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Stability of H, D, ¹⁴N, and ¹⁵N atoms in solid ammonia above 100 K

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The measurements reported below quantify the stability and decay of hydrogen, deuterium, and nitrogen atoms in frozen ammonia above 100 K. The decay of H atoms is observed on a time scale of minutes in the range of 100–110 K and follows first-order kinetics. Analogous decays of D and N atoms are observed in the ranges 105–120 and 140–160 K, respectively. Activation energies for the decay processes range from 0.1 to 0.4 eV. © *1998 American Institute of Physics.* [S0021-9606(98)51104-X]

I. INTRODUCTION

Ammonia at temperatures ≤ 1 K is used as a polarized target material to study spin effects in high-energy physics scattering experiments. Irradiation of solid ¹⁴NH₃, ¹⁴ND₃, ¹⁵NH₃, and ¹⁵ND₃ creates paramagnetic centers which, at low temperature and high microwave power, polarize the H and D nuclear spins. Electron paramagnetic resonance (EPR) studies of target samples are underway to reveal the electronic structures of the products of irradiated ammonia and their stability and decay processes. X-band spectra with wellresolved hyperfine structure have been obtained of ¹⁴NH₂, ¹⁴ND₂, ¹⁵NH₂, and ¹⁵ND₂ radicals. In addition there are resonances from H and D atoms at Breit-Rabi field strengths, and from ¹⁴N and ¹⁵N atoms. Resonances from H, D, ¹⁴N, and ¹⁵N have been observed previously in several kinds of solid matrix, but not in frozen ammonia. There are few reports of H and D, and none of N atoms stable above 77 K, and there is even less information about the temperature dependence of their disappearances. We find that the decay of all three atoms and of the free radicals in solid ammonia can be measured on a time scale of minutes over different temperature ranges in the interval of 100-160 K.

There is a significant literature on H, D, and N atoms at 4.2 K in frozen gas matrices.¹⁻⁹ The melting points of hydrogen, neon, and argon are in the range of 14–84 K. Even if variable temperature EPR measurements had been made on H, D, and N in these matrices, one would not have the opportunity to observe decay processes above 100 K, like those described below, because the phase transitions to the liquid state would have been accompanied by rapid diffusion and recombination of the atoms. Indeed, our first question after identifying the atoms, stable in irradiated frozen ammonia at 77 K, was whether their decay at higher temperatures would precede or accompany a phase transition in irradiated, solid ammonia. This question is answered here, but many questions remain about the stability and decay processes of atoms in other frozen matrices up to their melting points.

In the literature are two reports of H atoms stable in

solids above 100 K. EPR measurements by Livingston et al.¹⁰ at several temperatures between 94 and 124 K, show the time dependence of H atoms produced in acids exposed at 77 K to gamma irradiation; the data are represented reasonably well by second-order kinetics. Delbecq et al.¹¹ investigating with EPR and optical absorption the effects of ultraviolet irradiation at 80 K of KCl-KH and KCl-KD crystals, found significant concentrations of H and D atoms remaining after pulse annealing for 2 min at temperatures as high as 120 K; unaware of the rate process which was occurring, they interpreted their results in terms of temperaturedependent surviving fractions. Monolayers of H and D atoms are found to be stable on a clean Ni(100) surface up to about 160 K.¹² We find, at fixed temperatures as described below, exponential decay in time of free H and D (and N) atoms in solid ammonia. It takes about 1 min to record a spectral amplitude. This resolution is ample for the time scale of the processes we observe. Arrhenius plots (in rate constants versus reciprocal temperature) provide activation energies for the processes.

II. EXPERIMENT

Four types of ammonia, ${}^{14}NH_3$, ${}^{14}ND_3$, ${}^{15}NH_3$, and ${}^{15}ND_3$ were pre-prepared for this experiment. Each had been



FIG. 1. Free radical spectra of (A) $^{14}ND_2$ in irradiated $^{14}ND_3$ at 77 K, 9.488 GHz; (B) $^{15}ND_2$ in irradiated $^{15}ND_3$ at 77 K, 9.339 GHz.

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Free radical	g (isotropic)	g (anisotropic)	Reference ^a	
¹⁴ NH ₂	2.0044 2.0046±0.0003 2.0048		This paper 14 1	
¹⁴ ND ₂	2.0054 2.0042±0.0003 2.0047	$g_{\perp} = 2.0061 \ g_{\parallel} = 2.0040$	This paper 14 1	
¹⁵ NH ₂	2.0043 2.0052 ± 0.0005		This paper 14	
¹⁵ ND ₂	2.0053 2.0052 ± 0.0005	$g_{\perp} = 2.0063 g_{\parallel} = 2.0030$	This paper 14	
Atom (in free radical)		$A(10^{-4} \text{ cm}^{-1})$	Reference	
¹⁴ N		14.2 14.2 9.6±0.1	This paper 14 1	
¹⁵ N		22.2 19.9±0.7 $(22.2)^{b}$	This paper 14 1	
Н		21.6 23.8 22.3±0.1	This paper 14 1	
D		3.3 3.7 3.4	This paper 14 1	

TABLE I. g and A values for NH₂ free radicals.

^aReference 14 reports EPR measurements at 77 K (some at 118 K) on free radicals formed in the gas phase by 1 MeV He⁺ ion bombardment and then trapped at 77 K. Reference 1 reports EPR measurements at 4.2 K on the products of photolysis of ammonia in argon at 4.2 K.

^bThis entry includes a factor of 2 apparently missed in Ref. 1.

slowly frozen from a gas at room temperature to a pure and consistent microcrystalline form at liquid nitrogen temperature. The samples were then crushed into granules between 1 and 3 mm in diameter, and stored in a liquid nitrogen bath. The beads of ammonia were irradiated at liquid argon temperature and stored in liquid nitrogen.¹³ One of the ¹⁴NH₃ and ¹⁵ND₃ samples, and the ¹⁵NH₃ sample, received additional radiation at 1 K during scattering experiments, and every 16 h were warmed to ~80 K for 10 min to anneal away the deleterious effect of radiation damage on polarization; after their use as a target, the beads were again stored under liquid nitrogen.

It was found that a strong signal was obtained with only a few small beads of frozen ammonia. The beads could be pulled from the storage container with tweezers, and dropped into whatever dewar or sample cell (precooled to 77 K) was being used, with minimal exposure to room temperature air.

The EPR measurements were carried out with a Varian V-4500 X-band spectrometer. A Varian E-500 tracking NMR gaussmeter was used to measure the applied magnetic field, and a Hewlett–Packard X532B frequency meter to measure the microwave frequency. The microwave power entering the bridge hybrid junction was monitored through a 20 dB coupler with a Hewlett–Packard X486A thermistor mount attached, the output of which went to a Hewlett–



FIG. 2. Power saturation at 77 K and 9.298 GHz of the high-field Breit–Rabi resonance from H atoms in irradiated $^{14}NH_3$. The microwave powers reaching the cavity were: in (A) 0.8 mW; in (B) 1.3 mW; in (C) 3 mW.

Packard 431B power meter. To achieve sample temperatures above 77 K, a Varian V-4547 variable temperature system was employed; the temperature of the flowing cold nitrogen gas was determined with a copper–constantan thermocouple junction just below the sample tube.

III. RESULTS

EPR spectra from irradiated samples of all four ammonia isotopes were recorded at 77 K. Two examples are given in



FIG. 3. Low-field Breit–Rabi resonances at 77 K and 9.297 GHz from D atoms in irradiated $^{15}\mathrm{ND}_3.$

Fig. 1. Simulations of these spectra verified that the irradiation produced NH_2 and ND_2 free radicals. In Table I are listed the *g* and *A* values so obtained for each of the ammonia isotopes. The last column of Table I lists values of the parameters for the same free radicals produced from ammonia under other conditions.^{14,1}

The initial NH_2 and ND_2 simulations were made with isotropic *g* values, an assumption which produced perfectly antisymmetric first-derivative absorption curves. Because slight asymmetries were present in the experimental data, further simulations were carried out in order to determine the effects of very small contributions of orbital angular momen-

TABLE II. Breit-Rabi H-atom and D-atom resonances.

Source of atom	Matrix	Temperature (K) of EPR measurement	Microwave frequency (GHz)	B _{low} (G)	$egin{array}{c} B_{ m high} \ ({ m G}) \end{array}$	Reference for data	g	$A (10^{-4} \text{ cm}^{-1})$
			H-atom reson	ances				
Irradiated ¹⁴ NH ₃	$^{14}NH_3$	94-104	9.113	2979.4	3483.7	This paper	2.003	468.7
		101	9.111	2979.9	3482.7		2.003	467.3
		17	9.295	3044.9	3547.5		2.003	467.4
		4.2	9.190	3010	5515		2.005	407.0
Irradiated ¹⁵ NH ₃	¹⁵ NH ₃	94	9.111	2980.8	3483.7	This paper	2.002	467.3
		77	9.301	3047.2	3550.5		2.003	468.0
		4.2	9.195	3011.6	3515.6		2.001	468.1
Photolysis of HI	Argon	4.2	9.1775	3001.5	3508.9	3	2.0024	471.52
	U U			3000.8	3509.2		2.0024	472.46
				2997.6	3513.4		2.0018	479.10
Irradiated H ₂	H_2	4.2	9.1778	3000.9	3509.6	2	2.0023	472.70
Irradiated HClO ₄	$7.0 \text{ mol } H_2O$ /mol acid	77	23.034	7960.3	8462.7	10	2.0023	469.20
Irradiated H ₂ SO ₄	$\begin{array}{c} 2.1 \ mol \ H_2O \\ /mol \ acid \end{array}$	77	23.044	7961.4	8466.8	10	2.0025	472.05
Irradiated H ₃ PO ₄	$\begin{array}{c} 0.0 \ mol \ H_2O \\ /mol \ acid \end{array}$	77	23.065	7967.3	8475.6	10	2.0025	474.77
Irradiated H ₂ O	H ₂ O	4.2	24.494	8479.4	8983.6	5	2.0026	471.01
Irradiated HF	HF	4.2	24.72	8562.6	9068.3	5	2.002	472.2
Irradiated CH ₄	CH_4	4.2	24.52	8552	9056	5	1.988	467.5
Irradiated H ₂ O	D_2O	4.2	24.273	8398.7	8902.8	5	2.0030	471.01
			D-atom reson	ances				
Irradiated ¹⁴ ND ₃	¹⁴ ND ₃	94	9.113	3176	3318	This paper	2.004	66.43
		91	9.1105	3172.8	3327.0		2.001	72.07
			Weak pair	3184	3314		2.002	60.97
		77	9.296	3238	3382		2.006	67.44
		77	9.300	3240.3	3394.4		2.001	72.03
			Weak pair	3254	3383		2.002	60.29
		77	9.301	3240.4	3394.4		2.002	71.99
		4.2	9.194	3204.3	3358.4		2.000	72.00
Irradiated D ₂	D_2	4.2	9.1785	3196.4	3351.8	2	2.0012	72.636
Irradiated D ₂ O	D ₂ O	4.2	24.273	8577.6	8738.0	5	2.0020	74.999

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tum. For simplification, the symmetry was taken to be cylindrical; the isotropic g value was thus replaced by a g tensor with components perpendicular (g_{\perp}) and parallel (g_{\parallel}) to the symmetry axis such that $1/3*g_{\parallel}+2/3*g_{\perp}=\langle g \rangle$, the measured g value for a polycrystalline sample. These simulations were carried out only for the ND₂ isotopes; parameters for the most accurate simulations are given in the third column of Table I. The minor residual differences between experimental and calculated spectra are due, at least in part, to the presence of low levels of other EPR-active species (described below) absorbing in the same region of magnetic field strength as the NH₂ and ND₂ free radicals.

The presence of H and D atoms was established by observation of resonances at magnetic field strengths consistent with those predicted by the Breit-Rabi formula¹⁵ at the microwave frequency employed. These signals were considerably less intense than the resonances from the NH₂ and ND₂ radicals; the gain of the EPR spectrometer was increased by factors of 100 or more in order to see the Breit-Rabi resonances. Microwave power must be kept low to avoid power saturation of these signals, Fig. 2; at 77 K, the H atom resonances start to saturate at 30 μ W. For the frequencies employed in the experiments reported here (and for higher frequencies), the doublets from H atoms are split by about 500 G, and the triplets from D atoms by about 70 G. The pair of H atom resonances are well outside of the free radical spectra from ${}^{14}NH_2$ and ${}^{15}NH_2$ and readily resolved. The m_1 $=\pm 1$ D atom resonances fall in the wings of the free radical spectra and are thereby distorted but readily seen. The m_1 =0 D atom resonance is very near the center of the free radical spectra; the free radicals decay at a higher temperature than do the D atoms, so the $m_1=0$ resonances is not resolved, but it does have a small effect upon the center of the free radical spectra. Because the $m_1 = 0$ D atom resonance is not resolved, the discussion below deals only with low- and high-field resonances. Multiple high- and low-field D atom Breit-Rabi resonances were consistently found in samples of irradiated ¹⁵ND₃. Fig. 3; assignment of these resonances to particular high-field/low-field pairs is not unique and consideration of the possible pairings has not, thus far, proven useful. In ¹⁴ND₃, apart from a well-resolved high-field/low-field pair, there sometimes occurred an additional high-field and/or low-field Breit-Rabi resonance. However, only single low-field/high-field pairs were observed in ¹⁴NH₃ and ¹⁵NH₃ samples. Eigenenergies as functions of g and A values for H and D atoms were obtained from the isotropic spin Hamiltonian $H_{\text{atomic}} = (g \mu_B S_z)$ $-g_n\mu_N B + A\{S_zI_z + .5(S_+I + S_-I_+)\}$ and a program was written to calculate the g and A values from Breit-Rabi low-field/high-field pairs. In Table II are the results of applying the latter program to our most reliable data, and also to data in the literature from H and D atoms trapped in other kinds of matrix and obtained under other conditions. (In several cases our analysis of the data in the literature gives slightly different g and A than those in the papers cited; for this reason Table II includes the frequencies and magnetic fields from which we calculated the g and A values.) Adrian¹⁶ presented a theoretical treatment of matrix effects



FIG. 4. Time dependence at 106.5 K and 9.113 GHz of the amplitude of the high-field Breit–Rabi resonance from H atoms in irradiated $^{14}NH_3$.

producing small g- and A-value variations in the EPR spectra of H atoms stabilized in nonpolar matrices.

The EPR measurements at 77 K showed that the free radicals, H and D atoms (as characterized in the paragraphs above) are stable at this temperature (consistent with their survival for many months in storage at 77 K). Decay of the Breit-Rabi resonances from H atoms was observable during periods of 15-85 min within the temperature range 100-110 K. The time course of the decay in $^{14}NH_3$ matrix at 106.5 K is shown in Fig. 4. The first-order rate constants from data of this kind at 104, 106.5, and 109 K are 0.300, 1.04, and 1.68×10^{-3} s⁻¹, respectively, to which corresponds an activation energy of 8.7 kcal (0.38 eV). At the storage temperature of 77 K, the rate of decay of H atoms by this process is 0.5% per year. Analogous kinetic measurements were made on several of the species, and the activation energies obtained are given in Table III. The validity of taking the decay process as first order is seen in Fig. 5 which shows both firstand second-order nonlinear least-squares fits to data which

TABLE III. Thermal decay of paramagnetic species in irradiated ammonia.

Species	Matrix	Temperatures (K) at which decay was observed during periods of minutes	$E_{\rm activation}$ (kcal mol ⁻¹ /eV atom ⁻¹)
H atom	¹⁴ NH ₃	104-109	8.7/.38
		103-108	6.6/.29
	¹⁵ NH ₃	100-107	4.8/.21
¹⁵ N atom	¹⁵ ND ₃	139-149	5.5/.24
		142–157	4.8/.21
¹⁴ NH ₂	¹⁴ NH ₃	131–141	6.0/.26
¹⁵ ND ₂	¹⁵ ND ₃	119–132	6.0/.26
"Hydrazine radical"	¹⁵ ND ₃	144–157	3.3/.14
		147–155	4.9/.21

extends over a long period of time. The second-order fit, which clearly fails, is based upon $H+H\rightarrow H_2$ proceeding at the rate $d[H]/dt = -k[H]^2$.

As the NH₂ free radicals decayed and their spectra diminished in amplitude, the spectra of other paramagnetic species became evident. Records from irradiated ¹⁵ND₃ demonstrate the transition from a dominant ¹⁵ND₂ free radical spectrum at 124 K, Fig. 6(A), to a superposition of spectra at 135 K as in Fig. 6(B). Figure 6(B) shows a strong central ¹⁵N atom doublet (6.7 G splitting), a triplet (possibly from a hydrazine free radical) with outer bands at 3215 and 3286 G together with a more intense central band, and a small amount of residual ND₂. The weak peak at 3272 G is reproducible, but we have not yet been able to identify its source. ¹⁵N doublets from γ -irradiated 2% ¹⁵NH₃ in matrices of krypton and xenon at 4.2 K have been seen in EPR spectra taken at 24 GHz.⁸ After the ¹⁴NH₂ free radicals in irradiated ¹⁴NH₃ have decayed, a central resonance is observed which remains strong at 157 K but is gone at 160 K. The latter signal is analogous to the ¹⁵N atom resonance except that there is no resolved hyperfine splitting; this is not surprising



FIG. 5. First- and second-order nonlinear least-squares fits to the high-field Breit–Rabi resonance of the H atom in irradiated ${}^{14}NH_3$. The temperature of the sample was 101.7 ± 0.5 K: \blacksquare Peak-to-trough amplitudes;—first-order fit;---second-order fit.



FIG. 6. Effect of increased temperature upon the 9.122 GHz EPR spectrum in the region of resonances from ¹⁵ND₂ free radical in irradiated ¹⁵ND₃. Panel (A) shows ¹⁵ND₂ free radical as the dominant species at 124 K. Panel (B) shows residual ¹⁵ND₂ free radical together with ¹⁵N atom doublet and other resonances which have emerged at 135 K. The magnetic field modulation was 0.10 G in (A) and 1.2 G in (B); the microwave power level at the cavity was 10 mW in (A) and 70 μ W in (B). In (A) the signal level (receiver gain) was 3.1 times less than in (B), and the response times were 0.1 ms and 0.3 s, respectively.

because the splitting of the ¹⁴N atom triplet is expected to be 29% more closely spaced than that of the ¹⁵N atom doublet.

When the temperature of irradiated ammonia is raised from 77 to above 100 K, processes occur which result in the disappearance of all EPR detectable species. There may well be other, less stable sites for paramagnetic species in solid ammonia; if so, when ammonia is irradiated at liquid helium temperatures, the paramagnetic occupants of these sites would disappear when the temperature is raised through the range from 4.2 to 77 K. Clearly, such sites and decay processes can be characterized by EPR measurements at temperatures lower than those which were employed to obtain the results reported here, and the measurements should be made as soon as possible after the samples are irradiated. More generally, the methods of this paper are likely to be useful in learning about the conditions and rates of disappearance of "free" atoms (and radicals) in any matrix in which they are stable at 4.2 K when the temperature is raised above that point.

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