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A. Brooks Harris
University of Pennsylvania, harris@sas.upenn.edu

Earle Hunt

Horst Meyer

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Abstract

We have studied the ^{19}F chemical-shift anisotropy in NF$_3$ and CHF$_3$ trapped in β-quinol clathrates. It is known that molecules trapped in these compounds become aligned at low temperatures so that studies of relatively isolated oriented molecules become possible. The nuclear magnetic resonance was observed at several frequencies with the magnetic field applied at various angles relative to the crystal axis. The orientation of the molecules in the cavity and the dipolar broadening due to the lattice protons could be estimated rather closely by a qualitative analysis of the line shapes. The principal components of the chemical-shift tensor of NF$_3$ could be determined from the observed variation of the first and second moments of the line with the strength and orientation of the magnetic field. This determination was further substantiated by the good agreement between the calculated and observed line shapes for various values of the magnetic field. For CHF$_3$, where the chemical-shift anisotropy is smaller, only a cruder analysis was practicable. The values of the anisotropy of the chemical-shift tensor obtained were $\sigma_\parallel - \sigma_\perp = (390\pm60)$ ppm for NF$_3$ and $\sigma_\parallel - \sigma_\perp = (105\pm20)$ ppm for CHF$_3$, where $\sigma_\perp$ is the average of the two components of the chemical-shift tensor perpendicular to the fluorine bond direction. For NF$_3$ a difference of (140 ± 40) ppm between the two perpendicular components was found, indicating a deviation from uniaxial symmetry of the NF bond. The sign and order of magnitude of the chemical-shift anisotropy are discussed and can be understood on the basis of current ideas about the relationship between the bond characters and the chemical-shift anisotropy.

Disciplines
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Comments
At the time of publication, author A. Brooks Harris was affiliated with Duke University. Currently, (s)he is a faculty member in the Physics Department at the University of Pennsylvania.

argon. However, experimentally it is found that only 20% argon balances the negative pressure coefficient of viscosity of ammonia, and the mixture has a zero pressure coefficient. A quantitative treatment of the viscosity of argon–ammonia mixture similar to that applied to pure ammonia is not possible at present as no formulation of a dense gas theory for a ternary mixture is available. It may, however, be suggested that in ammonia–argon mixture most of the interactions like NH_3–Ar, Ar–Ar, $(NH_3)_2$–Ar, etc., should have positive pressure coefficient of viscosity. Consequently, a comparatively small percentage of argon can balance the effect of a higher percentage of ammonia.

4. CONCLUSION

The present calculations show that association due to hydrogen bonding plays a very significant role in determining the viscosity of highly polar gases like steam and ammonia. This effect is of such magnitude that at not too high temperatures the positive contribution to viscosity due to collisional transfer is overshadowed by the negative contribution due to dimerization resulting in negative pressure coefficients.

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Anisotropy of the ¹⁹F Chemical Shift of Trapped CHF₃ and NF₃ †

A. Brooks Harris,* Earle Hunt, and Horst Meyer‡

Department of Physics, Duke University, Durham, North Carolina

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We have studied the ¹⁹F chemical-shift anisotropy in NF₃ and CHF₃ trapped in β-quinol clathrates. It is known that molecules trapped in these compounds become aligned at low temperatures so that studies of relatively isolated oriented molecules become possible. The nuclear magnetic resonance was observed at several frequencies with the magnetic field applied at various angles relative to the crystal axis. The orientation of the molecules in the cavity and the dipolar broadening due to the lattice protons could be estimated rather closely by a qualitative analysis of the line shapes. The principal components of the chemical-shift tensor of NF₃ could be determined from the observed variation of the first and second moments of the line with the strength and orientation of the magnetic field. This determination was further substantiated by the good agreement between the calculated and observed line shapes for various values of the magnetic field. For CHF₃, where the chemical-shift anisotropy is smaller, only a cruder analysis was practicable. The values of the anisotropy of the chemical-shift tensor obtained were $\sigma_{||} - \sigma_{\perp} = (390 \pm 60)$ ppm for NF₃ and $\sigma_{||} - \sigma_{\perp} = (105 \pm 20)$ ppm for CHF₃, where $\sigma_{\perp}$ is the average of the two components of the chemical-shift tensor perpendicular to the fluorine bond direction. For NF₃ a difference of (140 ± 40) ppm between the two perpendicular components was found, indicating a deviation from uniaxial symmetry of the NF bond. The sign and order of magnitude of the chemical-shift anisotropy are discussed and can be understood on the basis of current ideas about the relationship between the bond characters and the chemical-shift anisotropy.

I. INTRODUCTION

RECENTLY measurements of the chemical-shift anisotropy of ¹⁹F in several molecules have been reported.[1–4] Obviously, a very direct way to obtain this type of information would be to study the nuclear magnetic resonance (NMR) of a single isolated molecule for different orientations of the applied magnetic field relative to the fluorine bonds. An approach to such an idealized experiment is realized by observing the NMR of molecules trapped in the cavities of β-quinol clathrate.[5] At helium temperature, the trapped molecules become aligned in one of several equivalent orientations, and one can study rather directly the anisotropy of the chemical shift. Two of the present authors have reported such an investigation of the chemical-shift anisotropy of ¹⁹F in CFH₃.[3] The interpretation of the experimental results was rather straightforward for two reasons. First, the chemical-shift tensor of the nucleus involved in such an uniaxial bond could be characterized by only two principal values $\sigma_{||}$ and $\sigma_{\perp}$, corresponding to the directions parallel and perpendicular to the CF bond, respectively.

[1] C. W. Wilson III, J. Polymer Sci. **61**, 403 (1962).
[2] E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. (London) **81**, 986 (1963).
[3] E. Hunt and H. Meyer, J. Chem. Phys. **41**, 353 (1964).
[4] R. Blinc, I. Zupanic, S. Maricic, and Z. Veksli, J. Chem. Phys. **39**, 2109 (1963); **40**, 3739 (1964). See also M. Karplus, C. W. Kern, and D. Lazdins, *ibid.*, p. 3738.
[5] D. E. Palin and H. M. Powell, J. Chem. Soc. **1947**, 208; **1948**, 571.

Second, all the molecules were oriented so that the CF bond was aligned parallel to the c axis of the clathrate. Hence the shift in frequency as the applied field was rotated from being parallel to the c axis to perpendicular to the c axis gave directly the anisotropy of the chemical-shift tensor.

In the present paper we present the results of a similar study of the NMR spectrum of ^{19}F for the molecules CHF_3 and NF_3. For these molecules, the interpretation of the experimental results is complicated by the presence of more than one fluorine bond and also by the unfavorable alignment of the molecules in the cavities of the clathrate. A further complication, caused by the lower degree of local symmetry at the fluorine nuclei, is that, for the molecules considered here, three constants are needed to determine the chemical-shift tensor. On the other hand, an interesting feature of the study of these molecules is the possibility of determining the degree to which the fluorine bonds of these molecules deviate from uniaxial symmetry. Since the paramagnetic component of its chemical shift is so large,[6] NF_3 is expected to be an especially favorable molecule for such an investigation. By studying the magnetic-field dependence of the frequency moments of the absorption spectrum, one can make a determination of all three principal values of the chemical-shift tensor, if the average shift is known. We have applied this method successfully to NF_3, but for CHF_3 the size of the shift is too small to make so complete an analysis practicable at present. Clearly, such detailed information about the chemical-shift tensor can provide a sensitive test for theoretical calculations of these quantities since the chemical-shift tensor depends critically on the electronic wavefunctions.

After a brief outline of the experimental techniques, we discuss the determination of the orientation of the trapped molecules relative to the clathrate crystal axes. We then proceed to deduce the principal values of the chemical-shift tensor using the method of moments. The accuracy of such a determination is discussed and the observed NMR spectrum is compared with calculations made using an electronic computer to find the eigenvalues of the nuclear spin Hamiltonian of the molecule. Using the previously determined values of the parameters, an almost quantitative agreement is obtained, small deviations being attributed to the approximate treatment of the dipolar interaction between the molecule and the protons of the clathrate lattice. Finally, we show that in their broad outline, the results of these experiments are consistent with current ideas about the relationship between the chemical-shift tensor and the bonding parameters.

II. EXPERIMENTAL

The CHF_3 and NF_3 clathrates were both grown from a saturated solution of hydroquinone in n-propanol

under a pressure of, respectively, 40 and 60 atm of gas. Although no volumetric analysis was made, we estimate that about 30%–40% of the cavities were filled. During the crystallization a small amount of oxygen was added in order to shorten the spin–lattice relaxation time, as described before.[3] The size of the clathrate crystals, their alignment in the rf cavity, and the technique of the NMR measurements were the same as in the experimental study of CFH_3 reported previously.[3] The signal-to-noise ratio was better here than for CFH_3 because of the larger number of fluorine nuclei. However, the shift of the average frequency of the line as a function of crystal orientation could not be determined more accurately than before. This is because the observed line shapes were asymmetrical and hence more difficult to analyze than those of CFH_3.

In order to study the magnetic-field dependence of the first and second moments, the NMR experiments on NF_3 were carried out at frequencies of approximately 4, 7, 15, 31, and 45 Mc/sec. We also observed the resonance for various orientations of the clathrate crystal axis relative to the magnetic field. In all cases, each absorption line was observed many times by sweeping the frequency alternatively towards higher and lower values. Since the line shapes thus obtained were nearly identical, we concluded that the degree of saturation was negligible. We estimated that the first, second, and third frequency moments of the absorption line could be determined to within 0.2 kc/sec, 5.0 $(kc/sec)^2$, and 100 $(kc/sec)^3$, respectively. Since the field dependence of the line shape for CHF_3 was less dramatic than for NF_3, we did not perform such an extensive series of measurements as for NF_3, and the determination of the frequency moments could not reliably be undertaken.

III. GEOMETRICAL CONSIDERATIONS

In Fig. 1 we show the molecules CHF_3 and NF_3, and in Table I we give the values of the structure parameters as determined from microwave spectroscopy.[7,8] Both these molecules form a pyramid, the base of which consists of an equilateral triangle of fluorine nuclei (henceforth referred to as the fluorine triangle). It was shown previously[3] that at low temperatures the CFH_3 molecule is oriented so that the
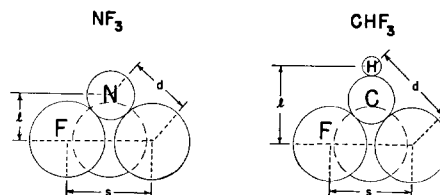

FIG. 1. Schematic diagram of the molecules NF_3 and CHF_3. The values of l, s, and d are given in Table I.

[6] J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, (McGraw-Hill Book Company, Inc., New York, 1959), p. 317 ff.

[7] S. N. Ghosh, R. Trambarulo, and W. Gordy, J. Chem. Phys. **20**, 605 (1952).

[8] J. Sheridan and W. Gordy, Phys. Rev. **79**, 513 (1950).

CF bond lies parallel to the c axis of the clathrate. This direction corresponds to that of the major axis of the somewhat ellipsoidal clathrate cavity.[5] This orientation of the trapped molecule is to be expected because the pyramid having the proton triangle as its base and the fluorine nucleus as its summit is a narrow one. However, since CHF_3 and NF_3 form rather squat pyramids, we expect that these molecules will be oriented so that the normal to the fluorine triangle is nearly perpendicular to the c axis of the clathrate. However, since the orientation of the molecules can not be reliably determined from such naive considerations, it is necessary to compute the NMR spectrum for various orientations of the trapped molecules relative to the crystal axes of the clathrate.

In such a calculation it is convenient to express the Hamiltonian in terms of the polar angle θ and the azimuthal angle ϕ which specify the direction of the magnetic field relative to axes fixed in the molecule. However, it is necessary to express these angles in terms of the angles specifying the orientation of the molecule and the field direction relative to the crystal axes. The axes fixed in the molecule are defined by the triad of unit vectors, $\mathbf{n}$, $\mathbf{n}_{12}$, and $\mathbf{n}_3$, where $\mathbf{n}$ is perpendicular to the fluorine triangle and directed towards the center of gravity of the molecule, $\mathbf{n}_{12}$ is directed from the first fluorine nucleus towards the second one, and $\mathbf{n}_3 = \mathbf{n} \times \mathbf{n}_{12}$. The axes fixed in the crystal are defined by the triad of orthogonal unit vectors, $\mathbf{x}_c$, $\mathbf{y}_c$, and $\mathbf{z}_c$, where $\mathbf{z}_c$ lies along the c axis of the clathrate lattice. Normally one would choose $\mathbf{x}_c$ and $\mathbf{y}_c$ to have some definite relation to the primitive vectors of the clathrate lattice which are perpendicular to the c axis. Then three Eulerian angles would be necessary to specify the orientation of the molecule relative to the axis fixed in the crystal. However, in the experimental setup only the c axis of the crystal is aligned, and the basal planes of the crystals are randomly oriented relative to the laboratory. Consequently, it is not
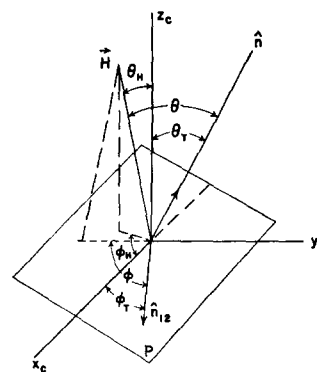

FIG. 2. The various coordinate systems used. The plane P which is perpendicular to $\mathbf{n}$ contains the vectors $\mathbf{n}_{12}$ and $\mathbf{x}_c$. The projection of H onto this plane makes an angle ϕ with $\mathbf{n}_{12}$. Its projection onto the $x_c - y_c$ plane makes an angle ϕ_H with $\mathbf{x}_c$.

possible to distinguish between the axes in the basal plane, and the orientation of the molecule can only be determined to within a rotation about the c axis.[9] Accordingly, we arbitrarily define the $\mathbf{y}_c$ axis to lie in the same plane as $\mathbf{z}_c$ and $\mathbf{n}$ and such that $\mathbf{y}_c \cdot \mathbf{n} \geq 0$. The two Eulerian angles, specifying the orientation of the molecule relative to the crystal axes, θ_T and ϕ_T, are defined so that $\cos\theta_T = \mathbf{n} \cdot \mathbf{z}_c$ and $\cos\phi_T = \mathbf{n}_{12} \cdot \mathbf{x}_c$ (see Fig. 2), whence

$$\mathbf{x}_c = \mathbf{n}_{12} \cos\phi_T - \mathbf{n}_3 \sin\phi_T, \tag{1a}$$

$$\mathbf{y}_c = \mathbf{n}_{12} \cos\theta_T \sin\phi_T + \mathbf{n}_3 \cos\theta_T \cos\phi_T + \mathbf{n} \sin\theta_T, \tag{1b}$$

$$\mathbf{z}_c = -\mathbf{n}_{12} \sin\theta_T \sin\phi_T - \mathbf{n}_3 \sin\theta_T \cos\phi_T + \mathbf{n} \cos\theta_T. \tag{1c}$$

The third Eulerian angle which would give the angle between $\mathbf{y}_c$ and one of the primitive lattice vectors in the basal plane cannot, as we have said, be determined by the present experiment.

The direction of the magnetic field relative to the crystal axes is specified by the angles θ_H and ϕ_H:

$$\mathbf{H}/H = \mathbf{x}_c \sin\theta_H \cos\phi_H + \mathbf{y}_c \sin\theta_H \sin\phi_H + \mathbf{z}_c \cos\theta_H. \tag{2}$$

If this vector is expressed in terms of the angles θ and ϕ relative to the axes fixed in the molecule, one obtains

$$\mathbf{H}/H = \mathbf{n}_{12} \sin\theta \cos\phi + \mathbf{n}_3 \sin\theta \sin\phi + \mathbf{n} \cos\theta. \tag{3}$$

Equating (2) and (3) and using (1) gives the relationships

$$\cos\theta = \sin\theta_H \sin\phi_H \sin\theta_T + \cos\theta_H \cos\theta_T, \tag{4a}$$

$$\sin\theta \cos\phi = \sin\theta_H \cos\phi_H \cos\phi_T + \sin\theta_H \sin\phi_H \cos\theta_T \sin\phi_T - \cos\theta_H \sin\theta_T \sin\phi_T, \tag{4b}$$

$$\sin\theta \sin\phi = -\sin\theta_H \cos\phi_H \sin\phi_T + \sin\theta_H \sin\phi_H \cos\theta_T \cos\phi_T - \cos\theta_H \sin\theta_T \cos\phi_T. \tag{4c}$$

TABLE I. Structure parameters of NF_3 and CHF_3.

	NF$_3$[a]		CHF$_3$[b]
$d = r_{NF}$	1.37 Å	$d = r_{HF}$	2.00 Å
$s = r_{FF}$	2.13 Å	$s = r_{FF}$	2.17 Å
l^c	0.60 Å	l^c	1.56 Å
$\angle FNF$	102.2°	$\angle FCF$	108.8°
ψ^d	26.1°	ψ^d	20.1°
Altitude of fluorine triangle	1.85 Å	Altitude of fluorine triangle	1.87 Å
		r_{CH}	1.10 Å

[a] See Ref. 8.

[b] See Ref. 7.

[c] l is the height of the pyramid formed by the molecule, taking the base to be the fluorine triangle (see Fig. 1).

[d] ψ is the angle between the NF or CF bond and the plane of the fluorine triangle.

[9] Strictly speaking the linewidth due to the lattice protons will be different even for two orientations of the trapped molecule which are obtained from one another by a rotation about the c axis (see for instance Ref. 10). This angular dependence, however, is too small to be experimentally observed at present.

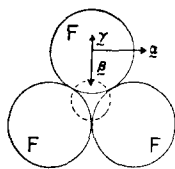[10] D. E. O'Reilly and T. Tsang, Phys. Rev. 128, 2639 (1962).

FIG. 3. The principal axes of the chemical-shift tensor. The central nucleus is nitrogen in the case of NF_3 and carbon in the case of CHF_3, α lies in the plane of the fluorine triangle, β is assumed to lie along the NF or CF bond, as the case may be, and γ is perpendicular to α and β.

To take account of the randomness of the orientation of the crystals one has, at a later stage, to perform an average over all values of ϕ_H.

For dipolar interactions one is interested in factors of the type $\cos\theta_{ij} \equiv \mathbf{H} \cdot \mathbf{r}_{ij}/H \cdot r_{ij}$, where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. If the fluorine nuclei are numbered 1, 2, and 3 and the odd nuclear magnetic moment (N for NF_3 and H for CHF_3) is numbered 4, one finds

$$\cos\theta_{12} = \sin\theta \cos\phi, \tag{5a}$$

$$\cos\theta_{13} = \sin\theta \cos(\phi - 120°), \tag{5b}$$

$$\cos\theta_{23} = \sin\theta \cos(\phi + 120°), \tag{5c}$$

$$\cos\theta_{14} = (l/d) \cos\theta - (s/d\sqrt{3}) \sin\theta \sin(\phi - 60°), \tag{5d}$$

$$\cos\theta_{24} = (l/d) \cos\theta - (s/d\sqrt{3}) \sin\theta \sin(\phi + 60°), \tag{5e}$$

$$\cos\theta_{34} = (l/d) \cos\theta + (s/d\sqrt{3}) \sin\theta \sin\phi, \tag{5f}$$

where l, s, and d are shown in Fig. 1 and have the values given in Table I.

For the chemical-shift Hamiltonian[11] it is necessary to specify for each nucleus the six independent components of the symmetric chemical-shift tensor. Alternatively, one can give for each nucleus the three principal values and the three Eulerian angles specifying the orientation of the principal axes. We define these axes by the triad of orthogonal unit vectors α_i, β_i, and γ_i for the ith nucleus. Since the molecules NF_3 and CHF_3 have a threefold axis, the chemical-shift tensor for one nucleus can be obtained from that of another one by a rotation of coordinates through 120°. Furthermore, neglecting the effects due to the presence of the clathrate lattice, the orientation of one of the principal axes can be shown to lie perpendicular to the plane of symmetry of the molecular environment of the nucleus in question. Hence we take α_i to lie in the plane of the fluorine triangle and perpendicular to the altitude of this triangle which intersects the nucleus in question (see Fig. 3). On physical grounds one expects another of the principal axes, which we call β_i, to lie very nearly along the CF bond for CHF_3 and along the NF bond for NF_3. It is then readily seen that the angle between $\mathbf{n}$ and the third axis, γ_i, is equal to ψ as defined in Table I. Hence the chemical-shift tensor can be completely specified by the three principal values σ_α, σ_β, and σ_γ corresponding to the axes α_i, β_i, and γ_i. If these axes are expressed in terms of the axes fixed in the molecule, one can show, using

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[11] N. F. Ramsey, Phys. Rev. **78**, 699 (1950); **86**, 243 (1952).

Eq. (3), that

$$\mathbf{H} \cdot \boldsymbol{\alpha}_1/H = \sin\theta \cos(\phi - 60°), \tag{6a}$$

$$\mathbf{H} \cdot \boldsymbol{\beta}_1/H = -\cos\theta \sin\psi + \sin\theta \cos\psi \sin(\phi - 60°), \tag{6b}$$

$$\mathbf{H} \cdot \boldsymbol{\gamma}_1/H = \cos\theta \cos\psi + \sin\theta \sin\psi \sin(\phi - 60°). \tag{6c}$$

The analogous equations for the second and third fluorine nuclei are obtained by replacing ϕ by $(\phi + 120°)$ and $(\phi - 120°)$, respectively.

Let us now consider how the symmetry properties of the cavity influence the calculation. Since by Eq. (4) θ and ϕ can be expressed in terms of θ_T, ϕ_T, θ_H, and ϕ_H, the Hamiltonian, and therefore the energy levels, can be considered to be functions of these four angles. From these energy levels one calculates the line shape as an average over ϕ_H. There will be several degenerate orientations of the molecule corresponding to the threefold axis of rotation about the c axis and to the inversion symmetry of the cavity, and consequently one should average over these degenerate orientations. However, as we use Hamiltonians which are invariant under spatial inversion [see Eqs. (7) and (26)] and since rotations about the c axis are irrelevant after the average over ϕ_H has been taken, this degeneracy can be ignored. Due to the invariance under spatial inversion, we can restrict θ_T to lie in the interval $0 \leq \theta_T \leq 90°$. Clearly we can also restrict ϕ_T to the interval $-60° \leq \phi_T \leq 60°$, since the molecule has a threefold axis of rotation. Furthermore, from Eq. (4) one sees that $\theta(\phi_T, \phi_H) = \theta(-\phi_T, 180° - \phi_H)$ and $\phi(\phi_T, \phi_H) = 180° - \phi(-\phi_T, 180° - \phi_H)$. However, the eigenvalues of the Hamiltonians of Eqs. (7) and (26) are invariant under the operation $\phi \rightarrow 180° - \phi$, corresponding to a plane of symmetry of the molecule. Hence, after the average over ϕ_H is taken, ϕ_T and $-\phi_T$ are equivalent and therefore we restrict ϕ_T to the interval $0 \leq \phi_T \leq 60°$.

IV. CALCULATIONS AND EXPERIMENTAL RESULTS FOR NF_3

A. General Remarks

As is apparent from the preceding section, there are two geometrical parameters, θ_T and ϕ_T, whose values must be deduced from the experiment. Also we must determine the parameter $\Delta\nu_{lat}$ characterizing the dipolar broadening due to the lattice protons. But our chief purpose is, of course, to determine the three principal values σ_α, σ_β, and σ_γ of the chemical-shift tensor. At first sight one might think that fitting the experimental data with so many parameters is not a sensitive way to determine them. However, this difficulty can be appreciably reduced by a systematic approach which we describe below. It is seen later that the large number of data, namely, the line shapes for different θ_H and at different magnetic fields, do in fact overdetermine the problem and give values of the anisotropy of the chemical-shift tensor that are quite reliable.

There are two ways to analyze the data, which complement one another: (1) a comparison of the line shapes calculated theoretically with those found experimentally and (2) a comparison of the calculated moments with the corresponding experimental values. In order to determine the anisotropy of the chemical-shift tensor, we have found the latter method to be especially valuable for several reasons. First, the use of this method enables one to fit quantities which are nearly independent of the assumed values of ϕ_T and $\Delta\nu_{\text{lat}}$. Secondly, this more analytic approach allows one to make rather definite estimates as to the reliability of the determination of the chemical-shift anisotropy. Thirdly, with so many parameters to determine it is necessary to proceed in a systematic way in order to minimize the computational effort. Finally, a rigorous calculation of the lowest moments is practicable whereas an exact calculation of the line shape involves serious difficulties. This is because in the latter case one can only treat approximately the effect of the lattice protons on the line shape.

It is convenient to determine first the values of $\Delta\nu_{\text{lat}}$ and θ_T which, however, can be done rather reliably using both the experimental line shapes at low magnetic fields and also the angular dependence of the second moment extrapolated to zero magnetic field. Having thus determined $\Delta\nu_{\text{lat}}$ and θ_T, it is then possible to make a reasonably accurate determination of the chemical-shift anisotropy using the method of moments. The validity of this procedure is confirmed by the satisfactory agreement between the experimental and calculated shapes for various fields and angles θ_H.

B. Theory

The nuclear spin Hamiltonian of NF_3 consists of the dipolar interaction, the chemical-shift Hamiltonian, the Zeeman energy, and the quadrupole interaction:

$$\mathcal{H} = \sum_{i<j} (\mu_i/I_i)(\mu_j/I_j) r_{ij}^{-3}[\mathbf{I}_i \cdot \mathbf{I}_j - 3(\mathbf{I}_i \cdot \mathbf{r}_{ij})(\mathbf{I}_j \cdot \mathbf{r}_{ij}) r_{ij}^{-2}]$$

$$+ \sum_i (\mu_i/I_i)[\mathbf{H} \cdot \boldsymbol{\delta}_i \cdot \mathbf{I}_i - \mathbf{H} \cdot \mathbf{I}_i]$$

$$+ h\nu'[(\mathbf{I}_4 \cdot \mathbf{n})^2 - \tfrac{1}{3}I_4(I_4+1)], \quad (7)$$

where μ_i, I_i, and $\boldsymbol{\delta}_i$ are, respectively, the magnetic moment, the spin, and the chemical-shift tensor of the ith nucleus and h is Planck's constant. The frequency of the nuclear quadrupole splitting of the nitrogen nuclear spin[12] ν' is taken to be 5.3 Mc/sec as determined for gaseous NF_3 by microwave spectroscopy.[8] This value is not very different from that found for solid NF_3[13] using pure quadrupole resonance data which suggests that the extramolecular electric-field gradients may be relatively unimportant. Hence we

assume that the value of ν' for NF_3 trapped in the clathrate is approximately the same as that for the molecule in the gaseous state.

Since the Zeeman term and the quadrupole term are by far the largest, we apply perturbation theory, taking these two terms to be the unperturbed Hamiltonian. One finds that I_z is a good quantum number, where $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3$, and that the eigenstates of the nitrogen nuclear spin are the solutions of

$$\{-\mu_4 I_{4z}H + h\nu'[(\mathbf{I}_4 \cdot \mathbf{n})^2 - \tfrac{2}{3}]\}\Phi_m = \lambda_m \Phi_m, \quad m = 1, 2, 3. \quad (8)$$

Since one keeps only that part of the Hamiltonian which commutes with the unperturbed Hamiltonian, one finds three energy-level schemes for the fluorine nuclear spins, one for each state of the nitrogen nuclear spin. These fluorine nuclear-spin states are the eigenvectors of the effective Hamiltonian

$$\mathcal{H}_{\text{eff}}(m) = \lambda_m - 2\mu_F H \sum_{i=1,3} I_{zi} + \sum_{i<j\leq 3} A_{ij}[\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{iz}I_{jz}]$$

$$+ \sum_{i=1,3} 2A_{i4}[I_{iz}\langle m \mid I_{4z} \mid m \rangle - 3I_{iz}z_{i4}r_{i4}^{-2}\langle m \mid \mathbf{I}_4 \cdot \mathbf{r}_{i4} \mid m \rangle]$$

$$+ 2\mu_F H^{-1} \sum_{i=1,3} [\sigma_\alpha(\boldsymbol{\alpha}_i \cdot \mathbf{H})^2 + \sigma_\beta(\boldsymbol{\beta}_i \cdot \mathbf{H})^2 + \sigma_\gamma(\boldsymbol{\gamma}_i \cdot \mathbf{H}^2], \quad (9)$$

where $\langle m \mid I_{4z} \mid m \rangle$ is calculated using the eigenvectors of Eq. (8) and

$$A_{ij} = (2\mu_F^2/s^3)(3\cos^2\theta_{ij}-1) \qquad i<j\leq 3, \quad (10a)$$

$$A_{i4} = (2\mu_F\mu_4/d^3)(3\cos^2\theta_{i4}-1) \qquad i\leq 3. \quad (10b)$$

Since this effective Hamiltonian is by construction diagonal in I_z, the states for which $I_z = \pm\tfrac{3}{2}$ are already eigenvectors and their eigenvalues are easily calculated. For both $I_z = \tfrac{1}{2}$ and $I_z = -\tfrac{1}{2}$ there are three state vectors, and hence to find their energy eigenvalues one must diagonalize two 3×3 matrices. Although this calculation can in principle be done analytically, it was more easily performed numerically using an electronic computer.

For an arbitrary orientation of the NF_3 molecule relative to the magnetic field, the resonance of the fluorine nuclei is governed only by the selection rule $\Delta I_z = \pm1$ so that in general one finds 15 absorption lines for each nitrogen nuclear-spin state. The intensity of the transition $r \to s$ is proportional to $\mid V_{rs} \mid^2$ or $\mid \langle r \mid I_x \mid s \rangle \mid^2$. In order to take account of the protons in the clathrate lattice we have broadened each of these lines with a Gaussian function, so that the intensity of absorption $\mathcal{g}(\nu)$ is given as

$$\mathcal{g}(\nu) = \frac{I_0}{\Delta\nu_{\text{lat}}}(2\pi)^{-\frac{1}{2}} \sum_{r,s} \int_0^{2\pi} \mid \langle r \mid I_x \mid s \rangle \mid^2$$

$$\times \exp\left[\frac{-(\nu-\nu_{rs})^2}{2\Delta\nu_{\text{lat}}^2}\right]d\phi_H, \quad (11)$$

where $h\nu_{rs} = E_r - E_s$, I_0 is a normalizing constant, and we have indicated an average over ϕ_H. We remark

[12] $h\nu' = 3eQV_{zz}/4I(2I-1)$ as is given by C. P. Slichter in *Principles of Nuclear Magnetic Resonance* (Harper and Row, Inc., New York, 1963), p. 171. For the value of eQV_{zz} see Ref. 8.

[13] P. J. Haigh, G. A. Matzkanin, and T. A. Scott, Bull. Am. Phys. Soc. **8**, 35 (1963).

that, although this broadening approximation is normally reasonable,[14] it may introduce a small error in the line shape since some of the lattice protons lie rather close to the molecule. Since the precise position of the NF_3 molecule and some of the lattice protons is uncertain, the linewidth $\Delta\nu_{lat}$ cannot be calculated accurately, and therefore we consider $\Delta\nu_{lat}$ to be an experimentally determined parameter.

As we have mentioned above, it is convenient to use the method of moments to analyze the experimental data. We can find expressions for the moments using the technique introduced by Van Vleck[14] and making the same assumptions. Thus, if $\mathcal{H}_t$ is the truncated Hamiltonian which commutes with the Zeeman term we have

$$h\nu_0 = \mathrm{Tr}V^+[\mathcal{H}_t, V]/\mathrm{Tr}V^+V, \tag{12a}$$

$$h^2 M_2 = (\mathrm{Tr}[V^+, \mathcal{H}_t][\mathcal{H}_t, V]/\mathrm{Tr}V^+V) - h^2\nu_0^2, \tag{12b}$$

$$h^3 M_3 = \mathrm{Tr}[V^+, \mathcal{H}_t]\{\mathcal{H}_t, [\mathcal{H}_t, V]\}/\mathrm{Tr}V^+V$$
$$\qquad - 3h^2(M_2 + \nu_0^2)\nu_0 + 2h^3\nu_0^3. \tag{12c}$$

Here ν_0 is the average frequency, and

$$V = \sum_i I_{ix} - iI_{iy}, \tag{13}$$

where the sum is taken over all fluorine nuclei. Using (12a) we find

$$h\nu_0(\theta_H, \theta_t, H) = 2\mu_F H\{1 + \bar{\sigma}$$
$$+ \tfrac{1}{4}(1 - 3\cos^2\theta_T)(1 - 3\cos^2\theta_H)$$
$$\times [\sigma_\alpha' \cos^2\psi + \sigma_\beta'(1 - 2\sin^2\psi)]\}, \tag{14}$$

where we have defined the average chemical shift $\bar{\sigma}$ to be

$$\bar{\sigma} = \tfrac{1}{3}\mathrm{Tr}\boldsymbol{\sigma}_i \tag{15}$$

and the anisotropic part of the chemical-shift tensor $\boldsymbol{\sigma}'$ as

$$\boldsymbol{\sigma}' = \boldsymbol{\sigma}_i - \bar{\sigma}\mathbf{1}. \tag{16}$$

The second moment, which is found using (12b), can be written in the form

$$M_2(\theta_H, \theta_T, \phi_T, H) = A_{FF}(\theta_H, \theta_F) + A_{FN}(\theta_H, \theta_T, \phi_T, H)$$
$$+ B(\theta_H, \theta_T, \phi_T)(2\mu_F H/h)^2 + \tfrac{1}{2}\Delta\nu_{lat}^2, \tag{17}$$

where the terms on the right-hand side of this equation are the contributions to the second moment from intramolecular dipole–dipole interactions among the fluorine nuclei, intramolecular dipole–dipole interactions between the fluorine nuclei and the nitrogen nucleus, the anisotropy of the chemical-shift tensor, and the extramolecular dipole–dipole interactions, respectively. Although $\Delta\nu_{lat}$ is actually a function of θ_H, θ_T, and ϕ_T, it is only its dependence on θ_H which is of interest since we treat it as an experimentally determined quantity. This dependence is found experimentally to be negligible, as one would expect since the nearest lattice protons can be considered to be uniformly spread over a sphere in first approximation. The contribution to the second moment from the interaction between the fluorine nuclei and the nitrogen nucleus is quite small. Accordingly, it introduces only a small error to replace this term by its average value which we have estimated to be 4.0×10^6 sec^{-2}. The other terms in Eq. (17) are rather complicated and hence have been evaluated only for the special cases $\theta_H = 0$ and $\theta_H = 90°$:

$$h^2 A_{FF}(0°, \theta_T) = (9\mu_F^4/4s^6)(11 - 30\cos^2\theta_T + 27\cos^4\theta_T), \tag{18a}$$

$$h^2 A_{FF}(90°, \theta_T) = (9\mu_F^4/32s^6)(49 - 42\cos^2\theta_T + 81\cos^4\theta_T), \tag{18b}$$

$$B(0°, \theta_T, \phi_T) = (\sigma_\alpha')^2[\tfrac{1}{8}\sin^4\theta_T(1 + \sin^2\psi)^2 - \sin^3\theta_T\cos\theta_T\cos3\phi_T\sin\psi\cos\psi(1 + \sin^2\psi) + 2\cos^2\theta_T\sin^2\theta_T\cos^2\psi\sin^2\psi]$$
$$+ \sigma_\alpha'\sigma_\beta'[-\tfrac{1}{4}\sin^4\theta_T(1 - 2\sin^2\psi)(1 + \sin^2\psi) - \sin^3\theta_T\cos\theta_T\cos3\phi_T\sin\psi\cos\psi(1 - 4\sin^2\psi)$$
$$+ 8\cos^2\theta_T\sin^2\theta_T\cos^2\psi\sin^2\psi] + (\sigma_\beta')^2[\tfrac{1}{8}\sin^4\theta_T(1 - 2\sin^2\psi)^2 + 8\cos^2\theta_T\sin^2\theta_T\cos^2\psi\sin^2\psi$$
$$+ 2\sin^3\theta_T\cos\theta_T\cos3\phi_T\sin\psi\cos\psi(1 - 2\sin^2\psi)], \tag{19a}$$

$$B(90°, \theta_T, \phi_T) = (\sigma_\alpha')^2[(\tfrac{21}{64} - \tfrac{7}{32}\sin^2\psi + \tfrac{5}{64}\sin^4\psi) + \cos^2\theta_T(-\tfrac{17}{32} + \tfrac{27}{16}\sin^2\psi - \tfrac{33}{32}\sin^4\psi)$$
$$+ \cos^4\theta_T(\tfrac{21}{64} - \tfrac{39}{32}\sin^2\psi + \tfrac{69}{64}\sin^4\psi) - \tfrac{3}{8}\cos\theta_T\sin^3\theta_T\cos3\phi_T\sin\psi\cos\psi(1 + \sin^2\psi)]$$
$$+ \sigma_\alpha'\sigma_\beta'[(\tfrac{15}{32} - \tfrac{19}{32}\sin^2\psi + \tfrac{10}{32}\sin^4\psi) + \cos^2\theta_T(-\tfrac{19}{16} + \tfrac{87}{16}\sin^2\psi - \tfrac{33}{8}\sin^4\psi) + \cos^4\theta_T(\tfrac{15}{32} - \tfrac{147}{32}\sin^2\psi + \tfrac{69}{16}\sin^4\psi)$$
$$- \tfrac{3}{8}\cos\theta_T\sin^3\theta_T\cos3\phi_T\sin\psi\cos\psi(1 + 4\sin^2\psi)] + (\sigma_\beta')^2[(\tfrac{21}{64} - \tfrac{5}{16}\sin^2\psi + \tfrac{5}{16}\sin^4\psi)$$
$$+ \cos^2\theta_T(-\tfrac{17}{32} + \tfrac{33}{8}\sin^2\psi - \tfrac{33}{8}\sin^4\psi) + \cos^4\theta_T(\tfrac{21}{64} - \tfrac{69}{16}\sin^2\psi + \tfrac{69}{16}\sin^4\psi)$$
$$+ \tfrac{3}{4}\cos\theta_T\sin^3\theta_T\cos3\phi_T\sin\psi\cos\psi(1 - 2\sin^2\psi)]. \tag{19b}$$

[14] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

Similarly, using (12c) one can show that, if the quadrupole interaction is neglected, the third moment is of the form

$$M_3(\theta_T, \theta_H, \phi_T, H) = C(\theta_H, \theta_T, \phi_T)(2\mu_F H/h) + D(\theta_H, \theta_T, \phi_T)(2\mu_F H/h)^3, \tag{20}$$

where

$$h^2 C(\theta_H, \theta_T, \phi_T) = \tfrac{3}{4}\left[\sum_i (\mathbf{H}\cdot\boldsymbol{\delta}_i\cdot\mathbf{H})\right]\left[\sum_{i,j} B_{ij}^2\right]/\left[(\sum_i 1)^2 H^2\right] - \tfrac{3}{4}\left[\sum_{ij}(\mathbf{H}\cdot\boldsymbol{\delta}_i\cdot\mathbf{H})B_{ij}^2\right]/\left[(\sum_i 1)H^2\right], \tag{21a}$$

$$D(\theta_H, \theta_T, \phi_T) = -\left[\sum_i (\mathbf{H}\cdot\boldsymbol{\delta}_i\cdot\mathbf{H})^3\right]/\left[(\sum_i 1)H^6\right] + 3\left[\sum_i (\mathbf{H}\cdot\boldsymbol{\delta}_i\cdot\mathbf{H})^2\right]$$

$$\times\left[\sum_i (\mathbf{H}\cdot\boldsymbol{\delta}_i\cdot\mathbf{H})\right]/\left[(\sum_i 1)^2 H^6\right] - 2\left[(\sum_i \mathbf{H}\cdot\boldsymbol{\delta}_i\cdot\mathbf{H})^3\right]/\left[(\sum_i 1)^3 H^6\right]. \tag{21b}$$

Here B_{ij} is defined the same way as by Van Vleck,[14] i is summed over fluorine nuclei only, and j is summed over all nuclear spins. From (21) one sees that crudely speaking the ratio of the linear terms to the cubic term in (20) is of the order of the ratio of the dipolar contribution to the second moment to that caused by the anisotropy of the chemical-shift tensor. Hence, for the purposes of estimation we neglect the term in H^3 in (20). Only terms in the summation of (21a) for which i and j refer to the same molecule are important, so that

$$C(0, \theta_T, \phi_T) = (27\mu_F^4/h^2 s^6)\{[\tfrac{3}{8}\sin^4\theta_T(3\sin^2\theta_T - 2)(1+\sin^2\psi) - \tfrac{9}{32}\cos6\phi_T\sin^6\theta_T(1+\sin^2\psi)$$

$$- \tfrac{3}{8}\sin\psi\cos\psi\sin\theta_T\cos\theta_T\cos3\phi_T(1 - 10\cos^2\theta_T + 9\cos^4\theta_T)]\sigma_\alpha' + [\tfrac{3}{8}\sin^4\theta_T(3\sin^2\theta_T - 2)(1 - 2\cos^2\psi)$$

$$- \tfrac{9}{32}\cos6\phi_T\sin^6\theta_T(1 - 2\cos^2\psi) - \tfrac{3}{4}\sin\psi\cos\psi\sin\theta_T\cos\theta_T\cos3\phi_T(1 - 10\cos^2\theta_T + 9\cos^4\theta_T)]\sigma_\beta'\}, \tag{22a}$$

$$C(90°, \theta_T, \phi_T) = (27\mu_F^4/h^2 s^6)(\sigma_\alpha'\{\tfrac{9}{64} + \cos^2\theta_T(\tfrac{33}{64} - \tfrac{15}{32}\sin^2\psi) + \cos^4\theta_T(-\tfrac{81}{64} + \tfrac{9}{8}\sin^2\psi) + \cos^6\theta_T(\tfrac{63}{64} - \tfrac{9}{32}\sin^2\psi)$$

$$+ \tfrac{45}{512}\sin^6\theta_T\cos6\phi_T(1 + \sin^2\psi) + \tfrac{27}{128}\sin\psi\cos\psi\cos3\phi_T\cos\theta_T\sin^3\theta_T(7 - 15\cos^2\theta_T) - \tfrac{27}{128}\cos^2\psi$$

$$\times \sin^4\theta_T(10 - 9\sin^2\theta_T)\} + \sigma_\beta'\{[-\tfrac{15}{32}\cos^2\theta_T + \tfrac{9}{8}\cos^4\theta_T + \tfrac{27}{128}\sin^4\theta_T(10 - 9\sin^2\theta_T) - \tfrac{9}{32}\cos^6\theta_T + \tfrac{45}{512}\sin^6\theta_T\cos6\phi_T]$$

$$\times (\sin^2\psi - \cos^2\psi) + \tfrac{9}{64}\sin\psi\cos\psi\cos3\phi_T\cos\theta_T\sin^3\theta_T(7 - 15\cos^2\theta_T)\}). \tag{22b}$$

One could calculate higher moments, but in order to get accurate formulas considerable algebra is required. Moreover, due to experimental uncertainties, such formulas would not be very helpful in determining the chemical-shift tensor.

C. Comparison with Experiment

We now proceed to deduce the values of the unknown parameters from the experimental data. It was easy to determine $\Delta\nu_{\text{lat}}$ from the general shape of the absorption curve, i.e., from the sharpness of the absorption peaks, even though the values of the other parameters were not yet well known. The value of $\Delta\nu_{\text{lat}}$ we found, (8.5 ± 1.0) kc/sec, is quite comparable to the value 8 kc/sec found previously[3] for CFH$_3$ trapped in the clathrate. Since the dependence of the line shape on θ_T is quite marked, it was also possible to determine the value of θ_T to be $80°\pm10°$ from the qualitative aspect of the line shapes. This value of θ_T also gave satisfactory agreement between the observed and calculated values of the second moment extrapolated to zero field, as can be seen in Table II. In making such a comparison it was, of course, necessary to subtract off the contribution to the second moment, due to the dipolar broadening of the lattice protons. Since the dependence of the line shapes on ϕ_T is less drastic, an unambiguous determination of ϕ_T by such a qualitative analysis is difficult. It was, however, possible to exclude the

values $15° \leq \phi_T \leq 45°$ which correspond to qualitatively incorrect line shapes.

Further progress was made using the method of moments. Since only two of the parameters σ_α', σ_β', and σ_γ' are independent, one can deduce their values and that of ϕ_T from three independent experimentally determined quantities. The first of these is the shift

TABLE II. Values of the second moment for zero field.

Molecule	θ_H	Experimental[a]	Theoretical[b]		
			$\theta_T = 70°$	$\theta_T = 80°$	$\theta_T = 90°$
			ϕ_T arbitrary		
NF$_3$	0°	171±8	154	175	190
NF$_3$	90°	107±8	99	105	107
			$\phi_T = 0°$		
CHF$_3$	0°	188±8	147	166	189
CHF$_3$	90°	143±8	123	131	138
			$\phi_T = 60°$		
CHF$_3$	0°	188±8	196	195	189
CHF$_3$	90°	143±8	141	142	138

[a] Values are quoted in units of (kilocycles per second)^2 and have been extrapolated to zero field. The contribution of the protons in the clathrate lattice, which was estimated from the experimental line shapes, has been subtracted off.

[b] These values, which are quoted in units of (kilocycles per second)^2 are calculated using Eqs. (17)–(19) for NF$_3$ and (28), (29), (18), and (19) for CHF$_3$.
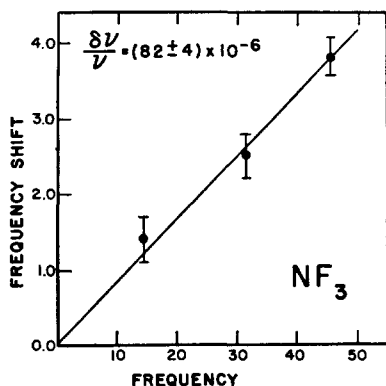
FIG. 4. The frequency shift $\delta\nu$ versus the frequency ν for NF_3. Each dot represents the analysis of about 25 resonance line shapes. Frequency in megacycles per second; frequency shift in kilocycles per second.

in the average frequency $\delta\nu$ as the field orientation θ_H is varied from $0°$ to $90°$. The graph of $\delta\nu$ vs ν (see Fig. 4) yields the value of $\delta\nu/\nu$ which can be compared with Eq. (14) to give

$$0.55\sigma_\alpha' + 0.42\sigma_\beta' = 8.2 \times 10^{-5}. \tag{23}$$

This relation, which is experimentally the most reliable, does not involve any ϕ_T dependence. The other two relations are found by plotting the second moment for θ_H equal to $0°$ and $90°$ vs ν^2 (see Fig. 5); comparing the result with Eq. (17) one finds, respectively,

$$(0.177 + 0.078 \cos3\phi_T)(\sigma_\alpha')^2$$

$$+ (-0.135 + 0.117 \cos3\phi_T)\sigma_\alpha'\sigma_\beta'$$

$$+ (0.080 - 0.080 \cos3\phi_T)(\sigma_\beta')^2 = 0.93 \times 10^{-8} \tag{24}$$

and

$$(0.282 + 0.029 \cos3\phi_T)(\sigma_\alpha')^2$$

$$+ (0.356 + 0.044 \cos3\phi_T)\sigma_\alpha'\sigma_\beta'$$

$$+ (0.283 - 0.031 \cos3\phi_T)(\sigma_\beta')^2 = 1.50 \times 10^{-8}. \tag{25}$$

Assuming a value of ϕ_T one has two variables σ_α' and σ_β' related by three equations, each of which determines a curve in the σ_α', σ_β' plane. The value of ϕ_T for which these curves most nearly intersect at a single point was found to be $\phi_T = 54°$, in which case one obtains Fig. 6. The values of the parameters resulting from this analysis are tabulated in Table III. The average chemical shift of NF_3 relative to F_2 is known[6] as well as the absolute magnitude of the average chemical shift for F_2.[15] Using these data we have also calculated the absolute magnitudes of the components of the chemical-shift tensor.

One interesting result we have found is that the two

[15] M. R. Baker, C. H. Anderson, and N. F. Ramsey, Phys. Rev. **133**, A1533 (1964).

components of the chemical-shift tensor perpendicular to the NF bond direction are not equal. This conclusion is particularly striking if one refers to Fig. 6. Here one sees that the intersection of the line for which $\sigma_\alpha' = \sigma_\gamma' = -\frac{1}{2}\sigma_\beta'$ with the line defined by the observed frequency shift corresponds to extremely large anisotropy of the chemical-shift tensor. We have calculated the line shapes for this value of the chemical-shift tensor and find line shapes that are very different from those actually observed. In other words, a simple uniaxial bond will not explain the results quoted here. Thus a successful quantum theory of the anisotropy of the chemical-shift tensor must take full account of the molecular character of the wavefunction.

Using the values of the parameters previously deduced, we have also calculated the line shapes for various values of the magnetic field and compared the results with the observed line shapes. As can be seen in Figs. 7–10, the observed line shapes are well reproduced by the calculated curves. The deviations between the two curves may be due to the inadequacy of the line-broadening approximation which we have mentioned above. We have also made calculations of the third moment, which happens to depend sensitively on the values of the parameters. Using Eqs. (22a) and (22b) we find the values $M_3/\nu = 7.0 \times 10^3$ sec^{-2} and $M_3/\nu = 9.4 \times 10^3$ sec^{-2} for θ_H equal 0 and $90°$, respectively. These values are not inconsistent with the corresponding experimental values of $(10\pm3)\times10^3$ and $(7\pm3)\times10^3$ sec^{-2}. We note that the agreement between the calculated and observed values of the third moment might be improved by including the second term in Eq. (20). Considering the uncertainty in the experimental value of the third moment, it was
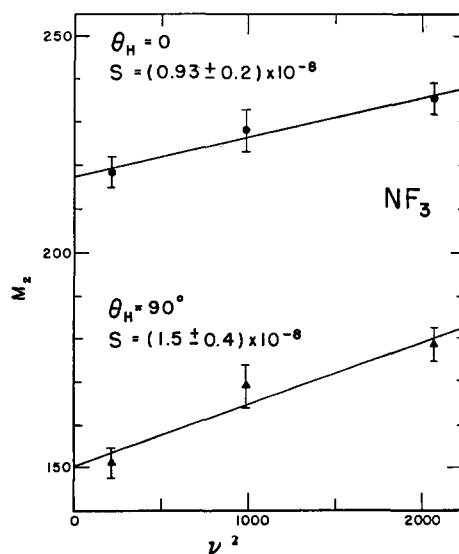

FIG. 5. The second moment M_2 for θ_H equal to $0°$ (top) and $90°$ (bottom) versus the square of the frequency ν^2 for NF_3. The slopes of the straight lines fitted to the data are indicated. Frequency in megacycles per second; M_2 in (kilocycles per second)^2.
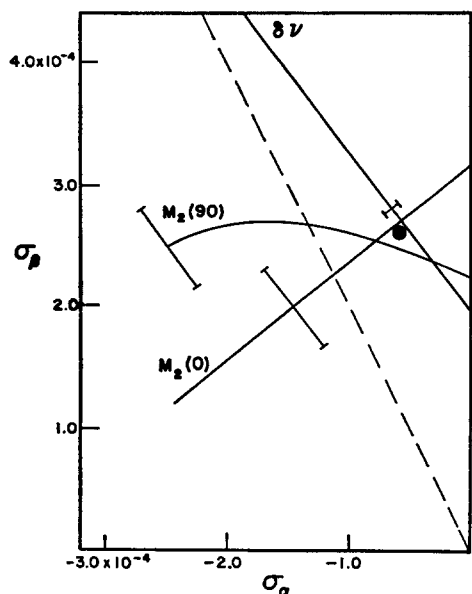
FIG. 6. The determination of σ_α' and σ_β' for NF$_3$ using the observed frequency shift $\delta\nu$ and the values of the second moment for θ_H equal to 0° and 90°. The error flags give an indication of the range of values of σ_α' and σ_β' consistent with each observed quantity. The uncertainty in the slopes of the lines which depends on the determination of θ_T and ϕ_T is not indicated here but is reflected in the values of the chemical-shift tensor quoted in Table III. The dashed line corresponds to a uniaxial NF bond for which $\sigma_\alpha' = \sigma_\gamma' = -\frac{1}{2}\sigma_\beta'$.

felt that it was not worthwhile to evaluate the very complicated expression for this term [see Eq. (21)].

V. CALCULATIONS AND EXPERIMENTAL RESULTS FOR CHF$_3$

A. Theory

The nuclear spin Hamiltonian for CHF$_3$ is somewhat simpler than that of NF$_3$ in that there is no quadrupole

TABLE III. Values of the parameters for NF$_3$ and CHF$_3$.

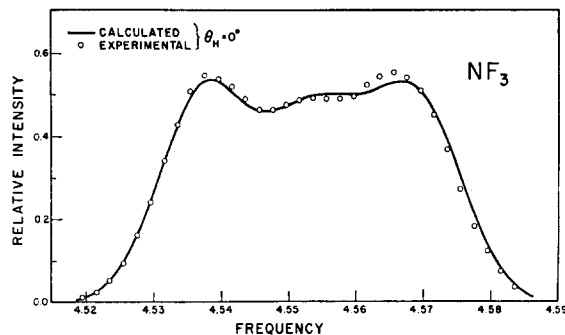| Molecule	NF$_3$	CHF$_3$
$\Delta\nu_{lat}$	(8.5 ± 1.0) kc/sec	(8.5 ± 1.0) kc/sec
θ_T	$80°\pm10°$	$80°\pm10°$
ϕ_T	$50°\pm10°$	$50°\pm10°$
σ_α'	$(-60\pm30)\times10^{-6}$	$(-35\pm10)\times10^{-6}$
σ_β'	$(260\pm40)\times10^{-6}$	$(70\pm14)\times10^{-6}$
σ_γ'	$(-200\pm30)\times10^{-6}$	$(-35\pm10)\times10^{-6}$
$\bar{\sigma}^{a}$	75×10^{-6}	299×10^{-6}
σ_α	15×10^{-6}	264×10^{-6}
σ_β	335×10^{-6}	369×10^{-6}
σ_γ	-125×10^{-6}	264×10^{-6}
$\sigma_\| - \sigma_\perp =$	$(390\pm60)\times10^{-6}$	$(105\pm20)\times10^{-6}$
$\bar{\sigma}-\bar{\sigma}$(HF)	-340×10^{-6} ^{b}	-116×10^{-6} ^{b}
$\sigma_\alpha-\sigma_\gamma$	$(140\pm40)\times10^{-6}$	$\cdots$

^{a} See Ref. 16.
^{b} See Ref. 6.

FIG. 7. Calculated and observed line shapes for NF$_3$ at frequency 4.5 Mc/sec. For values of the parameters used in the calculations see Table III.

term to consider. We have

$$\mathcal{H}=\sum_{i<j}(\mu_i/I_i)(\mu_j/I_j)r_{ij}^{-3}[\mathbf{I}_i\cdot\mathbf{I}_j-3r_{ij}^{-2}(\mathbf{I}_i\cdot\mathbf{r}_{ij})(\mathbf{I}_j\cdot\mathbf{r}_{ij})]$$
$$+\sum_i(\mu_i/I_i)[\mathbf{H}\cdot\mathbf{d}_i\cdot\mathbf{I}_i-\mathbf{H}\cdot\mathbf{I}_i]. \quad (26)$$

Since the Zeeman term is by far the largest, one sees, using perturbation theory, that I_z and I_{4z} are good quantum numbers and that in analogy with Eq. (9) the effective Hamiltonian is

$$\mathcal{H}_{eff}(I_{4z})=-\sum_i(\mu_i/I_i)I_{iz}H+\sum_{i\leq j\leq 3}A_{ij}[\mathbf{I}_i\cdot\mathbf{I}_j-3I_{iz}I_{jz}]$$
$$+2\mu_F H^{-1}\sum_{i=1,3}[\sigma_\alpha(\boldsymbol{\alpha}_i\cdot\mathbf{H})^2+\sigma_\beta(\boldsymbol{\beta}_i\cdot\mathbf{H})^2+\sigma_\gamma(\boldsymbol{\gamma}_i\cdot\mathbf{H})^2]$$
$$+2\sum_{i=1,3}A_{i4}I_{iz}I_{4z}, \quad (27)$$

where A_{ij} is given in Eq. (10). One finds two energy-level schemes, corresponding to the two possible values of I_{4z} in much the same way as we have done for NF$_3$. The selection rule is again $\Delta I_z=\pm1$ for arbitrary orientation of the molecule, and the spectrum is calculated using Eq. (11).

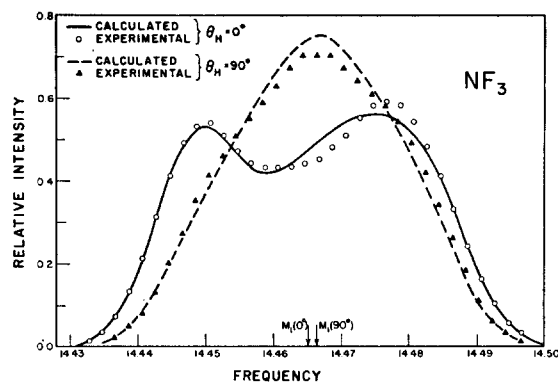One can calculate the moments of the line shapes, and in fact the formula for the first moment, Eq. (14),

FIG. 8. Calculated and observed line shapes for NF$_3$ at frequency 14.5 Mc/sec. For values of the parameters used in the calculations see Table III.

is still valid. However, the second moment for CHF_3 is given as

$$M_2(\theta_H, \theta_T, \phi_T, H) = A_{FF}(\theta_H, \theta_T) + A_{FP}(\theta_H, \theta_T, \phi_T) + B(\theta_H, \theta_T, \phi_T)(2\mu_F H/h)^2 + \tfrac{1}{2}(\Delta\nu_{lat})^2, \qquad (28)$$

where the contribution to the second moment due to the dipolar interaction between the fluorine nuclei and the proton has been evaluated for $\theta_H = 0$ and $\theta_H = 90°$ to be

$$h^2 A_{FP}(0, \theta_T, \phi_T) = (4\mu_F^2\mu_P^2 d^{-6})\left[1 - \frac{6l^2}{d^2}\cos^2\theta_T - \frac{s^2}{d^2}\sin^2\theta_T + \frac{9l^4}{d^4}\cos^4\theta_T + \frac{3s^4}{8d^4}\sin^4\theta_T \right.$$

$$\left. + \frac{9l^2s^2}{d^4}\cos^2\theta_T \sin^2\theta_T - \frac{\sqrt{3}ls^3}{d^4}\sin^3\theta_T \cos\theta_T \cos3\phi_T \right], \qquad (29a)$$

$$h^2 A_{FP}(90°, \theta_T, \phi_T) = (4\mu_F^2\mu_P^2 d^{-6})\left[1 - \frac{3l^2}{d^2}\cos^2\theta_T - \frac{s^2}{2d^2}(1 + \cos^2\theta_T) + \frac{27l^4}{8d^4}\sin^4\theta_T + \frac{3s^4}{64d^4}(3 + 2\cos^2\theta_T + 3\cos^4\theta_T) \right.$$

$$\left. + \frac{9l^2s^2}{8d^4}(\sin^2\theta_T + 3\sin^2\theta_T \cos^2\theta_T) + \frac{3\sqrt{3}ls^3}{8d^4}\sin^3\theta_T \cos\theta_T \cos3\phi_T \right], \qquad (29b)$$

and the other terms in Eq. (28) have been evaluated previously in Eqs. (18) and (19). The contribution to the second moment from A_{FP} is important and in fact happens to have a significant ϕ_T dependence for $\theta_T \neq 90°$. In Table II we give values of the second moment calculated for zero applied field which show the effect of this ϕ_T-dependent term.

B. Interpretation of the Experimental Results

Under these circumstances $\Delta\nu_{lat}$ and the approximate orientation of the molecule were rather easily determined from the general appearance and moments of the frequency spectrum. The values of $\Delta\nu_{lat}$, θ_T, and ϕ_T thus determined are given in Table III and as can be seen are much the same as those for NF_3.

From the observed line shapes one sees that the anisotropy of the chemical-shift tensor is much less for CHF_3 than for NF_3. For this reason we did not

attempt as systematic a determination of the field dependence of the moments as for NF_3. Consequently it was not possible to unambiguously determine all three principal values of the chemical-shift tensor. The most useful estimate of the anisotropy could be obtained by making the simplifying assumption of uniaxial symmetry of the CF bond, so that $\sigma_\alpha' = \sigma_\gamma' = -\tfrac{1}{2}\sigma_\beta'$. Then the anisotropy of the chemical-shift tensor $\Delta\sigma = \sigma_{||} - \sigma_\perp = \sigma_\beta' - \sigma_\alpha'$ could be determined by a one-parameter fit of the calculated line shapes to the experimental results. The best fit (see Figs. 11 and 12) was found for the values of the parameters quoted in Table III. This determination of the anisotropy of the chemical-shift tensor gives values of the frequency shift which are consistent with rough estimates obtained from the experimental data. The slight discrepancies between the calculated and observed line shapes may be due to the assumption of a uniaxial bond and the approximate treatment of the effects of the lattice protons.
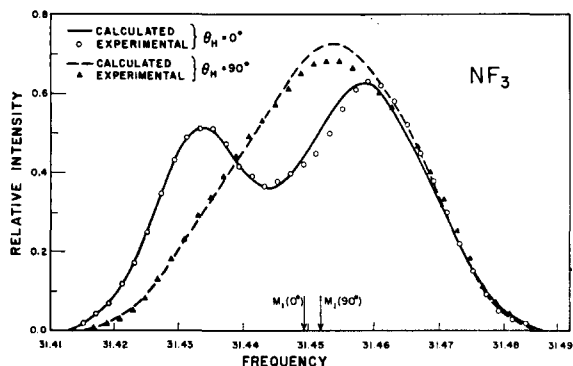
VI. DISCUSSION OF THE RESULTS AND CONCLUSIONS

Since the calculation of the chemical shift from the experimental results has been rather involved, no estimate has been made for the effect of the zero-point motion as was done previously.[3] However, it seems reasonable to assume that, because of the tight fitting of the trapped molecules in the clathrate cavities and their large moments of inertia, the rotational frequencies will be appreciably higher than those of trapped CHF_3, and consequently the influence of zero-point motion will be smaller.

The results for both NF_3 and CHF_3 are consistent with the theory of fluorine bonds first proposed by

FIG. 9. Calculated and observed line shapes for NF_3 at frequency 31 Mc/sec. For values of the parameters used in the calculations see Table III.
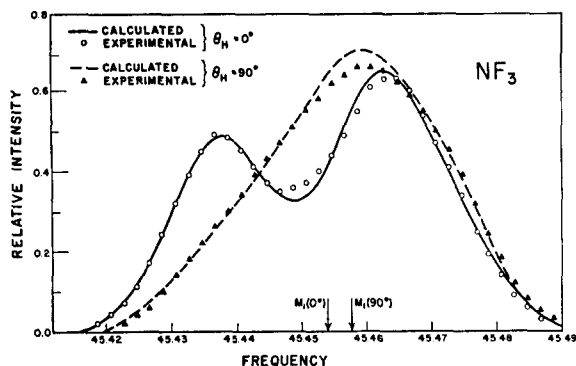
FIG. 10. Calculated and observed line shapes for NF_3 at frequency 45 Mc/sec. For values of the parameters used in the calculations see Table III.

FIG. 12. Calculated and observed line shapes for CHF_3 at frequency 45 Mc/sec. For values of the parameters used in the calculations see Table III.

Saika and Slichter.[16] Since the wavefunctions of these molecules are not known, only a qualitative comparison with theory can be made at present. The total chemical shift σ can be represented as the sum of two terms,[17] σ_d the diamagnetic part which is assumed to be isotropic[18] and σ_p the paramagnetic contribution due mainly to p electrons and which can be strongly anisotropic. Hence for nuclei in a uniaxial environment we write

$$\Delta\sigma = \sigma_{||} - \sigma_{\perp} \approx \sigma_{p||} - \sigma_{p\perp}, \qquad (30)$$

where the subscript p indicates the paramagnetic contribution. The theory of Das and Karplus[19] predicts that for a single bond with no double-bond character the paramagnetic component parallel to the bond direction due to p electrons is zero. For a strongly
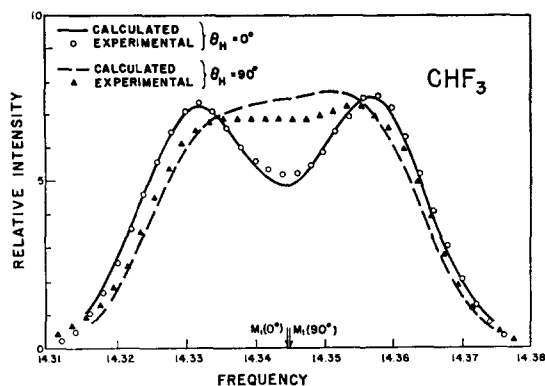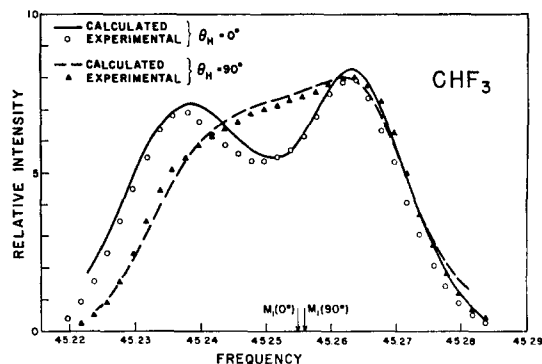

FIG. 11. Calculated and observed line shapes for CHF_3 at frequency 14 Mc/sec. For values of the parameters used in the calculations see Table III.

covalent bond, as in F_2, the paramagnetic component perpendicular to the bond, $\sigma_{p\perp}$, is large and negative. In contrast, for "ionic" fluorine, as exemplified by HF, $\sigma_{p\perp}$ is very small. Thus Eq. (30) becomes approximately

$$\Delta\sigma \approx -\sigma_{p\perp} \approx -\tfrac{3}{2}\bar{\sigma}_p. \qquad (31)$$

From calculations[20] of σ_d for HF and F_2 one sees that the difference in σ_d between these two compounds is an order of magnitude smaller than that of σ_p. Assuming this to be generally true, one can take the variation in σ_p to be approximately that of σ as determined experimentally. Hence, taking account of Eq. (31) one has

$$\Delta\sigma \approx -\tfrac{3}{2}\{\bar{\sigma} - \bar{\sigma}(\mathrm{HF})\}. \qquad (32)$$

To illustrate the usefulness of such a simple theory for fluorine compounds, we plot in Fig. 13 the known values of $\Delta\sigma$ vs $(\bar{\sigma} - \bar{\sigma}_{(\mathrm{HF})})$. According to Eq. (32) such a plot should give a straight line going through
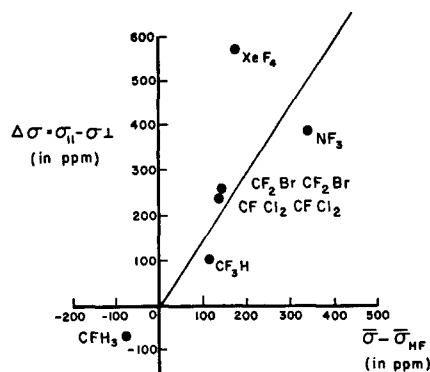

FIG. 13. The chemical-shift anisotropy $(\sigma_{||} - \sigma_{\perp})$ of fluorine nuclei in various molecules[2-4] versus $[\bar{\sigma} - \bar{\sigma}(\mathrm{HF})]$, the average chemical shift relative to that for fluorine in HF. The solid line is the result of the primitive theory discussed in the text.

[16] A. Saika and C. P. Slichter, J. Chem. Phys. **22**, 26 (1954).

[17] This separation is not gauge invariant (see Ref. 12, p. 78). We take the separation to be defined as in Ref. 11, for example.

[18] M. Karplus (private communication) has carried out calculations that show the diamagnetic shift to be anisotropic, although the absolute magnitude of the anisotropy is small.

[19] T. P. Das and M. Karplus, J. Chem. Phys. **34**, 1683 (1961).

[20] For values of σ_p and σ_d see Ref. 15, where references to calculations of σ_d are also given.

the origin with slope $-\frac{3}{2}$. Clearly, if one wishes to explain the experimental results in greater detail,[19] it will be necessary to undertake extensive calculations taking account of the individual molecular structures. It is also apparent that from both a theoretical and experimental standpoint molecules with a large paramagnetic shift, such as NF_3 and F_2, are ideal subjects for study.

Classical Equation of State for Molecules Interacting with Purely Repulsive Potentials*

CHARLES E. HECHT

Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, New York

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The virial development of the equation of state for molecules interacting with purely repulsive potentials is studied. The total number of positive terms contributing to any such virial coefficient is proven to exceed the total number of negative terms. Nevertheless, the virial coefficients are not necessarily all positive. From the fact that the asymptotic (finite system) equation of state for hard spheres and hard parallel cubes approaches the free volume form as the density increases to that of close packing, a reasonable asymptotic form for the virial coefficients B_l is deduced for l large. This form shows an unusual volume dependence. An isotherm for the parallel hard-cube gas is obtained which exhibits a van der Waals-like loop indicative of a first-order phase transition with a density change of roughly 12% across it. The entropy change in the transition is small and not in accord with the elementary account of a communal entropy change in the transition of a gas to a solid.

I. INTRODUCTION

THE question of the existence of a first-order phase transition from the gaseous state to a condensed phase in a system of molecules that interact with purely repulsive potentials has been a vexed one for more than 20 years. Experimentally, helium, far above its critical temperature and with a very minor region of attraction between its atoms as a function of interatomic distance, does have a sharp solidification transition at a volume larger than that of close packing. It is thus reasonable to consider the possible existence of a phase transition for the case of strictly repulsive potentials between particles. From theoretical considerations and using the so-called superposition approximation, Kirkwood and his students[1] first derived what was purported to be such a transition. However, this derivation has been suspect because of the approximation used to effect a closed relation for the two-particle distribution function from the set of exact integral equations relating the distribution functions of differing subgroups of molecules. Indeed, the superposition work gives a singularity at the same density[2] as would be predicted by keeping only the ring terms[3] in evaluating all the virial coefficients in the Kamerlingh-Onnes-type equation of state, using Mayer's general theory[4] of condensation. The same may be said about the density of the singularity indicated in the approximate equations of state derived by Abe,[5] Morita,[6] and Meeron.[7] The very poor results for the individual virial coefficients when only the ring terms are kept have also been discussed by Hoover and Poirier.[8] On the other hand, Mayer[9] and Alder and Wainwright[10] have given qualitative explanations as to how an *effective* attractive potential can arise even in the case of hard spheres based on considerations of an attractive potential of mean force[11] developing because of the geometric requirement that when two hard spheres are close to one another there are more collisions forcing them together than pushing them apart. More compelling yet are the computer calculations of Wood et al.[12] using a Monte Carlo method and of Wainwright and Alder[13] solving exactly the simultaneous equations

* Part of this work was done while the author was on the staff of the American University of Beirut, Beirut, Lebanon, and was receiving support from a grant from the Arts and Sciences Research Committee of that university.

[1] J. G. Kirkwood and E. Monroe, J. Chem. Phys. **9**, 514 (1941); J. G. Kirkwood, E. Maun, and B. J. Alder, *ibid.* **18**, 1040 (1950).

[2] H. S. Green, Proc. Roy. Soc. (London) **A189**, 103 (1947).

[3] E. W. Montroll and J. E. Mayer, J. Chem. Phys. **9**, 626 (1941).

[4] See, for example, J. E. Mayer, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12, p. 73.

[5] R. Abe, J. Phys. Soc. (Japan) **14**, 10 (1958).

[6] T. Morita, Progr. Theoret. Phys. (Kyoto) **20**, 920 (1958).

[7] E. Meeron, Phys. Fluids **1**, 139 (1958).

[8] W. G. Hoover and J. C. Poirier, J. Chem. Phys. **38**, 327 (1963).

[9] Reference 4, pp. 170–72.

[10] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).

[11] See, for example, T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 237.

[12] W. W. Wood, F. R. Parker, and J. D. Jacobson, Nuovo Cimento Suppl. No. 1, **9**, 133 (1958).

[13] T. E. Wainwright and B. J. Alder, Ref. 12, p. 116.