Last changed: September 25, 2018

N_2 Chemistry in Interstellar and Planetary Ices: Radiation-Driven Oxidation

Short title: Radiation-chemical N_2 oxidation in interstellar and planetary ices

by

Reggie L. Hudson[1,2]

Submitted to *The Astrophysical Journal*

---

[1] Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, Maryland, 20771 USA

[2] E-mail: Reggie.Hudson@NASA.gov

Abstract

As part of our work on nitrogen-rich ices, the infrared (IR) spectra and band strengths used in a recent paper to identify and quantify radiation-induced changes in a $N_2 + H_2O$ ice near 15 K are examined, along with reports of (i) a chemical tracer for $N_2 + H_2O$ ices, (ii) a new IR feature of solid N_2, and (iii) a striking ^{15}N isotopic enrichment. Problems are found for each IR band strength used and for each of the three claims made, to the extent that none is supported by the results presented to date. In contrast, new work presented here, combined with several older investigations, strongly supports the formation of di- and triatomic nitrogen oxides in irradiated N_2-rich ices. Observations and trends in the chemistry of N_2-rich icy solids are described and conclusions are drawn. A considerable amount of material from previous chemical studies of N_2-rich systems, spanning more than a century, is brought together for the first time and used to examine the chemistry of N_2-rich ices in extraterrestrial environments. Needs are identified and suggestions made for future studies of N_2-rich interstellar and planetary ice analogs

Key words: Astrochemistry; infrared: ISM; ISM: molecules; molecular data; astrobiology

1. Introduction

The use of laboratory methods to study the chemistry of ices in the the interstellar medium (ISM) and the outer Solar System is well-established and supported by an extensive set of publications. In our laboratory group, we have focused on reaction chemistry applicable to extraterrestrial ices and on the application of standard spectroscopic methods to identify and quantify the many solid-phase molecules and ions of astronomical interest. However, the diversity of icy solids and the range of astronomical environments make it unrealistic and tedious to attempt to examine all possible combinations of temperature, composition, molecular type, radiation doses, and radiation forms in terrestrial laboratories, and so it is imperative to seek patterns and trends in the chemistry of icy materials. As an example, some years ago we examined radiation-chemical reactions in cometary and interstellar ice analogs, showing how unsaturated compounds could be reduced to their saturated counterparts by solid-state radiolysis, such as the conversion of C_2H_2 into C_2H_6 (Hudson & Moore 1997) and CO into CH_3OH (Hudson & Moore 1999). More recently we have turned to radiation-driven oxidations, such as the conversion of solid propene into propylene oxide (Hudson et al. 2017a), which has been detected in the ISM (McGuire et al. 2016), and the low-temperature synthesis of aldehydes and ketones from alcohol-containing ices (Hudson & Moore 2018).

Background information on the radiation chemistry of icy solids is available in many earlier papers from our research group (e.g., Moore 1999; Hudson et al. 2001), from publications by other workers (e.g., Strazzulla 1998; Bennett et al. 2007; Bennett

et al. 2013), and from the many references therein, and so only a summary is given here. Cosmic radiation, magnetospheric radiation around planets, and stellar (including solar) far-UV photons and solar energetic particles all act to drive chemical reactions at low temperatures. In the case of cosmic and other magnetospheric radiation (particle radiations), the dominant components are hydrogen and helium ions. As each ion passes through an icy solid, it produces a track of ionizations and excitations. The ionizations generate secondary electrons that can continue to generate chemical change through a variety of reactions. In all cases, the initial ion's energy will be degraded and, in ices that are sufficiently thick, the ion will be trapped (thermalized) and implanted at the end of its trail. It is important to appreciate that the chemical products made by various radiations acting on extraterrestrial ices are largely the result of secondary electrons and that while reaction yields and spatial distributions of products can vary, the identities of those reaction products are expected to be largely the same across a wide variety of radiation types and energies. This makes it difficult, if not impossible, to distinguish among ices that have been irradiated by, for example, keV e^-, X- and γ-rays, and MeV H^+, He^+, and higher-mass ions.

Although most of our laboratory work on astronomical ices and radiation chemistry has focused on solids rich in highly polar molecules, such as H_2O, H_2O_2, alcohols, and nitriles, some astronomical ices are dominated by non-polar molecules. Specifically, Triton, Pluto, and Eris have surface ices rich in N_2 (Cruikshank et al. 1984; Owen et al. 1993; Tegler et al. 2012), and ice mantles on interstellar grains are thought to have regions that are deficient in H_2O-ice and rich in non-polar (or weakly polar) species, such as N_2, O_2, and CO (Ehrenfreund et al. 1998; Rosu-Finsen et al. 2016).

Our earlier work with such solids examined proton-irradiated N_2 + CH_4 and N_2 + CH_4 + CO ices to demonstrate the formation of both HCN and HNC (Moore & Hudson 2003). This soon was followed by a study of several organic nitriles in solid N_2 to demonstrate production of ketenimine (Hudson & Moore 2004), which subsequently was found in the ISM (Lovas et al. 2006). However, oxidation in nitrogen-rich ices has received relatively little attention, and so we recently have examined such reactions for applications to N_2-containing interstellar ices and to outer Solar-System bodies, such as trans-Neptunian objects (TNOs).

One example of the use of ionizing radiation to study N_2-rich ices, from a laboratory other than ours, is the work of de Barros et al. (2015) on the chemical changes produced by irradiating N_2 + H_2O ice at 15 K with 40 MeV $^{58}Ni^{11+}$. However, while comparing our work to that study, which we abbreviate as dB15, we encountered a large number of questionable items, about a dozen of which are described in our Appendix A. Instead of addressing each of them and trying to determine which are typographical errors and which are not, here we focus on the assignments of IR bands of reaction products reported by dB15 and on three claims in that paper that are, if valid, of considerable astrochemical significance. Note that the generation of a large amount of new numerical information based on reference data of questionable relevance or accuracy is specifically avoided. A primary goal is to extract results from dB15 that can be combined with published work from several laboratories, including new results presented here, to uncover some points of commonality in studies of radiolytic oxidation in N_2-rich icy solids and to identify some areas where new work is needed. A strong emphasis is placed on using a variety of spectroscopic methods to firmly assign

reaction products since without robust spectral assignments it will be difficult to move forward in our understanding of the chemistry of N_2-rich ices.

2. Laboratory Methods

The laboratory work for this paper used *in situ* mid-infrared spectroscopy to reveal chemical and physical changes in icy solids irradiated near 15 K by a 1-MeV H^+ beam. Ices were grown on a pre-cooled aluminum or gold substrate inside a vacuum chamber interfaced to a Van de Graaff accelerator, the source of the proton beam (current ~ 0.1 μA). An infrared (IR) spectrum of the sample was collected by reflecting the IR beam off the sample and underlying substrate (range = 5000 - 650 cm^{-1}, resolution = 0.5 cm^{-1}, 100 scans per spectrum). See our group's recent papers and references therein for details of our spectroscopic, cryogenic, vacuum, and radiation equipment (e.g., Hudson et al. 2017b; Hudson & Moore 2018). In all cases, ice thicknesses were smaller than the range of the incident radiation beam (~33 μm), ensuring irradiation throughout each ice sample. As in the past, the use of band strengths to determine the thickness of each of our ices has been avoided in favor of the method of interference fringes as a more-direct measurement (e.g., Tempelmeyer & Mills 1968; Hudson et al. 2017b). The index of refraction of our N_2-rich ices was taken as n = 1.22 (Satorre et al. 2008). Sigma Aldrich (USA) was the source of all reagents used, including those that were isotopically enriched.

To support our work, the electronic stopping power (S_{el}) of solid N_2 was calculated with the SRIM package of Ziegler et al. (1985; 2013 version), using a density of $\rho(N_2)$ = 0.94 g cm^{-3} (Satorre et al. 2008) and a compound correction of 1 (Ziegler &

Manoyan 1988). The results are, to two significant figures, S_{el} = 20 keV μm^{-1} for 1 MeV H^+ and S_{el} = 3600 keV μm^{-1} for the 40 MeV $^{58}Ni^{11+}$ of de Barros et al. (2015). The dose in eV molecule^{-1} received by an ice is found from the product "m S_{el} F", where m is the mass of a sample molecule (or average mass), S_{el} is the sample's electronic stopping power, and F is the flux of incident ions on the sample, typically with units of ions cm^{-2} sec^{-1}. This means that an incident proton fluence of 1.0 × 10^{14} H^+ cm^{-2} on our ices, all of which are N_2 rich, is equivalent to an absorbed dose of about 3.37 MGray, 337 Mrad, and 0.98 eV N_2-molecule^{-1}. Nuclear stopping powers are about 0.1% of S_{el} for our ices, and so are ignored.

3. Results

Before presenting new data from our own laboratory, we first consider some results from the paper of de Barros et al. (2015) that concern the identification and quantification of reactants and products in the irradiation of an N_2-rich ice sample. We show that significant questions accompany some of the results described there. However, and more positively, we also show that there are important common points between other results in that paper, some findings in other laboratories, and new experiments that we report here.

3.1. Reactant Column Densities

Figure 1 of dB15 shows IR spectra of the authors' ice sample at 15 K before and after irradiation. Three reactants, N_2, H_2O, and CO_2, were identified and quantified by integrating selected IR features and then using IR band strengths (denoted *A*) to

calculate column densities. More specifically, after integrating an absorbance band for the molecule of interest, and converting to an optical depth scale by multiplying the result by ln(10) = 2.303, one then divides the result by *A* for the IR band to get a molecular column density from the following equation:

$$N = \frac{2.303 \int_{band} (Absorbance)\ d\tilde{\nu}}{A}$$

This is a standard method, but for accurate results it requires the availability of appropriate band strengths (*A*) for the molecular components. With this in mind, we consider each of the three reactants of dB15.

The spectrum of the authors' unirradiated N_2 + H_2O sample resembles that published by Ehrenfreund et al. (1996), with the exception of a large peak in the ν_3 region of CO_2 (~2340 cm^{-1}). The unstated assumption in dB15 was that the band strength of the ν_3 feature of crystalline CO_2 (Yamada & Person 1964) was applicable to CO_2 trapped in an N_2 + H_2O ice, the result being a calculated N_{CO2} = 4.5 × 10^{14} molecules cm^{-2} for the ice's initial CO_2 column density. A different way to calculate CO_2 column density is to use IR peak heights. Figure 2 of Yamada & Person 1964) shows the spectrum of a CO_2 ice with a thickness h = 2.39 × 10^{-5} cm (0.239 μm) and a peak absorbance of ~1.35 near 2340 cm^{-1}, from which an absorption coefficient of α = (2.303 × 1.35 / h) = 1.30 × 10^5 cm^{-1} is found. Returning to Figure 1 of dB15, the CO_2 peak's height is about 0.32 on an absorbance scale so that the ice's equivalent CO_2 thickness is h = (2.303 × 0.32 / α) = 5.7 × 10^{-6} cm (~0.057 μm). Using a CO_2 mass density of ρ = 1.3 g cm^{-3} (Satorre et al. 2008), the equivalent initial column density of carbon dioxide in dB15 is estimated to be N_{CO2} = h ρ N_A / 44 = 1.0 × 10^{17} molecules cm^{-2}, where N_A =

6.022×10^{23} CO_2 molecules $mole^{-1}$. This N_{CO2} value based on a peak height is about 200 times larger than the 4.5×10^{14} molecules cm^{-2} that was based on band area. A similar calculation with the optical constants of Hudgins et al. (1993) leads to a discrepancy of a factor of about 400.

Turning to N_2, an estimate for the band strength $A(N_2, 2328\ cm^{-1})$ is made in dB15, and the complication of H_2O-ice being present is recognized. However, for an $N_2 + H_2O + CO_2$ ice, additional difficulties arise because the strength of the N_2 fundamental near 2328 cm^{-1} depends strongly on the presence of CO_2 (Fredin et al. 1974). This means that given the large uncertainty in the CO_2 abundance just described, the choice for $A(N_2, 2328\ cm^{-1})$ also is highly uncertain. For a CO_2 column density that is uncertain by a factor of 200 (see above), Table 2 of Sandford et al. (2001) shows that $A(N_2, 2328\ cm^{-1})$ also can be off by about that much, drastically altering the calculated initial N_2 column density

Admittedly these comments on the initial column densities for CO_2 and N_2 involve rough estimates, but the fact that they suggest values two orders of magnitude greater than those in dB15 is disconcerting. The differences might be from the choice of band strengths in dB15, the range over which IR bands were integrated (unstated), or the method of deconvolving bands that overlap (also unstated). The point is that such estimates, whether based on band areas or peak heights, require accurate band strengths or absorption coefficients, respectively, from appropriate standards. It is not clear that such laboratory data are available for $N_2 + H_2O$ or $N_2 + H_2O + CO_2$ ices. Moreover, without accurate reactant abundances it is impossible to use the method of dB15 to extract quantitative kinetic information for radiation products.

The estimate for the initial H_2O column density in dB15 also is uncertain. The band strengths used can be traced to the work of Hagen et al. (1981) on amorphous H_2O, but it is not clear to what extent their values, and specifically the band strength of the 1655.2 cm^{-1} feature of H_2O-ice, apply to H_2O trapped in N_2. There also is an inconsistency between the abundance ratio (N_2 / H_2O) = 10, from the abstract and Figure 1 of dB15, and the (N_2 / H_2O) ≈ 4.26, calculated from data in the authors' Table 3.

The other spectrum in Figure 1 of dB15 is for the authors' N_2 + H_2O ice after irradiation at 15 K. Our own Figure 1 compares that post-irradiation spectrum to one of amorphous H_2O-ice at a similar temperature. Except for four sharp peaks and one broad feature near 1400 cm^{-1} in the upper trace, the two spectra are essentially identical. A strong, broad band at 3300 cm^{-1} is easily seen in both, as are weaker broad features at 1600 and 800 cm^{-1}. Taking the absorbance of the peak at 3300 cm^{-1} in the upper trace of our Figure 1 as 0.44, and assuming it is from amorphous H_2O-ice, the post-irradiation column density of H_2O can be estimated with the method already applied to CO_2. The optical constant k(H_2O, 3300 cm^{-1}) of Hudgins et al (1993) gives α = 18,000 cm^{-1}, which yields $N_{H2O} \approx 1.9 \times 10^{18}$ H_2O molecules cm^{-2}, about 380 times greater than the $N_{H2O} = 5 \times 10^{15}$ H_2O molecules cm^{-2} listed in Table 3 of dB15, and about 8 times larger than water's stated initial column density. One explanation for this discrepancy is that contamination from background or atmospheric CO_2 and H_2O in those experiments might have been greater than realized. This possibility could have been addressed by irradiating solid N_2 with no H_2O added (a control experiment) or through experiments using D_2O, but no such work was reported.

3.2. Identifications and Abundances of Reaction Products

Having illustrated some of the difficulties in determining abundances of reactants in low-temperature ices, we turn to reaction products observed in ion-irradiated N_2 + H_2O ices by de Barros et al. (2015). Here too there are problems with abundances.

Thirteen reaction products are given in Table 2 of dB15, with ten of them being quantified in later tables and figures. Two spectral peaks were shown for N_2O, and laboratory data were cited for their positions, so that the N_2O assignment seems secure. Only one NO peak was observed, corresponding to the molecule's fundamental vibration, and only one was reported for NO_2, but since both peaks are rather sharp, well defined, and well documented then their assignments can be taken as correct. Assignments of the remaining seven quantified products are more difficult. The azide radical (N_3) assignment might be correct, but see our Appendix C for questions about it. Ozone (O_3) is claimed as a product of irradiated N_2 + H_2O, but only one IR peak was reported. Given the ease with which irradiated CO_2 produces ozone, that spectral assignment may be correct, but the O_3 might have come from CO_2 contamination and not from N_2 + H_2O. Experiments using $H_2{}^{18}O$ could decide, but none were reported.

The remaining five quantified nitrogen-oxygen products are NO_3, N_2O_2, N_2O_3, N_2O_4, and N_2O_5. Their spectral assignments in dB15 tend to be based on single peaks that are weak, broad, and overlapping with other bands, and the citation often used for their IR positions and band strengths is a density-functional study of gas-phase nitrogen oxides (Stirling et al. 1994) that has not been checked for use with solid-phase data. Formation of other oxides is expected if NO, NO_2, and N_2O are present, but without

additional support the authors' assignments to NO_3, N_2O_2, N_2O_3, N_2O_4, and N_2O_5 in dB15 are not secure and must be rejected.

The ten quantified products in Table 2 of dB15 also are listed in our own Table 1, where it can be seen that there are significant problems that extend beyond peak positions. The problems include misidentifications (e.g., N_3 vs. N_3^+, Dyke et al. 1982), information missing from the papers cited (e.g., N_2O_2, N_2O_4), disagreement of spectral positions with the literature (e.g., NO_3, N_2O_5), mistakes in copying from the literature (e.g., NO_2, N_2O), and the use of gas-phase band strengths to interpret solid-phase results (many). Here we consider band strengths of just two compounds, the first and last ones listed in Table 1.

The IR band strength of N_3 used by dB15 is particularly important as it influences the authors' claim that N_3 is the most-abundant product in their experiments. However, the band strength selected is from a reflection-transmission method and is not readily transferrable to a conventional transmission measurement (Hudson & Moore 2002). The result was $A(N_3, 1657\ cm^{-1}) = 7.2 \times 10^{-20}$ cm molecule^{-1}, which contrasts sharply with a later value of 4.0×10^{-17} cm molecule^{-1}, calculated with density-functional methods (Jamieson & Kaiser 2007). Depending on which value is selected, N_3 can be interpreted as either one of the more abundant or one of the least abundant products in irradiated $N_2 + H_2O$ ices.

The quantification of ozone (O_3) is another problem. The ozone band strength in Table 2 of dB15 is $A(O_3, 1039.7\ cm^{-1}) = 1.40 \times 10^{-17}$ cm molecule^{-1}, but details cannot be found in the two papers cited. Loeffler et al. (2006) reported only an effective A value for the experiments they carried out with a reflection-transmission arrangement.

The Sicilia et al. (2012) paper cited by dB15 gives only "Smith et al. (1985)" in a table as the source of the O_3 band strength, with no citation in the list of references. Our own literature search eventually determined that Smith et al. (1985) is a book chapter that cites even earlier work for $A(O_3, 1039.7\ cm^{-1})$. Additional searching finally revealed the original reference to be Secroun et al. (1981), who published the result of a gas-phase measurement for O_3 at 300 K. Our calculation from the latter paper gives $A(O_3, 1039.7\ cm^{-1}) = 1.48 \times 10^{-17}$ cm molecule^{-1}, slightly higher than the value in dB15.

To summarize, of the ten reaction products quantified in Table 2 of dB15, the NO, NO_2, and N_2O assignments seem secure. The N_3 and O_3 assignments also are probably correct, although a few questions remain. The remaining five assignments are questionable due to a lack of supporting data. Of the ten band strengths used for radiation products, eight are suspect as they are from calculations on gas-phase molecules and have not been checked for use with ices, a ninth seems to be miscopied, and a tenth is from a different type of measurement. We conclude that the band strengths used in dB15 for reaction products are on such uncertain ground that their application to kinetic data and reaction yields in ices is highly questionable, significantly lowering the accuracy and value of that paper's extensive numerical results (i.e., cross sections, abundances, and reaction yields). Also, without accurate abundances one cannot expect calculations of elemental budgets to yield meaningful results.

3.3. Proposed Tracers for Astronomical CO_2 and $N_2 + H_2O$

Among the conclusions drawn by dB15 (page 12) is "Comparing the current results with those of Boduch et al. (2012), it seems that ozone is a good indicator for the

presence of molecular oxygen, while nitrogen oxides give the best indication of the presence of molecular nitrogen mixed with water." Ozone certainly is made from molecular oxygen, but other sources exist, including CO_2. As for nitrogen oxides, our Figure 2 shows IR spectra we recorded before and after the 1-MeV H^+ irradiation of N_2 + O_2 (100:1) at 12 K. The spectrum of the irradiated ice (upper trace) shows sharp peaks from the formation of N_2O (2235 cm^{-1}), NO (1874 cm^{-1}), NO_2 (1615 cm^{-1}), and O_3 (1042 cm^{-1}). Less obvious are smaller peaks for N_3 (1657 cm^{-1}) and O_3 (2116 and 704 cm^{-1}). In Table 2 we list IR assignments for N_3, NO, NO_2, N_2O, and N_2O_2, supported by $^{15}N_2$ experiments and reference spectra recorded in our laboratory. Literature results are included for comparison. – Our O_3 assignment in Figure 2 was confirmed in a similar way, multiple O_3 peaks being observed and with positions that agreed with reference spectra we recorded. – From all of these observations we conclude that nitrogen oxides observed in an irradiated N_2-rich ice cannot be used to infer a previous composition of N_2 + H_2O either in a laboratory or an astronomical environment.

Identifications of the higher nitrogen oxides, N_2O_3, N_2O_4, and N_2O_5, in our experiments and those of others, are more problematic as each compound absorbs in the 1860 - 1620, 1320 - 1220, and 850 - 650 cm^{-1} regions marked by the asterisks in Figure 2. Our Figure 3 shows an example of the spectral confusion one meets. Going from spectrum (a) before irradiation to (b) after the first dose, three sharp peaks of comparable height are seen. These are assigned to N_2O_3, N_2O, and N_2O_4, with a smaller feature for N_2O_5, based mainly on ^{15}N isotopic shifts observed in an $^{15}N_2$ + O_2 experiment and comparisons with the literature. Results for these three oxides are

summarized in Table 3, but without appropriate reference spectra, the assignments are slightly more tentative than those in our Table 2. Also, the overlap of the many IR bands of these molecules makes some of their ^{15}N shifts difficult to measure. Four peaks are marked with numbers in Figure 3, but their assignments would be even less certain, such as the possibility that (iii) is from iso-N_2O_4 and (iv) is from NO_2^-. Our goal was not to assign every IR peak, but rather to obtain evidence that N_2O_3, N_2O_4, and N_2O_5 are radiation products. Future work will address assignments to specific isomers, such as *cis*- and *trans*-N_2O_2, asymmetric and symmetric N_2O_3, N_2O_4 and iso-N_2O_4, and ions such as NO^+, NO_2^+, NO_2^-, and NO_3^- (e.g., Terenishi & Decius 1954; Forney et al. 1993). However, it is clear that prolonged irradiation of N_2-rich ices can produce a wide range of nitrogen oxides.

3.4. Isotopic Enrichment of ^{15}N and the IR Spectrum of N_2

Two other results reported by de Barros et al. (2015) concern the mid-infrared spectrum of N_2 and a striking ^{15}N isotopic enrichment produced by ion irradiation of an N_2-rich ice. See our appendices B and C for a detailed analyses of these results.

4. Discussion

From the preceding section we conclude that many of the IR band strengths used to quantify product yields in such solids are of questionable relevance, having never been checked against solid-phase samples. However, our laboratory work strongly supports the claims of de Barros et al. (2015) and others of N_3, NO, NO_2, and N_2O formation by radiation processes. Here we first address reaction chemistry in N_2-

rich ices and follow with some comments on reaction products, radiation doses, chemical kinetics, and astronomical connections.

4.1. Reaction Chemistry in N_2-Rich Ices

Suffice it to say that the chemistry of irradiated N_2-rich mixtures is complex and its study has a long history. Perhaps the earliest relevant observation is that of Soddy (1911) who noted the formation of N_2O in irradiated air. However, the chemical evolution of irradiated $N_2 + O_2$ gas mixtures seems to have first been investigated by Lind & Bardwell (1929) who found that if sufficient O_2 is present then nitrogen oxidation will transform N_2 into NO and then into NO_2. If H_2O is present then it will convert NO_2 into nitric acid, HNO_3. Table 4 shows the rise in nitrogen oxidation number for this $N_2 \rightarrow NO \rightarrow NO_2 \rightarrow HNO_3$ sequence. In the late 1950s, Jones (1959) identified and quantified both NO_2 and N_2O as radiation products of $N_2 + O_2 + H_2O$ mixtures, and Harteck & Dondes (1958) reported the radiolytic formation of N_2O_5. By the 1970s, Willis and co-workers were able to list dozens of reactions in their papers on the irradiation of nitrogen-oxygen mixtures, many such studies being motivated by applications to nuclear facilities (Willis et al. 1970; Willis & Boyd 1976).

Despite all of this earlier work, it is not obvious *a priori* which of the many reactions occurring in irradiated N_2-rich gases are most relevant to the ices we have studied, but some processes seem beyond question. It also seems clear that both ionic and free-radical reactions are important and that the restricting environment of the solid state (i.e., the cage effect) will encourage more recombinations than in the gas phase.

A hallmark of radiation chemistry is that the action of the ionizing agent is non-specific, and so incident radiation acting on an $N_2 + O_2$ mixture will influence both components. In our irradiated ices, since N_2 is the more-abundant component then the nitrogen molecular ion N_2^+ is expected to be one a primary radiation products. Its neutralization can regenerate N_2 and, if that event is sufficiently energetic, yield N atoms. See reactions (1) - (3) below.

$$N_2 \rightarrow N_2^+ + e^- \quad (1)$$

$$N_2^+ + e^- \rightarrow N_2^* \rightarrow N_2 \quad (2)$$

$$N_2^+ + e^- \rightarrow N_2^* \rightarrow N + N \quad (3)$$

Accompanying (2) and (3) will be the reaction of N_2^+ with the O_2 present, giving nitric oxide (NO).

$$N_2^+ + O_2 \rightarrow NO + NO^+ \quad (4)$$

Since the ionization energy of N_2 is slightly higher than that of O_2, a more accurate sequence might be (5):

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+ \rightarrow NO + NO^+ \quad (5)$$

Reaction of the N_2^+ made in (1) with the N_2 matrix will produce the nitrogen dimer radical cation, N_4^+ (Varney 1953). Many reactions other than neutralization can follow, one being the combination of N_4^+ with an O_2 anion (O_2^-) to give both N_3 and NO_2 as follows:

$$N_2^+ + N_2 \rightarrow N_4^+ \quad (6)$$

$$O_2 + e^- \rightarrow O_2^- \quad (7)$$

$$N_4^+ + O_2^- \rightarrow N_3 + NO_2 \quad (8)$$

The neutral molecular products of reactions (4) - (8), other than N_2, are N_3, NO, and NO_2, and are easily seen in our spectra. Note that the positions of the strongest $^{14}N_4^+$ and $^{15}N_4^+$ infrared features are near the most intense IR peaks for $^{14}N_2O$ and $^{15}N_2O$, respectively, making the direct infrared detection of N_4^+ challenging (Thompson & Jacox 1990; Savchenko et al. 2014).

The preceding is based on reactions involving ions, but neutral free radicals also are important. As already stated, during an irradiation with MeV ions a track of excitations and ionizations will be produced by each ion as it travels through an ice, generating secondary electrons that produce their own trails of chemical change. The excitation and dissociation of N_2 represented as

$$N_2 \rightarrow N_2^* \rightarrow N + N \quad (9)$$

can be followed by

$$N + N_2 \rightarrow N_3 \quad (10)$$

again to make the N_3 we observed, although more-complex paths to N_3 exist (Mencos et al. 2017). For N_2-rich ices containing O_2, excitation and dissociation of molecular oxygen will give O atoms from which nitrous oxide and ozone can form in (11) - (13)

$$O_2 \rightarrow O_2^* \rightarrow O + O \quad (11)$$

$$N_2 + O \rightarrow N_2O \quad (12)$$

$$O_2 + O \rightarrow O_3 \quad (13)$$

by O-atom addition (DeMore & Davidson 1959). If H_2O is present then it too will be a source of O atoms, from which reaction (12) will follow (Zheng et al. 2011). Radiolysis of the N_2O produced will give the reverse of reaction (12), but will also yield nitric oxide (NO) as shown below.

$$N_2O \rightarrow N_2O^* \rightarrow N + NO \quad (14)$$

Several neutral oxidants exist in irradiated $N_2 + O_2$ ices, specifically O, O_2, and O_3, and these can lead to more-complex oxides. For example, starting from NO gives

$$NO + O \rightarrow NO_2 \quad (15)$$

$$NO_2 + O \rightarrow NO_3 \quad (16)$$

although we have no firm evidence for NO_3. Additional radical-radical reactions will lead to the more-complex oxides seen in our IR spectra:

$$NO + NO \rightarrow N_2O_2 \quad (17)$$

$$NO + NO_2 \rightarrow N_2O_3 \quad (18)$$

$$NO_2 + NO_2 \rightarrow N_2O_4 \quad (19)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (20)$$

See Minnisale et al. (2014) and Ioppolo et al. (2014) for similar reactions in a different context. See Cocke et al (2004) and references therein for solid-phase N_2O_5 formation without NO_3. Note that such radical-radical combinations are expected to proceed with no electronic activation barrier, being restricted mainly by their positions and mobility within the irradiated ice. Other possible reactions include, if sufficient energy is available, O-atom transfer from O_2 and especially O_3. See Koch et al. (1999) for a different path to N_2O_5, from which nitric acid (HNO_3) can be made by reaction with H_2O.

The formation of N_2O has been described, so it is appropriate to mention that that molecule's radiation chemistry also has been studied for nearly a century (Wourtzel 1919). Sambrook & Freeman (1974) reported that the major radiolytic products from N_2O include N_2, O_2, NO, and NO_2, the last three being secondary products in an ice

initially composed of N_2 + H_2O. Oxygen atoms from N_2O radiolysis will react to form NO according to

$$O + N_2O \rightarrow NO + NO \quad (21)$$

and from NO the other oxides already mentioned, as well as O_3, will follow, as already described. Similar arguments can be made for the formation of N_2O, NO, NO_2, and O_3, from other starting ice mixtures, such as N_2 + CO_2.

The complication added by the presence of CO_2 in the irradiated ices of dB15 is that it is a second source of O, O_2, and O_3, which will participate in many of the reactions already written. Also produced will be CO, which we suspect is the source of the peak near 2140 cm^{-1} in Figure 1 of dB15, but unlabeled, and also seen in the upper spectrum of our own Figure 1. However, the participation of CO_2 jeopardizes any interpretation of the resulting kinetic information and product yields solely in terms of N_2 + H_2O chemistry.

Note that all of the reactions in this section have ignored complications from electronic spin states, about which our methods provide no information. See the papers of Willis and co-workers for more-complex versions of most of these reactions with spin explicitly included (Willis et al 1970; Willis & Boyd 1976).

4.2. Other Possible Reaction Products from N_2 + H_2O

Since N atoms are made by the irradiation of N_2 + H_2O, and since both H and OH can form from H_2O, there are multiple possibilities for radical-radical reactions, such as these:

$$H + NO \rightarrow HNO \quad (22)$$

$$OH + NO \rightarrow HNO_2 \quad (23)$$

$$OH + NO_2 \rightarrow HNO_3 \quad (24)$$

The above three products are mentioned in dB15, but without reference spectra it is difficult to make firm assignments. Similarly, N and H atoms might react to make NH, NH_2, and NH_3, or the NH radicals might be captured by the N_2 matrix to make HN_3. On page 9 of dB15 it is said that HN_3 "bands were investigated", but no details were provided. It is not known if the authors looked up gas-phase positions of HN_3 infrared features, if they prepared solid mixtures of HN_3 in N_2 and recorded their IR spectra, or if something else was done. Van Thiel & Pimentel (1960) showed that the strongest IR feature of solid HN_3 is in the same region where CO absorbs, and so it could overlap, mask, or be masked by CO's fundamental band. Without appropriate reference spectra, little more can be said except that the CO label in our Figure 1 could be a simplification.

4.3. Reaction Products and Radiation Types

Table 5's first four lines list some results from radiation experiments with N_2-rich ices in four different laboratories. A recent study of a more-complex ice also is included (Vasconcelos et al. 2017). All five studies are seen to have reported radiolytic formation of NO, NO_2, and N_2O, suggesting that if N_2 and a source of oxygen are present then the ice can be driven to the same nitrogen oxides. One can safely predict that the same products will be observed from other irradiated nitrogen-rich ices, such as $N_2 + O_3$, $NH_3 + O_2$, and so forth. – For completeness, an ion-implantation study of Boduch et al. (2012) should be mentioned here. It included two IR spectra of $N_2 + O_2$ after irradiation

by 30-keV $^{13}C^{2+}$ at 15 K, but neither an initial N_2-to-O_2 ratio nor a radiation dose were given, and so that work is not included in our Table 5, although it too reported NO, NO_2, and N_2O formation.

The third column of Table 5 shows that radiations with a wide range of stopping powers were used in the five experiments listed. Since the composition of the ice of de Barros (2015) was uncertain (*vide supra*) the stopping power of 40-MeV Ni^{11+} in solid N_2 was calculated (3600 keV μm^{-1}) and is listed in Table 5. It is readily seen that in that experiment the energy deposition per unit distance was about 300% greater than the next largest value, raising the chances of sample heating and of sputtering, both of which would cause N_2 loss. This might explain why the post-irradiation spectrum of N_2 + H_2O in our Figure 1 so closely resembles that of unirradiated amorphous H_2O-ice. With such a substantial N_2 loss in the 40-MeV Ni^{11+} experiment, it is difficult to unravel the underlying reaction chemistry because the ice changes from being dominated by non-polar N_2 molecules to being composed of the highly-polar H_2O and reaction products. The chemical reactions occurring at the experiment's start play an increasingly smaller role as the radiolysis proceeds, and little or no role near its end.

4.4. Reaction Kinetics in N_2 + H_2O Ices

A problem with trying to understand chemistry in ices, in either a laboratory or astronomical setting, is that it can be hard to isolate specific reactions for study, so that a phenomenological approach is often necessary. For the N_2 + H_2O ice of interest here, no reactions were written by dB15 for this mixture's chemical evolution. The authors presented a set of equations similar to those for a reversible reaction that follows first-

order kinetics in both directions. A solution for this system has long been known (Harcourt & Esson 1866) and suggests that a semi-log plot of $N_t - N_\infty$ over time (N = reactant abundance) should be linear with a slope that is the sum of the forward and reverse rate constants. An assumption of parallel non-reversible destruction reactions would give a different solution and consecutive reactions would give yet a different result. Regardless, an explicit description of the kinetic system assumed to be relevant, to include specific reactions and the order of each, is critical for extracting accurate rate information from the laboratory data. Mathematical equations with adjustable parameters certainly can be used to fit data points, but without a basis in the chemistry of the system, the parameters extracted are not necessarily rate constants that are applicable to other chemical systems. See Rodiguin & Rodiguina, (1964), Capellos & Bielski (1972), and Andraos (1999) for examples of complex kinetic systems and solutions by Laplace and Laplace-Carson transforms.

Given the preceding observations and results, we conclude that although a full kinetic analysis to extract rate constants for the N_2 + H_2O system is of interest, it is impossible at present given the uncertainty over possible ice contaminants (i.e., CO_2, H_2O), convincing assignments of some of the IR features of products, and the lack of accurate product column densities.

4.5. Some Astrochemical Considerations

Having examined some results from N_2-rich ices in our lab and elsewhere, we consider some astrochemical implications. First and foremost is the ease of formation of nitrogen oxides in a variety of chemical systems. The N_2 + CO_2, N_2 + CO, N_2 + H_2O,

and N_2 + O_2 combinations have been studied in four independent laboratories and found, from the action of ionizing radiation, to produce N_2O, NO, and NO_2, and probably more-complex nitrogen oxides. Again, see Table 5, which also includes the four-component ice recently studied by Vasconcelos et al. (2017). These same products can be expected in irradiated ices of TNOs that are N_2 rich. Although these three oxides might be observed spectroscopically in the gas phase, direct detection in ices could be difficult. In any case, radiolytic oxidation in solid N_2 would seem to be firmly established.

A related implication of the ease of forming nitrogen oxides is that small amounts of H_2O in N_2-rich ices will be consumed by radiation-driven chemistry. This makes it challenging to identify H_2O mixed with N_2-rich ices on TNOs, such as Pluto. The clearest detections to date are the broad and weak, but distinct, near-IR features of H_2O-ice observed with the New Horizons fly-by mission (Grundy et al. 2016).

In contrast to the situation for N_2-rich TNOs, that for trans-Neptunian objects that are rich in solid NH_3, such as Charon, is less clear. Free-radical reactions can dominate in non-polar ices, such as those studied here, but icy solids rich in polar molecules, like NH_3, likely would find a larger contribution from ions, such as NH_4^+, and electron-transfer reactions. The reason for this is that an ionization, such as $N_2 \rightarrow N_2^+ + e^-$, involved in a radiolytic reaction scheme is more likely to be followed by electron-cation recombination in non-polar solids than in those of higher dielectric constant where the cation and e^- are, in a sense, shielded from one another (Williams 1964; Swallow 1973, p 77; Mozumder 1999, pp 232-234). Seen this way, one can predict quite different chemistries for Pluto and Charon due to their different surface ices.

In previous papers, we estimated proton radiation doses for multiple astronomical objects and environments (Moore et al. 2001, Moore & Hudson 2006, Hudson et al. 2008, and references therein). Table 6 summarizes some of our estimates, with doses being given both for 16-amu and 28-amu scales, the latter being the more relevant for the N_2-rich ices of the present work. The table's final column shows that the dose of ~1 eV (N_2 molecule)$^{-1}$ for our Figure 2 is reasonable for a 1-m depth on Pluto over ~90 million years and for a 1-m depth over ~50 million years for more-distant TNOs. Each orbit of Pluto is accompanied by the sublimation of N_2-rich surface material, which can carry nitrogen-oxide radiation products into the gas phase, but also can lead to the enrichment of the less volatile nitrogen oxides left behind on the surface. This suggests that the greatest abundance of gas-phase nitrogen oxides from Pluto might well be found near perihelion.

For interstellar ices, Table 6 shows that the ice mantles on interstellar grains receive a dose of a few eV per N_2 molecule over the lifetime of a dark cloud (10^6 - 10^7 years), an estimate that compares well to that of Sicilia et al. (2012). This dose is similar to that used in experiments that we and others have carried out. Since our estimates consider only H^+, the most abundant component of cosmic rays, the actual dose might be somewhat higher. This strengthens the possibility (Zheng et al. 2008) that N_2 mixed with H_2O-rich ices in interstellar grain mantles can be radiolytically oxidized, and so might never be observed in the solid state as N_2. In such cases, any nitrogen present might exist as NO, NO_2, N_2O or maybe NO_2^- and other ions. See Halfen et al. (1991) for a study of gas-phase NO and N_2O in the Sagittarius B2 interstellar cloud.

A slightly different picture emerges for apolar interstellar ices, which are thought to have a relatively high abundance of N_2 and O_2 (Ehrenfreund et al. 1998). Radiation-driven reactions would yield products from our Tables 2 and 4, with any H_2O trapped in such ices, at low abundance, also succumbing to radiation-driven chemistry. In apolar ices, O atoms would react with N_2 to make N_2O and other products, perhaps helping to explain why O_3 has not yet been identified as an interstellar molecule.

5. Summary and Conclusions

1. The IR band strengths used in de Barros et al. (2015) to quantify the radiation products of an $N_2 + H_2O$ ice vary from unchecked to suspect, casting doubt on the authors' subsequent data analyses.

2. Nitrogen oxides cannot be used as tracers of $N_2 + H_2O$ ices.

3. Conversely, by combining new work from our laboratory (e.g., see Table 5) with results from elsewhere we have shown that the irradiation of N_2-rich icy solids readily produces the simpler nitrogen oxides, N_2O, NO, and NO_2.

4. An extensive array of spectroscopic tools and techniques are available and required for firm assignments in the IR spectra of interstellar and planetary ice analogs, particularly if those spectra contain broad, overlapping bands. Such aids include isotopic substitution, thermal annealings, control experiments (blanks), comparisons with similar chemical systems, careful attention to the underlying chemistry, and reference spectra recorded under the same conditions, and preferably with the same equipment, used for the ices being studied.

5. Detailed kinetic results should be accompanied by a statement of the reaction order(s) and types of reactions assumed since kinetic order determines the mathematical relations used for curve fits and the extraction of rate constants.

6. Infrared studies of solid nitrogen oxides, in the laboratory and elsewhere, are hindered by the lack of appropriate reference spectra. New measurements of IR band strengths and optical constants for nitrogen oxides also are needed before studies of the low-temperature formation of these compounds in amorphous ices can be quantified. Claims of nitrogen-oxide formation and quantification in ices should be judged with this in mind. Unfortunately, since many nitrogen oxides are both toxic and detrimental to laboratory equipment, continued slow progress is expected.

In our appendices we justify the following concluding statements:

1. The report (de Barros et al. 2015) of an IR band near 2347.5 cm^{-1} for solid N_2 conflicts with the bulk of the spectroscopic literature and is unsupported by the results presented to date. Astronomical searches for solid N_2 should continue to focus on the molecule's well-known fundamental and first overtone bands.

2. The striking and specific ^{15}N enrichment reported for N_3 seems highly unlikely, and conflicts with published results on N_3 formation in radiation experiments.

This work was supported by NASA's Planetary Science Division Internal Scientist Funding Program through the Fundamental Laboratory Research (FLaRe) work package at the NASA Goddard Space Flight Center. Also acknowledged is the NASA Astrobiology Institute through funding to the Goddard Center for Astrobiology under

proposal 13-13NAI7-0032. Stephen Brown, Eugene Gerashchenko, and Martin Carts of NASA Goddard's Radiation Effects Facility are thanked for the operation and maintenance of the Van de Graaff accelerator. Many helpful conversations with Marla Moore and Perry Gerakines are acknowledged.

APPENDIX A

During the course of this study, a relatively large number of questionable items were found in a paper published in this journal by de Barros et al. (2015). For example, on page 2 in column 2, the units of stopping power are incorrect, or at least ambiguous. The infrared spectra of Figure 1 on page 2 for two N_2 + H_2O mixtures are not compared to spectra published earlier by Ehrenfreund et al. (1996). On page 3, the order of the line-types in the legend at the top of Figure 2 disagrees with the top three panels in the figure itself. Figure 2d has a peak near 1875 cm^{-1} labeled N_2O_3, but Table 2 gives 1834.2 cm^{-1} as the position. On page 3 in column 2, a spectral band is designated ν_1 + σ, but that label's meaning is never explained. The last sentence on page 3 employs "blueshift" in a sense that is opposite to conventional usage, and "wavelength" is used where "wavenumber" is meant. On page 4, the first entry in Table 1 is attributed to the lead author's previous work and one other paper, but the measurement cited is originally from Hagen et al. (1981). Five rows later, the "ν_2 monomer" assignment should be designated "ν_1 monomer" instead, unless the band position (3633.3 cm^{-1}) is in error. Further, the 3723.8 and 3633.3 cm^{-1} peaks in that table are from isolated H_2O (Van Thiel et al. 1957), not from dangling OH bonds (Rowland et al. 1991). On page 4

in the first column, 9.8×10^{17} is considered to be "almost one order of magnitude higher" than 2.3×10^{17}. On page 6 in column 1, the last paragraph's ^{18}CO should be $^{18}CO_2$ instead. Also on page 6 in column 1, the ratios 2200 and 220 are really 2200 and 511 according to Table 3. At the top of page 9, the *cis* and *trans* isomers of N_2O_2 are noted and data for them are plotted in Figure 6, but the wavenumbers of the peaks used to follow those two molecules and generate the points plotted are not unequivocally stated. Figure 6's caption refers to some of the curves in the figure as predictions. They are, in fact, curve fits used to extract kinetic information from the lab measurements, as opposed to being *a priori* mathematical statements.

APPENDIX B

Infrared Features of Molecular Nitrogen (N_2)

The N_2 abundance in planetary and interstellar ices is of considerable interest and importance, and so the IR absorbance of solid N_2 has been studied for applications to both the ISM (Sandford et al. 2001) and the outer Solar System (Tryka et al. 1995). However, isolated N_2 molecules are IR-inactive and solid N_2 has only weak IR activity, hindering its astronomical detection by infrared methods. This means that the discovery of a new N_2 infrared feature would be of great interest.

Figure 1 and Table 1 of dB15 have an IR peak near 2347 cm^{-1} that is labeled N_2 + CO_2, with a component at 2347.5 cm^{-1} that the authors assigned to N_2. However, no such position is known for N_2 and the authors' assignment is not supported with either their own reference spectra or isotopic substitution experiments (e.g., $^{15}N_2$). Further, no IR spectra are shown of either the unirradiated ice at multiple temperatures or of ices

with different N_2:H_2O ratios, which might clarify the proposed N_2 assignment. The author's Table 1 cites a 1999 paper of Hadjiivanov and Knzinger (*sic*) for an N_2 peak in that region, but that paper's experimental conditions (adsorption on a zeolite at 7.5 torr) differ significantly from those in dB15 (bulk N_2-ice under vacuum). A paper of Zheng et al. (2008) also is cited for support, but those authors give only a footnote in a table of their own that cites an unpublished calculation for an IR peak at 2374 cm^{-1} to assign a feature at 2348 cm^{-1} in irradiated NH_3, again with no reference spectra provided. Finally, the band strength $A = 1.5 \times 10^{-20}$ cm molecule^{-1} calculated in dB15 for the IR feature at 2347.5 cm^{-1}, which the authors assigned to solid N_2, is about seven times (~600%) larger than the band strength of the N_2 fundamental near 2328 cm^{-1}. Therefore, since an overtone was seen for the 2328 cm^{-1} peak then one is expected for the much stronger 2347.5 cm^{-1} feature, but none was reported. Reference spectra of N_2-rich ices (e.g., Fredin et al. 1974; Bernstein & Sandford 1999), as well as spectra showing N_2 formation in irradiated NH_3 (Bordalo et al. 2013), all give the position of the N_2 fundamental vibration as near 2328 cm^{-1}, not 2347.5 cm^{-1}, and so it is not clear to what N_2 vibration the latter could apply.

The more likely explanation for the IR features near 2347 cm^{-1} in dB15 is that they are all from CO_2. One interpretation is that the spectral structure comes from some CO_2 molecules being trapped solely by N_2 and others being surrounded by both H_2O and N_2, while another explanation is that CO_2 dimers or multimers are partly responsible. Within the astrochemical community, early work by Van der Zwet et al. (1989) found three CO_2 features in the 2347 cm^{-1} region of the IR spectrum of N_2 + CO_2 mixtures. Schriver et al (2000) later reported that CO_2 that is matrix-isolated within N_2,

even at high dilutions, exhibits multi-component patterns in that same spectral region, with all IR peaks coming from one or more CO_2 molecules. Also, Zhang and Sander (2011) have reported multiple CO_2 positions near 2347 cm^{-1} in N_2 + CO_2 + H_2O ices at 4.5 K, with N_2 as the matrix material. In short, without additional information the proposal of an IR feature of N_2 overlapping the ν_3 band of CO_2 in the spectrum of an N_2 + H_2O ice must be rejected.

APPENDIX C

Reported Enrichment of ^{15}N in Radiation-Chemical Products

Isotopic abundances are relevant to many astrochemical subfields, ranging from meteorites to planetary atmospheres to comets to the ISM. Isotope measurements can help reveal and constrain evolutionary paths and physical conditions. Therefore, laboratory work that reveals pathways for altering isotopic ratios is of much interest.

Along these lines, the ice experiments of dB15 began with an N_2-ice matrix that had, apparently, a normal ^{14}N-to-^{15}N ratio of ~250 based on terrestrial nitrogen isotopic abundances. However, in the authors' Figures 7a and 7b and the accompanying text several IR peaks are assigned to $^{15}N_3$, $^{15}N_2{}^{14}N$, and $^{15}N^{14}N_2$. It is surprising that the IR bands of these ^{15}N-azide radiation products are comparable to or larger than those from the expected $^{14}N_3$. Since the natural abundance of ^{15}N is only about 0.4%, this assignment suggests that the experiments produced a stunning ^{15}N isotopic enrichment for N_3, and that the enrichment did not extend to other radiation products, such as NO and NO_2. It is unclear why radiolysis should produce any such large ^{15}N enrichment, much less one that is specific to a single product. Our own study of N_3 formation gave

no detectable ^{15}N enrichment (Hudson & Moore 2002), and we know of none reported by others (e.g., Tian et al. 1988; Jamieson & Kaiser 2007; Wu et al. 2012).

The ^{15}N enrichment just described rests on the soundness of the assignments of weak IR features to N_3. Although the text of dB15 says that "doublets of four isotopologues of the azide radical are clearly marked", the relevant figure labels only five of the eight expected peaks, with one of those at roughly the same position as NO_2 and another at the same position as a residual peak of the unirradiated sample. Of the remaining three labeled peaks, their assignment to N_3 can be tested by seeing if slight increases in temperature cause them to disappear, due to thermal decay of the N_3 radicals. No such test was presented. We conclude that the ^{15}N isotopic enrichment reported is not convincing, although N_3 is an expected radiolysis product.

ORCID iDs

R. L. Hudson https://orcid.org/0000-0003-0519-9429

References

Andraos, J. 1999, J. Chem. Educ., 76, 1578

Arakawa, E. T., & Nielsen, A. H. 1958, J. Molec. Spectr., 2, 413

Beckers, H., Willner, H., & Jacox, M. E. 2009, ChemPhysChem, 10, 706

Begun, G. M., & Fletcher, W. H. 1960, J. Molec. Spectr., 4, 388

Bencivenni, L., Sanna, N., Schriver-Mazzuoli, A., & Schriver, A. 1996, JCP, 104, 7836

Bennett, C. J., Chen. S., Sun, B., Chang, A. H. H, & Kaiser, R. I. 2007, ApJ, 660, 1588

Bennett, C. J., Pirim, C., & Orlando, T. M. 2013, 113, 9086

Bernstein, M. P., & Sandford, S. A. 1999, Spect. Acta, 55A, 2455

Boduch, P., Domaracka, A., Fulvio, D., Langlinay, T., Lv, X. Y., Palumbo, M. E., Rothard, H., & Strazzulla, G. 2012, A&A, 544, A30

Bordalo, V., da Silveira, E. F., Lv, X. Y., Domaracka, A., Rothard, H., Seperuelo Duarte, E., & Boduch, P. 2013, ApJ, 774, 105

Capellos, C., & Bielski, B. H. J. 1972, *Kinetic Systems: Mathematical Description of Chemical Kinetics in Solution* (New York: Wiley)

Cocke, D. L., Gomes, J. A. G., Gossage, J. L., Li, K., Lin, C., & Tandel, S. 2004, Appl. Spec., 58, 528

Cruikshank, D. P., Brown, R. H., & Clark, R. N. 1984, Icarus, 58, 293

de Barros, A. L. F., da Silveira, E. F., Bergantini, A., Rothard, H., & Boduch, P. 2015, ApJ, 810, 156

DeMore, W. B., & Davidson, N. 1959, JACS, 81, 5869

Dyke, J. M., Jonathan, N. B. H., Lewis, A. E., & Morris, A. 1982, Molec. Phys., 47, 1231

Ehrenfreund, P., Gerakines, P. A., Schutte, W. A., van Hemert, M. C., & van Dishoeck 1996, A&A, 312, 263

Ehrenfreund, P., Boogert, A., Gerakines, P., & Tielens, A. 1998, Faraday Disc., 109, 463

Forney, D., Thompson, W. E., & Jacox, M. E. 1993, JCP, 99, 7393

Fredin, L., Nelander, B., & Ribbegard, G. 1974, J. Molec. Spec., 53, 410

Grundy, W. M. et al. and the New Horizons Science Team 2016, Science, 351, aad9189

Hadjiivanov, K., & Knözinger, H. 1999, Catalyst. Letters, 59, 21

Hagen, W., Tielens, A. G. G. M., & Greenberg, J. M. 1981, Chem. Phys., 56, 567

Halfen, D. T., Apponi, A. J., & Ziurys, L. M., 2001, ApJ, 561, 244

Harcourt, A. V., & Esson, W. 1866, Phil. Trans., 156, 193

Harteck P., & Dondes S. 1958, JCP, 28, 975

Hudgins, D. M., Sandford, S. A., Allamandola, L. J., & Tielens, A. G. G. M. 1993, ApJSS, 86, 713

Hudson, R. L., & Moore, M. H. 1997, Icarus, 126, 233

Hudson, R. L., & Moore, M. H. 1999, Icarus, 140, 451

Hudson, R. L., & Moore, M. H. 2002, ApJ, 568, 1095

Hudson, R. L., & Moore, M. H. 2004, Icarus, 172, 466

Hudson, R. L., Ferrante, R. F., & Moore, M. H. 2014, Icarus, 228, 276

Hudson, R. L., & Moore, M. H. 2018, ApJ, 857, 89

Hudson, R. L,. Moore, M. H., & Gerakines, P. A. 2001, JGR-Planets, 106, 33275

Hudson, R. L., Palumbo, M. E, Strazzulla, G., Moore, M. H., Cooper, J., & Sturmer, S. J. 2008, "Laboratory Studies of the Chemistry of TNO Surface Materials" in *The Solar System Beyond Neptune*, eds. M. A. Barucci, H. Boehnhardt, D. P. Cruikshank, & A. Morbidelli (Tucson, Arizona, USA: University of Arizona Press)

Hudson, R. L., Loeffler, M. J., & Yocum, K. M. 2017a, ApJ, 835, 225

Hudson, R. L., Loeffler, M. J., & Gerakines, P. A. 2017b, JCP, 146, 0243304.

Ioppolo, S., Fedoseev, G., Minnisale, M., Congiu, E., Dulieu, & Linnartz, H. 2014, PCCP, 16, 8270

Jamieson, C. S., Bennett, C. J., Mebel, A. M., & Kaiser, R. I. 2005, ApJ, 624, 436

Jamieson, C. S., & Kaiser, R. I. 2007, Chem. Phys. Lett., 440, 98

Jones, A. R. 1959, Rad. Res. 10, 655

Koch, T. G., Horn, A. B., Chesters, M. A., McCoustra, M. R. S., & Sodeau, J. R. 1995, JPC, 99, 8362

Krim, L. 1998, J. Molec. Struct., 471, 267

Łapinski, A., Spanget-Larsen, J., Waluk, J., & Radziszewski, J. G. 2001, JCP, 115, 1757

Lind, S. C., & Bardwell, D. C. 1929, JACS, 58, 2751

Loeffler, M. J., Teolis, B. D., & Baragiola, R. A. 2006, JCP, 124, 104702

Lovas, F. J., Hollis, J. M., Remijan, A. J., & Jewell, P. R. 2006, ApJ, 645, L137

McGuire B. A., Carroll, P. B., Loomis, R. A., Finneran, I. A., Jewell, P. R., Remijan, A. J., & Blake, G. A. 2016, Science, 352, 1449

Mencos, A., Nourry, S., & Krim, L. 2017, MNRAS, 467, 2150

Minissale, M., Fedoseev, G., Congiu, E., Ioppolo, S., Dulieu, F., & Linnartz, H. 2014, PCCP, 16, 8257

Moore, M. H., & Hudson, R. L. 2003, Icarus, 161, 486

Moore, M. H. 1999, The Physics and Chemistry of Ices in the Interstellar Medium in *Solid Interstellar Matter: The ISO Revolution* (Berlin: Springer Verlag)

Moore, M. H., & Hudson, R. L. 2006, "Production of Complex Molecules in Astrophysical Ices" in *Astrochemistry: Recent Successes and Current Challenges*, Proceedings IAU Sym. 231, Cambridge University Press

Moore, M. H., Hudson, R. L., & Gerakines, P. A. 2001, Spect. Acta, 57A, 843

Mozumder, A. 1999, *Fundamentals of Radiation Chemistry* (San Diego: Academic Press)

Owen, T. C., Roush, T. L., Cruikshank, D. P., Elliot, J. L., Young, L. A., de Bergh, C., Schmitt, B., Geballe, T. R., Brown, R. H., & Bartholomew, M. J. 1993, Science, 261, 745

Rodiguin, N. M., & Rodiguina, E. N. 1964, *Consecutive Chemical Reactions: Mathematical Analysis and Development* (Toronto: Van Nostrand)

Rowland, B., Fisher, M., & Devlin, J. P. 1991, JCP, 95, 1378

Rosu-Finsen, A., Marchione, D., Salter, T. L., Stubbing, J. W., Brown, W. A., & McCoustra, M. R. S. 2016, PCCP, 18, 31930

St. Louis, R. V., & Crawford Jr., B. 1965, JCP, 42, 857

Sambrook, T. E. M., & Freeman, G. R. 1974, JPC, 78, 28

Sandford, S. A., Bernstein, M. P., Allamandola, L. J., Goorvitch, D., & Teixeira, T. C. V. 2001, ApJ, 548, 836

Satorre, M. Á., Domingo, M., Millan, C., Luna, R., Vilaplana, R., & Santonja, C. 2008, PSS, 56, 1748

Savchenko, E. V., Khyzhniy, I. V., Uyutnov, S. A., Barabashov, A. P., Gumenchuk, G. B., Beyer, M. K., Ponomaryov, A. N., & Bondeybey, V. E. 2014, JPC, 119, 2475

Secroun, C., Barbe A., Jouve, P., Arcas, P., & Arie, E. 1981, J. Molec. Spec., 85, 8

Schriver, A., Schriver-Mazzuoli, L., & Vigasin, A. A. 2000, Vibr. Spec., 23, 83

Sicilia, D., Ioppolo, S., Vindigni, T., Baratta, G. A., & Palumbo, M. E. 2012, A&A, 543, A155

Smith, M. A. H., Rinsland, C. P., Fridovich, B., & Rao, K. N. 1985, "Intensities and Collision Broadening Parameters from Infrared Spectra" in *Molecular Spectroscopy: Modern Research*, vol. 3, ed. K. N. Rao (Orlando, Florida, USA: Academic Press)

Soddy, S. 1911, Ann. Rep. Chem. Soc. for 1910, 8, 269 (see pp 299-300)

Stirling, A., Papai, I., Mink, J., & Salahub, D. 1994, JCP, 100, 2910

Strazzulla, G. 1998, “Chemistry of Ice Induced by Bombardment with Energetic Charged Particles” in *Solar System Ices*, eds. B. Schmitt, C. de Bergh, & M. Festou (Dordrecht, The Netherlands: Kluwer)

Swallow, A. J. 1973, *Radiation Chemistry* (New York: John Wiley & Sons)

Swanepoel, R. 1983, J. Phys. E: Sci. Instrum. 16, 1214

Tegler, S. C., Grundy, W. M., Olkin, C. B., Young, L. A., Romanishin, W., Cornelison, D. M., & Khodadadkouchaki, R. 2012, ApJ, 751, 1

Tempelmeyer, K. E., & Mills, D. W. 1968, J. Appl. Phys., 39, 2968

Terenishi, R., & Decius, J. C. 1954, JCP, 22, 896

Thompson, W. E., & Jacox, M. E. 1990, JCP, 93, 3856

Tian, R., Facelli, J. C., & Michl, J. 1988, JPC, 92, 4073

Tryka, K. A., Brown, R. H., & Anicich, V. 1995, Icarus, 116, 409

Van der Zwet, G. P., Allamandola, L.J., Baas, F., & Greenberg, J. M. 1989, J.Molec. Struct., 195, 213

Van Thiel, M., Becker, E. D., & Pimentel, G. C. 1957, JCP, 27, 486

Van Thiel, M., & Pimentel, G. C. 1960, JCP, 32, 133

Varetti, E. L., & Pimentel, G. C. 1971, JCP, 55, 3813

Varney, R. N. 1953, Phys. Rev., 89, 708

Vasconcelos, F. A., Pilling, S., Rocha, W. R. M., Rothard, H., & Boduch, P. 2017, PCCP, 19, 24154

Williams, F. 1964, JACS, 86, 3954

Willis, C., & Boyd, A. W. 1976, Int. J. Rad. Phys. Chem., 8, 71

Willis, C., Boyd, A. W., & Young 1970, Can. J. Chem., 48, 1515

Wourtzel, E. 1919, Radium, 11, 289

Wu, Y., Wu, C. Y. R., Chou, S., Lin, M., Lu, H., Lo, J., & Cheng, B. 2012, ApJ, 746, 175

Yamada, H., & Person, W. B. 1964, JCP, 41, 2478

Zhang, X., & Sander, S. P. 2011, JPC, 115A, 9854

Zheng, W., Jewitt, D., Osamura, Y., & Kaiser, R. I. 2008, ApJ, 674, 1242

Zheng, W., Kim, Y. S., & Kaiser, R. I. 2011, PCCP, 13, 15749

Zhu, I., Zhou, X., & Liu, R. 1996, JCP, 105, 11366

Ziegler, J. F., Biersack, J. P., & Littmark, U. 1985, *The Stopping and Range of Ions in Solids* (New York: Pergamon); see also: http://www.srim.org/.

Ziegler, J. F., & Manoyan, J. M. 1988, Nucl. Instru. Meth. Phys. Res., B35, 218

Table 1

Comments on Table 2 of the N_2 + H_2O Study of de Barros et al. (2015) [a]

Molecule	Comments on Assignments and Band Strengths
N_3	The first peak listed is incorrectly assigned. It is not from the N_3 radical, but from the N_3^+ cation. The other band strengths (*A*) listed are based on an estimate from a reflection-transmission type IR spectrum, and the accuracy of that estimate has not been checked.
NO	The position and *A* given for the first peak is not in the paper cited, and in any case that paper reports a gas-phase calculation, not a solid-phase measurement. The source listed for the second *A*'(NO) has no details about the measurement and only an incomplete reference in a table.
NO_2	The band strength selected for use is not in the *Icarus* paper cited. (Also, the wrong volume and year are given for that reference.) The other band strength given was miscopied and is 10 times too large.
NO_3	The spectral position disagrees with the literature (Beckers et al. 2009) by about 25 cm^{-1}, making this one-peak spectral assignment questionable. The *A* value listed is from a gas-phase calculation.
N_2O	The band strength selected for use is from a gas-phase calculation, not a solid-phase measurement. The other three *A* values listed are from a mixed amorphous-crystalline ice. The *A*(2573.3 cm^{-1}) value was miscopied and is 10 times larger than in the original publication.
N_2O_2	The band strength selected for use is from a gas-phase calculation, not a solid-phase measurement. The first peak's position is not in the paper cited. The second peak listed is not in the work cited, which is not about N_2O_2.
N_2O_3	The N_2O_3 assignment is based on just one peak, which is either incorrectly labeled in Figure 2d or is incorrectly assigned. The band strength listed is from a gas-phase calculation.
N_2O_4	One band strength is not in the paper cited, which is not about N_2O_4. The other band strength is from a gas-phase calculation, not a solid-phase measurement.
N_2O_5	The N_2O_5 assignment is based on a single peak about 30 cm^{-1} lower than in the reference cited. Again the *A* value is from a gas-phase calculation, not a solid-phase measurement.
O_3	Measurement of the band strength listed is not in either of the papers cited.

Note.

[a] In earlier work we have drawn a distinction between absolute (*A*) and apparent (*A*') infrared band strengths (e.g., Hudson et al. 2014). For simplicity, in this paper only *A* is used.

Table 2

Infrared Identifications of Products with 2 - 4 Atoms from 1-MeV H^+ Irradiation of $N_2 + O_2$ (100:1) Ice at 12 K

		Position (cm^{-1})		^{15}N Shift (cm^{-1})	
Molecule	Mode	This Work	Literature	This Work	Literature
N_3	ν_1	1657	1657 [a]	54	54 [a]
NO	ν_1	1874	1875 [b]	33	33 [b]
NO_2	$\nu_1 + \nu_3$	2908	2905 [c]	46	47 [d]
	ν_3	1615	1616 [c]	35	37 [d]
	ν_2	750	750 [e]	10	9.6 [d]
N_2O	ν_3	2235	2236 [f]	70	70 [f]
	ν_1	1291	1291 [f]	20	20 [f]
cis-N_2O_2	ν_1	1866	1866 [b]	--- [g]	32.9 [b]
	ν_5	1779	1780 [b]	31	31.5 [b]
trans-N_2O_2	ν_5	1760?	1760 [b]	--- [g]	31.1 [b]

Notes.

[a] Tian et al. (1988); N_2 matrix

[b] Krim (1998); N_2 matrix

[c] Varetti & Pimentel (1971); N_2 matrix

[d] Arakawa & Nielsen (1958); gas phase

[e] St. Louis & Crawford (1965); O_2 matrix; overlaps slightly with a feature of N_2O_4.

[f] Łapinski et al. (2001); N_2 matrix

[g] Overlaps with other features or too weak for accurate measurement

Table 3

Infrared Identifications of Products with 5 - 7 Atoms from 1-MeV H^+ Irradiation of $N_2 + O_2$ (100:1) Ice at 12 K

Assignments slightly more tentative than those in Table 2

		Position (cm^{-1})		^{15}N Shift (cm^{-1})	
Molecule	Mode	This Work	Literature	This Work	Literature
asymm N_2O_3	ν_1	1841	1840 [a]	32	32 [a]
	ν_2	1630	1630 [a]	32?	36 [a]
	ν_3	1302	1302 [a]	15	16 [a]
N_2O_4	ν_{11}	1261	1261 [a]	12	11 [b]
	ν_{12}	751 (weak)	751 [a]	~11	11 [b]
N_2O_5	ν_1	~1740	1742 [c]	~35	40 [c]
	ν_9	1703	1702 [c]	39	40 [c]
	ν_{10}	1245	1245 [c]	6	8 [c]
	ν_{11}	738	732 [c]	9	8.5 [c]

Notes.

[a] Varetti & Pimentel (1971); N_2 matrix

[b] Begun & Fletcher (1960); gas phase

[c] N_2O_5 literature values are from Bencivenni et al. (1996) with some reassignments by Zhu et al. (1996); Ar matrix

Table 4

Nitrogen Oxidation Numbers for Selected Molecules and Ions [a]

Nitrogen Oxidation Number	Molecules and Ions			
0	N_2			
+1	N_2O			
+2	NO	N_2O_2		
+3	N_2O_3	NO^+	NO_2^-	HNO_2
+4	NO_2	N_2O_4		
+5	N_2O_5	NO_2^+	NO_3^-	HNO_3
+6	NO_3			

Note.

[a] The nitrogen atom in N, NH, NH_2, and NH_3 has an oxidation number of 0, -1, -2, and -3, respectively.

Table 5

Examples of Reports of Radiation Products in Cosmic Ice Analogs [a]

Publication	Experimental Conditions	Stopping Power (keV μm^{-1})	NO	NO_2	N_2O
Jamieson et al. (2005)	5 keV e^- $N_2 + CO_2$ (1:1), 10 K	6.4 [b]	✓	✓	✓
Sicilia et al. (2012)	200 keV H^+ $N_2 + CO$ (8:1), 16 K	57 [c]	✓	✓	✓
de Barros et al. (2015)	40 MeV Ni^{11+} $N_2 + H_2O$ (10:1), 15 K	3600 [d]	✓	✓	✓
This work	1 MeV H^+ $N_2 + O_2$ (100:1), 12 K	20 [d]	✓	✓	✓
Vasconcelos et al. (2017)	15.7 MeV O^{5+} $N_2 + H_2O + CO_2 + NH_3$ (100:1.5:0.2:0.4), 16 K	944 [c]	✓	✓	✓

Notes.
[a] The ✓ symbol indicates that the product was reported by the authors
[b] Linear energy transfer reported by the authors
[c] Value reported by the authors
[d] Calculated for pure N_2 for the ion and energy listed

Table 6

Radiation Doses for Ices of Three Astronomical Objects [a]

Object	Time	Distance	Depth	Dose (eV / 16 amu)	Dose (eV / 28 amu)
Pluto	4.6 Gy	~40 AU	1 m	30	52.5
TNO	4.6 Gy	~1000 AU	1 m	50	87.5
Dense IS Cloud	10^6 yr	--	0.02 μm	0.3	0.525
Dense IS Cloud	10^7 yr	--	0.02 μm	3	5.25

Note.

[a] Based on Moore et al. (2001), Moore & Hudson (2006), Hudson et al. (2008), and references therein. The 0.02-μm depth for an interstellar ice grain considers both the entrance and exit layers. See Moore et al. (2001).

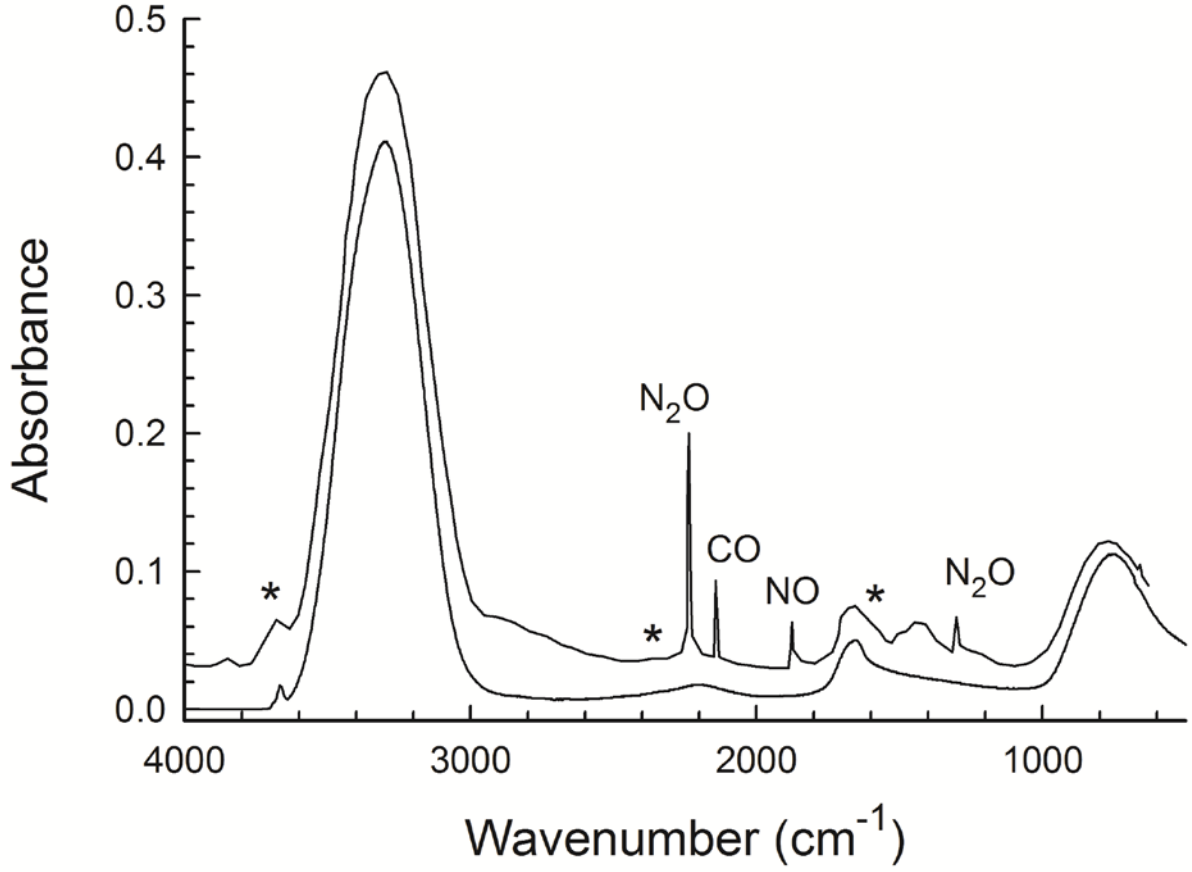


Figure 1. The lower spectrum was calculated (Swanepoel 1983) from the optical constants of Hudgins et al. (1993) for an amorphous H_2O-ice at 10 K, with a thickness of 0.45 µm. The upper spectrum is from an ion-irradiated N_2 + H_2O ice at 15 K, digitized from Figure 1 of de Barros et al. (2015) and offset for clarity. Asterisks indicate three regions, each about 50 cm^{-1} wide, of inaccurate digitization caused by overlapping lines in the original version. See the original publication for enlargements of several regions.

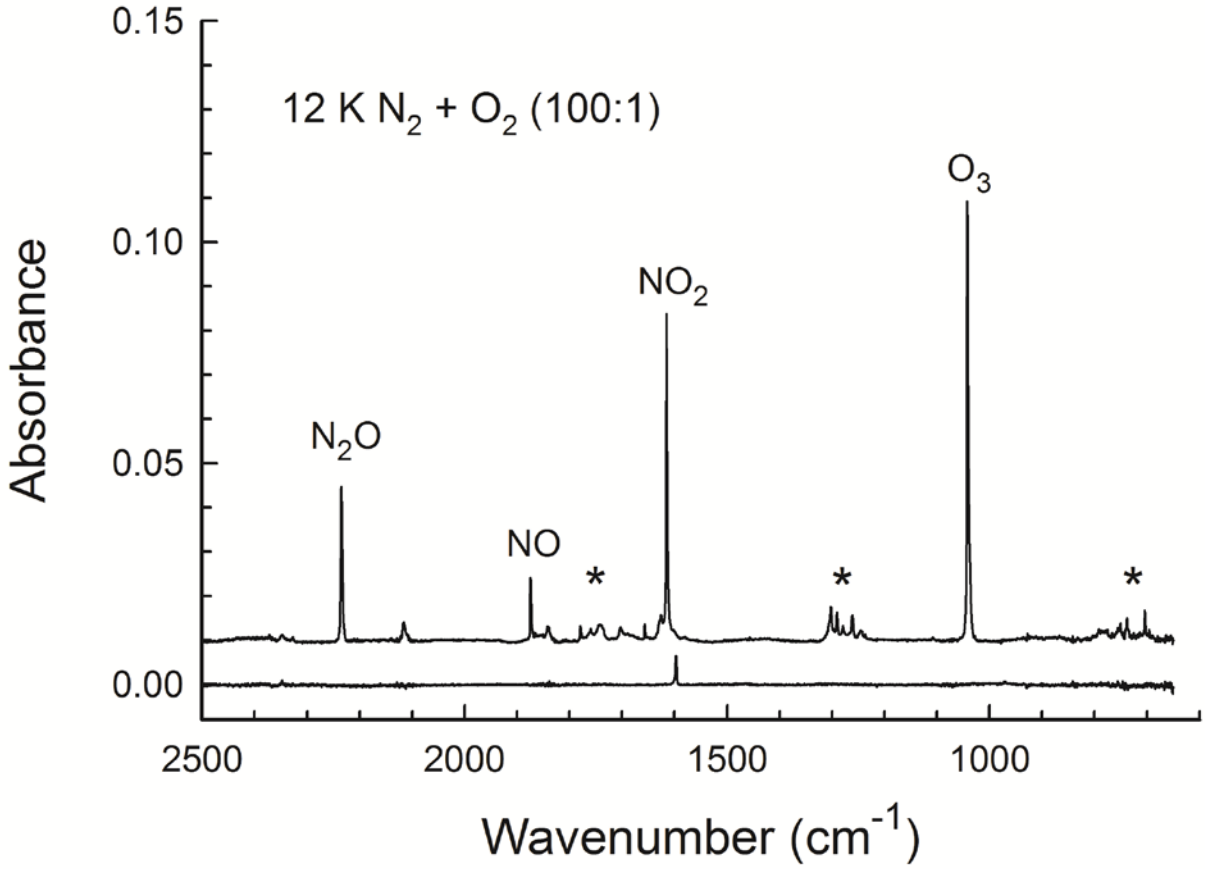


Figure 2. Infrared spectra of an N_2 + O_2 (100:1) ice at 12 K before (lower) and after (upper) irradiation by 1 MeV H^+ to a fluence of about 1×10^{14} H^+ cm^{-2}. A small peak near 1600 cm^{-1} in the lower spectrum is from trapped H_2O (N_2:H_2O ~ 2400:1). Asterisks mark three regions of overlapping IR bands of nitrogen oxides. See the text. The sample's original thickness was about 3 μm. The upper spectrum has been offset for clarity.

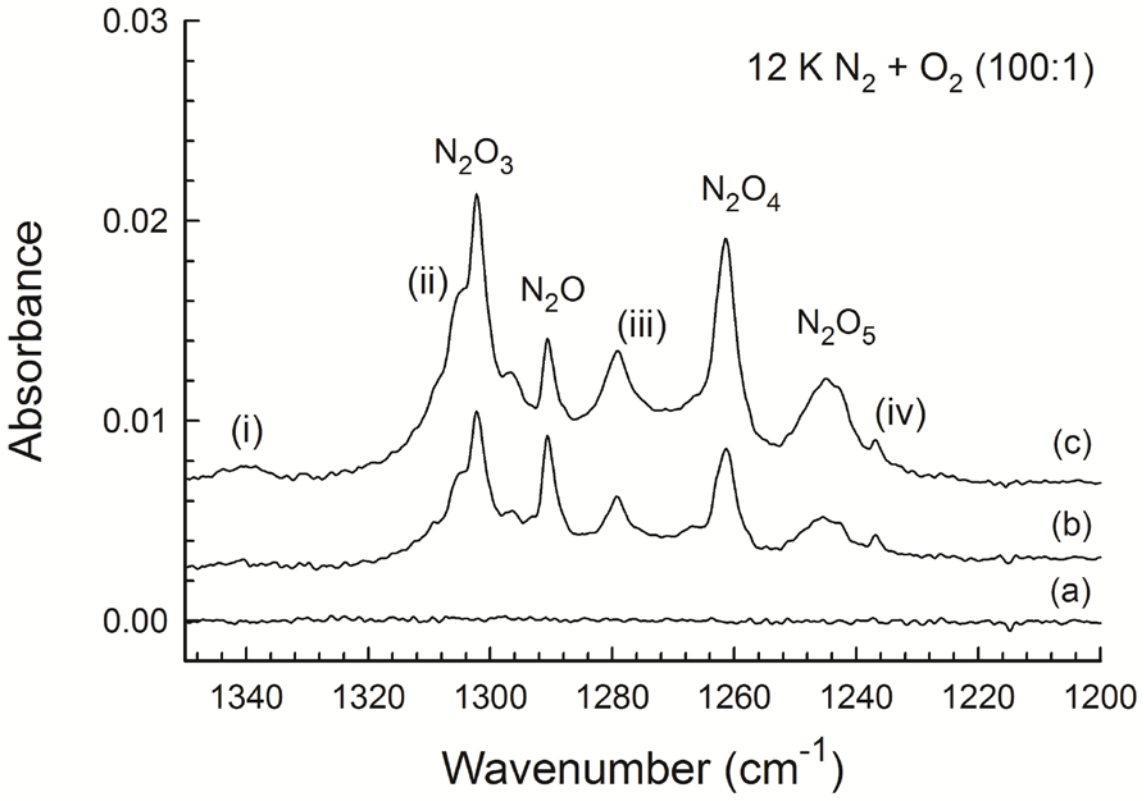


Figure 3. Infrared spectra of an N_2 + O_2 (100:1) ice at 12 K (a) before and after irradiations by 1 MeV H^+ to a fluence of about (b) 1×10^{14} and (c) 2×10^{14} H^+ cm^{-2}. See the text for comments on (i) - (iv). The sample's original thickness was about 3 μm. The spectra have been offset for clarity.

(RLH, 9/25/2018)