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ELECTRON SPIN RESONANCE SPECTRA OF THE NH_2 AND ND_2 FREE RADICALS AT 4.2°K*

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Electron spin resonances of NH_2 and ND_2 stabilized in argon at liquid helium temperature have been observed. The identification of the radicals has been established by a detailed analysis of the hyperfine spectra.

The essential features of the apparatus have been described.[1-3] Preliminary experiments in which the products of electric discharges in ammonia were condensed in an argon matrix gave evidence for trapped NH_2 radicals. In addition to a nine-line spectrum which was tentatively assigned to NH_2, we observed strong atomic hydrogen lines, atomic nitrogen lines, and a broad unresolved resonance near the free electron value. When the products of a discharge in ND_3 were condensed in argon, the presence of a strong center deuterium atom line and the broad unresolved resonance line obscured the ND_2 resonances.

In view of these difficulties, an attempt was made to produce the radicals by photolysis of ammonia in argon at 4.2°K. A gaseous mixture of about 0.5% NH_3 or ND_3 and argon was deposited on the liquid-helium-cooled sapphire rod and subsequently photolyzed through a quartz window with 1849-A resonance radiation from a low-pressure mercury lamp.

Figure 1 shows the spectrum obtained by photolysis of NH_3. The spectrum consists of three groups of triplet lines, consistent with the expected spectrum for the NH_2 radical since $I(N^{14})=1$ and $I(H)=1/2$ resulting in nine resonance lines. Because the widths of the resonance lines are different, the intensity distributions obtained from peak amplitudes are misleading. In particular, the lines in a triplet group are actually comparable in intensity. It is not evident from the spectrum whether to attribute the splitting into triplet groups to hydrogen and the subsplitting to nitrogen or vice versa. Experiments with deuterated ammonia supplied the answer to this problem and established that the large splitting in NH_2 was due to hydrogen. The spectrum obtained by photolysis of ND_3 in argon is shown in compressed form in Fig. 2. The ND_2 spectrum is expected to consist of 15 lines since $I(N^{14}) = 1$ and $I(D) = 1$. From an analysis of several of the stronger lines of the spectrum, two hyperfine

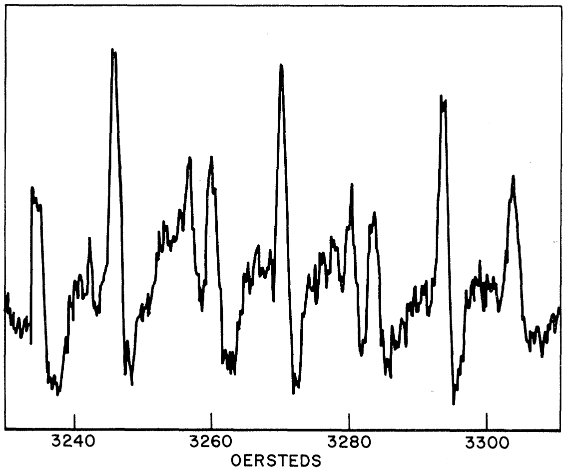

FIG. 1. Electron spin resonance spectrum of NH_2 in an argon matrix at 4.2°K. ν = 9177.82 Mc/sec.

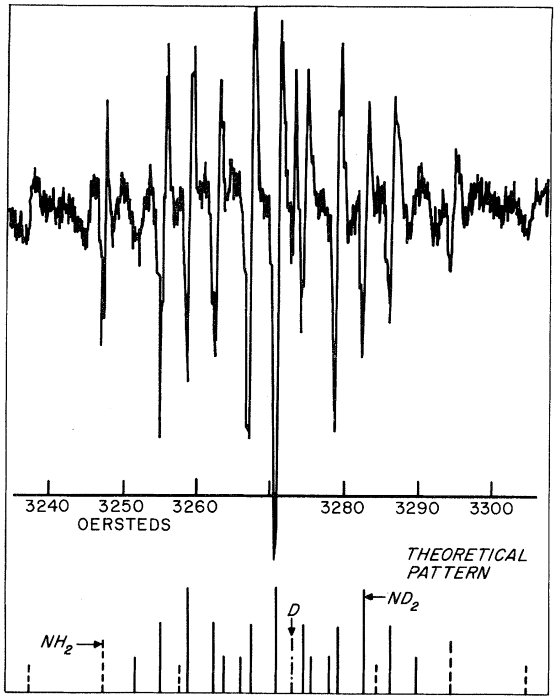

FIG. 2. Electron spin resonance spectrum of ND_2 in an argon matrix at 4.2°K. Also present are spectra of D and NH_2 and weak traces of NHD.

coupling constants were evaluated, as discussed later, and the complete spectrum calculated. The predicted positions of the spectral lines are indicated in the bottom of the figure. Eleven of the lines are clearly recognized in the recording. The others are too close to other lines to be resolved. In addition, one sees the center deuterium atom line, slight traces of NHD, and several lines from NH_2 arising from some remanent NH_3 in the system. The lines of NH_2 and ND_2 were recorded individually on expanded sweeps to determine their field positions with high precision.

If one solves the spin Hamiltonian for the magnetic energy, W, to the first order approximation, one obtains

$$W = M_J g_J \mu_0 H + AM_J \sum_i m_i + BM_J M_I(\mathrm{N}) + \mu_0 H \left[g_I \sum_i m_i + g_I(\mathrm{N}) M_I(\mathrm{N}) \right] \qquad (1)$$

where m_i is the nuclear magnetic quantum number of hydrogen (± 1/2) in the case of NH_2 or of deuterium (1, 0, -1) in the case of ND_2, and the other symbols have their usual significance. The hyperfine coupling constants A and B and the electronic g-factor, g_J, can be calculated from the data. The results are given in Table I.

Table I. Electron spin resonance results for NH_2 and ND_2

Radical	A (Mc/sec)	B (Mc/sec)	g_J
NH_2	67.03(20)	28.90(20)	2.00481 (8)
ND_2	10.27(20)	33.28(20)	2.00466 (8)

The ratio of the hydrogenic coupling constants, $A_H/A_D = 6.526$, is in excellent agreement with the predicted ratio, $g_I(\mathrm{H})/g_I(\mathrm{D}) = 6.514$. The difference between the values for the nitrogen coupling constants is unexpected, indicating that the electronic wave functions for the two radicals are somewhat different. It is clear that the inclusion of higher-order terms in the solution of the spin Hamiltonian would not bring the B values into closer agreement. Apparently, the hyperfine interaction with the nitrogen atom is rather sensitive to some small perturbation in the electronic state. Thus far, we have been unable to account for the discrepancy by considering zero-point vibration and the differences in the rotational states of these molecules.

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[1] Jen, Foner, Cochran, and Bowers, Phys. Rev. 104, 846 (1956).

[2] Foner, Jen, Cochran, and Bowers, J. Chem. Phys. 28, 351 (1958).

[3] Jen, Foner, Cochran, and Bowers, (to be published).

SPIN EXCHANGE IN SUPERCONDUCTORS

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The only known superconductor among the rare earth elements is lanthanum. The elements following lanthanum in the periodic system are either strongly paramagnetic or ferromagnetic, with magnetic moments which are due to their $4f$ electrons. In lutetium, 14 electrons have filled this $4f$ shell entirely and the element does not show pronounced paramagnetism. Lutetium, however, is not superconducting above 1.02°K because its metallic radius has become much smaller and at the same time it is much heavier than lanthanum.