Variations in the Strength of the Infrared Forbidden 2328.2 cm⁻¹ Fundamental of Solid N₂ in Binary Mixtures

by

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Abstract

We present the 2335-2325 cm⁻¹ infrared spectra and band positions, profiles, and strengths (A values) of solid nitrogen and binary mixtures of N₂ with other molecules at 12 K. The data demonstrate that the strength of the infrared forbidden N₂ fundamental near 2328 cm⁻¹ is moderately enhanced in the presence of NH₃, strongly enhanced in the presence of H₂O and very strongly enhanced in the presence of CO₂, but is not significantly affected by CO, CH₄, or O₂. The mechanisms for the enhancements in N₂-NH₃ and N₂-H₂O mixtures are fundamentally different from those proposed for N₂-CO₂ mixtures. In the first case, interactions involving hydrogen-bonding are likely the cause. In the latter, a resonant exchange between the N₂ stretching fundamental and the ¹⁸O=¹²C asymmetric stretch of ¹⁸O¹²C¹⁶O is indicated. The implications of these results for several astrophysical issues are briefly discussed.

Key Words: Nitrogen; Carbon dioxide; Water; Infrared Spectroscopy; Interstellar Ices; Matrix Isolation

1. Introduction

While infrared forbidden in the gas phase, the N₂ fundamental stretching vibration near 2328 cm⁻¹ can be perturbed into infrared activity in the solid state through interactions with neighboring species. The nature of this interaction has received considerable attention over the years and has been studied in pure N₂ ices [1-4] and in a number of N₂-containing ice mixtures [5-11]. This earlier work, combined with the realization that N₂-rich mixed-molecular ices are present in the outer solar system [12] and probably in cold, dense clouds of dust, gas, and ice in the interstellar medium [13], have led us to conduct a laboratory study on the variation in the absorption intensity of the infrared forbidden N≡N fundamental stretch near 2328 cm⁻¹.
The methods and materials used in this study are described in the following section (§2). In §3 we present spectra of the 2328 cm\(^{-1}\) N=N stretching band produced by N\(_2\) in a variety of binary ice mixtures, and examine the change of this feature's intensity as a function of the identity and concentration of the second molecule. A discussion of the results of the work is provided in §4, and §5 contains some brief comments on the implications of this work for several astrophysical issues. Our findings are summarized in §6.

2. Materials and Methods

The techniques and equipment employed for this study have been described in detail as part of our previous studies of mixed-molecular ices [13-15]. Details associated with the materials and methods used that are unique to this particular study are provided below.

2.1 Starting Materials

The N\(_2\) gas used (Airco, 99.95\%) was further purified by passing it through a liquid nitrogen-cooled trap to remove condensable contaminants prior to mixing with other gases. Most of the other gases used in our experiments, \(^{15}\)N\(_2\) (Aldrich, 98.0\%), \(^{13}\)CO\(_2\) (Aldrich, 99.0\%), CO\(_2\) (Matheson, 99.8\%), CH\(_4\) (Matheson, 99.99\%), O\(_2\) (Matheson, 99.99\%), NH\(_3\) (Matheson, 99.99\%), and CO (Matheson, 99.99\%), were taken directly from lecture bottles without further purification. Distilled H\(_2\)O was further purified by three freeze-pump-thaw cycles under vacuum (P<10\(^{-5}\) mbar) prior to mixing in order to remove dissolved gases.

2.2 Sample Preparation

All the compounds had sufficient volatility at room temperature that samples could be prepared by mixing, in the gas phase, appropriate amounts of N\(_2\) with the compound of interest. The relative gas abundances were controlled using a greaseless glass gas-handling system described elsewhere [14] and the gases were mixed in volume-calibrated, greaseless glass bulbs. All bulbs were mixed at room temperature and allowed to equilibrate for at least 24 hours before use. The background pressure in the gas-handling system was \(~10^{-6}\) mbar. The total pressure in the sample bulbs varied
depending on the relative concentration of N2 to the second gas and its identity, but the sample bulbs never contained less than 20, or more than 1000, mbar of total pressure. Thus, the contaminant levels in the bulbs associated with the mixing process are always less than about one part in 10^7, i.e., are negligible compared to the original impurities of our starting materials.

Once prepared, glass sample bulbs were transferred to the stainless steel vacuum manifold where the sample mixture was vapor-deposited onto a CsI window cooled to 12 K by an Air Products Displex CSW 202 closed-cycle helium refrigerator. Typical samples were deposited at a rate of about 1.0 mmole/hour, corresponding to an ice growth rate of approximately 5 μm/hour. Under these conditions, N2-rich ices are expected to be in the α structural form.

2.3 Determination of N2 Band Strengths

Infrared spectra were obtained from the condensed samples using a Nicolet 7100 Fourier transform spectrometer at a resolution of 0.9 cm\(^{-1}\) (the width of an unresolved line) and normalized by ratioing to a spectrum of the blank cold finger obtained prior to gas deposition. The intrinsic strength, \(A\), of any bands of interest in the spectra were determined by measuring the integrated area of the band in absorbance and dividing by the column density of the molecule responsible, i.e.,

\[
A = \frac{\tau(v) \, dv}{N} \quad (1)
\]

where \(\tau(v)\) is the frequency dependent optical depth across the absorption feature, \(v\) is the frequency in cm\(^{-1}\), and \(N\) is the column density in molecules/cm\(^2\). The intrinsic strength is then given in units of cm/molecule.

In this work, the \(A\) values for the N=N stretching vibration near 2328 cm\(^{-1}\) produced by N2 in different ice mixtures were determined using two independent methods. In the first, we scaled the area of the N2 band at 2328 cm\(^{-1}\) to that of a known absorption band produced by the other molecule in the ice. Using the known relative concentration of the N2 and the second molecule, and the known \(A\) value of the band produced by the second molecule, it was then a simple matter to derive the \(A\) value for the N2 by scaling. The derivation of \(A_{N2}\) using this method did not require a direct measurement of the actual column densities of the materials in the measured sample but was only as accurate as the \(A\) value used for the strength of the band of the second molecule.
In this paper, we use the following $A$ values: $A_{\text{ACO}}(2140 \text{ cm}^{-1} \text{ band}) = 1.0 \times 10^{-17} \text{ cm/molecule}$, $A_{\text{ACO}_2}(2344 \text{ cm}^{-1} \text{ band}) = 1.4 \times 10^{-16} \text{ cm/molecule}$, $A_{\text{ACH}_4}(1301 \text{ cm}^{-1} \text{ band}) = 3.8 \times 10^{-18} \text{ cm/molecule}$, $A_{\text{ANH}_3}(1070 \text{ cm}^{-1} \text{ band}) = 1.7 \times 10^{-17} \text{ cm/molecule}$, and $A_{\text{AH}_2\text{O}}(1660 \text{ cm}^{-1} \text{ band}) = 1.4 \times 10^{-16} \text{ cm/molecule}$. These are based on $A$ values measured for these molecules in similar ice mixtures [16,17], and are expected to involve uncertainties of no more than a factor of about 50%.

In some of our thicker $N_2:CO_2$ ices the 2344 cm$^{-1}$ $^{12}\text{CO}_2$ band was saturated and could not be measured. In these cases, we integrated the strength of the weaker $^{13}\text{CO}_2$ band and scaled by the $^{12}\text{CO}_2/^{13}\text{CO}_2$ band strength ratios measured from thinner samples where the $^{12}\text{CO}_2$ band near 2344 cm$^{-1}$ was not saturated.

For the second method, we used interference fringes formed in the baseline of the infrared spectrum by multiple reflections of the infrared beam within the solid sample film to determine a sample thickness and then derived the column density of the sample using an assumed index of refraction and density of the sample. The $A$ value for the $N_2$ fundamental was then determined by dividing the integrated area of the $N_2$ absorption band by the column density of $N_2$. For this method we generally assumed the samples had an index of refraction of 1.23 (that of pure $N_2$) [18] and densities of 1.0271 g/cm$^3$ [19]. The values of these two parameters undoubtedly differ slightly from sample to sample, especially for those with high concentrations of guest molecules, but with the exception of $H_2O$ as a guest molecule, these effects are expected to result in uncertainties of less than a few percent. Since pure $H_2O$ ice has a significantly higher index of refraction than $N_2$, we used the relative concentrations of $N_2$ and $H_2O$ in our $N_2-H_2O$ samples to interpolate an index of refraction between the value of 1.23 for pure $N_2$ and a value of 1.32 for pure $H_2O$ [16]. Overall, for those samples that produced good interference fringes in their spectra, this technique results in final $N_2$ $A$ values having uncertainties of 25% at most.

It was necessary to use both of these methods because neither method could be applied to all of the ice mixtures examined. For example, it was not possible to use the interference fringe technique for samples where the ice contained large concentrations of $H_2O$ since this molecule produces a number of strong and broad bands that mask the fringes. Similarly, the technique of ratioing band
areas requires prior information about the intrinsic strengths of bands produced by the second molecule in the mix, information that is not available for all the mixes and concentrations studied here. Nonetheless, we are confident that both techniques provided reliable results within better than a factor of three since (i) when both techniques could be used on the same sample, they yielded strengths that always agreed to better than a factor of three (typically better than a factor of 1.5-2.0) and both yielded identical trends and (ii) both techniques yielded values for our samples with high N$_2$ concentrations that agree with those already published for high concentration N$_2$ ices [20].

3. Results

3.1 The Position and Profile of the Nitrogen Fundamental

Since the N$_2$ stretching fundamental is only seen in ices because interactions with neighboring molecules lead to symmetry breaking, it would not be surprising if the position and profile of this feature were a function of the samples' composition. Fig. 1 presents the 2338-2322 cm$^{-1}$ (4.277-4.307 μm) infrared spectra of six N$_2$-rich ices deposited and maintained at 12 K. The top spectrum is that of pure N$_2$; the N≡N stretch produces an absorption band centered at 2328.2 cm$^{-1}$ (4.2952 μm) with a full-width-at-half-maximum (FWHM) of ~1.5 cm$^{-1}$ (0.0028 μm). As can be seen from Fig. 1, the addition of ~5% CO, CH$_4$, O$_2$, or NH$_3$ has little affect on the position or profile of the N$_2$ stretching band, although the presence of NH$_3$ does cause the band to broaden slightly. Nitrogen ices containing 5% H$_2$O produce an N$_2$ band that is about twice as broad as the other ices.

The presence of CO$_2$ does not produce a wider N$_2$ band. However, in addition to the N≡N stretching band, the 2338-2322 cm$^{-1}$ spectra of N$_2$-CO$_2$ ices contain a second band at 2332.0 cm$^{-1}$ (4.2882 μm). The 2332.0 cm$^{-1}$ band is interpreted as being due to the $^{18}$O isotopic band of the CO$_2$ asymmetric C=O stretching mode [5-8]. Fig. 2 presents the 2338-2322 cm$^{-1}$ (4.277-4.307 μm) infrared spectra of a number of 12 K N$_2$-rich ices containing CO$_2$ in concentrations ranging from 1 part in 400 up to 1 part in 2. Note that the N$_2$ band near 2328 cm$^{-1}$ and the $^{18}$O$^{12}$C$^{16}$O band near 2332 cm$^{-1}$ have similar strengths over most of this range of relative concentrations. This peculiar behavior will be discussed in more detail in §3.2 and §4.2.2.
The positions, widths, and strengths of the N=N stretching band of the N$_2$-rich ice mixtures shown in Fig. 1 are summarized in Table I. The interpretation of the infrared and Raman positions and profiles of the N$_2$ fundamental and of the bands of molecules interacting with N$_2$ has received substantial attention over the years. For considerably more detailed discussions of these interactions, the reader is encouraged to see references 1-10.

### 3.2 Changes in the Intrinsic Strength of the N$_2$ Fundamental

Since the N$_2$ stretching fundamental is classically infrared forbidden, its absolute strength in solids is, not surprisingly, a strong function of composition. Indeed, it was the observation that the N$_2$ fundamental becomes 'infrared active' in the presence of CO$_2$ [5,6] that stimulated much of the early work on this band. Subsequent observations of the N$_2$ band enhancement in the presence of CO$_2$ [3,7,8] were extended to include other guest molecules including HF, DF, HCL, and DCl [10], ICN and BrCN [9], C$_2$N$_2$ [7,9], and H$_2$O and D$_2$O [7,9,10]. This earlier work was largely confined to issues associated with the N$_2$ band position, however, and the enhancements in strength were noted but not quantified. Here we attempt to quantify the extent of the enhancements as a function of the identity of the guest molecule and its relative concentration.

It is apparent from the intrinsic strengths (A values) of the N=N stretching bands in Table I that the strength of the N$_2$ band depends critically on the identity of the second molecule in the sample. The N$_2$ stretching fundamental in ices containing ~5% CO, CH$_4$, O$_2$, or NH$_3$ has a strength that is similar that of pure N$_2$. In contrast, the presence of 5% H$_2$O or CO$_2$ produces significant enhancements in the strength of the N$_2$ feature, factors of about 10 and 100, respectively. In order to further understand these effects, we carried out a series of spectral measurements of ices having a wide variety of ratios of N$_2$ to CO, CH$_4$, O$_2$, NH$_3$, H$_2$O, and CO$_2$. The results of these experiments are summarized in Table II. The results based on the fringe technique are presented graphically in Fig. 3.

It is apparent from Table II and Fig. 3 that the presence of CO, CH$_4$, and O$_2$ in N$_2$-containing ices have little affect on the intrinsic strength of the N$_2$ band, even at large concentrations. In
contrast, the presence of NH$_3$, H$_2$O, or CO$_2$ cause the strength of the N$_2$ band to measurably increase as their concentration rises. The effect produced by NH$_3$ is moderate; substantial growth in N$_2$ band strength is not seen until the NH$_3$ concentration exceeds about 10% and the enhancement increases to a factor of slightly over 40 as the N$_2$/NH$_3$ ratio drops to 1. H$_2$O has a greater effect than NH$_3$. It produces measurable enhancement in the N$_2$ fundamental at concentrations as low as a few percent and causes increases in the N$_2$ band intensity greater than a factor of 80 in ices rich in H$_2$O.

The most dramatic effect, however, is produced by the presence of CO$_2$. Even at concentrations as low as 0.25%, the presence of CO$_2$ measurably enhances the strength of the N$_2$ fundamental, and at concentrations above 5% it enhances the N$_2$ fundamental by factors of hundreds. In very CO$_2$-rich ices, the enhancement exceeds a factor of 1000. It should be noted that the 2332.0 cm$^{-1}$ band attributed to $^{18}$O=$^{12}$C=$^{16}$O in the spectra of N$_2$-CO$_2$ mixtures (see also §4.2.2 and Fig. 2) is not included in the N$_2$ band areas reported in Tables I and II. All band intensities listed in these tables and displayed in Fig. 3 include only the absorption of the band at 2328.2 cm$^{-1}$. However, there is a certain ambiguity in the values reported in Table II in our samples with N$_2$/CO$_2$ $<$ 5. Fig. 2 shows that the bands due to $^{18}$O$^{12}$C$^{16}$O and N$_2$ begin to overlap and coalesce at high CO$_2$ concentrations. These two bands increase in strength together at lower concentrations (Fig. 2). As they begin to coalesce at N$_2$/CO$_2$ = 5/1, their relative proportions appear to be about $1/3$ to $2/3$ [21] and we assume they maintain this proportion at higher CO$_2$ concentrations. Therefore, the values in Table II for N$_2$/CO$_2$ $<$ 5 are calculated assuming that $2/3$ of the combined band at high CO$_2$ concentrations is due to the N$_2$.

Two additional items are worthy of note. First, while our spectrometer is not very sensitive above 4000 cm$^{-1}$, we were occasionally able to detect the N$_2$ overtone band near 4656 cm$^{-1}$. In several samples having N$_2$/H$_2$O ratios between 10 and 20 we observed overtones having strengths of between $2.7 \times 10^{-23}$ and $3.9 \times 10^{-23}$ cm/molecule, values that are enhanced relative to those reported for pure N$_2$ (see [20]) by at most a factor 2, whereas the fundamentals in these samples are enhanced by factors of about 8. Similarly, the overtones seen in a few of our N$_2$/CO$_2$ = 20/1 and N$_2$/CO$_2$ = 5/1 samples yield strengths of a maximum of $4.2 \times 10^{-22}$ and $1.4 \times 10^{-21}$
cm/molecule, respectively. These correspond to enhancements of less than a factor of about 20 and 70 for the overtones, while the fundamentals are enhanced by factors of about 110 and 660, respectively. Thus, it appears that the N$_2$ overtone is less enhanced by the presence of H$_2$O and CO$_2$ than is the fundamental. Additional spectral measurements with higher signal to noise in the 4700-4600 cm$^{-1}$ region will be needed to better quantify this observation, and for the remainder of this paper we will restrict ourselves to discussion of the N$_2$ fundamental.

Second, in a limited number of experiments we monitored the strength of the N$_2$ band as the samples were warmed to 20, 25, and 30 K. The H$_2$O- and CO$_2$-induced enhancements in the strength of the N$_2$ fundamental were seen to decrease slightly with warm up, the effect being less than 30% for CO$_2$ and perhaps as much as 50% for H$_2$O. Again, additional experiments will be required to better quantify this effect as a function of sample composition.

3.3 Isotopic Labeling

In order to gain a better understanding of the mechanisms responsible for the enhancement of the nitrogen fundamental in the presence of H$_2$O and CO$_2$, we carried out several experiments using isotopically-labeled N$_2$ and CO$_2$. When the nitrogen in the N$_2$-H$_2$O = 20/1 mixtures was replaced with isotopically-labeled $^{15}$N$_2$, the N≡N fundamental at 2328.2 cm$^{-1}$ was observed to shift down to ~2250 cm$^{-1}$ (4.444 μm) with essentially no change in strength (Fig. 4a,b and Table II), i.e., the same enhancements were seen when either $^{14}$N$_2$ or $^{15}$N$_2$ were used (enhancement factors of 8.9 ± 2.2 versus 6.1 ± 1.1, respectively). $^{15}$N$_2$-CO$_2$ mixtures demonstrated the same shift in the nitrogen band position, but in this case with a substantial reduction in the band's strength. For a $^{15}$N$_2$/CO$_2$ = 20/1 mixture, the N$_2$ stretching band decreases in strength by a factor of about 6 relative to an isotopically-normal N$_2$/CO$_2$ = 20/1 mixture (Fig. 4c,e and Table II), but is still enhanced relative to pure N$_2$ by a factor of about 18. The 2332 cm$^{-1}$ band, which we earlier attributed to the $^{18}$O=$^{12}$C asymmetric stretch of $^{18}$O$^{12}$C$^{16}$O, remains at 2332 cm$^{-1}$ when $^{15}$N$_2$ is used, as expected. Finally, in N$_2$-$^{13}$CO$_2$ mixtures there is no change in the position of the 2328 cm$^{-1}$ N≡N stretch, but its intensity diminishes. For an N$_2$/$^{13}$CO$_2$ = 20/1 mixture, the N$_2$ stretching band decreases by a factor of ~6 in strength.
relative to an isotopically-normal N$_2$/CO$_2$ = 20/1 mixture (Fig. 4c,d and Table II), but is still enhanced relative to pure N$_2$ by a factor of about 18.

4. Discussion

4.1 Band Positions and Profiles

The relative invariance of the N$_2$ band profiles (Fig. 1) and strengths (Table II) make it clear that there is no strong interaction between N$_2$ and CO, CH$_4$, or O$_2$ in our samples. The broadening in the position of the N$_2$ feature in the presence of NH$_3$ and H$_2$O is probably due to hydrogen-bonding interactions. Such effects are commonly observed for other molecules frozen at these temperatures in H$_2$O-containing matrices [16,17]. The N$_2$-H$_2$O system has been previously studied by Andrews and Davis [10], who used Ar matrix-isolation techniques to demonstrate that N$_2$ interacts with hydrogen-bonding molecules in a way that suggests that an electronic structure readjustment in a monomeric complex occurs that results in a slightly stronger N≡N bond within the complex. This effect was observed to be the strongest in HF, but weaker hydrogen bonded complexes were observed for HCl and H$_2$O as well.

The position and profile of the N$_2$ band produced by N$_2$-CO$_2$ ices are not significantly different from those of pure N$_2$ and they provide little evidence for a strong N$_2$-CO$_2$ interaction. However, as we will see in the next section, the strength of the N$_2$ feature in these ices indicates otherwise.

4.2 Band Intensities

Again, CO, CH$_4$, and O$_2$ have little effect on the strength of the N$_2$ fundamental over a wide range of concentrations, while the presence of NH$_3$, H$_2$O, or CO$_2$ can result in a considerable increases in the band's intensity. The interactions whereby NH$_3$ and H$_2$O enhance the strength of the N$_2$ stretching band are thought to be fundamentally different from the CO$_2$ interaction.

4.2.1 The Intensity of the 2332.0 cm$^{-1}$ N$_2$ Band in the Presence of NH$_3$ and H$_2$O

In N$_2$-H$_2$O mixtures rich in H$_2$O, the intensity of the 2328 cm$^{-1}$ N$_2$ fundamental reaches a value of at least $A_{N_2} = 1.4 \times 10^{20}$ cm/molecule at N$_2$/H$_2$O = 1, i.e., almost 80 times greater than
for pure solid N$_2$ (see Table II and Figure 3). The enhancements produced by NH$_3$ are less
dramatic, but still exceed a factor of 40 at high NH$_3$ concentrations. These N$_2$ band strength
enhancements are probably the result of the same interactions that are producing band shifting [10]
and broadening (see also Fig. 1), namely hydrogen-bonding interactions. These interactions should
produce a far greater breaking of the symmetry of the N≡N stretching vibrations of nitrogen
molecules near or complexed with NH$_3$ and H$_2$O than is produced by N$_2$ with only N$_2$ neighbors,
resulting in greater infrared activation. Band strength enhancements mediated by hydrogen-bonding
have been previously observed in a number of molecules frozen in H$_2$O-containing ices. For
example, the intrinsic strengths of the infrared-active stretching modes of CO and CO$_2$ increase by
factors of ~2 and 3, respectively, in H$_2$O-rich ices when compared to the same modes in pure ices
[22,23]. Even more dramatically, it has long been known that the intrinsic strength of the 3250 cm$^{-1}$
O-H stretching mode of H$_2$O in an H$_2$O-only ice is ~100 times greater than the same mode when
H$_2$O is in the gas phase or frozen in argon [24]. In the case of the N$_2$-H$_2$O system, an
enhancement by hydrogen-bonding interactions is already suggested by the observation from band
position measurements that N$_2$ interacts with hydrogen bonding molecules [10]. Furthermore, the
smaller enhancement produced by NH$_3$ compared to H$_2$O is consistent with this interpretation since
the earlier band position work indicates that the strength of the interaction between HF, HCl, and
H$_2$O qualitatively correlates with electron affinity [10].

4.2.2 The Intensity of the 2332.0 cm$^{-1}$ N$_2$ Band in the Presence of CO$_2$

For N$_2$/CO$_2$= 5/1 mixtures, the intensity of the 2328 cm$^{-1}$ band is over 600 times greater than
that of pure N$_2$. Beyond N$_2$/CO$_2$ = 5, the intensity reaches a 'plateau' value of about 2.5x10$^{-19}$
cm/molecule, although it becomes difficult to accurately determine the area of the 2328 cm$^{-1}$ N$_2$
feature because the 2328 and 2332.0 cm$^{-1}$ bands begin to seriously overlap (see Fig. 2 and §3.2).
This overlap provides a clue to the CO$_2$ interaction causing the observed N$_2$ band strength
enhancements. Since the band at 2332.0 cm$^{-1}$ is due to the asymmetric stretch of $^{18}$O$^{12}$C$^{16}$O, one
would expect it to grow, relative to the N$_2$ feature at 2328 cm$^{-1}$, with increasing CO$_2$ concentration.
However, Fig. 2 shows that this is not the case; the two bands remain fairly constant in strength relative to each other over a 40 fold change in N2/CO2 ratio. The 'expected' strength of the 2332.0 cm\(^{-1}\) 18O\(^{12}\)C\(^{16}\)O band relative to the main 16O\(^{12}\)C\(^{16}\)O band near 2348 cm\(^{-1}\) can be assessed measuring the 2348 and 2332 cm\(^{-1}\) band areas in the spectra of Ar-CO\(_2\) mixtures (where no N\(_2\) is present) or 15N\(_2\)-CO\(_2\) mixtures where there is no confusion with the N\(_2\) fundamental (see Fig. 4e). We find that the strength of the 2332.0 cm\(^{-1}\) 18O\(^{12}\)C\(^{16}\)O band is near that which would be expected on the basis of the observed 2348 cm\(^{-1}\) CO\(_2\) band for a wide range of N\(_2\)/CO\(_2\) ratios. Thus, both the shift of the 2332 cm\(^{-1}\) 18O\(^{12}\)C\(^{16}\)O band at high CO\(_2\) concentrations and the 'lock step' fashion with which the strength of the 2328 cm\(^{-1}\) N\(_2\) feature increases with CO\(_2\) concentration suggest a interactive relationship between the N\(_2\) fundamental and the 18O\(^{12}\)C\(^{16}\)O band.

We suspect that the enhancement of the N\(_2\) fundamental is related to resonant interaction of the 2328 cm\(^{-1}\) N\(_2\) band with the nearby O=O asymmetric stretches of 18O\(^{12}\)C\(^{16}\)O at 2332 cm\(^{-1}\) and, possibly, 16O\(^{12}\)C\(^{16}\)O at 2348 cm\(^{-1}\). The resonant nature of this interaction is suggested by the observation that the enhancement of the N\(_2\) band decreases with increasing frequency difference (\(\Delta V\)) between the N=O fundamental and the nearby CO\(_2\) bands. For example, for 20/1 ices, an enhancement of a factor of ~100 is seen in normal N\(_2\)-CO\(_2\) samples [\(\Delta V(14N_2,18O^{12}C^{16}O) = 4\) cm\(^{-1}\), \(\Delta V(14N_2,16O^{12}C^{16}O) = 17\) cm\(^{-1}\)] relative to pure N\(_2\), while the enhancement decreases to a factor of about 18 for both N\(_2\)-13CO\(_2\) samples [\(\Delta V(14N_2,16O^{13}C^{16}O) = 46\) cm\(^{-1}\)] and 15N\(_2\)-CO\(_2\) samples [\(\Delta V(15N_2,16O^{12}C^{16}O) = 94\) cm\(^{-1}\)]. The fact that in samples with N\(_2\)/CO\(_2\) > 5, the 2332 cm\(^{-1}\) 18O\(^{12}\)C\(^{16}\)O band is seen to produce enhanced absorption (albeit more modest) that essentially matches step with the enhancement of the N\(_2\) band is further suggestive of a resonant exchange of energy between N\(_2\) molecules and adjacent CO\(_2\) molecules. These observations are consistent with the results described by DiLella and Tevault [7] for N\(_2\) ices containing 16O\(^{12}\)C\(^{16}\)O, 16O\(^{12}\)C\(^{18}\)O, and 18O\(^{12}\)C\(^{18}\)O, and they ascribe this behavior to an electrostatic mechanism whose behavior is similar to that of a Fermi resonance. Note that this behavior is very different from that seen in our N\(_2\)-H\(_2\)O experiments were there is essentially no difference in the enhancement factor between the 14N\(_2\) and 15N\(_2\) variants (see Table II).
Our concentration studies allow us to place some constraints on the nature of the N$_2$-CO$_2$ interaction. Assume for the moment that the observed N$_2$ absorption band in N$_2$-CO$_2$ ices is due to the superposition of absorption contributions from N$_2$ molecules having only N$_2$ neighbors ($A_{N_2N_2} = 1.8 \times 10^{-22}$ cm/molecule) plus 'enhanced' absorption contributions from N$_2$ molecules having a significant interaction with an adjacent CO$_2$ molecule ($A_{N_2CO_2} = 2.5 \times 10^{-19}$ cm/molecule). Using this simple "on-off" model in which a given N$_2$ molecule either is or is not enhanced, it is possible to use simple nearest-neighbor calculations of the type used to predict the fractional abundance of monomers, dimers, trimers, etc. in matrix-isolation studies [25] to calculate the expected enhancement of the $A_{N_2}$ value as a function of N$_2$/CO$_2$ ratio. The most favorable fit to the N$_2$/CO$_2$ concentration data is provided when it is assumed that each CO$_2$ in the sample can enhance at most two N$_2$ molecules (see Fig. 5). Since the resonant interaction involves the N$_2$ stretching fundamental and the CO$_2$ asymmetric stretching vibration, it is not entirely unexpected that the effect might be restricted to the N$_2$ molecules at the two ends of the CO$_2$ molecule. However, this simple model clearly deviates from our observations as the CO$_2$ concentration increases beyond N$_2$/CO$_2 < 5$, presumably because this simple model doesn't fully describing the interaction of N$_2$ with CO$_2$ multimers. Nonetheless, it appears that it is possible to explain the main facets of the observed enhancements using a simple model based on resonant interactions of the ends of the guest CO$_2$ molecules with their nearest N$_2$ neighbors.

5. Astrophysical Implications

Most of the material in dense interstellar dust clouds is at very low temperatures (T < 50 K). At these temperatures the majority of gas phase species condense out onto the dust grains in the form of mixed molecular ices [17]. Studies of the position and profile of the interstellar band near 2140 cm$^{-1}$ (4.67 µm) due to CO in these ices show that they can be divided into two main types, those dominated by polar, H$_2$O-rich matrices and those dominated by apolar molecules like CO, CO$_2$, N$_2$, and O$_2$ [13,22,26]. The presence of N$_2$ in interstellar ices is supported by the observation that one of the best fits to the CO band position and profile in the apolar ices is
provided by a N$_2$:O$_2$:CO$_2$:CO = 1:5:1/2:1 mixture [13], a mixture having a composition similar to that expected for the apolar ices on the basis of time-dependent chemistry models [27].

A major fraction of the N$_2$ molecules in an N$_2$:O$_2$:CO$_2$:CO = 1:5:1/2:1 mixture should have at least one CO$_2$ neighbor and, as a result, the N$_2$ fundamental in such astrophysical ices is likely to be enhanced by factors of hundreds over that of pure nitrogen. This is good news for astronomers in that this is a sufficiently large enhancement that it raises the very real possibility that it may be possible to directly detect the N$_2$ in interstellar ices. On the other hand, it will be very difficult to derive interstellar N$_2$ column densities from any N$_2$ feature detected without first doing a thorough job of characterizing the other molecular components in the ice.

Closer to home, the enhancements described here may also play a significant role in the interpretation of the spectra of Pluto and Neptune's satellite Triton, both of which show evidence for surface ices that contain both CO$_2$ and abundant N$_2$ [12,28,29]. A more detailed discussion of the astrophysical implications of this work will appear elsewhere [30].

6. Conclusions

We have studied the position, profile, and strength of the N≡N fundamental stretch of N$_2$ in binary ice mixtures containing CO, CH$_4$, O$_2$, NH$_3$, H$_2$O, and CO$_2$. Mixtures of N$_2$ with NH$_3$, H$_2$O, or CO$_2$ produce significant enhancements in the strength of the 2328 cm$^{-1}$ absorption feature relative to that observed for pure N$_2$ ices or mixtures of N$_2$ with O$_2$, CH$_4$, or CO.

In the case of NH$_3$ and H$_2$O, the N$_2$ band strength enhancement is probably the result of hydrogen-bonding interactions which produce a far greater breaking of the symmetry of the N≡N stretching vibrations of nitrogen molecules near NH$_3$ and H$_2$O than is produced by N$_2$ with only N$_2$ neighbors. The enhancement of the N$_2$ fundamental in the presence of CO$_2$ is probably related to resonant interaction of the 2328 cm$^{-1}$ N$_2$ band with the nearby O=C asymmetric stretches of $^{18}$O$^{12}$C$^{16}$O at 2332 cm$^{-1}$ and $^{16}$O$^{12}$C$^{16}$O at 2348 cm$^{-1}$. 
These results may have significant implications for the interpretation of astronomical data of N$_2$-containing ices in dense molecular clouds in the interstellar medium and on the surfaces of planets and satellites in the outer Solar System.

Acknowledgments

This work was supported by NASA grants 344-37-44-01 (Origins of Solar Systems Program) and 344-38-12-04 (Exobiology Program). The authors are grateful for useful discussions with L. Allamandola, D. Cruikshank, E. Young, and P. Ehrenfruend, and excellent technical support from R. Walker.

References


[21] The 1/3 proportion in the N2/CO2 = 5/1 ice is consistent with the expected strength of the 2332 cm⁻¹ ¹⁸O¹²C¹⁶O band relative to the 2340 cm⁻¹ CO₂ fundamental based on the ¹⁸O¹²C¹⁶O/¹⁸O¹²C¹₆O band area ratio seen in Ar-CO₂ ices.


Table I - Positions, FWHM, and Strengths of the N≡N Stretching Features in Fig. 1

<table>
<thead>
<tr>
<th>Ice mixture</th>
<th>Position in cm⁻¹ (µm)</th>
<th>FWHM (cm⁻¹)</th>
<th>A value of N₂ from band areas (cm/molecule)ᵃ</th>
<th>A value of N₂ from fringes (cm/molecule)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure $^{14}$N₂</td>
<td>2328.2 (4.295)</td>
<td>1.5</td>
<td>---</td>
<td>(1.8 ± 0.3) x 10⁻²² b</td>
</tr>
<tr>
<td>pure $^{15}$N₂</td>
<td>2250.6 (4.443)</td>
<td>1.8</td>
<td>---</td>
<td>(1.6 ± 0.1) x 10⁻²² b</td>
</tr>
<tr>
<td>N₂/CO = 25/1</td>
<td>2328.2 (4.295)</td>
<td>1.6</td>
<td>(2.9 ± 0.8) x 10⁻²²</td>
<td>(2.1 ± 0.7) x 10⁻²²</td>
</tr>
<tr>
<td>N₂/CH₄ = 20/1</td>
<td>2327.9 (4.296)</td>
<td>1.3</td>
<td>(3.3 ± 0.3) x 10⁻²²</td>
<td>(4.1 ± 0.7) x 10⁻²²</td>
</tr>
<tr>
<td>N₂/O₂ = 20/1</td>
<td>2328.2 (4.295)</td>
<td>1.4</td>
<td>---</td>
<td>(2.4 ± 0.3) x 10⁻²²</td>
</tr>
<tr>
<td>N₂/NH₃ = 22/1</td>
<td>2328.2 (4.295)</td>
<td>2.0</td>
<td>(5.5 ± 1.2) x 10⁻²²</td>
<td>(5.1 ± 0.9) x 10⁻²²</td>
</tr>
<tr>
<td>N₂/H₂O = 20/1</td>
<td>2328.4 (4.295)</td>
<td>3.3</td>
<td>(4.7 ± 0.7) x 10⁻²¹</td>
<td>(1.6 ± 0.4) x 10⁻²¹</td>
</tr>
<tr>
<td>N₂/CO₂ = 20/1</td>
<td>2328.6 (4.294)</td>
<td>2.7</td>
<td>(2.7 ± 0.2) x 10⁻²⁰ c</td>
<td>(1.9 ± 0.1) x 10⁻²⁰ c</td>
</tr>
<tr>
<td></td>
<td>2332.0 (4.288)</td>
<td>1.4</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ) Stated uncertainties represent the standard deviations of multiple measurements. A values used for the band area derivations and indices of refraction used for the fringe derivations are discussed in §2.3.

ᵇ) For comparison, Bohn et al. [15] report a value of $A_{N₂} = (1.3 ± 0.6) x 10^{-22}$ cm/molecule.

ᶜ) Does not include any contribution from the area of the 2332.0 cm⁻¹ band (see §3.2).
Table II - The Strength of the Infrared N≡N Stretching Feature as a Function of Guest Molecule Composition and Concentration

<table>
<thead>
<tr>
<th>Ice Composition and Ratios</th>
<th>Fraction of Guest Molecule (%b)</th>
<th>$A$ value of N$_2$ from band areas (cm/molecule)$^a$</th>
<th>$A$ value of N$_2$ from fringes (cm/molecule)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure $^{14}$N$_2$</td>
<td>0.0</td>
<td>---</td>
<td>$(1.8 \pm 0.3) \times 10^{-22}$</td>
</tr>
<tr>
<td>pure $^{15}$N$_2$</td>
<td>0.0</td>
<td>---</td>
<td>$(1.6 \pm 0.1) \times 10^{-22}$</td>
</tr>
<tr>
<td>N$_2$/CO</td>
<td>% CO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>0.1</td>
<td>$(3.0 \pm 1.2) \times 10^{-22}$</td>
<td>$(1.6 \pm 0.2) \times 10^{-22}$</td>
</tr>
<tr>
<td>25</td>
<td>3.8</td>
<td>$(2.9 \pm 0.8) \times 10^{-22}$</td>
<td>$(2.1 \pm 0.7) \times 10^{-22}$</td>
</tr>
<tr>
<td>5.0</td>
<td>16.7</td>
<td>$(4.1 \pm 0.2) \times 10^{-22}$</td>
<td>$(4.2 \pm 0.3) \times 10^{-22}$</td>
</tr>
<tr>
<td>N$_2$/CH$_4$</td>
<td>% CH$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>4.8</td>
<td>$(3.3 \pm 0.3) \times 10^{-22}$</td>
<td>$(4.1 \pm 0.7) \times 10^{-22}$</td>
</tr>
<tr>
<td>5.0</td>
<td>16.7</td>
<td>$(5.7) \times 10^{-22}$</td>
<td>$(7.8 \pm 0.1) \times 10^{-22}$</td>
</tr>
<tr>
<td>N$_2$/O$_2$</td>
<td>% O$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>4.8</td>
<td>---</td>
<td>$(2.4 \pm 0.3) \times 10^{-22}$</td>
</tr>
<tr>
<td>5.0</td>
<td>16.7</td>
<td>---</td>
<td>$(5.4 \pm 1.6) \times 10^{-22}$</td>
</tr>
<tr>
<td>N$_2$/NH$_3$</td>
<td>% NH$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>4.3</td>
<td>$(5.5 \pm 1.2) \times 10^{-22}$</td>
<td>$(5.1 \pm 0.9) \times 10^{-22}$</td>
</tr>
<tr>
<td>10.4</td>
<td>8.8</td>
<td>$(2.0 \pm 0.2) \times 10^{-21}$</td>
<td>$(1.6 \pm 0.1) \times 10^{-21}$</td>
</tr>
<tr>
<td>4.8</td>
<td>17.2</td>
<td>$(2.9 \pm 0.1) \times 10^{-21}$</td>
<td>$(2.6 \pm 0.3) \times 10^{-21}$</td>
</tr>
<tr>
<td>0.97</td>
<td>50.8</td>
<td>$(8.6 \pm 1.6) \times 10^{-21}$</td>
<td>$(8.0 \pm 0.2) \times 10^{-21}$</td>
</tr>
<tr>
<td>N$_2$/H$_2$O</td>
<td>% H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>0.3</td>
<td>$(7.7 \pm 0.1) \times 10^{-22}$</td>
<td>$(2.0 \pm 0.1) \times 10^{-22}$</td>
</tr>
<tr>
<td>130</td>
<td>0.8</td>
<td>$(6.6 \pm 2.4) \times 10^{-22}$</td>
<td>$(3.3) \times 10^{-22}$</td>
</tr>
<tr>
<td>100</td>
<td>1.0</td>
<td>$(8.4 \pm 2.1) \times 10^{-22}$</td>
<td>$(4.0 \pm 0.8) \times 10^{-22}$</td>
</tr>
<tr>
<td>43</td>
<td>2.3</td>
<td>$(2.0 \pm 0.5) \times 10^{-21}$</td>
<td>$(9.5 \pm 1.3) \times 10^{-22}$</td>
</tr>
<tr>
<td>N$_2$/CO$_2$</td>
<td>% CO$_2$</td>
<td>(e)</td>
<td>(e)</td>
</tr>
<tr>
<td>-------------</td>
<td>---------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>400</td>
<td>0.25</td>
<td>(1.8 ± 0.2) x 10$^{-21}$</td>
<td>(1.4 ± 0.1) x 10$^{-21}$</td>
</tr>
<tr>
<td>200</td>
<td>0.5</td>
<td>(3.2 ± 0.1) x 10$^{-21}$</td>
<td>(4.0 ± 0.4) x 10$^{-21}$</td>
</tr>
<tr>
<td>75</td>
<td>1.3</td>
<td>(8.9 ± 1.3) x 10$^{-21}$</td>
<td>(5.3 ± 0.4) x 10$^{-21}$</td>
</tr>
<tr>
<td>20</td>
<td>4.8</td>
<td>(2.7 ± 0.2) x 10$^{-20}$</td>
<td>(1.9 ± 0.1) x 10$^{-20}$</td>
</tr>
<tr>
<td>10</td>
<td>9.1</td>
<td>(6.6 ± 0.3) x 10$^{-20}$</td>
<td>(4.4 ± 0.1) x 10$^{-20}$</td>
</tr>
<tr>
<td>5.0</td>
<td>16.7</td>
<td>(1.6 ± 0.4) x 10$^{-19}$</td>
<td>(1.2) x 10$^{-19}$c</td>
</tr>
<tr>
<td>3.6</td>
<td>21.7</td>
<td>(2.5 ± 0.3) x 10$^{-19}$</td>
<td>(1.7) x 10$^{-19}$c</td>
</tr>
<tr>
<td>3.0</td>
<td>25.0</td>
<td>(3.4 ± 0.1) x 10$^{-19}$</td>
<td>(2.1 ± 0.1) x 10$^{-19}$</td>
</tr>
<tr>
<td>2.55</td>
<td>28.2</td>
<td>(3.6) x 10$^{-19}$c</td>
<td>---</td>
</tr>
<tr>
<td>2.25</td>
<td>30.8</td>
<td>(3.9 ± 0.7) x 10$^{-20}$</td>
<td>(2.7 ± 0.1) x 10$^{-19}$c</td>
</tr>
<tr>
<td>2.0</td>
<td>33.3</td>
<td>(3.7 ± 0.1) x 10$^{-19}$</td>
<td>(2.2) x 10$^{-19}$c</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N$_2$/13CO$_2$</th>
<th>% 13CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1.3</td>
</tr>
<tr>
<td>20</td>
<td>4.8</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>15N$_2$/CO$_2$</th>
<th>% CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>15N$_2$/H$_2$O</th>
<th>% H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.8</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>
a) Stated uncertainties represent the standard deviations of multiple measurements. A values used for the band area derivations and indices of refraction used for the fringe derivations are discussed in §2.3.

b) This work. For comparison, Bohn et al. [15] report a value of $A_{N_2} = (1.3 \pm 0.6) \times 10^{-22}$.

c) Result of a single measurement.

d) For our most dilute N$_2$:NH$_3$ = 22:1 samples we found that the value of $A_{NH_3}(1070 \text{ cm}^{-1} \text{ band}) = 1.7 \times 10^{-17} \text{ cm/molecule}$ provided very different results from those obtained using fringes. Study of a series of N$_2$-NH$_3$-CO samples, where the CO was used as a 'trace' band area standard, indicated that the A values of all the NH$_3$ bands fall off significantly as the NH$_3$ is diluted to N$_2$/NH$_3$ = 20/1 and beyond. For the N$_2$/NH$_3$ = 22/1 value we have scaled against the CO band area in an N$_2$/NH$_3$/CO = 22/1/0.2 ice sample.

e) Does not include any contribution from the area of the 2332.0 cm$^{-1}$ band (see §3.2).

f) Calculations assume $A^{13}CO_2(2280 \text{ cm}^{-1}) = 1.0 \times 10^{-16} \text{ cm/molecule}$ based on work done here.
Figure Captions

Fig. 1 - The 2338-2322 cm\(^{-1}\) (4.277-4.307 \(\mu\)m) infrared spectra of the N=N stretching fundamental of (a) pure N\(_2\), (b) N\(_2\)/CO = 25/1, (c) N\(_2\)/CH\(_4\) = 20/1, (d) N\(_2\)/O\(_2\) = 20/1, (e) N\(_2\)/NH\(_3\) = 22/1, (f) N\(_2\)/H\(_2\)O = 20/1, and (g) N\(_2\)/CO\(_2\) = 20/1 ices deposited and maintained at 12 K.

Fig. 2 - The 2338-2322 cm\(^{-1}\) (4.277-4.307 \(\mu\)m) infrared spectra of N\(_2\)/CO\(_2\) ice samples deposited and maintained at 12 K. The N\(_2\)/CO\(_2\) ratios of the samples are (a) 400/1, (b) 200/1, (c) 20/1, (d) 10/1, (e) 5/1, and (f) 2/1. The increasingly strong fall off to higher frequency as CO\(_2\) concentration increases is due to the growth of the strong \(^{16}\)O\(^{12}\)C\(^{16}\)O stretching fundamental near 2344 cm\(^{-1}\).

Fig. 3 - The change in the intensity of the N-N stretch near 2328.2 cm\(^{-1}\) (4.295 \(\mu\)m) as a function of the concentration of added CO (○), CH\(_4\) (+), O\(_2\) (×), NH\(_3\) (▲), H\(_2\)O (▲), and CO\(_2\) (●). Note that the values plotted for the N\(_2\)-CO\(_2\) ices represent only the contribution from the band near 2328 cm\(^{-1}\), i.e., they do not include the area of 2332 cm\(^{-1}\) band. The dotted horizontal line near the bottom of the figure denotes the absorption strength of the 2328 cm\(^{-1}\) N\(_2\) fundamental in pure nitrogen ices (Reference 20 and this work). All the values in this figure were determined using the interference fringe technique (see Table II).

Fig. 4 - The 2400-2200 cm\(^{-1}\) (4.17-4.55 \(\mu\)m) infrared spectra of the N=N stretching fundamental for several normal and isotopically spiked samples deposited and maintained at 12 K. The samples are (a) N\(_2\)/H\(_2\)O= 20/1, (b) \(^{15}\)N\(_2\)/H\(_2\)O= 20/1, (c) N\(_2\)/CO\(_2\) = 20/1, (d) N\(_2\)/\(^{13}\)CO\(_2\) = 20/1, and (e) \(^{15}\)N\(_2\)/CO\(_2\) = 20/1. The various spectra have been scaled by arbitrary amounts and the stronger bands in (c), (d), and (e) have been truncated for clarity.

Fig. 5 - A comparison of the observed N\(_2\) band enhancement as a function of N\(_2\)/CO\(_2\) ratio with predictions from a simple model based on nearest-neighbor considerations. The model assumes \(A_{N_2} = 1.8 \times 10^{-22}\) cm/molecule for all the N\(_2\) molecules in the sample except those that are resonantly enhanced by an interaction with CO\(_2\). Resonantly enhanced N\(_2\) are all assumed to have \(A_{N_2} = 2.5 \times 10^{-19}\) cm/molecule. The theoretical curves correspond to different assumptions regarding how many N\(_2\) molecules are enhanced by each CO\(_2\). From the upper to lower curve they correspond to every CO\(_2\) enhancing 6, 4, 2, and 1 neighboring N\(_2\) molecule, respectively. It is clear that the best fit is provided when each CO\(_2\) molecule is assumed to enhance two adjacent N\(_2\) molecules.
Figure 1

(a) Pure N₂
(b) N₂ / CO = 25
(c) N₂ / CH₄ = 20
(d) N₂ / O₂ = 20
(e) N₂ / NH₃ = 22
(f) N₂ / H₂O = 20
(g) N₂ / CO₂ = 20

2338 2336 2334 2332 2330 2328 2326 2324 2322
Wavelength (μm)

(a) $N_2/CO_2 = 400$
(b) $N_2/CO_2 = 200$
(c) $N_2/CO_2 = 20$
(d) $N_2/CO_2 = 10$
(e) $N_2/CO_2 = 5$
(f) $N_2/CO_2 = 2$

Frequency (cm$^{-1}$)
Figure 3
Figure 4

(a) $N_2/H_2O = 20$

(b) $^{15}N_2/H_2O = 20$

(c) $N_2/CO_2 = 20$

(d) $N_2/^{13}CO_2 = 20$

(e) $^{15}N_2/CO_2 = 20$
Figure 5

- $A_{N_2}$ from fit lines
- CO$_2$ interacts with 1 neighbor
- CO$_2$ interacts with 2 neighbors
- CO$_2$ interacts with 4 neighbors
- CO$_2$ interacts with 6 neighbors

Graph axes:
- X-axis: $z(N_A \times 10^{22}$ cm$^{-2}$ molecule$^{-1}$)
- Y-axis: N$_2$/CO$_2$