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THE N_3 RADICAL AS A DISCRIMINATOR BETWEEN ION-IRRADIATED AND UV-PHOTOLYZED ASTRONOMICAL ICES

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ABSTRACT

Infrared spectroscopy has been used to show that irradiation of solid N_2 and N_2-rich ices with 0.8 MeV protons produces the N_3 (azide) radical. In contrast, no N_3 was observed after solid N_2 and N_2-rich ices were photolyzed by far-UV photons. Isotopic substitution experiments support the N_3 identification, as does an analysis of the reactions occurring in the ices. This is the first documented difference in reaction products between the radiation chemistry and photochemistry of a nonpolar astronomical ice analog. We suggest that this difference in reaction chemistries could be used to identify ion-irradiated ices on interstellar grains and in the outer solar system. Further, N_3 might be used as a tracer of solid-phase interstellar N_2, which is expected to exist in dark, molecular clouds but is difficult to observe directly. Although the absolute strength of the N_3 band in solid N_2 is unknown, we estimate that it is at least 100 times greater than that of the fundamental vibration of N_2.

Subject headings: ISM: molecules — line: formation — line: identification — molecular processes

1. INTRODUCTION

Ices on interstellar grains, cometary nuclei, and the surfaces of icy solar system objects are exposed to and altered by both UV photons and cosmic rays. Similar reaction products are predicted for UV and ion processing of these ices, a prediction which is confirmed by three recent papers. Gerakines, Moore, & Hudson (2000) compared and contrasted the photochemistry and radiation chemistry of $H_2O + CO_2$ ices, finding the major products to be CO and H_2CO_3 in both cases. A more complex chemistry was found by Hudson & Moore (2000a) for an $NH_3 + CO$ ice, but IR spectra showed that the radiation and photochemical products, and their relative amounts, were virtually identical in the two types of experiments. A very recent paper (Gerakines & Moore 2002) on the radiation and photochemistries of pure CO showed that C_3O_2 and CO_2 are formed in both types of experiments.

Although product identification is important in ice chemistry, differences in product yields in photochemical and radiation chemical experiments are also of interest. In the cases of $H_2O + CO_2$ mixtures (Gerakines et al. 2000) and pure CO (Gerakines & Moore 2002) quantitative differences have already been discovered for photochemical and radiation chemical processing. Yet while it is important to document quantitative differences in ice chemistries, *qualitative* differences are also relevant. If a qualitative difference could be found between the products of a photolyzed ice and an ion-irradiated ice, then it might be used to distinguish between the two types of chemistry in an astronomical environment. In other words, can laboratory experiments uncover a reaction product which is unique to either ice radiolysis or ice photolysis?

To date no such indicator of either UV or radiation processing is known, although at least four candidates have come and gone: acetone, H_2CO_3, "XCN," and hexamethylenetetramine (HMT). First, the tentative identification of acetone in ion-irradiated CH_3OH (Baratta et al. 1994), as well as its absence from UV-photolyzed ices containing CH_3OH, was considered as a possible discriminator for the two types of energetic processing (Bernstein et al. 1995). However, we have recently shown (Hudson & Moore 2000b) that there is no IR evidence for acetone formation in irradiated methanol ices. At one point it was thought that H_2CO_3 might be formed by ion irradiation and not UV photolysis, yet Gerakines et al. (2000) showed that UV-photolyzed $H_2O + CO_2$ mixtures do indeed contain H_2CO_3. A third candidate is so-called XCN, characterized by an IR band for interstellar ices at ~2165 cm^{-1} (~4.62 μm). Pendleton et al. (1999) observed that this IR feature can be matched by the cyanate ion, OCN^-, seen in UV-photolyzed $CO + NH_3$ ices, but added that "it is unclear whether the 4.62 μm band produced by ion bombardment is also due to the OCN^- ion." Were UV and ion processing capable of making products that differed chemically but were spectroscopically identical, then one might hope that unique and identifiable products of each process might eventually be uncovered. Unfortunately, the XCN feature gives no reason for such hope as an extensive laboratory study (Hudson, Moore, & Gerakines 2001) has shown that OCN^- is formed in *both* irradiated and photolyzed laboratory ices, and by extension in interstellar ices. Finally, Bernstein et al. (1995) tentatively suggested that HMT might be formed only in UV photolysis experiments and thus would discriminate photolyzed ices from ion-irradiated ices. However, recent experiments of Cottin, Czopa, & Moore (2001) conclusively show that HMT is formed by both UV and radiation processing.

Heretofore most studies of energetically altered ices have concentrated on polar molecules, such as H_2O and CH_3OH, and all have failed to uncover a product unique to either UV photolysis or ion irradiation. In this paper we report on the chemistry of N_2, a *nonpolar* molecule, and describe a qualitative chemical difference between ion-irradiated and UV-photolyzed N_2 and N_2-rich ices. Specifically, the azide radical, N_3, is observed in ices that have been ion bombarded but not in those that have been photolyzed. This observa-

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tion is doubly significant as it suggests that N_3 might not just be an indicator of cosmic-ray processing in ices but could also be a tracer for solid N_2.

2. EXPERIMENTAL

Our experimental methods have been described in many previous papers (e.g., Moore & Hudson 1992, 1998), so only a summary will be given here. N_2 and N_2-containing ices were prepared by vapor-phase condensation of the appropriate gas(es) onto a precooled ($\sim$12 K) aluminum substrate (area $\approx$5 cm^2) in a high-vacuum chamber. Ices were grown to thicknesses of several micrometers in about 1 hr, with thicknesses being determined by a conventional laser interference system assuming an index of refraction of 1.23 for solid N_2 (Roux et al. 1980). Mid-IR spectra of ices were recorded with an FTIR spectrometer before and after exposure to a 0.8 MeV H^+ beam from a Van de Graaff accelerator. Spectra were typically 120 scan accumulations from 4000 to 400 cm^{-1} at a resolution of 1 cm^{-1}. Chemical reagents were purchased largely from Aldrich, Matheson, and Cambridge Isotopes.

The use of proton irradiation to mimic cosmic-ray bombardment and energetic processing has been discussed in previous papers (Moore et al. 1983; Moore, Hudson, & Gerakines 2001). Since our samples' thicknesses were on the order of a few micrometers, the incident protons, having a range of $\sim$20 μm (Northcliffe & Shilling 1970), penetrated the ices, initiated chemical reactions, and then came to rest in the underlying metal substrate, not in the ices themselves. For radiation dose calculations, we used standard relations to estimate the stopping power of 0.8 MeV protons in solid N_2 to be 323 MeV cm^{-1} (Chatterjee 1987). This assumes Scott's (1976) value, 1.03 g cm^{-3}, for the density of solid N_2.

The hydrogen discharge lamp used for UV photolysis gave mainly Lyα photons (121.6 nm, 10.6 eV) with a flux of approximately 3.1×10^{14} photons cm^{-2} s^{-1} (Gerakines et al. 2000; M. H. Moore & H. Cottin 2002, unpublished). Exposure times were on the order of hours, as is common in ice experiments of this type. Allamandola, Sandford, & Valero (1988) suggested that, for a similar lamp, 1 hr of laboratory photolysis is comparable to about 1000 yr of UV exposure for the outermost part of an interstellar cloud around a protostellar object. Deeper parts of such a cloud are more shielded from UV exposure so that the conversion can easily climb to 1 hr of laboratory photolysis being equivalent to 10^6 yr, or roughly the cloud's lifetime.

3. RESULTS

3.1. *Ion Irradiation of Pure* N_2

The fundamental vibration of gas-phase N_2 is IR inactive, as the molecule has no dipole moment. Smith, Keller, & Johnston (1950) reported that solid-phase N_2 displays a weak mid-IR band at 2328 cm^{-1}, a feature which has been confirmed by others (e.g., Bohn et al. 1994) and was observed by us as part of the present work.

It is known that bombardment of pure solid N_2 with either 4 keV Ne/Ne$^+$ (Tian, Facelli, & Michl 1988) or 120 eV N atoms (Khabashesku et al. 1997) produces the N_3 radical, whose most intense IR feature is at 1657 cm^{-1}. For our radiation experiments, we used a beam of 0.8 MeV H^+, this ion being more typical of cosmic radiation than N, Ne, or Ne$^+$. Proton irradiation of solid N_2 at 12 K indeed produced an IR band at 1657 cm^{-1}, the expected position for N_3, and this feature is shown in the upper trace of Figure 1. A similar irradiation of solid $^{15}N_2$ produced the band shown in the lower trace of Figure 1 at 1603 cm^{-1}, the expected position of $^{15}N_3$. In a third experiment (not shown), irradiation of a $^{14}N_2 + {}^{15}N_2$ mixture gave bands at 1657, 1649, 1615, and 1603 cm^{-1}, the expected positions for $^{14}N_3$, $^{15}N^{14}N_2$, $^{14}N^{15}N_2$, and $^{15}N_3$, respectively (Tian et al. 1988). All of these results confirm that proton irradiation of N_2 produces the N_3 radical in our experiments. Other IR bands of N_3 are known (Tian et al. 1988) but are too weak to be seen in our ices.

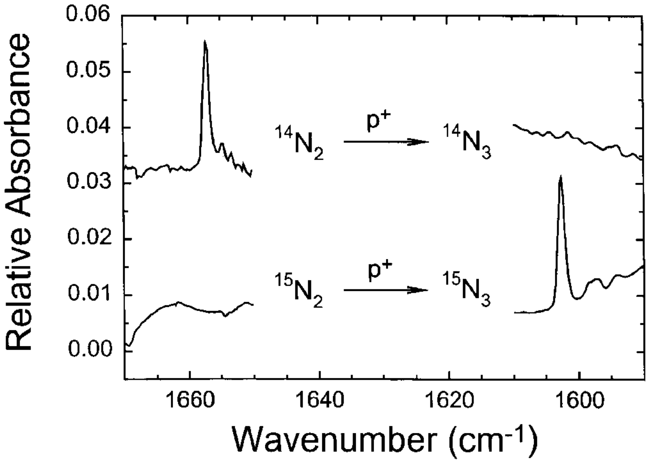

FIG. 1.—IR spectra of proton-irradiated N_2 at $\sim$12 K. The upper trace is for irradiated $^{14}N_2$, and the lower trace is for irradiated $^{15}N_2$.

Figure 2 shows the growth of the 1657 cm^{-1} $^{14}N_3$ band during the irradiation of solid $^{14}N_2$ at 12 K. Warming an irradiated N_2 ice gave little change in the N_3 feature until the matrix began to sublime away near 30 K, at which point the N_3 band rapidly decayed. A green emission was observed as the sample reached $\sim$25 K, was most intense between 30 and 35 K, and quickly decayed above 35 K.

3.2. *Ion Irradiation of* N_2*-containing Mixtures*

To assess the ability of known or suspected interstellar molecules to block N_3 formation, we proton-irradiated the

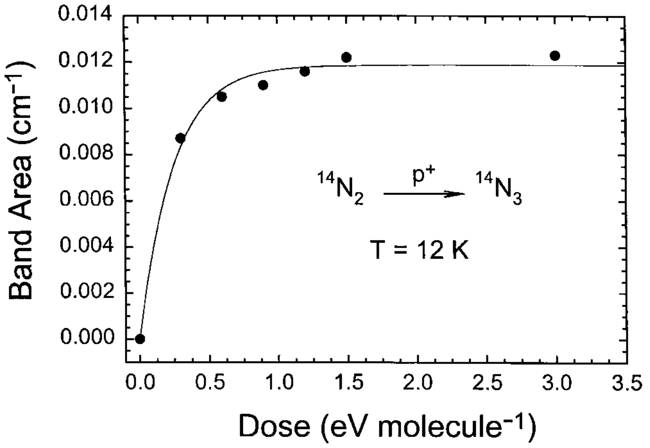

FIG. 2.—Growth of the 1657 cm^{-1} $^{14}N_3$ band during the 0.8 MeV H^+ irradiation of solid $^{14}N_2$ at 12 K. The equation $y = 0.01187(1 - e^{-4.052x})$ is also plotted.

TABLE 1

Ion-irradiated N_2-containing Ices[a]

Ice Composition	Ratio	ν_3 of N_3 (cm^{-1})
N_2	...	1657.3
$N_2 + CO$	100 : 1	1656.7
$N_2 + CO$	1 : 1	1656.5
$N_2 + CO_2$	100 : 1	1656.7
$N_2 + CO_2$	1 : 1	Not seen
$N_2 + O_2$	100 : 1	1656.8
$N_2 + O_2$	1 : 1	1656.7
$N_2 + CH_4$	100 : 1	1656.8
$N_2 + CH_4$	4 : 1	1656.6
$N_2 + H_2O$	100 : 1	1656.8
$N_2 + H_2O$	1 : 1	Not seen
$N_2 + NH_3$	100 : 1	1657.3
$N_2 + NH_3$	1 : 1	1656.2[b]
$N_2 + CH_3OH$	100 : 1	1655.8
$N_2 + CH_3OH$	1 : 1	Not seen
$N_2 + CH_4 + CO$	100 : 1 : 1	1656.9
$N_2 + CH_4 + CO$	10 : 1 : 1	1656.7
$N_2 + CH_4 + CO$	4 : 1 : 1	1656.1[b]
$N_2 + CH_4 + CO$	1 : 1 : 1	Not seen

[a] Irradiations were done and spectra were recorded at 12–18 K.

[b] Very weak.

18 N_2-containing ice mixtures of Table 1. Pure N_2 is included in Table 1 for comparison. Of the 18 mixtures listed, N_3 was detected in 14, as well as in all of the N_2-rich ices. For each type of binary mixture, the 100 : 1 ice gave a more intense N_3 feature than the corresponding 1 : 1 ice. Table 2 lists some of the observed radiation products in 100 : 1 mixtures, these products having been selected for the light they shed on the underlying solid-phase chemistry.

TABLE 2

Selected Products in on-irradiated Ices

Ice Composition	Products[a]
$N_2 + CO$ (100 : 1)	OCN (1934)[b]
	NO (1874)
	N_2O (2239)
$N_2 + CO_2$ (100 : 1)	OCN (1933)[b]
	NO (1874)
	N_2O (2235)
$N_2 + O_2$ (100 : 1)	NO (1874)
	N_2O (2235)
	NO_2 (1615)
$N_2 + CH_4$ (100 : 1)	CH_3 (611)[c]
	NH_2 (1499)[d]
	NH_3 (971)
$N_2 + H_2O$ (100 : 1)	HN_3 (2151)[e]
$N_2 + NH_3$ (100 : 1)	HN_3 (2151)[e]
$N_2 + CH_3OH$ (100 : 1)	HNCO (2266)
	NO (1874)

[a] Values in parentheses represent positions (in cm^{-1}).

[b] Milligan & Jacox 1967b.

[c] Milligan & Jacox 1967a.

[d] Milligan & Jacox 1965.

[e] Moore & Rosengren 1966.

Where no reference is given in Table 2, the product was identified by comparison with an ice of known composition. The FWHM of N_3 in pure N_2 was 1.2 cm^{-1}, with a mean value of 1.8 ± 0.3 cm^{-1} for the mixtures.

As checks on the N_3 assignment, experiments were done with mixtures containing isotopically labeled molecules. In each experiment an N_3 band was seen at the expected position. The mixtures studied were $N_2 + {}^{13}CH_4$, $N_2 + CD_4$, $N_2 + C_2D_2$, ${}^{15}N_2 + CH_4$, ${}^{15}N_2 + C_2H_6$, and ${}^{15}N_2 + O_2$.

3.3. *UV Photolysis Experiments*

In contrast to our radiation results, when we photolyzed solid N_2 or N_2-containing mixtures with UV light from a hydrogen discharge lamp, the 1657 cm^{-1} band of N_3 was never observed (exposure times of 1–2 hr), and no green emissions were seen on warming photolyzed solid N_2 or N_2-containing ices. Our IR work agrees with previous studies of photolyzed N_2 (Gerakines, Schutte, & Ehrenfreund 1996) and N_2 mixtures (Bohn et al. 1994) done in other laboratories. Moreover, during the past 40 years, thousands of experiments in many laboratories have involved UV photolysis of N_2 matrices. To the best of our knowledge, none of these have resulted in publication of an N_3 IR band.

4. DISCUSSION

4.1. *Formation of* N_3 *in Laboratory Ices*

The IR spectra of ion-irradiated N_2 in Figure 1 leave no doubt that N_3 was produced. The most reasonable explanation for N_3 synthesis is that during radiolysis N_2 molecules undergo dissociation to produce N atoms, some of which react with nearby N_2 molecules to form N_3 radicals:

$$N_2 \rightarrow N + N \ ,$$
$$N + N_2 \rightarrow N_3 \ .$$

The green glow seen on warming irradiated N_2 is almost certainly the ${}^2D - {}^4S$ emission of N atoms reported by Pevron & Broida (1959), lending support to the above reactions. These reactions also imply that in a ${}^{14}N_2 + {}^{15}N_2$ mixture only four of the six possible N_3 isotopomers are expected according to

$${}^{14}N_2 \rightarrow {}^{14}N + {}^{14}N \ ,$$
$${}^{14}N + {}^{14}N_2 \rightarrow {}^{14}N_3 \ ,$$
$${}^{14}N + {}^{15}N_2 \rightarrow {}^{14}N{}^{15}N{}^{15}N \ ,$$

and

$${}^{15}N_2 \rightarrow {}^{15}N + {}^{15}N \ ,$$
$${}^{15}N + {}^{14}N_2 \rightarrow {}^{15}N{}^{14}N{}^{14}N \ ,$$
$${}^{15}N + {}^{15}N_2 \rightarrow {}^{15}N_3 \ ,$$

and indeed only the four expected N_3 isotopomers were observed (vide supra).

Our failure to observe N_3 in UV-photolyzed N_2-containing ices can be attributed to the lack of N atom formation in the photolytic process, which is largely due to the high bond energy of N_2 (9.8 eV). However, this is probably not the entire reason for the rather limited chemistry of N_2. The bond energy of CO (11.1 eV) is slightly higher than that of N_2, yet CO has a much richer solid-state photochemistry

(Gerakines et al. 1996) involving the formation of C atoms to give C_2O and higher suboxides beginning with the following reactions:

$$\begin{aligned} CO &\rightarrow CO^* , \\ CO^* + CO &\rightarrow CO_2 + C , \\ C + CO &\rightarrow C_2O , \\ C_2O + CO &\rightarrow C_3O_2 . \end{aligned}$$

Undoubtedly the existence of a highly stable product molecule, CO_2, helps drive these reactions, while the lack of a comparably stable product in pure N_2 limits the molecules synthesized, even with radiolysis. Along these lines, while we cannot say that *no* N_3 is produced in UV-photolyzed N_2, we can say that its abundance is so small as to be essentially undetectable by conventional IR spectroscopy.

Table 1 shows that the presence of a second or third molecule at the 1% level did not prevent the formation of N_3 in irradiated N_2. However, as the abundance of the second molecule was raised, the decrease in the relative abundance of N_2 probably reduced the efficiency of N atom reactions, lowering the N_3 yield. This dilution effect was seen, for example, in the $N_2 + CH_4 + CO$ experiments of Table 1, where the N_3 band was easily observed in the 100 : 1 : 1 ice but became progressively weaker, with lower initial N_2, until it was not seen at all in the 1 : 1 : 1 mixture.

The presence of molecules other than N_2 in a sample allowed additional reactions to occur, lowering the final N_3 abundance. The weakness of the N_3 band in $N_2 + CO$ (1 : 1), as well as its absence in $N_2 + CO_2$ (1 : 1), was probably due to N atom scavenging by the carbon oxides. The appropriate reactions for the $N_2 + CO$ (1 : 1) mixture are

$$\begin{aligned} N_2 &\rightarrow N + N , \\ N + CO &\rightarrow OCN , \end{aligned}$$

which explains the OCN radical observed. For the $N_2 + CO_2$ (1 : 1) mixture, the reactions

$$\begin{aligned} N_2 &\rightarrow N + N , \\ N + CO_2 &\rightarrow NO + CO \end{aligned}$$

explain the observation of the NO radical at the expense of N_3. The NH_2 and NH_3 seen in irradiated $N_2 + CH_4$ mixtures imply that N atoms reacted with CH_4, probably via H atom abstraction through

$$N + CH_4 \rightarrow NH + CH_3$$

to make NH and CH_3 radicals. A similar reaction in $N_2 + NH_3$ mixtures

$$N + NH_3 \rightarrow NH + NH_2$$

will generate NH radicals, which react by

$$NH + N_2 \rightarrow HN_3$$

to make HN_3 (Moore & Pimentel 1964).

Quantitative comparisons among the ices studied are hampered by the lack of appropriate band strengths for the N_3 radical in various mixtures. If the intrinsic band strength, A, in cm molecule^{-1}, were known for N_3, then dividing a measured N_3 band area, in cm^{-1}, by A would give a column density for N_3 in units of molecules cm^{-2}:

$$\text{column density}\left(\text{molecules cm}^{-2}\right) = \frac{\text{IR band area}\left(\text{cm}^{-1}\right)}{A\left(\text{cm molecule}^{-1}\right)} .$$

To approximate A(1657 cm^{-1}) for N_3, we assume that the maximum concentration of N_3 radicals in ion-irradiated N_2 is ~1%, a number that is, if anything, overly generous (Jackson 1960). A typical experiment with pure N_2 gave band areas of N_3 and N_2 in roughly a 4 : 1 ratio, so assuming $A(N_2,\ 2328\ \text{cm}^{-1}) = 1.8 \times 10^{-22}$ cm molecule^{-1} (Sandford et al. 2001), we calculate $A(N_3,\ 1657\ \text{cm}^{-1}) = 7.2 \times 10^{-20}$ cm molecule^{-1}. This value will be larger if the actual N_3 concentration is less than 1% of the ice. Furthermore, $A(N_3,\ 1657\ \text{cm}^{-1})$ may well be sensitive to ice composition, as was recently shown for the N_2 band at 2328 cm^{-1} by Sandford et al. (2001).

4.2. *Potential Value of* N_3 *for Astronomical Observations*

The radiation doses used to reach final "equilibrium" N_3 concentrations in our experiments are only a few eV molecule^{-1}, values comparable to those in certain astronomical environments. For instance, the radiation dose to the outer 0.02 μm of an ice grain in a cold, dense interstellar cloud is estimated to be ~3 eV molecule^{-1} over 10^7 yr (Moore et al. 2001). For Oort cloud comets, Strazzulla & Johnson (1991) have calculated that a dose of ~5 eV molecule^{-1} is received by ices 5 m beneath a nuclear surface, integrated over the age of the solar system, with higher doses at smaller depths and vice versa. Finally, for Pluto, a Kuiper belt object, the cosmic radiation dose is estimated to be ~160 eV molecule^{-1} at ~10 cm from the surface, integrated over the age of the solar system (Johnson 1989). Thus, N_2-rich regions on Pluto, on or beneath a cometary nucleus, or on an interstellar grain are expected to receive sufficient radiation to produce N_3 radicals. It is interesting to note that regions of high N_2 abundance are suggested by observations of both Pluto (Douté et al. 1999) and Triton (Quirico et al. 1999) and that interstellar ices rich in N_2 are suggested by *Infrared Space Observatory* (*ISO*) observations (Ehrenfreund et al. 1998).

Since N_3 is produced by ion irradiation of N_2 and N_2-rich ices, but not by far-UV photolysis, an astronomical observation of the 1657 cm^{-1} band would be strong evidence that an ice had been ion irradiated. Our experiments imply that the strength of any observed N_3 feature will depend on the ice's temperature, composition, and radiation dose received. The most favorable cases for detection will be in highly nonpolar ices (N_2-rich) below 30 K. Dark interstellar clouds come to mind, but subsurface ices on Kuiper belt objects are also in a cold, dark environment and experience ion irradiation. N_3 will form in such regions, although detection with current technology would be challenging, to say the least.

A second potential application of our work concerns the so-called missing nitrogen problem, namely, the discrepancy between the expected and measured abundances of nitrogen species in interstellar ices. To date only NH_3 and OCN^- are known interstellar solid-phase nitrogen contributors. Solid-phase N_2 is expected in nonpolar ice mantles on interstellar grains, but it has not yet been observed, and the chances of direct IR detection are slim as a result of the N_2 band's intrinsic weakness. It is known that the strength of the N_2 band at 2328 cm^{-1} is significantly enhanced by the presence of CO_2 (Sandford et al. 2001) in an ice, but even so CO_2 has a strongly interfering band nearby at 2343 cm^{-1}. Our experiments show that the intensity of the N_3 1657 cm^{-1} absorption can easily exceed that of the N_2 2328 cm^{-1} band, while lying in a region free from CO_2 interference. This suggests that astronomical observation of N_3 could be a way to infer solid-phase molecular nitrogen.

The minimum number of N_3 radicals for observation will depend, of course, on the signal-to-noise ratio and sensitivity of one's detector. As a rough estimate of a detection limit, we doubled the area of a noise feature near 1657 cm^{-1} in an *ISO* spectrum of the young stellar object W33A (Gibb et al. 2000) and then divided by our $A(N_3,\ 1657\ cm^{-1}) = 7.2 \times 10^{-20}$ cm $molecule^{-1}$. This gives an N_3 column density of 5×10^{18} molecules cm^{-2} over the line of sight to W33A, compared to the 11×10^{18} molecule cm^{-2} abundance reported for H_2O (Gibb et al. 2000). Clearly our experiments show that N_3 radicals form by ice irradiation, but their detection, as with N_2 itself, will be challenging. N_2 and N_3 certainly are candidates for future IR missions where higher signal-to-noise ratio measurements are anticipated, especially for targets of high flux levels.

4.3. *Other Nonpolar Molecules*

Since N_2 distinguishes between UV and ion processing, one wonders if the same might be true for other astronomical (suspected or identified) nonpolar molecules, such as O_2 and CO_2. Molecular oxygen (O_2) forms ozone (O_3) on both photolysis and radiolysis, and so it is not promising. Neither is CO_2, which makes CO and CO_3 on both photolysis and radiolysis (Gerakines & Moore 2002 and references therein).

5. SUMMARY AND CONCLUSIONS

In this paper we have shown that the N_3 radical (azide) is detectable by IR spectroscopy after ion irradiation of N_2 and N_2-rich mixtures, but not after far-UV photolysis. Suggested applications are that N_3 may be both an indicator of radiation exposure of astronomical ices and a tracer of solid-phase N_2.

Additional work is desirable to further characterize the N_3 radical in ion-irradiated mixtures. Future experiments will be aimed toward a better understanding of the role of temperature on the formation of N_3 and the role of both temperature and UV exposure on the destruction of N_3. Finally, an accurate band strength is needed for comparisons of N_3 yields among various ices.

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