PHYSICAL REVIEW VOLUME 79, NUMBER 3 AUGUST 1, 1950

The Nuclear Quadrupole Moment of N^{14} and the Structure of Nitrogen Trifluoride from Microwave Spectra*

JOHN SHERIDAN** AND WALTER GORDY
Department of Physics, Duke University, Durham, North Carolina

(Received April 10, 1950)

Measurements of the $J=1\rightarrow 2$ rotational transitions of $N^{14}F_3$ and $N^{15}F_3$ yield the following molecular and nuclear properties. For $N^{14}F_3$, $B_0=10{,}680.96$ Mc/sec., $I_B=78.5475\times 10^{-40}$ g cm^2; for $N^{15}F_3$, $B_0=10{,}629.35$ Mc/sec., $I_B=78.9291\times 10^{-40}$ g cm^2. The molecular dimensions are: $d_{NF}=1.371$A and $\angle FNF=102°\,9'$. The nuclear quadrupole coupling of N^{14} is -7.07 Mc/sec. This yields $+0.01\times 10^{-24}$ cm^2 as the most probable value of the nuclear quadrupole moment of N^{14}.

I. INTRODUCTION

PREVIOUS workers have proposed various molecular configurations for the pyramidal molecule nitrogen trifluoride, NF_3. The infra-red spectrum[1] is reported to indicate an angle FNF of 110° or more, and the distance, d_{NF}, of 1.45A is suggested by the application of Badger's rule to the observed NF stretching force-constant. An equally large FNF angle has also been favored on account of the small electric dipole moment found for the molecule.[2] A recent electron diffraction study,[3] on the other hand, indicates an angle FNF of only $102.5°\pm 1.5°$ and a distance d_{NF} of 1.37 ± 0.02A.

We have measured the $J=1\rightarrow 2$ transitions in the pure rotation spectra of $N^{14}F_3$ and $N^{15}F_3$. The moments of inertia prove that the molecule has a structure very close to that found by the electron diffraction method. The nuclear quadrupole coupling of N^{14} has also been obtained from the hyperfine structure of the $N^{14}F_3$ spectrum, and provides additional evidence of the nature of the bonding. A new evaluation of the nuclear quadrupole moment of N^{14} has been made.

II. EXPERIMENTAL METHOD AND RESULTS

Nitrogen trifluoride was prepared by the electrolysis of fused ammonium bifluoride[4] using an anode of carbon impregnated with copper, which did not polarize readily. The nitrogen trifluoride, which was formed in a yield of only some 10 to 15 percent of that expected from the electrical charge passed, was purified by distillation at $-150°$C.

The $N^{15}F_3$ (7.5 atom percent N^{15}) was prepared by condensation of anhydrous ammonia into the required amount of anhydrous hydrogen fluoride at $-78°$C with subsequent electrolysis of the fused product in the same copper vessel.

The experimental measurements on the microwave spectra were made using methods previously described.[5]

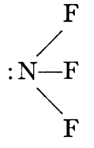
Table I lists the frequencies found for the unperturbed rotational absorptions, and also the B_0 and I_B values. Table II summarizes the molecular dimensions obtained by substitution of the appropriate I_B and mass values into the relationship

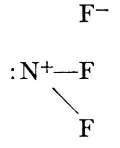
$$I_B=1.6599\left[\frac{3}{2}M_F d_{NF}^2\sin^2\beta+d_{NF}^2\cos^2\beta\left(M_N-\frac{M_N^2}{3M_F+M_N}\right)\right],$$

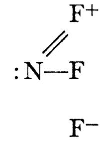
where $\sin\beta=(2/3^{\frac{1}{2}})\sin(\frac{1}{2}\angle FNF)$. Table III gives the calculated and observed hyperfine structure of the $J=1\rightarrow 2$ transition of $N^{14}F_3$.

III. DISCUSSION OF MOLECULAR STRUCTURE

The distance d_{NF} is close to that predicted by the Schomaker-Stevenson rule[6] for a single N—F bond with partial ionic character. This would be in accord with the assumption that structure I and three structures of type II are the main contributing states:


(I)


(II)


(III)

The electronegativity difference[7] of N and F, indicates that the NF link will be about 20 percent ionic, and accordingly it is reasonable to regard the three forms of type II as the most important. Three structures of type III may also contribute to some extent without greatly changing the nuclear separations. Any marked contribution of forms III, however, might be expected

---

* The research reported in this document has been made possible through support and sponsorship extended by the Geophysical Research Directorate of the Air Force Cambridge Research Laboratories under Contract No. W19-122-ac-35. It is published for technical information only and does not represent recommendations or conclusions of the sponsoring agency.

** On leave from Department of Chemistry, University of Birmingham, Birmingham, England.

[1] Bailey, Hale, and Thompson, J. Chem. Phys. **5**, 275 (1937).

[2] K. L. Ramaswamy, Proc. Ind. Acad. Sci. **2A**, 364 (1934).

[3] C-S. Lu and V. Schomaker, quoted by P. W. Allen and L. E. Sutton, Acta Crys. **3**, 65 (1950).

[4] O. Ruff *et al.*, Zeits. f. anorg. allgem. Chemie **172**, 417 (1928).

[5] Gordy, Simmons, and Smith, Phys. Rev. **74**, 243 (1948).

[6] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).

[7] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1940), p. 70.

TABLE I. Molecular constants.

Molecule	Unperturbed frequency for $J=1\rightarrow 2$ Mc/sec.	B_0 Mc/sec.	D_{JK} Mc/sec.	I_B* g cm²
$N^{14}F_3$	42,723.84±0.10	10,680.96	−0.025	78.5475×10^{-40}
$N^{15}F_3$	42,517.38±0.10	10,629.35		78.9291×10^{-40}

* Calculated by taking Planck's constant as 6.6242×10^{-27} erg/sec.

TABLE II. Molecular dimensions.*

Molecule	d_{NF}	∠FNF
NF_3	1.371A	102° 9′

* Taking $M_F=19.00452$ a.m.u., $M_N=14.0075$ a.m.u. and 15.00489 a.m.u., from M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. 9, 373 (1937).

to cause d_{NF} to become shorter than the Schomaker-Stevenson rule predicts, since similar resonance has been thought to be the cause of the abnormally short CF distance in fluorocarbons.[8] The contribution of forms of the type of III thus appears to be less in NF_3 than in analogous carbon fluorides.

The angle FNF of 102° 9′ is significantly less than tetrahedral and indicates that the NF bonds have more than 75 percent *p*-character. This is important in connection with the discussion of the nuclear quadrupole coupling in the molecule (below).

The only serious difficulty encountered by the above theory is in accounting for the smallness of the electric dipole moment, 0.21 D, reported for the molecule[2] by the gas-temperature method. The observed intensities of the rotational absorptions also suggest that the moment is not much greater than this. With the observed valency angle, the predominance of forms of type II and the bond-moments predicted approximately from electronegativity differences[9] would be expected to give rise to a larger moment. This effect would not be offset by contributions of I and III unless these are larger than has been supposed. It is probable that a reduction in moment results from dipole interactions such as have been postulated in other cases of a similar nature. In view of the position, however, we propose to redetermine the dipole moment of the molecule using Stark modulation of the microwave spectrum.

IV. NUCLEAR COUPLING AND QUADRUPOLE MOMENT OF N^{14}

Table IV summarizes the calculated nuclear constants of N^{14}. The N^{14} nuclear quadrupole coupling in NF_3, −7.07 Mc/sec., is much larger than that found for N^{14} in any other molecule. Its magnitude is 73 percent greater than that, 4.10 Mc/sec., in the similar NH_3 molecule. This coupling can be accounted for by assuming about 17 percent *s*-character for each of the bonding orbitals, so that the non-bonding orbital would have about 50 percent *p*-character. In this calculation we have neglected distortion effects and have assumed structures of type II to be the most important ones. However, sizeable contributions from I or III would not significantly affect the results. We have assumed[10] 10 Mc/sec. coupling per unbalanced *p*-electron, and have multiplied by a factor of 1.25 to correct for the positive formal charge on N in structure II. The resulting hybridization is in good agreement with the observed bond angles.

Except for N_2O, in which the bonding is extremely complex and the observed coupling is so small that it could be caused almost entirely by distortion effects, Townes and Dailey were able to account satisfactorily for all of the N^{14} couplings then measured, by assuming either 10 Mc/sec. or 24 Mc/sec. coupling per unbalanced *p*-electron, and by postulating different kinds of *sp*-hybridization. This situation causes large uncertainties in the value, $+0.02\times 10^{-24}$ cm², which they estimated for the N^{14} quadrupole moment. The higher value, 24 Mc/sec., can be ruled out by the NF_3 coupling. Less than 10 percent *s*-character in bonding orbitals would be required to account for the observed coupling, whereas the observed bond angles indicate that the bonding orbitals have 15 to 20 percent *s*-character. Hence, it appears that the lower value 10 Mc/sec. is closer to the correct one. We accordingly assign $+0.01\times 10^{-24}$ cm² as the most probable value for the nuclear quadrupole moment of N^{14}.

The value of 10 Mc per unbalanced *p* electron would

TABLE III. Observed and calculated hyperfine structure of the $J=1\rightarrow 2$ transition of $N^{14}F_3$.

K	$F\rightarrow F'$	Frequency (Mc/sec.) Calculated*	Frequency (Mc/sec.) Observed	Relative intensity Calculated	Relative intensity Observed
0	1→1	42,727.39	42,727.39	18	15
1	0→1	42,726.61	42,726.60	18	20
1	2→3	42,724.39	42,724.36	75	70
0	2→3	42,724.00	42,723.94	100	150
0	1→2	42,723.85		54	
1	2→2	42,723.25	42,723.28	13	18
1	1→2	42,722.18	42,722.16	40	75
0	0→1	42,722.08		24	
0	2→2	42,721.73	42,721.73	18	20

* Calculated by using $eQ(\partial^2V/\partial z^2)=-7.07$ Mc/sec. and $D_{JK}=-0.025$ Mc/sec.

---

[8] L. O. Brockway, J. Phys. Chem. **41**, 747 (1937).

[9] L. Pauling, reference 7, p. 68.

[10] The 10 Mc/sec. per unbalanced electron is the lower value employed by Townes and Dailey, J. Chem. Phys. **17**, 782 (1949). The factor 1.25 is that used by these authors to correct for a positive formal charge of one unit.

require the σ-bond wave function of multiple bonded N to be $(1/\sqrt{2})\psi_s+(1/\sqrt{2})\psi_p$ rather than[10] $\frac{1}{2}\psi_s+(\sqrt{3}/2)\psi_p$, and would favor structures of the type

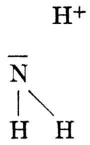


TABLE IV. Nuclear constants of N^{14}.

Nucleus	Spin	Coupling in NF_3 $eQ(\partial^2V/\partial z^2)$	Quadrupole moment
N^{14}	1	-7.07 ± 0.10 Mc/sec.	0.01×10^{-24} cm^2

for ammonia rather than that written $N\equiv H_3$ by Townes and Dailey.

PHYSICAL REVIEW VOLUME 79, NUMBER 3 AUGUST 1, 1950

An Application of the W.K.B. Method to the Cohesive Energy of Monovalent Metals

T. S. KUHN*
Harvard University, Cambridge, Massachusetts

(Received March 2, 1950)

A new method is developed which, within the limits of the spherical cell approximation first presented by Wigner and Seitz, will permit the evaluation of the cohesive energy, lattice constant, and compressibility of a monovalent metallic solid without the explicit computation of a central field for the atom. Analytic formulas for approximate solid state wave functions are produced in the region outside the atomic core by utilizing Imai's form of the W.K.B. method with the phase constant determined explicitly in terms of the known quantum defect of the free atom. These wave functions are applied to the determination of the minimum ground state energy in the alkali metals and of the sphere radius at which this occurs as functions of the quantum defects of the free atoms. These functions, when applied to Fröhlich's semi-empirical formula, yield a rapid and accurate method for the computation of the ground-state energy as a function of sphere radius.

I. Introduction: A previous paper[1] has developed the "function matching method" which permits computation of solid state wave functions to be undertaken without a knowledge of the potential function of the atomic core. Before the discovery of that technique an attempt had been made to achieve the same result with wave functions of the W.K.B. type. This proved to be feasible only in theory, for the region in which the wave functions are of physical interest lies near the outer turning point of the wave equation where the W.K.B. approximation tends to break down. Even Langer's[2] W.K.B. formalism yielded significant errors in this region, so the attempt was abandoned in favor of the function matching technique.

Recently Imai[3] has suggested a revision of the W.K.B. method which materially improves the approximation near the turning point. His formalism is applied in the present paper to the computation of wave functions for the solid state and, in a sample specialization, yields numerical results almost identical with those computed by more exact methods. Because the computations involved are less arduous and because this revised W.K.B. technique proves less critically sensitive to small changes in the experimental data, it is presented here as an improvement on our earlier method. No attempt has been made, however, to duplicate the computations made in the earlier paper (**A**), for there is every evidence that the two formalisms will yield almost identical results.

The objectives and the physical presuppositions of this paper are identical with those discussed in (**A**). Readers acquainted with (**A**) will note that the general solution of the radial wave equation, there produced as an arbitrary linear combination of Whittaker's two solutions of the confluent hypergeometric equation, is here replaced by Imai's W.K.B. solution with an undetermined phase constant. The condition that the wave function be zero at the origin is then seen to determine explicitly the phase constant used in the W.K.B. expansion about the inner turning point, so that the phase constant to be used about the outer turning point can be determined as a function of the quantum defect of the atom by an obvious modification of the usual phase-integral quantum condition. This procedure serves to determine the wave functions for the solid without the computation of the logarithmic derivative function required by the earlier, function matching procedure.

II. The Imai Procedure for the Solid State:

Imai has shown that a differential equation,

$$d^2U/(dx^2)+k^2P(x)U=0, \tag{1}$$

---

* Junior Fellow, Society of Fellows.

[1] T. S. Kuhn and J. H. Van Vleck, Phys. Rev., **79**, 382 (1950). This paper will be referred to as (**A**).

[2] R. E. Langer, Phys. Rev. **51**, 669 (1937).

[3] I. Imai, Phys. Rev. **74**, 113 (1948).