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DETECTION OF ABUNDANT CO_2 ICE IN THE QUIESCENT DARK CLOUD MEDIUM TOWARD ELIAS 16[1]

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ABSTRACT

We report the first detection of solid carbon dioxide (CO_2) in quiescent regions of a dark cloud in the solar neighborhood, a result that has important implications for models of ice formation and evolution in the interstellar medium. The K-type field star Elias 16 was previously known to display solid-state absorption features of H_2O and CO ices arising in the Taurus Dark Cloud. Our detection of the CO_2 feature at 4.27 μm in this line of sight implies a column density $N(CO_2) = 4.6^{+1.3}_{-0.6} \times 10^{17}$ cm^{-2}, equivalent to ~18% and 70% of the H_2O and CO column densities, respectively. Comparison with laboratory data indicates that (unlike CO) the CO_2 resides primarily in a polar (H_2O-rich) component of the ices. CO_2 is formed easily in the laboratory by the photolysis of ice mixtures containing CO, but the detection toward Elias 16 indicates that CO_2 formation can occur in dark clouds in the absence of a local embedded source of radiation. Possible alternative mechanisms for CO_2 production include grain surface reactions and energetic processing driven by the interstellar radiation field or cosmic rays.

Subject headings: dust, extinction — infrared: ISM: lines and bands — ISM: individual (Taurus Dark Cloud) — ISM: molecules

1. INTRODUCTION

Icy mantles are an important component of the interstellar dust in molecular clouds (see Chiar 1997 and Whittet 1997 for recent reviews). Observations show that, typically, some 10% of the elemental oxygen is locked up in solid H_2O, comparable to that locked up in gas-phase CO. Mantles are believed to form initially by catalysis reactions on the surfaces of cold (~15 K) grain cores in molecular clouds. These reactions involve abundant gas-phase species such as H, C, O, N, CO, O_2, and N_2 and may lead to a variety of simple molecular species in the solid phase, such as CO, CO_2, CH_4, NH_3, O_2, and N_2, as well as H_2O (Tielens & Hagen 1982). The existence of distinct polar and nonpolar ices, dominated by H_2O and CO, respectively, is indicated by the comparison of observations (Tielens et al. 1991; Chiar et al. 1995) with laboratory spectra (Sandford et al. 1988). Polar and nonpolar ices are thought to form under different physical conditions characterized by the presence or absence of atomic hydrogen in the gas. When these "primary" ices are subject to irradiation and warm up with the onset of local star formation, partial sublimation and separation of constituents may occur as a function of volatility (see Tielens & Whittet 1997), and photochemical reactions may generate additional species, including both CO_2 and a variety of complex organic compounds (e.g., d'Hendecourt et al. 1986; Sandford et al. 1988; Bernstein et al. 1995; Gerakines, Schutte, & Ehrenfreund 1996).

The fact that CO_2 is produced easily in the laboratory by ultraviolet (UV) irradiation of ices containing CO and H_2O (d'Hendecourt et al. 1986; Sandford et al. 1988) suggests that the CO_2 abundance in interstellar ices might measure the degree of UV photolysis. Observations are hindered by the fact that strong CO_2 absorption in the Earth's atmosphere precludes detection from ground-based or suborbital platforms. Studies of the CO_2 bending mode at 15 μm with the low-resolution spectrometer on board the *Infrared Astronomical Satellite* provided conflicting results (d'Hendecourt & Jourdain de Muizon 1989; Whittet & Walker 1991), and convincing detection of both stretching and bending modes had to await the launch of the *Infrared Space Observatory* (*ISO*) in 1995 (de Graauw et al. 1996b; d'Hendecourt et al. 1996; Gürtler et al. 1996). The abundance of solid CO_2 typically exceeds that of gas-phase CO_2 by factors of ~20–100 (van Dishoeck et al. 1996), in keeping with chemical models that predict low CO_2 production efficiency via gas-phase reactions (e.g., Herbst & Leung 1986). Solid CO_2 detections reported to date are almost exclusively toward "protostellar" objects embedded in molecular clouds, in which the ices may be at least partially processed by radiation from the source itself, consistent with the hypothesis that CO_2 is the product of photolysis. Confirmation would require the *nondetection* of CO_2 in a line of sight remote from sources of UV radiation.

The Galactic center source Sgr A* might be considered a test case. It shows solid-state absorption features arising in both dense and diffuse clouds along the line of sight (e.g., Lutz et al. 1996). The detection of solid CO_2 toward Sgr A* (Lutz et al. 1996; de Graauw et al. 1996b) hints that the presence of an embedded source may not be a prerequisite for CO_2 formation; however, interpretation is complicated because multiple clouds along the line of sight contribute to the observed solid-state features, and the environment of the CO_2 is thus unknown. Since much of the total visual extinction ($A_V \approx 30$ mag) in the line of sight is thought to arise in diffuse clouds (Sandford et al. 1991) that lack solid CO_2 (Whittet et al. 1997), the denser CO_2 clouds must have modest extinctions ($A_V \lesssim 10$ mag) and

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may be translucent, in which case they do not provide a good diagnostic of CO_2 as a tracer of photolysis.

Field stars located serendipitously behind dense molecular material provide an invaluable resource for probing the properties of icy mantles in quiescent regions of molecular clouds in the solar neighborhood, since these lines of sight are generally remote from embedded stars that might affect the local environment (Whittet, Longmore, & McFadzean 1985; Whittet et al. 1983, 1988, 1989; Kerr, Adamson, & Whittet 1993; Smith, Sellgren, & Brooke 1993; Chiar et al. 1994, 1995). Elias 16, in particular, has been adopted as a standard for the quiescent cloud medium. This source, a K1 III star hidden by some 21 mag of visual extinction, was first detected and classified in a near-infrared survey of the Taurus Dark Cloud by Elias (1978). We know with some confidence that the grain mantles toward Elias 16 have not been thermally or radiatively processed by an embedded source: this is indicated by (i) the shape of the 3.0 μm H_2O ice feature, consistent with a lack of annealing (Smith, Sellgren, & Tokunaga 1989); (ii) the presence of abundant solid CO in nonpolar form (Chiar et al. 1995), requiring grain temperatures below 20 K; and (iii) the absence of 4.62 μm absorption, associated with CN-bearing molecules thought to be produced by irradiation of primary ices containing N (Tegler et al. 1995). Elias 16 is thus the ideal test case for the link between CO_2 production and photolysis. This Letter reports the unequivocal detection of abundant CO_2 in ice mantles toward Elias 16, a result that challenges existing models of ice formation and evolution in molecular clouds.

2. OBSERVATIONS AND RESULTS

Elias 16 was observed by *ISO* with the Short Wavelength Spectrometer (SWS) on 1997 October 1, during revolution 686 of the mission. A difficulty encountered while preparing for these observations was the fact that the position of Elias 16 was previously not known with sufficient precision: since it is not possible to "peak-up" on a source prior to observation with the SWS, positions better than $\pm 2''$ are required to ensure maximum sensitivity, whereas the original position of Elias 16 (Elias 1978) has quoted errors of $\pm 5''$. The source lacks a counterpart on Palomar Observatory Sky Survey prints, precluding the determination of an optical position. Improved coordinates were determined from the mean of eight peak-up positions in the near-infrared, extracted from the data archive of the UK Infrared Telescope at Mauna Kea Observatory:

$$\text{R.A.} = 04^{\rm h}36^{\rm m}34^{\rm s}.4, \text{ decl.} = +26^\circ 05' 36'' \text{ (1950)}.$$

This position is considered accurate to $\pm 1''$; it agrees very well with the original Elias (1978) position, which we deduce to have conservative nominal errors.

A detailed description of the SWS is given by de Graauw et al. (1996a). The instrument was used to observe Elias 16 in mode S06 (selective grating scans), covering the wavelength ranges 2.6–3.5, 4.0–4.5, and 4.6–5.3 μm[10] at mean resolving power $\lambda/\Delta\lambda \approx 1800$ μm. The detectors used by the SWS are InSb from 2.6 to 4.05 μm (band 1) and Si:Ga from 4.05 to 5.3 μm (band 2A). The total on-target time was 8894 s.

The final spectrum is plotted in Figure 1 and compared with the ground-based observations from Whittet et al. (1983, 1985).

[10] Data were also obtained serendipitously in the 14–19 μm region but are of poor quality because of the faintness of the object at these wavelengths; regrettably, this precludes the detection of the CO_2 bending mode near 15 μm.

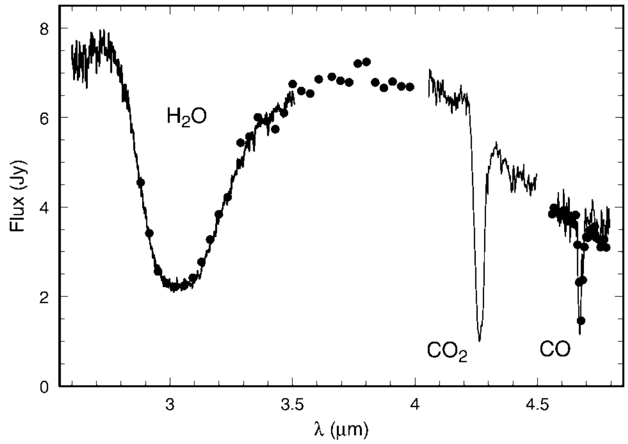

FIG. 1.—Superposition of the SWS and ground-based spectra of Elias 16 in the 2.6–4.8 μm region: SWS data (*solid curves*); ground-based data (*filled circles*) in the 2.9–4.0 and 4.6–4.8 μm windows (Whittet et al. 1983, 1985). Features due to H_2O, CO_2, and CO ices are labeled.

The data were reduced using the SWS Interactive Analysis package (de Graauw et al. 1996a) and the latest version of the Relative Spectral Response Function (RSRF; Schaeidt et al. 1996). The observations consist of "up" and "down" scans, treated separately in the analysis and subsequently combined to give the final spectrum. Dark current variations can be especially troublesome for a source as faint as Elias 16 (relative to other SWS targets) in band 2A. Preliminary reductions suggested that too much dark current is subtracted by the standard product pipeline, resulting in low apparent flux levels in the band 2A continuum compared with those in band 1 and the ground-based data. A correction offset (0.35 μV s^{-1}) was applied before dividing by the RSRF and applying gain correction factors to give absolute flux calibration. Agreement between the final SWS spectrum and ground-based data is excellent in the 2.9–3.5 and 4.6–4.8 μm regions (Fig. 1), where they overlap, and the continuum level in the 4.0–4.5 μm region is consistent with an interpolation of the ground-based data to within 10%. Wavelength calibration (Valentijn et al. 1996) is good to ± 0.01%. We found generally satisfactory agreement between the up and down scans, appreciable deviations occurring only in the trough of the deep 4.27 μm feature (where the signal-to-noise ratio is lowest) and in the adjacent short-wavelength continuum at 4.18–4.22 μm. We deduce that the apparent shallow "emission wing" near 4.2 μm is probably not real. Other details of the spectrum, notably weak, narrow features at 4.295, 4.352, and 4.393 μm (see Fig. 2), do appear to be real. We identify the latter with photospheric CO lines in the K1 III star. The 4.393 μm line may be blended with a broader, shallower feature at 4.39 μm associated with the stretching resonance in solid $^{13}CO_2$.

3. ANALYSIS

The spectrum in Figure 1 contains a deep feature corresponding to the C=O stretching mode of solid CO_2 at 4.27 μm, in addition to previously known features at 3.0 and 4.67 μm identified with H_2O and CO. An optical depth plot centered on the 4.27 μm feature is shown in Figure 2, deduced by assuming that the 4.05–4.18 and 4.33–4.45 μm regions represent the continuum (ignoring narrow features). We estimate the peak optical depth in the CO_2 feature to be $\tau_{4.27} = 1.7^{+0.5}_{-0.2}$.

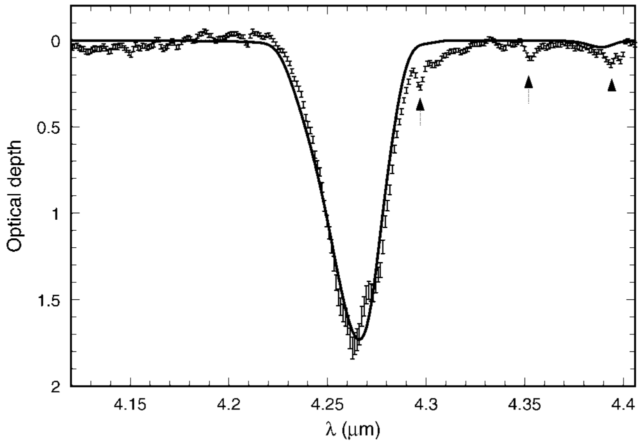

FIG. 2.—Optical depth plot (*points with error bars*) deduced from the SWS data in the region of the CO_2 stretching mode. Arrows indicate the positions of photospheric CO lines in the K1 III star. The solid curve is the best-fitting laboratory ice mixture (H_2O:CO_2:CO = 100:20:3 at 20 K).

The asymmetric uncertainty allows for possible systematic error in vertical placement as well as random noise.

Fits to the feature were attempted using data for various laboratory ice analogs containing CO_2 (Ehrenfreund et al. 1996, 1997) and a χ^2 minimization routine (Kerr et al. 1993; Chiar et al. 1995). Both polar and nonpolar ice mixtures containing CO_2 are included in the set of analog spectra, and the routine may select an individual mixture or any pair of polar and nonpolar mixtures. Grains following a continuous distribution of ellipsoids in the small particle limit are assumed in the calculations (see Ehrenfreund et al. 1997). The best fit to the profile (Fig. 2, *solid line*) is obtained with a single polar ice composed of H_2O:CO_2:CO (100:20:3) at 20 K. A number of similar mixtures give fits that are not substantially worse than that shown, but no combination with a significant nonpolar component is capable of giving a satisfactory fit. The conclusion that the feature is dominated by H_2O-rich polar ice at low temperature ($\lesssim$20 K) therefore appears to be robust. It is informative to compare our Figure 2 with Figure 1 of de Graauw et al. (1996b), which presents corresponding results for several embedded protostars. Satisfactory fits to the protostars require a substantial contribution from nonpolar ices: in the case of GL 2136, for example, a pronounced short-wavelength wing in the profile requires a polar (almost pure) CO_2 ice component that is absent in the spectrum of Elias 16.

The column density of solid CO_2 is calculated from the formula $N = \int \tau(\nu)d\nu/A$, where A is the band strength and the integration is carried out over the profile of the observed feature. We adopt $A = 7.6 \times 10^{-17}$ cm molecule^{-1}, a value only weakly dependent on the composition of the matrix containing the CO_2 (Gerakines et al. 1995). The resulting column density toward Elias 16 is $N(CO_2) = 4.6^{+1.3}_{-0.6} \times 10^{17}$ cm^{-2}. For comparison, the 3.0 and 4.67 μm features lead to column densities of 25 and 6.5 (in units of 10^{17} cm^{-2}) for H_2O and CO ices, respectively (Chiar et al. 1995). Hence, the CO_2 abundance is ~18% relative to the H_2O abundance, consistent with the composition of our best-fitting mixture. The abundance of CO_2 in polar mantles toward Elias 16 is similar to the *total* (polar + nonpolar) CO_2 abundance in protostars (de Graauw et al. 1996b; d'Hendecourt et al. 1996). Overall abundances of solid CO and CO_2 are comparable in Elias 16, but the CO resides predominantly in nonpolar ices (Chiar et al. 1995) and must therefore be segregated from the CO_2. The CO_2/CO ratio in the polar component alone is ~6.

4. DISCUSSION

In general, three processes are thought to play important roles in the formation and evolution of interstellar ice mantles: (i) grain surface reactions, (ii) energetic processing by UV photolysis or particle bombardment, and (iii) thermal processing that leads to sublimation, segregation, and/or annealing. Of these, processes (i) and (ii) are the most probable sources of CO_2 in grain mantles, with process (ii) highly favored in the literature on the topic over the past 10 years (§ 1). The detection of solid CO_2 toward young embedded stars supports energetic processing driven by the source itself (de Graauw et al. 1996b; d'Hendecourt et al. 1996), but this explanation is clearly inappropriate in the case of Elias 16. An important implication of our detection is that *the presence of* CO_2 *in grain mantles does not require the presence of an embedded source of luminosity*. CO_2 can evidently be produced in other ways, perhaps by grain surface reactions, or by energetic processing driven by penetrating UV photons or cosmic rays rather than any local embedded source.

Within the context of a surface chemistry model, accreted CO reacts with accreted O to form CO_2. This reaction possesses an activation energy barrier (Grim & d'Hendecourt 1986). However, at interstellar densities, grain surface chemistry is in the diffusion limit rather than in the reaction limit (Tielens & Charnley 1997), unlike the typical laboratory situation. The long timescales ($\simeq$1 day) between successive accretion events may allow the reaction to proceed; i.e., an accreted O atom has a day to react with any CO present before the accretion of another atom (O or H) with which it may react. Theoretical studies have shown that it may be possible to form appreciable quantities of CO_2 (~10%) in this way (Tielens & Hagen 1982).

We noted in § 3 that CO_2 toward Elias 16 resides in a polar (H_2O-rich) mantle, whereas CO resides almost entirely in a nonpolar (H_2O-poor) mantle. In the surface chemistry scheme, CO_2 must therefore form simultaneously with H_2O in an environment where a significant abundance of atomic H is present in the accreting gas. The nonpolar mantle is presumed to arise in a different (denser) environment with very low gas-phase atomic H and O abundances, leading to ices dominated by accreted CO and O_2 and containing very little CO_2 in the absence of an energy source. A problem faced by the surface chemistry model is the requirement to form CO_2 in a situation where hydrogenation is important (to form H_2O), yet CO is preferentially oxidized to CO_2 rather than hydrogenated to methanol.[11] The accretion of O, O_2, and CO in the presence of abundant atomic H ensures efficient H_2O formation (via hydrogenation of O_2 or O_3, where the latter is formed by the reaction of O with O_2), while CO must be inhibited from reaction with H to form CH_3OH. The barrier for the reaction of H with O_3 is indeed less than that for the reaction of H with CO (450 K compared with 1000 K; Tielens & Hagen 1982). However, the probability of the reaction that forms O_3 relative to the reaction that forms CO_2 is presently uncertain, and this precludes a detailed quantitative evaluation of the chemistry scheme. Further progress is dependent on new laboratory measurements.

[11] The abundance of methanol (CH_3OH) was found to be no more than 3% of the H_2O abundance in ices toward Elias 16 (Chiar, Adamson, & Whittet 1996).

Finally, we reconsider energetic processing as a possible source of CO_2 in *quiescent* clouds. In this scenario, CO_2 forms by the reaction of CO with atomic oxygen liberated by the dissociation of other molecules (primarily H_2O and O_2 in the polar and nonpolar mantles, respectively). It is important to note that CO_2 is also dissociated back to CO by energetic processing; thus, $CO \rightarrow CO_2$ conversion is never complete. The energy sources available are the external interstellar radiation field (ISRF; Mathis, Mezger, & Panagia 1983), attenuated by dust in the cloud itself, and cosmic rays; the latter may contribute to CO_2 production either directly, by ion bombardment of the ices (Palumbo & Strazzulla 1993), or indirectly, by generation of a UV radiation field through the liberation of energetic secondary electrons that excite H_2 (Prasad & Tarafdar 1983; Sternberg, Dalgarno, & Lepp 1987).

Information on some UV-photolyzed laboratory ices is available from the Leiden database.[12] As a basis for discussion, a polar laboratory mixture with an initial composition of H_2O:CO = 100:30 reaches a CO_2/CO ratio of 2.1 after exposure for 3 hr to ∼6 eV radiation of flux 10^{15} photons cm^{-2} s^{-1}. Equilibrium is not established at this stage, and a simple extrapolation suggests that the observed CO_2/CO ratio of ∼6 in polar ices toward Elias 16 (§ 3) might be reached in $\sim 3 \times 10^4$ s, i.e., after an exposure of $\sim 3 \times 10^{19}$ photons cm^{-2}. The cosmic-ray–induced UV flux in a molecular cloud amounts to $\sim 10^3$ photons cm^{-2} s^{-1} (Prasad & Tarafdar 1983): the time to reach an exposure of 10^{19} photons cm^{-2} is thus $\sim 10^9$ yr, which exceeds typical cloud lifetimes, and we conclude that photolysis via this route alone is probably insufficient to account for the abundance of CO_2 in polar ices. In contrast, the ISRF delivers $\sim 8 \times 10^7$ photons cm^{-2} s^{-1} to the cloud surface (Mathis et al. 1983), attenuated to $\sim 3 \times 10^4$ photons cm^{-2} s^{-1} at $A_V = 5$ mag (assuming $A_{UV}/A_V = 1.6$). Thus, the required exposure level is reached in $\sim 3 \times 10^7$ yr at $A_V = 5$, comparable to cloud lifetimes. This result is not necessarily in conflict with the observed total line-of-sight extinction ($A_V \approx 21$) to Elias 16, since at any location along the path, the extinction *to the cloud edge* is never more than half of this value; moreover, filamentary structure and clumpiness within the cloud will tend to enhance intracloud penetration of the ISRF relative to that in a homogeneous cloud.

The dearth of CO_2 in the nonpolar component of the ices seems consistent with production by photolysis that is driven by penetrating UV photons. Solid CO, the primary tracer of the nonpolar component, is detected only at optical depths equivalent to $A_V \gtrsim 5$ mag (Whittet et al. 1989; Chiar et al. 1995). Thus, the segregation of CO and CO_2 might arise naturally as a result of physical conditions, as a function of shielding from the external radiation field at different optical depths into the cloud. However, if CO_2 is indeed produced by UV photolysis, it is somewhat surprising that the 4.62 μm “XCN” feature, normally considered an indicator of energetic processing of grain mantles, is absent in Elias 16 (Tegler et al. 1995). Perhaps the preirradiation ices contain little NH_3, which may be an essential ingredient for the formation of XCN (Grim et al. 1989).

The detection of CO_2 in ice mantles toward Elias 16 clearly presents a challenge to existing models of ice formation and evolution in molecular clouds. Both surface chemistry and photolysis schemes for CO_2 production require further investigation to determine which is the most important source of CO_2 in quiescent regions of the interstellar medium.

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[12] See the ice analogs database at http://www.strw.leidenuniv.nl/∼lab/, which is maintained by the Laboratory Astrophysics group of Leiden Observatory.

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