Electron-Diffraction Study of Ammonia and Deuteroammonia*

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The gas-phase structures of NH_3 and ND_3 molecules were determined by the sector-microphotometer method of electron diffraction. The following internuclear distances r_g and mean amplitudes l_e with estimated standard errors were obtained: For NH_3, $r_g(\text{N–H}) = 1.030_2 \pm 0.002$ Å, $r_g(\text{H–H}) = 1.662 \pm 0.010$ Å, $l_e(\text{N–H}) = 0.073_1 \pm 0.002$ Å, $l_e(\text{H–H}) = 0.125 \pm 0.006$ Å, and for ND_3, $r_g(\text{N–D}) = 1.026_6 \pm 0.003$ Å, $r_g(\text{D–D}) = 1.654 \pm 0.008$ Å, $l_e(\text{N–D}) = 0.061_1 \pm 0.002$ Å, $l_e(\text{D–D}) = 0.101 \pm 0.006$ Å, with the parameter κ representing bond-stretching anharmonicity fixed at 1.0×10^{-5} and 0.5×10^{-5} Å³ for N–H and N–D, respectively. Effects of anharmonicity and isotope differences in the structural parameters analogous to those in CH_4 and CD_4 were observed. The r_a^0 and r_e bond distances calculated from the above r_g distances are found to be consistent with the corresponding r_z and r_e distances derived from the spectroscopic rotational constants of Benedict and Plyler. The isotope effects reported by Bell and by Halevi for the dipole moment and polarizability of ammonia are discussed briefly in the light of the present results.

INTRODUCTION

The internuclear distances of NH_3 and ND_3 were determined by gas electron diffraction by Bastiansen and Beagley,[1] who investigated the isotope differences in the structure and in the mean vibrational amplitude. They found that the N–H and N–D bond distances (r_a) were essentially equal $(1.019_1 \pm 0.002_4$ Å for N–H and $1.020_2 \pm 0.002_4$ Å for N–D), and that the effective HNH angle $(109.1° \pm 1.0°)$ was about 3 degrees greater than the effective DND angle $(106.1° \pm 1.0°)$. No significant anharmonicity of the bond-stretching vibration was detected. The above results for NH_3 and ND_3 were apparently in striking contrast to the effects of anharmonicity observed for CH_4 and CD_4 by Bartell, Kuchitsu, and deNeui[2] and this made Bastiansen and Beagley remark that the vibrational properties of the two pairs of compounds appeared to be different. They made no attempt to compare their results with the structures determined by spectroscopy, although in the earlier work of Almenningen and Bastiansen[3] the peak value of the N–H radial-distribution curve, 1.015 Å, was claimed to be in good agreement with the effective r_0 value, 1.014 Å, determined by infrared spectroscopy.[4]

The purpose of the present experimental study is to investigate the hydrogen–deuterium isotope effect on the structure and to compare the electron-diffraction structures with those obtained from infrared spectroscopy by Benedict and Plyler,[5] who reported the r_0 and r_e structures as well as the normal frequencies and the quadratic force constants. Average structures for the ground vibrational state (r_z) have also been calculated by Morino, Kuchitsu, and Yamamoto[6] from the experimental rotational constants given by Benedict and Plyler.[5]

EXPERIMENTAL PROCEDURE

Samples of NH_3 and ND_3 were purchased from the Matheson Company and Merck and Company Limited, respectively. Both compounds were 99.9% pure and the isotope purity of ND_3 was greater than 98%.

Electron-diffraction photographs were taken at room temperature using the apparatus at Iowa State University.[2] The 40-kV electrons of the 0.36-μA beam current were scattered by gas molecules, and the diffraction patterns were recorded on 4×5-in. Kodak process plates through an r^3 sector. The samples were introduced into the diffraction chamber through a platinum nozzle with throat dimensions of 0.3 mm diam and 0.9 mm length. Initial sample pressures were 40 and 60 torr, respectively, for the long camera (21 cm) and short camera (11 cm) distances. Exposure times varied from 11–15 sec for the long camera distance and 30–50 sec for the short camera distance. Care was taken to record the photographs for the hydride and deuteride samples

[1] O. Bastiansen and B. Beagley, Acta Chem. Scand. **18**, 2077 (1964).

[2] L. S. Bartell, K. Kuchitsu, and R. J. deNeui, J. Chem. Phys. **35**, 1211 (1961).

[3] A. Almenningen and O. Bastiansen, Acta Chem. Scand. **9**, 815 (1955).

[4] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1945), p. 439.

[5] W. S. Benedict and E. K. Plyler, Can. J. Phys. **35**, 1235 (1957).

[6] Y. Morino, K. Kuchitsu, and S. Yamamoto, Spectochim. Acta **A24**, (1968).

at identical settings of the apparatus in order to avoid systematic errors.

The photographic plates were read with a microphotometer–converter system,[7] and relative electron intensities were obtained by a method described previously.[2] The molecular intensities obtained from the long ($q_{min}\sim 12$) and short ($q_{max}\sim 130$) camera distances agreed in the overlapping region ($q=29$–49) within the limit of their experimental uncertainties [about 0.001 in $M(q)$ values]. A small and uniform correction was made for the extraneous scattering at larger scattering angles ($q>\sim 100$).

ANALYSIS

The radial distribution curves $f(r)$ shown in Fig. 1 were calculated with small corrections for nonnuclear scattering[8] based on theoretical scattering factors for nitrogen[9] and hydrogen atoms[10] and with an artificial damping factor of $\exp[-0.0023(\pi q/10)^2]$. Isotope effects on the $f(r)$ curves similar to those observed for CH_4 and CD_4 are apparent. The N–H and N–D peaks are slightly distorted from Gaussian, indicating the effect of anharmonicity in the bond-stretching vibrations[12] (Fig. 2). The order of systematic distortion, with an effective parameter of asymmetry a of 3 Å^{-1}, is similar to that found in the C–H and C–D radial distribution peaks[2] in CH_4 and CD_4. On the other
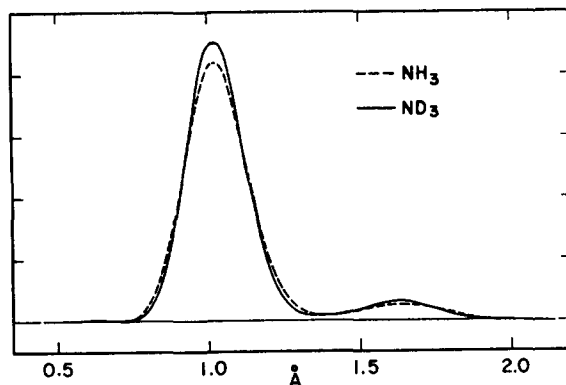

FIG. 1. Experimental radial distribution curves $f(r)$ for NH_3 (broken line) and for ND_3 (solid line) with an artificial damping parameter of 0.0023. The isotope effects on the bonded (N–H, N–D) and nonbonded (H–H, D–D) peaks are shown.

hand, the H–H and D–D peaks appear to be nearly symmetric when the contribution from the bonded distance on the left side of the peak is subtracted, in spite of the previous observations and conjecture.[1,3] This approximate symmetry is expected from a simple theoretical calculation, which shows that the effect of inversion[13] should not distort the peak significantly.

Several different methods were applied to the least-squares analysis of the intensity data with the following theoretical expressions for the molecular intensity,[14]

$$qM(q) = k \sum_i (A_i/r_{ai}) \exp(-\pi^2 l_i^2 q^2/200)$$

$$\times \sin\{(\pi q/10)[r_{ai} - (\pi^2 \kappa_i q^2/100)]\}. \quad (1)$$

It was found crucially important to include a nonzero κ value for the bonded distance in order to determine its r_a value accurately. The correlation between the κ and r_a parameters[14] was so strong that a change in κ of $\pm 1\times 10^{-5}$ Å^3 caused the $r_a(\text{N–H})$ and $r_a(\text{N–D})$ to shift by ± 0.0026 and ± 0.0033 Å, respectively.

The total intensities obtained from the short and long camera distances were first fitted separately by the theoretical expressions using analytical background functions with polynomials of various degrees.[11,15] The output r_a values from the long camera distance (for fixed κ parameters) were consistently longer than those from the short camera distance by about $0.2_5\%$, indicating the presence of a slight systematic error, which may have been caused by a magnetic disturbance of the sector ball-bearing race used in the experiment as discussed elsewhere.[7]

For this and other reasons, an alternative least-squares analysis on the molecular intensity curve[14] with the data from the two camera distances joined together at $q=40$ did not converge to any reasonable κ values

TABLE I. Experimental internuclear distances in ammonia and deuteroammonia (in angstrom units).

		r_a	r_g	σ[a]
NH_3	N–H	1.025_0	1.030_2	0.002
	H–H	1.654	1.662	0.010
ND_3	N–D	1.022_8	1.026_6	0.003
	D–D	1.648	1.654	0.008

[a] Estimated standard errors including systematic errors.

[7] L. S. Bartell and H. K. Higginbotham, J. Chem. Phys. **42**, 851 (1965).

[8] L. S. Bartell, L. O. Brockway, and R. H. Schwendeman, J. Chem. Phys. **23**, 1854 (1955).

[9] J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, Acta Cryst. **8**, 478 (1955); A. J. Freeman, *ibid.* **12**, 929 (1959).

[10] The effect of the uncertainties in the scattering factors is estimated to be negligible. For example,[11] the use of an effective atomic number of 1.2 for hydrogen produced a change in $r_g(\text{N–H})$ of less than 0.0002 Å and a change in $r_g(\text{H–H})$ of not more than 0.002 Å.

[11] J. P. Guillory, U.S. At. Energy Comm. IS-T-8, 72 (1965); thesis, Iowa State University, 1965.

[12] It is difficult to estimate the degree of anharmonicity precisely from the deviation of the N–H and N–D radial distribution peaks from a Gaussian shape, among other reasons, because the peaks are probably influenced by the systematic error in the molecular intensity (see text). Least-squares analysis on molecular intensities in which κ was varied did not converge to reliable values for this anharmonicity parameter. Nevertheless, there is no question that a major part of the uniform deviation of the N–H peak from Gaussian shown in Fig. 2 is a real effect of bond-stretching anharmonicity.
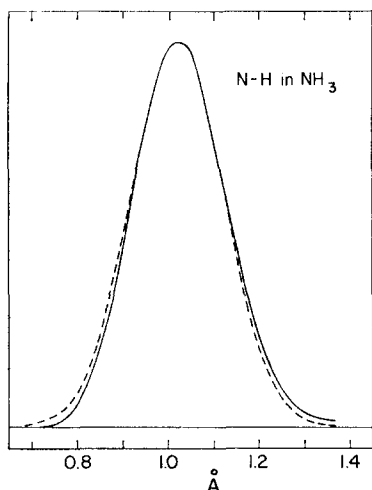
[13] J. D. Swalen and J. A. Ibers, J. Chem. Phys. **36**, 1914 (1962).

[14] Y. Morino, K. Kuchitsu, and Y. Murata, Acta Cryst. **18**, 549 (1965).

[15] L. S. Bartell, D. A. Kohl, B. L. Carroll, and R. M. Gavin, Jr., J. Chem. Phys. **42**, 3079 (1965).

FIG. 2. Asymmetry of the N–H radial distribution peak (solid line) stemming primarily from the anharmonicity in the N–H bond-stretching vibration. The broken line is a Gaussian curve with an identical maximum position and half-width. See Reference 12.

when the κ parameters were varied freely; the analysis resulted in $\kappa(N-H) = (2.0\pm0.2)\times10^{-5}$ Å^3 with $r_a(N-H) = 1.027$ Å and $\kappa(N-D) = (1.4\pm0.2)\times10^{-5}$ Å^3 with $r_a(N-D) = 1.026$ Å. Since the κ parameters were extremely sensitive to small systematic errors, it was difficult to estimate reliable κ and r_a values from this analysis.[16] However, the r_a values were obtained with no difficulty once the κ values were fixed to the values expected for a Morse oscillator. These values, $(1.0\pm0.4)\times10^{-5}$ Å^3 and $(0.5\pm0.2)\times10^{-5}$ Å^3 for N–H and for N–D, respectively, were based on the formula[17–19]

$$\kappa\sim\tfrac{1}{6}al_a^4, \qquad (2)$$

with an estimated a value of 2.5 ± 0.5 Å^{-1}. The variations in the output parameters of the analyses by different methods and with different statistical weights assigned to individual observations, the uncertainties in the scale factor, and the uncertainties in the κ values were taken into the estimates of the errors in the structural parameters listed in Tables I and II, where final results of the r_a and r_g distances and the mean amplitudes are given. The observed and the best-fit molecular intensities are shown in Fig. 3.

In all the above analyses with the $\kappa(N-H)$ parameter taken about twice as large as $\kappa(N-D)$, as indicated by Eq. (2), the difference between $r_a(N-H)$ and $r_a(N-D)$ was consistently $+0.002_2$ Å, showing the r_a isotope

effect. The corresponding r_g isotope effect is 0.003_6 Å according to the equation[17]

$$r_g=r_a+l^2/r. \qquad (3)$$

This difference is similar to that observed[2] for CH_4 and CD_4, where $r_g(C-H) - r_g(C-D) = 0.004_1$ Å.

The present r_a values are several thousandths of an angstrom larger than those reported.[1] The principal origin of this discrepancy seems to be in the effect of the κ parameter, which was entirely ignored in the analysis of Ref. 1. If the κ values estimated above are included in the earlier result,[1] the corrected r_a distances become 1.022 Å for N–H and N–D, much closer to the present values, 1.025 and 1.023 Å.

The mean amplitudes derived from the least-squares analysis were corrected for the failure of the Börn approximation[20] and were converted into l_e parameters. The correction for the Börn failure[21] involves values for δ in $\exp(-\delta s^2)$, of 2.7×10^{-4} and 2.5×10^{-4} Å^2 for N–H and N–D, respectively. The mean amplitudes listed in Table II agree well with the experimental values of Bastiansen and Beagley,[1] with the l_e values calculated in the present study, and with the harmonic amplitudes calculated by Cyvin[22] and Sundaram.[23] The indices of resolution k are found to be essentially unity (0.988 ± 0.01 for NH$_3$ and 0.998 ± 0.01 for ND$_3$).

COMPARISON WITH SPECTROSCOPIC STRUCTURE

The r_g distances obtained in the above analysis were converted into r_α^0 distances by using the relation[24]

$$r_\alpha^0 = [\lim(T\to0^\circ K)r_g] - K_0 - \delta r_{cent}$$
$$\simeq r_g - \tfrac{3}{2}a(\langle\Delta z^2\rangle_T - \langle\Delta z^2\rangle_{0^\circ K}) - K_0 - \delta r_{cent}, \qquad (4)$$

where

$$K_0 = [\langle\Delta x^2\rangle_{0^\circ K} + \langle\Delta y^2\rangle_{0^\circ K}]/2r. \qquad (5)$$

The perpendicular amplitudes[25] in Eq. (5) and the centrifugal corrections[26] δr_{cent} in the above equations were calculated by means of the F matrix given in Ref. 6. The r_α^0 distances are compared with their spectroscopic counterparts r_z calculated by Morino, Kuchitsu, and Yamamoto[6] from the experimental rotational constants B_0 and C_0 determined by Benedict and Plyler.[5] The agreement between the r_α^0 and r_z structures is satisfactory within the experimental uncertainties, as shown in Table III. Contrary to the previous observation,[1] no significant difference was

[16] Judging from the standard errors attached to κ, however, statistically significant κ values for the N–H and N–D pairs might have been obtained from this experiment if the experimental data had been free from the above-mentioned systematic error in the scale factor.

[17] L. S. Bartell, J. Chem. Phys. 23, 1219 (1955).

[18] K. Kuchitsu and L. S. Bartell, J. Chem. Phys. 35, 1945 (1961).

[19] K. Kuchitsu, Bull. Chem. Soc. Japan, 40, 498, 505 (1967).

[20] J. A. Ibers and J. A. Hoerni, Acta Cryst. 7, 405 (1954).

[21] L S Bartell and L. O. Brockway, Nature 171, 978 (1953).

[22] S. J. Cyvin and J. Bakken, Acta Chem. Scand. 12, 1759 (1958). S. J. Cyvin, Acta Polytech. Scand. Ph6 (1960).

[23] S. Sundaram, J. Mol. Spectry. 7, 53 (1961).

[24] Y. Morino, K. Kuchitsu, and T. Oka, J. Chem. Phys. 36, 1108 (1962).

[25] Y. Morino and E. Hirota, J. Chem. Phys. 23, 737 (1955).

[26] M. Iwasaki and K. Hedberg, J. Chem. Phys. 36, 2961 (1962).

TABLE II. Mean amplitudes of ammonia and deuteroammonia (in angstrom units).

	l_e (obs)[a]	l_e (calc)[a]	l (obs)[b]	l (calc)[c]	l (calc)[d]
NH$_3$	$0.073_1 \pm 0.002$	0.072_2	$0.078_9 \pm 0.002_7$	0.0727	0.0726
	0.125 ± 0.006	0.11_7	0.10 ± 0.02	0.1236	0.1261
ND$_3$	$0.061_1 \pm 0.002$	0.061_7	$0.066_7 \pm 0.002_7$	0.0618	0.0626
	0.101 ± 0.006	0.099	0.09 ± 0.02	0.1040	0.1074

[a] Present study.   [b] Reference 1.   [c] Reference 22.   [d] Reference 23.

observed in the HNH and DND average angles beyond their experimental errors.

Since all the eight cubic constants (k_{1ii} and k_{2ii} for $i = 1$–4) necessary to calculate the linear mean values of normal coordinates have been given[6] for NH$_3$ and ND$_3$, the equilibrium structure was estimated from the r_g values determined above by calculating $r_g - r_e$ in the manner described previously for water[27] and methane.[28] The linear mean values of the normal coordinates Q_1 and Q_2, given by[29]

$$\langle Q_s \rangle = -(h/16\pi^2 c\omega_s{}^3)^{1/2}(3k_{sss}T_s + k_{ss's}T_{s'}$$
$$+2k_{s33}T_3 + 2k_{s44}T_4), \qquad (s=1, 2; s'=2, 1), \quad (6)$$

where

$$T_i = \coth(hc\omega_i/2kT) \approx 1, \qquad (7)$$

were calculated by using the cubic constants derived from the experimental values by Benedict and Plyler[5] (the set "obs" in Table 6 of Ref. 6) and the estimated cubic constants ("empirical-fit model" in the same table). By applying the mean values summarized in

Table IV, the r_e bond distance of ammonia is estimated from the electron-diffraction r_g distances to be: $r_e(\text{N–H}) = r_e(\text{N–D}) = 1.011 \pm 0.003$ Å. This agrees with the corresponding r_e structures, $r_e(\text{N–H}) = 1.012_4 \pm 0.002$ Å and $r_e(\text{N–D}) = 1.010_8 \pm 0.004$ Å, based on the spectroscopic B_e and C_e constants reported in Ref. 5, the errors being estimated from the probable experimental errors of about 0.02 cm^{-1} in the rotational constants.[5] The spectroscopic results reported for the equilibrium H–N–H and D–N–D angles are $106.6_7°(\pm 0.2°)$ and $106.7_0°(\pm 0.5°)$, respectively. The N–H and N–D bond distances of ammonia with various different definitions, r_g, r_a, $r_\alpha{}^0$, r_z, r_0, and r_e, are compared in Fig. 4.

ISOTOPE EFFECTS ON OTHER OBSERVABLES

Deuterium isotope effects play an important role in the diagnosis of reaction mechanisms. Since they are frequently difficult to interpret in detail, a large amount of effort has gone into the study of isotope effects on physical and chemical properties of substances in the
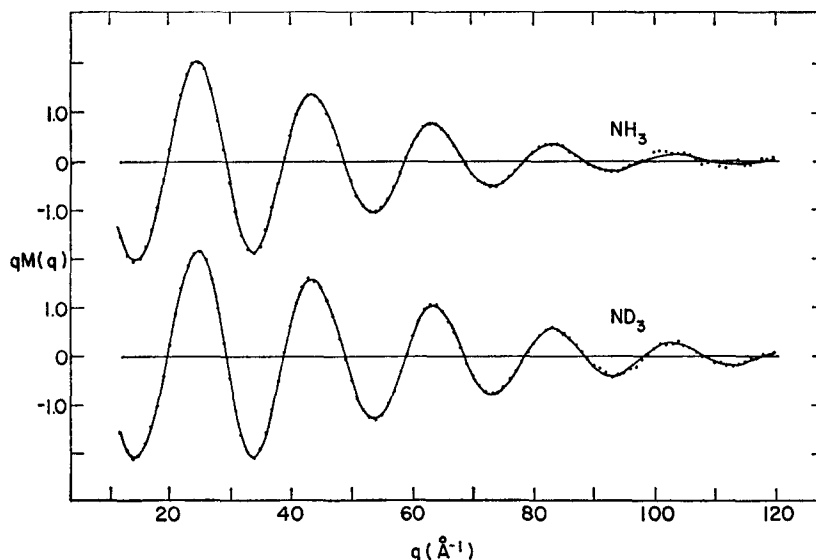

FIG. 3. Comparison of the experimental and theoretical molecular intensity curves $qM(q)$. The experimental data shown in dots are average values with random standard errors of about ± 0.03 at $q = 60$ and ± 0.06 at $q = 120$. The solid lines represent the best-fit curves from the least-squares analysis with fixed κ parameters.

[27] K. Kuchitsu and L. S. Bartell, J. Chem. Phys. **36**, 2460 (1962).
[28] K. Kuchitsu and L. S. Bartell, J. Chem. Phys. **36**, 2470 (1962).
[29] M. Toyama, T. Oka, and Y. Morino, J. Mol. Spectry. **13**, 193 (1964).

TABLE III. Average structures of ammonia and deuteroammonia (distances in angstrom units).

		K_0	δr_{cent}	r_α^0	r_z^a	r_0^b
NH₃	N–H	0.0068	0.0007	$1.022_7 \pm 0.003$	$1.024_9 \pm 0.0009$	1.0173
	H–H	0.0033	0.0005	1.658 ± 0.011	$(1.649_7 \pm 0.001_9)$	(1.643_7)
	∠H–N–H	⋯	⋯	$(108._2° \pm 1.1°)$	$107.3_2° \pm 0.1_1°$	107.78°
ND₃	N–D	0.0050	0.0006	$1.021_0 \pm 0.003$	$1.020_6 \pm 0.001_9$	1.0155
	D–D	0.0022	0.0007	1.651 ± 0.009	$(1.643_2 \pm 0.004_0)$	(1.638_8)
	∠D–N–D	⋯	⋯	$(107._9° \pm 1.0°)$	$107.2_2° \pm 0.2_4°$	107.59°

[a] Reference 6. [b] Reference 5.

hope that some insight will be gained. In the course of such studies, ND₃ has been found to have a larger dipole moment (by 0.015 D)[30,31] and a lower electrical polarizability (by 0.2 cm³/mole)[30,31] than NH₃. Also, by analogy with amines, the *deutero* compound is expected to be more basic.[32] Halevi has tentatively accounted for the shifts in dipole moment and polarizability in terms of a flatter structure for NH₃ than ND₃ and longer N–H than N–D bonds, respectively.[33] His approximate scheme for using anharmonicity constants to estimate mean atomic displacements from equilibrium positions at 0°K yielded the values 0.008 Å for $\langle \Delta r \rangle$ and $+1.42°$ for $\langle \Delta\alpha \rangle$ of NH₃, and 0.006 Å and $+1.11°$ for ND₃. These values were questioned by Bartell,[34] who applied Ehrenfests' theorem to a model force field and obtained 0.022_4 Å[35] and $-1.26°$ for NH₃, and 0.0167 Å[35] and $-0.92°$ for ND₃. The corresponding values deduced from the experimental cubic constants by a first-order perturbation calculation are listed in Table IV. They confirm that $\langle \Delta r \rangle$ is substantial but, unfortunately, they do not unequivocally

TABLE IV. Mean values of coordinates for ammonia and deuterammonia.[a]

	$\langle Q_1 \rangle$	$\langle Q_2 \rangle$	$\langle \Delta z \rangle^c$	$\langle \Delta r \rangle^c$	$\langle \Delta\alpha \rangle^d$
NH₃ Set I[b]	0.0216	0.0161	0.0113	0.0188	0.37°
Set II	0.0225	0.0120	0.0122	0.0196	0.21°
ND₃ Set I	0.0255	0.0188	0.0096	0.0153	0.31°
Set II	0.0227	0.0085	0.0090	0.0147	0.01°

[a] Calculated at room temperature. Units: $\langle Q_1 \rangle$ and $\langle Q_2 \rangle$ in amu$^{1/2} \cdot$Å, $\langle \Delta z \rangle$ and $\langle \Delta r \rangle$ in angstroms.

[b] Sets I and II correspond to the sets of cubic constants listed in Table 6 of Ref. 6: "observed" and "empirical-fit model," respectively.

[c] $\langle \Delta r \rangle$ is the difference between r_g and r_e including δr_{cent} and $\langle \Delta z \rangle$ is the mean displacement projected onto the equilibrium bond axis.

[d] The mean displacement of the valence angle.

[20] R. P. Bell and I. E. Coop, Trans. Faraday Soc. **34**, 1209 (1938).

[31] E. A. Halevi, E. N. Haran, and B. Ravid, Chem. Phys. Letters **1**, 475 (1967).

[32] E. A. Halevi, Tetrahedron **1**, 174 (1957).

[33] E. A. Halevi, Trans. Faraday Soc. **54**, 1441 (1958). See also Footnote 23 in Ref. 34.

[34] L. S. Bartell, J. Chem. Phys. **38**, 1827 (1963).

[35] The values cited here contain the correction $(109/24)a^3 l^4$ for truncation of the potential energy as discussed in Ref. 34. The asymmetry constant a used in Ref. 34 was derived from the empirical potential function of Lippincott and Schroeder [J. Chem. Phys. **23**, 1131 (1955); **26**, 1678 (1957)]. The experimental cubic constants derived by Morino *et al.* in Ref. 6 suggest that the empirical a value is approximately 9% too large.

resolve the problem of the isotope effect on the apex angle and its possible relation to the dipole moment.

There can be no doubt that the values of $\langle \Delta\alpha \rangle$ on Table IV are based on considerably firmer evidence than are the earlier estimates of Halevi and Bartell. The difficulty lies in the relatively great uncertainties in the experimental cubic constants k_{211} and, more importantly, k_{244}. From the order of magnitude of these uncertainties (inferred from the inconsistencies in Tables 6 and 7 of Ref. 6) we conclude that the derived values of $\langle \Delta\alpha \rangle$ may be in error by as much as a degree. Model force fields are also subject to large uncertainties. Although stretching anharmonicities are now quite well understood, virtually no generalities have been established for bending anharmonicities. If ammonia's reliably known quadratic force field is supplemented by adding a Morse-like bond-stretching anharmonicity, a reasonable value $\langle \Delta r \rangle$ is obtained, but the calculated value for $\langle \Delta\alpha \rangle$ becomes $-1.6_1°$ for NH₃. This gives a mean angle which is almost certainly far too small.

The isotope effect on the polarizability seems to be reasonably well explained by the bond length shift $\Delta\langle \Delta r \rangle$, according to Halevi.[31] On the other hand, if the almost negligible values of $\langle \Delta\alpha \rangle$ suggested by the experimental cubic constants are correct, the isotope effect on the dipole moment may be inadequately accounted for by Halevi's proposed anharmonic contribution $(\partial\mu/\partial\alpha)_e \langle \Delta\alpha \rangle$ alone. The contributions
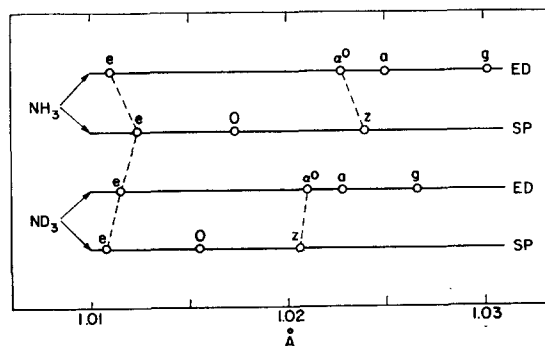

FIG. 4. Diagram of the bond distances of ammonia showing the dependence of the distances on their definitions and on the isotope substitution: r_g, r_α, r_α^0, and r_e from electron diffraction (ED) and r_z, r_0, and r_e from infrared spectroscopy (SP) for NH₃ and ND₃. The open circles represent their most probable values, to which standard errors of $\simeq 0.002$ or 0.003 Å should be assigned.

$(\partial^2\mu/\partial\alpha^2)_e\langle\Delta\alpha^2\rangle$ may be significant, in view of the 8° root-mean-square value of $\Delta\alpha$. It is probable that a careful SCF MO calculation of μ as a function of α would shed light on the matter.

Theory of Temperature-Dependent g-Tensor Splittings in p-Phenylenediamine–Chloranil

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A theory is developed to interpret the unusual temperature dependence of the g-tensor splittings—the electron paramagnetic resonance lines *narrow* slightly as they merge into a single line—observed in the paramagnetic organic crystal p-phenylenediamine–chloranil. Dipolar interactions are shown to delocalize the magnetic excitations over magnetically inequivalent chains of radicals. The g tensor for a delocalized excitation is calculated in terms of the g tensors of the radicals over which it is delocalized. The splittings decrease, and finally vanish, as the interchain dipolar field becomes sufficiently strong to delocalize the excitation entirely. The dipolar field strength depends on temperature through the strong magnetic dilution arising from large, antiferromagnetic, intrachain exchange. The theory, which accounts for the entire temperature range of the spectrum, is contrasted with the qualitatively different line merging predicted by random modulation among fixed frequencies (i.e., localized excitations), which necessarily leads to an initial line broadening greater than the line shift.

I. INTRODUCTION

Hughes[1,2] has recently observed the electron paramagnetic resonance (EPR) spectrum of single-crystal p-phenylenediamine–chloranil (PDC). The three EPR lines due to magnetically inequivalent chains of radicals merge smoothly into a single line as the temperature is raised. The temperature dependence of the spectrum is very unusual: the widths of the individual lines *decrease* during the line merging. The collapse of splittings as a function of an external parameter such as temperature, viscosity, or radical concentration is often observed in both NMR and EPR. Theoretical models[3–6] based on random modulation at least qualitatively account for the collapse of previously observed splittings. Such theories, however, require that the lines *broaden* as they merge, with an initial broadening larger than the line shift.

The purpose of this paper is to account for the unusual line merging observed in crystalline PDC. Since PDC is composed of free radicals, the spin Hamiltonian has the familiar form

$$\mathcal{3C}=\mathcal{3C}_e+\mathcal{3C}_Z+\mathcal{3C}_d, \qquad (1)$$

where $\mathcal{3C}_e$ represents the exchange interaction between radicals; $\mathcal{3C}_Z$ is the Zeeman interaction; and $\mathcal{3C}_d$ represents dipolar interactions among both electronic and nuclear moments. Each term contributes to the observed EPR spectrum. The unusual magnetic properties of PDC, as of other organic free-radical crystals, reflect the strong, antiferromagnetic, one-dimensional exchange interactions, characteristic of these crystals.[7] Both $\mathcal{3C}_Z$ and $\mathcal{3C}_d$ are small perturbations splitting the degeneracies of the excited states of $\mathcal{3C}_e$. In Sec. II, we construct approximate excited states of $\mathcal{3C}_e$ and discuss the delocalization of the magnetic excitations and the strong, temperature-dependent magnetic dilution. In Sec. III, the Zeeman Hamiltonian $\mathcal{3C}_Z$ for an unpaired electron in a delocalized state is found by relating its g tensor to those of the radicals over which it is delocalized. The dipolar interactions $\mathcal{3C}_d$ are introduced in

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