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ABSTRACT

Dilute samples of NH₃ and ND₃ in solid neon near 4 K were irradiated at 200 or 173 or 143 nm with light from a synchrotron. We recorded emission spectra of atomic N, involving states ${}^{4}S^{o}$, ${}^{2}P^{o}$ and ${}^{2}D^{o}$, and of molecular N₂, involving states X ${}^{1}\Sigma_{g}^{+}$, A ${}^{3}\Sigma_{u}^{+}$, B ${}^{3}\Pi_{g}$ and C ${}^{3}\Pi_{u}$ in systems with vibrational progressions in the lower states. The emission spectra covered the near-ultraviolet, visible and near-infrared regions from 200 to 1100 nm; the far-ultraviolet absorption spectrum for the precursor NH₃ in solid neon was also measured. Recorded for samples in darkness after irradiation at 143 nm during warming from ~5 K to ~8 K, thermoluminescent spectra consisted mostly of lines emitted by molecular N₂. The analysis of these spectra, and their temporal development, provides information about the nature of dissociative and trapping processes in solid neon under cryogenic conditions involving monochromatic synchrotron radiation.

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INTRODUCTION

The products of decomposition of ammonia with ultraviolet light have been investigated extensively for both gaseous ammonia and ammonia in solid dispersions. Gaseous product NH₂ but not NH was identified with its electronic absorption spectra after flash photolysis of NH₃.¹ Triatomic NH₂ but not NH was identified as a primary photochemical product of the photolysis of also N₂H₄.² Following the flash photolysis of gaseous NH₃ and ND₃, an analysis of the complicated electronic absorption spectra of NH₂ and ND₂ incorporated both vibrational and rotational aspects.³ The photolysis of NH₃ in solid Ar with radiation of wave length less than 200 nm sufficed to generate spectra in the visible and near-ultraviolet region of NH₂ but a wave length less than 155 nm was required to produce NH,⁴ in contrast with 160 nm from gaseous NH₃.⁵ Mid-infrared spectral lines were assigned⁶ to both NH₂ and NH after photolysis of NH₃ in solid N₂; a similar experiment involving photolysis of HN₃ in solid Ar generated lines attributed to NH and ND.⁷ Irradiation from 149 to 164 nm of NH₃ in Ar at 4 K generated NH₂ and NH in approximately equal proportions, although prolonged photolysis decreased the yield of NH₂, likely due to secondary photolysis.⁸ Visible absorption spectra of NH₂, NHD and ND₂ in Ar,⁸ and of emission and excitation of photoluminescence of NH and ND^{9,10} in solidified noble gases have been reported; chemiluminescent spectra of N, O₂, NO, N₂ and NH have also been observed during the warming of mixtures of NH₃ and H₂O in solid argon subjected to photolysis with vacuum-ultraviolet light in a broad band.¹¹

Using intense and tunable radiation from a synchrotron, we have applied our advanced apparatus to record not only absorption

spectra of samples near 4 K throughout the near-ultraviolet, visible and near-infrared regions up to 1100 nm but also emission spectra in the same range, and absorption spectra in the mid-infrared region, from 500 to 4000 cm⁻¹.^{12–15} In preceding work, we irradiated ammonia dispersed in solid neon with far-ultraviolet light and identified photolysis products NH and NH₂ radicals; the features of their electronic and vibrational absorption spectra were recorded in the near-ultraviolet, visible and infrared region.¹⁶ In this work, the emission spectra were recorded both during irradiation and whilst the sample in darkness warmed from ~5 K to ~8 K. These advanced techniques have enabled us to detect both nitrogen atoms and dinitrogen molecules as a significant presence in this photolysis system.

EXPERIMENTS

We recorded the far-ultraviolet absorption spectrum of condensed samples and irradiated these samples with light from the synchrotron in Taiwan Light Source at National Synchrotron Radiation Research Center (NSRRC). The apparatus for this absorption measurement is described elsewhere.¹² To record the absorption of a condensed sample of NH3 dispersed in Ne in the far-ultraviolet region, we deposited a gaseous mixture on a cold LiF window attached to a rotatable refrigerator system (Janis RDK-415 or APD HC-DE204S) coupled to beam line BL03. The far-ultraviolet light was dispersed with a high-flux cylindrical-grating monochromator (focal length 6 m) at beam line BL03 with maximum photon rate about ~10¹² photons s⁻¹ and maximum resolving power about ~50,000; a LiF or CaF₂ disc served to remove the light of higher orders. The light transmitted through the LiF substrate was incident on a glass window coated with sodium salicylate; the converted visible light was detected with a photomultiplier tube (Hamamatsu R943-02) in a photon-counting mode. The absorption was measured at spectral resolution 0.1 nm; the accuracy of reported spectral positions is ± 0.04 nm.

The apparatus for photochemical experiments on solid samples is described elsewhere.^{13–15} The radiation for photolysis at 200 or 173 or 143 nm was selected from an undulator on beam line BL21A2; after absorption by a gaseous and a crystalline filter to suppress harmonics from the undulator, the selected far-ultraviolet light delivered about ~10¹⁵ photons s⁻¹ (bandwidth 2%) to samples. Gaseous mixtures of NH3 dispersed in designed proportion 1:1000 of neon were deposited for 1-4 h on a KBr window that was cooled with a closed-cycle refrigerator (Janis RDK-415) to ~4 K within an enclosure evacuated to <4 µPa. During irradiation with far-ultraviolet light from the beam line, we recorded simultaneously the nearultraviolet, visible and near-infrared emission in spectral range 200 - 1100 nm from the sample in solid neon; afterward, we raised the temperature of the irradiated sample from 4 K to 8 K and monitored its emission. The emissions were analysed with a monochromator (iHR320) and recorded with a charge-coupled device as detector (1024×256 pixels, Horiba Symphony II, image mode). The light emitted in the near-ultraviolet, visible and near-infrared regions was collected with an optical fibre and conveyed to a monochromator and detector.

The chemical substances in these experiments were NH₃ (99.99%, Matheson), ND₃ (isotopic purity 99%, Cambridge Isotope Laboratories, Inc.) and Ne (99.999%, Scott Specialty Gases). Ne was

used without purification. NH_3 and ND_3 were purified with a freezepump-thaw procedure at 77 K, followed by vacuum distillation from 206 to 77 K.

RESULTS

Our samples of NH₃ in Ne were irradiated with light at wave lengths 200 or 173 or 143 nm. Figure 1 shows the absorption of NH₃ in solid neon at 4 K in the far-ultraviolet region. At 200 nm the absorption is finite but weak within a transition from ground state X ¹A₁ to excited state A ¹A₂".¹⁷ Wave length 173 nm is near the maximum absorption, 173.8 nm, in this electronic system that



FIG. 1. Far-ultraviolet absorption spectrum of $\rm NH_3$ dispersed in solid Ne (1:1000) near 4 K.



FIG. 2. After sample NH₃:Ne=1:1000 was irradiated at 143 nm and 4 K, thermoluminescent emission spectra from 250 to 400 nm were recorded during warming to (a) 6-7 K, (b) 7-8 K; for clarity the ordinate scale of curve b is offset upward by 65 counts s⁻¹ from curve a; the dark current of the detector corresponds to 900 counts s⁻¹.

exhibits vibrational structure less diffuse than for NH₃ in solid argon at 10 K.¹⁸ The discernible diffuse structure superimposed on a continuous curve between 150 and 200 nm has mean interval 1830 \pm 30 cm⁻¹; this interval is roughly twice the vibrational wavenumber associated with the symmetric deformation mode in the electronic ground state and reflects the planar structure of electronically excited state A ¹A₂".¹⁷ Below 170 nm three further excited states, B ¹E", C ¹A₁' and D ¹A₂", known for gaseous NH₃ might all contribute to the absorption of light at 143 nm.^{17,19,20}

Analysis of the spectra recorded in our experiments with a comparison of literature data indicates the presence, during or after irradiation of NH₃ or ND₃ with NH₂D and NHD₂ dispersed in solid neon near 4 K, of N, N₂, NH, ND, NH₂, NHD and ND₂ from ammonia precursors, and of OH and CO from vestigial impurities H_2O and CO_2 present before irradiation. A novel feature of these experiments was the recording of emission spectra when a sample of initially either NH₃ or ND₃ in Ne that had been previously irradiated at 143 nm but was otherwise maintained in darkness for several minutes was allowed to warm gradually from ~5 K, according to a Si diode embedded in the KBr substrate supporting the solid neon, to 6-7 K during a first recording of the thermoluminescence, and

then to 7-8 K during a second recording of further thermoluminescence. As displayed in Figure 2, these spectra are notable for their flat baselines, unlike the emission spectra recorded during irradiation of a sample that tended to exhibit a prominent pattern of fringes. Nearly all lines in these first and second spectra are readily assigned mostly to emissions of N₂ in systems A ${}^{3}\Sigma_{u}{}^{+}$ - X ${}^{1}\Sigma_{g}{}^{+}$ and C ${}^{3}\Pi_{u}$ - B ${}^{3}\Pi_{g}{}^{21}$ listed in Table I.

Lines of electronic transition N₂ A-X were emitted during irradiation only at 143 nm and afterward as thermoluminescence, whereas lines of transition C - B were emitted during and after irradiation at both 173 and 143 nm. Whereas transition A ${}^{3}\Sigma_{u}^{+}$ - X ${}^{1}\Sigma_{g}^{+}$ involves an altered multiplicity, from a triplet state to a singlet state, transition C ${}^{3}\Pi_{u}$ - B ${}^{3}\Pi_{g}$ is expected to have a large intrinsic intensity; according to this condition the production of measurable intensity of lines of the transition C – B might correspond to a small fraction of N₂ molecules involved. Although excited electronic states A, of term value 50203.63 cm⁻¹, and B, of term value 59619.35 cm⁻¹, of N₂ have electronic energies less than the maximum photon energy of irradiation in this experiment, at wave length 143 nm corresponding to ~70,000 cm⁻¹, state C of gaseous N₂ has electronic energy, corresponding to term value 89136.88 cm⁻¹,

N ₂ in Ne near 6-8 K			gaseous N ₂		A ${}^{3}\Sigma_{u}$ + - X ${}^{1}\Sigma_{g}$ +	
λ/nm^a	v/cm ^{-1b}	$\Delta v/cm^{-1c}$	$(v',v'')^{\mathrm{d}}$	ν/cm^{-1e}	$\Delta v/cm^{-1c}$	$\Delta \nu/cm^{-1f}$
			0,0	49754.7		
			0,1	47424.8	2329.9	
			0,2	45123.6	2301.2	
233.0	42905		0,3	42851.3	2272.3	-64
245.7	40688	2217	0,4	40607.9	2243.4	-80
259.7	38494	2194	0,5	38393.8	2214.1	-100
275.5	36287	2178	0,6	36209.9	2184.8	-78
293.2	34097	2190	0,7	34054.0	2155.0	-43
312.5	31991	2106	0,8	31929.2	2124.8	-62
335.0	29842	2149	0,9	29834.6	2094.6	-17
359.4	27816	2026	0,10	27771.1	2063.5	-45
387.9	25773	2043	0,11	25739.1	2032.0	-34
420.9	23752	2021	0,12	23738.9	2000.2	-13
N ₂ in Ne near 6-8 K			gaseous N ₂		$C^{3}\Pi_{u}$ - $B^{3}\Pi_{g}$	
344.6	29011		0,0	29677.9		667
366.4	27285	1726	0,1	27973.0	1704.9	688
391.1	25562	1723	0,2	26296.7	1676.3	735
418.4	23895	1667	0,3	24649.1	1647.6	754
450.0	22216	1679	0,4	23030.5	1618.6	809
485.4	20596	1620	0,5	21440.9	1589.6	839
526.5	18988	1608	0,6	19880.0	1560.9	887
574.0	17416	1572	0,7	18347.7	1532.3	926

TABLE I. Emission lines of N₂ from photolysis of NH₃ in solid Ne near 6-8 K compared with data for gaseous N₂.

 $^aWave \, length \, \lambda/nm$ is measured in air.

 $^{\rm b}Wavenumber \,\nu/cm^{-1}$ pertains to vacuum.

^cWavenumber difference $\Delta v/cm^{-1}$ is the progressive difference from the preceding row.

 $^{d}v',v''$ denotes the vibrational numbering for transitions between the vibrational ground state v' = 0 of N₂ of an excited electronic state and vibrational state v'' in a lower electronic state.

ev/cm⁻¹ denotes the wavenumber calculated for gaseous N2¹⁵ for transitions in the preceding column.

 $^{f}\Delta v$ is the difference/cm⁻¹ between the value for N₂ calculated for the gaseous phase and that for N₂ dispersed in Ne.

λ/nm^{a}	v/cm^{-1b}	transition	v/cm^{-1c}	$\Delta \nu/cm^{-1d}$
N in solid Ne		gaseous N		
518.6	19278	${}^{2}D^{o}_{3/2} \rightarrow {}^{4}S^{o}_{3/2}$	19233.2	-45
519.6	19240	${}^{2}\text{D}^{0}{}_{5/2} \rightarrow {}^{4}\text{S}^{0}{}_{3/2}$	19224.5	-16
1039.2	9620 (second order)	${}^{2}\text{D}^{0}{}_{3/2} \rightarrow {}^{4}\text{S}^{0}{}_{3/2}$		
1042.5	9599 (second order)	${}^{2}\text{D}^{0}{}_{5/2} \rightarrow {}^{4}\text{S}^{0}{}_{3/2}$		
1037.6	9635	${}^{2}P^{o}{}_{1/2,3/2} \rightarrow {}^{2}D^{o}{}_{5/2}$	9615.2	-20
1038.3	9628	${}^{2}\mathrm{P}^{\mathrm{o}}{}_{1/2,3/2} \rightarrow {}^{2}\mathrm{D}^{\mathrm{o}}{}_{3/2}$	9606.4	-22

TABLE II. Emission lines of N during irradiation of NH₃ and ND₃ in solid Ne near 4 K compared with data for gaseous N.

^aWave length λ /nm is measured in air.

^bWavenumber v/cm⁻¹ pertains to vacuum; lines appearing in the second order of the grating are indicated.

^cv/cm⁻¹ is the wavenumber¹⁶ for gaseous N for the transition in the preceding column.

 $^{d}\Delta\nu$ is the difference/cm $^{-1}$ between the value for N_{2} calculated for the gaseous phase and that for N_{2} dispersed in Ne.

substantially greater than that photon energy. Two progressions A - X and C - B are readily distinguishable because the relative intensities of the progression of transition C - B decreased from the first to the second recorded thermoluminescent spectra whereas the relative intensities of the progression of transition A - X increased under the same conditions, as shown in Figure 2. Apart from the several lines in the vibrational progressions of these two electronic transitions of N₂ in the thermoluminescent spectra, which appeared in both first and second orders of the grating, the only other significant line, at 336.2 nm or 29736 cm⁻¹, at a wave length less than 750 nm is readily assignable to NH in its transition A ${}^{3}\Pi_{i}$ - X ${}^{3}\Sigma^{-}$; the origin for gaseous NH is known at 29777 cm⁻¹.

Lines emitted by atomic nitrogen recorded during irradiation, at 173 and 143 nm but not 200 nm, of samples of both NH_3 and ND_3 in neon, are listed in Table II. On irradiation at 143 nm, the feature near 520 nm was the most prominent in the emission spectrum, whereas on irradiation at 173 nm this feature was less prominent



FIG. 3. Emission spectra (a) from 516 to 521 nm and (b) from 1034 to 1044 nm, recorded during irradiation at 143 nm of NH_3 in Ne (1:1000) near 4 K; the dashed lines indicate an approximate deconvolution into the significant components, each with a lorentzian profile.

than only the emission lines of NH or ND near 335 nm. A lack of isotopic shift with H or D is consistent with this intense feature being associated with N. There is likely some contribution to the intensity of the feature near 520 nm from emission line 0,5 of the progression of system A ${}^{3}\Sigma_{u}{}^{+}$ - X ${}^{1}\Sigma_{g}{}^{+}$ for N₂, expected near 520 nm in the second order of the grating. The same feature of N appears in these experiments also in the second order of the grating, near 1040 nm, near other features attributable to atomic nitrogen. The atomic transitions near 520 nm as a doublet at 518.3 and 519.3 nm are assigned to N in transitions ${}^{2}D^{o}{}_{5/2} \rightarrow {}^{4}S^{o}{}_{3/2}$ and ${}^{2}D^{o}{}_{3/2} \rightarrow {}^{4}S^{o}{}_{3/2}$; the atomic transitions near 1040 nm as a doublet 1037.6 and 1038.5 nm are assigned to N in transitions ${}^{2}P^{o}_{1/2,3/2}$ - ${}^{2}D^{o}_{5/2}$ and ${}^{2}P^{o}_{1/2,3/2}$ - ${}^{2}D^{o}_{3/2}$;¹⁶ the details appear in Table II; the emission profiles with roughly fitted components are shown in Figure 3. The relative intensities of the components of these doublets are in each case consistent with the Einstein A coefficients for N in the gaseous phase.²

Other than those transitions of atomic and molecular nitrogen, the emission spectra recorded during irradiation of our samples at 200, 173 and 143 nm included many lines, shown in overviews in Figures 4 and 5. During irradiation of NH₃ in Ne at 200 nm, lines at 334.7, 336.0 and 339.0 nm of NH in transition A ${}^{3}\Pi_{i}$ - X ${}^{3}\Sigma^{-}$ were



FIG. 4. Emission spectrum from 320 to 800 nm during irradiation of NH_3 in solid Ne near 4 K; annotation 2^{nd} implies the second order of the diffraction grating.



FIG. 5. Emission spectrum from 320 to 800 nm during irradiation of ND₃ in solid Ne near 4 K; annotation 2^{nd} implies the second order of the diffraction grating.

TABLE III	Assigned	emission	lines (of NH.	OH	and CO.
	. Assiuncu	01111331011				

most prominent, of which the lines at 334.7 and 336.0 nm appeared first with comparable stature, but the latter became more intense in subsequent irradiation; the counterpart of these lines appeared also in the second order of the grating near 672 nm. In the nearinfrared region weak lines at 783.9, 787.4 and 788.6 nm were barely discernible, assigned to NH in transition a ${}^{1}\Delta$ - X ${}^{3}\Sigma$; the intensity of the feature at 783.9 nm seemed to decrease on protracted irradiation whereas the intensities of the other two main features at 787.4 and 788.6 nm increased monotonically. During irradiation at 173 nm of NH₃ in Ne, the most prominent emission feature was that near 335 nm, due to NH, followed by the line of atomic N near 520 nm and another feature of NH near 789 nm. In the near-ultraviolet region the only other emission lines, at 307.9 and 309.2 nm, were much less intense than the nearby lines of NH; these lines are assigned to OH radicals¹⁵ that were produced on photolysis of H₂O impurity. During irradiation at 173 nm of ND₃ in Ne, the most prominent emission feature was near 335 nm, due to ND, followed by the lines of atomic N near 520 nm and ND near 789 nm.

λ/nm^a	v/cm ^{-1b}	$\Delta \nu/cm^{-1c}$	$(v',v'')^{\mathrm{d}}$	ν/cm^{-1e}	$\Delta v/cm^{-1c}$	$\Delta v/cm^{-1f}$
	NH in Ne near	4 K		gaseous NH	$a^{1}\Delta - X^{3}\Sigma^{-}$	
788.4	12681		0,0	12589	-92 b ${}^{1}\Sigma^{+}$ – X ${}^{3}\Sigma^{-}$	
	NH in Ne near 4 K			gaseous NH		
468.1	21357		0,0	21238		-119
	NH in Ne near	4 K		gaseous NH	$A^{3}\Pi_{i} - X^{3}\Sigma^{-}$	
336.1	29744		0,0	29776.8	33	
	ND in Ne near 4 K			gaseous ND	$a^{1}\Delta - X^{3}\Sigma^{-}$	
788.7	12676		0,0	12613	-63	
	ND in Ne near 4 K			gaseous ND $b^{1}\Sigma^{+} - X^{3}\Sigma^{-}$		$-X^{3}\Sigma^{-}$
468.3	21348		0,0	21225	-123	
	ND in Ne near 4 K			gaseous ND	$A^{3}\Pi_{i} - X^{3}\Sigma^{-}$	
336.5	29709		0,0	29798.8		90
	OH in Ne near 4 K			gaseous OH	$A^2\Sigma^+ - X^2\Pi_i$	
307.8	32478		0,0	32616.4		
309.2	32331	147	0,0	32477.2		144
CO in Ne near 4 K			gaseous CO	$a^{3}\Pi_{r}$ – $X^{1}\Sigma^{+}$		
206.2	48473		0,0	48473.2		0
215.7	46339	2134	0,1	46330.0	2143.2	-9
226.1	44209	2130	0,2	44213.4	2116.6	4
237.3	42123	2086	0,3	42123.4	2090.0	0
249.4	40080	2043	0,4	40060.0	2063.4	-20
262.9	38023	2057	0,5	38023.2	2036.8	0
CO in Ne near 4 K				gaseous CO	$e^{3}\Sigma^{-} - a^{3}\Pi_{r}$	
646.5	15463		0,0	15231.6		-231
726.8	13748	1715	0,1	13517.0	1714.6	-231
829.4	12054	1694	0,2	11831.2	1685.8	-223
961.1	10401	1653	0,3	10174.2	1657.0	-227

^aWave length λ /nm is measured in air.

 b Wavenumber $\nu/cm^{\text{-1}}$ pertains to vacuum.

^cWavenumber difference $\Delta \nu/cm^{-1}$ is the progressive difference from the preceding row.

 ${}^{d}v',v''$ denotes the vibrational numbering for transitions between the vibrational ground state v' = 0 of an excited electronic state and vibrational state v'' in a lower electronic state.

 $^{e}v/cm^{-1}$ is the wavenumber calculated for gaseous N₂ for the transitions in the preceding column.

 $^{f}\Delta\nu$ is the difference/cm⁻¹ between the value for N₂ calculated for the gaseous phase and that for N₂ dispersed in Ne.

During irradiation at 143 nm of NH₃ in Ne, the most prominent feature in emission was that of atomic N near 520 nm, followed by the features due to NH near 789 and 335 nm; the transition b ${}^{1}\Sigma^{+}$ - X ${}^{3}\Sigma^{-}$ of NH was another appreciably intense feature at 468.3 and 469.6 nm.⁹ During irradiation at 143 nm of ND₃ in Ne, the most prominent feature was due to ND near 789 nm, followed by atomic N near 520 nm and ND near 335 nm; the transition of ND b - X was also a significant feature at 469.6 and 470.9 nm. Because of isotopic mixing in precursor ND3 to include ND2H and NH2D before deposition of the mixture,¹⁶ the lines attributed to electronic transitions of ND above included contributions from NH. During irradiation of NH₃ or ND₃ at 143 nm, six weak lines in a progression accompanying electronic transition a ${}^{3}\Pi_{r}$ - X ${}^{1}\Sigma^{+}$ of CO were recorded in the ultraviolet region in the first order of the grating, and also in the visible and near-infrared regions in the second and third orders of the grating, as reported previously.¹⁴ During irradiation at 143 nm, a substantial line at 646.9 nm, equivalent to 15454 cm⁻¹, was observed, which we assign also to electronic transition $e^{3}\Sigma^{-}$ - $a^{3}\Pi_{r}$ of CO, with three more lines in a vibrational progression; the origin for gaseous CO is known at 15232 cm⁻¹.²¹ State e ${}^{3}\Sigma^{-}$ has term value 64230 cm⁻¹, corresponding to appreciably less energy than the photon energy at 143 nm. A list of assigned emission lines other than those of N and N₂ is presented in Table III.

DISCUSSION

According to Heisenberg in 1925,²³ the observable properties of atoms and molecules are their spectral lines, which are characterised by their frequencies and their intensities. Our experiments involve active chemical species that are present to an extent less than 5 µmol, mixed with an inert diluent, neon, rather than a gaseous sample on a macroscopic scale. Although Heisenberg's comment was applicable to free atoms and molecules, as in a dilute gaseous phase, the inert environment provided by neon atoms in a polycrystalline lattice enables the generation and persistence of nearly free and isolated atoms and molecules, as attested by the small spectral shifts between the wavenumbers in the preceding tables associated with gaseous and isolated species, whether atomic or molecular. The corresponding perturbations of the electronic structure by the neon environment and of the properties of these isolated species are hence also slight, because the energy of the photons, less than 9 eV, from the synchrotron radiation in our experiments is much less than the energy at the onset of absorption of solid neon. On this basis we interpret our spectra in terms of participating atoms and molecules that absorb and emit light, rather than of bulk matter.

In our experiments we recorded spectra in absorption in the mid-infrared region, from 500 to 5000 cm⁻¹,¹⁶ and in absorption¹⁶ and emission in the near ultraviolet, visible and near-infrared regions, from 200 to 1100 nm. The emission spectra were recorded not only during irradiation of our samples at a particular wave length – 200 or 173 or 143 nm, but also whilst the sample in darkness was gradually warming from about 5 K to 8 K. Chemiluminescence signifies the production of light as a result of a chemical reaction; photoluminescence implies the emission of light by an atom or molecule that is excited to an emitting state as a result of absorption of light, at the same or different wave length, whereas thermoluminescence comprises light emitted by a species as a result of an increased temperature or a warming process. In our experiments

the emission detected during irradiation at 200 or 173 or 143 nm might include photoluminescence, if a particular species absorbed a photon at one such wave length and directly emitted a photon, or chemiluminescence, if a species that was produced on photolysis reacted with another species to generate an excited atom or molecule that emitted a photon. In our experiments, emission lines observed as thermoluminescence resulted from the reaction of a previously trapped atom or molecule that became mobile, through increased thermal energy with rising temperature, so as to migrate through the neon lattice and then to react with another previously trapped species to generate an excited atom or molecule that emitted a photon. After irradiation at 143 nm, our recorded thermoluminescent emission lines are definitively assigned to excited molecular N2 in two electronic systems, A ${}^{3}\Sigma_{u}^{+} \rightarrow \widetilde{X} {}^{1}\Sigma_{g}^{+}$ and C ${}^{3}\Pi_{u} \rightarrow B {}^{3}\Pi_{g}$, that must form from the reaction of N atoms that became mobile with increasing temperature - even such a small increase as from 6 to 7 K – according to the unambiguous evidence of our spectra. The emission of N atoms directly observed in transitions ²D - ⁴S and ²P - ²D proves that these atoms in excited states ²P and ²D were produced during irradiation of ammonia at 173 or 143 nm, but not at 200 nm; these N atoms could be trapped and isolated within the Ne lattice, ready to migrate and to react to form excited N₂ when the increased temperature enabled their mobility. A combination of two N atoms in ground state ⁴S suffices to produce excited N₂ molecules in state A, whereas for emission of excited N2 molecules in state C two atoms in states ${}^{4}S$ and ${}^{2}P$ are required.²⁴ The emission of N₂ molecules from state C during the thermoluminescence stage of the experiment seems to indicate that not only N atoms in ground state ⁴S but also atoms in excited state ²P were stored in solid neon for some finite interval.^{25} Other reactions N + NH \rightarrow N_2^* + H and N + NH_2 \rightarrow N_2^{\star} + H_2 to produce electronically excited molecules N₂^{*} that emit during warming cannot be excluded. A combination of a previously trapped N atom with a likewise liberated H atom can generate excited NH in state $A^3\Pi_i$ that was the only other emitter identified in our thermoluminescent spectra. The N atoms that result from secondary photolysis of NH and NH₂ combine to generate electronically excited N₂ molecules that relax radiatively through transitions $C \rightarrow B$ and $A \rightarrow X$, according to our direct spectral observations. Whereas the absorption spectrum of NH3 in solid neon is well characterised in the far-ultraviolet region, cf. Figure 1, and states c and d of NH are known to be amenable to absorption at wave lengths less than 230 nm,¹⁷ the absorption characteristics of NH₂ radicals are unknown in this region. The monochromatic and tunable nature of the radiation from the synchrotron in our experiments enabled a much improved analysis of the production of excited states of N and N2 beyond published reports of their emission spectra excited with a broad source of vacuum-ultraviolet light.

During irradiation at 200 nm the most notable feature in the emission spectra from 300 to 800 nm was also the composite line near 335 nm, assigned to NH, but during irradiation at 173 nm the line at 518.3 nm, assigned to atomic N, was more prominent. During irradiation at 143 nm the most prominent lines were the composite feature near 786 nm, assigned to NH, the line of atomic N at 518.3 nm and the composite feature near 335 nm, assigned to NH. During irradiation of ND₃ at 143 nm, the line at 646 nm, assigned to CO, was also prominent. The absorption lines due to NH₂, NHD and ND₂ are expected on the basis that these triatomic radicals become

the primary photochemical product of photolysis of NH_3 and its deuterated variants, as discussed in the previous work.¹⁶ If not a primary photochemical product of photolysis of NH_3 , NH must be a primary product of photolysis of NH_2 . Photolysis of any nitrogen hydride molecules under our conditions of protracted irradiation would be expected ultimately to yield N atoms, which combine to form N₂. The temporal profiles of N, N₂, NH and NH₂ in Figure 6 clearly indicate that NH_2 and NH were formed directly on initiation of irradiation at 173 nm, and that NH_2 is subject to secondary decomposition through photolysis. The profiles of N and N₂ show that these species appeared only after the prior formation of NH and NH_2 ; when the proportion of N in the solid dispersion became sufficiently great, the combination of these atoms to form N₂ occurred. These processes are summarised in this qualitative scheme, in which each arrow except the rightmost implies a photolytic action.

$$NH_3 \rightarrow NH_2 \rightarrow NH \rightarrow N \rightarrow N_2$$

The spectra of amidogen radicals in solid dispersions of noble gases are explored at length elsewhere.⁸ The spectra of imidogen radicals in solid dispersions of noble gases other than Ne are likewise discussed elsewhere;⁹ the attribution of lines due to NH in particular cavities in solid argon is speculative because no direct evidence from a crystal structure was provided.⁹ Multiple trapping sites for both atoms²⁶ and molecules⁴⁷ in solid dispersions in noble gases have long been known, but the particular nature of the trapping sites is inevitably difficult to identify.

The observation of emission of N and N₂ in solid Ne or other solidified gas has been reported; excitation of dilute mixtures of N₂ in Ne with X-rays from a W target induced emission of systems A – X, and C – B but only for Ne dispersant, of N₂ and transition ²D – ⁴S of N, but not ²P – ²D.²⁸ Another contrasting feature is that, in our experiments, N₂ must have been formed from precursor ammonia rather than being present after the deposition of the particular samples. As a notable result of published experiments of N₂ in Ne,²⁸ the lifetime of the emission from excited N₂ was evaluated as 341 s;



FIG. 6. Temporal profiles of N, N₂, NH and NH₂ during or after irradiation at 173 nm of NH₃ in Ne near 4 K; the points indicate areas of selected characteristic spectral lines of the pertinent species in emission or absorption as a function of duration of irradiation.

our experiments in which the delay between irradiation and recording of emission in the measurements of thermoluminescence was greater than 400 s are consistent with such a great lifetime. Following the condensation of N₂ subjected to an electric discharge and its mixtures with other constituents, a line near 348 nm was tentatively identified²⁹ as due to atomic N, trapped in solid N₂, in transition ${}^{2}P^{o}{}_{1/2,3/2} \rightarrow {}^{4}S^{o}{}_{3/2}$; this line is not reproduced in our experiments, despite our observation of the transition ${}^{2}P^{o}{}_{1/2,3/2} \rightarrow {}^{2}D^{o}{}_{3/2,5/2}$ near 1040 nm with the same upper state that is within the energy of our irradiating photons. The effective energies of both the X-rays²⁸ and the electrons that induced dissociation of N₂ in the electrode-less discharge²⁹ are much greater than the energy, < 9 eV, of the photons in our experiments in which we observed the emission of light in transitions of both N and N₂, as explained above.

CONCLUSION

Under our particular conditions of intense and tunable radiation from a synchrotron and samples of absorbing molecules NH_3 and ND_3 dispersed in solid neon near 4 K, we have extended the range of products from the photochemical decomposition of ammonia to include, in secondary processes, nitrogen atoms and dinitrogen molecules, unambiguously identified according to their emission spectra not only during irradiation but also, for N_2 , in a succeeding thermoluminescent stage of our experiments.

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