}\mu\text{m}$  thick carbonate films: the 6.9- $\mu\text{m}$  absorption bands of these materials were narrower than those in the KBr-dispersion<sup>2</sup> spectra used by Keane et al. (2001) and provided a good match to a similar 6.9  $\mu\text{m}$  absorption band produced by dust obscuring the carbon-rich atmosphere of Sakurai’s Object (V4334 Sgr) in 2005–2008 Spitzer observations. Interpretation of Sakurai’s Object spectra (Bowey 2021; Bowey & Hofmeister 2022) was simplified by the absence of ices as exemplified by the absence of a 6.0- $\mu\text{m}$   $\text{H}_2\text{O}$ –ice absorption band. PAH absorption was added to match finer structure in its 6–7  $\mu\text{m}$  spectra and fits improved if overtone features due to large (25  $\mu\text{m}$ -sized) SiC grains were included in the model.

Here, I shall use the same carbonate spectra to model the sources in environments where the fitting is complicated by the co-existence of ices in the same lines of sight, and add SiC grains when necessary. The contribution of PAHs will be briefly considered, but is not a focus of this research.

An absence of experimental studies of carbonate formation under astronomical conditions, is frustrating, but unsurprising (see Bowey & Hofmeister (2022) for a detailed discussion). However, carbonates are candidate carriers of a broad 90- $\mu\text{m}$  emission band in the spectra of planetary nebulae (PNe) (e.g Kemper et al. 2002) and YSOs (e.g Ceccarelli et al. 2002). Carbonates were also included in models of the spectra of freshly produced dust from the deep impact experiment on comet Tempel 1 (Lisse et al. 2007) because they produce a 6.9- $\mu\text{m}$  absorption band in the spectra of pyroxene

<sup>1</sup>True melilite overtones were a pair of narrow (<0.1  $\mu\text{m}$ ) peaks at 6.4 and 6.8  $\mu\text{m}$ .

<sup>2</sup>Transmission spectra derived from dispersions of powder mixed with other matrix material (KBr, polyethylene) have broader spectral peaks than those of thin films due to the effect of scattering between the grains and the matrix. Bowey, Hofmeister & Keppel (2020) contains a detailed discussion of experimental methods and comparison between KBr and thin-film spectra for pyroxenes. Band-widths also increase if the grain-sizes or sample-thicknesses or grain sizes are too large because light is not transmitted at the band centre; Hofmeister’s preliminary spectra of thicker 0.2–0.3  $\mu\text{m}$  carbonate films were significantly broader than the data in Bowey & Hofmeister (2022) and do not match astronomical spectra. Spectral artefacts are discussed in detail by Hofmeister, Keppel & Speck (2003). In the astronomical literature from the 1980s to 2000s, this phenomenon is frequently referred to as ‘grain-shape and size effects’ and is one of the reasons why the use of particulate-spectra was frowned on in astronomy.

and layer-lattice interplanetary dust particles (Sandford & Walker 1985). They are found with hydrated minerals in meteorites (e.g. Rubin & Ma 2017), and form rapidly from CaO exposed to the air under ambient terrestrial conditions (Galván-Ruiz et al. 2009).

## 3 SELECTION OF MW SOURCES

Due to the overlapping wavelengths of the  $\text{CH}_3\text{OH}$  and carbonate 6.9- $\mu\text{m}$  bands, fits to the 5–8- $\mu\text{m}$ -spectra were compared with  $\text{CH}_3\text{OH}$  to  $\text{H}_2\text{O}$  abundance-ratios from 3- to 4- $\mu\text{m}$  data for the MW targets. Hence, MW spectra were selected according to the following criteria:

(i) There must be good spectra of the 6–8- $\mu\text{m}$  absorption bands which are unsaturated, i.e. the absorption peaks are curved rather than flat-topped. Laboratory spectra of rounded and flattened peaks indicate that the grains are too large or the sample is too thick for light to pass through to give a reliable spectral shape (e.g Hofmeister et al. 2003) and footnote 2.

(ii) There must be good unsaturated data for the 3.0- $\mu\text{m}$   $\text{H}_2\text{O}$  band and estimates, or upper limits of the  $\text{CH}_3\text{OH}$  abundance from the 3.54- and 3.95- $\mu\text{m}$  bands.

The sample includes the quiescent sightline through the Taurus molecular cloud towards Taurus Elias 16 and spectra of YSOs in high-mass star forming regions (S140 IRS 1, Mon R2 IRS 3, AFGL 989). Unfortunately, these criteria eliminated observations of low-mass YSOs like  $\rho$ -Elias 29 (the 6–8- $\mu\text{m}$  spectrum was weak and relatively noisy), well-known high-mass YSOs like W 33A (saturated 3.0  $\mu\text{m}$  band), which have more ice features than discussed here, and quiescent-molecular cloud sources (no 3.0  $\mu\text{m}$  spectra), and sightlines where the 6–8- $\mu\text{m}$  absorption bands were coincident with PAH emission. The 3–4- $\mu\text{m}$  saturation constraint limits the range of explored  $\text{H}_2\text{O}$  ice column densities and three of the four 3–4- $\mu\text{m}$   $\text{CH}_3\text{OH}$  estimates are upper limits.

## 4 SIGHTLINE CHARACTERISTICS

### 4.1 PKS 1830–211

The line of sight towards blazar PKS 1830–211 at  $z = 2.507$  is physically and chemically interesting at radio, submm and IR wavelengths because its light passes through a face-on lensing spiral galaxy at a redshift of  $z = 0.886$  (Winn et al. 2002). Two or three lensed components are observed in ALMA images with a maximum separation of 1" (Muller et al. 2020). The SW component of PKS 1830–211 is currently the only high redshift object in which gas-phase methanol ( $\text{CH}_3\text{OH}$ ) absorption has been detected in the submm (Muller et al. 2021); this together with other submm and radio absorption bands due to 60 gas-phase molecular species indicate conditions within the galaxy-absorber are similar to those in MW cold molecular clouds and hot UV-rich HII regions associated with young stellar objects (YSOs) (Tercero et al. 2020; Muller et al. 2021).

PKS 1830–211 was a single object in the  $3.7'' \times 57''$  aperture of the Short-Low (SL) module of the infrared spectrometer (IRS) on Spitzer; its spectrum is known for its unusual 10  $\mu\text{m}$  silicate absorption feature, which resembles crystalline olivine (Aller et al. 2012), rather than the glassy silicates common to other galaxies and the interstellar medium of the MW; early MIRI/JWST observations are scheduled (Aller & Kulkarni 2021). Aller et al. (2012) also remarked on the similarity between the galaxy-absorber’s additional 6.0 and 6.9  $\mu\text{m}$  bands and those in MW embedded ice-rich YSOs and associated the 6.0- $\mu\text{m}$  band with  $\text{H}_2\text{O}$  ice. The data selection process for this work is explained in Appendix A.

#### 4.2 MW dark molecular cloud: Taurus Elias 16

The interstellar line of sight towards the field-star Elias 16 is the archetypal quiescent dark and dusty molecular cloud environment because it is a bright and highly reddened field star ( $E(J-K_s)=4.76$ ;  $A_V \sim 19$ ) of spectral type K1 III behind the Taurus Molecular Cloud (Chiar et al. 2007). Spectral studies of ices, PAHs, and silicates, and spectropolarimetric studies of ices have all been made towards Elias 16 (e.g. Knez et al. 2005; Chiar et al. 2021; Bowey, Adamson & Whittet 1998; Hough et al. 2008, respectively). Spitzer data in this work are from the CASSIS archive; the original observations were published by Knez et al. (2005). Short Wavelength Spectrometer (de Graauw et al. 1996) Infrared Space Observatory (ISO) data published by Gibb et al. (2004) were used for analysis in the 2–5- $\mu\text{m}$  range.

#### 4.3 MW massive star-forming regions

SWS/ISO spectra published by Gibb et al. (2004) were used for S140 IRS 1, AFGL 989, and Mon R2 IRS 3.

S140 is an H II region located 910 pc away behind  $\sim 23$  mag of extinction in a molecular cloud, which is forming high- and low-mass stars (Evans et al. 1989). K' band images (Preibisch & Smith 2002) show several high mass YSOs (8–10  $M_\odot$ ) within the 30"–40" ISO beam. S140 IRS 1 has a dust disc, which has been resolved at 1.3 mm (Maud & Hoare 2013).

AFGL 989, otherwise known as Allen's Source, is the brightest IR source in NGC 2264 (IRS 1). It is a high-mass YSO (10  $M_\odot$ ), which is invisible in the optical. Mid-infrared interferometric observations indicate that the object is surrounded by a flat circumstellar disc that has properties similar to discs typically found around lower-mass young stellar objects (Grellmann et al. 2011). The luminosity is consistent with a 9.5- $M_\odot$  B2 zero-age main-sequence star (Allen 1972) with 20–30 mag of visual extinction (Thompson et al. 1998).

In the near-infrared, Mon R2 IRS 3 is a bright 500-au conical reflection nebula containing two to three massive early-type stars (IRS 3N, IRS 3S, and possibly IRS 3 NE). Infrared speckle imaging suggests that the conical-shaped nebula is due to collimation of the light of IRS 3 by a 500-au disc (Koresko et al. 1993) and the presence of three further sources within 2.6 arcsec of IRS 3S; the  $A_V$  to the primary is  $>30$  mag (Preibisch et al. 2002).

### 5 ICE AND CARBONATE MODELS OF 6–8 $\mu\text{M}$ SPECTRA

The infrared continua of objects with strong absorption features are poorly constrained longward of 5  $\mu\text{m}$  (e.g. see Gibb et al. 2004; Boogert et al. 2008) and it is common practice to use a low-order polynomial or spline fit over as wide a wavelength range as possible and then to add the absorbers for each of the bands. In contrast to this approach, I select laboratory data for thin films of candidate absorbers and simultaneously fit the optical depths and continua. My continua are represented by simple mathematical formulae over the narrower wavelength range of the absorption features; these represent an ill-defined combination of the effects of baseline subtraction from the laboratory spectra, source physics, and foreground extinction.

Since ice abundances are usually given in terms of number of molecular absorbers (i.e. molecular density) whilst abundances of the refractory components (i.e. the grain cores) are quoted as mass and grain number densities, I give estimates of all three parameters. The relationship between these quantities is described in Appendix B.

#### 5.1 Laboratory spectra used to model the absorption bands

Each continuum function,  $C_v$ , was extinguished by up to three components represented by  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ , and one of the carbonate spectra listed in Table 1.

$$F_v = C_v \exp\left(-\sum_{i=1}^3 c_i \tau_i(\lambda)\right), \quad (1)$$

where  $\tau_i$  is the shape of the  $i$ th absorber, normalized to unity at the tallest peak in the wavelength range of interest.

Three combinations of materials were fitted to each source spectrum: (i)  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  and a carbonate, (ii)  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ , and (iii)  $\text{H}_2\text{O}$  and a carbonate. The ice spectra (Hudgins et al. 1993) were measured at 10 K, the carbonate spectra (Bowey & Hofmeister 2022) were obtained at room temperature (there are no suitable low-temperature data). The carbonate samples included magnesite ( $\text{MgCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), and calcite ( $\text{CaCO}_3$ ). Peak wavelengths vary between 6.87  $\mu\text{m}$  (magnesite, dolomite) and 6.97  $\mu\text{m}$  (calcite); most of the spectra were obtained from 0.1- to 0.15- $\mu\text{m}$  thick powder films. The effect of grain-size on the calcite fits was explored by using the spectrum of an additional  $\sim 0.04$ - $\mu\text{m}$  thick calcite film ( $n\text{CaCO}_3$ ). Only the best carbonate fits are included in the paper; fit qualities are governed primarily by the match to peak-wavelength and secondly by feature-width. Small components of other materials may also contribute to the spectra, especially to the 6.0- $\mu\text{m}$   $\text{H}_2\text{O}$  band.<sup>3</sup> In tests extra components fell to zero or the fit was unconstrained.

#### 5.2 Continua and fitting process

##### 5.2.1 Power-law galaxy and YSO continua

The observed spectra of PKS 1830–211, and the YSOs, were modelled by inserting a wavelength-dependent power-law continuum,

$$C_v = c_0 \lambda^\alpha, \quad (2)$$

into equation (1). Constant,  $c_0$ , and optical-depth scale factors  $c_1$ – $c_3$  were constrained to positive values (to prevent the introduction of spurious emission features) and optimized by the downhill-simplex method of  $\chi^2$ -minimization as implemented by the AMOEBA routine in Interactive Data Language (IDL). Power-law index,  $\alpha$ , values were selected by trial and error to give the best fit to each source.

##### 5.2.2 Taurus-Elias 16 continuum

Power-law models, which match the featureless Elias 16 spectrum between 5.0 and 5.6  $\mu\text{m}$  and the 6.0- $\mu\text{m}$  band are too shallow to match the 6.9- $\mu\text{m}$  band and continuum beyond 7.0  $\mu\text{m}$   $\chi^2$  values are poor. Unlike the other sources which are characterized by largely optically thick power-law emission local to the source, Elias 16 is a heavily reddened field star, which is better represented by a second order polynomial in wavelength:

$$C_v = a_0 + a_1 \lambda + a_2 \lambda^2. \quad (3)$$

in equation (1)

<sup>3</sup>Organic residues may broaden and deepen the feature (Gibb & Whittet 2002) but were included by them to explain extra depth in the 6.0- $\mu\text{m}$  band in comparison to predictions from the 3.0- $\mu\text{m}$   $\text{H}_2\text{O}$  band. I did not include an (organic refractory material) ORM component because the fits were degenerate.

**Table 2.** Fits to 6–8  $\mu\text{m}$  spectra with  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  and carbonates ( $-\text{CO}_3$ ) in order of decreasing fit quality for each source. The best fits, plotted in Fig. 1, are indicated in bold. Italics indicate optical depths predicted from 3 to 4  $\mu\text{m}$  spectra.  $\sigma$ -values are the one-sigma confidence intervals quoted as a percentage of each fitted optical depth to one significant figure (see Section 5.2.3).

Source	Index $\alpha$	$\text{H}_2\text{O}$ component			Additional components			Quality			
		$\tau_6(\text{H}_2\text{O})$	$\sigma$	$\tau_{6,0}(B)^a$	$\tau_6(\text{CH}_3\text{OH})$	$\sigma$	$\tau_{6,85}(P)^b$	$\tau_6(-\text{CO}_3)$	$\sigma$	$\chi_v^2$	
PKS 1830–211	<b>1.44</b>	<b>0.21</b>	1	–	<b><math>\text{CH}_3\text{OH}+\text{CaCO}_3</math></b>	<b>0.11</b>	2	–	<b>0.063</b>	4	<b>1.1</b>
	1.32	0.19	1	–	$\text{CH}_3\text{OH}$	0.15	2	–	–	–	1.3
	1.52	0.22	1	–	$\text{CaCO}_3$	–	–	0.17	1	–	2.1
Elias 16	–	<b>0.18</b>	1	<i>0.15 (10 K)</i>	<b><math>\text{CaMg}(\text{CO}_3)_2</math></b>	–	–	<b>0.10</b>	2	<b>3.52</b>	
	–	0.18	–	–	$\text{CH}_3\text{OH}+\text{CaMg}(\text{CO}_3)_2$	0.017	10	<i>&lt;0.006</i>	0.086	2	3.54
	–	0.16	2	–	$\text{CH}_3\text{OH}$	0.096	1	–	–	–	4.37
S140 IRS 1	<b>2.07</b>	<b>0.12</b>	0.1	<i>0.16 (100 K)</i>	<b><math>\text{nCaCO}_3</math></b>	–	–	<b>0.10</b>	0.2	<b>13.052</b>	
	2.05	0.12	0.2	–	$\text{CH}_3\text{OH}+\text{nCaCO}_3$	0.0073	3	<i>&lt;0.01</i>	0.092	0.3	13.055
	2.04	0.11	0.2	–	$\text{CH}_3\text{OH}$	0.092	0.2	–	–	–	18.27
AFGL 989	<b>1.25</b>	<b>0.16</b>	0.2	<i>0.18 (40 K)</i>	<b><math>\text{CH}_3\text{OH}</math></b>	<b>0.071</b>	0.6	–	–	<b>10.538</b>	
	1.25	0.16	0.2	–	$\text{CH}_3\text{OH}+\text{nCaCO}_3$	0.071	0.6	<i>0.046</i>	$<10^{-6}$	–	10.540
	1.23	0.17	0.2	–	$\text{nCaCO}_3$	–	–	0.061	0.7	12.44	
Mon R2 IRS 3	1.65	0.18	0.2	<i>0.20 (100 K)</i>	$\text{CH}_3\text{OH}+\text{nCaCO}_3$	$<10^{-6}$	–	<i>&lt;0.01</i>	0.21	0.2	26.9
	1.66	0.18	0.2	–	$\text{nCaCO}_3$	–	–	0.21	0.2	27.0	
	1.65	0.16	0.2	–	$\text{CH}_3\text{OH}$	0.20	0.2	–	–	–	42
	<b>1.88</b>	<b>0.17</b>	0.2	–	<b><math>\text{nCaCO}_3 + \text{bSiC}</math></b>	<b>0.064</b>	0.6	–	<b>0.27</b>	0.1	<b>20.0</b>

<sup>a</sup>Published estimate deduced from 3.0  $\mu\text{m}$  band and the temperature of the 3.0- $\mu\text{m}$  laboratory spectrum, see Section 6.1. Value for Elias 16 is from Boogert et al. (2011); others are from Boogert et al. (2008).

<sup>b</sup>Estimate defined in Section 6.2. It is based on published ratios of the 3.54- $\mu\text{m}$   $\text{CH}_3\text{OH}$  ice to the 3.0- $\mu\text{m}$   $\text{H}_2\text{O}$  ice band.

Six parameter fits of coefficients  $a_0$ – $a_2$  and optical-depth scale factors  $c_1$ – $c_3$  were poorly constrained due to the excessive number of degrees of freedom; five parameter fits were constrained. Therefore, values of the 6.0- $\mu\text{m}$   $\text{H}_2\text{O}$  optical depth were pre-selected by trial-and-error to give the lowest  $\chi_v^2$  in the  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and carbonate models.  $\text{H}_2\text{O}$  components in two-component models including either  $\text{CH}_3\text{OH}$ , or a carbonate were allowed to vary freely.

Unsophisticated tests of power-law reddened Spitzer library spectra of KIII giants produced continua similar to the polynomial models over this wavelength range.

### 5.2.3 Calculation of fit uncertainties

Fit robustness was checked by determining one-sigma confidence intervals after convergence at  $\chi^2(\text{fit})$ . Each parameter was shifted from the solved value by a few per cent and a new  $\chi^2(\text{shifted})$  calculated. Then the AMOEBA routine was invoked to minimize  $|\chi^2(\text{shifted}) - \chi^2(\text{fit}) - 1.0|$ . The value at convergence is an estimate of the one sigma confidence interval. Formal uncertainties of well-constrained parameters are usually small (0.1 per cent–3 per cent) in comparison to my estimates of systematic uncertainties; these include the true number of dust components, the true continuum, and uncertainties intrinsic to baseline subtraction in the laboratory data. Hence, parameters are quoted to no more than two significant figures despite the confidence intervals indicating smaller uncertainties. Quoted uncertainties are based on propagating the most pessimistic fit (5 per cent) and realistic systematic (15 per cent) errors.

### 5.3 Fitted components and optical depth profiles

Fits are listed in Table 2 where the best fits (with the lowest  $\chi_v^2$  values) are indicated in bold and shown with the observed fluxes in Fig. 1. Optical depth profiles and absorption components obtained

from visually distinguishable models are shown in Fig. 2; they were derived by taking the natural log of the ratio of the observed, or fitted flux (equation (1)) to the continuum model (equations (2) or (3), as appropriate).

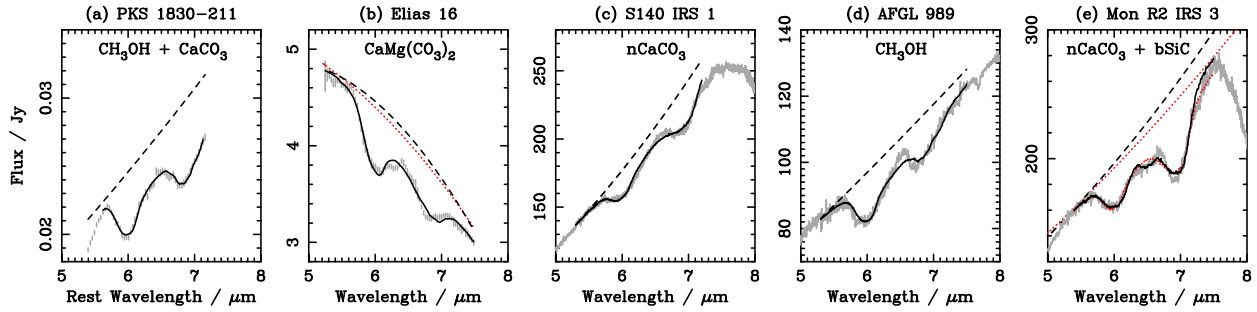
$$\tau(\lambda) = \ln(C_v/F_v). \quad (4)$$

The spectrum of the PKS 1830–211 galaxy-absorber was fitted best with a three-component model including  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CaCO}_3$  (Fig. 1a). Carbonate-bearing fits to Elias 16 (with  $\text{CaMg}(\text{CO}_3)_2$ ; Fig. 1b) and S140 IRS 1 (with  $\text{nCaCO}_3$ ; Fig. 1c) were nearly statistically identical irrespective of the inclusion or exclusion of  $\text{CH}_3\text{OH}$ . Hence, I represent the data with two-component  $\text{H}_2\text{O}$  and carbonate models. In contrast, the carbonate component in AFGL 989 (Fig. 1e) was negligible ( $\tau(\text{nCaCO}_3) < 10^{-6}$ ) so the two-component  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  model was selected.

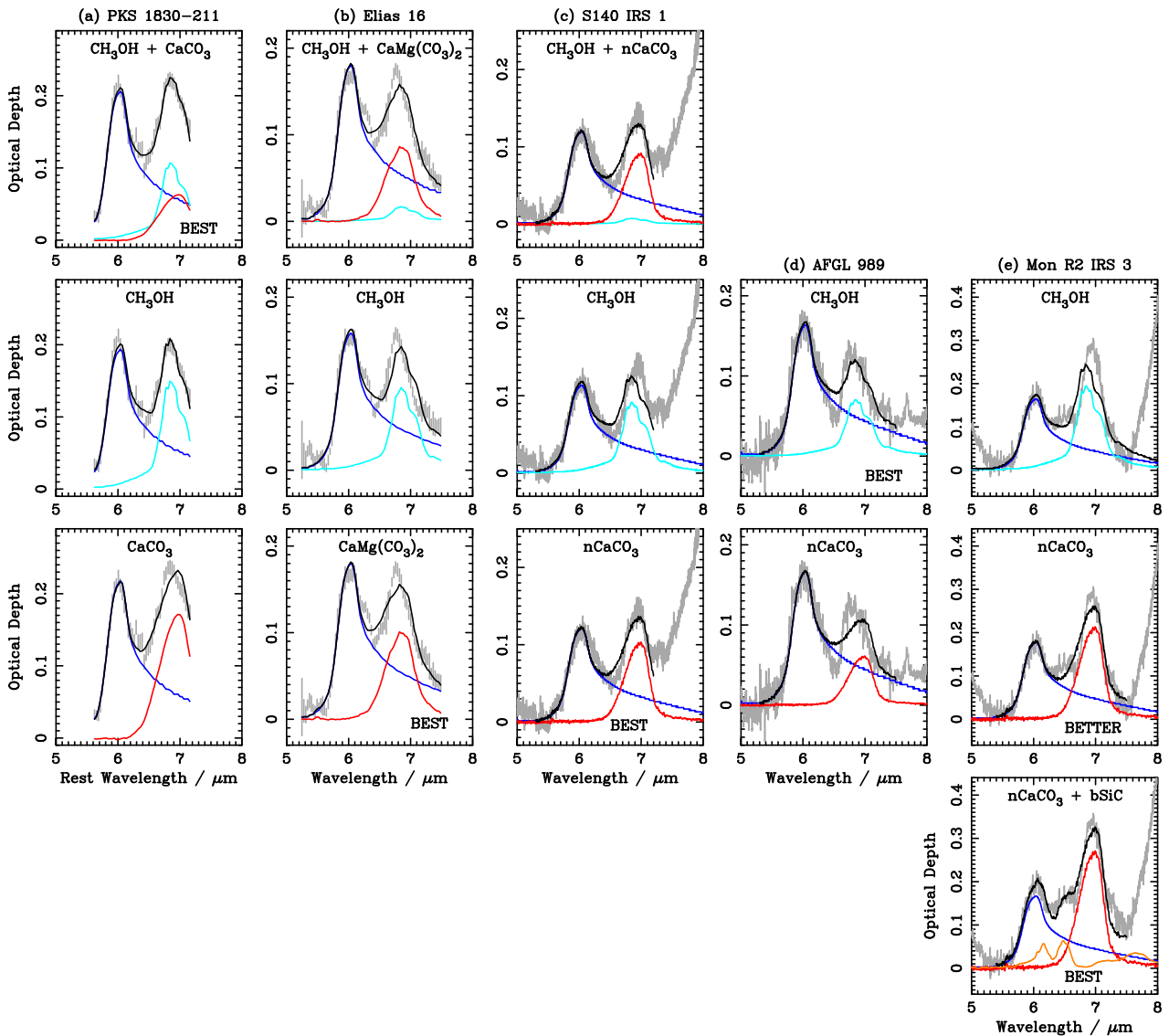
The Mon R2 IRS 3 observation was initially matched with a two-component  $\text{H}_2\text{O}$  and  $\text{nCaCO}_3$  model due to the negligible fitted  $\text{CH}_3\text{OH}$  component ( $\tau(\text{CH}_3\text{OH}) < 10^{-6}$ ) (labelled **BETTER** in Fig. 1e). However, this fit does not match a plateau centred at 6.4  $\mu\text{m}$  indicating the need to add a third absorber.

### 5.4 20 $\mu\text{m}$ -sized SiC grains in Mon R2 IRS 3

Isotope measurements of thousands of 0.1–20  $\mu\text{m}$ -sized meteoritic SiC grains (e.g. Hoppe et al. 1994; Speck, Thompson & Hofmeister 2005) suggest that they exist in protostellar environments. However, the SiC stretching band near 11.5  $\mu\text{m}$  has not been detected beyond carbon stars (e.g. Whittet, Duley & Martin 1990); due to the high opacity of the band only nanometre-sized grains produce unsaturated 11.5  $\mu\text{m}$  features (see Hofmeister et al. 2009) so the meteoritic grains would be opaque. Noting that larger  $\lesssim 25 \mu\text{m}$  SiC grains, hereinafter denoted bSiC (for ‘big’ SiC grains), might be detectable by using their weak overtone peaks near 6.2 and 6.5  $\mu\text{m}$



**Figure 1.** Best fits (solid black) to absorption features in the 6–8- $\mu\text{m}$  spectra of PKS 1830–211 and MW sources: Taurus Elias 16, S140 IRS 1, AFGL 989, and Mon R2 IRS 3 (grey; error bars are plotted on the Spitzer data, but not the ISO data) with 10 K  $\text{H}_2\text{O}$  and a carbonate or  $\text{CH}_3\text{OH}$  or both 6.9  $\mu\text{m}$  components. Dashed curves are continua derived with the best models. Only Mon R2 IRS 3 required a bSiC component. Red dotted curves indicate the continuum derived for Elias 16 with the poor two-component  $\text{CH}_3\text{OH}$  model and the continuum and fit to Mon R2 IRS 3 if the bSiC component were excluded.



**Figure 2.** 5–8  $\mu\text{m}$  optical depth spectra (grey) with combinations including 10 K  $\text{H}_2\text{O}$  (blue), a carbonate (red), and/or  $\text{CH}_3\text{OH}$  (cyan). Black curves are the sum of the components over the fitted range. The ‘BEST’ Mon R2 IRS 3 fit included an additional bSiC component (orange) to fit a plateau at 6.4  $\mu\text{m}$ . Three-component fits to AFGL 989 and Mon R2 IRS 3 are not included because they are indistinguishable from the ‘BEST’ (AFGL 989), or ‘BETTER’ (Mon R2 IRS 3) two-component fits.

(Hofmeister et al. 2009; Bowey 2021; Bowey & Hofmeister 2022) included them in three-component models of Sakurai's Object and I include them here.<sup>4</sup>

Significantly better fits ( $\chi^2_{\nu} = 20.0$  instead of 26.9 and labelled **BEST** in Fig. 1e) were obtained by adding the overtone spectrum of  $\sim 20\text{-}\mu\text{m}$ -sized silicon carbide grains to the nCaCO<sub>3</sub> and H<sub>2</sub>O model. This component increased the power-law index slightly, reduced  $\tau_6(\text{H}_2\text{O})$  by 5 per cent and increased  $\tau_6(-\text{CO}_3)$  by 29 per cent, to 0.27. In test fits to other MW objects the bSiC component fell to zero.

### 5.5 Unfitted structure in the PKS 1830–211 and Elias 16 sightlines

Spectra of Elias 16 and PKS 1830–211 contain weak 0.2- $\mu\text{m}$  wide peaks centred at 6.3  $\mu\text{m}$  that are not captured by the model fits. While the PKS 1830–211 peak could be explained by noise, structure in the Elias-16 spectrum appears to be significant. In addition, the Elias-16 6.9- $\mu\text{m}$  peak is narrower than the dolomite and magnesite laboratory spectra and is blueshifted by 0.1  $\mu\text{m}$  in comparison to these carbonates. 6.9  $\mu\text{m}$ -fits might be improved with spectra of smaller ( $\lesssim 0.04\mu\text{m}$ ) magnesite or dolomite grains, or low-temperature measurements because these factors sharpen the bands. However, it is unlikely that they can explain the wavelength shift. Since unmatched areas below and above the dolomite fit to the 6.9- $\mu\text{m}$  peak in Elias 16 are similar, I consider derived carbonate abundances and uncertainties representative of the true values.

The two excesses at 6.3 and 6.75  $\mu\text{m}$  might be explained by a contribution from PAHs. Preliminary attempts to obtain an upper-limit by adding a Carpentier et al. (2012) PAH spectrum were unconstrained, but fits with the narrower bands of individual PAHs (aka Mattioda et al. 2020; Chiar et al. 2021) might provide a solution.

### 5.6 Summary

H<sub>2</sub>O ice is present in all these lines of sight. Every sightline, except AFGL 989, required a carbonate component. The best models of Mon R2 IRS 3 included large (20  $\mu\text{m}$ -sized) SiC grains. Only PKS 1830–211 and AFGL 989 have a substantial CH<sub>3</sub>OH component. There is unexplained excess absorption in the spectrum of Elias 16 at 6.3 and 6.75  $\mu\text{m}$ .

## 6 ABUNDANCES

### 6.1 H<sub>2</sub>O

Fitted H<sub>2</sub>O optical depths,  $\tau_6(\text{H}_2\text{O})$ , in Table 2 are compared with published estimates,  $\tau_{6,0}(B)$ . Boogert et al. (2008) define

$$\tau_{6,0}(B) = \tau_6(I_3, T) + C1 + C2, \quad (5)$$

where  $\tau_6(I_3, T)$  is the optical depth of H<sub>2</sub>O ice at 6.0  $\mu\text{m}$  inferred from the observed depth of the 3.0- $\mu\text{m}$  H<sub>2</sub>O band using a laboratory spectrum obtained at temperature  $T$ . Components C1 ( $\lambda_{pk} = 5.8 \mu\text{m}$ , fwhm  $\sim 0.3 \mu\text{m}$ ) and C2 ( $\lambda_{pk} = 6.2 \mu\text{m}$ , fwhm  $\sim 0.4 \mu\text{m}$ ) are the optical depths of two observationally defined profiles of unknown materials. The contribution of C1 + C2 to  $\tau_{6,0}(B)$  in Elias 16,

<sup>4</sup>Overtone features due to other materials did not match the Mon R2 IRS 3 spectrum (Bowey & Hofmeister 2005), with the exception of the 'melilite' spectrum, which was later found to be contaminated with carbonates (Bowey & Hofmeister 2022).

**Table 3.** Mass,  $\Sigma$ ; and molecular,  $m$ ; densities of H<sub>2</sub>O ice evaluated from the 6- to 7- $\mu\text{m}$  spectra with published values,  $m_3$ , from 3.0- $\mu\text{m}$  spectra (Gibb et al. 2004). Uncertainties in  $\Sigma$  and  $m$  are  $\lesssim 20$  per cent (see Section 5.2.3).

Object	$\Sigma/10^{-6} \text{ g cm}^{-2}$	$m/10^{18} \text{ cm}^{-2}$	$m_3/10^{18} \text{ cm}^{-2}$
PKS 1830–211	120	2.7	
Elias 16	110	2.4	$2.5 \pm 0.06$
S140 IRS 1	70	1.6	$1.9 \pm 0.03$
AFGL 989	96	2.1	$2.4 \pm 0.1$
Mon R2 IRS 3	98	2.2	1.9

**Table 4.** Mass and molecular densities of CH<sub>3</sub>OH ice evaluated from the 6- to 7- $\mu\text{m}$  spectra.  $R_6(\text{CH}_3\text{OH})$  and  $R_3(\text{CH}_3\text{OH})$  are my CH<sub>3</sub>OH/H<sub>2</sub>O molecular ratios from the 6- to 7- $\mu\text{m}$  spectra and the ratios obtained by Gibb et al. (2004) from the 3- to 4- $\mu\text{m}$  spectra, respectively. Uncertainties in  $\Sigma$ ,  $m$ , and  $R_6(\text{CH}_3\text{OH})$  are  $<20$  per cent,  $<20$  per cent, and  $<30$  per cent, respectively (see Section 5.2.3).

Object	$\Sigma$ $10^{-6} \text{ g cm}^{-2}$	$m$ $10^{18} \text{ cm}^{-2}$	$R_6(\text{CH}_3\text{OH})$ Per cent	$R_3(\text{CH}_3\text{OH})$ per cent
PKS 1830–211	36	1.1	41	
Elias 16 <sup>a</sup>	$<5.7$	$<0.18$	$<7.5$	$<2.9$
S140 IRS 1	$<2.4$	$<0.077$	$<4.9$	$<7.7$
AFGL 989	24	0.74	35	$23 \pm 2.5$
Mon R2 IRS 3	$\sim 0$	$\sim 0$	$\sim 0$	$<4.9$

<sup>a</sup>Upper limits are based on the marginally poorer 3-component fit.

S140 IRS 1, AFGL 989, and Mon R2 IRS 3 were 0.01, 0.02, 0.03, and 0.01, respectively.

My  $\tau_6(\text{H}_2\text{O})$  values are similar to  $\tau_{6,0}(B)$ . Small discrepancies ( $-0.04$  to  $+0.03$ ) are suggestive of differences in the continua adopted, rather than the H<sub>2</sub>O temperature, because (temperature-) broadened profiles tend to reduce fitted optical depths.

Mass and molecular densities derived from my fits are in Table 3 with the molecular densities,  $m_3$ , derived by Gibb et al. (2004) from the 3.0- $\mu\text{m}$  feature of the MW sources. The 6.0–7.0- $\mu\text{m}$  values are  $\pm 20$  per cent of  $m_3$ . The molecular H<sub>2</sub>O density in the PKS 1830–211 absorber is  $2.7 \times 10^{18}$  molecules  $\text{cm}^{-2}$ . This is 110 per cent of the, molecular density towards Elias 16, and 120–170 per cent the molecular density in the MW YSOs.

### 6.2 CH<sub>3</sub>OH

Fitted CH<sub>3</sub>OH optical depths,  $\tau_6(\text{CH}_3\text{OH})$ , are compared with values,  $\tau_{6,85}(P)$ , predicted from 3.54  $\mu\text{m}$  data in Table 2 and defined below. Mass- and molecular-densities are in Table 4.

I used the three component fits to obtain an upper limits for the column densities in cases where three-component fits included a very small, but finite, CH<sub>3</sub>OH component but were statistically marginally poorer than two-component H<sub>2</sub>O and carbonate fits. These sources were Elias 16– $\tau_6(\text{CH}_3\text{OH}) = 0.017$  with  $\chi^2_{\nu} = 3.54$  versus 3.52 and S140 IRS 1  $\tau_6(\text{CH}_3\text{OH}) = 0.0073$  with  $\chi^2_{\nu} = 13.055$  versus 13.052.

#### 6.2.1 Calibration of 6.85 $\mu\text{m}$ CH<sub>3</sub>OH abundance

$\tau_{6,85}(P)$  is derived from the 3.54- to 3.0- $\mu\text{m}$  CH<sub>3</sub>OH- to H<sub>2</sub>O-molecular ratios,  $R_3(\text{CH}_3\text{OH})$ , obtained by Gibb et al. (2004), and reproduced in Table 4. Since the integrated band strengths of the 6.85- and 6.0- $\mu\text{m}$  CH<sub>3</sub>OH- and H<sub>2</sub>O- bands in Table 1 are similar,

$$\tau_{6,85}(P) \approx 1.25 \times \tau_6(\text{H}_2\text{O}) \times \frac{R_3(\text{CH}_3\text{OH})}{100}, \quad (6)$$

where the factor of 1.25 is obtained from the ratio of the fwhms of the pseudo-Gaussian 6.0- and 6.85- $\mu\text{m}$  bands.

Fitted  $\text{CH}_3\text{OH}$  optical depths in S140 IRS 1 ( $<0.0073$ ) and Mon R2 IRS 3 ( $<10^{-6}$ ) are consistent with predicted values ( $<0.01$ ); Towards Elias 16 the  $\tau_6(\text{CH}_3\text{OH})$  upper limit is 2.8 times the predicted value ( $<0.006$ ). Fits to AFGL 989 in which carbonates were absent, were 1.5 times the predicted value (0.046).

### 6.2.2 Sources of uncertainty in particle abundance estimates

Even if the optical paths of light transmitted at different wavelengths are identical (unlikely within a YSO disc or envelope), abundance discrepancies between estimates from different spectral features occur due to: (i) the choice of continuum. For example, my polynomial fit to the Elias 16 spectrum adds curvature, which explains the larger ice optical depths. (ii) the effect of very large column densities of small grains or a smaller number of large grains, which cause the band to saturate. The effect occurs in thin film laboratory samples (see Hofmeister et al. 2003; Bowey et al. 2020; Bowey & Hofmeister 2022) because strong bands become rounded and eventually opaque as the film thickness (aka column density) is increased. Hence, if the column density is high, weak peaks will give a truer (and larger) estimate of the total abundance.

### 6.3 $\text{CH}_3\text{OH}$ ice in the PKS 1830–211 galaxy-absorber

Due to the consistency of the determined 6.85 and 3.54  $\mu\text{m}$   $\text{CH}_3\text{OH}$  abundances, I conclude that the high  $\text{CH}_3\text{OH}$  optical depth ( $\tau_6(\text{CH}_3\text{OH})=0.11$ ) towards PKS 1830–211 is supported by the MW fits. The galaxy-absorber  $R_6(\text{CH}_3\text{OH})$  ratio of 41 per cent is similar to the value for AFGL 989 (35 per cent), but much higher than ratios in the quiescent molecular cloud towards Elias 16 ( $<7.5$  per cent) and the other YSOs (S140 IRS 1 (4.9 per cent) and Mon-R2 IRS 3 ( $\sim 0$ )). It is 3–8 times the  $R_3(\text{CH}_3\text{OH})$  value in MW isolated starless molecular clouds and 14 times the value in giant molecular clouds (5 per cent–12 per cent; Boogert et al. 2011; Goto et al. 2021), while the ratio in the giant Lupus and Taurus molecular clouds and IC 5146 is ( $<3$  per cent; Boogert et al. 2013; Chiar et al. 2011). The high ratio is consistent with the detection of gas-phase  $\text{CH}_3\text{OH}$  absorption in the submm lensed SW image because observations of massive star-formation regions combined with gas-grain chemical models (e.g. van der Tak, van Dishoeck & Caselli 2000) indicate  $\text{CH}_3\text{OH}$  forms on  $\lesssim 15$  K grain surfaces in molecular clouds when HI densities  $\lesssim 10^4 \text{cm}^{-3}$  with  $\text{CO}_2$  forming preferentially at higher densities. Evaporation occurs at  $\sim 100$  K as a consequence of star-formation. Muller et al. (2020) obtain a total methanol gas column density  $\sim 5 \times 10^{14}$  molecule  $\text{cm}^{-2}$  in the SW component. Assuming the SW lensed submm component, is responsible for the infrared absorption feature, the  $\text{CH}_3\text{OH}$  solid-to-gas ratio along this line of sight is  $\sim 2000$ .

### 6.4 Carbonates

Carbonate column densities are listed in Table 5. Calcite ( $\text{CaCO}_3$ ) grains, with a peak wavelength of 6.97  $\mu\text{m}$  and grain size of 0.11  $\mu\text{m}$ , provided the best fit to PKS 1830–211. MW YSOs S140 IRS1 and Mon R2 IRS 3 were matched with smaller ( $\sim 0.04 \mu\text{m}$ -sized) calcite grains. Elias 16 was fitted with dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), with a peak wavelength of 6.87  $\mu\text{m}$  and a grain size of 0.15  $\mu\text{m}$ . AFGL 989 models do not contain carbonate dust.

The carbonate-to- $\text{H}_2\text{O}$  molecular-density ratio ( $R_6(-\text{CO}_3)$ ) towards PKS 1830–211 is 35 per cent of the value towards Elias 16 and

**Table 5.** Mass, grain, and molecular densities of carbonates. AFGL 989 models do not contain carbonate dust.  $R_6(-\text{CO}_3)$  is the  $-\text{CO}_3/\text{H}_2\text{O}$  molecular ratio obtained from the 6- to 7- $\mu\text{m}$  spectra. Uncertainties in  $\Sigma$ ,  $n_g$ , and  $R_6(-\text{CO}_3)$  are  $<20$  per cent,  $<20$  per cent,  $<20$  per cent, and  $<30$  per cent, respectively (see Section 5.2.3).

Object	Carbonate	$\Sigma$ $10^{-6}$ $\text{gcm}^{-2}$	$n_g$ $10^6$ $\text{cm}^{-2}$	$m$ $10^{15}$ $\text{cm}^{-2}$	$R_6(-\text{CO}_3)$ Per cent
PKS 1830–211	$\text{CaCO}_3$	1.3	350	2.5	0.091
Elias 16	$\text{CaMg}(\text{CO}_3)_2$	3.0	310	6.3	0.26
S140 IRS 1	n $\text{CaCO}_3$	1.6	9300	3.1	0.19
Mon R2 IRS 3	n $\text{CaCO}_3$	4.2	24000	8.1	0.37

**Table 6.** Mass, grain, and molecular densities of bSiC in Mon R2 IRS 3.  $R_6(\text{SiC})$  is the  $\text{SiC}/\text{H}_2\text{O}$  molecular ratio obtained from the 6- to 7- $\mu\text{m}$  spectra. Uncertainties in  $\Sigma$ ,  $n_g$ ,  $m$ , and  $R_6(\text{SiC})$  are  $<20$  per cent,  $<20$  per cent,  $<20$  per cent, and  $<30$  per cent, respectively (see Section 5.2.3).

$\Sigma$ $10^{-6}$ $\text{gcm}^{-2}$	$n_g$ $10^6$ $\text{cm}^{-2}$	$m$ $10^{18}$ $\text{cm}^{-2}$	$R_6(\text{SiC})$ Per cent
300	0.0089 <sup>a</sup>	1.5	68

<sup>a</sup>Grain number densities are not directly comparable with those for Sakurai’s Object because the samples were different; the grain volume ratio is  $\sim 1.95$ .

48 per cent of the value in S140 IRS 1, and  $\sim 25$  per cent the ratio towards Mon R2 IRS 3. The mass-densities towards PKS 1830–211, Elias 16, and S140 IRS 1 are similar to those in the circumstellar environment of Sakurai’s Object ( $1.2$ – $2.8$ )  $\times 10^{-6}$   $\text{gcm}^{-2}$  between 2005 April and 2008 October (Bowey & Hofmeister 2022). The carbonate mass-density towards Mon R2 IRS 3 is 1.5 times the peak value in Sakurai’s Object.

### 6.5 SiC in Mon R2 IRS 3

bSiC abundances for Mon R2 IRS 3 are given in Table 6. Due to the 20- $\mu\text{m}$  size of these grains, the molecular and mass-densities are substantial in comparison to the measured  $\text{H}_2\text{O}$  abundances:  $R_6(\text{SiC})\sim 68$  per cent; the mass density is  $300 \times 10^{-6}$   $\text{gcm}^{-2}$ . For comparison, bSiC mass densities within Sakurai’s Object were  $54$ – $167 \times 10^{-6}$   $\text{gcm}^{-2}$ , or 0.18–0.6 times the inferred value towards Mon R2 IRS 3.

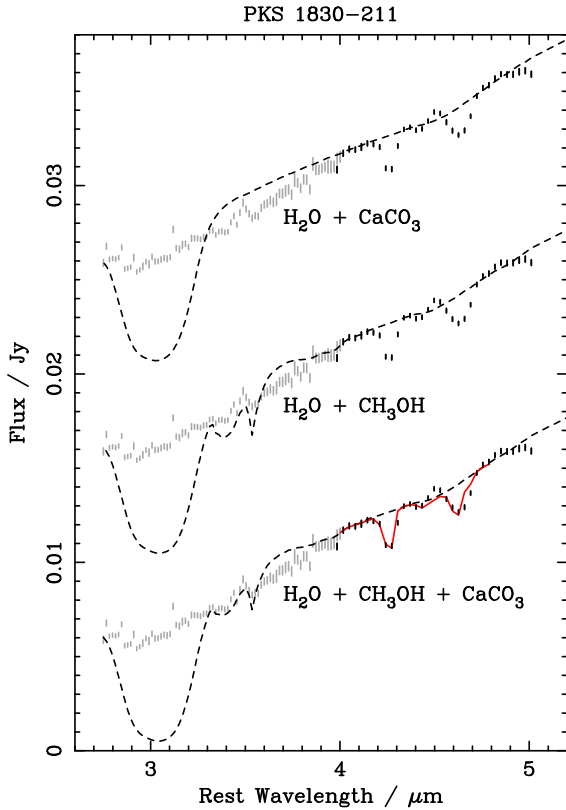
## 7 ICES IN THE 2.5–5- $\mu\text{m}$ PKS 1830–211 SPECTRUM

Fig. 3 shows the rest-frame 2–5  $\mu\text{m}$  flux spectrum of the PKS 1830–211 galaxy-absorber with laboratory spectra scaled to optical depths obtained with the 6–7- $\mu\text{m}$  fits and a modified power-law index,  $\beta$  (defined, below). I attribute the peculiar absence of a 3.0- $\mu\text{m}$   $\text{H}_2\text{O}$ -ice band to flux contamination from an object of unknown type in the SL 2 slit (see Appendix A). Despite the absence of  $\text{H}_2\text{O}$ , the PKS 1830–211 spectrum contains structures similar in shape and strength to  $\text{CH}_3\text{OH}$  bands in the extrapolated 3-component ‘continuum’.  $\text{CH}_3\text{OH}$  bands in the carbonate-free  $\text{CH}_3\text{OH}$ -rich model are too strong.

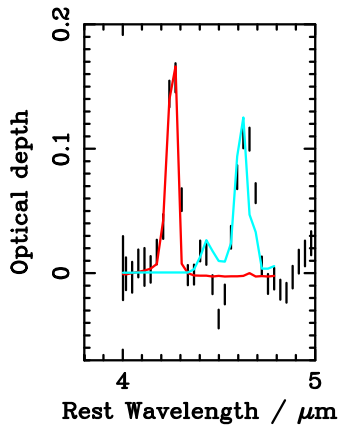
There are clear absorption features near 4.3 and 4.6  $\mu\text{m}$ . I added two extra absorbers and selected the power-law index,  $\beta$  to produce the lowest  $\chi^2_\nu$  values in this wavelength range:

$$F_{\nu,4-4.8\mu\text{m}} = b_o \lambda^\beta \exp\left(-\sum_{i=1}^5 c_i \tau_i(\lambda)\right). \quad (7)$$





**Figure 3.** Fits (solid red) to absorption features in the 4–4.8- $\mu\text{m}$  SL 1 spectrum of PKS 1830–211 (black error bars). Dashed curves include extrapolated absorption components derived from the 5–8- $\mu\text{m}$  fits. SL 2 data (grey error bars) for wavelengths below 4  $\mu\text{m}$  were not fitted. y-axis offsets from the bottom are, 0.00, 0.01, and 0.02, respectively.



**Figure 4.** 4–5  $\mu\text{m}$  optical depth spectrum of PKS 1830–211 (error bars), with fitted components of CO:10CO<sub>2</sub> (red) and OCN<sup>−</sup> in irradiated formamide (cyan). The spectrum was derived with equation (4) using the three-component H<sub>2</sub>O, CH<sub>3</sub>OH, and calcite ‘continuum’ in Fig. 3.

Parameters  $c_1$ – $c_3$  are fixed to values for H<sub>2</sub>O, CH<sub>3</sub>OH, and CaCO<sub>3</sub> obtained from the 5–8- $\mu\text{m}$  fits. The scale factor,  $b_o$  and  $c_4$  and  $c_5$  are fitted.

Optical depth spectra of the observations and fits, obtained with the 4–4.8- $\mu\text{m}$  continuum by setting  $c_4$  and  $c_5$  to zero, are in Fig. 4. The best-matching laboratory spectra (Table 1) were the 4.27- $\mu\text{m}$  CO<sub>2</sub> band in a CO:10 CO<sub>2</sub> mixture ( $\tau = 0.17$ ) and the 4.61- $\mu\text{m}$

OCN<sup>−</sup> band ( $\tau = 0.13$ ) with  $\beta = 1.54$  and  $\chi_v^2 = 7.1$ , which have been identified in MW molecular-clouds. The fwhms of these bands are  $\sim 0.03 \mu\text{m}$  and  $0.06 \mu\text{m}$  similar to the spacing between 2 and 4 wavelength-intervals, respectively; this resolution is insufficient to derive reliable abundance estimates.

## 8 SUMMARY OF RESULTS

Light from blazar PKS 1830–211 passes through a face-on lensing spiral galaxy at a redshift of  $z = 0.886$ . Observations of absorption features from IR to radio wavelengths indicate the optical path through the galaxy includes massive star-forming regions and molecular clouds similar to those in the MW. MW sightlines included for comparison with the PKS 1830–211 spectrum are the quiescent molecular-cloud towards Taurus-Elias 16, and YSOs in massive star-forming regions (S140 IRS 1, AFGL 989, and Mon R2 IRS 3).

### 8.1 Carbonates and ices in star-forming regions

I have: (i) associated the 6.9- $\mu\text{m}$  band with a combinations of CH<sub>3</sub>OH ice and/or carbonate dust; (ii) deciphered the carriers of solid-state absorption features near 4.3, 4.6, 6.0, and 6.9  $\mu\text{m}$  in the PKS 1830–211 absorber-rest-frame and compared the results with those for the MW sightlines; (iii) shown CH<sub>3</sub>OH:H<sub>2</sub>O ratios derived in my 6–8  $\mu\text{m}$  models are comparable to those obtained at 3–4  $\mu\text{m}$  if the observation has unsaturated 3–4 and 6–8  $\mu\text{m}$  bands.

### 8.2 H<sub>2</sub>O, CO<sub>2</sub>, and OCN<sup>−</sup>

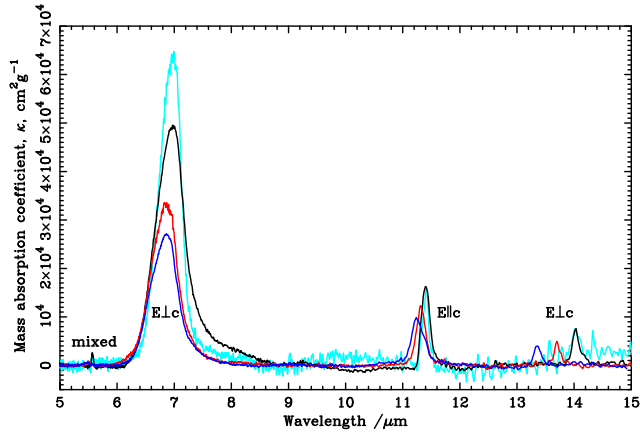
Due to the constraint on the spectral characteristics, the range of MW H<sub>2</sub>O column densities was limited to  $1.6$ – $2.4 \times 10^{18}$  molecules  $\text{cm}^{-2}$ . 6.0  $\mu\text{m}$  estimates of H<sub>2</sub>O column density are within  $\pm 20$  per cent of the 3.0- $\mu\text{m}$  values. The H<sub>2</sub>O column density in the PKS 1830–211 galaxy-absorber is  $2.7 \times 10^{18}$  molecules  $\text{cm}^{-2}$ .

NIR features in the PKS 1830–211 absorber were matched with the 4.27- $\mu\text{m}$  CO<sub>2</sub> peak in a CO:10 CO<sub>2</sub> mixture, a 4.61- $\mu\text{m}$  OCN<sup>−</sup> peak but the spectral resolution is too low to obtain estimates of their abundances.

### 8.3 CH<sub>3</sub>OH to H<sub>2</sub>O ratios

The PKS 1830–211 galaxy-absorber and MW YSO AFGL 989, have a substantial CH<sub>3</sub>OH:H<sub>2</sub>O molecular ratios of 41 per cent and 35 per cent, respectively. For the MW sources Elias 16, and YSOs S140 IRS 1 and Mon R2 IRS 3, the respective ratios are  $< 7.5$  per cent,  $< 4.9$  per cent, and  $\sim 0$ .

Whilst the MW sources have ratios within the range expected, the PKS 1830–211 galaxy-absorber has an extremely high CH<sub>3</sub>OH:H<sub>2</sub>O ratio: typical 3–4  $\mu\text{m}$  ratios for isolated starless molecular-clouds within the MW are [5 per cent–12 per cent; Boogert et al. 2011; Goto et al. 2021], with values  $< 3$  per cent within the giant Lupus and Taurus molecular clouds and IC 5146 is (Boogert et al. 2013; Chiar et al. 2011)]. These substantial quantities of CH<sub>3</sub>OH ice appear consistent with the submm detection of gas-phase CH<sub>3</sub>OH absorption in the SW lensed component observed by Muller et al. (2021). Assuming the SW lensed submm component, is responsible for the infrared absorption feature, the CH<sub>3</sub>OH solid-to-gas ratio along this line of sight is  $\sim 2000$ .



**Figure 5.** Wavelength comparison of 0.11- $\mu\text{m}$  calcite (black),  $\sim 0.04$ - $\mu\text{m}$  calcite (cyan), 0.15- $\mu\text{m}$  dolomite (red), and 0.15- $\mu\text{m}$  magnesite (blue) in data from Bowey & Hofmeister (2022).

#### 8.4 Carbonates in MW molecular-clouds, YSOs, and the PKS 1830–211 galaxy absorber

With the exception of AFGL 989, fits to the 6.9- $\mu\text{m}$  band of every sightline required a contribution from carbonate dust. The best fit to PKS 1830–211 was obtained with calcite ( $\text{CaCO}_3$ ) grains, with a peak wavelength of 6.97  $\mu\text{m}$  and grain size of 0.11  $\mu\text{m}$ . S140 IRS1 and Mon R2 IRS 3 were matched with smaller (0.04  $\mu\text{m}$ -sized) calcite grains. Elias 16 was fitted with dolomite  $\text{CaMg}(\text{CO}_3)_2$ , with a peak wavelength of 6.87  $\mu\text{m}$  and a grain size of 0.15  $\mu\text{m}$ . The carbonate-to- $\text{H}_2\text{O}$  molecular-density ratio towards PKS 1830–211 is 39 per cent of the value towards Elias 16, 50 per cent of the value towards S140 IRS 1, and  $\sim 24$  per cent of the ratio towards Mon R2 IRS 3.

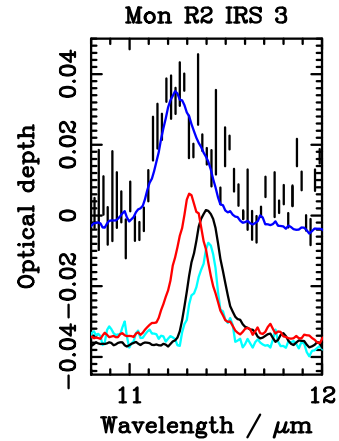
#### 8.5 20 $\mu\text{m}$ -sized SiC grains in Mon R2 IRS 3?

The best models of Mon R2 IRS 3 included large (20  $\mu\text{m}$ -sized) SiC grains to fit a plateau at 6.4  $\mu\text{m}$ . Modelled molecular densities of 20  $\mu\text{m}$ -sized SiC grains in Mon R2 IRS 3 are 68 per cent of the measured  $\text{H}_2\text{O}$  abundances; the mass density is  $300 \times 10^{-6} \text{ g cm}^{-2}$ . For comparison, bSiC mass densities within Sakurai’s Object were  $54\text{--}167 \times 10^{-6} \text{ g cm}^{-2}$ , or 0.18–0.6 times the inferred value towards Mon R2 IRS 3.

### 9 DISCUSSION: IMPACT OF ASTRONOMICAL CARBONATE DUST

#### 9.1 Additional spectral features

Since carbonates contribute to the astronomical 6.9- $\mu\text{m}$  band weaker bands near 5.6, 11.3, and 13.2–14  $\mu\text{m}$  might also be detected (see Fig. 5). However, due to the very large difference in band strength, the concurrence of both sets of features in a single sightline is likely to be infrequent. This extreme difference in band strength was the reason a very small carbonate fraction ( $< 0.1$  per cent) was missed by Bowey & Hofmeister (2005) in their melilite overtones study. Grains with strong 5.6, 11.3, and 13.2–14  $\mu\text{m}$  peaks are very likely to be opaque at 6.9  $\mu\text{m}$ . Under controlled laboratory conditions this property of particulate samples is a useful method for band-strength calibration, provided it is possible to measure the thickness of extremely thin films. After appropriate calibration, this property might become useful in the interpretation of astronomical data.



**Figure 6.** Optical depth spectrum derived from the 11.2- $\mu\text{m}$  excess absorption in Mon R2 IRS 3 (error bars) identified by Bregman et al. (2000), which is well-matched by the 0.15- $\mu\text{m}$  thick magnesite optical depth spectrum ( $\text{MgCO}_3$ ; blue). 0.15  $\mu\text{m}$  dolomite (red), and 0.11  $\mu\text{m}$  and  $\sim 0.04$   $\mu\text{m}$  calcite spectra (black and cyan, respectively) are offset in the  $y$ -axis by  $-0.03$  for clarity.

The effect of cation substitution of  $\text{Ca}^{2+}$  with  $\text{Mg}^{2+}$  relatively difficult to discern within the broad 6.9- $\mu\text{m}$  band, but is much more visible in the narrow longer wavelength-bands. Bregman, Hayward & Sloan (2000) identified excess absorption 11.3  $\mu\text{m}$  in the radioed spectrum of Mon R2 IRS 3 and identified it with PAHs due to its resemblance to emission bands in planetary nebulae, HII regions, and the ISM. I took the natural logarithm of their ratio to obtain the optical depth spectrum in Fig. 6; it closely resembles the 11.25- $\mu\text{m}$  band in magnesite. Scaling the laboratory spectrum by eye, gives a match to the 11.3- $\mu\text{m}$  optical depth, when  $\tau_{6.9} = 0.11$  and mass- and molecular-densities of  $4.1 \times 10^{-6} \text{ g cm}^{-2}$  and  $8.6 \times 10^{15}$ , respectively. These values are  $\pm 5$  per cent of the densities evaluated using  $n\text{CaCO}_3$  in the 6.9- $\mu\text{m}$  fits of the Mon R2 IRS 3 ISO data, which is suggestive of a match to carbonates with the caveat that the  $\text{H}_2\text{O} + \text{MgCO}_3$  fit to the 5–8- $\mu\text{m}$  spectrum was poorer ( $\chi_v^2 \sim 70$ ) than that for  $\text{H}_2\text{O}$  and  $n\text{CaCO}_3$  ( $\chi_v^2 \sim 27$ ), or  $\text{CH}_3\text{OH}$  ( $\chi_v^2 \sim 42$ ) due to mis-matches in peak wavelength and feature width.

#### 9.2 Grain orientation and potential for polarization effects

Carbonate crystals are optically anisotropic: the 6.9- $\mu\text{m}$  and 13.2–14- $\mu\text{m}$  peaks are sensitive to  $E \perp c$  while the 11.3- $\mu\text{m}$  peak is responsive to  $E \parallel c$ . Hence, if the optical path is the same for the 6.9 and 11.3- $\mu\text{m}$  bands similar measurements of column density at both wavelengths is indicative of random crystal orientation. In astronomical observations, e.g. towards Mon R2 IRS 3, this might indicate an insensitivity of carbonate dust to the local magnetic field and an absence of Fe in these grains. Fe-bearing carbonates were not measured by Bowey & Hofmeister (2022) because the strongest peak in the Fe-carbonate end-member (siderite,  $\text{FeCO}_3$ ) is at  $\sim 7.03$   $\mu\text{m}$  and longward of the astronomical bands, but clearly more observations and laboratory data are needed to confirm these hypotheses.

Carbonate dust may also provide an explanation for a narrow polarization feature at 11.3  $\mu\text{m}$  in the N-band polarization spectrum of AFGL 2591, which was tentatively attributed to an annealed (i.e. crystalline) silicate component (Aitken et al. 1988) before the infrared-space-observatory revealed that crystalline silicates were reasonably common in circumstellar environments. The feature is known to be persistent over time due to the use of the source as a

position-angle standard ( $170^\circ$ ) (Smith et al. 2000). Carbonate orientation might be due to a physical association with flowing gas rather than magnetic fields because Fe-free carbonates would be insensitive to the magnetic field unless they contained magnetic inclusions.

### 9.3 Impact on chemical depletion measurements

Observations of abundances in the transitions between the diffuse medium (atomic hydrogen column density,  $N_H < 10^{21} \text{ cm}^{-2}$ ; visual extinction,  $A_V < 1$ ), the translucent medium ( $10^{21} < N_H < 10^{22} \text{ cm}^{-2}$ ;  $A_V$  3–5) and dark molecular clouds ( $N_H > 10^{22} \text{ cm}^{-2}$ ;  $A_V > 5$ ) established the concurrence of a rapid removal of 30 per cent–50 per cent of the available oxygen atoms from the interstellar gas as the density increases (Jenkins 2009; Whittet 2010). Jones & Ysard (2019) argued for the presence of (possibly undetectable) cyclic organic carbonates (COCs), or other carrier with a C:O ratio of 1:3, which minimizes the required carbon depletion into an O-rich phase, but could find no observational studies of COC spectroscopic signatures which might occur at 5.5–5.8 and 7.8–8.2  $\mu\text{m}$ .<sup>5</sup> The 6.9- $\mu\text{m}$  band of inorganic carbonates were mentioned in a footnote, presumably because they had been ruled out of contention by Keane et al. (2001) or due to the absence of laboratory data for them. My analysis of the 6.9- $\mu\text{m}$  feature in molecular cloud environments and identification of carbonate dust seems to seem to fulfill the abundance constraints, especially since the authors allowed a minor depletion (< 20 per cent) of other metals including Mg on to the grains in these transition regions.

## 10 CONCLUSION

Solid-state infrared absorption features within dense molecular clouds are useful tracers of the physical and chemical conditions within the MW and other galaxies because the dust is a repository of information about stellar evolution and metallicity, and is the source material for new planets. IR spectra are used to determine the mineralogy of oxygen-rich refractory materials because these materials do not have characteristic spectral features in radio and submm bands and their optical bands are obscured by the high visual extinction and stronger atomic and molecular lines. The analysis has required data from several laboratories, which specialize in chemical synthesis, infrared spectroscopy of ices and organics, and the Earth and planetary sciences, as well as reinterpretation of astronomical observations with simple empirical models ( $\chi^2$ -fitting).

I have interpreted spectral features near 6.0 and 6.9  $\mu\text{m}$ , which appear in molecular clouds and YSOs within the MW and the  $z = 0.886$  galaxy absorber in the line of sight to PKS 1830–211. To determine the proportions of three-component models, four MW sources were selected using two criteria: (i) the peaks must be curved (not flattened) because distorted spectral shapes indicate grain densities or grain sizes, which are too large for light transmission, and (ii) there must be published  $\text{H}_2\text{O}$ – $\text{CH}_3\text{OH}$  ice ratios derived from 3.0 to 4.0- $\mu\text{m}$  observations to calibrate the 5–8- $\mu\text{m}$  fits. These constraints limit the range of explored MW  $\text{H}_2\text{O}$ -ice column densities to  $1.6$ – $2.4 \times 10^{18} \text{ molecules cm}^{-2}$ ; the  $\text{H}_2\text{O}$  ice column density in the galaxy absorber is  $2.7 \times 10^{18} \text{ molecules cm}^{-2}$  with an uncertainty of  $\pm 10$  per cent to  $\pm 20$  per cent.

Uncertainties in molecular ratios are estimated to be  $\sim \pm 30$  per cent of the quoted values. Evaluations of  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  ratio

<sup>5</sup>These bands do not appear in the 6–7- $\mu\text{m}$ -features in the circumstellar environment of Sakurai’s Object either, Bowey (2021).

in the ices from 6–8  $\mu\text{m}$  spectra of PKS 1830–211 and AFGL 989 are high at 41 per cent and 35 per cent, respectively. For Elias 16, S140 IRS 1, and Mon R2 IRS 3 the respective ratios are < 7.5 per cent, 4.9 per cent, and  $\sim 0$ .

Every sightline, except AFGL 989, required a carbonate component with grain-sizes in the 0.04–0.15- $\mu\text{m}$  range. PKS 1830–211, S140 IRS 1, and Mon R2 IRS 3 spectra were all matched with calcite ( $\text{CaCO}_3$ ). The molecular-cloud sightline towards Elias 16 was better matched with 0.15  $\mu\text{m}$ -sized dolomites ( $\text{CaMg}(\text{CO}_3)_2$ ). However, the carbonate fit to Elias 16 might be improved by using narrower laboratory spectra produced by small ( $\sim 0.04 \mu\text{m}$ -sized) and/or low-temperature ( $\sim 10 \text{ K}$ ) Mg-bearing carbonates which were unavailable. Unexplained excesses in the spectrum of Elias 16 at 6.3 and 6.75  $\mu\text{m}$  could potentially be associated with PAHs.

The Mon R2 IRS 3 spectrum may indicate a population of much larger (20  $\mu\text{m}$ -sized) SiC grains which contribute to a plateau near 6.4  $\mu\text{m}$ . Due to their large size, the SiC to  $\text{H}_2\text{O}$  molecular ratio is 68 per cent.

Observations with NIRSpec and MIRI on JWST and future far-infrared instruments could enhance our understanding of the dust mineralogy and improve the link between meteoritics, planetary science, and astrophysics of systems beyond the Solar system as far as high-redshift galaxies. IR spectra of solid-state features in statistically significant samples of high redshift galaxies could aid studies of star-formation rate, metallicity, and physical conditions at extended look-back times if there are suitable background sources. Laboratory experiments are required to determine mechanisms for carbonate formation in astronomical environments, and to reduce systematic uncertainties in the abundance of dust species in dense environments.

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## DATA AVAILABILITY

Carbonate data published by Bowey & Hofmeister (2022) are available from <https://zenodo.org/communities/mineralspectra/>. Other data underlying this article will be shared on reasonable request to the corresponding author.

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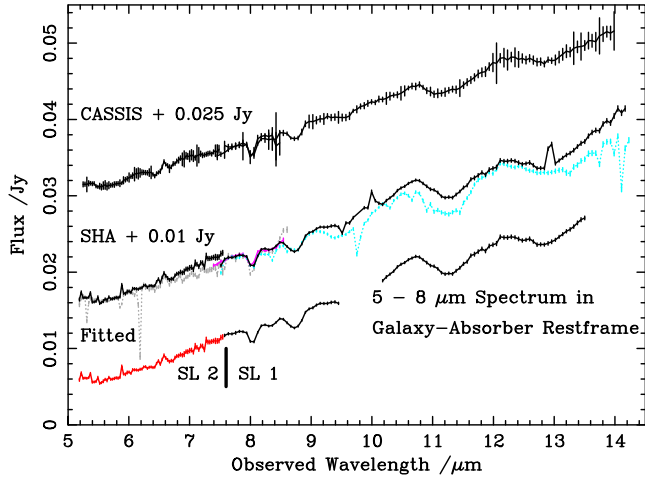
## APPENDIX A: PKS 1830–211 SPITZER OBSERVATIONS

PKS 1830–211 was observed with the IRS (Houck et al. 2004) on the Spitzer Space Telescope (Werner et al. 2004) on 2008 October 5 as part of programme 50783 (PI Kulkarni, V. P.); Astronomical Observation Request (AOR) 26905856 was originally reduced, published and interpreted by Aller et al. (2012).

Data from the Combined Atlas of Sources with Spitzer/IRS Spectra (CASSIS) Archive (Lebouteiller et al. 2011) from pipeline S18.18.0 and Level 2 data from the Spitzer Heritage Archive (SHA) retrieved in 2020 are compared in Fig. A1. Due to the redshift of the absorber ( $z = 0.886$ ), the 4–5- $\mu\text{m}$  and 6–7- $\mu\text{m}$  features of interest were observed by order SL 1 at wavelengths of 8–9  $\mu\text{m}$  and 10–14  $\mu\text{m}$ , respectively.

### A1 Data selection

IRS observations were obtained by nodding between two beams; SL 1 beams in the SHA spectrum in Fig. A1 are denoted **004** (dotted cyan) and **005** (solid black) in the SHA archive. If the source had been perfectly centred on the slit spectra from the two beams would be nearly identical. However, beyond 9  $\mu\text{m}$  the **004**-fluxes are lower and noisier than the **005** data indicating a loss of signal. Since the CASSIS



**Figure A1.** Selection of PKS 1830–211 Spitzer data for modelling. SL 1 and SL 2 data from the Spitzer Heritage Archive Data for beams **005** and **003** (black solid curves) were used to produce the observations modelled in the paper. **003** data which overlap SL 1 **005** (solid magenta), and the grey- and cyan-dotted curves for beams **002** and **004**, respectively, were discarded. The red portion of the ‘Fitted Data’ indicates the SL-2 spectrum contaminated by an extra source and the bar is at join between the SL 2 and SL 1 spectra.

pipeline combines the **004** and **005** beams, the long-wavelength part of the spectrum is 6 per cent lower than **005** and there is reduced contrast in the spectral features. Hence, I discarded **004** data except for using it to justify an interpolation across the 13- $\mu\text{m}$  bad-pixel spike in **005**. The result was trimmed to the 10.2–13.5- $\mu\text{m}$  range to exclude a spectral curvature due to an artefact known as the 14- $\mu\text{m}$  teardrop (see IRS 2011) and blue shifted to the rest-frame of the galaxy-absorber. Error bars are the root-mean-square uncertainties in **005**. The SL 2 spectrum from the **003** beam (red) were scaled by a factor of 0.92 to match SL 1 and trimmed at 7.6  $\mu\text{m}$ . Data from SL 2 **002** (grey) were discarded due to the larger number of bad points.

## A2 Contamination of the SL 2 slit by an unknown source

Order SL 2 observations covered 3.0–5  $\mu\text{m}$  bands in the absorber rest-frame. Unfortunately, these data are contaminated by the presence of an additional object of unknown type in the SL 2 slit. The source, at J2000 coordinates 18:33:40.444–21:04:35.24, is variously catalogued as a star and a galaxy; it increases in brightness from 17.4 mag in the B band to 14.372 mag at K in the NOMAD catalogue (Zacharias et al. 2005), but does not seem to affect spectral shapes in the (magenta) region of SL 2 which overlaps SL 1.

## APPENDIX B: CALCULATION OF COLUMN DENSITIES

### B1 Mass density and mass absorption coefficient

The mass column density,  $\Sigma_i$ , of each fitted component is,

$$\Sigma_i = \frac{c_i}{\kappa_{pk}}, \quad (\text{B1})$$

where  $\kappa_{pk}$  is the mass absorption coefficient of the appropriate laboratory spectrum at the peak wavelength of the absorber,  $\kappa_{pk}$

is given by,

$$\kappa_{pk} = \frac{10^4 T_{pk}}{\rho d}, \quad (\text{B2})$$

where  $T_{pk}$  is the optical depth of the sample of thickness  $d$  (in  $\mu\text{m}$ ) at wavelength  $\lambda_{pk}$ .

### B2 grain number density

The grain number density,  $n_g$  of each component is

$$n_g = \frac{\Sigma_i}{\rho d^3}, \quad (\text{B3})$$

where  $\rho d^3$ , is the mass of a single grain. This mass calculation includes three approximations: (i) that the mass densities of terrestrial materials are similar to those of interstellar materials, (ii) that the thickness of a powder film thin can be used as a representative grain size, and (iii) that the geometry is approximately cubic. Film thickness is assumed to be representative of the largest grain sizes in the sample because boundary reflections between grains smaller than the thickness of a compressed powder are minimized due to the absence of airspaces (or matrix material) with a significantly different refractive index. However, unlike a single-crystal measurement, the powder-measurement will represent the average opacity of a range of crystal orientations. Cubic grains are isotropic so the orientations should be random, but elongated grains will preferentially lie with their long axes perpendicular to the compression axis so that some orientations will be under-represented. Film thickness is difficult to measure in very small samples (e.g. the nCaCO<sub>3</sub> sample) and air spaces will be imperfectly removed. I think these approximations are no worse than the typical astrophysical assumptions of spheroidal or ellipsoidal shapes and the use of Mie theory in strong IR bands where the absorption component dominates the scattering. By definition crystals have specific angular shapes and are not spheroidal, e.g. some forms of SiC are cubic, carbonates are rhombohedral. Grinding mineral samples will knock corners off the crystals, but care is taken to minimize the effect on the IR bands (e.g. see Bowey et al. 2020). Overgrinding destroys the crystal structure and alters the infrared spectrum (e.g. Farmer 1958; Imai, et al. 2009).

### B3 Number of molecular absorbers and integrated band strength

The number of absorbers,  $m_i$ , is obtained from the integrated band strength,  $A_i$ , ( $\text{cm molecule}^{-1}$ ). The integrated band strength of a laboratory sample is given by

$$A_i = \frac{10^4 m_r}{Zd} \int_{\nu_1}^{\nu_2} T_i(\nu) d\nu, \quad (\text{B4})$$

where  $\nu_1$  and  $\nu_2$  are the frequencies at the edges of the band,  $m_r$  is the relative molecular mass of the sample and  $Z$  is Avogadro’s number. The optical depth,  $T(\nu)$ , at frequency  $\nu$ , has a sample-thickness  $d$  in  $\mu\text{m}$ . For a Gaussian peak the integral can be approximated by  $\Delta_\nu T_{pk}$  where,  $\Delta_\nu$  is the full-width-half-maximum in wavenumbers ( $\text{cm}^{-1}$ ) and  $T_{pk}$  is the peak optical depth. The number of molecular absorbers is given by

$$m_i = c_i \Delta_\nu / A_i. \quad (\text{B5})$$

It can also be shown, by ratioing equations (B2) and (B4), that for Gaussian peaks,

$$A_i \approx \frac{m_i \Delta v \rho}{Z} \kappa_{pk}. \quad (\text{B6})$$

and that  $m_i$  and  $\Sigma$  are equivalent, but non-identical measures of abundance due to the different calculation methods.

This paper has been typeset from a  $\text{\TeX}/\text{\LaTeX}$  file prepared by the author.