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# $^1\text{H}$ , $^{19}\text{F}$ and $^2\text{H}$ NMR of monofluoromethane and deuterated analogues partially oriented in nematic liquid crystals

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A  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^2\text{H}$  nuclear magnetic resonance study of eight isotopomers of fluoromethane ( $\text{CH}_3\text{F}$ ) has been carried out under virtually identical experimental conditions. An analysis of the observed anisotropic couplings on the basis of bond additivity has been performed and the underlying assumption of bond additivity has been found to be adequate. In an accurate description of the solute orientation ‘non-rigid’ contributions such as vibration–rotation interaction, and harmonic and especially anharmonic vibrational corrections have to be included. The present study indicates the presence of a contribution to the observed anisotropic carbon–fluorine couplings due to an anisotropy in  $J_{\text{CF}}$ .

## 1. Introduction

Since the introduction of liquid crystals as solvents causing the partial orientation of solute species [1], nuclear magnetic resonance (NMR) has proved to be an important technique for an abundance of investigations. From the observed spectral NMR parameters, detailed information about anisotropic molecular properties can be deduced [2–5]. Additionally, from the observed anisotropic NMR splittings, insight about the solute–solvent interactions responsible for the observed partial orientation can be obtained. This interaction can be assumed to consist of long- and short-range contributions. In a simple picture [6–8] the long-range contribution, which is electrostatic in nature, can be viewed as a tensor product of some electronic solute property which couples with some solvent ‘mean field’, and possible deviations from this mean-field approach are not considered. Moreover, the short-range contributions to the average orientation are assumed to depend on the size and shape of the solute molecule.

In the framework of this simplified picture, the use of molecular hydrogen and its deuterated analogues as probe molecules has revealed the presence of a non-zero electric field gradient (efg) in nematic liquid crystals [8–10]. For molecular hydrogen, the orientation appears to be dominated by the interaction between this liquid crystal efg and the solute molecular quadrupole moment. This interaction explains both the sign and most of the magnitude of the orientation in a large variety of nematic solvents. An important breakthrough in the study of possible contributions to the orientation of solutes has been the use of *mixtures* of liquid crystals possessing average efg’s of opposite sign. When the component liquid crystal materials are mixed in appropriate amounts, zero-efg mixtures can be formed, as illustrated in a number of cases [8–11]. In this study we employ the zero-efg liquid crystal mixture made up of 54.7 wt.% Merck ZLI 1132 in *N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline (EBBA) at 302 K. In this ‘magic mixture’ the orienting interaction between the solvent efg and the solute molecular quadrupole moment can be removed selectively. In the case of

molecular deuterium, this interaction accounts for most of the orientation, and only small anisotropic couplings remain [8–10]. When solutes other than molecular deuterium are dissolved in a ‘magic mixture’ it has been assumed that they also experience a zero efg. However, their degree of orientation usually is not reduced to the same extent as that of molecular deuterium. Extensive previous research has shown that the remaining orientation can be described in terms of a single size and shape-dependent mechanism. Moreover, this mechanism can be adequately modelled in a phenomenological fashion using a very limited number (one or two) of adjustable parameters [11–14].

The above simple picture has met with a reasonable degree of success [11–14]. The solute orientation in nematic phases has been described by invoking two mechanisms: (i) the interaction between solvent efg and solute quadrupole moment; and (ii) a size and shape-dependent contribution. In a zero-efg mixture, only the second orientation mechanism remains. In such a solvent the orientation for a large body of solutes with very different multipole moments, and unrelated in size and shape, can be predicted at approximately the 10% level. However, one should not be blind to the fact that the solute–solvent interaction could take on a more complicated form than has been assumed in the simple models. The above approach has been criticized, mainly on theoretical grounds, in a number of papers [15–18] in which the simple product form used for the long-range solute–solvent interaction has been questioned [15–18], and in which the importance of the shape of the solvent molecules has been emphasized [18]. However, the predictive power of these more sophisticated approaches when applied to a wide range of solutes and solvents is still limited to date.

In the present study monofluoromethane and its deuterated analogues have been studied by NMR in the above zero-efg nematic mixture, as well as in the pure component liquid crystals ZLI 1132 and EBBA. A total of 34 dipolar couplings might be observed if all of the  $^2\text{H}$  and  $^{13}\text{C}$  isotopically-substituted monofluoromethane species were available. Here, eight isotopomers are studied and 29 out of these couplings have been measured, including satellites from  $^{13}\text{C}$  nuclei in natural abundance.

The experimental anisotropic spin–spin couplings  $D_{ij}^{\text{exp}}$  give information on relative internuclear distances and bond angles of the solute. However, a careful interpretation should pay proper attention to a number of points, as only their cumulative effects are revealed in the NMR observables: (i) the  $D_{ij}^{\text{exp}}$  are (thermal) averages over all vibrational motions; (ii) the couplings may be affected by vibration–rotation correlation effects due to anisotropic interactions of the solute with the liquid crystalline environment which are also responsible for the anisotropic orientation of the solute; and (iii) some of the couplings may include significant contributions from the anisotropy,  $\Delta J_{ij}$ , of the corresponding indirect spin–spin coupling tensor. To estimate these effects accurately for a probe molecule, sufficient data from other sources must be available. In this respect monofluoromethane is a judicious choice. The molecular geometry [19, 20], and both the quadratic harmonic [20] and cubic anharmonic [21] force fields have been determined accurately and consequently can be used to calculate vibrational corrections. Anisotropies in the indirect spin–spin coupling between  $^1\text{H}$  and  $^1\text{H}$ ,  $^{13}\text{C}$  or  $^{19}\text{F}$ , respectively, can be safely neglected [4], but may well be significant for the coupling between  $^{13}\text{C}$  and  $^{19}\text{F}$  [22]. Effects of vibration–rotation interaction are known to play a dominant role for methane in nematic solvents and theoretical models have been developed by Snijders *et al.* [7] and by Lounila and Diehl [23] based on the correlation between molecular rotation and

(small-amplitude) vibrations to explain the observed NMR spectra of methane and its deuterated analogues successfully. These effects may well be also significant in other, less symmetrical solutes.

The present study has been motivated by a number of considerations. First, to study the problem at hand, experimental data on different isotopomers obtained under virtually identical experimental conditions are essential. Secondly, the relative importance of the different 'rigid' and 'non-rigid' contributions (following the somewhat crude shorthand terminology introduced previously [7]) which may influence the observed anisotropic couplings should be assessed in some detail. Thirdly, attention should be given to the possible importance of an anisotropy in the indirect  $^{13}\text{C}$ -F coupling. Fourthly, in order to reduce the number of adjustable parameters required to fit the experimental data the assumption of bond additivity has to be invoked and should be tested.

## 2. Experimental

The liquid crystals used were: (i) EBBA: *N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline, synthesized according to the procedure described in [24]; (ii) 1132: Merck ZLI 1132, used without further purification; and (iii) a mixture of 54.7 wt% 1132 and 45.3 wt% EBBA.

Methyl fluoride and its deuterated analogues were synthesized from the corresponding isotopically-substituted methanol in two steps as outlined by Edgell and Parts [25, 26]. The appropriate methanol was first converted to methyl *p*-toluenesulphonate. This, in turn, gives the desired fluoromethane upon reaction with potassium fluoride. Methanol and methanol- $d_4$  were obtained from Aldrich,  $\text{CH}_2\text{-DOH}$  and  $\text{CHD}_2\text{OH}$  were obtained from Merck, Sharp and Dohme, Canada. All methanols were used without further purification.

Methyl *p*-toluenesulphonate was prepared following [27], with minor adaptations: 1.75 g (54.6 mmol) of methanol and 11.4 g (59.8 mmol) of *p*-toluenesulphonyl chloride were added to 100 ml of anhydrous 2,4,6-trimethylpyridine. The resulting solution was stirred for 7 h at 20–25 °C under nitrogen and then poured into 200 ml of an ice-water mixture. The cold mixture was acidified with 100 ml of concentrated hydrochloric acid and then extracted with ether (4 × 50 ml). The combined ethereal extracts were washed successively with aqueous (2 M) hydrochloric acid and with saturated sodium chloride solution until the extract was no longer acidic, dried over sodium sulphate and, after evaporation of the ether, fractionally distilled. From the fraction collected at 80–100 °C (0.2 mmHg) the methyl *p*-toluenesulphonate was isolated by preparative column chromatography using a Jobin-Yvon Miniprep equipped with a silica gel column (Merck 60H) using petroleum ether (b.p. 40–60 °C) with 15% ethyl acetate as the eluting solvent. Yields were between 15 and 40%. The product was identified and tested for purity by GC/MS and by NMR.

Methyl fluoride was prepared as follows: 1.90 g (10.2 mmol) of methyl *p*-toluenesulphonate and 1.20 g (20.6 mmol) of anhydrous potassium fluoride were added to a dry 50 ml round-bottomed flask. The flask was connected to a vertically mounted reflux condenser, which in turn was connected by a short PVC tube that included a nitrogen gas inlet, to a cold trap cooled with liquid nitrogen. The trap was connected to a vacuum line and the pressure in the system was reduced to about 50 mmHg. The flask was heated gradually to 250 °C in 2 h and maintained at this temperature for another 5 h. Then the cold trap was closed and transferred to a small

vacuum rack. The monofluoromethane was isolated by a fractional gas distillation using an isopropyl alcohol/liquid nitrogen mixture to warm the cold trap slowly. Assuming methyl fluoride to be an ideal gas, a yield in the second step of 70–85% was obtained. The overall yield was 10–35%.

Samples containing a mixture of all the isotopically-substituted monofluoromethanes were prepared in 1132, EBBA and the 54.7 wt% 1132/EBBA mixture. The liquid crystals were placed in 9 mm o.d. Pyrex glass tubes and thoroughly degassed by several freeze–pump–thaw cycles. The tubes were then cooled to liquid nitrogen temperature and the methyl fluorides condensed into them. The tubes were then flame-sealed and pressure-tested in an oven at approximately 400 K for 15 min.

$^1\text{H}$ ,  $^2\text{H}$  and  $^{19}\text{F}$  free induction decays for the samples were recorded on a Bruker MSL400 wide-bore NMR spectrometer operating at 9.4 T (400.13 MHz for  $^1\text{H}$ , 61.42 MHz for  $^2\text{H}$  and 376.43 MHz for  $^{19}\text{F}$ ). The spectra of the samples were obtained using either a 10 or 20 mm broadband probe, the  $^2\text{H}$  signal being measured through the observe channel and both the  $^1\text{H}$  and  $^{19}\text{F}$  signals through the decouple channel. Thus  $^1\text{H}$ ,  $^2\text{H}$  and  $^{19}\text{F}$  NMR spectra were obtained without removing the sample from the probe, ensuring that these spectra were recorded under the same experimental conditions. All experiments were performed with sample tubes spinning around an axis parallel to the external magnetic field. The temperature was controlled by means of a variable-temperature gas-flow unit. All samples were heated to the isotropic phase and mixed thoroughly before being placed into the probe and left to equilibrate for at least half an hour before the NMR spectra were recorded.

### 3. Analysis of NMR spectra

The NMR spectra observed for a partially aligned system of nuclear spins such as monofluoromethane (with nuclear magnetic spin quantum number  $I_i$  for nucleus  $i$ ) and with the nematic director parallel to the external magnetic field along a space-fixed axis  $Z$  are interpreted using a Hamiltonian  $\mathbf{H}$  (in Hz) given in the usual notation by:

$$\mathbf{H} = -\sum_i v_i (1 - \sigma_{ZZ}) I_{Zi} + \sum_{i < j} (J_{ij}^{\text{iso}} + T_{ij}) I_{Zi} I_{Zj} + \frac{1}{2} \sum_{i < j} (J_{ij}^{\text{iso}} - \frac{1}{2} T_{ij}) (I_i^+ I_j + I_i I_j^+) + \frac{1}{3} \sum_i B_i (3I_{Zi}^2 - I_i^2), \quad (1)$$

with the total anisotropic spin–spin coupling given by  $T_{ij} = 2D_{ij} + J_{ij}^{\text{aniso}}$ . The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra are all first order.

For  $^{12}\text{CH}_3\text{F}$ , the  $^1\text{H}$  spectrum shows two 1:2:1 triplets with a spacing between the triplets of  $|\frac{3}{2}T_{\text{HH}}|$  and a separation of successive lines of  $|J_{\text{HF}} + T_{\text{HF}}|$  within each triplet. The  $^{19}\text{F}$  spectrum shows a 1:3:3:1 quartet with a spacing of  $|J_{\text{HF}} + T_{\text{HF}}|$  between the lines.

For  $^{12}\text{CH}_2\text{DF}$ , the  $^1\text{H}$  spectrum consists of a doublet with a spacing of  $|\frac{3}{2}T_{\text{HH}}|$ . Each doublet line is split into a doublet with a spacing of  $|J_{\text{HF}} + T_{\text{HF}}|$ . Furthermore, each line is split into a 1:1:1 triplet with a spacing of  $|J_{\text{HD}} + T_{\text{HD}}|$ . The  $^{19}\text{F}$  spectrum consists of a 1:2:1 triplet with a spacing of  $|J_{\text{HF}} + T_{\text{HF}}|$ . Each triplet line is split into a 1:1:1 triplet with a separation of  $|J_{\text{DF}} + T_{\text{DF}}|$ .

For  $^{12}\text{CHD}_2\text{F}$ , the  $^1\text{H}$  spectrum shows two 1:2:3:2:1 pentets with a separation of  $|J_{\text{HF}} + T_{\text{HF}}|$  and a spacing of  $|J_{\text{HD}} + T_{\text{HD}}|$  between the successive lines within each pentet. The  $^{19}\text{F}$  spectrum shows two 1:2:3:2:1 pentets separated by  $|J_{\text{HF}} + T_{\text{HF}}|$  and a spacing of  $|J_{\text{DF}} + T_{\text{DF}}|$  within each pentet.

For  $^{12}\text{CD}_3\text{F}$ , the  $^{19}\text{F}$  spectrum shows a 1:3:6:7:6:3:1 septet with a splitting of  $|J_{\text{DF}} + T_{\text{DF}}|$  between successive lines.

For  $^{12}\text{CH}_2\text{DF}$ , a first-order  $^2\text{H}$  NMR spectrum occurs with a main doublet splitting of  $|2B_D|$ . Each doublet line is resolved into a doublet with a spacing of  $|J_{\text{DF}} + T_{\text{DF}}|$ . Furthermore, each line is split into a 1:2:1 triplet with a spacing of  $|J_{\text{HD}} + T_{\text{HD}}|$ . The  $^2\text{H}$  spectra of  $^{12}\text{CHD}_2\text{F}$  and  $^{12}\text{CD}_3\text{F}$  are not first order and hence more complicated. These spectra were analysed with the aid of the Bruker PANIC program. In both the  $^1\text{H}$  and  $^{19}\text{F}$  spectra satellites from  $^{13}\text{C}$  in natural abundance are observed. The  $^{13}\text{C}$ -monofluoromethanes show an additional splitting of the lines with a magnitude  $|J_{\text{CF}} + T_{\text{CF}}|$  in the  $^1\text{H}$  spectra and  $|J_{\text{CH}} + T_{\text{CH}}|$  in the  $^{19}\text{F}$  spectra.

The values for the indirect spin-spin coupling constants were taken from the literature and assumed to be independent of the liquid crystal solvents used:  $^1J_{\text{CH}} = 149.15$  Hz,  $^2J_{\text{HF}} = 46.30$  Hz,  $^1J_{\text{CF}} = -160.77$  Hz [22] and  $^2J_{\text{HH}} = -9.6$  Hz [28]. From these spin-spin coupling constants, values for  $^2J_{\text{HD}}$ ,  $^2J_{\text{DD}}$  and  $^2J_{\text{DF}}$  were obtained by scaling with the appropriate magnetogyric ratios, neglecting other isotope effects.

#### 4. Theory

We shall base our analysis on the theory for the orientation of solutes undergoing intramolecular motions in nematic liquid crystal solvents as developed by Snijders *et al.* [7]. The main points of this theory relating to the present analysis of the observed anisotropic couplings for monofluoromethanes are summarized in the present section.

The interaction potential determined by the intermolecular interactions between the solvent and solute is required to describe the anisotropic couplings observed by NMR for solutes present in a nematic solvent. Snijders *et al.* assume in their model that the solute experiences a mean field from the surrounding liquid crystalline environment that possesses cylindrical symmetry around the space-fixed magnetic field direction  $Z$  and propose an anisotropic interaction potential  $U$  given by:

$$U = -\frac{1}{3}G\Sigma_{k,l}\beta_{kl}(Q_m)\mathbf{S}_{kl}(\Omega), \quad (2)$$

with the orientation operator

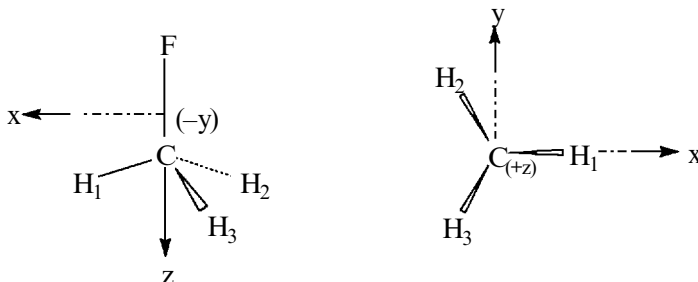
$$\mathbf{S}_{kl}(\Omega) = \frac{3}{2}\cos\theta_{kZ}\cos\theta_{lZ} - \frac{1}{2}\delta_{kl},$$

where  $k$  and  $l$  are molecule-fixed axes  $x, y, z$  for the solute and  $\cos\theta_{kZ}$  is the direction cosine between the molecule-fixed  $k$  axis and the space-fixed  $Z$  axis. The quantity  $G = F_{\parallel} - F_{\perp}$  is the anisotropy of the mean field liquid crystal property interacting with the solute. This potential is a function of both the orientation  $\Omega$  and the normal coordinates  $Q_m$  of the solute and thus couples its rotational and vibrational motions. The potential is then treated as a small perturbation acting on the freely rotating and vibrating solute molecule – the unperturbed wavefunctions taken as simple products of harmonic oscillator and rigid rotator wavefunctions – and standard first-order perturbation theory is used to obtain the perturbed wavefunctions in the presence of this orienting potential. Expectation values of NMR observables, such as dipolar and quadrupolar couplings, can then be obtained by evaluating the matrix elements for the associated operators using the perturbed wavefunctions for the rotational and vibrational motions of the solute molecule and calculating the thermal average.

It must be pointed out that only the general form of the orienting potential in equation (2) is specified, as the values of the  $G\beta_{kl}(Q_m)$  are unknown without additional assumptions regarding the specific nature of the orienting interaction that plays a role. The products  $G\beta_{kl}(Q_m)$  form a second-rank tensor that depends on the properties of both the environment and the solute molecule. Moreover, it is likely that more than

Table 1. Molecular geometry, quadratic harmonic and cubic anharmonic force field for monofluoromethanes used in the present study.

Definition of molecule-fixed axes  $x$ ,  $y$ ,  $z$  and convention for the labelling of nuclei for  $\text{CH}_3\text{F}$  in its equilibrium configuration. On the right the three protons are above the plane of the page and the  $z$  axis points out of the page.



(Curvilinear) symmetry coordinates  $S_i$  for monofluoromethanes adapted to point group  $C_{3v}$  symmetry

$A_1$  symmetry:

$$S_1 = 3^{-1/2} (\Delta r_{\text{CH}_1} + \Delta r_{\text{CH}_2} + \Delta r_{\text{CH}_3})$$

$$S_2 = (3(1 + K^2))^{-1/2} [K(\Delta\alpha_{\text{H}_2\text{CH}_3} + \Delta\alpha_{\text{H}_1\text{CH}_3} + \Delta\alpha_{\text{H}_1\text{CH}_2}) - (\Delta\beta_{\text{H}_1\text{CF}} + \Delta\beta_{\text{H}_2\text{CF}} + \Delta\beta_{\text{H}_3\text{CF}})], K = -3 \sin \beta \cos \beta / \sin \alpha$$

$$S_3 = \Delta r_{\text{CF}}$$

$E$  symmetry:

$$S_{4a} = 6^{-1/2} (2\Delta r_{\text{CH}_1} - \Delta r_{\text{CH}_2} - \Delta r_{\text{CH}_3})$$

$$S_{4b} = 2^{-1/2} (\Delta r_{\text{CH}_2} - \Delta r_{\text{CH}_3})$$

$$S_{5a} = 6^{-1/2} (2\Delta\alpha_{\text{H}_2\text{CH}_3} - \Delta\alpha_{\text{H}_1\text{CH}_3} - \Delta\alpha_{\text{H}_1\text{CH}_2})$$

$$S_{5b} = 2^{-1/2} (\Delta\alpha_{\text{H}_1\text{CH}_3} - \Delta\alpha_{\text{H}_1\text{CH}_2})$$

$$S_{6a} = 6^{-1/2} (2\Delta\beta_{\text{H}_1\text{CF}} - \Delta\beta_{\text{H}_2\text{CF}} - \Delta\beta_{\text{H}_3\text{CF}})$$

$$S_{6b} = 2^{-1/2} (\Delta\beta_{\text{H}_2\text{CF}} - \Delta\beta_{\text{H}_3\text{CF}})$$

Equilibrium geometry used ([19], table 5 of [20]):

$$r_{\text{CH}} = 1.0837 \text{ \AA}$$

$$r_{\text{CF}} = 1.3890 \text{ \AA}$$

$$\alpha = \angle \text{H}_i\text{CH}_j = 110^\circ 19'; \beta = \angle \text{H}_i\text{CF}, 1 - \cos \alpha = 3/2 \sin^2 \beta$$

Quadratic harmonic force field in symmetry coordinates for methyl fluoride taken from table 5 of [20].

Cubic anharmonic force field in symmetry coordinates for methyl fluoride taken from table IV, column V of [21].

Atomic masses used (table XI of [33]):

$$^1\text{H} \ 1.00782519 \text{ amu} \quad ^2\text{H} \ 2.01410222 \text{ amu}$$

$$^{12}\text{C} \ 12.0 \text{ amu} \quad ^{13}\text{C} \ 13.0033544 \text{ amu}$$

$$^{19}\text{F} \ 18.9984046 \text{ amu}$$

one interaction is responsible for the observed orientation and accordingly the parameters  $G\beta_{kl}(Q_m)$  should be considered as a sum of contributions  $G^{(i)}\beta_{kl}^{(i)}(Q_m)$  for every orienting interaction  $i$ . In their theory for the correlation between vibration and rotation for partially oriented molecules, Lounila and Diehl [23] apply the same form for the vibration–rotation interaction as in equation (2) and describe all the contributing interactions by a single second-rank interaction tensor  $\mathbf{A}_{kl}$ .

The  $\beta$  tensor, assumed to be an electronic property of the solute molecule, can be expanded in terms of the normal coordinates  $Q_m$  for small displacements away from equilibrium as:

$$\beta_{kl}(Q_m) = \beta_{kl:e} + \sum_m (\partial\beta_{kl}/\partial Q_m)_e Q_m + \dots \quad (3)$$

This Taylor series is truncated after the linear term. Apart from the reliance on the mean-field approximation and on perturbation theory, this approximation is necessary to keep the number of unknown parameters required in the model description by Snijders *et al.* within reasonable limits for the present study of monofluoromethanes. The inclusion of higher-order terms has been a matter of some debate in the case of methane [29]. By truncation of the Taylor expansion in equation (3) after the linear term, the unknown parameters in the model are reduced to  $G\beta_{\text{kl};\text{e}}$  and  $G(\partial\beta_{\text{kl}}/\partial Q_{\text{m}})_{\text{e}}$ , with the shorthand notation e for evaluation at the equilibrium geometry of the solute. These parameters are not all independent as an examination of their dependence upon isotopic substitution reveals. Within the Born–Oppenheimer approximation, the  $\beta$  tensor is of course transferable from one isotopic species to another for the same nuclear configuration. For the derivatives of the  $\beta$  tensor with respect to the various normal coordinates, the isotopic dependence is more subtle due to the Eckart conditions [30]. These derivatives can be related to the derivatives of the  $\beta$  tensor with respect to the symmetry coordinates  $S_{\text{n}}$  of an appropriate reference molecule [31], e.g. the most symmetrical species, using the  $\mathbf{L}$  tensor introduced by Hoy *et al.* [32]. The  $\mathbf{L}$  tensor relates the symmetry adapted linear combinations  $S_{\text{n}}$  of a set of geometrically defined curvilinear internal coordinates to the normal coordinates  $Q_{\text{m}}$  by:

$$S_{\text{n}} = \sum_{\text{m}} \mathbf{L}_{\text{nm}} Q_{\text{m}} + \frac{1}{2} \sum_{\text{m}, \text{m}'} \mathbf{L}_{\text{nm}\text{m}\text{m}'} Q_{\text{m}} Q_{\text{m}'} + \dots \quad (4)$$

The  $\mathbf{L}$  tensor can be calculated from a preliminary harmonic vibration analysis using the equilibrium geometry, the appropriate atomic masses and the quadratic force field defined in terms of the  $S_{\text{n}}$ . For the present study of monofluoromethanes these data have been taken from various sources and are summarized in table 1. Owing to molecular symmetry not all of the derivatives of the  $\beta$  tensor with respect to these symmetry coordinates are independent. Only nine independent derivatives (one for each  $A_1$  symmetry mode and two for each E mode) suffice to describe all the  $(\partial\beta_{\text{kl}}/\partial S_{\text{n}})_{\text{e}}$  and their symmetry relations are summarized in table 2. Together with the anisotropy of the  $\beta$  tensor,  $\beta_{\text{zz};\text{e}} - \frac{1}{2}(\beta_{\text{xx};\text{e}} + \beta_{\text{yy};\text{e}})$ , a total of ten independent parameters is required to describe the anisotropic couplings in this way. Note that the isotropic part of the  $\beta$  tensor can be omitted because it does not contribute to the molecular orientation in an anisotropic environment and consequently also not to the observed dipolar or quadrupolar NMR couplings.

Dipolar couplings  $D_{\mu\nu}$  for a pair of nuclei  $\mu, \nu$  result from a sum of two different kinds of contributions. The first kind arises from the ordering of the solute for independent vibrational and rotational motions and is given by

$$D_{\mu\nu} = \sum_{\text{k}, \text{l}} \langle d_{\text{kl};\mu\nu} \rangle_{\text{vibrations}} \langle \mathbf{S}_{\text{kl}} \rangle_{\text{rotations}} \quad (5)$$

with

$$d_{\text{kl};\mu\nu} = -(h\gamma_{\mu}\gamma_{\nu}/4\pi^2) (\cos\theta_{\mu\nu, \text{k}} \cos\theta_{\mu\nu, \text{l}}/r_{\mu\nu}^3),$$

where  $\cos\theta_{\mu\nu, \text{k}}$  is the direction cosine between the internuclear vector for the pair of nuclei  $\mu\nu$  and the molecule-fixed  $k$  axis and  $r_{\mu\nu}$  is the instantaneous internuclear distance. The average over vibrations in equation (5) can be obtained by expanding  $d_{\text{kl};\mu\nu}$  about the equilibrium geometry in a Taylor series in terms of the normal coordinates  $Q_{\text{m}}$  and this series is normally truncated after terms of power two:

$$\begin{aligned} \langle d_{\text{kl};\mu\nu} \rangle_{\text{vibrations}} &= d_{\text{kl};\mu\nu; \text{e}} + \sum_{\text{m}} (\partial d_{\text{kl};\mu\nu} / \partial Q_{\text{m}})_{\text{e}} \langle Q_{\text{m}} \rangle \\ &+ \frac{1}{2} \sum_{\text{m}, \text{n}} (\partial^2 d_{\text{kl};\mu\nu} / \partial Q_{\text{m}} \partial Q_{\text{n}})_{\text{e}} \langle Q_{\text{m}} Q_{\text{n}} \rangle + \dots \end{aligned} \quad (6)$$

Then the terms in equation (6) of power zero, one and two in the normal coordinates  $Q_{\text{m}}$  result in the usual equilibrium, anharmonic and harmonic contributions



Table 2. Symmetry relations among the derivatives  $(\partial\beta_{kl}/\partial S_n)_e$  for a traceless, symmetric rank-two tensorial molecular electronic property  $\beta$  with respect to the symmetry coordinates  $S_n^a$ .

Symmetry coordinate	Character	$\beta_{kl}$ tensor component					
		xx	xy	xz	yy	yz	zz
$S_1^{A_1}$	CH <sub>3</sub> symmetric stretch	$-\frac{1}{2}\beta_1$			$-\frac{1}{2}\beta_1$		$\beta_1$
$S_2^{A_1}$	CH <sub>3</sub> symmetric bend	$-\frac{1}{2}\beta_2$			$-\frac{1}{2}\beta_2$		$\beta_2$
$S_3^{A_1}$	CF stretch	$-\frac{1}{2}\beta_3$			$-\frac{1}{2}\beta_3$		$\beta_3$
$S_{4a}^E$	CH <sub>3</sub> deformational stretch	$\beta_4$		$\beta_7$	$-\beta_4$		
$S_{4b}^E$	CH <sub>3</sub> deformational bend		$-\beta_4$			$\beta_7$	
$S_{5a}^E$		$\beta_5$		$\beta_8$	$-\beta_5$		
$S_{5b}^E$	CH <sub>3</sub> rock		$-\beta_5$			$\beta_8$	
$S_{6a}^E$		$\beta_6$		$\beta_9$	$-\beta_6$		
$S_{6b}^E$			$-\beta_6$			$\beta_9$	

<sup>a</sup> Similar relations hold for the derivatives with respect to the normal coordinates  $Q_m$ .

respectively to the dipolar coupling  $D_{\mu\nu}$  after the appropriate thermal average over vibrations and rotations has been taken into account. For a harmonic vibrational potential,

$$\langle Q_m Q_n \rangle = \delta_{mn} \langle v_m | Q_m^2 | v_m \rangle \quad \text{with} \quad \langle v_m | Q_m^2 | v_m \rangle = \left( \left( \frac{h}{2\pi} \right) / \omega_m \right) (v_m + \frac{1}{2}), \quad (7)$$

where  $v_m$  is the vibrational quantum number and  $\omega_m$  is the angular frequency for normal mode  $m$ . By taking a Boltzmann thermal average over all vibrational states [34, 35] at temperature  $T$ , we obtain:

$$\langle v_m + \frac{1}{2} \rangle_T = \frac{1}{2} \coth \left( \left( \frac{h}{2\pi} \right) \omega_m / 2kT \right) \quad (8)$$

and the corresponding thermal average  $\langle Q_m Q_n \rangle_T$  for equation (7) is readily evaluated.

For a harmonic potential, the vibrational quantum average of any product of normal coordinates  $Q_m$ , each taken to a certain power, reduces to zero when any one of these powers is odd. However, for an anharmonic potential, the totally symmetric normal coordinates of the molecule under consideration can be nonvanishing. The non-zero vibrational quantum averages  $\langle Q_m \rangle$  can be obtained from the quadratic and cubic force fields using the  $\mathbf{L}$  tensor of Hoy *et al.* They specify the displacements of the average geometry away from equilibrium (cf. [34–36]) and are given by:

$$\langle Q_m \rangle = -1/(2\omega_m^2) \sum_l \Phi_{mll} \langle v_l | Q_l^2 | v_l \rangle, \quad (9)$$

where the  $\Phi_{mll}$  are the semidiagonal cubic anharmonic force constants of the vibrational potential in normal coordinates. The Boltzmann thermal average  $\langle Q_m \rangle_T$  is readily obtained by combining the results in equations (7) and (8) with equation (9).

The thermal average over all vibrational states for  $\langle Q_m \rangle$  and  $\langle Q_m Q_n \rangle$  in equation (5) at temperature  $T$  results in [36]:

$$\begin{aligned}\langle Q_m \rangle_T &= -\left(\frac{\hbar}{2\pi}\right) / (4\omega_m^2) \Sigma_l (\Phi_{ml} / \omega_l) \coth\left(\left(\frac{\hbar}{2\pi}\right) \omega_l / 2kT\right) \\ \langle Q_m Q_n \rangle_T &= \left(\frac{\hbar}{2\pi}\right) / (2\omega_m) \delta_{mn} \coth\left(\left(\frac{\hbar}{2\pi}\right) \omega_m / 2kT\right).\end{aligned}\quad (10)$$

Apart from the direct effects discussed above of the harmonic and anharmonic force fields on the NMR observables, there is another contribution to  $D_{\mu\nu}$  which arises from the correlation between vibrations and rotations and is given by [7]:

$$D_{\mu\nu}^{\text{nonrigid}} = \frac{1}{3} G \Sigma_{i,j} \Sigma_{k,l} \Sigma_m (\partial\beta_{ij} / \partial Q_m)_e (\partial d_{kl;\mu\nu} / \partial Q_m)_e \left(\frac{1}{\omega_m^2}\right) \langle \mathbf{S}_{ij} \mathbf{S}_{kl} \rangle_{\text{rotations}}. \quad (11)$$

For monofluoromethanes, the thermal averages over rotations in equations (5) and (11) can be evaluated classically using Boltzmann statistics:

$$\begin{aligned}S_{kl} &= \langle \mathbf{S}_{kl} \rangle_{\text{rotations}} = \left( \int \mathbf{S}_{kl} \exp(-U(\Omega)/kT) d\Omega \right) / \left( \int \exp(-U(\Omega)/kT) d\Omega \right) \\ \langle \mathbf{S}_{ij} \mathbf{S}_{kl} \rangle_{\text{rotations}} &= \left( \int \mathbf{S}_{ij} \mathbf{S}_{kl} \exp(-U(\Omega)/kT) d\Omega \right) / \left( \int \exp(-U(\Omega)/kT) d\Omega \right),\end{aligned}\quad (12)$$

where  $U(\Omega)$  is the orientation-dependent interaction potential in equation (2) for the molecule in its average geometry obtained by taking the appropriate average over vibrations for  $\beta_{kl}$  in equation (3). The  $\langle \mathbf{S}_{kl} \rangle_{\text{rotations}}$  in equations (5) and (12) are the familiar Saupe order parameters  $S_{kl}$  that describe the orientation of the solute in a liquid crystal solvent. The integrals in equation (12) have been calculated numerically in the present study using Gauss–Legendre quadrature with an interpolating Legendre polynomial of degree 25.

In summary, the contributions to the dipolar coupling  $D_{\mu\nu}$  are

$$D_{\mu\nu} = D_{\mu\nu}^e + D_{\mu\nu}^a + D_{\mu\nu}^h + D_{\mu\nu}^{\text{non-rigid}}, \quad (13)$$

with

$$\begin{aligned}D_{\mu\nu}^e &= \Sigma_{k,l} d_{kl;\mu\nu;e} S_{kl} \\ D_{\mu\nu}^a &= \Sigma_{k,l} \Sigma_m (\partial d_{kl;\mu\nu} / \partial Q_m)_e \langle Q_m \rangle_T S_{kl} \\ D_{\mu\nu}^h &= \Sigma_{k,l} \frac{1}{2} \Sigma_m \Sigma_n (\partial^2 d_{kl;\mu\nu} / \partial Q_m \partial Q_n)_e \langle Q_m Q_n \rangle_T S_{kl}\end{aligned}$$

and with  $D_{\mu\nu}^{\text{non-rigid}}$  given by equation (11). Expressions for the derivatives  $(\partial d_{kl;\mu\nu} / \partial Q_m)_e$  required for the anharmonic contribution  $D_{\mu\nu}^a$  and the non-rigid contribution  $D_{\mu\nu}^{\text{non-rigid}}$  [37–40], as well as for  $(\partial^2 d_{kl;\mu\nu} / \partial Q_m \partial Q_n)_e$  required for the harmonic contribution  $D_{\mu\nu}^h$  to the dipolar couplings  $D_{\mu\nu}$  [37, 38, 40, 41] have been given in various places. The quantities needed for the calculation of these derivatives can be obtained from a preliminary harmonic vibration analysis.

For monofluoromethanes, ten independent parameters are required for an analysis of the anisotropic couplings in the model of Snijders *et al.*:  $G < \beta_{zz} - \frac{1}{2}(\beta_{xx} + \beta_{yy}) >$  with the anisotropy of the  $\beta$  tensor averaged over vibrations, and nine independent products of  $G$  and the derivatives with respect to symmetry coordinates. A reduction of this number of parameters is desirable. In this respect the assumption of bond or segmental addition for the molecular properties involved in the orientation is

appealing. The number of parameters required in the theoretical models to describe the anisotropic interactions between solute and liquid crystal environment is reduced in this way, preferably to only those that are mainly responsible for the observed orientation. If the bonds are assumed axially symmetric with respect to the bond axis, every bond can be represented by two parameters [42], the bond anisotropy  $\Delta\beta = \beta_{\parallel} - \beta_{\perp}$  and the derivative of the bond anisotropy with respect to bond stretch at the equilibrium geometry  $(\partial\Delta\beta/\partial r)_e$ . In this way the number of parameters needed reduces to twice the number of different bonds present in the solute molecule, i.e. four for monofluoromethanes:

$$\left. \begin{aligned} G\Delta\beta_{\text{CH}} &= \frac{1}{3}G((\beta_{\parallel;\text{CH}_1} - \beta_{\perp;\text{CH}_1}) + (\beta_{\parallel;\text{CH}_2} - \beta_{\perp;\text{CH}_2}) + (\beta_{\parallel;\text{CH}_3} - \beta_{\perp;\text{CH}_3})), \\ G\Delta\beta_{\text{CF}} &= G(\beta_{\parallel;\text{CF}} - \beta_{\perp;\text{CF}}), \\ G(\partial\Delta\beta_{\text{CH}}/\partial r_{\text{CH}})_e &= \frac{1}{3}G((\partial(\beta_{\parallel;\text{CH}_1} - \beta_{\perp;\text{CH}_1})/\partial r_{\text{CH}_1})_e + (\partial(\beta_{\parallel;\text{CH}_2} - \beta_{\perp;\text{CH}_2})/\partial r_{\text{CH}_2})_e \\ &\quad + (\partial(\beta_{\parallel;\text{CH}_3} - \beta_{\perp;\text{CH}_3})/\partial r_{\text{CH}_3})_e) \\ G(\partial\Delta\beta_{\text{CF}}/\partial r_{\text{CF}})_e &= G(\partial(\beta_{\parallel;\text{CF}} - \beta_{\perp;\text{CF}})/\partial r_{\text{CF}})_e \end{aligned} \right\} \quad (14)$$

The four bond additivity parameters above can be expressed in the ten independent  $G\beta_i$  ( $i = 1-9$ ) and  $\beta$  anisotropy parameters. Relevant expressions for the bond additivity parameters have been given in the literature [29, 42]. It should be noted that these expressions differ for each isotopomer.

An obvious advantage of the assumption of bond additivity is the reduction of the number of independent parameters. Introduction of bond additivity has another attractive feature which is less apparent. In a treatment based on the full set of parameters, the consequences of the Eckart conditions must be heeded, resulting in separate (but mutually dependent) sets of parameters for each isotopomer. The purely geometrical bond additivity parameters remain unchanged throughout the series of isotopomers.

## 5. Results and discussion

In the present work monofluoromethane and a number of its deuterated analogues have been studied in three different nematic solvents at 302 K. In each liquid crystal solvent a total of 29 experimental dipolar couplings were observed. The complete set of couplings is listed in table 3. Despite the fact that in the present work only the dipolar couplings are used, the observed quadrupolar couplings  $B_D$  are included as well for future reference. As discussed in the previous section, the assumption of bond additivity is required in order to reduce the number of independent parameters to a manageable degree. An analysis has been carried out in terms of the four bond additivity parameters  $G\Delta\beta_{\text{CH}}$ ,  $G\Delta\beta_{\text{CF}}$ ,  $G(\partial\Delta\beta_{\text{CH}}/\partial r_{\text{CH}})_e$  and  $G(\partial\Delta\beta_{\text{CF}}/\partial r_{\text{CF}})_e$ . In such an analysis there are various options. First, there are a number of different contributions to the dipolar couplings summarized in equation (13) which may or may not be significant. It is therefore important to carry out fitting procedures in which the different contributions are either included or omitted to assess their importance. Secondly, the experimental dipolar couplings may contain contributions due to anisotropies in indirect couplings which cannot be determined independently on experimental grounds. Such an anisotropy would be expected to occur in particular for the  $^{13}\text{C}$ -F indirect coupling. This leaves room for two possible strategies in which fits are performed which either include or exclude the  $^{13}\text{C}$ -F experimental coupling.

First, the question as to which contributions to the dipolar couplings are important will be addressed. The dipolar couplings observed for solutes in nematic solvents are

Table 3(a). Experimental anisotropic couplings  $D$  and quadrupolar couplings  $B_D$  for monofluoromethanes in 1132 at  $302 \pm 1$  K.

Molecule	Spectral parameter	Observed nucleus			Average
		$^1\text{H}$	$^2\text{H}$	$^{19}\text{F}$	
$^{12}\text{CH}_3\text{F}$	$D_{\text{HH}}$	701.42(3)			
	$D_{\text{HF}}$	-562.97(5)		-562.94(7)	-562.94(6)
$^{13}\text{CH}_3\text{F}$	$D_{\text{HH}}$	701.40(4)			
	$D_{\text{HF}}$	-562.89(6)		-562.74(8)	-562.84(7)
	$D_{\text{CH}}$	524.00(6)			
	$D_{\text{CF}}$			-716.79(8)	
$^{12}\text{CH}_2\text{DF}$	$D_{\text{HH}}$	701.02(4)			
	$D_{\text{HD}}$	108.70(5)	108.63(10)		108.67(8)
	$D_{\text{HF}}$	-565.01(5)		-564.97(7)	-564.99(6)
	$D_{\text{DF}}$		-87.77(10)	-87.01(5)	-87.39(8)
	$B_D$		-2914.26(10)		
$^{13}\text{CH}_2\text{DF}$	$D_{\text{HH}}$	700.99(5)			
	$D_{\text{HD}}$	108.71(7)			
	$D_{\text{HF}}$	-564.98(7)		-564.65(8)	-564.82(8)
	$D_{\text{DF}}$			-87.38(8)	
	$D_{\text{CH}}$	523.10(7)			
$^{12}\text{CHD}_2\text{F}$	$D_{\text{DD}}$		16.84(4)		
	$D_{\text{HD}}$	108.64(5)	108.58(10)		108.61(8)
	$D_{\text{HF}}$	-567.00(5)		-566.95(7)	-566.98(6)
	$D_{\text{DF}}$		-87.26(10)	-87.32(5)	-87.29(8)
	$B_D$		-2910.43(11)		
$^{13}\text{CHD}_2\text{F}$	$D_{\text{HD}}$	108.64(9)			
	$D_{\text{HF}}$	-567.01(9)		-566.18(25)	-566.60(17)
	$D_{\text{DF}}$			-87.20(9)	
	$D_{\text{CH}}$	522.22(10)			
	$D_{\text{CF}}$			-718.80(10)	
$^{12}\text{CD}_3\text{F}$	$D_{\text{DD}}$		16.77(4)		
	$D_{\text{DF}}$		-87.45(10)	-87.62(8)	-87.54(9)
	$B_D$		-2905.02(8)		
$^{13}\text{CD}_3\text{F}$	$D_{\text{DF}}$			-87.10(10)	
	$D_{\text{CF}}$			-720.13(9)	

determined by their anisotropic molecular properties interacting with their environment. For the monofluoromethanes the predominant contribution to the calculated couplings stems from properties that refer to the equilibrium structure. In addition, equation (13) contains three possible 'non-rigid' contributions to the dipolar couplings: harmonic and anharmonic vibrational corrections, as well as a contribution that results from the correlation between solute vibrational and reorientational motion. Since the equilibrium structure is identical for all isotopomers, one would expect on the basis of this contribution alone that all molecules of the series would show identical dipolar couplings. However, the experimental data sets in the present study indicate that, for similar dipolar couplings in a series of monofluoromethanes measured under the same conditions in a nematic solvent, small but noticeable effects of isotopic substitution are observed. These effects must be due to the influence of

Table 3(b). Experimental anisotropic couplings  $D$  and quadrupolar couplings  $B_D$  for monofluoromethanes in 54.7 wt% 1132/EBBA at  $302 \pm 1$  K.

Molecule	Spectral parameter	Observed nucleus			Average
		$^1\text{H}$	$^2\text{H}$	$^{19}\text{F}$	
$^{12}\text{CH}_3\text{F}$	$D_{\text{HH}}$	453.90(7)			
	$D_{\text{HF}}$	-364.39(10)		-364.59(11)	-364.49(11)
$^{13}\text{CH}_3\text{F}$	$D_{\text{HH}}$	452.47(8)			
	$D_{\text{HF}}$	-363.48(13)		-362.93(12)	-363.21(13)
	$D_{\text{CH}}$	345.41(13)			
	$D_{\text{CF}}$			-463.12(12)	
$^{12}\text{CH}_2\text{DF}$	$D_{\text{HH}}$	451.00(7)			
	$D_{\text{HD}}$	70.59(11)	70.35(8)		70.47(10)
	$D_{\text{HF}}$	-367.16(11)		-367.38(13)	-367.27(12)
	$D_{\text{DF}}$		-55.85(8)	-55.98(13)	-55.92(11)
	$B_D$		-1870.35(8)		
$^{13}\text{CH}_2\text{DF}$	$D_{\text{HH}}$	449.47(9)			
	$D_{\text{HD}}$	70.51(13)			
	$D_{\text{HF}}$	-365.86(13)		-366.02(13)	-365.94(13)
	$D_{\text{DF}}$			-55.87(13)	
	$D_{\text{CH}}$	342.50(13)			
$^{12}\text{CHD}_2\text{F}$	$D_{\text{CF}}$			-464.12(14)	
	$D_{\text{DD}}$		10.95(3)		
	$D_{\text{HD}}$	70.20(13)	70.07(9)		70.14(11)
	$D_{\text{HF}}$	-369.92(13)		-370.16(13)	-370.04(13)
	$D_{\text{DF}}$		-56.36(9)	-56.44(13)	-56.40(11)
	$B_D$		-1853.37(9)		
$^{13}\text{CHD}_2\text{F}$	$D_{\text{HD}}$	69.96(13)			
	$D_{\text{HF}}$	not assigned		-368.70(14)	
	$D_{\text{DF}}$			-56.06(13)	
	$D_{\text{CH}}$	340.58(13)			
	$D_{\text{CF}}$			-465.44(13)	
$^{12}\text{CD}_3\text{F}$	$D_{\text{DD}}$		10.92(3)		
	$D_{\text{DF}}$		-56.86(8)	-56.88(13)	-56.87(11)
	$B_D$		-1836.59(8)		
$^{13}\text{CD}_3\text{F}$	$D_{\text{DF}}$			-56.42(13)	
	$D_{\text{CF}}$			-466.30(13)	

isotopic substitution on the vibrations and/or the coupling between these vibrations and rotations. Apparently, there is a need to include some or all of the 'non-rigid' contributions.

Since harmonic force fields are commonly known or can be calculated with reasonable accuracy, in most studies of solutes oriented in liquid crystals the harmonic vibrational corrections to the dipolar couplings are included. For the quadratic force field of Blom and Müller [20] available for fluoromethane, the contribution due to harmonic vibrations is less than about 1% of all of the total calculated dipolar couplings for monofluoromethanes, except for  $D_{\text{CH}}$  where it amounts to  $\sim 3\%$ . The anharmonic force field is a molecular property which in many cases is unknown and whose calculation is not trivial. However, in recent years more information on anharmonic force fields in small molecules has become available. For the fluoro-

Table 3(c). Experimental anisotropic couplings  $D$  and quadrupolar couplings  $B_D$  for monofluoromethanes in EBBA at  $302 \pm 1$  K.

Molecule	Spectral parameter	Observed nucleus			Average
		$^1\text{H}$	$^2\text{H}$	$^{19}\text{F}$	
$^{12}\text{CH}_3\text{F}$	$D_{\text{HH}}$	106.43(5)			
	$D_{\text{HF}}$	-85.41(8)		-85.41(10)	-85.41(9)
$^{13}\text{CH}_3\text{F}$	$D_{\text{HH}}$	106.57(7)			
	$D_{\text{HF}}$	-85.29(16)		-85.60(10)	-85.45(13)
	$D_{\text{CH}}$	100.44(10)			
	$D_{\text{CF}}$			-111.59(25)	
$^{12}\text{CH}_2\text{DF}$	$D_{\text{HH}}$	97.83(6)			
	$D_{\text{HD}}$	17.43(9)	17.44(4)		17.44(7)
	$D_{\text{HF}}$	-90.58(9)		-90.57(12)	-90.58(11)
	$D_{\text{DF}}$		-12.13(3)	-12.11(12)	-12.12(8)
	$B_D$		-412.87(3)		
$^{13}\text{CH}_2\text{DF}$	$D_{\text{HH}}$	97.86(45)			
	$D_{\text{HD}}$	17.39(50)			
	$D_{\text{HF}}$	-90.62(45)		-90.75(50)	-90.69(47)
	$D_{\text{DF}}$			-12.08(13)	
	$D_{\text{CH}}$	92.63(50)			
$^{12}\text{CHD}_2\text{F}$	$D_{\text{DD}}$		2.81(2)		
	$D_{\text{HD}}$	16.08(9)	16.14(4)		16.11(7)
	$D_{\text{HF}}$	-95.66(9)		-95.64(11)	-95.65(10)
	$D_{\text{DF}}$		-12.87(5)	-12.92(12)	-12.90(9)
	$B_D$		-364.53(4)		
$^{13}\text{CHD}_2\text{F}$	$D_{\text{HD}}$	16.06(50)			
	$D_{\text{HF}}$	-95.73(51)		-95.65(43)	-95.69(47)
	$D_{\text{DF}}$			-12.99(48)	
	$D_{\text{CH}}$	85.22(50)			
	$D_{\text{CF}}$			-113.32(47)	
$^{12}\text{CD}_3\text{F}$	$D_{\text{DD}}$		2.62(2)		
	$D_{\text{DF}}$		-13.63(5)	-13.69(12)	-13.66(9)
	$B_D$		-318.11(4)		
$^{13}\text{CD}_3\text{F}$	$D_{\text{DF}}$			-13.79(12)	
	$D_{\text{CF}}$			-114.28(13)	

methanes, we are in the favourable situation that the cubic force field has been determined in detail by Kondo [21], hence allowing the assessment of its effect on the observed dipolar couplings in the fluoromethanes for the first time. The anharmonic contributions to the dipolar couplings, as calculated from this anharmonic force field are approximately 3% for all dipolar couplings. These contributions appear to be even larger than the corresponding harmonic corrections and their inclusion is obviously important. Finally, the vibration-rotation interaction, if included, leads to least-squares fits for the four bond additivity parameters of significantly better quality than when this contribution is left out. In the present paper we have therefore, apart from the rigid contribution, included all the above 'non-rigid' effects in our calculations and least-squares fits.

A second point of concern in an analysis of experimental anisotropic couplings for

monofluoromethanes is the possibility that these couplings may contain a contribution due to anisotropic  $J$  couplings, in particular for the  $^{13}\text{C}$ -F coupling. In a recent analysis of these anisotropic couplings for  $^{13}\text{CH}_3\text{F}$  in nine different nematic solvents by Jokisaari *et al.* [22], a value of  $\Delta J_{\text{CF}} = 402 \pm 35$  Hz was obtained. Their analysis incorporated corrections for both the harmonic vibrations and for the correlation between vibration and rotation, but did not include the effects of vibrational anharmonicity. To see if the anisotropic couplings in the present study contain significant anisotropic  $J_{\text{CF}}$  couplings, the four carbon-fluorine couplings were excluded from the experimental set of anisotropic couplings obtained in each of the three solvents. The results of the least-squares fits using the remaining 25 couplings were found to improve significantly in all cases. On the basis of the four bond additivity parameters obtained in these fits, we have recalculated the values for the four dipolar carbon-fluorine couplings. The anisotropies  $\Delta J_{\text{CF}}$  for the appropriate monofluoromethanes could then be estimated by attributing the difference between these calculated dipolar and the corresponding experimentally observed couplings to  $\Delta J_{\text{CF}}$  according to

$$\frac{2}{3}\Delta J_{\text{CF}}S_{zz} = D_{\text{CF}}^{\text{exp}} - D_{\text{CF}}^{\text{calc}}. \quad (15)$$

(For the asymmetrically deuterated monofluoromethanes that require two additional but smaller independent order parameters to describe their orientation properly, this is only true to a good degree of approximation.) The results summarized in table 4 show that the estimated anisotropies  $\Delta J_{\text{CF}}$  obtained in this way for the four monofluoromethanes in one particular liquid crystal solvent all have the same sign and are to a reasonable extent similar in magnitude. However, there are large differences between the results in the various solvents. In 1132 values for  $\Delta J_{\text{CF}}$  are estimated very similar to those obtained in the study by Jokisaari *et al.* [22] and to the theoretical estimates for  $\Delta J_{\text{CF}}$  cited in that reference. In EBBA probably unrealistically large negative anisotropies are obtained. In the ‘magic mixture’ positive  $\Delta J_{\text{CF}}$  values in the range 140–200 Hz are estimated. Of course, our estimates may be affected in part by the fact that we attributed *all* of the difference between calculated and observed anisotropic couplings to the anisotropies  $\Delta J_{\text{CF}}$ . For reasons to be discussed below, one might be tempted to believe the results obtained in the ‘magic mixture’ to be more reliable than those obtained in the component nematic phases. Whatever the case may be, our results indicate that an anisotropy in the indirect spin-spin coupling does contribute to the observed anisotropic carbon-fluorine couplings. Therefore, in the following the  $^{13}\text{C}$ -F dipolar couplings have been omitted from all least-squares fits.

In table 4 we present three least-squares fits for our series of fluoromethanes dissolved in the nematic solvents 1132, a 54.7 wt% mixture of 1132 in EBBA, and EBBA, based on four adjustable bond additivity parameters for each solvent. In the table the various ‘rigid’ and ‘non-rigid’ contributions are listed separately. Least-squares fits to the data sets with the couplings involving deuterons scaled with the appropriate magnetogyric ratios to bring them in line with the corresponding proton values gave similar results. As can be seen the overall agreement between the calculated and experimental values is quite good in every case. Closer inspection reveals that the rms value obtained for the fit in the 54.7 wt% mixture of 1132 in EBBA is of excellent quality. The rms value for the fit in 1132 appears to be equally good, but the fit quality in EBBA is appreciably lower. A pleasing aspect of all the fits is the fact that the four bond additivity parameters appear to be quite stable if slight modifications, such as leaving out some dipolar couplings, are made to the fitting procedure. This is a strong indication that the physical basis of the theoretical

Table 4(a). Results of least-squares fit to data in table 3(a) for monofluoromethanes in 1132 at  $302 \pm 1$  K. Fit to 25 dipolar couplings (excluding 4  $D_{CF}$  values), including rigid, harmonic and anharmonic and vibration–rotation correlation contributions in equation (13). (Optimal) bond additivity parameters:

$$\begin{aligned}
 G\Delta\beta_{CH} &= 0.1515 \times 10^{-20} \text{ J} & (\text{standard error: } 0.013) & & G(\partial\Delta\beta_{CH}/\partial r_{CH}) &= 0.3755 \times 10^{-10} \text{ J m}^{-1} & (\text{standard error: } 0.039) \\
 G\Delta\beta_{CF} &= 0.5920 \times 10^{-20} \text{ J} & (\text{standard error: } 0.010) & & G(\partial\Delta\beta_{CF}/\partial r_{CF}) &= 2.069 \times 10^{-10} \text{ J m}^{-1} & (\text{standard error: } 0.465).
 \end{aligned}$$

Molecule	Spectral parameter	Calculated					Experimental/ Hz	Experimental/ – calculated	Estimate $\Delta/\text{CF}/\text{Hz}$
		Equilibrium	Anharmonic	Harmonic	Total	'Non-rigid'			
		'rigid and vibrational'					Total calculated/ Hz		
$\text{C}^1\text{CH}_3\text{F}$	$D_{HH}$	73571	–2433	–672	70466	–329	70137	70142(3)	005
	$D_{HF}$	–58146	1609	174	–56323	037	–56286	–56294(6)	–008
$\text{C}^1\text{CH}_2\text{F}$	$D_{HH}$	73634	–2420	–687	70257	–327	70201	70140(4)	–061
	$D_{HF}$	–58155	1599	185	–56371	035	–56336	–56284(7)	052
	$D_{CH}$	57334	–1915	–1828	53598	–1181	52416	52400(6)	–016
	$D_{CF}$	–73818	1236	–384	–72966	–823	(–73790)*	–71679(8)	(2111)*
$\text{C}^1\text{CH}_2\text{DF}$	$D_{HH}$	73583	–2298	–830	70455	–417	70038	70102(4)	064
	$D_{HD}$	11319	–334	–070	10915	–046	10869	10867(8)	–002
	$D_{HF}$	–58274	1562	237	–56475	008	–56467	–56499(6)	–032
	$D_{DF}$	–89409	204	–011	–8717	015	–8702	–8739(8)	–037
	$D_{HH}$	73643	–2283	–844	70515	–416	70100	70099(5)	–001
	$D_{HD}$	11328	–332	–072	10925	–046	10879	10871(7)	–008
$\text{C}^1\text{CH}_2\text{DF}$	$D_{HF}$	–58320	1551	247	–56521	008	–56514	–56482(8)	032
	$D_{DF}$	–8947	203	–010	–8725	015	–8710	–8738(8)	–028
	$D_{CH}$	57288	–1848	–1894	53547	–1225	52321	52310(7)	–011
	$D_{CF}$	–73930	1220	–353	–73063	–850	(–73913)*	–71861(8)	(2052)*
	$D_{DD}$	1742	–046	–005	1690	–007	1684	1684(4)	000
	$D_{HD}$	11318	–320	–088	10910	–059	10851	10861(8)	010
$\text{C}^1\text{CHD}_2\text{F}$	$D_{HF}$	–58431	1536	285	–56610	–025	–56636	–56698(6)	–062
	$D_{DF}$	–8934	199	–005	–8740	011	–8729	–8729(8)	–000
	$D_{HD}$	11326	–318	–089	10919	–058	10861	10864(9)	003
	$D_{HF}$	–58475	1525	294	–56657	–025	–56681	–56660(17)	021
$\text{C}^1\text{CHD}_2\text{F}$	$D_{DF}$	–8941	198	–003	–8747	011	–8736	–8720(9)	016
	$D_{CH}$	57219	–1813	–1936	53469	–1268	52201	52222(10)	021
	$D_{CF}$	–74030	1204	–323	–73149	–876	(–74025)*	–71880(10)	(2145)*
	$D_{DD}$	1741	–044	–008	1689	–008	1681	1677(4)	–004
$\text{C}^1\text{CD}_3\text{F}$	$D_{DF}$	–8957	196	001	–8761	006	–8754	–8754(9)	000
	$D_{DF}$	–8964	194	002	–8768	006	–8762	–8710(10)	052
$D_{CF}$	–74124	1187	–296	–73233	–899	(–74132)*	–72013(9)	(2119)*	

\* Not included in least-squares fit to experimental data but calculated from obtained (optimal) fit parameters.  
Rms error of fit = 0.303 Hz.



Table 4(b). Results of least-squares fit to data in table 3(b) for monofluoromethanes in 547 wt% 1132/EBBA at  $302 \pm 1$  K. Fit to 25 dipolar couplings (excluding 4  $D_{CF}$  values), including rigid, harmonic and anharmonic and vibration-rotation correlation contributions in equation (13). (Optimal) bond additivity parameters:

$$\begin{aligned}
 G\Delta\beta_{CH} & 0.2067 \times 10^{-20} \text{ J} & (\text{standard error: } 0.023) & G(\partial\Delta\beta_{CH}/\partial r_{CH}) & 1.193 \times 10^{-10} \text{ J m}^{-1} & (\text{standard error: } 0.070) \\
 G\Delta\beta_{CF} & 0.4840 \times 10^{-20} \text{ J} & (\text{standard error: } 0.018) & G(\partial\Delta\beta_{CF}/\partial r_{CF}) & 2.350 \times 10^{-10} \text{ J m}^{-1} & (\text{standard error: } 0.860).
 \end{aligned}$$

Molecule	Spectral parameter	Calculated					Experimental/ Hz	Experimental - calculated	Estimate $\Delta r_{CF}/\text{Hz}$
		Equilibrium	Anharmonic	Harmonic	Total	Total calculated/ Hz			
$\text{I}^2\text{CH}_3\text{F}$	$D_{HH}$	478.51	-15.82	-4.37	458.31	-4.31	453.90(7)	-0.10	
	$D_{HF}$	-377.92	10.46	1.13	-366.32	3.26	-364.49(11)	-1.43	
	$D_{HH}$	478.08	-15.71	-4.46	457.91	-4.30	452.47(8)	-1.13	
	$D_{HF}$	-377.58	10.38	1.20	-366.00	3.25	-363.21(13)	-0.47	
	$D_{CH}$	372.25	-12.43	-11.83	347.99	-2.39	345.41(13)	-0.18	
	$D_{CF}$	-479.27	8.03	-2.49	-473.74	6.44	-463.12(12)	(4.19)*	140.3
$\text{I}^2\text{CH}_2\text{DF}$	$D_{HH}$	476.64	-14.88	-5.39	456.37	-5.56	451.00(7)	0.19	
	$D_{HD}$	7.403	-2.19	-0.46	71.39	-0.57	70.47(10)	-0.35	
	$D_{HF}$	-381.02	10.21	1.54	-369.28	2.85	-367.27(12)	-0.84	
	$D_{DF}$	-57.75	1.32	-0.07	-56.49	0.61	-55.92(11)	0.03	
	$D_{HH}$	476.25	-14.77	-5.48	456.01	-5.56	449.47(9)	-0.98	
	$D_{HD}$	7.397	-2.17	-0.47	71.33	-0.57	70.51(13)	-0.26	
$\text{I}^3\text{CH}_2\text{DF}$	$D_{HH}$	-380.70	10.12	1.60	-368.98	2.86	-365.94(13)	0.18	
	$D_{DF}$	-57.70	1.31	-0.06	-56.45	0.60	-55.87(13)	0.02	
	$D_{CH}$	370.32	-11.95	-12.25	346.12	-3.15	342.50(13)	-0.47	
	$D_{CF}$	-481.21	7.94	-2.30	-473.56	6.22	-464.12(14)	(5.22)*	174.1
	$D_{DD}$	11.45	-0.30	-0.04	11.12	-0.08	10.95(3)	-0.09	
	$D_{HD}$	7.365	-2.09	-0.57	70.99	-0.75	70.14(11)	-0.10	
$\text{I}^3\text{CHD}_2\text{F}$	$D_{HF}$	-383.90	10.08	1.84	-371.98	2.42	-370.04(13)	-0.48	
	$D_{DF}$	-58.16	1.30	-0.03	-56.90	0.55	-56.40(11)	0.05	
	$D_{HD}$	7.359	-2.07	-0.58	70.94	-0.75	69.96(13)	-0.23	
	$D_{HF}$	-383.60	9.99	1.90	-371.72	2.44	-368.70(14)	0.58	
	$D_{DF}$	-58.12	1.28	-0.02	-56.86	0.55	-56.31	0.25	
	$D_{CH}$	367.56	-11.66	-12.45	343.45	-3.86	340.58(13)	0.99	
$\text{I}^2\text{CD}_3\text{F}$	$D_{CF}$	-482.70	7.85	-2.10	-476.95	6.01	-465.44(13)	(5.50)*	182.8
	$D_{DD}$	11.39	-0.29	-0.05	11.05	-0.10	10.92(3)	-0.02	
	$D_{DF}$	-58.58	1.28	0.01	-57.29	0.49	-56.87(11)	-0.07	
$\text{I}^3\text{CD}_3\text{F}$	$D_{DF}$	-58.53	1.27	0.01	-57.25	0.49	-56.42(13)	0.35	
	$D_{CF}$	-484.02	7.75	-1.93	-478.21	5.83	-466.30(13)	(6.08)*	201.5

\* Not included in least-squares fit to experimental data but calculated from obtained (optimal) fit parameters.  
Rms error of fit = 0.549 Hz.

Table 4(c). Results of least-squares fit to data in table 3(c) for monofluoromethanes in EBBA at  $302 \pm 1$  K. Fit to 25 dipolar couplings (excluding 4  $D_{CF}$  values), including rigid, harmonic and anharmonic and vibration–rotation correlation contributions in equation (13). (Optimal) bond additivity parameters:

$$\begin{aligned}
 G\Delta\beta_{CH} &= 0\text{-}3086 \times 10^{-20} \text{ J} & (\text{standard error: } 0\text{-}046) & & G(\hat{C}\Delta\beta_{CH}/\hat{C}r_{CH}) &= 2\text{-}993 \times 10^{-10} \text{ J m}^{-1} & (\text{standard error: } 0\text{-}145) \\
 G\Delta\beta_{CF} &= 0\text{-}3601 \times 10^{-20} \text{ J} & (\text{standard error: } 0\text{-}010) & & G(\hat{C}\Delta\beta_{CF}/\hat{C}r_{CF}) &= 8\text{-}516 \times 10^{-10} \text{ J m}^{-1} & (\text{standard error: } 1\text{-}863).
 \end{aligned}$$

Molecule	Spectral parameter	Calculated					Total calculated/ Hz	Experimental/ Hz	Experimental – calculated	Estimate $\Delta/\text{CF}/\text{Hz}$
		Equilibrium	Anharmonic	Harmonic	Total	*Non-rigid*				
$^{12}\text{CH}_3\text{F}$	$D_{HH}$	11840	-390	-1408	11302	-516	10786	10643(5)	-143	-2985
	$D_{HF}$	-9349	258	028	-9033	698	-8335	-8541(9)	-206	
$^{13}\text{CH}_3\text{F}$	$D_{HH}$	11625	-382	-1408	11135	-516	10619	10657(7)	038	
	$D_{HF}$	-9182	252	029	-8900	698	-8202	-8545(13)	-343	
	$D_{CH}$	9052	-302	-288	8462	1439	9901	10044(10)	143	
	$D_{CF}$	-11655	195	-061	-11520	2529	(-8991)*	-11159(25)	(-2168)*	
$^{12}\text{CH}_2\text{DF}$	$D_{HH}$	11198	-350	-132	10717	-710	10007	9783(6)	-224	
	$D_{HD}$	1954	-058	-012	1884	-062	1822	1744(7)	-078	
	$D_{HF}$	-9995	266	037	-9693	637	-9056	-9058(11)	-002	
	$D_{DF}$	-1375	032	-001	-1344	122	-1222	-1212(8)	010	
	$D_{HH}$	11037	-342	-132	10562	-710	9853	9786(45)	-067	
	$D_{HD}$	1929	-057	-012	1860	-062	1798	1739(50)	-059	
$^{13}\text{CH}_2\text{DF}$	$D_{HH}$	-9867	260	038	-9569	638	-8931	-9069(47)	-138	
	$D_{DF}$	-1356	031	-001	-1325	121	-1204	-12408(13)	-004	
	$D_{CH}$	8563	-277	-286	8040	1309	9308	9263(50)	-045	
	$D_{CF}$	-12086	199	-058	-11945	2515	(-9430)*	-11252(15)	(-1822)*	
	$D_{DD}$	322	-008	-001	312	-007	305	281(2)	-024	
	$D_{HD}$	1838	-052	-015	1771	-091	1680	1611(7)	-069	
$^{13}\text{CHD}_2\text{F}$	$D_{HF}$	-10627	275	043	-10309	576	-9733	-9565(10)	168	
	$D_{DF}$	-1463	033	-000	-1431	112	-1319	-1290(9)	029	
	$D_{HD}$	1815	-051	-016	1748	-091	1657	1606(50)	-051	
	$D_{HF}$	-10509	270	044	-10195	580	-9615	-9569(47)	046	
$^{12}\text{CD}_3\text{F}$	$D_{DF}$	-1445	032	-000	-1413	112	-1300	-1299(48)	001	
	$D_{CH}$	7866	-252	-271	7342	1186	8528	8522(50)	-006	
	$D_{CF}$	-12412	202	-054	-12264	2502	(-9762)*	-11332(47)	(-1570)*	
	$D_{DD}$	302	-008	-001	293	-011	281	262(2)	-019	
$^{13}\text{CD}_3\text{F}$	$D_{DF}$	-1553	034	000	-1519	103	-1416	-1366(9)	050	
	$D_{DF}$	-1536	033	000	-1502	103	-1399	-1379(12)	020	
$D_{CF}$	-12698	203	-051	-12546	2490	(-10055)*	-11428(13)	(-1373)*		

\* Not included in least-squares fit to experimental data but calculated from obtained (optimal) fit parameters. Rms error of fit = 1.150 Hz.

description is sound. The least stable parameter is the  $G(\partial\Delta\beta_{CF}/\partial r_{CF})_e$ , which is not surprising in view of the difficulties encountered with the  $^{13}\text{C}$ -F experimental dipolar couplings described above. Clearly, the assumption of bond additivity for describing the orientation of the fluoromethanes is quite reasonable.

The set of four bond additivity parameters obtained in the three nematic solvents show large differences. Also, a glance at the sets of experimental dipolar couplings for monofluoromethanes in table 3 for the three different nematic solvents used here shows that the values obtained in the 54.7 wt% 1132 in EBBA mixture are intermediate between those obtained in the component liquid crystals, all at 302 K. These observations naturally lead to a discussion on orientation mechanisms which may not be identical in the three solvents.

It has been shown extensively in previous work that a mixture of 55 wt% 1132 in EBBA at 301.4 K forms a nematic solvent of a somewhat special nature. The picture which has emerged from the use of this and other liquid crystal mixtures is that two mechanisms are important for the orientation of solutes in nematic phases. One mechanism appears to be the interaction between an average electric field gradient (efg) present in the solvent and the solute molecular quadrupole moment [8–10]. The second mechanism is short range in character, depends on the size and shape of the solute molecule, and can be modelled effectively in a phenomenological fashion. The above mixture possesses the special property that its average efg equals zero, thus presenting the experimentalist with a situation in which only a *single* orientation mechanism is important.

If we assume that the above considerations also apply to the monofluoromethanes, we would expect that in the liquid crystals 1132 and EBBA *two* orientation mechanisms would be at play, whereas in the mixture only *one* mechanism remains. It should be stated, however, that from the present work alone it is not possible to decide how many independent orientation mechanisms are of importance. If in the framework of the ‘mean-field’ approach more than one mechanism would be present, and if all these mechanisms would obey the assumption of bond additivity, the dipolar couplings could still be fitted with a set of four ‘effective’ bond additivity parameters. However, the physical meaning of such parameters, which now depend on *all* the contributing mechanisms in a complicated fashion, would be lost. If one or more of the contributing mechanisms would not fulfil the assumption of bond additivity, a set of four parameters would be insufficient to fit the dipolar couplings adequately, and relatively large deviations between measured and calculated couplings would result.

It is obvious that, if for any of the contributions to the orientation the assumption of bond additivity does not hold, one has to resort to less simplifying assumptions or, in the worst case, to give up the appealing notion of bond additivity altogether and use the complete set of independent effective parameters required to describe the orienting interactions. A careful look at the results of table 4 shows that the fits based on 4 bond additivity parameters for the mixture and for 1132 are of excellent quality, and lead to appreciably smaller rms values than obtained for EBBA. We are tempted to think that the agreement with experiment would be better in the zero-efg mixture than in the pure component solvents because in the zero-efg mixture one orienting interaction has been removed that may possibly not be described by bond additivity. However, this notion is confirmed only if we compare our results for the zero-efg mixture and EBBA, but not in the comparison with 1132.

## 6. Conclusions

A series of eight isotopically substituted fluoromethanes has been studied under virtually identical experimental circumstances in three different liquid crystal solvents, namely, two component nematic phases and a mixture of the two. Using bond additivity to reduce the number of parameters required to describe 29 dipolar couplings observed for these solutes, these anisotropic couplings can be reproduced adequately by only four adjustable parameters. These results lend definite support to the underlying assumption of bond additivity.

In a simple theoretical treatment of the solute orientation the main contribution arises from 'rigid' equilibrium properties of the solute molecules. However, the quality of the description deteriorates significantly if 'non-rigid' contributions such as vibration-rotation interaction, and harmonic and especially anharmonic vibrational corrections are omitted. In addition, the present study indicates a contribution to the observed dipolar carbon-fluorine couplings due to the anisotropy in  $J_{CF}$ .

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