



NMR Studies of Iron (III) NMethyINPhenyIdithiocarbamate and Its meta and paraFluorophenyI Derivatives

R. M. Golding, W. C. Tennant, J. P. M. Bailey, and A. Hudson

Citation: The Journal of Chemical Physics **48**, 764 (1968); doi: 10.1063/1.1668709 View online: http://dx.doi.org/10.1063/1.1668709 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/48/2?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in Fourier transform infrared spectroscopic and theoretical study of water interactions with glycine and its N-methylated derivatives J. Chem. Phys. **134**, 115104 (2011); 10.1063/1.3567202

Electronic spectra of butadiene and its methyl derivatives: A multiphoton ionization study J. Chem. Phys. **73**, 5508 (1980); 10.1063/1.440070

NMR Studies of a Series of Phenyl Substituted Ferric NEthylNPhenyldithiocarbamates J. Chem. Phys. **56**, 4147 (1972); 10.1063/1.1677827

Transient Species Produced in the Photochemistry of 5Bromouracil and Its NMethyl Derivatives J. Chem. Phys. **51**, 4893 (1969); 10.1063/1.1671880

NMR Studies of a Series of Iron (III) Dithiocarbamate Complexes J. Chem. Phys. **45**, 2688 (1966); 10.1063/1.1727993



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 129.22.67.7 On: Tue, 02 Dec 2014 12:34:43

NMR Studies of Iron (III) N-Methyl-N-Phenyldithiocarbamate and Its meta- and para-Fluorophenyl Derivatives

R. M. GOLDING, W. C. TENNANT, J. P. M. BAILEY,* AND A. HUDSON† Chemistry Division, Department of Scientific and Industrial Research, Wellington, New Zealand (Received 25 September 1967)

The proton and fluorine magnetic resonance spectra of these compounds are interpreted using a model where the iron atom is in an intermediate crystal field of octahedral symmetry. The various proton and fluorine isotropic hyperfine-interaction constants in the ${}^{6}A_{1}$ and the ${}^{2}T_{2}$ states are calculated, and the approximations to determine these constants are examined. A method is outlined whereby an estimate of the ratio of the molecular vibrational partition functions in the ${}^{2}T_{2}$ and ${}^{6}A_{1}$ states can be ascertained from the NMR and the magnetic moment measurements. From the aromatic proton and fluorine hyperfine-interaction constants the electron spin densities in the ${}^{6}A_{1}$ state are estimated and the results discussed. It is shown that fluorine substitution in the aromatic ring has little effect on the various hyperfine-interaction constants in both states.

In an earlier paper¹ the temperature dependence of the proton NMR spectra of a series of iron (III) dithiocarbamates was interpreted on a model with the iron atom in an intermediate field of octahedral symmetry. The treatment fully accounted for the temperature dependence of ΔH (the change in effective magnetic field at the nucleus due to unpaired electrons) for all of the protons in the NMR spectra and gave numerical values for the hyperfine-interaction coupling constants for each compound in the ground and first excited states. In the ${}^{6}A_{1}$ state the hyperfine-interaction constants arise from the Fermi contact interaction and their variation for the various protons along the alkyl ligands was shown to arise mainly from *d*-electron delocalization from the iron nucleus.

In the case of the N-alkyl-N-phenyl compounds the data was incomplete due to uncertainty in assigning the ortho and meta aromatic protons. Hence, it was desirable to carry out further work on these compounds with a view to making unambiguous assignments of the aromatic proton resonances. This would be possible if a suitable atom, such as fluorine, were substituted for hydrogen in the aromatic fragment of the molecule. In this case the ¹⁹F resonance could be measured and, hence, an estimate of the electron spin density on the fluorine atom made. The influence of fluorine on the electron spin densities on the adjacent carbon atoms would follow. Little work of this nature has been reported, and many uncertainties exist.²

In this paper we have concentrated attention on one of the previously studied compounds, namely, iron (III) N-methyl-N-phenyldithiocarbamate and its meta- and para-fluorophenyl derivatives. From a detailed temperature-dependence study of the NMR spectra of these compounds, hyperfine-interaction con-

stants for the ${}^{2}T_{2}$ and ${}^{6}A_{1}$ states are evaluated for each of the protons and fluorine nuclei of the molecules and the electron spin densities on the various carbon atoms of the aromatic fragment calculated. The electron spin density on the carbon atoms is shown to be little influenced by the presence of fluorine in the aromatic system. By comparing the NMR and magnetic moment data³ for the N-methyl-N-phenyl compound, the ratio of the molecular vibrational partition functions for the ground and first excited state is evaluated.

EXPERIMENTAL

The preparation of iron (III) N-methyl-N-phenyldithiocarbamate has been described elsewhere.³ Its meta- and para-fluorophenyl derivatives were prepared as follows: The corresponding fluoroaniline (Koch-Light Labs., Ltd.) was methylated with CH₃I and the secondary amine separated by column chromatography on activated alumina. The secondary amine was reacted in the cold with the calculated amounts of NaOH and CS₂ and the sodium salt of the dithiocarbamate formed. The iron (III) dithiocarbamates were then precipitated, by adding the calculated amount of Fe³⁺ as ferric sulphate to an aqueous solution of the sodium salt, and crystallized from chloroform solution.

The apparatus and experimental procedure for the measurement of NMR spectra are the same as those previously used.¹ Diamagnetic proton chemical shifts were measured from sodium N-methyl-N-phenyldithiocarbamate in D₂O solution. These values were found to be (in cps from tetramethylsilane in each case) -N-CH₃, -225 and -N- aromatic, -445. Diamagnetic fluorine chemical shifts were measured in the corresponding sodium salts of the dithiocarbamates with p-fluoroaniline as internal standard and were found to be -702 cps and -907 cps for the *para*- and *meta*-

^{*} Present address: Mathematical Institute, Oxford, England. † Present address: University of Sussex, Brighton, Sussex, England.

¹R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, J. Chem. Phys. **45**, 2688 (1966). ²D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, Mol. Phys. **5**, 407 (1962).

⁸ A. H. White, R. Roper, E. Kokot, and H. Waterman, Australian J. Chem. 17, 294 (1964).



FIG. 1. The room-temperature 60-Mc/sec proton NMR spectra of the iron (III) dithiocarbamates in dilute deuterochloroform solution; (a) N-methyl-N-phenyl, (b) N-methyl-N-m-fluorophenyl, (c) N-methyl-N-p-fluorophenyl.

fluorine shifts, respectively. ΔH values were calculated from

$$\Delta H = H_e - H_d,$$

where H_e is the experimentally measured chemical shift in the paramagnetic compound and H_d the diamagnetic chemical shift. Figure 1 shows the proton NMR spectra of the three compounds studied in dilute deuterochloroform solution.

THEORY

Before we can analyze the NMR spectra of this series of iron (III) dithiocarbamates, we must derive the general expression for the temperature dependence of the effective magnetic field ΔH at the nucleus due to the unpaired electrons. Here,4

$$\Delta H = hA \langle S_z \rangle / g_N \beta_N, \qquad (1)$$

⁴ R. M. Golding, Mol. Phys. 8, 561 (1964).

765

into

where A is the isotropic hyperfine-interaction coupling constant and $\langle S_z \rangle$ is the time-average value of the z component of the electron spin. The magnetic susceptibility results⁵ of a similar series of iron (III) dithiocarbamates suggest that the iron atom is in a crystal field of octahedral symmetry: The Mössbauer results^{6,7} indicate that the degree of distortion of the crystal field from octahedral symmetry is small, and to a good approximation, we may assume octahedral symmetry. In this case,⁴

$$\langle S_{z} \rangle = \frac{\sum_{J} (2J+1) \langle S_{z} \rangle_{J} \exp(-E_{i}/kT)}{\sum_{J} (2J+1) \exp(-E_{i}/kT)}, \quad (2)$$

where

<

$$S_{z}\rangle_{J} = \frac{-\beta H}{3kT} \left(\frac{(g-\gamma)}{(2-\gamma)} gJ(J+1) + \frac{2(g-\gamma)(g-2)}{(2-\gamma)} \frac{kT}{\nu} \right)$$

Equation (2) was derived by using the isomorphic

properties of p and d electrons, namely, that the ${}^{2S+1}T_1$ and ${}^{2S+1}T_2$ terms are equivalent to ${}^{2S+1}P_J$ terms (J= 1+S, S, |1-S| and the isomorphic transformation transforms the spin-orbit coupling and magnetic field interaction Hamiltonian,

 $3\mathbb{C} = \zeta ls + \beta (l+2s) H,$

$$\mathcal{K} = \nu L S + \beta (\gamma L + 2S) H,$$

where ν is a function of ζ , the spin-orbit coupling constant for the transition metal ion, and γ is a specific number arising from the transformation.

The magnetic susceptibility measurements of iron (III) N-methyl-N-phenyl dithiocarbamate in a chloroform solution yields a magnetic moment result at room temperature of 3.33 Bohr magnetons which indicates that the d^5 ion is in an intermediate crystal field where the lowest lying ${}^{2}T_{2}$ and the ${}^{6}A_{1}$ states are of comparable energies. Therefore, we must consider both these states. The $\langle S_z \rangle_J$ values and the relative energies E_i for the ${}^{2}T_{2}$ and ${}^{6}A_{1}$ states are as follows:

$${}^{2}T_{2}, \quad E_{i} = -\nu \qquad \langle S_{z} \rangle_{J=1/2} = -\left(\beta H/9kT\right) \left[\frac{1}{2}(1-2\gamma) - \frac{8}{3}(\gamma-2)\left(kT/\nu\right)\right],$$

$$E_{i} = \frac{1}{2}\nu \qquad \langle S_{z} \rangle_{J=3/2} = -\left(\beta H/9kT\right) \left[\frac{5}{2}(1+\gamma) + \frac{4}{3}(\gamma-2)\left(kT/\nu\right)\right],$$

$${}^{6}A_{1}, \quad E_{i} = E \qquad \langle S_{z} \rangle_{J=5/2} = -\frac{35}{6}(\beta H/kT), \qquad (3)$$

where E is the energy separation of the ${}^{6}A_{1}$ and ${}^{2}T_{2}$ states. (E is positive when the ground state is ${}^{2}T_{2}$.) To determine ΔH for the complete system we consider a Boltzmann distribution over all states, and from Eqs. (1), (2), and (3) we obtain

$$\Delta H = -\frac{h\beta HA_2}{3g_N\beta_N kT} \left[\left(\frac{1}{3} (1-2\gamma) - \frac{16}{9} (\gamma-2) \frac{kT}{\nu} \right) \exp\left(\frac{\nu}{kT} \right) + \left(\frac{10}{8} (1+\gamma) + \frac{16}{9} (\gamma-2) \frac{kT}{\nu} \right) \exp\left(-\frac{\nu}{2kT} \right) + 105z \left(\frac{Q_a}{Q_t}\right) \exp\left(-\frac{E}{kT} \right) \right] \\ \times \left[2 \exp\left(\frac{\nu}{kT}\right) + 4 \exp\left(-\frac{\nu}{2kT}\right) + 6 \left(\frac{Q_a}{Q_t}\right) \exp\left(-\frac{E}{kT}\right) \right]^{-1}.$$
(4)

In Eq. (4),

 $z = A_6/A_2$.

H is the applied magnetic field, T the absolute temperature, A_2 and A_6 are the isotropic hyperfine-interaction coupling constants in the ${}^{2}T_{2}$ and ${}^{6}A_{1}$ states, respectively, and Q_{a} and Q_{t} are the molecular vibrational partition functions of the ${}^{6}A_{1}$ and ${}^{2}T_{2}$ states, respectively.

In deriving Eq. (4) we have neglected higher states and considered spin-orbit mixing from other states as negligible. If we consider configurational mixing, the appropriate values for γ and ν in Eq. (4) for the Fe³⁺ ion are about -1.3 and 1.1; respectively.⁸ These values do not differ greatly from $\gamma = -1$ and $\nu = \zeta$, the case when configurational mixing is neglected. We shall, therefore, choose the case when $\gamma = -1$ and $\nu = \zeta$ in Eq. (4). This leads to

$$\Delta H = -\frac{k\beta H A_2}{3g_N \beta_N \zeta} \frac{\left[x + (16/3)\right] \exp(x) - (16/3) \exp(-\frac{1}{2}x) + 105xz(Q_a/Q_t) \exp(-E/kT)}{2 \exp(x) + 4 \exp(-\frac{1}{2}x) + 6(Q_a/Q_t) \exp(-E/kT)},$$
(5)

where $x = \zeta/kT$. The approximations in deriving Eq. (5) are not expected to have a marked effect on the temperature dependence over the temperature range we are investigating.8

766

⁶ A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, Proc. Roy. Soc. (London) A280, 235 (1964).
⁶ R. M. Golding and H. J. Whitfield, Trans. Faraday Soc. 62, 1713 (1966).
⁷ R. M. Golding, Mol. Phys. 12, 13 (1967).
⁸ L. M. d. Liele, and P. M. Golding, Phys. Rev. B 40, 100 (1997).

⁸ J. M. de Lisle and R. M. Golding, Proc. Roy. Soc. (London) A296, 457 (1967).

The ratio of the molecular vibrational partition functions over the temperature range of interest approximates⁸ to $Q_a/Q_t = P \exp(-b/kT)$. Therefore, in Eq. (5) we may replace Q_a/Q_t by the constant P and let b be incorporated in E.

A similar expression, with the same approximations, for the magnetic moment is

$$\mu^{2} = \frac{\left[3 + (8/x)\right] \exp(x) - (8/x) \exp(-\frac{1}{2}x) + 105P \exp(-E/kT)}{\exp(x) + 2 \exp(-\frac{1}{2}x) + 3P \exp(-E/kT)}.$$
(6)

If the experimental magnetic moment at a particular temperature is known, then we may relate Eqs. (5) and (6) and hence calculate the constant P.

RESULTS

The temperature-dependent data for the three compounds studied were analyzed by computing a "least mean squares" fit of Eq. (5) to the experimental figures using an Elliott 503 computer. In Eq. (5) we have five unknown parameters A_2 , A_6 , E, ζ , and P. Initially we consider the case when P=1, i.e., we neglect the molecular vibrational partition function ratio. (We show later that this choice of P has little affect on the values of the hyperfine-interaction constants.) Assuming first the free-ion value of 400 cm⁻¹ for ζ , the value of E was varied to produce the "best fit" for the methyl protons and the corresponding values of A_2 and A_6 calculated. Using these values as a first approximation, the data was then analyzed according to a second program in which A_2 , A_6 , and E were simultaneously varied and the best fit values again obtained. Using this second value of E, the A_2 and A_6 values were then calculated for all the other protons and the fluorine nuclei. Finally, the whole procedure was repeated for ζ values of 350, 300, 250,

TABLE I. The hyperfine-interaction coupling constants for the iron (III) dithiocarbamates studied ($\zeta = 400 \text{ cm}^{-1}$ in each case).

Nucleus	E (cm ⁻¹)	$\stackrel{A_2}{(cps imes 10^5)}$	$A_{\mathfrak{b}}$ (cps $ imes$ 10 ⁵)					
Iron (III) N-methyl-N-phenyldithiocarbamate								
Methyl proton	261.0	2.133	7.475					
Aromatic (ortho) proton	261.0	-1.691	0.452					
Aromatic (meta) proton	261.0	0.268	0.210					
Aromatic (para) proton	261.0	0.055	-0.782					
Iron (III) N-methyl-N-m-fluorophenyldithiocarbamate								
Methyl proton	217.7	2.135	5.175					
Aromatic (ortho) proton	217.7	-1.456	0.112					
Aromatic (meta) proton	217.7	0.204	0.113					
Aromatic (para) proton	217.7	0.029	-0.602					
Aromatic (meta) fluorine	217.7	0.997	0.079					
Iron (III) N-methyl-N-p-fluorophenyldithiocarbamate								
Methyl proton	267.9	2.442	7.071					
Aromatic (ortho) proton	267.9	-1.467	0.214					
Aromatic (meta) proton	267.9	0.181	0.141					
Aromatic (para) fluorine	267.9	1.190	1.604					

and 200 cm⁻¹. The hyperfine-interaction coupling constants, A_2 and A_6 , for all of the protons and fluorine nuclei for the three compounds (with P=1 and $\zeta =$ 400 cm⁻¹) are tabulated in Table I. Experimental points and calculated curves for all of the protons and fluorine nuclei are shown in Figs. 2(a), 2(b), and 2(c). The relationship between A_2 and A_6 and for the methyl protons of each molecule is shown in Fig. 3.

DISCUSSION

From Figs. 2(a)-2(c) it is apparent that Eq. (5) accounts for the temperature dependence of the NMR of all the protons and fluorine nuclei of the three compounds studied. Figure 1 shows that fluorine substitution has little effect on the form of the NMR spectra at room temperature and Fig. 2 shows that the temperature dependence of the ΔH 's are very similar for all three compounds. In calculating the hyperfineinteraction constants and the energy E as given in Table I we assumed a value of unity for the partition function ratio.

In the case of the N-methyl-N-phenyl derivative, the magnetic moment at room temperature was known,⁸ and hence, using Eqs. (5) and (6), an estimate of Pcan be ascertained. From Fig. 4 we observe that the value of P is about 3 and is almost independent of the choice of the spin-orbit coupling constant. This value

TABLE II. Comparison of E, A_2 , and A_6 for iron (III) N-methyl-N-phenyldithiocarbamate for P=1 and P=3 ($\zeta = 400$ cm⁻¹).

Proton	<i>E</i> (cm ⁻¹)	$A_2 \text{ (cps $\times 10^5)}$	$A_6 \text{ (cps} imes 10^5)$
Methyl			
P = 1	261.0	2.133	7.475
P=3	359.0	2.682	4.187
Aromatic (ortho)			
P = 1	261.0	-1.691	0.452
P=3	359.0	-1.633	0.171
Aromatic (meta)			
P=1	261.0	0.268	0.210
P=3	359.0	0.281	0,127
Aromatic (para)			
P = 1	261.0	0.055	-0.782
P=3	359.0	-0.006	-0.425

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded IP: 129 22 67 7 On: Tue, 02 Dec 2014 12:34:43





FIG. 2. The temperature dependence of ΔH at the various protons and fluorine nuclei; (a) *N*-methyl-*N*-phenyl, (b) *N*-methyl-*N*-*m*-fluorophenyl, (c) *N*-methyl-*N*-*p*-fluorophenyl. Solid line, theoretical curve from Eq. (5); open circles, experimental points.





FIG. 3. The dependence of A_2 and A_6 on ζ for the methyl protons of the compounds studied; (a) *N*-methyl-*N*-phenyl, (b) *N*-methyl-*N*-*m*-fluorophenyl, (c) *N*methyl-*N*-*p*-fluorophenyl.

agrees with the value estimated from the vibrational modes.⁵ Substituting this value of P in Eq. (5), the parameters A_2 , A_6 , and E may be recalculated for the iron (III) *N*-methyl-*N*-phenyldithiocarbamate molecule. The values are compared with the previous case (P=1) in Table II for a ζ value of 400 cm⁻¹. Because of the method of calculation, A_6 is more affected by variations in P than is A_2 . Except in the case of the para proton where A_2 is close to zero, the signs of A_2 and A_6 are unchanged by variation of P and the errors arising from taking P=1 are not serious.

Covalency effects in the complexes may be allowed for by a reduction in ζ , the spin-orbit coupling constant, from the free-ion value of 400 cm⁻¹. A value of $\zeta = 250$ cm⁻¹ is suggested from Mössbauer studies⁶ of the solid N-methyl-N-phenyl compound but with some uncertainty. Fortunately, the choice of ζ does not greatly affect values of A_2 and A_6 as can be seen from Fig. 3.

The isotropic hyperfine-interaction constants arise from the Fermi contact term and the pseudocontact term, the latter term depending on the anisotropy of the g tensor. Both the ${}^{2}T_{2}$ and the ${}^{6}A_{1}$ states have isotropic g tensors, and hence, we would expect that the isotropic hyperfine-interaction constants, A_{2} and A_{6} , would arise entirely from the Fermi contact term. However, the ${}^{2}T_{2}$ state g tensor is markedly dependent on small distortions from octahedral symmetry. From Mössbauer studies⁶ the quadrupole splitting in the *N*-methyl-*N*-phenyl compound is about 0.6 mm/sec indicating a splitting of about 120 cm⁻¹ in the ${}^{2}T_{2}$ state. In this case the pseudocontact term may be comparable in magnitude to the Fermi contact term. Unfortunately, we are unable to distinguish between these two terms in the isotropic hyperfine-interaction constants in the ${}^{2}T_{2}$ state, and hence, we shall confine any detailed discussion to the A_{6} hyperfine-interaction constants.

In the ${}^{6}A_{1}$ state the electron spin densities ρ_{c} on the aromatic C atoms can be evaluated from⁹

$$A = Q\rho_c, \tag{7}$$

where Q = -65 Mc/sec.¹⁰ These values are given in Table III, and it is seen that for each compound the electron spin density is positive on the *para* C atom and small and negative on the *ortho* and *meta* C atoms. Further, the spin densities are little influenced by fluorine substitution although (from Table I) fluorine substitution affects A_6 more than A_2 . However, as noted above this may arise from a change in the relative

TABLE III. Carbon and fluorine spin densities in the ${}^{6}A_{1}$ state for the compounds studied.

Compound	Spin density $(\times 10^{-4})$					
	0	m	Þ	<i>m</i> - fluorine	p- fluorine	
N-phenyl	-6.96	-3.23	12.0			
N-m-fluorophenyl	-1.72	-1.74	9.3	-0.17	•••	
N-p-fluorophenyl	-3.29	-2.17	•••	•••	1.55	

⁹ H. M. McConnell, J. Chem. Phys. **24**, 632 (1956). ¹⁰ J. P. M. Bailey and R. M. Golding, Mol. Phys. **12**, 49 (1967).



FIG. 4. The dependence of P on E and ζ for the methyl protons in iron (III) N-methyl-N-phenyldithiocarbamate.

populations of the two ground states. As pointed out previously¹ the spin densities on the aromatic C atoms are consistent with the hypothesis that the spin density on N is positive and the substituent attached to the aromatic ring is electron attracting.

The calculation of spin densities on the fluorine atoms is not so certain. The problem has been discussed in detail by Kaplan et al.¹¹ Eaton et al.² used the relation

$$A_F = Q^c \rho_c + Q^F \rho_F, \tag{8}$$

where the first term arises from spin polarization of the C-F σ -bonding electrons due to unpaired spin on the carbon atom while the second term is due to spin polarization of the fluorine 1s and 2s electrons due to unpaired spin in the $2p\pi$ orbital on fluorine. Accurate values of Q^c and Q^F are not known, but Cook *et al.*¹² estimate $Q^c = -410$ Mc/sec and $Q^F = 3800$ Mc/sec. Since ρ_c is little affected in our compounds by fluorine

substitution, we may take $\rho_c(para) = 10.5 \times 10^{-4}$ and $\rho_e(meta) = -1.74 \times 10^{-4}$ (see Table III) and hence calculate approximate values for ρ_F from Eq. (8). These values of ρ_F are given in Table III. Carrington et al.¹³ found that the fluorine splittings in the radical anions of fluoronitrobenzenes could be interpreted in terms of the relation $Q\rho_e = A_F$ with the proportionality constant Q=140 Mc/sec, the ratio ρ_F/ρ_c being approximately constant for the ortho, meta, and para positions. In the present work taking again the same values of ρ_c we calculate $A_F(meta) = -2.43 \times 10^5$ and $A_F(para) =$ 1.47×10⁵. $A_F(para)$ is in close agreement with our experimental value of 1.6×10^5 but the calculated value of $A_F(meta)$ has the wrong sign. It would appear, therefore, that the simplified relationship $A_F = Q\rho_c$ is inadequate to describe the nuclear hyperfine-interaction in our compounds, and the complete relationship of Eaton et al. must be employed. Such a situation could arise from a difference in the π -bond orders of the meta and para C-F bonds.

771

¹¹ M. Kaplan, J. R. Bolton, and G. K. Fraenkel, J. Chem. Phys. 42, 955 (1965). ¹² R. J. Cook, J. R. Rowlands, and D. H. Whiffen, Mol. Phys.

^{7, 31 (1963).}

¹³ A. Carrington, A. Hudson, and H. C. Longuet-Higgins, Mol. Phys. 9, 377 (1965).