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Integrated infrared intensities and atomic polar tensors in fluoroform

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The integrated intensities of the fundamental modes in HCF_3 and DCF_3 have been measured by Wilson–Wells–Penner–Weber method, and the atomic polar tensors were derived. The effective atomic charge for fluorine was found to be $\chi_F/e = 0.598 \pm 0.018$, in good agreement with that in other fluorocarbons. The effective atomic charge for hydrogen was found to be $\chi_H/e = 0.049 \pm 0.006$, a value somewhat lower than that found in other hydrocarbons and their derivatives.

INTRODUCTION

The analysis of integrated infrared intensities in terms of atomic polar tensors[1,2] and effective atomic charges[3] has revealed a hitherto unnoticed order in the structural parameters that control vibrational transition moments. The atomic polar tensor for atom η in a molecule is defined as the conjugate (transposed) gradient of the molecular dipole moment vector, $\hat{P}$, written in various notations as[1]

$$P_X^\eta = \nabla_\eta^* \hat{P} \equiv \begin{bmatrix} \partial P_X/\partial X_\eta & \partial P_X/\partial Y_\eta & \partial P_X/\partial Z_\eta \\ \partial P_Y/\partial X_\eta & \partial P_Y/\partial Y_\eta & \partial P_Y/\partial Z_\eta \\ \partial P_Z/\partial X_\eta & \partial P_Z/\partial Y_\eta & \partial P_Z/\partial Z_\eta \end{bmatrix} \tag{1}$$

and the square of the effective atomic charge is defined as one-third of the sum of squares of the polar tensor components[4]; that is,

$$\chi_\eta^2 \equiv (1/3)\nabla_\eta^* \hat{P} : \nabla_\eta \hat{P} \ . \tag{2}$$

The analysis of the integrated intensities of a variety of hydrocarbons, fluorocarbons, and other materials with diverse structures revealed that the effective charges for the hydrogen and fluorine atoms in these systems fell within the fairly narrow range of values[3,5] $\chi_H/e = 0.088 \pm 0.015$ and $\chi_F/e = 0.57 \pm 0.05$, respectively. Furthermore, the components of their polar tensors were sufficiently insensitive to structural differences that they could be used to predict meaningfully accurate vibrational transition moments in hydrocarbons and various fluorine compounds.[6–10]

Two exceptions were noted early in the interpretation of intensities as atomic properties. The effective charges observed for the hydrogen atoms in HCCH and HCN, $\chi_H/e = 0.198 \pm 0.002$[11] and $\chi_H/e = 0.231 \pm 0.009$,[12] respectively, clearly differ substantially from the values common to the other carbon–hydrogen systems. Indeed, the larger values of the effective charges (and the approximately isotropic polar tensors) of the hydrogen atoms in HCCH and HCN more closely resemble those expected for a free charge in an ionic compound than the smaller values (and the highly directional, anisotropic polar tensors) associated with the atoms in strong covalent bonds. Consequently, the peculiar values of χ_H in HCCH and HCN were rationalized using the chemical argument that, because of their acidity and the stability of acetylydes and cyanides, the protons in HCCH and HCN are markedly "different" from the protons in other hydrocarbons, and their effective charges, after all, should have been expected to be different.[12]

The discovery that the effective hydrogen atom charge in fluoroform was likewise anomalous clearly challenges the usefulness of the arguments used to explain the acetylydes and cyanides. The effective hydrogen charge derived from intensity data in the literature is $\chi_H/e = 0.297$, a value closer to that in HCCH and HCN than other fluorine-substituted hydrocarbons. The above value for χ_H was derived from the differences in the intensities in HCF_3 and DCF_3 reported in the literature,[13] using an intensity sum rule given in the following section.[3] Although effective charges derived from this sum rule are free of many of the uncertainties that plague intensity analyses, they depend upon differences between measured intensities and are especially sensitive to experimental error. Consequently, it seems worthwhile to remeasure the integrated intensities of both HCF_3 and DCF_3 in order to determine if the effective hydrogen charge in fluoroform really is as large as that in acetylene and hydrogen cyanide, and if a new rationalization is required to account for the effective charges in all three substances.

This paper summarizes the results of the remeasurement of the integrated intensities of the fluoroforms. It includes, in addition, the results of an *ab initio* calculation of the atomic polar tensors in HCF_3. It was found that the effective hydrogen atom charge is $\chi_H/e = 0.049 \pm 0.006$, a value that is more representative of that in other hydrocarbons than that in either HCCH or HCN, although outside of the range of values common to the fluorocarbons. Furthermore, the signs of the dipole transition moments obtained by *ab initio* calculation are those that minimize the error between calculated and observed integrated intensities.

INTEGRATED BAND INTENSITIES

Experimental intensities are found by the determination of the concentration dependence of the integrated absorbance,

$$\int \ln(I_0/I)\, d\nu = A_1(Cl) + A_2(Cl)^2 + A_3(Cl)^3 + \cdots \ , \tag{3}$$

where A_1 is the desired integrated intensity. The coefficients A_2, A_3, etc., are measures of dimer, trimer,

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etc., absorption or, more often, of the effects of instrumental distortion. Absorbance due to polymeric species is eliminated by reducing the concentration C of the absorbing species with a compensationg adjustment of the sample thickness l. Instrumental distortion is normally suppressed by pressure broadening the spectrum with a transparent foreign gas. This is the basis of the so-called Wilson–Wells–Penner–Weber method.[14,15] The experimental test that the above effects have been eliminated from band intensity measurements is that the integrated intensity is accurately described by the first term, $A_1(Cl)$, in Eq. (3) only; that is, the integrated absorbance satisfies Beer's law.[16]

The connection between integrated band intensities and molecular parameters has been expressed in several ways because of the use of a variety of systems of units.[5,17] In an effort to accommodate all systems, this relationship is written in an invariant, dimensionless form,

$$A_1/(N_A a_0) = [(\pi\alpha^2/3)(m_e/u)] \left| (\partial\hat{P}/\partial Q)/(eu^{-1/2}) \right|^2 \qquad (4)$$

In Eq. (4), N_A is Avogadro's number, a_0 is the Bohr radius; $\alpha \equiv (\mu_0 c^2/4\pi)(e^2/\hbar c)$ is the fine structure constant, expressing the reciprocal of the velocity of light in atomic units; m_e/u is the electron rest mass in atomic mass units, u; e is the electronic charge; while $\partial\hat{P}/\partial Q$ is the derivative of the molecular dipole vector $\hat{P}$ with respect to the vibrational normal coordinate Q and contains the structural information. Because the term in brackets is a fixed, dimensionless constant,[18] $[(\pi\alpha^2/3)(m_e/u)] = 3.059139 \times 10^{-8}$, the integrated intensity in any of the various systems of units can be found by expressing the quantity $N_A a_0$ appropriately. In particular, if the band intensity is expressed in km mol^{-1} units, then $N_A a_0 = 3.185728 \times 10^{-10}$ km mol^{-1}, so that

$$A_1/\text{km mol}^{-1} = 974.8644 \left| (\partial\hat{P}/\partial Q)/eu^{-1/2} \right|^2 . \qquad (5)$$

The atomic polar tensors are found by transforming the derivatives in Eq. (4) to a Cartesian representation. This may be expressed in a variety of ways also, our favorite being

$$\nabla_\eta^* P = (\partial\hat{P}/\partial Q)(\partial Q/\partial R)\nabla_\eta R + (\partial\hat{P}/\partial\rho)\nabla_\eta\rho + (\partial\hat{P}/\partial\tau)\nabla_\eta\tau , \qquad (6)$$

in which the matrix derivatives are defined in the usual way; for example, $(\partial\hat{P}/\partial Q) = \{(P_Q)_{\alpha j}\} \equiv \{\partial P_\alpha/\partial Q_j\}$, where $\alpha = X, Y, Z$, and Q_j denotes the jth normal coordinate. The three terms on the right of Eq. (6) describe the separate contributions to the polar tensor of internal valence bond–angle displacement (R), and rigid-body rotation (ρ) and translation (τ), respectively. Except for the explicit inclusion of rigid-body translation, Eq. (6) may be recognized as the same as that given by Person and Newton,[1]

$$P_X = P_Q L^{-1} B + P_\rho \beta , \qquad (7)$$

where, for instance, $L^{-1} \equiv (\partial Q/\partial R)$, $B \equiv (\partial R/\partial X)$, and $\beta \equiv (\partial\rho/\partial X)$ are matrices introduced by Wilson.[19]

Effective atomic charges are found either from the computed polar tensors using Eq. (2), or directly from experimental data using an intensity sum rule. This sum rule follows from Eq. (6) or (7) and expresses the invariance of the traces of the products of matrices under orthogonal transformations, the result of which is[3]

$$\sum A_j/(N_A a_0) + \Omega/(N_A a_0) = [\pi\alpha^2(m_e/u)] \sum_\eta (u/m_\eta)(\chi_\eta/e)^2 , \qquad (8)$$

where (m_η/u) denotes the mass of atom η. The second term on the left of Eq. (8) defines the absorption intensity due to rigid body motion,

$$\Omega/(N_A a_0) \equiv (\pi\alpha^2/3)(m_e/u)(u/e^2) \times \left(\frac{P_Y^2 + P_Z^2}{I_{XX}} + \frac{P_Z^2 + P_X^2}{I_{YY}} + \frac{P_X^2 + P_Y^2}{I_{ZZ}} + 3\,\frac{(q^2)}{M} \right) , \qquad (9)$$

in which P_Y denotes a component of the permanent electric moment of the molecule, I_{XX} is a principal moment of inertia, and q^2/M is the net molecular charge squared, divided by the molecular mass M. Thus, if the intensities of all of the fundamentals of a molecule and any of its isotopic derivatives are known, the effective charge of the isotopically substituted atom, at least, can be easily determined by difference, using the sum rule, Eq. (8).

Any uncertainty in the effective atomic charges derived from the sum rule is due to error in the experimental intensities. Unlike those computed from the polar tensors using (2), these effective charges are independent of errors in the normal coordinates, uncertainties in the signs of the dipole derivatives, $(\partial\hat{P}/\partial Q)$ derived from (4), or errors introduced by inaccurately separating the intensities of overlapping absorption bands. On the other hand, the effective charges derived from the intensity sum rule depend upon differences in intensities, and are often quite sensitive to small errors in the experimental data. Consequently, in addition to the requirement mentioned above, that the experimental integrated absorbances satisfy Beer's law, a second, necessary condition that the integrated intensities are both accurate and have been analyzed correctly is that the effective atomic charges computed from the polar tensors for each isotopic species and from the sum rule all be commensurate. In the summary of our study of the fluoroforms, it will be demonstrated that both of these criteria are satisfied with excellent precision.

EXPERIMENTAL DETAILS

The HCF_3 samples used in these measurements were obtained from the Matheson Chemical Co., further purified by trap-to-trap distillation. The DCF_3 samples were prepared by the decarboxylation of CF_3COOK in dideuteroethylene glycol[20–23]

$$CF_3COOK + (CH_2OD)_2 \rightarrow DCF_3 + CO_2 + KO(CH_2)_2OD .$$

For these measurements 0.125 mol CF_3COOK and 0.125 mol $(CH_2OH)_2$ were dissolved in 2.5 mol D_2O, and the mixture distilled under reduced pressure at 70 °C to remove excess water. The residue was then heated at 160 °C for about 4 h, and the DCF_3 and CO_2 evolved was collected. The CO_2 was removed by passing the gas mixture through an Ascarite® column, and the DCF_3 was further purified by trap-to-trap distillation. The gas samples used were found to contain $95 \pm 2\%$ of DCF_2 and $5 \pm 2\%$ of

TABLE I. Concentration dependence of the integrated absorbance of the fundamental modes of HCF_3 as defined in Eq. (3).[a]

	Model	A_0 (cm^{-1})	A_1 ($km\ mol^{-1}$)	A_2 ($dam^3\ mol^{-2}$)
	I		23.85 (0.10)	
ν_1 (3036 cm^{-1})	II	0.3(0.3)	23.65 (0.21)	
	III		24.21 (0.24)	−2.01 (1.29)
	I		626.82 (0.51)	
$\nu_2+\nu_5$ (1150 cm^{-1})	II	−0.02 (0.11)	627.29 (2.27)	
	III		626.73 (2.71)	18. (612.)
	I		12.11 (0.05)	
ν_3 (700 cm^{-1})	II	0.1 (0.3)	12.06 (0.17)	
	III		12.30 (0.24)	−1.00 (1.29)
	I		81.96 (0.07)	
ν_4 (1372 cm^{-1})	II	−0.002 (0.057)	81.96 (0.17)	
	III		81.83 (0.30)	4.02 (9.48)
	I		4.17 (0.02)	
ν_6 (507 cm^{-1})	II	−0.01 (0.29)	4.17 (0.07)	
	III		4.19 (0.09)	

[a] The dispersions estimated by least-squares adjustment are given in parentheses.

HCF_3, evidently caused by the incomplete conversion of $(CH_2OH)_2$ to $(CH_2OD)_2$, as determined by the relative intensities of the 52*u* and 51*u* peaks (DCF_2 and HCF_2) in the mass spectra of the final mixture. The concentration of HCF_3 in this mixture was further verified by the band intensity of its ν_4 mode, following the procedures described next.

The details of the intensity measurements on the fluoroforms are similar to those reported earlier on measurements on other systems.[11,12,24] In summary, the spectra were obtained using a Perkin-Elmer Model 301 spectrometer with a spectral resolution of about 1 cm^{-1}. The gas samples were contained in a Teflon-coated cell with a nominal length of 5 cm and the spectra were pressure-broadened with helium at total pressures of 6.89 MPa. These high pressures were observed to be adequate for collision broadening but still too low to cause noticeable induced absorption.

Because the band absorbances of the ν_4 and the overlapping $\nu_2+\nu_5$ bands in HCF_3, and the ν_4 band in DCF_3 are very strong, correspondingly low fluoroform concentrations were used to determine the intensities of these bands from Eq. (3). To avoid excessive error in determining these low concentrations by direct pressure measurement, the gas samples were first diluted about 10-fold with helium, so that all pressure measurements on either pure or diluted samples fell within the same range, 1–20 kPa, and had the same precision, ± 6 Pa. The uncertainty in the composition of the helium–fluoroform samples, introduced by dilution, was taken to be less than 1%, as determined by the precision of the pressure measurements made in preparing the mixtures, and from the integrated absorbances in the mixtures of the ν_1 mode of HCF_3 and the ν_5 mode of DCF_3, the intensities of which were determined from the nondiluted samples. In all, the integrated absorbances of each fundamental were measured at eight different fluoroform concentrations.

The integrated intensities were determined by the least-squares analysis of the integrated absorbances. In order to test these measurements for one class of systematic error, three alternative models based on Eq. (3) were examined. In the first (Model I), it was assumed that the data satisfied Beer's law exactly, by including only the term containing A_1 in Eq. (3). In the second (Model III), it was assumed that the data do not satisfy Beer's law, and a second term containing A_2 was also included. Finally, a third possibility was examined (Model II) by including a constant A_0 to Eq. (3), along with the linear term. The values of the constants based upon these models are summarized in Tables I and II.

The results given in these two tables indicate that our measurements satisfy the Beer's law criterion with good precision.[16] The integrated intensities A_1 obtained from the three models are not only in good agreement with

TABLE II. Concentration dependence of the integrated absorbance of the fundamental modes of DCF_3 as defined in Eq. (3).[a]

	Model	A_0 (cm^{-1})	A_1 ($km\ mol^{-1}$)	A_1 ($dam^3\ mol^{-2}$)
	I		29.45 (0.11)	
ν_1 (2257 cm^{-1})	II	0.08 (0.46)	29.38 (0.45)	
	III		29.50 (0.57)	−0.4 (4.7)
	I		75.67 (0.18)	
ν_2 (1109 cm^{-1})	II	0.3 (0.2)	75.02 (0.43)	
	III		76.74 (0.42)	−18.59 (6.75)
	I		12.78 (0.02)	
ν_3 (693 cm^{-1})	II	0.2 (0.2)	12.69 (0.10)	
	III		12.89 (0.12)	−0.50 (0.57)
	I		577.22 (0.50)	
ν_4 (1209 cm^{-1})	II	0.05 (0.07)	576.21 (1.63)	
	III		578.76 (2.04)	−301. (373)
	I		47.31 (0.23)	
ν_5 (974 cm^{-1})	II	0.1 (0.6)	47.16 (0.66)	
	III		47.49 (1.14)	−1.5 (9.6)
	I		4.48 (0.01)	
ν_0 (503 cm^{-1})	II	0.1 (0.2)	4.44 (0.04)	
	III		4.53 (0.06)	−0.10 (0.11)

[a] The dispersions estimated by least-squares adjustment are given in parentheses.

TABLE III. The integrated band intensities of the fundamental modes in CHF_3 and CDF_3 in km mol^{-1} units.

		Sign $\partial P/\partial Q$	Theoretical values SCF	Experimental values			
				This work[a]	Others		
CHF_3	ν_1	+	38.8	23.9 ± 0.4	23.5[b]	24.8[c]	35.2[d]
	$\nu_2+\nu_5$	(+, −)	167. + 563 = 730	626.8 ± 6.6	540.	695.	860
	ν_3	+	29.6	12.1 ± 0.2	14.6	13.2	14.9
	ν_4	−	136.	82.0 ± 0.3	87.6	87.5	97.2
	ν_6	+	16.6	4.17 ± 0.07	4.9	4.6	5.2
	$\sum A$		951.	749 ± 7	671.	825.	1013.
CDF_3	ν_1	+	56.3	29.5 ± 0.7		24.9[c]	
	ν_2	+	145.	75.7 ± 1.7		85.5	
	ν_3	+	31.2	12.8 ± 0.3		12.4	
	ν_4	+	674.	577. ± 13		531.7	
	ν_5	−	26.0	47.3 ± 1.3		43.7	
	ν_6	+	15.9	4.48 ± 0.10		5.04	
	$\sum A$		948.	747 ± 13		703.	

[a] The uncertainties represent the estimated 99% confidence interval, based upon the dispersions given in Tables I and II, and the estimated magnitude of systematic error; see text.

[b] Reference 25.

[c] Reference 13.

[d] Reference 26.

TABLE IV. Structural data for the fluoroforms.

Masses (u)[a]: $m_H = 1.007825$, $m_D = 2.014102$, $m_F = 18.998405$, $m_C = 12$

Structure: $R_{CH} = 0.1098$ nm, $R_{CF} = 0.1332$ nm, $F\hat{C}F = 108.8°$, Dipole[b]: 5.504×10^{-30} cm

Harmonic frequencies (cm^{-1})[c]:

HCF$_3$						DCF$_3$					
A_1	ν_1	3077	E	ν_4	1397.5	A_1	ν_1	2268	E	ν_4	1235.5
	ν_2	1154.7		ν_5	1187.5		ν_2	1123.3		ν_5	989
	ν_3	709.7		ν_6	518.9		ν_3	704.4		ν_6	513.7

Symmetry coordinates[d]:

$S_1 = (1/\sqrt{3})\,(R_{CF_1} + R_{CF_2} + R_{CF_3})$

$S_2 = (1/\sqrt{6})\,[a(F_1\hat{C}F_2 + F_1\hat{C}F_3 + F_2\hat{C}F_3) - b(F_1\hat{C}H + F_2\hat{C}H + F_3\hat{C}H]$

$S_3 = R_{CH}$

$S_4 = (1/\sqrt{2})\,(R_{CF_2} - R_{CF_3})$

$S_5 = (1/\sqrt{2})\,(F_1\hat{C}F_3 - F_2\hat{C}F_2)$

$S_6 = (1/\sqrt{2})\,(F_2\hat{C}H - F_3\hat{C}H)$

$a = 1.01188, \quad b = 0.93797$

[a] Reference 28.

[b] Reference 29.

[c] Reference 27.

[d] Reference 30.

TABLE V. Normal coordinates, $(\partial S/\partial Q)$, in HCF_3 and DCF_3 in units of $u^{-1/2}$.

		HCF$_3$[a]				DCF$_3$[a]		
		Q_1	Q_2	Q_3		Q_1	Q_2	Q_3
A_1	S_1	0.04899	0.26261	−0.10424	S_1	0.07848	0.25721	−0.09958
	S_2	−0.13982	−0.43412	−0.32719	S_2	−0.21306	−0.40032	−0.33077
	S_3	−1.03705	0.00252	−0.00486	S_3	−0.76038	0.03973	0.00183
		Q_4	Q_5	Q_6		Q_4	Q_5	Q_6
E	S_4	0.15051	0.37212	0.03999	S_4	−0.38447	0.11610	0.03780
	S_5	0.16340	0.27661	−0.30213	S_5	−0.32403	0.01852	−0.29860
	S_6	−1.18702	0.12287	−0.10395	S_6	0.55582	0.70181	−0.12906

[a] The indices labelling the normal coordinates correspond to the labels identifying the normal frequencies in Table IV.

TABLE VI. The atomic polar tensors derived from the band intensities in HCF_3 and DCF_3, and from *ab initio* calculations, given in atomic units (e).[a]

	X_H	Y_H	Z_H	X_{F_1}	Y_{F_1}	Z_{F_1}	X_C	Y_C	Z_C
HCF_3[b]	0.032(0.006)	0	0	−0.885(0.024)	0	0.266(0.012)	1.730(0.035)	0	0
	0	0.032(0.006)	0	0	−0.290(0.004)	0	0	1.730(0.035)	0
	0	0	−0.072(0.003)	0.106(0.010)	0	−0.341(0.007)	0	0	1.095(0.021)
DCF_3	0.040(0.005)	0	0	−0.888(0.013)	0	0.273(0.005)	1.730(0.019)	0	0
	0	0.040(0.005)	0	0	−0.292(0.005)	0	0	1.730(0.019)	0
	0	0	−0.061(0.004)	0.105(0.006)	0	−0.343(0.004)	0	0	1.091(0.012)
SCF	−0.007	0	0	−0.823	0	0.214	1.898	0	0
	0	−0.007	0	0	−0.437	0	0	1.898	0
	0	0	−0.079	0.103	0	−0.486	0	0	1.537

[a] The uncertainties in the tensor components, given in parentheses, represent the 99% confidence interval, see text.

[b] The H, C, and F atoms define the XZ plane.

one another, the largest difference being 1.6% for the ν_3 mode of HCF_3, but the other parameters A_0 and A_2 are also of dubious statistical significance. Consequently, significant uncertainty is not introduced if we assume our measurements satisfy Beer's law, and only the intensities computed using Model I are considered in the following analysis.

RESULTS

The integrated intensities of the fundamental bands in the fluoroforms are collected in Table III, where they are compared with other measurements reported in the literature.[13,25,26] The uncertainties in the band intensities given in Tables I and II represent the calculated dispersions, under the assumption that the measurements are subject only to random experimental error. These estimates are a useful measure of the precision with which our results satisfy Beer's law, but they probably do not indicate the true accuracy because of the systematic errors described in the preceding section. The uncertainty in the concentrations of the gas samples used to measure the $\nu_2 + \nu_5$ modes in HCF_3 and the ν_4 mode in DCF_3 due to dilution with helium is at most 1%, and the uncertainty in the purity of the DCF_3 used here was at most 2%. To obtain a more realistic confidence interval of the intensities of each mode, these systematic errors were combined with the generally smaller uncertainties due to random error where applicable, and are given in Table III.

In order to extract structural information from the integrated intensities, the atomic polar tensors need to be computed and analyzed. For this purpose, the normal coordinates for HCF_3 and DCF_3 were computed by the usual methods, using the force constants reported by Kirk and Wilt.[27] Relevant structural information and the resulting normal coordinates are summarized in Tables IV and V, respectively.

The actual calculation of the polar tensors using Eqs. (4) and (6) is ambiguous because of the uncertainty of the signs of the $(\partial \hat{P}/\partial Q)$ components, and because only the sum of the ν_2 and ν_5 band intensities was measured. To help resolve the sign ambiguities, *ab initio* values for the polar tensors were derived. Using the GAUSSIAN-70 program system and the standard 6-31 Gaussian basis set,[31] the dipole derivatives in Eq. (1) were estimated, with a precision of about ±0.003e, by the finite displacement of the atoms from their positions in the equilibrium configuration described in Table IV. The resulting polar tensors are given in Table VI, and the signs in the $(\partial \hat{P}/\partial Q)$ array and the integrated intensities derived from the computed polar tensors are included in Table III.

To test the validity of these *ab initio* calculations, and estimate the separated intensities of the ν_2 and ν_5 modes in HCF_3, the observed intensities were analyzed using all possible sign combinations for the $(\partial \hat{P}/\partial Q)$ derivatives. For each of the 64 sign combinations, the polar tensors in DCF_3 were computed using the measured band intensities. Assuming that the ratio of band intensities for the ν_2 and ν_5 modes in HCF_3 is equal to that computed using the polar tensors of DCF_3, the intensity in the overlapping $\nu_2 + \nu_5$ band was partitioned between the two

TABLE VII. Effective atomic charges, mean dipole derivatives, and atom anisotropies.[a]

	χ_H/e	$\bar{P}_H/e$	β_H/e	χ_F/e	$\bar{p}_F/e$	β_F/e
HCF_3, Eq. (2)	0.049 ± 0.004	− 0.003 ± 0.003	0.104 ± 0.009	0.596 ± 0.016	− 0.505 ± 0.012	0.670 ± 0.110
DCF_3, Eq. (2)	0.048 ± 0.005	0.006 ± 0.005	0.101 ± 0.009	0.599 ± 0.009	− 0.508 ± 0.007	0.675 ± 0.064
Sum Rule, Eq. (8)	0.049 ± 0.029					
SCF, Eq. (2)	0.046	− 0.031	0.072	0.622	− 0.582	0.479
FCH_3, Eq. (8)[b]	0.094 ± 0.006	− 0.019 ± 0.008	0.195 ± 0.014	0.577 ± 0.040	− 0.481 ± 0.035	0.679 ± 0.082

[a] The uncertainties define extreme values computed from the uncertainties in the polar tensor components Table VI, or the intensity sums, Table III.

[b] Reference 32.

modes, and the polar tensors were computed from the HCF_3 measurements.

We were pleased to find that the sign combination derived in the *ab initio* calculation gave the best results. Not only were the polar tensors from HCF_3 and from DCF_3 in closest agreement, but the band intensities of HCF_3 computed from DCF_3 polar tensors, and conversely, were closest to the experimental values. Thus, we adopted the signs obtained from the *ab initio* calculations as the proper combination, and give the polar tensors derived from this set in Table VI. The uncertainties in their components represent the estimated 99% confidence interval, as obtained from the uncertainties in the measured band intensities in Table III, assuming an additional 5% error in the intensities of the ν_2 and ν_5 bands in HCF_3 representing the estimated error introduced from the intensity separation procedure described above.

DISCUSSION

Overall, the atomic polar tensors given in Table VI are in good agreement with one another. The experimentally derived polar tensors for the F and C atoms in HCF_3 and DCF_3 are in essentially exact agreement with one another, while the hydrogen and deuterium tensors just miss agreeing within their estimated uncertainties. To improve the agreement between the H and D atom polar tensors would require a substantial improvement in the accuracy of these measurements, and perhaps the inclusion of anharmonicity in the analysis, because the intensities are reasonably insensitive to the hydrogen atom polar tensor. Indeed, the sums of intensities, given in Table III, appear to be independent of isotopic substitution.

The polar tensors derived by the *ab initio* calculations are also in fair agreement with the experimental results. The intensities derived from them, included in Table III for comparison, differ substantially in magnitude from the measured values, but are highly correlated with the experimental values ($r \simeq 0.999$). Clearly, then, the most serious disagreement between the theoretical and experimental results is the sign discrepancy in the H atom polar tensor. Although this discrepancy does not influence the signs of the $(\partial\hat{P}/\partial Q)$ derivatives, for which the F atom polar tensors are dominant in this system, it nonetheless points out a potential hazard in developing a structural model of vibrational intensities based only upon theoretical calculations.

One of the main purposes of these measurements, as stated in the beginning, is a redetermination of the effective atomic charges in fluoroform. The effective charges derived from these measurements are given in Table VII, along with two other tensor invariants,[32] the mean dipole derivative,

$$\bar{P}_\eta \equiv (1/3)[(\partial P_X/\partial X_\eta)+(\partial P_Y/\partial Y_\eta)+(\partial P_Z/\partial Z_\eta)] , \qquad (10)$$

and the atom anisotropy,

$$\beta_\eta^2 \equiv (9/2)(\chi_\eta^2-\bar{P}_\eta^2) . \qquad (11)$$

These results summarized in Table VII indicate that our measurements satisfy the second necessary condition, mentioned at the end of the introduction. Not only do these measurements satisfy Beer's law, the first condition, but also the effective charges derived separately from the polar tensors of the isotopes, Eq. (2), and from the intensity sum rule, Eq. (8), are all in excellent agreement with one another, as are most of the other tensor invariants. The single exception seems to be the mean dipole derivative for hydrogen, $\bar{P}_H$, but even here they all agree, that it is very small.

For comparison, the invariants derived from the polar tensors in FCH_3 are also given in Table VII.[32] To the extent indicated by the invariants, the transferability of the fluorine atom polar tensor is clearly demonstrated, but that for the hydrogen atom is not. The effective hydrogen charge found here differs significantly from that in FCH_3, and falls outside of the range, $\chi_H/e = 0.088 \pm 0.015$, observed for most other hydrocarbons.[3] This value also differs significantly from the value $\chi_H/e = 0.297$ derived from intensity measurements reported in the literature,[13] but is more representative of the small effective charges associated with atoms in strong covalent bonds, rather than those associated with "acidic" protons. Thus, while the effective hydrogen charge appears to be structure dependent, these measurements suggest that less drastic assumptions will be required to account for that dependence than the earlier intensity measurements indicated.

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