CO Diffusion and Desorption Kinetics in CO₂ Ices

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Abstract
The diffusion of species in icy dust grain mantles is a fundamental process that shapes the chemistry of interstellar regions; yet, measurements of diffusion in interstellar ice analogs are scarce. Here we present measurements of CO diffusion into CO₂ ice at low temperatures (T = 11–23 K) using CO₂ longitudinal optical phonon modes to monitor the level of mixing of initially layered ices. We model the diffusion kinetics using Fick’s second law and find that the temperature-dependent diffusion coefficients are well fit by an Arrhenius equation, giving a diffusion barrier of 300 ± 40 K. The low barrier along with the diffusion kinetics through isotopically labeled layers suggest that CO diffuses through CO₂ along pore surfaces rather than through bulk diffusion. In complementary experiments, we measure the desorption energy of CO from CO₂ ices deposited at 11–50 K by temperature programmed desorption and find that the desorption barrier ranges from 1240 ± 90 K to 1410 ± 70 K depending on the CO₂ deposition temperature and resultant ice porosity. The measured CO–CO₂ desorption barriers demonstrate that CO binds equally well to CO₂ and H₂O ices when both are compact. The CO–CO₂ diffusion–desorption barrier ratio ranges from 0.21 to 0.24 dependent on the binding environment during diffusion. The diffusion–desorption ratio is consistent with the above hypothesis that the observed diffusion is a surface process and adds to previous experimental evidence on diffusion in water ice that suggests surface diffusion is important to the mobility of molecules within interstellar ices.

Key words: astrochemistry - ISM: molecules - methods: laboratory: solid state - molecular processes

1. Introduction
The motion of atoms and molecules on and within icy grain mantles is a fundamental process that regulates the chemical evolution in astrophysical environments. Diffusion of these species within the bulk ice or along icy surfaces influences the rates of desorption, chemistry, and ice reorganization. The interplay between the diffusion and reaction of radical fragments within the ice is a critical factor to explain the existence and abundances of several complex organic molecules in star-forming regions (Garrod et al. 2008; Garrod 2013a).

The diffusion of molecules in ice mantles is, however, poorly constrained. For most species and ice matrices, both the diffusion mechanism and the diffusion barrier are unknown. Astrochemical models therefore often adopt diffusion barriers that are fractions of the better constrained desorption barriers (Tielens & Hagen 1982; Katz et al. 1999; Ruffle & Herbst 2000; Cuppen et al. 2009; Garrod & Pauly 2011; Chang & Herbst 2012). Previous studies have explored diffusion–desorption barrier ratios between 0.3 and 0.8, and have demonstrated that the chemistry and ice composition is very sensitive to this parameter, e.g., Garrod & Pauly (2011); experimental constraints of diffusion and desorption for several major ice species are essential to better understand the temperature-dependent evolution of ices.

To obtain a complete understanding of diffusion in interstellar ices, data is required on diffusion in all common interstellar ice environments since molecular diffusion and desorption barriers are expected to depend strongly on the ice composition and morphology. Observations of ice absorption bands toward protostars indicate that the main ice constituents are H₂O, CO, and CO₂. Furthermore, the ice mantles are typically divided into H₂O-rich and CO-rich phases, both of which are mixed with CO₂, as well as a pure CO₂ ice phase in some lines of sight (D’Hendecourt & Jourdain 1989; Boogert et al. 2004; Pontoppidan et al. 2008). To understand the importance of diffusion in astrochemically relevant ices, experiments, and models are required for all three ice phases. The diffusion of molecules through H₂O ices has been the subject of several recent studies (Livingston et al. 2002; Mispaëlera et al. 2013; Karssemeijer et al. 2014; Lauck et al. 2015); however, diffusion in CO- and CO₂-rich ice environments has not been treated experimentally. Considering the differences between the ice matrices of CO- and CO₂-rich ices and the hydrogen-bonded, porous H₂O-rich ices, it is unclear whether the barriers and diffusion mechanisms in CO and CO₂ ices are similar to those found in the experiments with H₂O ices.

Molecular diffusion in astrochemical ice analogs has been studied predominantly by two methods: first, by diffusion–desorption experiments in which the decreasing IR absorbance of the diffusing species is recorded over time (Mispelaer et al. 2013; Karssemeijer et al. 2014); and, second, by spectroscopic techniques that exploit the fact that some IR bands are very sensitive to their molecular environment (Lauck et al. 2015). The latter effects have been shown to be strong when CO or CO₂ is mixed with hydrogen bonding molecules like water or methanol, producing blueshifts and broadening of the CO and CO₂ infrared modes (Sandford et al. 1988; Sandford & Allamandola 1990; Ehrenfreund et al. 1999; Palumbo & Baratta 2000; Öberg et al. 2009). However, the CO and CO₂ normal vibrational modes are not as sensitive to mixing with other, non-polar or weakly polar ice constituents, making diffusion measurements in these environments more challenging (Ehrenfreund et al. 1997).

Recently, we have shown that CO₂ longitudinal optical (LO) phonons can be used to sensitively probe ice mixing characteristics, including the amount of CO molecules that are mixed within CO₂ ices (Cooke et al. 2016). LO phonons arise in the CO₂ ice when the substrate is positioned at an
oblique angle to the infrared beam. We found that the CO₂ LO phonons redshift linearly with the ice mixing fraction, suggesting that they may be utilized to study diffusion dynamics in CO₂ ices.

Here, we present a study of CO diffusion into CO₂ ices by measuring changes in the CO₂ ν₃ LO phonons. We also measure the desorption energy of CO from CO₂ ices and present the diffusion–desorption energy barrier ratio. Section 2 presents the experimental setup, procedures, and spectral analyses used to study CO diffusion through CO₂ ices (Section 2.2) and desorption from CO₂ ices by temperature programmed desorption (TPD; Section 2.3). Section 3 presents the results of the diffusion experiments and their dependencies on ice temperature and thickness as well as the diffusion modeling strategies. In Section 4, we outline the results and analysis of the TPD experiments and extract the desorption barriers for CO from CO₂ ices. The results and their astrophysical implications are discussed in Section 5.

2. Experimental Setup and Procedures

2.1. Experimental Setup

The experiments were conducted using the setup described previously in Lauck et al. (2015). Briefly, the setup consists of an ultrahigh vacuum chamber with a base pressure of ~4 x 10⁻¹⁰ Torr at room temperature. The ices are deposited onto a CsI window cooled to as low as ~11 K using a closed-cycle helium cryostat. These ices are grown using a 4.8 mm gas doser that is positioned close to the CsI substrate at normal incidence. The temperature of the crystal is monitored and controlled using a LakeShore Model 335 controller with two calibrated silicon diode sensors that have an estimated accuracy of 2 K and a relative uncertainty of 0.1 K. Transmission infrared spectra of the ices are obtained using a Fourier transform infrared (FTIR) spectrometer (Bruker Vertex 70v) with a resolution of 1 cm⁻¹ and with 60 scans taken per spectra. Gas partial pressures were monitored during the diffusion experiments using a quadrupole mass spectrometer (Pfeiffer QMG 220M1). The desorbing molecules are monitored using a quadrupole mass spectrometer (Hiden IDP 300, model HAL 301 S/3) with a pinhole that is moved via a translational stage to ~0.5 inches away from the ice. The experiments were performed using CO₂ gas (99.99 atom % %¹²C, Sigma), %¹³CO₂ (99 atom % %¹³C, <3 atom % %¹⁸O, Sigma), and %¹²CO (99 atom % %¹³C, <5 atom % %¹⁸O, Sigma).

2.2. Diffusion Experimental Procedures

The diffusion experiments consist of initially layered CO:CO₂ ices whose mixing is monitored using infrared spectroscopy. In each of these experiments %¹³CO and CO₂ were deposited sequentially at 11 K at a rate of ~1 ML/minute to form the layered ice structures. The deposited ice thicknesses were determined using IR absorption spectroscopy and Equation (1), which relates the column density to the ice absorbance:

\[ N_i \text{ (cm}^{-2}\text{)} = \frac{\cos \theta \int \tau_i(\nu) \, d\nu}{A_i}, \]

where \( N_i \) is the column density of the ice species \( i \), \( \theta \) is the angle of incidence between the IR field vector and the ice surface normal (here 45°), \( \int \tau_i(\nu) \, d\nu \) is the integrated area of the chosen IR band (in optical depth), and \( A_i \) is the associated band strength adopted from Gerakines et al. (1995) and Bouilloud et al. (2015). The column densities, \( N_i \), were then converted to thicknesses in monolayers assuming 10⁻¹⁵ molecules/ML, or to nanometers using the mass densities of CO and CO₂ ice from Satorre et al. (2008) and Roux et al. (1980). Following deposition, the layered ices were kept at 11 K for ~10 minutes and were subsequently heated at 5 K minute⁻¹ to the desired temperature and maintained there for 2–4 hr. Time zero was taken when the isothermal temperature was reached. Infrared scans were taken every minute to monitor the ice composition.

The different families of experiments are illustrated in Figure 1. The target and actual layer thicknesses, as well as the temperature at which mixing was monitored are listed in Table 1. The fiducial experiment consisted of ices with target thicknesses of 30 ML %¹³CO followed by 30 ML of CO₂ and held at 20 K. We then carried out a series of experiments at different temperatures and with different ice thicknesses as well as experiments with isotopically labeled layers in order to extract the barrier for diffusion and elucidate the diffusion mechanism. We ran the temperature-dependent experiments with the 30 ML:30 ML composition from \( T = 18–23 \) K. Above 23 K non-negligible CO desorption occurs and the diffusion rate is so rapid that the fits have large uncertainties. Below 18 K, the diffusion rate is too slow to measure during our experimental timescale. In addition to the temperature-dependent experiments, we also ran diffusion experiments for different CO:CO₂ thickness configurations at 20 K using the thicknesses shown in Figure 1.

2.3. TPD Experimental Procedures

Temperature programmed desorption experiments are used to obtain the desorption energy of %¹³CO from CO₂ ice. Ices are grown using the same conditions described in Section 2.2. In each experiment, we first deposited ~50 ML of CO₂ followed by ≤1 ML of CO. The CO₂ ice substrates were deposited at 11, 21, 23, 25, 40, and 50 K to obtain different CO₂ ice structures; the ice deposited at the lowest temperature is expected to be the most porous. Following CO₂ deposition, the ice was cooled down to 11 K before depositing %¹³CO. The ices were heated at a constant rate of 1 K minute⁻¹. We subtract the mass background for %¹³CO and normalize the integrated QMS signal to the amount of CO deposited using the infrared spectra taken prior to heating.

3. Diffusion Analysis and Results

In this section, we describe the results and analysis of the CO:CO₂ diffusion experiments. In Section 3.1, we present the spectral analysis used to follow CO diffusion into the CO₂ based on changes in the ν₃ LO phonon mode. In Section 3.2, we describe the outcome of all bilayered diffusion experiments using the spectral analysis from Section 3.1. In Section 3.3, we describe the model framework used to quantify the diffusion rate in each experiment. In Section 3.4, we apply the models to the experimental data and extract the CO–CO₂ diffusion barrier. Finally, in Section 3.5, we present the results of experiments in which isotopically labeled CO₂ layers are employed to further constrain the diffusion mechanism.

3.1. Spectral Analysis

During the isothermal diffusion experiments, we monitor changes in the CO₂ LO phonon mode. Figure 2(a) shows
spectra of CO:CO2 ice mixtures of various CO concentration, reproduced from Cooke et al. (2016); the CO2 LO phonon mode is perturbed when CO2 is mixed with CO and thus can be used as a tracer of CO diffusion in CO2 ices.

Figures 2(b)–(c) show an example of the CO2 LO phonon mode during the diffusion experiment at 20 K. The LO phonon frequency at \( t = 0 \) is taken as reference for the pure CO2 ice and is \( \sim 2381 \text{ cm}^{-1} \) (4.2 \( \mu \text{m} \)). With time, we observe a decrease

Table 1
Initial Ice Thicknesses and Diffusion Temperatures Used in the Diffusion Experiments and Modeling

| Experiment | Target Ice (ML) | \( T_{\text{diff}} \) (K) | CO (1–0) Area (cm\(^{-1}\)) | CO\(_2\) (ν\(_3\)) Area (cm\(^{-1}\)) | CO Thickness\(^a\) (d nm) | CO\(_2\) Thickness\(^a\) (h – d) (nm) |
|------------|-----------------|----------------|-----------------------------|---------------------------------|----------------|-------------------------------|
| Temperatures CO:CO\(_2\) |
| 1          | 30:30           | 18            | 0.27                        | 1.39                            | 16             | 14                            |
| 2          | 30:30           | 19            | 0.27                        | 1.60                            | 16             | 16                            |
| 3          | 30:30           | 20            | 0.27                        | 1.38                            | 15             | 14                            |
| 4          | 30:30           | 21            | 0.26                        | 1.45                            | 15             | 14                            |
| 5          | 30:30           | 22            | 0.28                        | 1.42                            | 16             | 14                            |
| 6          | 30:30           | 23            | 0.27                        | 1.47                            | 15             | 15                            |
| Ice thicknesses CO:CO\(_2\) |
| 3          | 30:30           | 20            | 0.27                        | 1.38                            | 15             | 14                            |
| 7          | 10:50           | 20            | 0.09                        | 2.30                            | 5              | 23                            |
| 8          | 50:10           | 20            | 0.45                        | 0.50                            | 26             | 5                             |
| 9          | 20:20           | 20            | 0.13                        | 0.78                            | 8              | 8                             |
| Isotope layers CO:CO\(_2\):CO\(_{\text{i}}\)\(^b\) |
| 10         | 30:15:15        | 20            | 0.28                        | 0.77 + 0.70                     | 16             | 8 + 7                         |
| 11         | 30:15:15        | 20            | 0.28                        | 0.71 + 0.77                     | 16             | 7 + 8                         |
| 12         | 30:40:15        | 20            | 0.27                        | 1.89 + 0.79                     | 16             | 19 + 8                        |

Notes. There are two experimental series aimed at elucidating temperature and ice thickness dependencies, as well as an isotopically labeled experimental series. We use the following band strengths and ice densities to calculate the CO and CO2 thicknesses: \( A_{1\nu CO}(ν) = 1.1 \times 10^{-16} \), \( A_{1\nu CO}(ν) = 1.15 \times 10^{-16} \), \( A_{1\nu CO}(1-0) = 1.7 \times 10^{-17} \text{ cm molecule}^{-1} \) from Gerakines et al. (1995) and corrected for density in Bouilloud et al. (2015), \( \rho_{\text{CO2}} = 1.1 \text{ g cm}^{-3} \) (Satorre et al. 2008), \( \rho_{\text{CO}} = 0.8 \text{ g cm}^{-3} \) (Roux et al. 1980).

\(^a\) The uncertainty on the ice thickness in nanometers is estimated to be \( \sim 15\% \).

\(^b\) \( i \) and \( j \) refer to carbon mass 13-Carbon or 12-Carbon.
in the LO phonon intensity at 2381 cm\(^{-1}\) and an apparent broadening of the feature toward lower frequencies. The subtraction spectra (Figure 2(d)) reveal two distinct features: a loss centered at \(\sim 2381\) cm\(^{-1}\) and a growth centered around 2375 cm\(^{-1}\). Two Gaussians are fit to the subtraction spectra (Figure 2(e)) and their sum is optimized in Python using the `scipy.optimize.nnls` optimization package. The resulting negative Gaussian (Gaussian 1) is considered as a loss of the original pure CO\(_2\) ice environment, while the positive Gaussian (Gaussian 2) arises from the new CO–CO\(_2\) mixed environment. The new redshifted LO feature, while growing in intensity during diffusion experiment, does not shift in frequency, which can be contrasted to CO:CO\(_2\) mixtures we deposited from gases in Cooke et al. (2016), where the frequency changed with mixture concentration.

While both Gaussians can be used to model mixing of CO into the CO\(_2\) layer, we use the negative Gaussian 1 to extract the diffusion coefficients; the integrated area of Gaussian 1 is larger than that of Gaussian 2, allowing us to better fit the fast mixing kinetics within the first 10 minutes of the diffusion experiments.

### 3.2. CO Diffusion Experimental Results

Figure 3 and Table 2 show the results of the diffusion experiments. The top two rows of Figure 3 show the outcome of diffusion experiments with close to identical ice thicknesses but run at six different temperatures between 18 and 23 K. At 18 K, mixing is not complete after 250 minutes, while at 23 K it is complete within the first \(\sim 10\) minutes. The final mixing fraction, as traced by the loss of the LO mode, is almost constant above 18 K, i.e., the ice morphology is almost independent of ice temperature within the explored range; by contrast, the loss rate depends strongly on temperature. This is the expected behavior for a system in which diffusion is driven by the random movement of the more volatile species, motivating our model choices below.

The bottom row of Figure 3 shows the experiments for different CO:CO\(_2\) thicknesses; Experiment 7: 10 ML CO and 50 ML CO\(_2\), Experiment 8: 50 ML CO and 10 ML CO\(_2\), and Experiment 9: 20 ML CO and 20 ML CO\(_2\). The final mixed fraction depends on the CO\(_2\) ice thickness as expected, i.e., thicker CO\(_2\) ices can host more CO molecules. We explore the dependence of the diffusion rate on ice thickness and CO:CO\(_2\) ratio quantitatively in Section 3.4.

### 3.3. Fickian Diffusion Modeling

We use a Fick’s second law model to extract the diffusion coefficients and barrier for CO diffusion into CO\(_2\) ice. Fick’s law has been applied by Karssemeijer et al. (2014), Mispaèla et al. (2013), and Lauck et al. (2015) to model CO diffusion in amorphous solid water (ASW) ices. This law should apply if the ice mixing is dominated by random walk diffusion of the more volatile CO into the CO\(_2\) matrix resulting in a concentration gradient across the ice depth. We also fit the kinetic data with exponentials to give a rate coefficient and time associated with CO mixing into the CO\(_2\) layer.

We adopt a Fickian diffusion model modified from Lauck et al. (2015) and Bergner et al. (2016). The general form of Fick’s second law for a 1D system is

\[
\frac{\partial c(z, t)}{\partial t} = D(T) \frac{\partial^2 c(z, t)}{\partial z^2},
\]
where \( c(z, t) \) is the concentration of the diffusant CO as a function of time, \( t \), and position, \( z \), and \( D(T) \) is the temperature-dependent diffusion coefficient. In the layered CO:CO2 system, we define \( z = 0 \) as the substrate height, \( z = d \) as the interface height between CO and CO2 layers, and \( z = h \) as the vacuum interface. To calculate the height of the CO/CO2 and vacuum interfaces, we use densities of \( 1.1 \text{ g cm}^{-3} \) (Satorre et al. 2008) and \( 0.8 \text{ g cm}^{-3} \) (Roux et al. 1980) for CO2 and CO, respectively. For a system where CO desorption is negligible, we impose boundary conditions such that the flux of CO at the CsI substrate and at the vacuum interface is zero, i.e., 

\[
\frac{\partial c(z, t)}{\partial t} = 0 \quad \text{at} \quad z = 0 \quad \text{and} \quad z = h.
\]

At \( t = 0 \), we assume the concentration of CO is \( c_0 \) in the CO layer and zero everywhere else. Applying these boundary conditions gives a general solution that may be integrated to find the amount of CO in the CO2 layer. Dividing this by the total amount of CO gives a mixed fraction, \( N_{\text{mix}} \):

\[
N_{\text{mix}}(t) = \frac{1}{d c_0} \int_0^h c(z, t) dz = \frac{h - d}{h} \\
- \sum_{n=1}^{\infty} \frac{2h}{n^2 \pi^2 d} \sin\left(\frac{n \pi d}{h}\right) \exp\left(-\frac{n^2 \pi^2 d^2}{h^2} D t\right).
\]

This is adjusted to account for mixing during the fast temperature ramp by using a time offset, \( t_0 \), and for uncertainties in the measured ice thickness using a nuisance parameter, \( N_0 \), yielding

\[
N_{\text{mix}}(t) = N_0 \frac{h - d}{h} - \sum_{n=1}^{\infty} \frac{2N_0 h}{n^2 \pi^2 d} \sin\left(\frac{n \pi d}{h}\right) \exp\left(-\frac{n^2 \pi^2 d^2}{h^2} D (t + t_0)\right).
\]

Here \( D \), \( N_0 \), and \( t_0 \) are free parameters that are fit to the experimental mixing fraction of CO over time. We use the python nonlinear least squares routine \texttt{scipy.optimize.curve_fit} to fit Equation (4).

We also fit the mixing of CO into CO2 using exponentials. Fitting exponentials to the data allows us to directly extract a time constant associated with the diffusion process. A similar method has been used to fit the kinetics of molecules diffusing into ASW ice (Mispelaer et al. 2013). The exponential equation describing the time dependent mixed fraction, \( N_{\text{mix}} \), is

\[
N_{\text{mix}}(t) = N_0 e^{-k_{\text{mix}}(t + t_0)^n},
\]

where \( k_{\text{mix}} \) is the mixing rate coefficient in \text{s}^{-1} and \( n \) is the kinetic order. The diffusion coefficient, \( D \), can be roughly approximated from the mixing rate coefficient using Einstein’s relationship:

\[
D \approx \frac{k_{\text{Av}} (h - d)^2}{2}.
\]

![Figure 3](image-url)
where \( h - d \) is the thickness of the CO\(_2\) ice in which the CO diffuses. This equation generally gives us the same order of magnitude diffusion coefficients as those obtained using the Fickian model.

**3.4. Diffusion Kinetics and Barriers**

Consistent with the qualitative analysis above the Fickian diffusion coefficients increase with temperature from \( \sim 1 \times 10^{-15} \) cm\(^2\) s\(^{-1}\) at 18 K to \( \sim 3 \times 10^{-15} \) cm\(^2\) s\(^{-1}\) at 23 K. The mixing rates obtained from exponentials fits to the kinetic data likewise increase with temperature and are shown in Table 2. There are two major sources of uncertainty on the diffusion coefficients that are propagated into the uncertainty on the diffusion barrier. At the higher temperatures (\( T > 20 \) K), the largest source of uncertainty is the choice of the \( t = 0 \) point, which can change the diffusion coefficient by up to 50\%. The largest source of uncertainty for the experiments is where \( T \lesssim 20 \) K arises from the thickness determination and is a combination of uncertainties in the CO and CO\(_2\) band strengths and their densities.

A weighted linear regression to the Fick’s Law Arrhenius plot (Figure 4) yields a diffusion energy barrier of 300 ± 40 K. We also fit an Arrhenius Law to the mixing rate coefficients (not shown here) and find a barrier of 380 ± 30 K, indicating that the derived barrier is robust to the choice of model.

Comparing the ices with different thickness configurations, we find that the mixing timescale decreases with decreasing CO\(_2\) ice thickness. Based on the exponential fit, the characteristic mixing time constant is 4.5 minutes for the thin 10 ML CO\(_2\) ice and 72 minutes for mixing into the thick 50 ML CO\(_2\) ice. Likewise, the Fickian diffusion coefficients increase from \( 3 \times 10^{-17} \) cm\(^2\) s\(^{-1}\) in the 10 ML CO: 50 ML CO\(_2\) ice to \( 1 \times 10^{-15} \) cm\(^2\) s\(^{-1}\) in the 50 ML CO: 10 ML CO\(_2\) ice, i.e., it is larger for larger CO:CO\(_2\) ratios. The diffusion rates extracted for experiments with the same CO:CO\(_2\) thickness ratio but different total ice thicknesses (30 ML:30 ML and 20 ML:20 ML) are the same within experimental error, indicating that the CO:CO\(_2\) thickness ratio together with temperature control the diffusion rate and that total ice thickness is not an important factor.

**3.5. Isotopic Studies**

The isotopically labeled layered ice experiments provide further insight into the mechanism of CO:CO\(_2\) diffusion. Experiments were conducted with layered isotopic CO\(_2\) ices as shown in Figure 1 and Table 1. We test two different isotopic thickness configurations in which we layered 30 ML of CO with (1) 40 ML \(^{13}\)CO\(_2\) then 15 ML \(^{12}\)CO\(_2\) (Figure 5(a)) and (2) 15 ML \(^{13}\)CO\(_2\) then 15 ML \(^{12}\)CO\(_2\) (Figure 5(b)).

Figure 5 shows the kinetic curves for CO mixing into the two CO\(_2\) layers. In Figure 5(a), we see that the middle 40 ML layer has a larger final LO Gaussian area, corresponding to a larger number of mixed CO molecules, than the top 15 ML layer. By contrast, in Figure 5(b), the top 15 ML is able to host more CO than the bottom 15 ML despite their equal thicknesses. We also switched the isotopic order and layered 15 ML \(^{12}\)CO\(_2\) then \(^{13}\)CO\(_2\) and found that the top 15 ML layer always hosts more CO regardless of the order of the two isotopologues. In each of these three experiments, we found that the final mixed fraction in the top 15 ML layer was the
same. We discuss the physical interpretation of these results further in Section 5.

We calculate the diffusion coefficients for CO through the total ice thickness by summing the LO loss feature in both layers, reported in Table 2. We do this purely to check whether the diffusion coefficients calculated from summing the two 15 ML layers are the same as the 30 ML experiment at 20 K and we find that two are indeed the same within experimental uncertainties.

4. TPD Analysis and Results

4.1. TPD Analysis

The TPD traces for CO desorbing from CO2 ices are shown in the left panel of Figure 6. The spectra display one or two peaks between 25 and 50 K, depending on the ice surface area and corresponding CO coverage. CO desorption from CO2 ices deposited at 40 and 50 K display two TPD peaks in this temperature regime. The first peak corresponds to multilayer CO desorption and occurs around 28 K, which is consistent with previous measurements in the literature (Öberg et al. 2005; Noble et al. 2012; Collings et al. 2015; Fayolle et al. 2016). The higher temperature peak is associated with submonolayer desorption of CO from the CO2 ice surface. This peak is broader than in the multilayer regime, indicating a larger range of binding sites and associated energies, even when the CO2 ice is quite compact.

CO2 ices deposited at temperatures ≤25 K have a single desorption peak associated with sub-monolayer CO desorption from the surface of the CO2 ices. An additional desorption peak is seen near the CO2 desorption temperature (not shown here), probably due to CO diffusion into the CO2 pores and subsequent entrapment due to pore collapse. Similar entrapment has been seen for other volatile species within porous ASW ices (Collings et al. 2003; Fayolle et al. 2011; Martín-Domènech et al. 2014). No multilayer peak is observed for these ices, which is consistent with the expectation that ices deposited at lower temperatures are more porous and therefore present a larger surface for adsorbing molecules.

4.2. Desorption Barriers

Figure 6 shows the TPD curves for CO desorption from CO2 ices deposited at 11, 21, 23, 25, 40, and 50 K. The TPD curves are fit using the Polanyi–Wigner equation:

\[ \frac{d\theta}{dT} = \frac{\nu}{\beta} e^{-E_{\text{des}}/T}, \]

where \( \theta \) is the CO ice coverage, \( T \) is the temperature in K, \( \nu \) is a pre-exponential frequency factor in s\(^{-1}\), \( \beta \) is the heating ramp rate in Ks\(^{-1}\), \( n \) is the desorption order, and \( E_{\text{des}} \) is the desorption energy in K. We see that the peak desorption temperature increases as the CO2 deposition temperature is decreased. The trailing edges of the submonolayer CO peaks
Figure 6. $^{13}$CO temperature programmed desorption curves (left) and related desorption energy distributions (right) from CO$_2$ ices at various deposition temperatures listed in Table 3. The TPD spectrum of CO desorption from CO$_2$ ice grown at 11 K also displays a small peak below 25 K that we attribute to CO co-desorption with hydrogen that is deposited from the chamber background.
also extends to higher temperature for more porous CO2 ices deposited at lower temperatures.

To derive the desorption energy distribution for CO on CO2 we fit the TPD traces with a linear combination of first-order kinetics using the methods of Doronin et al. (2015) and described in detail in Fayolle et al. (2016). We use an energy step interval of 30 K to fit desorption kinetics between 900 and 1800 K. The resulting desorption energy distributions are shown in the right panel of Figure 6.

The mean desorption energies and desorption energy distributions, defined by the peak FWHM, for the various CO2 deposition temperatures are shown in Figure 7 and in Table 3. The desorption energies for CO from CO2 ices increase with decreasing deposition temperature and range from 1239 to 1407 K for CO2 ices deposited at 50 and 11 K respectively. We show the desorption energies of CO from H2O ice deposited at 11 K (porous) and at 100 K (compact) from Fayolle et al. (2016) for comparison. The increase in CO–CO2 desorption energy with decreasing CO2 deposition temperature is likely due to an increase in porosity and therefore number of strongly bound sites. In the submonolayer regime, mobile molecules tend to fill the deeper adsorption sites, resulting in a shift in the mean $E_{des}$ to higher energies (e.g., Fillion et al., 2009).

In the experiments where CO2 is deposited at temperatures between 11 and 25 K, CO is slowly out-gassing between the CO and CO2 desorption peaks, probably due to a combination of slow CO diffusion and CO2 ice rearrangement during the TPD warm-up. CO out-gassing is the largest for the experiment where CO2 ice was deposited at 11 K (porous) and at 100 K (compact) from Fayolle et al. (2016) for comparison. The increase in CO–CO2 desorption energy with decreasing CO2 deposition temperature is likely due to an increase in porosity and therefore number of strongly bound sites. In the submonolayer regime, mobile molecules tend to fill the deeper adsorption sites, resulting in a shift in the mean $E_{des}$ to higher energies (e.g., Fillion et al., 2009).

Figure 7. Desorption energies of $^{13}$CO from CO2 ice for various CO2 deposition temperatures. The blue panels show the average desorption energy with FWHM distributions for porous H2O ice deposited at 11 K and for compact H2O ice deposited at 100 K reported in Fayolle et al. (2016).

| CO2 Temp (K) | CO Column Density (10$^{15}$ molecules cm$^{-2}$) | $E_{des}$ (K) | FWHM (K) |
|--------------|---------------------------------------------|---------------|-----------|
| 11           | 1.0                                        | 1407          | 71        |
| 21           | 0.7                                        | 1385          | 86        |
| 23           | 0.8                                        | 1347          | 84        |
| 25           | 0.5                                        | 1361          | 73        |
| 40           | 0.8                                        | 1240          | 105       |
| 50           | 0.8                                        | 1239          | 94        |

Table 3

in the desorption energy estimate compared to our reported value.

5. Discussion

5.1. Diffusion Mechanisms

There are three main diffusion mechanisms proposed in the literature that are relevant for low temperature interstellar ices and their laboratory analogs: swapping of lattice molecules (Fuchs et al. 2009; Öberg et al. 2009; Garrod 2013a), movement into empty vacancy sites in the lattice (e.g., Lamberts et al. 2013, 2014; Chang & Herbst 2014), and surface hopping along adsorption sites in pores (Garrod 2013b). The former two are bulk diffusion processes, which are expected to have large barriers compared to pore surface hopping.

Our experiments provide three different lines of evidence that, in the case of CO diffusion into CO2, the main diffusion mechanism is that of surface diffusion in pores and on the ice surface: the magnitude of the extracted diffusion barrier, the evolution of the LO mode during diffusion, and the observed diffusion pattern through isotopically labeled ice layers.

First, the low diffusion barrier and the low diffusion–desorption energy barrier ratio of 0.21–0.24 is consistent with surface diffusion, but not with models of bulk diffusion in which ratios ranging from 0.5 for diffusion by swapping (Garrod 2013a) up to 1 for movement into interstitial sites (Chang & Herbst 2014) have been employed. Similar low diffusion barriers have been measured for the diffusion of volatile species into porous water ices (Mispelaer et al. 2013; Lauck et al. 2015).

Second, pore diffusion is the best explanation for how the CO2 LO phonon mode evolves during the isothermal diffusion experiments. Our previous experiments reported in Cooke et al. (2016) have shown that bulk mixing of CO into CO2 ices redshifts the CO2 LO mode linearly with the concentration of CO. If diffusion occurred through swapping, there should be a smooth change in the CO2 ice lattice with time, which should increasingly redshift the LO mode as more CO diffuses into the CO2. This is not observed; rather, we observe the growth of a new feature at a single redshift. The diffusion mechanism then, does not change the bulk lattice structure during CO diffusion, and this is only consistent with either surface hopping or movement into interstitial sites.

The third line of evidence comes from the behavior of the isotopically labeled CO2 layered experiments in Section 3.5. If diffusion occurs by the random walk into the CO2 layer with a homogeneous distribution of binding sites, we would expect that diffusion into the top layer should be delayed with respect
to the bottom layer, and the final mixing fractions should be the same for two layers of the same thickness. In Figure 8, we show a toy model to demonstrate this point. On the left-hand side of Figure 8 (panels (a) and (c)), we input our experimentally measured ice thicknesses into Fick’s law to model the mixing of CO into the CO$_2$ isotopic layers and compare with the actual experiments. Contrary to model predictions, in our experiment the top isotopic layer hosts more CO molecules per ML of CO$_2$ compared to the bottom CO$_2$ layer; the Fick’s law model (solid lines) expects equal final mixing of CO into CO$_2$ layers of the same thickness. The second discrepancy is the predicted time delay for CO mixing into the top layer, which is not seen in our experimental data.

One possible explanation for the discrepancy in the final mixing fractions is that the top layer has a larger number of surface sites, i.e., the binding sites for CO are not distributed homogeneously across the CO$_2$ ice height. We incorporate this into the toy model by assigning the top layer an “effective thickness” to best match the experimental mixing fractions by eye. In the case of 15 ML:15 ML ice, we need to roughly double the thickness of the top layer to reproduce the relative mixing fractions seen in the experimental curves. In the 40 ML:15 ML case, we increase the top layer by around 33%. In the pore-diffusion scenario, this effect can be explained physically by a larger number of surface sites per CO$_2$ ML in the top isotopic layer due to additional surface binding sites at the vacuum interface. Changing the effective thicknesses of the two layers does not resolve the above noted mismatch between predicted and experimental mixing delay times. The immediate appearance of mixing in the top ice layer (within the measurement timescale) is best explained by a rapid pore diffusion, which is faster than expected using our solution to Fick’s law. One possible explanation for the rapid pore diffusion is that initially absorbed CO molecules at the CO–CO$_2$ boundary could facilitate faster diffusion of subsequent CO molecules via decreased van der Waals forces.

Figure 8. Fick’s Law model for CO diffusion into isotopic layers of CO$_2$. Panels (a) and (c) are modeled using the CO$_2$ thicknesses used in the experiment and a relevant diffusion coefficient from the measurements at 20 K. Panels (b) and (d) show adjustments to the Fickian model by scaling the heights to an “effective” thickness by assuming that the top layer has an additional surface area that is not present in the lower layer. The diffusion coefficient is increased to assume that once the CO reaches pores in the lower CO$_2$ it can move more rapidly along the pore surface to the top layer. The faint open circles display the experimental kinetic traces for comparison.
interactions. Because the CO–CO adsorption energy is lower than that of CO–CO₂, the diffusion kinetics would reflect the CO–CO self-diffusion barrier. This possibility has been suggested previously by Lauck et al. (2015) for the case of CO diffusing through porous water ices.

In summary, diffusion of CO through CO₂ ice most likely occurs through internal pores; this theory is supported by the low diffusion–desorption energy barrier ratio, the evolution of the CO₂ ν₃ LO mode during CO diffusion, and the surface accumulation of CO in the isotopically labeled ice experiments.

5.2. CO₂ LO Phonons for Tracing Diffusion

We have presented a new method for studying diffusion processes in CO₂ bearing ices based on the sensitivity of the CO₂ LO phonon mode to the ice environment. Diffusion kinetics in ices have most commonly been measured via decreases in IR absorption of the diffusing molecule after desorption. Typically, a layered or mixed ice is heated to temperatures above the desorption temperature of the volatile species. In these experiments, the volatile species diffuses through the ice and subsequently desorbs; the diffusion is then traced by the decreasing infrared absorption. These experiments are usually not able to distinguish well between the mechanisms of diffusion as the molecule can diffuse from both weakly and strongly bound sites. In our method, we monitor diffusion by observing changes in the CO₂ lattice IR modes. This method resembles that used by Lauck et al. (2015), where the IR feature of the diffusing molecule, CO, was monitored, but presents a number of advantages.

First, this technique could be extended to study ice systems in which the diffusing molecule itself is IR inactive, e.g., O₂, N₂, but produces a still produces a shift in the CO₂ LO mode upon mixing with CO₂.

Second, LO phonon modes are very sensitive to the exact mixing morphology of the ice, which enabled us to distinguish between mixing through pore diffusion and mixing through bulk diffusion.

Using LO phonons to trace ice mixing and diffusion also presents some unique challenges. The LO phonon frequency shifts are the result of changes in the ice lattice to intermolecular forces between CO₂ and the diffusing CO molecules and there are potentially other processes that can also change the lattice structure. In particular, at temperatures similar to those employed in our experiments, the CO₂ ice may undergo pore collapse or reorganization, which could change the LO phonon frequency. To check the potential impact of CO₂ morphology changes, we also ran an isothermal experiment in which we deposited pure CO₂ ice. In this experiment, we did not see a redshift of the LO mode, indicating that CO diffusion into CO₂ is indeed responsible for the observed redshift during the diffusion experiments. At longer timescales, we did, however, see a slow blueshift and narrowing of the LO mode develop attributed to CO₂ crystallization. Fortunately, the CO₂ crystallization is slower than the CO diffusion process in our temperature regime and it appears that CO diffusion into CO₂ further slows the CO₂ crystallization rate.

5.3. Diffusion and Desorption Barriers and Their Astrophysical Implications

The CO:CO₂ diffusion barriers extracted in this work, combined with the complementary measurements of the CO–CO₂ desorption barriers places CO:CO₂ ice diffusion into a growing family of systems with low, <0.3, ice diffusion–desorption barrier ratios. This suggests that diffusion may be underestimated in current gas–grain astrochemical models, which typically adopt diffusion–desorption energy barrier ratios of 0.3 or higher (Katz et al. 1999; Ruffle & Herbst 2000; Garrod & Pauly 2011; Chang & Herbst 2012). However, it is important to note that these low diffusion barriers are only valid for ices with pores, and may be sensitive to porosity differences between laboratory and interstellar ices (Garrod 2013b).

It is further important to note that the diffusion–desorption barrier ratio for the CO:CO₂ system is larger by a factor of two compared to the diffusion–desorption barrier ratio for the CO:COH₂O system that can be derived from experiments of Lauck et al. (2015) and Fayolle et al. (2016). This strongly suggests that there is no universal ratio that can be applied in models, but rather that experiments and molecular dynamics models are needed for several other major ice constituents and for mixed ices to evaluate the range of possible ratios.

Through our measurements to determine the diffusion–desorption barrier ratio for the CO:CO₂ ice system, we systematically measured CO–CO₂ desorption barriers for the first time. We found that the CO–CO₂ Eₜ des barriers are substantially higher than the previous estimates of Cleeves et al. (2014), who report a CO–CO₂ desorption energy of 1110 K based on the peak desorption temperature of CO from CO₂. Considering only the individual pairwise interactions between CO and the ice substrate, we would expect that the CO desorption energy from water ice should be higher than that from CO₂. Instead, the ice morphology appears to be more important in controlling the CO desorption from H₂O and CO₂ ices. This implies that the CO desorption temperature in, for example, protoplanetary disks, may be high even when CO is not in direct contact with water ice. A recent study places the CO snowline in the iconic protoplanetary disk TW Hya at 22 au (Zhang et al. 2017) and explains its location as a result of CO binding directly to water ice. Our results show that the same desorption temperature could result from binding to CO₂ ice, which might be a likelier scenario when considering the freeze-out temperatures and chemistry of H₂O, CO₂, and CO.

6. Conclusions

In this work, we report the diffusion of CO into CO₂ from initially layered ices at low temperatures. We make the following conclusions:

1. We show that the CO₂ ν₃ LO phonon mode can be used to trace CO diffusion. This system could be used to study mixing phenomena between other astrophysically relevant ice constituents and CO₂.
2. The diffusion coefficients depend on temperature as well as the CO:CO₂ ice thickness ratio.
3. The temperature-dependent rates CO diffusion through CO₂ ice are well fit by an Arrhenius Law, which allows us to derive a diffusion barrier of 300 ± 40 K.
4. The CO from CO₂ desorption energies ranges from 1239 to 1407 K depending on the CO₂ ice deposition temperature. Some of the CO–CO₂ desorption barriers are similar to those from water ices, demonstrating that CO binds equally well to compact CO₂ as it does to compact water ice.
5. Combining these sets of experiments, we derive a diffusion–desorption barrier ratio for CO:CO₂ ices of 0.21–0.24. This ratio is low compared to what has been used in astrochemical models, suggesting that diffusion driven processes may be more efficient than what is currently assumed.

6. The low diffusion barrier, combined with constraints on the diffusion kinetics supports a scenario where CO diffusion into CO₂ occurs along internal pores and across the CO₂ ice surface rather than through the bulk ice. The CO mobility and mixing in CO₂ ices depends on the number of surface binding sites resulting in an accumulation of CO at the CO₂ ice surface.

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