The Journal of Physical Chemistry A

VOLUME 101, NUMBER 16, APRIL 17, 1997

LETTERS

Electron Spin Resonance of the H···NH_2 Radical Pair

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Received: January 3, 1997[⊗]

Exchange within the radical pairs H···NH_2 and D···ND_2 trapped in solid argon and krypton at 4 K was observed via electron spin resonance. They were produced from ammonia by radiation from a corona discharge through the rare gas. From the zero-field splittings of the triplet species, it is concluded that the H atom and NH_2 are separated by one rare-gas atom in each of these matrices.

Introduction

Magnetic-dipole-coupled radical pairs are often observed in the solid state after irradiation.[1,2] That weak interaction has been observed via electron spin resonance (ESR) spectroscopy for H···CH_3 pairs in solid CH_4[3] and for H···H pairs in solid rare-gas matrices.[4] Here we report a similar radical pair in the form of H···NH_2, as detected in its triplet state via ESR.

Gas-phase spectra, observed by Dressler and Ramsey,[5] have established that the NH_2 molecule is bent at an angle of 103° and has a $^2B_1$ ground state. NH_2 has been isolated and observed in matrices many years ago, optically by Robinson and McCarty[6] and via ESR by Foner, Cochran, Bowers, and Jen[7] and Cochran, Adrian, and Bowers.[8] Since it is a $S = ^1/_2$ molecule, all of the ESR spectra were observed near $g = 2$ (i.e., at ~3300 G, $\nu \cong$ 9 GHz). NH_2, NHD, and ND_2 were produced by photolysis of NH_3 and ND_3 in argon at 4 K, and the hyperfine splittings due to interaction of the unpaired spin with H, D, and ^{14}N were analyzed. Cochran et al.[8] give the following values for the isotropic magnetic constants of NH_2: $g = 2.0049(1)$, $A(^{14}N) = 10.4(1)$ G, and $A(H) = 23.8(1)$ G. It is not clear whether the molecule is rotating freely or hindered in these matrices (see McConnell,[9] Jen,[10] and Cochran et al.[8]).

A corona discharge[11,12] of the rare gas was used here as a source of excitation of NH_3 when forming the matrices, and the ESR spectra revealed lines near $g = 4$ (i.e., near 1700 G, $\nu \cong 9$ GHz) corresponding to $\Delta m_s = \pm 2$ transitions of an $S = 1$ species. In principle, both $\Delta m_s = \pm 1$ and $\Delta m_s = \pm 2$ transitions can be observed for randomly oriented triplet molecules if the zero-field-splitting parameter, D, is less than $h\nu$,[13] which is the case in these radical pairs. Gordy and Morehouse[3] observed only the $\Delta m_s = \pm 1$ transitions for the H-atom−methyl-radical complex ($D = 91$ G) whereas Knight et al.[4] observed only the $\Delta m_s = \pm 2$ transitions for the H···H interactions ($D \cong 80$ G). In the latter case, $\Delta m_s = \pm 1$ transitions were probably obscured by intense atom and other radical signals at $g = 2$. In our case of H···NH_2, the $\Delta m_s = \pm 2$ transitions near $g = 4$ were clearly observed in solid argon and krypton at 4 K; however, it was difficult to assign definitely the $\Delta m_s = \pm 1$ transitions to lines observed in the $g = 2$ region. In addition to H···NH_2 , intense signals due to hydrogen atoms, NH_2, NH, and CH_3 radicals were observed. All of these signals appeared near $g = 2$, except for the $^3\Sigma$ NH molecule which appears at higher fields. The dipole-coupled spectra were not detected in neon matrices.

A significant feature of the ESR spectra is that the H-atom hyperfine splitting is about one-half of that in the isolated atom, thus indicating the exchange with a neighboring doublet radical. The zero-field splitting (zfs), $|D|$, obtained from the matrix data is about 140 G. From it, assuming that magnetic-dipole interaction is dominant, one can obtain an effective separation distance of the two spins, i.e. a H···NH_2 distance.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

S1089-5639(97)00066-2 CCC: $14.00

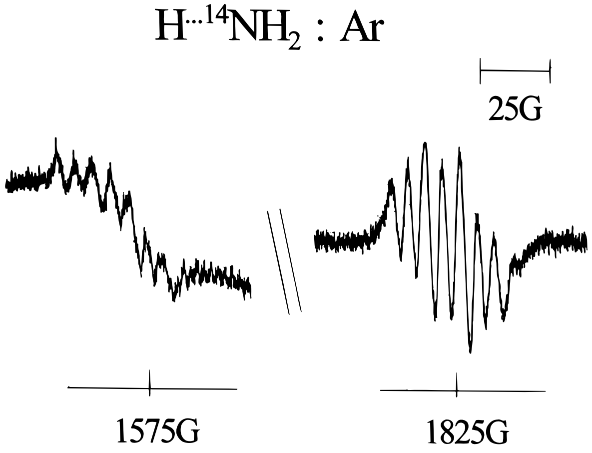

Figure 1. ESR (ν = 9.5863 GHz) of matrix at 4 K formed during corona-discharge irradiation of condensing NH_3 and argon gases. The doublet (of seven lines) is due to the H hyperfine splitting of ~250 G in the H···$^{14}NH_2$ radical pair. The seven-line pattern is the hyperfine splitting of the $^{14}NH_2$.

Experimental Section

The Heli-tran, X-band ESR spectrometer, and deposition equipment have been previously described.[14] The new feature in these experiments is a corona discharge unit,[11] operating at ~3 KV, through which only pure rare gas was passed. The rare-gas ammonia mixture was passed into the vacuum system in parallel with the corona discharge in nearly equal amounts so that both gas flows were condensed simultaneously on the copper surface at 4 K. Normal ammonia (Matheson, 99.99% purity), isotopically enriched $^{15}NH_3$ (Cambridge Isotopes, Inc., 99% enrichment, 98+% purity), and deuterated ammonia (Cambridge, 99% enrichment, 98+% purity) were diluted to ~5% with neon (Matheson, 99.9995% purity), argon (Airco, 99.999% purity), or krypton (Matheson 99.999% purity).

ESR Spectra

All spectra were measured at 4 K; attempts to observe them at higher temperatures, even a few degrees higher, resulted in their disappearance. Figure 1 shows the ESR spectrum attributed to H···$^{14}NH_2$ in an argon matrix. The matrix was produced by condensing a 2% concentration of $^{14}NH_3$ at 4 K while being subjected (and diluted) by a corona discharge through pure argon. The doublet of septets, $\Delta m_s = \pm 2$ transitions centered at $g \cong 4$ (1700 G), in Figure 1 is quite clear. The large doublet splitting is 257 G, and the septet splitting is about 6 G. (The ESR spectrum of the NH radical was also observed in these matrices.) The crudely derived relative intensities of the seven lines centered at 1570 G appear to be nearly 1:1:1:1:1:1:1, and the septet pattern at 1825 G is determined more accurately with an intensity ratio of 1:2:3:2:3:2:1. A series of seven weak lines also appears in this matrix centered at 3222 ± 6 G with a spacing of about 6 G which can perhaps be assigned to the lower field (xy_1) line. This more reliably determined $\Delta m_s = \pm 1$ transition (xy_1 perpendicular line) is shown in Figure 2.

The corresponding spectrum near $g = 4$ of $^{15}NH_3$ deposited in an argon matrix is shown in Figure 3. It is identical to the $^{14}NH_3$ pattern but with the seven lines reduced to four with approximate relative intensities of 1:2:2:1. These patterns are in accord with hyperfine interaction with one nitrogen nucleus in each case [$^{14}N(I=1)$ and $^{15}N(I=^1/_2)$].

The ESR of irradiated $^{14}ND_3$ in argon is shown in Figure 4. It consists of a triplet centered at $g \cong 4$ with a spacing of 39 G. No lines in the $g = 2$ region could be assigned.

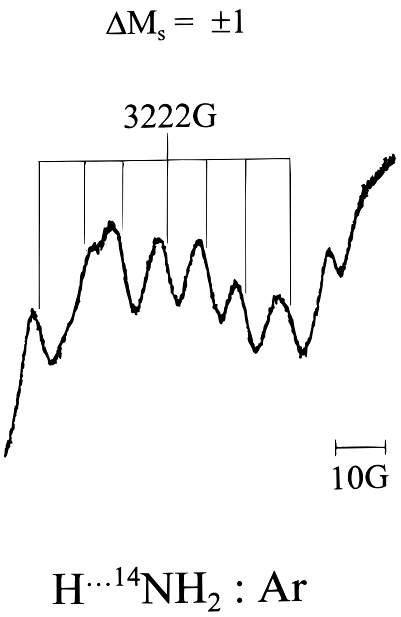

Figure 2. Assigned as one of xy_1 perpendicular lines ($\Delta m_s = \pm 1$). The center of the seven-line pattern is not certain.

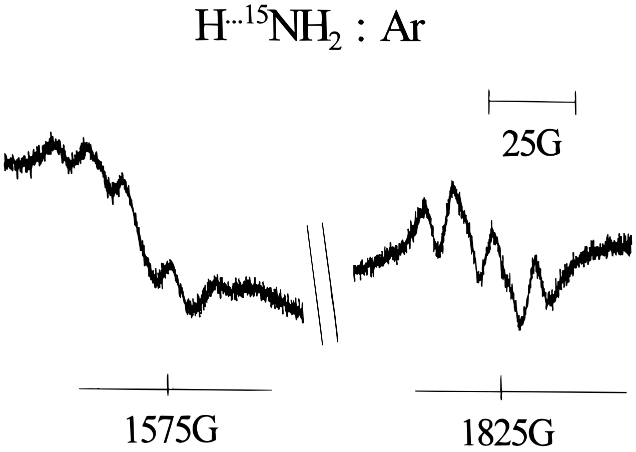

Figure 3. Same as Figure 1 (ν = 9.5870 GHz) except with $^{15}N(I=^1/_2)$ substituted for $^{14}N(I=1)$. The four-line patterns are thereby proven to be due to the $^{15}NH_2$ moiety.

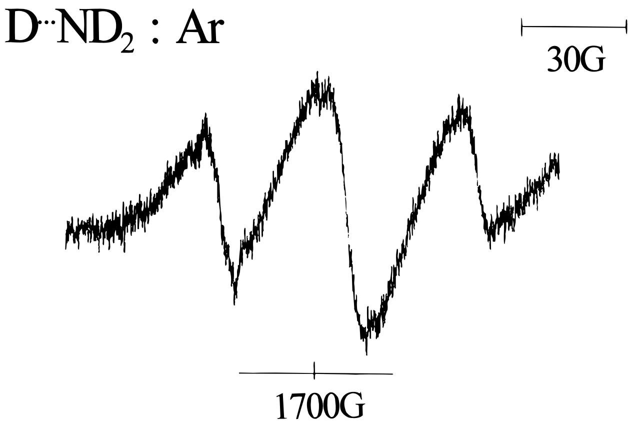

Figure 4. ESR (ν = 9.5868 GHz) of matrix formed during irradiation of ND_3 in argon gas. The three lines are hyperfine splitting from interaction with lone deuterium atom (I = 1) in the D···ND_2 complex. The $^{14}ND_2$ hyperfine is within the broad lines.

Deposition of $^{15}NH_3$ in krypton, subjected to a pure krypton corona discharge, yielded the spectrum in Figure 5. The result is basically the same as in argon.

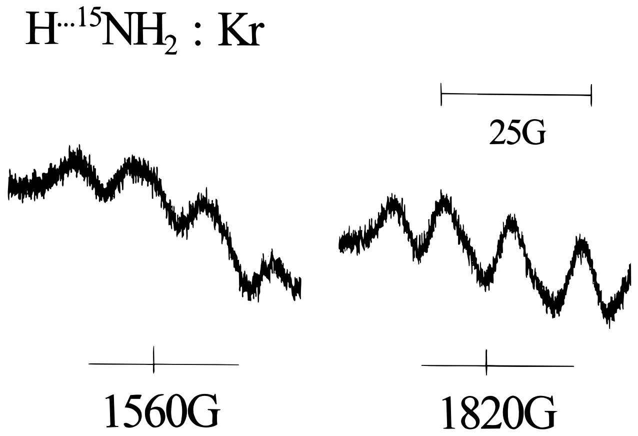

Figure 5. Irradiated $^{15}NH_2$ in a krypton matrix ($\nu = 9.5862$ GHz). Similar to Figure 3.

Analysis

The spin Hamiltonian

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta H_x S_x + D[S_z^2 - S(S+1)/3] + \sum_i A_{\parallel}^i S_z^i I_z^i + A_{\perp}^i[(S_x^i I_x^i) + (S_y^i I_y^i)]$$

was used to fit the data. $A_{\parallel}^i$ and $A_{\perp}^i$ are axial hyperfine (hf) parameters for the *i*th nucleus which is the lone H, the nitrogen atom, or the two equivalent H atoms on the nitrogen atom. (Truly axial hf parameters would strictly apply only if the NH_2 radical were rotating.) Because the hyperfine splittings (hfs) from the two equivalent hydrogens and from the nitrogen atom are small, they were determined by perturbation theory. The hyperfine splittings in the $\Delta m_s = \pm 2$ lines are produced by a combination of $A_{\parallel}^i$ and $A_{\perp}^i$[13] so that only some average values are measured from the spectra. That is not important since the ^1H and ^2H hf interaction is isotropic and the ^{14}N and ^{15}N hfs is small.

Although the $\Delta m_s = \pm 2$ (H_{min}[13]) lines were always observed and clearly identified in the $g = 4$ region, the $\Delta m_s = \pm 1$ transitions (xy_1 and xy_2 perpendicular lines) were difficult to identify because of the often overlapping extraneous signals in the $g = 2$ region. One expects, again, two xy_1 lines separated by ~250 G (one-half of the H hfs) and a corresponding set of xy_2 lines at higher field, the spacing between the centers of the two sets yielding $|D|$, the zero-field-splitting parameter. (Gordy and Morehouse[3] used a g_{iso} for $H\cdots CH_3$ formed by averaging the g values of isolated H and CH_3 in the matrix and then obtained $|D|$ from the observed $\Delta m_s = \pm 1$ transitions. Knight et al.[4] observed only $\Delta m_s = \pm 2$ transitions and used the measured g values for isolated H atoms in the various matrices to calculate the $|D|$ values in the H···H case.) Here we have tried to establish both $g_{\perp}$ and $|D|$ values from our observations of $\Delta m_s = \pm 2$ and $\Delta m_s = \pm 1$ transitions, but the latter are not usually detectable.

(a) $H\cdots{}^{14}NH_2$. The lone ^1H hfs yields two sets of seven lines [spacing = 6(1) G] centered at 1563 and 1821 G [spacing = 258(5) G] (see Figure 1). The seven line patterns arise from overlapping of the third and fourth and the sixth and seventh lines in a nine-line pattern (a triplet of triplets). This is attributed to a combination of a 1:2:1 triplet spaced by 12 G from the two equivalent hydrogens on $^{14}NH_2$ and 1:1:1 triplets spaced by 5 G from the single $^{14}N(I{=}1)$ nucleus. These hf splittings for the $^{14}NH_2$ moiety are, just as for the lone H, one-half of the gas-phase values (quoted earlier) due to exchange coupling. The intensity ratios within a given seven-line pattern are difficult to measure but appear to be either 1:1:2:1:2:1:1, 1:1:3:2:3:1:1, or something in between. From the stronger pattern in Figure 1, one does see clearly that the central line is weaker than its neighbors.

TABLE 1: Observed and Calculated Line Position for $H\cdots{}^{14}NH_2$ in Solid Argon ($\nu = 9.5834$ GHz)

M_I	M_J	M_I	XY_1 (G)		XY_2 (G)		H_{min} (G) ($\theta = 62°$)	
$(H)_1$	$(H)_2$	(^{14}N)	obsvd[a]	calcd	obsvd[b]	calcd	obsvd	calcd
		1	3204(3)	3204.2		3335.4	1544(4)	1541.6
	1	0		3210.3		3341.5	1550	1547.7
		1,1	3216	3216.4		3347.6	1557	1553.8
1/2	0	0	3224	3222.5		3353.7	1564	1559.9
		−1,1	3228	3228.6		3359.8	1569	1566.0
	−1	0	3233	3234.7		3365.9	1575	1572.1
		−1	3240	3240.8		3372.0	1581	1578.2
		1		3431.6	3580	3583.2	1803(3)	1804.7
	1	0		3437.7	3585	3588.6	1809	1810.8
		−1,1		3443.8	3593	3594.7	1815	1816.9
−1/2	0	0		3449.9	3602	3601.3	1821	1823.0
		−1,1		3456.0	3608	3606.9	1827	1829.1
	−1	0		3462.1	3615	3613.0	1833	1835.2
		−1		3468.2	3619	3619.4	1839	1841.3

[a] These could be incorrect by one spacing unit, i.e., 7 G (see Figure 2). [b] Weak, overlapping spectra.

TABLE 2: Observed and Calculated Transitions for $H\cdots{}^{15}NH_2$ in Solid Argon at 4 K ($\nu = 9.5870$ GHz)

M_I	M_J	M_I	XY_1 (G)		XY_2 (G)		H_{min} (G) ($\theta = 62°$)	
$(H)_1$	$(H)_2$	(^{15}N)	obsvd[a]	calcd	obsvd[a]	calcd	obsvd	calcd
		+1/2	3207(3)	3209.5		3360.0	1546(5)	1551.5
	1							
		−1/2, +1/2	3218	3219.7		3370.5	1556	1561.7
1/2	0							
		+1/2, −1/2	3229	3229.9		3380.4	1566	1571.9
	−1							
		−1/2	3241	3240.1		3390.6	1577	1582.1
		+1/2		3437.0	3586(3)	3587.2	1802	1808.6
	1							
		−1/2, +1/2		3447.2	3596	3597.4	1816	1818.8
−1/2	0							
		+1/2, −1/2		3457.4	3607	3607.6	1826	1829.1
	−1							
		−1/2		3467.6	3617	3617.8	1837	1839.2

[a] Weak, overlapping spectra.

Our clearest (lowest-field) xy_1 line is shown for $H\cdots{}^{14}NH_2$ in Figure 2, and even there the assignment of the seven hf lines is not definite. (The spacing of ~6 G is in accord with that in Figure 1.) The center of that pattern is either at 3222 or 3228 G. The corresponding high-field xy_2 line seems to lie centered at about 3600 G which, if correct, implies that $|D| \cong (3600 - 250) - 3222 \cong 130$ G. This is uncertain to perhaps ±20 G. Table 1 gives the observed line positions and calculated values using the parameters in Table 3.

The nuclear spin statistics pertaining to NH_2 in rotational states in a solid at low temperature have been reviewed by Jen.[10] In this radical pair one expects, considering the overlapping, a static molecule to yield a 1:1:3:2:3:1:1 pattern. However, in the $J = 0$ rotational state this would be 1:1:2:1:2:1:1. If some molecules were in the $J = 1$, state then the relative intensities of the three central lines would be uniformly enhanced. The population of that state at 4 K is not very significant since the gas-phase $J = 0-1$ spacing is 21 cm^{-1}, meaning that only about 0.2% of the molecules would occupy that level. All in all, the pattern of observed relative intensities is in agreement with the

TABLE 3: Derived Magnetic Parameters of the Radical Pairs

	$^{14}NH_3$/Ar	$^{15}NH_3$/Ar	$^{14}ND_3$/Ar	$^{15}NH_3$/Kr
$g_{\parallel}$	2.007[a]	2.007[a]	2.001[a]	2.006[a]
$g_{\perp}$	2.007(2)	2.007(2)	2.001(2)	2.006(2)
$\|D\|$ (cm^{-1})	0.013(2)	0.013(2)	0.013[a]	0.010(2)
$\|A\|^{(1 \text{ or } 2)}H_1$ (MHz)	721.5(9)	721.5(9)	109(1)	713.2(9)
$\|A\|(^1H)_2$ (MHz)	34(9)	39(9)	(see text)	28(9)
$A(^{14 \text{ or } 15}N)$ (MHz)	17(9)	29(9)	(see text)	28(9)

[a] Assumed.

statistics but does not allow anything definite to be said about the motion in the matrices.

(b) H···^{15}NH$_2$. Again the lone ^1H yields two sets of lines centered at 1562 and 1820 G in Ar and 1566 and 1820 G in Kr (see Figures 3 and 5). The spacing between these lines is ~256 G as in the $^{14}NH_3$ case. However, there are only four hf lines within each of the doublets, with relative intensities within these quartets somewhere between 1:1:1:1 and 1:2:2:1. The four-line patterns with a spacing of 10(1) G are accounted for if the two hydrogens on NH_2 give a 1:2:1 pattern spaced by 10 G (as in $^{14}NH_2$) with each line correspondingly split into a doublet (^{15}N, $I = {}^1/_2$) by about 5 G. The static pattern, considering overlap, would be 1:3:3:1. However, nuclear statistics for $^{15}NH_2$ require a 1:2:2:1 intensity ratio in $J = 0$ and an equal increase in intensity in the two central lines due to any molecules in the $J = 1$ state.[10] None of these intensity ratios fit those observed.

Some four-line patterns in the 3200 and 3400 G regions could be assigned to $\Delta m_s = \pm 1$ transitions, and they did fit satisfactorily with the g and $|D|$ values obtained from $^{14}NH_3$ spectra (see Table 2).

(c) D···^{14}ND$_2$. The lone deuterium atom ($I = 1$) yields the three-line pattern with each line broadened by the hyperfine of the $^{14}ND_2$ radical. The spacing between the three broad lines is 39 G, again approximately one-half of that for the free deuterium atom. The width of each line is about 20 G, limiting the $^{14}N(I=1)$ 1:1:1 triplet to a spacing of about 6 G, with each triplet line broadened by the small hf produced by the two deuterium nuclei on ND_2.

Discussion

The evidence is convincing that the H···NH_2 radical pair is being observed in solid argon and krypton at 4 K. The derived magnetic parameters for these triplet state complexes are given in Table 1. The patterns of hf lines in Figures 1–5 are in general agreement with those expected from the known properties of the isolated NH_2 radical, but the state of motion of the complex is not clear.

Not discussed above is the difference in the intensities of the low-field (~1575 G) and high-field (~1825) lines in the H···$^{14}NH_2$ spectrum in argon in Figure 1, which also occurs in H···$^{15}NH_2$ in argon and krypton in Figures 3 and 5. Because of the similarity in this intensity difference in argon and krypton matrices, it is not likely to be a motional effect but is possibly attributable to the anisotropy in the ESR spectrum. Thus, the $\Delta m_s = 2$ patterns at $g = 4$ are downfield by about 1600 G from $g_{\parallel}$, and the intensity pattern is very anisotropic, having most of its strength at the lower fields (see ref 15 and/or ref 13). Then we speculate that the doublet at 1700 G split by 250 G exhibits unequal intensity (the lower-field line weaker) simply because of this anisotropy.

Distances between Exchanging Radical Pairs. If the two unpaired spins on $H^{\bullet}$ and $NH_2^{\bullet}$ are considered as point dipoles, then the zero-field-splitting parameter $|D|$ is a measure of the distance between them, according to $|D| = 3(g\beta)^2/2r^3$. Then the derived r values (in Å) from Table 1 are, assuming isotropic g components:

H···H_2N/Ar 5.8(2)

H···H_2N/Kr 6.5(2)

Taking the radii of H and NH_2 as 1.2 and 1.5 Å, respectively, one can derive the spacing between the pairs in the two matrices as 3.1 Å in argon and 3.8 Å in krypton. In the rare-gas crystals, Ar has a diameter of 3.08 Å and Kr 3.4 Å. Thus, as found for H···CH_3,[3] it appears that one rare-gas atom in each matrix is separating the radical pairs.

Acknowledgment. This research was supported by NSF Grant CHE-9418451.

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