MOLECULAR PHYSICS, 1985, VOL. 56, NO. 5, 1083–1095

Rovibrational averaging of molecular magnetic properties of CH_3F, CH_2F_2, and CHF_3

by CYNTHIA J. JAMESON
Department of Chemistry, University of Illinois at Chicago,
Box 4348 Chicago, Illinois 60680, U.S.A.

and H. JÖRG OSTEN
Academy of Sciences of the GDR, Central Institute of Physical Chemistry,
1199 Berlin, Rudower Chaussee 6, German Democratic Republic

(*Received 28 June 1985; accepted 27 July 1985*)

The mean bond displacements in the series of molecules CH_3F, CH_2F_2, CHF_3 have been calculated using the available harmonic force fields augmented by cubic terms in the stretching and non-bonded interactions, ignoring cubic terms in the bond angle deformation. With these dynamic factors we interpret the previously reported temperature dependence of ^{19}F shielding in the zero-pressure limit as well as the ^{13}C- and ^{2}H-induced ^{19}F isotope shifts in these molecules. We obtain values for the shielding derivatives $(\partial\sigma^F/\partial\,\Delta r_{CF})_e = -338$, -725, and -1274 for CH_3F, CH_2F_2, and CHF_3 respectively. These shielding derivatives are shown to correlate linearly with n in CH_nF_{4-n}, and with the shielding tensor components parallel to the CF bond and perpendicular to the CF bond in the FCF plane. Together with the halomethanes CF_3X, CF_2Cl_2, and $CFCl_3$, they show a non-linear correlation with the absolute shielding and a nearly linear one with $^1J(CF)$. From the D-induced ^{19}F isotope shift in CHF_3 we obtain an estimate $(\partial\sigma^F/\partial\,\Delta r_{CH})_e = -84$ ppm Å^{-1}. We also estimate $(\partial\sigma^F/\partial\,\Delta r_{CF})_e \simeq -1520$ and -1400 ppm Å^{-1} $CHFCl_2$ and CHF_2Cl respectively. The errors associated with the empirical values of shielding derivatives are discussed.

1. INTRODUCTION

Of the fluorocarbons, the molecular systems which are amenable to *ab initio* calculations of molecular electronic properties are the CH_3F, CH_2F_2, and CHF_3 molecules. These molecules are interesting from the point of view of electrical properties as the electric dipole moment changes significantly along the series. The analysis of integrated infrared intensities in terms of atomic polar tensors (gradients of the molecular dipole moment vector) and effective atomic charges (one third the trace of the squares of the polar tensor components) in these molecules have been supported by *ab initio* calculations [1–3]. The analogous magnetic properties such as the temperature dependence of the rovibrationally-averaged shielding, the absolute shielding at the equilibrium structure, the derivatives of the nuclear shielding with respect to bond extension, the individual shielding tensor components, the spin–spin coupling constants $^1J(CF)$ and $^2J(HF)$, and the ^{19}F chemical shifts upon ^{13}C- or D- substitution, are likewise of interest. There are as yet no *ab initio* calculations of the shielding surface of ^{19}F

or any of the other magnetic properties of these molecules, although there are *ab initio* calculations of ${}^1J(\mathrm{CF})$ and ${}^2J(\mathrm{HF})$ at the equilibrium configuration in CH_3F [4, 5]. In this paper, we interpret the temperature dependent N.M.R. chemical shifts at the isolated molecule limit and the related isotope effects on shielding in terms of the rovibrationally-averaged bond displacements. From this, an empirical estimate of $(\partial\sigma^{\mathrm{F}}/\partial\, \Delta r_{\mathrm{CF}})_{\mathrm{e}}$ can be obtained for each of these molecules. We relate these derivatives to the ^{19}F nuclear shielding tensor components and the coupling constants ${}^1J(\mathrm{CF})$ and ${}^2J(\mathrm{HF})$, and include comparisons with other halomethanes [6] for a more general correlation.

The observed isotropic nuclear shielding in the zero-pressure limit is a thermal average shielding. Employing the Born–Oppenheimer separation and assuming small nuclear displacements during vibration, one can write the ^{19}F thermal average nuclear shielding as follows:

$$\sigma_0(T) = \sigma_{\mathrm{e}} + (\partial\sigma/\partial\, \Delta r_{\mathrm{CF}})_{\mathrm{e}}\langle\Delta r_{\mathrm{CF}}\rangle^T + \dots . \qquad (1)$$

There are terms in the derivative with respect to bond angle deformation, $(\partial\sigma/\partial\, \Delta\alpha)_{\mathrm{e}}$, and in second derivatives $(\partial^2\sigma/\partial\, \Delta r^2)_{\mathrm{e}}$, etc. However, for the nearly tetrahedral molecules which we are considering here the terms in the bond angle deformation can be neglected [6, 7]. For ^{19}F shielding in CH_nF_{4-n} the small deviations from equilibrium bond angles are even less important than in the halomethanes such as CF_3X or CF_nCl_{4-n} since there are no Cl, Br, or I atomic orbitals which tend to be brought closer or further away by angle deformations around the C atom. Further, we neglect the terms in the second derivatives. For diatomic molecules Ditchfield has calculated many higher order derivatives and shown that the temperature dependence of $\sigma_0(T)$ based on all these derivatives and that calculated only with the first derivative are indistinguishable within the experimental errors normally associated with such measurements [8]. Therefore, we limit our interpretation only to the one term shown in equation (1). Thus, it is possible to extract from an experimentally determined $[\sigma_0(T) - \sigma_0(300\ \mathrm{K})]$ the quantity $(\partial\sigma/\partial\, \Delta r)_{\mathrm{e}}$, provided one can evaluate the thermal mean bond displacements $\langle\Delta r_{\mathrm{CF}}\rangle^T$. It is also possible to interpret the small isotope effects on ^{19}F shielding by calculating differences in the mean bond displacements in ${}^{13}CH_3F$ and ${}^{12}CH_3F$, and in ${}^{12}CH_3F$ and ${}^{12}CD_3F$, for example.

2. CALCULATION OF THERMAL MEAN BOND DISPLACEMENTS

The general valence harmonic force fields (GVFF) of CH_3F, CH_2F_2, and CHF_3 are available. For CH_3F the experimental GVFF of Duncan *et al.* [9] was improved by Blom and Müller [10] using a recent value of the centrifugal distortion constant D_{K} and r_{e} geometry to fix F_{12}; the new value of the latter thus comes into agreement with the *ab initio* value, resolving a discrepancy which had previously been noted between the sign of all *ab initio* values of F_{12} and the empirical value. This also brings all interaction force constants in CH_3F into the same signs as the comparable ones in CH_3Cl. For CH_2F_2 the values of F_{12}, F_{13}, and F_{14} which are still indeterminable from experiment were constrained by Blom and Müller to the *ab initio* values [10]. For CHF_3, the GVFF of Kirk and Wilt [11] is still the best available. Recent measurements of some anharmonicity constants by IR double resonance experiments [12] yield values which are very close to the values estimated by Kirk and Wilt from their force field. For comparison with our previous results for the halomethanes CF_3X, (X = F, Cl, Br, I), CF_2Cl_2, and $CFCl_3$ [6], we determined sets of Urey–Bradley force constants which are consistent with the GVFF for CH_3F and CHF_3, and for CH_2F_2 linearly interpolated between the values for CH_3F and CHF_3. Trends in these values are consistent with those found by Shimanouchi and Suzuki [13] for CH_nCl_{4-n} and CH_nBr_{4-n}.

The usual approximate anharmonic potential terms are added to the harmonic potential function. We use Bartell's anharmonic approximation for stretching and non-bonded interactions [14], ignoring cubic terms in the bending altogether.

$$V_{\text{anh}} = \tfrac{1}{2}\sum_{i=1}^{4} - a_i K_i(\Delta r_i)^3 + \tfrac{1}{2}\sum_i \sum_{j\neq i} (1/6q_{ij})F_{ij}^3(\Delta q_{ij})^3 \tag{2}$$

where a_i is the Morse parameter for each bond, determined from the exponential functions given by Herschbach and Laurie [15], K_i is the quadratic stretch force constant, q_{ij} is the non-bonded distance and F_{ij}^3 is the cubic force constant appropriate to non-bonded interactions. F_{ij}^3 are obtained as follows:

$$F^3 = q[\partial^3 V(q)/\partial q^3] \tag{3 a}$$

$$V(q) = A \exp(-Bq) - Cq^{-6} \quad \text{for H–F and H–H interactions} \tag{3 b}$$

$$V(q) = 4\varepsilon[(q_0/q)^{12} - (q_0/q)^6] \quad \text{for F–F interactions.} \tag{3 c}$$

The parameters A, B, and C are given by Boyd and Kesner [16], ε and q_0 by Kestin *et al.* [17]. We use the same form for F–F interactions as for F–X interactions for direct comparison with our halomethane results and because this Lennard–Jones form has been found to reproduce fairly well the quadratic UB constants for interhalogen non-bonded interactions. For H-other atom interactions the exp/-6 form has been found to work best [18].

We can compare the cubic force constant for CF stretch (F_{333}) obtained from the above approximation with the *ab initio* value calculated for CH_3F by Kondo *et al.* [19]. With our anharmonic terms we get

$$F_{333} = 3[-aK_{\text{CF}} + (1/q_{\text{FH}})(s_{\text{FH}})^3 F_{\text{HF}}^3], \tag{4}$$

where the symbols have their standard definitions [18]. This yields $F_{333} = -28{\cdot}45$ mdyn Å^{-2}. Kondo *et al.* recommend 'normalizing' their *ab initio* cubic symmetry force constants for CH_3F by using the experimental values of the harmonic force constants as follows:

$$F_{ijk} = (F_{ijk})_{\text{th}} \times \{(F_{ii}F_{jj}F_{kk})_{\text{expt}}/(F_{ii}F_{jj}F_{kk})_{\text{th}}\}^{1/2} \tag{5}$$

in order to correct for the poor diagonal force constants (these are always overestimated by *ab initio* methods). With this, their 'normalized' F_{333} for CH_3F is $-32{\cdot}21$ mdyn Å^{-2}. Thus, we find that Bartell's anharmonic terms give ~90 per cent of the theoretical anharmonic value for the CF stretching. It is not known exactly how much of an over-estimate the theoretical value is. It is well known that *ab initio* methods give much better agreement with off-diagonal force constants whereas they always give too large diagonal force constants. For CH_2F_2, we can make a similar comparison. Here an empirical value for the cubic CF stretching force constant has been derived from experimental vibration–rotation constants: $-37{\cdot}5$ mdyn Å^{-2}, the only one determined significantly by a least squares analysis. In CH_2F_2 our approximation for the cubic constants for the CF stretching is

$$F_{333} = -3aK_{CF} + (1/q_{FF})(s_{FF})^3 F^3_{FF} + (2/q_{FH})(s_{FH})^3 F^3_{HF}, \qquad (6)$$

which gives a value equal to $-31{\cdot}3$ mdyn Å^{-2}, about 85 per cent of the experimental estimate.

3. RESULTS

3.1. *Temperature dependence of ^{19}F nuclear shielding*

We calculated the mean bond displacements in the same way as for the halomethanes [6] using Bartell's method [14]. There are two coupled equations to solve in $\langle \Delta r_{CF} \rangle$ and $\langle \Delta r_{CH} \rangle$ in terms of the mean square amplitude matrix elements. As usual we include all terms in the mean square amplitudes and evaluate their thermal average values using

$$\langle Q_i^2 \rangle = (h/8\pi^2 c\omega_i) \coth (hc\omega_i/2kT). \qquad (7)$$

The centrifugal stretching is calculated in the usual way [20]. The results are shown in table 1. The mean CF bond displacements at 300 K, $6{\cdot}076 \times 10^{-3}$ to $6{\cdot}722 \times 10^{-3}$ Å are comparable to the ones obtained in the halomethanes, $5{\cdot}7$–$6{\cdot}4 \times 10^{-3}$ Å. The mean C–H bond displacements at 300 K, $2{\cdot}2$–3×10^{-2} Å are comparable to the ones obtained for CH_4, $2{\cdot}21 \times 10^{-2}$ Å by Bartell [14] and ourselves [7], $2{\cdot}14 \times 10^{-2}$ Å. This supports our previous assessment that the mean bond displacement varies only slightly for a given type of bond (e.g. C–F) in different molecules. In table 1 we also give the temperature dependence of the mean bond displacements. $\Delta_T \equiv (\langle \Delta r \rangle^{400} - \langle \Delta r \rangle^{200})$ is $7{\cdot}5$–$9{\cdot}0 \times 10^{-4}$ Å for the CF bonds in CH_3F, CH_2F_2, and CHF_3, whereas for the halomethanes they are $7{\cdot}8$–$8{\cdot}4 \times 10^{-4}$ Å. The fraction of the temperature dependence which is due to rotation is 65, 49 and 31 per cent for the CF bond; 71, 26 and 10 per cent for the CH bond in CH_3F, CH_2F_2, and CHF_3 respectively. There is less error associated with the neglect of the vibrational contributions involving the higher derivatives (such as $(\partial^2\sigma/\partial \Delta r^2)\langle \Delta r^2 \rangle$, etc.) in the interpretation of the experimental temperature dependence of the ^{19}F resonance frequency when the term involving the first derivative has a significant rotational contribution. We see that this condition is satisfied for the fluoromethanes. The isotope effect on the mean bond displacement is also comparable to the halomethanes. Here we find the difference between the CF mean bond displacements in $^{13}CH_nF_{4-n}$ and $^{12}CH_nF_{4-n}$ is $8{\cdot}2$–$9{\cdot}3 \times 10^{-5}$, the ^{13}CF bond being somewhat shorter. In the halomethanes, these are $7{\cdot}0$–$10{\cdot}0 \times 10^{-5}$ Å. The rotational contribution to the ^{13}C-isotope effect on the CF bond is not significant (less than 10 per cent for all these fluoromethanes). The differences between the CH and CD mean bond displacements in CH_3F, CH_2F_2, and CHF_3, $5{\cdot}4$–$6{\cdot}0 \times 10^{-3}$ Å, are comparable to $5{\cdot}5 \times 10^{-3}$ Å in CH_4 [7].

With these dynamic factors we are able to interpret the previously reported temperature dependence of ^{19}F shielding in the zero-pressure limit in CH_3F, CH_2F_2 [21] and CHF_3 [22] as well as the ^{13}C-induced and ^{2}H-induced ^{19}F chemical shifts in these molecules. Using equation (1), by least squares fitting to the observed ^{19}F resonance frequencies over the following range of temperatures:

Table 1. Mean bond displacements and equilibrium bond lengths in CH_nF_{4-n}. The temperature and mass dependence of the mean bond displacements are given respectively by:

$$\Delta_T \equiv \langle \Delta r \rangle^{400} - \langle \Delta r \rangle^{200}, \quad \delta_D = \langle \Delta r_{CF} \rangle_{CH_nF_{4-n}} - \langle \Delta r_{CF} \rangle_{CDH_{n-1}F_{4-n}},$$

$$\Delta_C \equiv \langle \Delta r_{^{12}CX} \rangle - \langle \Delta r_{^{13}CX} \rangle,$$

$$\Delta_D \equiv \langle \Delta r_{CH} \rangle - \langle \Delta r_{CD} \rangle.$$

All numbers are given in Ångströms

	$\langle \Delta r_{CF} \rangle$			$\langle \Delta r_{CH} \rangle$		
	CH_3F†	CH_2F_2	CHF_3	CH_3F†	CH_2F_2	CHF_3
$T = 200$	$5{\cdot}702 \times 10^{-3}$	$6{\cdot}389 \times 10^{-3}$	$6{\cdot}229 \times 10^{-3}$	$2{\cdot}278 \times 10^{-2}$	$2{\cdot}204 \times 10^{-2}$	$2{\cdot}316 \times 10^{-2}$
240	$5{\cdot}837 \times 10^{-3}$	$6{\cdot}506 \times 10^{-3}$	$6{\cdot}331 \times 10^{-3}$	$2{\cdot}281 \times 10^{-2}$	$2{\cdot}204 \times 10^{-2}$	$2{\cdot}317 \times 10^{-2}$
300	$6{\cdot}076 \times 10^{-3}$	$6{\cdot}722 \times 10^{-3}$	$6{\cdot}530 \times 10^{-3}$	$2{\cdot}287 \times 10^{-2}$	$2{\cdot}207 \times 10^{-2}$	$2{\cdot}320 \times 10^{-2}$
340	$6{\cdot}266 \times 10^{-3}$	$6{\cdot}895 \times 10^{-3}$	$6{\cdot}692 \times 10^{-3}$	$2{\cdot}292 \times 10^{-2}$	$2{\cdot}209 \times 10^{-2}$	$2{\cdot}324 \times 10^{-2}$
400	$6{\cdot}601 \times 10^{-3}$	$7{\cdot}201 \times 10^{-3}$	$6{\cdot}978 \times 10^{-3}$	$2{\cdot}300 \times 10^{-2}$	$2{\cdot}215 \times 10^{-2}$	$2{\cdot}333 \times 10^{-2}$
r_e	1·382	1·351	1·328	1·090	1·084	1·091
$\langle \Delta r \rangle_{rot}$	$2{\cdot}959 \times 10^{-6}$ T	$2{\cdot}008 \times 10^{-6}$ T	$1{\cdot}153 \times 10^{-6}$ T	$8{\cdot}092 \times 10^{-7}$ T	$1{\cdot}485 \times 10^{-7}$ T	$8{\cdot}905 \times 10^{-8}$ T
Δ_T	$8{\cdot}99 \times 10^{-4}$	$8{\cdot}12 \times 10^{-4}$	$7{\cdot}49 \times 10^{-4}$	$2{\cdot}27 \times 10^{-4}$	$1{\cdot}12 \times 10^{-4}$	$1{\cdot}69 \times 10^{-4}$
$(\Delta_T)_{rot}$	65 per cent	49 per cent	31 per cent	71 per cent	26 per cent	10 per cent
Δ_C	$9{\cdot}3 \times 10^{-5}$	$8{\cdot}6 \times 10^{-5}$	$8{\cdot}2 \times 10^{-5}$	$6{\cdot}3 \times 10^{-5}$	$6{\cdot}2 \times 10^{-5}$	$6{\cdot}4 \times 10^{-5}$
Δ_D				$5{\cdot}4 \times 10^{-3}$	$5{\cdot}6 \times 10^{-3}$	$6{\cdot}0 \times 10^{-3}$
δ_D	$4{\cdot}67 \times 10^{-5}$	$1{\cdot}54 \times 10^{-4}$	$2{\cdot}15 \times 10^{-4}$			

† The earlier analysis of the CH_3F data in 1978, *J. chem. Phys.*, **69,** 1655 had several errors in it. Equation (12) should read $-[3(1+\kappa^2)]^{1/2} \cdot \sin\beta_e \cos\beta_e$ for the (2, 1) element and $[3(1+\kappa^2)]^{1/2} \sin\beta_e \cos\beta_e$ for the (2, 2) element. Table III and figures 3 and 4 are all wrong because of this error and also because the anharmonic contributions from only the first term in (3) of the paper, i.e., $(-3/2\omega_i)k_{iii} \coth(hc\omega_i/2kT)$ had been included.

280–380 K (CH_3F), 230–380 K (CH_2F_2), and 240–380 K (CHF_3), we obtain empirical values for the derivatives $(\partial\sigma/\partial\,\Delta r_{CF})_e = -338$, -725, and -1274 ppm Å^{-1} for CH_3F, CH_2F_2, and CHF_3. In the calculation of the mean bond displacement $\langle\Delta r_{CF}\rangle$ and $\langle\Delta r_{CH}\rangle$ for these molecules and in fitting to the experimental temperature dependence of the ^{19}F nuclear resonance frequencies, we have neglected the mean bond angle deformations although we have included all mean square amplitudes involving bond angles. This neglect is not expected to be important in the determination of $(\partial\sigma^F/\partial\,\Delta r_{CF})_e$ from the fitting of $\langle\Delta r_{CF}\rangle^T$ to the experimental $\sigma_0(T)$. The significant rotational contribution (which is linear in T) to $(\partial\sigma^F/\partial\,\Delta r_{CF})_e[\langle\Delta r_{CF}\rangle^T - \langle\Delta r_{CF}\rangle^{300\text{ K}}]$ makes this term dominant in the temperature dependence of shielding. Thus, we feel confident that we are obtaining good estimates of $(\partial\sigma/\partial\,\Delta r_{CF})_e$. These also yield estimates of the rovibrational corrections to the shielding at 300 K, $[\sigma(300\text{ K}) - \sigma_e] \simeq -2{\cdot}1, -4{\cdot}8, -8{\cdot}3$ ppm. These are only part of the vibrational corrections because second derivatives of the shielding have not been included here. Nevertheless, it is worthwhile to note the magnitudes of errors incurred when comparing theoretical values of ^{19}F chemical shifts between molecules (obtained by taking differences of shielding at equilibrium configurations of the molecules) with the experimental chemical shifts (which are differences of σ_0 (300 K)), even when extrapolation to the zero-pressure limit has eliminated solvent effects. For the halomethanes these vibrational corrections are $-6{\cdot}8$ ppm (CF_4) to $-15{\cdot}4$ ppm ($CFCl_3$) [6]. When only CF bonds are being compared, e.g. CH_3F with $CFCl_3$, this error is of the order of 13 ppm or less. On the other hand, when comparing F_2 with CH_3F this error is about 40 ppm [23]. Thus, it is important to know the rovibrational corrections necessary to convert the observed σ_0 (300 K) to σ_e. Differences in σ_0 (300 K) can be obtained to good precision if the experiments are carried out properly [24, 25]. Due to the uncertainties in the $[\sigma_0(300\text{ K}) - \sigma_e]$ calculated here, the derived σ_e values are necessarily less precise than one would like. Nevertheless, it is more correct to compare theoretical values with differences in the (less precise) derived σ_e.

3.2. *Isotope shifts*

With these derivatives, we have also calculated the ^{13}C-induced one-bond ^{19}F isotope shifts and the ^2H-induced 2-bond ^{19}F isotope shifts using equations (8) and (9)

$$^1\Delta^{19}F(^{13/12}C) \cong (\partial\sigma^{F_1}/\partial\,\Delta r_{CF_1})[\langle\Delta r_{^{12}CF_1}\rangle - \langle\Delta r_{^{13}CF_1}\rangle], \tag{8}$$

$$\begin{aligned} ^2\Delta^{19}F(^{2/1}H) = {} & (\partial\sigma^{F_1}/\partial\,\Delta r_{CF_1})_e[\langle\Delta r_{CF_1}\rangle_{CH_nF_{4-n}} - \langle\Delta r_{CF_1}\rangle_{CDH_{n-1}F_{4-n}}] \\ & + (\partial\sigma^{F_1}/\partial\,\Delta r_{CH})_e[\langle\Delta r_{CH}\rangle - \langle\Delta r_{CD}\rangle]. \end{aligned} \tag{9}$$

The results are shown in table 2 in comparison with experiment. Using equation (9) and the experimental value of $^2\Delta^{19}F(^{2/1}H) = -0{\cdot}78$ ppm in the CDF_3–CHF_3 system, we calculate $(\partial\sigma^F/\partial\,\Delta r_{CH})_e = -84$ ppm Å^{-1}. The two contributions in (9) are $-0{\cdot}27$ and $-0{\cdot}51$ ppm respectively, if we assume that only these two contributions are important.

For the isotope shift the discrepancies between experiment and calculation come from two sources: The terms in the second derivatives which are not important to the temperature dependent chemical shifts can be important to the

Table 2. Comparison of N.M.R. observables for CH_nF_{4-n} molecules.

	CH_3F	CH_2F_2	CHF_3
$(\partial\sigma/\partial\,\Delta r)_e$/ppm Å^{-1}	−338	−725	−1274
$[\sigma_0(300\text{ K}) - \sigma_e]$/ppm	−2·1	−4·8	−8·3
σ_0/ppm	471 (*a*)	339·1 (*b*)	274·4 (*a*)
σ_e/ppm	473	349	283
$^1\Delta^{19}F(^{13/12}C)$obs/ppm	−0·074(−0·072 (*c*))	−0·112(−0·115 (*c*))	−0·127(−0·126 (*c*))
$^1\Delta^{19}F(^{13/12}C)$calc/ppm	−0·031	−0·062	−0·104
$^1J(CF)$/Hz	161(158 (*c*))	235(235 (*c*))	275(274 (*c*))
σ_{aa}/ppm	426(∥ C–F) (*d*)	225(⊥) (*e*)	201(in-plane FCF) (*f*)
σ_{bb}/ppm	493(⊥)	388 (*g*)	277(⊥)
σ_{cc}/ppm	493(⊥)	398 (*h*)	344(∥C–F)
$^2\Delta^{19}F(^{2/1}H)$obs/ppm			−0·78 ppm (*i*)
$^2J(HF)$/Hz (*c*)	46·36	50·22	79·72

(*a*) [25]; (*b*) [24]; (*c*) [26]; (*d*) [29]; (*e*) Perpendicular to the molecular plane [30]; (*f*) [28]; (*g*) In the molecular plane bisecting the FCF angle; (*h*) In the molecular plane perpendicular to the C=C bond; (*i*) [32].

isotope shift. These terms $(\partial^2\sigma^{F_1}/\partial\,\Delta r^2_{CF_1})_e \cdot [\langle(\Delta r_{^{12}CF_1})^2\rangle - \langle(\Delta r_{^{13}CF_1})^2\rangle]$, are expected to have the same sign as the term which is included in equation (8). We base this on the evidence from diatomic molecules for which Ditchfield has calculated many higher order derivatives. He finds that the first and second derivatives are both negative [8]. Since the dynamic factors $[\langle(\Delta r_{^{12}CF})^2\rangle - \langle(\Delta r_{^{13}CF})^2\rangle]$ are negative, then there is reason to believe that the $(\partial^2\sigma/\partial\,\Delta r^2_{CF})$ term should make a contribution of the same sign as the first term. Neglect of this term would lead to underestimation of the magnitude of the isotope shift. The other terms which we have not included are the isotope effects on the other bonds which are transmitted to the ^{19}F nucleus via a secondary derivative of the nuclear shielding,

$$\sum_{i\neq 1} (\partial\sigma^{F_1}/\partial\,\Delta r_{CF_i})_e[\langle\Delta r_{^{12}CF_i}\rangle - \langle\Delta r_{^{13}CF_i}\rangle]$$
$$+\sum_{j} (\partial\sigma^{F_1}/\partial\,\Delta r_{CH_j})_e[\langle\Delta r_{^{12}CH_j}\rangle - \langle\Delta r_{^{13}CH_j}\rangle].$$

These neglected terms are expected to be the same sign as and much smaller than the term in (8). Therefore, it is not surprising that we have underestimated the isotope shifts.

The comparison of calculated with experimental isotopic shifts in these molecules and the halomethanes are summarized in figure 1. We see that there is a systematic trend that when one or two heavier nuclei like Cl are attached to the carbon, the calculated isotope shifts are in good agreement with experiment whereas hydrogens lead to underestimation (as expected).

The higher the percentage of rotational contribution to Δ_T, the more accurate the empirical $(\partial\sigma/\partial\,\Delta r)_e$ that is obtained from fitting $\sigma_0(T) - \sigma_0(300)$ data since the term linearly dependent on temperature [20],

$$(\partial\sigma/\partial\,\Delta r)_e\{\langle\Delta r\rangle^T_{\text{rot}} - \langle\Delta r\rangle^{300}_{\text{rot}}\} = (\partial\sigma/\partial\,\Delta r)_e\langle\Delta r\rangle^{300}_{\text{rot}}((T-300)/300)$$

dominates the observed $\sigma_0(T) - \sigma_0(300)$. For CH_3F this is very good, 65 per cent of $\Delta_T(r_{CF})$ is due to rotation. For the others the percentages are 49 per cent for CF_2H_2, 31 per cent for CF_3H, 22 per cent for CF_4, 18 per cent for CF_3Cl, 14·5

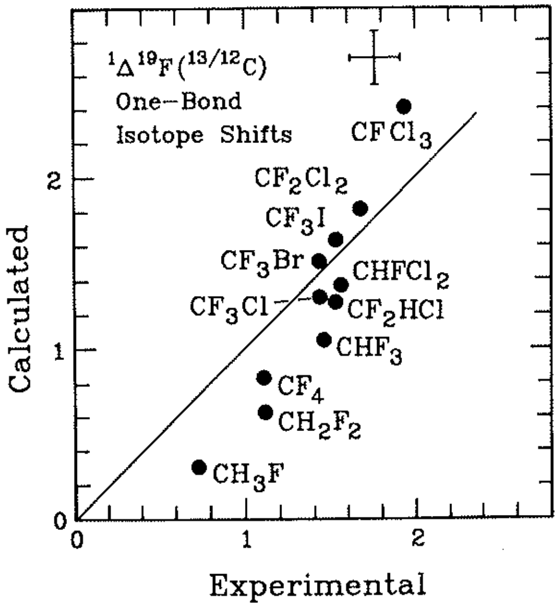

Figure 1. Comparison of calculated and observed one-bond ^{13}C-induced ^{19}F isotope shifts in the fluoromethanes.

per cent for CF_2Cl_2, 10 per cent for $CFCl_3$, 16 per cent for CF_3Br, and 15 per cent for CF_3I. We note that the situation is less favourable for the CCl_nF_{4-n} series.

Including the quadratic terms in equation (1)

$$\sigma_0(T) - \sigma_0(300) \simeq (\partial\sigma/\partial\,\Delta r)_e\{\langle\Delta r\rangle^T - \langle\Delta r\rangle^{300}\} + \tfrac{1}{2}(\partial^2\sigma/\partial\,\Delta r^2)_e\{\langle(\Delta r)^2\rangle^T - \langle(\Delta r)^2\rangle^{300}\},$$

where $\langle\Delta r\rangle^T = \langle\Delta r\rangle^T_{\text{vib}} + \langle\Delta r\rangle^T_{\text{rot}}$ and $\langle(\Delta r)^2\rangle^T = \langle(\Delta r)^2\rangle^T_{\text{vib}}$. In polyatomic molecules there are of course many more quadratic terms than this. For the purpose of estimating the discrepancies between experimental and calculated isotope shifts in figure 1 let us consider only the term in $\langle\Delta r^2\rangle$. Furthermore, let us use the diatomic molecule approximation for the relationship between $\langle\Delta r\rangle$ and $\langle\Delta r^2\rangle$ [14]

$$\langle\Delta r\rangle^T_{\text{vib}} \simeq (3/2)a\langle(\Delta r)^2\rangle^T.$$

Then,

$$\sigma_0(T) - \sigma_0(300) \simeq \{(\partial\sigma/\partial\,\Delta r)_e + (1/3a)(1-f_T)(\partial^2\sigma/\partial\,\Delta r^2)_e\}\{\langle\Delta r\rangle^T - \langle\Delta r\rangle^{300}\},$$

where f_T is that fraction of the total temperature dependence $\{\langle\Delta r\rangle^T - \langle\Delta r\rangle^{300}\}$ which is due to rotation. Thus the empirical derivative $(\partial\sigma/\partial\,\Delta r)_{e,\,\text{emp}}$, obtained from fitting $\sigma_0(T) - \sigma_0(300)$ will be

$$(\partial\sigma/\partial\,\Delta r)_{e,\,\text{emp}} = \{(\partial\sigma/\partial\,\Delta r)_e + (1/3a)(1-f_T)(\partial^2\sigma/\partial\,\Delta r^2)_e\},$$

which is in the range

$$|(\partial\sigma/\partial\,\Delta r)_e| \leqslant |(\partial\sigma/\partial\,\Delta r)_{e,\,\text{emp}}| < |(\partial\sigma/\partial\,\Delta r)_e + (1/3a)(\partial^2\sigma/\partial\,\Delta r^2)_e|.$$

Since a is typically around 2·0 Å^{-1}, and the second derivative is of the same order of magnitude as the first derivative [8], then the neglected terms are about a factor $[1-f_T]/6$ smaller than $(\partial\sigma/\partial\,\Delta r)_e$. When the rotational contribution to Δ_T is sizeable (i.e. $f_T \gtrsim 0{\cdot}3$) then $(\partial\sigma/\partial\,\Delta r)_{e,\,emp}$ should be very close to $(\partial\sigma/\partial\,\Delta r)_e$. For much smaller rotational contributions, the magnitude of the empirical first derivative is overestimated.

In accounting for the ^{13}C-induced ^{19}F isotope shift using only $(\partial\sigma/\partial\,\Delta r)_e\,\Delta_C$, we should expect to get values that are too small, since $(\partial^2\sigma/\partial\,\Delta r^2)_e\{\langle\Delta r^2_{12CF}\rangle - \langle\Delta r^2_{13CF}\rangle\}$ terms have not been included. When we use the empirical derivative from the temperature dependent shielding to calculate the isotope shift, then we underestimate the magnitude of the isotope shift by an amount

$$(f_T - f_{iso})(1/3a)(\partial^2\sigma/\partial\,\Delta r^2)_e\{\langle\Delta r\rangle_{light} - \langle\Delta r\rangle_{heavy}\},$$

where f_{iso} is that fraction of $\{\langle\Delta r\rangle_{light} - \langle\Delta r\rangle_{heavy}\}$ which is due to rotation. In diatomic molecules f_{iso} is identically zero, and in polyatomic molecules it is typically less than 0·01. The different magnitudes of f_T lead to the systematic deviations observed in figure 1. For the CH_nF_{4-n} series the discrepancies between the calculated and experimental isotope shifts correlate with f_T values 0·31 to 0·65. On the other hand, in the $CF_{4-n}Cl_n$ series, in which f_T ranges from 0·10 to 0·18, the agreement between calculated and experimental isotope shifts is within the experimental errors.

4. DISCUSSION

The shielding derivatives which we obtained here serve as electronic indices of the CF bond. Therefore, we expect to find that this magnetic property is related to other magnetic properties. In figure 2 we correlate the empirical values of the shielding derivatives for CH_3F, CH_2F_2, and CHF_3 with the absolute shielding for these molecules and compare with the halomethanes. It is encouraging that the CH_nF_{4-n} molecules fit in with the rest of the halomethanes in a smooth trend covering a range of 196–471 ppm in the absolute ^{19}F shielding, and -350 to -2400 ppm Å^{-1} in the shielding derivative. CH_3F is at one extreme of ^{19}F shielding in CF bonds whereas $CFCl_3$ is at the other end. As discussed above, the empirical derivatives for CH_nF_{4-n} are probably fairly good whereas those for the CCl_nF_{4-n} are overestimated. Thus; the correlation plot in figure 2 may be too steep for the less shielded fluorines. In figure 3 we plot these derivatives with the corresponding ^1J(CF) which spans a range of -160 to -345 Hz [26], and find that CH_nF_{4-n} fits into the trend observed in the halomethanes. This correlation allows us to estimate from ^1J(CF) alone the derivatives $(\partial\sigma/\partial\,\Delta r_{CF})_e$ for $CHFCl_2$ and CF_2HCl. We have observed the one-bond CF coupling constants and ^{13}C-induced ^{19}F isotope shifts in these molecules. From $^1J(CF) = 294$ Hz [27] and 284 Hz (this work), respectively, we read from figure 3 the estimates of the derivatives $(\partial\sigma^F/\partial\Delta r_{CF})_e = -1520$ and -1400 ppm Å^{-1} respectively for $CHFCl_2$ and CHF_2Cl. With these derivatives and typical values of $[\langle\Delta r_{12CF}\rangle - \langle\Delta r_{13CF}\rangle] \simeq 9\times10^{-5}$ Å we calculate the ^{13}C-induced one-bond isotope shifts using equation (8) as $-0{\cdot}137$ and $-0{\cdot}126$ ppm, to be compared with the experimental values of $-0{\cdot}156$ ppm [27] and $-0{\cdot}143$ ppm (this work) respectively for $CHFCl_2$ and CHF_2Cl.

In figure 4 we find that the CH_nF_{4-n} derivatives give a linear plot with n. It is encouraging that this behaviour is similar to that found in CCl_nF_{4-n} [6].

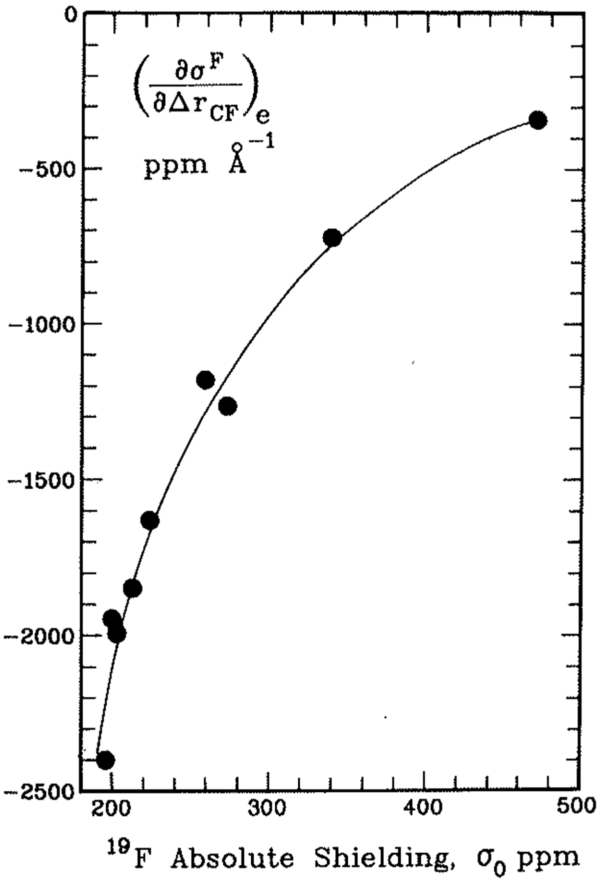

Figure 2. Correlation of the ^{19}F nuclear shielding derivatives (this work and [6]) with the ^{19}F absolute shielding [24, 25] in the methanes.

Finally, we correlate the derivatives with the components of the shielding tensor [28–30] in figure 5. For CH_2F_2 the shielding tensor in the principal axis system has been rotated into the axis system of the halomethanes using the known molecular geometries. We find that the component of shielding parallel to the CF bond correlates with the shielding derivatives for CH_nF_{4-n} as well as CF_3X, although the two sets fall on different straight lines. The shielding tensor perpendicular to the CF bond in the FCF plane also correlates with the derivatives in CH_nF_{4-n}. On the other hand, the shielding tensor component perpendicular to the CFX plane correlates with the derivatives in CF_3X. That CF_3X *and* CH_nF_{4-n} derivatives correlate to *different* components of shielding can be traced to the lone pair orbitals on X which do not exist in H atom. These orbitals contribute to paramagnetic shielding in CF_3X and such a contribution varies with X in a systematic way for the component parallel to the CF bond and for the component perpendicular to the CFX plane. This is also the reason why the correlations to the component parallel to the CF bond do not have the same slope in the two sets of molecules, the contributions to the paramagnetic term are different. While the slopes of all these linear relations are different, they all have the same sign, giving rise to the smooth curve which is shown in figure 2 for the correlation with the isotropic average absolute shielding. It is worthwhile noting the order of CF_4 and CF_3H in straight lines relating the derivatives and the components of the ^{19}F shielding tensor. In both linear relationships CF_4 and CF_3H fall in reverse order. This is the case in the correlation of these derivatives

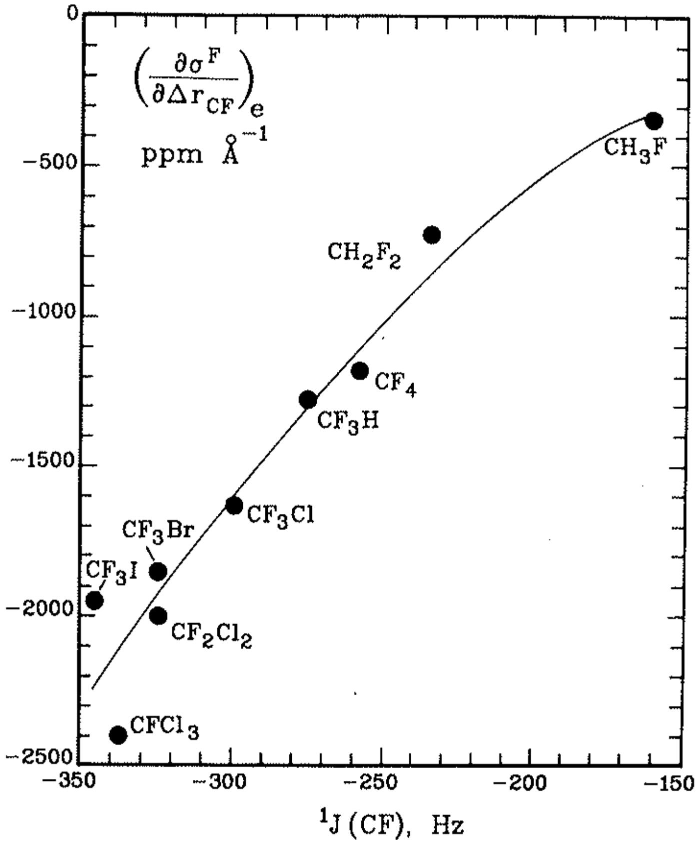

Figure 3. Correlation of the ^{19}F nuclear shielding derivatives with the one-bond ^{13}C–F spin–spin coupling constant [26]).

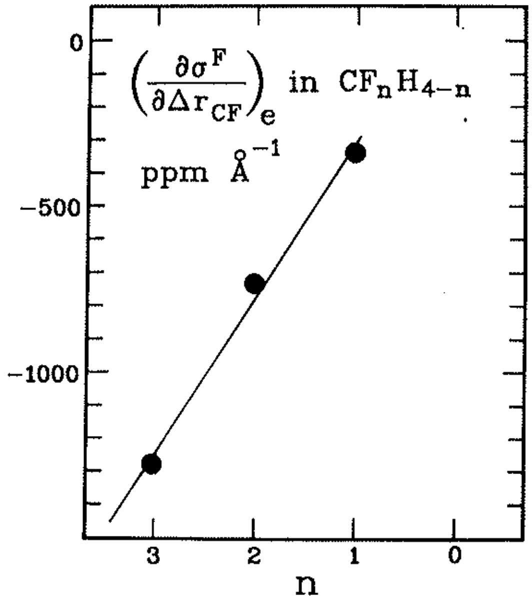

Figure 4. Linear relation between the ^{19}F nuclear shielding derivatives and the extent of H substitution.

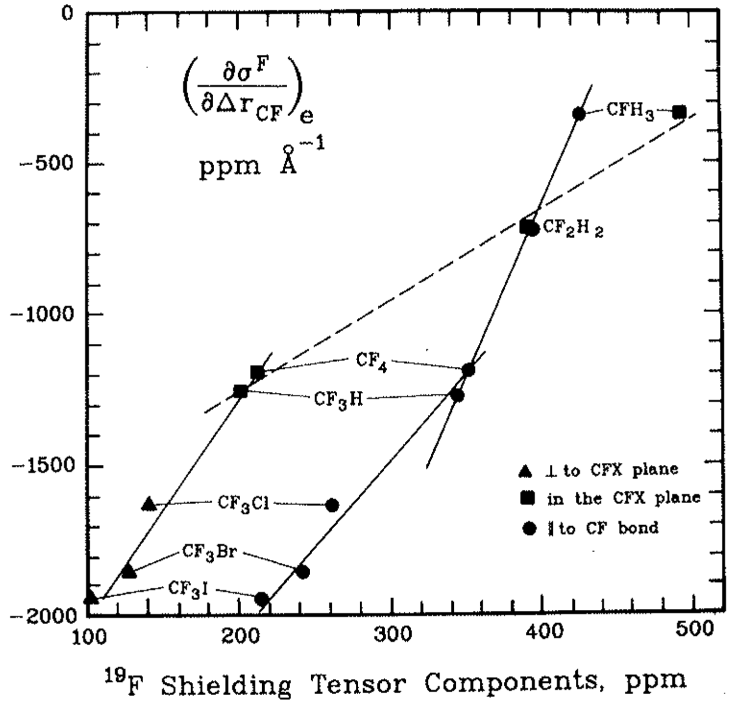

Figure 5. Comparison of the individual components of the ^{19}F shielding tensor in CF_3X and CH_nF_{4-n} [28–30] with the nuclear shielding derivatives in these molecules (this work and [6]).

with $^1J(CF)$ as well. Thus, we are confident that this is the proper order. In the isotropic absolute shielding $(\sigma_{aa} + \sigma_{bb} + \sigma_{cc})/3$ only two of 3 components correlate with the derivative, leading to a somewhat poorer relation of σ_0 to $(\partial\sigma^F/\partial\,\Delta r_{CF})_e$ in figure 2.

5. CONCLUSION

Unlike the effective atomic charges and components of the atomic polar tensors which are found to be sufficiently insensitive to structural differences that they could be used to predict meaningfully accurate vibrational transition moments in hydrocarbons and various fluorine compounds, the shielding derivatives are not so transferable. The difference between this magnetic property and the analogous electrical derivatives, the atomic polar tensors, is that the electric dipole moment is a property of the electronic ground state, whereas in nuclear magnetic shielding, only the diamagnetic part, σ^d, is a property of the electronic ground state. The additive nature of σ^d which had been proposed by Flygare [31] and is generally accepted, could undoubtedly be cast in a form such that the various components of $(\partial\sigma^d/\partial\,\Delta r)_e$ could be defined in an exactly analogous form to the atomic polar tensors. However, the important paramagnetic part, σ^p, which undoubtedly gives a large (very probably a dominant) contribution to the derivative, is a second-order property characteristic of the unperturbed excited states, and has not been found to be made up of additive contributions. The only useful approach at this time is to correlate this second order property with other second order properties such as $^1J(CF)$ which are more directly and easily accessible from experiment.

This research has been supported in part by the National Science Foundation (grant CHE81–16193). This paper was written while CJJ was visiting the Central Institute of Physical Chemistry of the Academy of Sciences of the G.D.R. under the National Academy of Sciences Interacademy Exchange Program. The support of the Academy of Sciences of the G.D.R. and the National Academy of Sciences is gratefully acknowledged.

REFERENCES

[1] NEWTON, J. H., and PERSON, W. B., 1976, *J. chem. Phys.*, **64,** 3036.
[2] KONDO, S., NAKANAGA, T., and SAEKI, S., 1980, *J. chem. Phys.*, **73,** 5409.
[3] KIM, K., and KING, W. T., 1980, *J. chem. Phys.*, **73,** 5591.
[4] LAAKSONEN, A., and KOWALEWSKI, J., 1981, *J. Am. chem. Soc.*, **103,** 5277.
[5] DITCHFIELD, R., and SNYDER, L. C., 1972, *J. chem. Phys.*, **56,** 5823.
[6] JAMESON, C. J., and OSTEN, H. J., 1985, *Molec. Phys.*, **55,** 383.
[7] OSTEN, H. J., and JAMESON, C. J., 1984, *J. chem. Phys.*, **81,** 4288.
[8] DITCHFIELD, R., 1981, *Chem. Phys.*, **63,** 185.
[9] DUNCAN, J. L., MCKEAN, D. C., and SPEIRS, G. K., 1972, *Molec. Phys.*, **24,** 553.
[10] BLOM, C. E., and MÜLLER, A., 1978, *J. molec. Spectrosc.*, **70,** 449.
[11] KIRK, R. W., and WILT, P. M., 1975, *J. molec. Spectrosc.*, **58,** 102.
[12] HARRADINE, D., FOY, B., LAUX, L., DUBS, M., and STEINFELD, J. I., 1984, *J. chem. Phys.*, **81,** 4267.
[13] SHIMANOUCHI, T., and SUZUKI, I., 1961, *J. molec. Spectrosc.*, **6,** 277.
[14] BARTELL, L. S., 1963, *J. chem. Phys.*, **38,** 1827; 1979, **70,** 4581. KUCHITSU, K., and BARTELL, L. S., 1962, *J. chem. Phys.*, **36,** 2460, 2470.
[15] HERSCHBACH, D. R., and LAURIE, V. W., 1961, *J. chem. Phys.*, **35,** 458.
[16] BOYD, R. H., and KESNER, L., 1980, *J. chem. Phys.*, **72,** 2179.
[17] KESTIN, J., RO, S. T., and WAKEHAM, W., 1972, *Physica*, **58,** 165.
[18] SHIMANOUCHI, T., 1970, *Physical Chemistry, An Advanced Treatise*, Vol. 4 (Academic Press), Chap. 6.
[19] KONDO, S., KOGA, Y., and NAKANAGA, T., 1984, *J. chem. Phys.*, **81,** 1951.
[20] TOYAMA, M., OKA, T., and MORINO, Y., 1964, *J. molec. Spectrosc.*, **13,** 193.
[21] JAMESON, C. J., JAMESON, A., K., and OPPUSUNGGU, D., 1984, *J. chem. Phys.*, **81,** 85.
[22] JAMESON, C. J., and JAMESON, A. K., 1984, *J. chem. Phys.*, **81,** 1198.
[23] JAMESON, C. J., 1977, *J. chem. Phys.*, **66,** 4977.
[24] JAMESON, C. J., JAMESON, A. K., and HONARBAKHSH, J., 1984, *J. chem. Phys.*, **81,** 5266.
[25] JAMESON, C. J., JAMESON, A. K., and BURRELL, P. M., 1980, *J. chem. Phys.*, **73,** 6013.
[26] FRANKISS, S. G., 1963, *J. phys. Chem.*, **67,** 752.
[27] HARRIS, R. K., 1963, *J. molec. Spectrosc.*, **10,** 309.
[28] GARG, S. K., RIPMEESTER, J. A., and DAVIDSON, D. W., 1983, *J. chem. Phys.*, **79,** 4101.
[29] WOFSY, S. C., MUENTER, J. S., and KLEMPERER, W., 1971, *J. chem. Phys.*, **55,** 2014.
[30] KUKOLICH, S. G., WANG, J. H. S., and RUBEN, D. J., 1973, *J. chem. Phys.*, **58,** 5474.
[31] FLYGARE, W. H., and GOODISMAN, J., 1968, *J. chem. Phys.*, **49,** 3122. GIERKE, T. D., TIGELAAR, H. L., and FLYGARE, W. H., 1972, *J. Am. chem. Soc.*, **94,** 330. GIERKE, T. D., and FLYGARE, W. H., 1972, *J. Am. chem. Soc.*, **94,** 7277.
[32] CRESSWELL, C. J., and ALLRED, A. L., 1962, *J. Am. chem. Soc.*, **84,** 3966.