# Anisotropy of the Indirect Nuclear Spin-Spin Coupling Constants. III. Problems in the Structure Determination of the Molecule Dissolved in a Nematic Solvent

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Anisotropy of the indirect nuclear spin-spin coupling constant was studied theoretically. All the contributions to the coupling tensors were calculated for various molecules by using the INDO molecular orbitals. As shown in part I of this series, the calculated $^{13}$C–H coupling anisotropy of $^{13}CH_3F$ is too small to be compared with the value obtained experimentally by Krugh and Bernheim. Thus we examined the substituent effect on the anisotropy in the $^{13}CH_3X$ series. It is concluded that the experimentally estimated value of the $^{13}$C–H coupling anisotropy in $^{13}CH_3F$ as large as 1890 Hz is erroneous and that it contains some other effects which are more important than electronic effect. We believe that the change in molecular geometry from gas state to the solute state in a nematic solvent is the most probable origin for the differences between theories and experiments. For the directly bonded C–X couplings (X is C, N or F), their anisotropies are in the same order of magnitude as their isotropic couplings. For the non-bonded C–X nuclei, they seem negligible in magnitude. For the F–F couplings, their anisotropies are exceptionally large and the orbital term is a very important source of anisotropy. Furthermore, even for the isotropic F–F couplings, the orbital and spin dipolar terms are very important and sometimes make decisive contributions exceeding the Fermi contact term.

Since the experiment of Saupe and Englert,[1,2] extensive investigations of the molecules dissolved in liquid-crystal solvents have been carried out by means of nuclear magnetic resonance (NMR) technique.[3–5] Chemically fundamental data such as molecular motion and molecular geometry in liquid-crystal phase have accumulated, in addition to a more detailed knowledge of NMR parameters than those available by the usual NMR measurements in isotropic liquid phase. However, some difficulties exist in the determination of molecular geometry. In order to calculate molecular geometry (strictly speaking, ratios of the geometrical parameters) from spectral splittings, one needs the value of the anisotropy of the indirect nuclear spin-spin coupling constant ($J$).[3,6] The most frequent assumption is a disregard of the anisotropy of the indirect coupling constant. However, the molecular geometries obtained under this assumption sometimes differ slightly from those obtained by other measurements in gas phase (*e.g.* electron diffraction method, microwave method *etc*).[6,7] On the other hand, if one assumes that the geometry obtained by other measurements in gas phase can be used without any correction, one may calculate the anisotropy of the indirect coupling constant from spectral splittings. This treatment, however, has sometimes given extremely large anisotropy.[8]

For a solution of this situation, the following points must be clarified. (1) Can the anisotropy of the indirect coupling constant be assumed to be nearly zero ? (2) If so, why does the geometry obtained by means of NMR in liquid crystal solvent differ from that given by other measurements in gas phase ?

The main purpose of this series of investigation is to solve these problems theoretically. Possible origins of the coupling anisotropy were studied by both sum-over-state[9] and finite perturbation[10] methods on the basis of molecular orbital (MO) theory. The Fermi-spin dipolar cross term is important. For doubly and triply bonded nuclei, the orbital term is also important. However, for the $^{13}$C–H coupling in $CH_3F$, the calculated anisotropy was too small to be compared with 1890 Hz obtained by assuming microwave geometry.[8a] Similar results were also obtained by Barfield[11] by valence-bond method, and by Buckingham and Love[12] with a similar MO treatment.

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Theory of coupling anisotropy is described in the next section. It is applied to various molecules by using the INDO MO's of Pople *et al.*[13] The substituent effect in the $^{13}CH_3X$ series[14] will be discussed for the directly bonded $^{13}C$–H coupling anisotropy in paticular. Another important aspect is the coupling anisotropy between F–F nuclei. For Problem (2), the possible factors are twofold; the vibrational effect and the effect due to the structural change from gas state to the solute state in a nematic solvent. Their relative importance is examined in the last section.

## Theoretical Background

The essential part of the theory of the anisotropy of the indirect nuclear spin-spin coupling constant were given by us[9,10] and by Buckingham and Love.[12]

Anisotropy of the indirect coupling constant originates from three mechanisms: Fermi-spin dipolar cross (FSD) term, spin dipolar (SD) term and orbital (OB) term.[9,15] The Fermi-contact (FC) term is isotropic. These contributions can be developed in terms of molecular orbital theory, along lines similar to the treatment of Pople and Santry.[16] We introduce a reduced coupling constant $\boldsymbol{K}_{AB}$ defined by

$$\boldsymbol{K}_{AB} = (2\pi/\hbar\gamma_A\gamma_B)\boldsymbol{J}_{AB} \tag{1}$$

First we set the following three approximations (*Level A* approximation). (1) Use of the sum-over-state perturbation method, taking single Slater determinant built up from SCF MO's as zeroth order wavefunction. An improvement over this treatment may be achieved by using the finite perturbation[17] (or coupled Hartree-Fock[18]) method.[10] (2) LCAO-MO approximation. Actually the INDO SCF MO's expanded by all the valence AO's will be used. (3) One-center integral approximation. This approximation may be crude especially for the coupling tensor between directly bonded nuclei. However, since all the Hamiltonians considered (Eqs. (1)—(4)[9]) lay stress on the electronic structure in the vicinity of nuclei, and we use the INDO MO's based on the zero-differential overlap approximation (theoretically based on the orthogonalized AO's[19]), this approximation may be approved. It should be noted that under this approximation, the anisotropy of the H–H coupling constant becomes zero, which may be justified by the study of Barfield.[11]

As an example, the elements of coupling tensor obtained under Level A approximation are given for the FSD term as follows.

$$(\boldsymbol{K}_{AB}{}^{(2,3)})_{\alpha\alpha} = -(64\pi\beta^2/15)s_A(0)\langle r^{-3}\rangle_B \sum_i^{occ}\sum_j^{vac}({}^3\Delta E_{i\to j})^{-1}$$
$$C_{is_A}C_{js_A}(2C_{ip\alpha_B}C_{jp\alpha_B} - \sum_{\delta(\mp\alpha)}{}' C_{ip\delta_B}C_{jp\delta_B}) + [\text{interchange term of A and B}] \tag{2-a}$$

$$\underset{(\alpha\mp\beta)}{(\boldsymbol{K}_{AB}{}^{(2,3)})_{\alpha\beta}} = -(32\pi\beta^2/5)s_A(0)\langle r^{-3}\rangle_B \sum_i^{occ}\sum_j^{vac}({}^3\Delta E_{i\to j})^{-1}$$
$$C_{is_A}C_{js_A}(C_{ip\alpha_B}C_{jp\beta_B} + C_{ip\beta_B}C_{jp\alpha_B}) + [\text{interchange term of A and B}] \tag{2-b}$$

The other contributions are summarized in Appendix. In Eq. (2), $s_A(0) = (s_A|\delta(\boldsymbol{r})|s_A)$, $s_A$ and $p_{\alpha A}$ are the s-type AO and $2p_\alpha$AO ($\alpha$ is $x, y$ or $z$) centered on atom A. $\sum_{\delta(\mp\alpha)}{}'$ means the summation over the directions $x, y$, and $z$ except $\alpha$. The other notations are the same as those used by Pople and Santry.[16]

Although we use Level A approximation in actual calculations, it is sometimes convenient to introduce further approximations: (4) Average excitation energy ($\Delta E$) approximation.[20] (5) zero-differential overlap (ZDO) approximation. Hereafter we call this level of approximation Level B approximation, where the elements of coupling tensor are given for the FSD term by

$$(\boldsymbol{K}_{AB}{}^{(2,3)})_{\alpha\alpha} = (16\pi\beta^2/15)s_A(0)\langle r^{-3}\rangle_B({}^3\Delta E)^{-1}$$
$$\times (2P^2_{s_Ap\alpha_B} - \sum_{\delta(\mp\alpha)}{}' P^2_{s_Ap\delta_B}) + [\text{interchange term of A and B}] \tag{3-a}$$

$$\underset{(\alpha\mp\beta)}{(\boldsymbol{K}_{AB}{}^{(2,3)})_{\alpha\beta}} = (16\pi\beta^2/15)s_A(0)\langle r^{-3}\rangle_B({}^3\Delta E)^{-1}$$
$$\times (P_{s_Ap\alpha_B}P_{s_Ap\beta_B}) + [\text{interchange term of A and B}] \tag{3-b}$$

The other contributions are summarized in Appendix. In Eq. (3), $P_{s_Ap\alpha_B}$ denotes the bond order between $s_A$ and $2p_{\alpha B}$ AO's.

$$P_{s_Ap\alpha_B} = \sum_i 2C_{is_A}C_{ip\alpha_B} \tag{4}$$

When localized AO's are introduced, the chemical picture of the coupling mechanisms becomes clear. Namely, each contribution to the $\sigma\sigma$-element of the coupling tensor, $(J_{AB})_{\sigma\sigma}$ becomes as follows.

$$[\text{FC term}] \propto P^2_{ss'}$$
$$[\text{FSD term}] \propto P^2_{s\sigma'} + [\text{interchange term}]$$
$$[\text{SD term}] \propto 8P^2_{\sigma\sigma'} + 2(P^2_{\pi\pi'} + P^2_{\bar{\pi}\bar{\pi}'}) + 9P_{\sigma\sigma'}(P_{\pi\pi'} + P_{\bar{\pi}\bar{\pi}'})$$
$$[\text{OB term}] \propto P_{\pi\pi'}P_{\bar{\pi}\bar{\pi}'}$$

These equations may be considered as showing the "paths" and "width" along which two nuclear moments interact. However, it should be noted that although this chemical picture is very intuitive, it sometimes leads to erroneous results, especially for the coupling constants between nuclei in polar bonds.[16] Thus, in the following applications, we use Level A approximation. The values of the one-center

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integrals, $s_A(0)$ and $\langle r^{-3}\rangle_A$ are quoted from those summarized by Morton[21] except for $s_H(0)=0.550$ (a.u.).

## Results and Discussion

*General Features.* In Tables 1—4, the coupling constants calculated in Level A approximation are summarized for various nuclear pairs. First, the relative importance of the coupling mechanisms is examined. As is well-known, the most important mechanism for the *isotropic* coupling constants is the FC term, the SD and OB mechanisms giving only small contributions. However, exceptions are found for the F–F couplings (Tables 3 and 4), where the OB and SD terms are very important and sometimes give predominant contributions exceeding the FC term. For the *anisotropies*, the FSD term is important (Tables 1–4). The OB term is important for the multiply bonded nuclear pairs (Tables 1 and 4) and for the F–F couplings (Tables 3 and 4). The SD term is less important.

Secondly, the anisotropies between non-bonded nuclear pairs are calculated to be very small as compared with those between directly bonded ones (Tables 1 and 2), except for the F–F coupling anisotropies (Tables 3 and 4).

Thirdly, for isotropic couplings, the calculated values are smaller than experimental ones. The disagreement may be due to the too large excitation energies calculated by the INDO method and/or the neglect of the self-consistency requirement[22] in the present perturbation treatment. An improvement can be achieved in the finite perturbation method.[10] However, the defect is not very serious for semi-quantitative discussions.

*X–H Couplings.* As seen from Eqs. (6), (A-1)—(A-4), the sources of the isotropic and anisotropic couplings between X and H nuclei are only the FC and FSD terms, respectively.

The calculated isotropic C–H coupling constants of methane, ethylene, and acetylene are 64.6, 80.1, and 141.9 Hz and the experimental values are 125.0, 156.2, and 249.0 Hz, respectively. Their calculated anisotropies, defined by $J_{xx}-1/2(J_{yy}+J_{zz})$, are 33.0, 24.5, and 18.0 Hz, respectively, where the $x$-axis of the coupling tensor is taken to be parallel to the C–H bonds. This sequence of change reflects that expected from changes in hybridization for the FC and FSD terms.

The calculated coupling constants between X–H nuclei in $CH_3Y$ (Y=H, $CH_3$, CN, OH, NC, F, and I) are summarized in Table 1. The $^{13}$C–H coupling anisotropy of $CH_3F$ is also too small to be compared with the experimentally estimated value.[8a] Similar results were also obtained by Barfield,[11] and Buckingham and Love.[12] The difference between theories

TABLE 1. X–H COUPLINGS IN THE METHYL DERIVATIVES

| Molecule | Nuclei[a] | $(J_{XH})_{iso}$ Exptl | $(J_{XH})_{iso}$ Calcd | $(J_{XH})_{aniso}$ Exptl | $(J_{XH})_{aniso}$ Calcd | $S_{zz}$ |
|---|---|---|---|---|---|---|
| $CH_4$ | $^{13}$C–H | 125.0[b] | 64.6 | — | −9.9 | — |
| $C_2H_6$ | $^{13}$C–H | 124.9[b] | 57.8 | — | −8.7 | — |
|  | ($^{13}$C–H) |  | 0.3 | — | 0.3 |  |
| $CH_3CN$ | $^{13}$C–H | 136.0[c] | 58.9 | −50[d] | −8.7 | 0.1009[d] |
|  | ($^{15}$N–H) | −1.75[c] | −0.2 | — | 2.1 |  |
|  | ($^{13}$C–H) | −10.0[c] | 1.4 | — | 1.1 |  |
| $CH_3OH$ | $^{13}$C–H | 141.0[b] | 68.9 | — | −10.7[e] | 0.0050[d] |
| $CH_3NC$ | $^{13}$C–H | 145.2[f] | 64.7 | −108[g] | −9.8 | 0.0997[g] |
|  | ($^{13}$C–H) |  | −0.1 | — | −1.8 |  |
|  | ($^{15}$N–H) | 3.8[f] | −0.6 | $\begin{pmatrix}-401\\ \pm 142\end{pmatrix}^{h)}$ | −0.5 |  |
| $CH_3F$ | $^{13}$C–H | 148.8[i] | 75.2 | 1890[i]<br>±130 | −11.0 | 0.0166[i] |
|  | ($^{19}$F–H) | 46.3[i] | 7.3 | −18[i]<br>±54 | −9.0 |  |
| $CH_3I$ | $^{13}$C–H | 151.4[j] | — | 555[k] | — | 0.0323[k] |

a) The nuclei in parentheses are non-bonding.
b) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).
c) W. McFarlane, *Mol. Phys.*, **10**, 603 (1966): G. Englert and A. Saupe, *Mol. Cryst.*, **8**, 233 (1969).
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e) Free rotation about the C-O bond is assumed.
f) W. McFarlane, *J. Chem. Soc.*, **1967**, 1660.
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h) C. S. Yannoni, *J. Chem. Phys.*, **52**, 2005 (1970).
i) T. R. Krugh and R. A. Bernheim, *J. Amer. Chem. Soc.*, **91**, 2385 (1969).
j) S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes, and J. Kraitchman, *J. Chem. Phys.*, **20**, 1112 (1952).
k) I. Morishima, A. Mizuno, H. Nakatsuji, and T. Yonezawa, *Chem. Phys. Lett.*, to be published.
l) $J_{aniso}=J_{/\!/}-J_{\perp}$, where $/\!/$ and $\perp$ mean parallel and prependicular with the molecular symmetry axis, respectively.

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Table 2. C-X coupling constants (Hz)

| Molecule | C-X | Isotropic, $(J_{XX'})_{iso}$ | | | | | Anisotropic, $(J_{CX})_{aniso}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcd | | | | Exptl | Calcd | | | | Exptl |
| | | Fermi | Spin dipolar | Orbital | Total | | Fermi-spin dipolar | Spin dipolar | Orbital | Total | |
| $C_2H_6$ | $^{13}C$-$^{13}C$ | 6.6 | 0.4 | −0.7 | 6.2 | 34.6a) | 12.7 | 0.7 | 1.5 | 14.8 | — |
| $C_2H_4$ | $^{13}C$-$^{13}C$ | 20.8 | 1.4 | −5.4 | 16.8 | 67.6a) | 14.4 | −2.2 | 8.9 | 22.7 | — |
| $C_2H_2$ | $^{13}C$-$^{13}C$ | 56.1 | 4.2 | 6.1 | 66.5 | 171.5a) | 14.2 | −6.2 | 43.2 | 51.1 | — |
| $CH_3F$ | $^{13}C$-$^{19}F$ | −99.2 | 9.4 | −6.3 | −96.0 | −161.9b) | 93.5 | −16.2 | 4.6 | 114.2 | 700±<br>130b) |
| $CH_3CN$ | $^{13}C$≡$^{15}N$ | 1.8 | −1.9 | −0.2 | −0.3 | −17.5c) | −11.0 | 3.7 | −27.7 | −35.1 | — |
| | $^{13}C$-$^{13}C$ | 15.3 | 0.3 | −0.5 | 15.2 | 57.3d) | 16.7 | 0.1 | 1.9 | 18.7 | — |
| | ($^{13}C$-$^{15}N$) e) | 0.0 | −0.2 | 0.0 | −0.2 | — | −0.6 | −0.2 | 0.8 | 0.0 | — |
| $CH_3NC$ | $^{15}N$≡$^{13}C$ | 10.5 | −1.7 | −0.3 | 8.5 | ±5.8f) | −10.5 | 3.4 | −25.5 | −32.6 | — |
| | $^{13}C$-$^{15}N$ | −2.3 | −0.3 | 0.4 | −2.2 | −10.7g) | −9.2 | −0.3 | −1.0 | −10.5 | — |
| | ($^{13}C$-$^{13}C$) | 1.2 | 0.0 | 0.1 | 1.3 | — | 1.1 | 0.3 | 1.1 | 2.5 | — |

a) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.*, **A269**, 385 (1962).
b) T. R. Krugh and R. A. Bernheim, *J. Amer. Chem. Soc.*, **91**, 2385 (1969).
c) W. McFarlane, *Mol. Phys.*, **10**, 603 (1966).
d) K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).
e) The nuclei in parenthesis are non-bonding.
f) I. Morishima, T. Yonezawa, and K. Goto, to be published.
g) W. McFarlane, *J. Chem. Soc. A*, **1967**, 1660.
h) $J_{^{13}C^{14}N} = -0.713 J_{^{13}C^{15}N}$
i) $(J_{CX})_{aniso} = J_{xx} - 1/2(J_{yy} + J_{zz})$, where $x$-axis is taken to be parallel with the C-X bond.

and experiments seem to be far beyond the accuracy of the theories.

Recently, the substituent effect on the directly bonded $^{13}C$–H coupling anisotropies $(J_{CH})_{aniso}$ in methyl derivatives are obtained by analyzing the NMR spectra in the same way as for $CH_3F$.14) They are also given in Table 1. First, we examine the isotropic $^{13}C$–H couplings $(J_{CH})_{iso}$. From the experimental values, we can estimate the order of magnitude of the change in the electron distribution near the C–H bond induced by substitution. It is 2—6 %. The change of the same order is also reproduced by the INDO MO's. On the other hand, the substituent effect on the coupling anisotropy $(J_{CH})_{aniso}$ estimated from the experimental analyses is unusually large. In fact, in order to explain this substituent effect, a very large change must be assumed in the electronic structure in the vicinity of C–H bond. However, this contradicts the substituent effect seen for $(J_{CH})_{iso}$, while the calculated effect on $(J_{CH})_{aniso}$ is the same order as that on $(J_{CH})_{iso}$.

Thus, it is concluded that the experimentally estimated values of $(J_{CH})_{aniso}$ given in Table 1 still contain some other effects which are more important than the electronic effect. Then, a value of $(J_{CH})_{aniso}$ of $CH_3F$ as large as 1890 Hz8a) is erronious. We see in Table 1 that there is an approximate parallelism between the experimentally estimated values of $(J_{CH})_{aniso}$ and the orientation parameters $S_{zz}$ in nematic solvent.

*C–X Couplings.* The calculated values of the C–X coupling constants of ethane, ethylene, acetylene, and methyl derivatives are summarized in Table 2, from which we see: 1) compared with C–H couplings, the magnitude of the C–X coupling anisotropies are comparable to those of the isotropic coupling constants. 2) the calculated value of $^{13}C$–F coupling anisotropy is still small compared with the experimental value,8a) although the value 207 Hz is obtained by finite perturbation method,10) and 3) for the anisotropies of the $^{13}C$-$^{15}N$ couplings in $CH_3CN$ and $CH_3NC$, the OB term contributes to a great extent, due to the triple bond character of these bonds. The sign of the isotropic $^{15}C$≡$^{13}N$ coupling constant of $CH_3NC$ is expected to be positive and is the reverse of that of the same nuclear pair in $CH_3CN$.

*Coupling Tensors of the Molecules Including Fluorine Nuclei.* So far, we have seen that the coupling anisotropies between non-bonded nuclei are very small in magnitude compared with those between directly bonded nuclei. However, this is not always the case for the F–F couplings. Experimentally, Snyder and Anderson8d) pointed out that the anisotropy of the F–F coupling in hexafluorobenzene might be considerably large. Similar suggestions were also given for symm-tetrafluorobenzene,8b) 1,3,5-trifluorobenzene,8b) 1,1-difluoroethylene,8f) and tetrafluoroethylene.8g)

The calculated coupling tensors of the molecules including fluorine nuclei are summarized in Tables 3 and 4. The following points are remarkable: 1) For the *isotropic* F–F couplings,23) the OB and SD contributions are very important.24) In the geminal F–F

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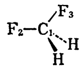
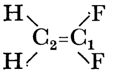
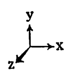
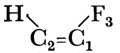
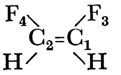
23) J. N. Murrell, P. E. Stevenson, and G. T. Jones, *Mol. Phys.*, **12**, 265 (1967).

24) Importance of the orbital term in the isotropic F–F coupling constants has been stressed independently by Blizzard and Santry. (A. C. Blizzard and D. P. Santry, *Chem. Communications*, **1970**, 87).

TABLE 3. CALCULATED COUPLING TENSORS (Hz) OF THE FLUOROMETHANES AND DIFLUOROETHYLENES[a)]

| Molecule | Nuclei | Fermi | Fermi-spin dipolar | Spin dipolar | Orbital | Total | $J_{\rm iso}$ Exptl. |
|---|---|---|---|---|---|---|---|
| $CH_3F$ | C-F[b)] | −99.1 | $\begin{bmatrix}62.3&0&0\\0&-31.1&0\\0&0&-31.1\end{bmatrix}$<br>0.0 (93.5) | $\begin{bmatrix}20.3&0&0\\0&4.1&0\\0&0&4.1\end{bmatrix}$<br>9.5 (16.2) | $\begin{bmatrix}-3.2&0&0\\0&-7.7&0\\0&0&-7.7\end{bmatrix}$<br>−6.2 (4.6) | $\begin{bmatrix}-19.8&0&0\\0&-133.9&0\\0&0&-133.9\end{bmatrix}$<br>−95.8 (114.2) | −161.9[c)] |
| $CH_2F_2$ | $C_1$-$F_2$ | −95.3 | $\begin{bmatrix}67.1&11.8&0\\11.8&-32.2&0\\0&0&-34.2\end{bmatrix}$<br>0.0 (100.3) | $\begin{bmatrix}12.5&-1.1&0\\0.4&1.1&0\\0&0&2.8\end{bmatrix}$<br>5.4 (10.6) | $\begin{bmatrix}-0.4&-2.6&0\\-0.7&-1.4&0\\0&0&-39.9\end{bmatrix}$<br>−13.9 (20.3) | $\begin{bmatrix}-16.1&8.1&0\\11.4&-127.7&0\\0&0&-167.4\end{bmatrix}$<br>−103.7 (131.5) | −234.8[d)] |
|  | $F_2$-$F_3$ | −103.9 | $\begin{bmatrix}32.3&-0.7&0\\-0.7&32.3&0\\0&0&-65.1\end{bmatrix}$<br>0.0 (48.7) | $\begin{bmatrix}53.9&3.6&0\\18.6&46.0&0\\0&0&9.2\end{bmatrix}$<br>36.4 (26.3) | $\begin{bmatrix}-24.4&11.6&0\\7.1&-31.0&0\\0&0&286.1\end{bmatrix}$<br>76.9 (−152.0) | $\begin{bmatrix}-42.1&14.5&0\\24.9&-56.6&0\\0&0&126.4\end{bmatrix}$<br>9.2 (−77.0) | (+150)[e)] |
| 1,1-$C_2H_2F_2$ | C=C | 31.8 | $\begin{bmatrix}10.7&0&0\\0&-5.4&0\\0&0&-5.4\end{bmatrix}$<br>0.0 (16.1) | $\begin{bmatrix}0&0&0\\0&1.0&0\\0&0&2.5\end{bmatrix}$<br>1.2 (−1.8) | $\begin{bmatrix}2.0&0&0\\0&-10.7&0\\0&0&-1.2\end{bmatrix}$<br>−3.3 (8.0) | $\begin{bmatrix}44.6&0&0\\0&16.7&0\\0&0&27.7\end{bmatrix}$<br>29.7 (22.4) | — |
|  | $C_1$-$F_3$ | −59.2 | $\begin{bmatrix}-16.4&42.4&0\\42.2&53.7&0\\0&0&-37.3\end{bmatrix}$<br>0.0 (−24.6) | $\begin{bmatrix}3.0&4.8&0\\1.9&4.7&0\\0&0&-1.3\end{bmatrix}$<br>2.1 (1.3) | $\begin{bmatrix}-15.1&12.2&0\\12.4&-11.8&0\\0&0&-25.6\end{bmatrix}$<br>−17.4 (3.6) | $\begin{bmatrix}-87.7&59.1&0\\56.5&-12.6&0\\0&0&-123.3\end{bmatrix}$<br>−74.6 (−19.8) | −287.0[d)] |
|  | $F_3$-$F_4$ | −24.3 | $\begin{bmatrix}-19.0&0&0\\0&78.4&0\\0&0&-59.3\end{bmatrix}$<br>0.0 (−28.6) | $\begin{bmatrix}29.4&-2.0&0\\2.0&51.0&0\\0&0&-3.4\end{bmatrix}$<br>25.7 (5.6) | $\begin{bmatrix}-79.0&0.1&0\\-0.1&-36.3&0\\0&0&174.0\end{bmatrix}$<br>19.6 (−147.9) | $\begin{bmatrix}-92.9&-2.0&0\\2.0&68.7&0\\0&0&87.0\end{bmatrix}$<br>20.9 (−170.8) | +36.4[f)] |
| *trans*-$C_2H_2F_2$ | $C_1$=$C_2$ | 35.5 | $\begin{bmatrix}9.4&-1.8&0\\-1.8&-4.6&0\\0&0&-4.8\end{bmatrix}$<br>0.0 (14.1) | $\begin{bmatrix}0&0.1&0\\0.1&1.0&0\\0&0&2.4\end{bmatrix}$<br>1.1 (−1.7) | $\begin{bmatrix}0.9&-1.5&0\\-1.5&-11.7&0\\0&0&-1.0\end{bmatrix}$<br>−3.9 (7.3) | $\begin{bmatrix}45.8&-3.6&0\\-3.2&20.1&0\\0&0&32.1\end{bmatrix}$<br>32.7 (19.7) | — |
|  | $C_1$-$F_3$ | −65.4 | $\begin{bmatrix}-5.4&56.6&0\\56.6&47.0&0\\0&0&-41.7\end{bmatrix}$<br>0.0 (−8.1) | $\begin{bmatrix}4.2&6.2&0\\3.8&7.5&0\\0&0&-1.9\end{bmatrix}$<br>−3.3 (1.4) | $\begin{bmatrix}-11.4&0.1&0\\-1.0&-10.4&0\\0&0&-7.5\end{bmatrix}$<br>−9.8 (−2.5) | $\begin{bmatrix}-78.0&62.9&0\\59.4&-21.3&0\\0&0&-116.4\end{bmatrix}$<br>−71.9 (−9.2) | — |
|  | $F_3$-$F_4$ | 13.4 | $\begin{bmatrix}12.1&35.5&0\\35.5&11.8&0\\0&0&-23.8\end{bmatrix}$<br>0.0 (18.1) | $\begin{bmatrix}9.2&-3.4&0\\-0.8&7.7&0\\0&0&-4.2\end{bmatrix}$<br>4.2 (7.5) | $\begin{bmatrix}-92.7&95.6&0\\95.6&-118.2&0\\0&0&-7.7\end{bmatrix}$<br>−72.9 (−29.8) | $\begin{bmatrix}-58.1&127.8&0\\130.3&-85.3&0\\0&0&-22.3\end{bmatrix}$<br>−55.2 (−4.3) | −124.8[g)] |
| *cis*-$C_2H_2F_2$ | $C_1$=$C_2$ | 30.6 | $\begin{bmatrix}10.2&0&0\\0&-5.0&0\\0&0&-5.2\end{bmatrix}$<br>0.0 (15.3) | $\begin{bmatrix}0&-0.1&0\\0.1&1.0&0\\0&0&2.6\end{bmatrix}$<br>1.2 (−1.8) | $\begin{bmatrix}1.7&-2.1&0\\2.1&-10.7&0\\0&0&-0.8\end{bmatrix}$<br>−3.3 (7.5) | $\begin{bmatrix}42.5&-2.2&0\\2.2&15.9&0\\0&0&27.2\end{bmatrix}$<br>28.5 (21.0) | — |
|  | $C_1$-$F_3$ | −70.7 | $\begin{bmatrix}-5.9&48.6&0\\48.6&41.9&0\\0&0&-36.0\end{bmatrix}$<br>0.0 (−8.9) | $\begin{bmatrix}5.0&7.1&0\\3.6&7.9&0\\0&0&-1.8\end{bmatrix}$<br>3.7 (2.0) | $\begin{bmatrix}-12.6&1.0&0\\0.6&-10.9&0\\0&0&-7.5\end{bmatrix}$<br>−10.3 (−3.4) | $\begin{bmatrix}-84.2&56.6&0\\52.7&-31.8&0\\0&0&-115.9\end{bmatrix}$<br>−77.3 (−10.4) | — |
|  | $F_3$-$F_4$ | 49.0 | $\begin{bmatrix}-27.9&0&0\\0&46.4&0\\0&0&-18.5\end{bmatrix}$<br>0.0 (−41.9) | $\begin{bmatrix}-1.0&-3.7&0\\3.7&-6.5&0\\0&0&11.2\end{bmatrix}$<br>1.2 (−3.4) | $\begin{bmatrix}-54.2&-42.1&0\\42.1&11.9&0\\0&0&39.7\end{bmatrix}$<br>−2.6 (−80.0) | $\begin{bmatrix}-34.0&-45.8&0\\45.8&100.8&0\\0&0&81.4\end{bmatrix}$<br>47.6 (−125.1) | ±18.7[g)] |

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a) The notation of the tensor elements is as follows.

$$J_{\rm AB}=\begin{bmatrix}(J_{\rm AB})_{xx}&(J_{\rm AB})_{xy}&(J_{\rm AB})_{xz}\\(J_{\rm AB})_{yx}&(J_{\rm AB})_{yy}&(J_{\rm AB})_{yz}\\(J_{\rm AB})_{zx}&(J_{\rm AB})_{zy}&(J_{\rm AB})_{zz}\end{bmatrix}$$

The value given under each tensor is the contribution to the isotropic coupling constant, and the value given in parenthesis is the contribution to the coupling anisotropy defined by $J_{xx}-1/2(J_{yy}+J_{zz})$.

b) The C-F axis is parallel to the $x$-coordinate axis.

c) T. R. Krugh and R. A. Bernheim, *J. Amer. Chem. Soc.*, **91**, 2385 (1969).

d) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).

e) Assumed from the observed coupling constants of the substituted ethanes: J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Pergamon Press, p. 886 (1966).

f) G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 226 (1963).

g) G. W. Flynn, M. Matsushima, and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 2295 (1963); Y. Kanazawa, J. D. Baldeschwieler, and N. C. Craig, *J. Mol. Spect.*, **16**, 325 (1965) (this reports a negative sign for the isotropic F-F coupling constant in *cis*-$C_2H_2F_2$); M. Fukuyama, *Reports Govt. Chem. Ind. Res. Inst. Tokyo*, **61**, 129 (1966) (this reports a positive sign for the above coupling constant).

TABLE 4. CALCULATED COUPLING TENSORS[a)](Hz) OF THE MONO- AND DI-FLUOROACETYLENE

| Molecule | Nuclei[b)] | Fermi | Fermi-spin dipolar | | Spin dipolar | | Orbital | | Total | | $J_{\mathrm{iso}}$ | $J_{\mathrm{aniso}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $xx$ | $yy$[c)] | $xx$ | $yy$[c)] | $xx$ | $yy$[c)] | $xx$ | $yy$[c)] | | |
| $C_2HF$ | C-C | 71.4 | 9.7 | −4.8 | 0.4 | 5.6 | 30.3 | −5.5 | 111.7 | 66.6 | 81.7 | 45.1 |
| | C-F | −64.8 | 127.5 | −63.8 | 9.1 | −1.6 | −16.1 | −12.5 | 55.8 | −142.6 | −76.5 | 198.4 |
| | C-H | 153.7 | 10.7 | −5.3 | 0.0 | 0.0 | 0.0 | 0.0 | 164.4 | 148.4 | 153.7 | 16.0 |
| | (C-F) | −18.1 | 6.0 | −3.0 | −1.2 | 8·4 | 50.0 | −22.1 | 36.7 | −34.8 | −10.9 | 71.5 |
| $C_2F_2$ | C-C | 101.3 | 8.1 | −4.0 | 0.6 | 5.5 | 29.3 | −4.0 | 139.2 | 98.8 | 112.3 | 34.4 |
| | C-F | −69.9 | 146.8 | −73.4 | 9.6 | −1.3 | −17.3 | −6.6 | 69.2 | −151.2 | −77.7 | 220.3 |
| | (C-F) | −21.2 | 15.2 | −7.6 | 0.2 | 7.9 | 43.6 | −11.3 | 37.8 | −32.3 | −8.9 | 70.1 |
| | (F-F) | 17.7 | −1.3 | 0.6 | −30.6 | −4.1 | 76.6 | −173.6 | 62.5 | −159.3 | −85.4 | 221.8 |

a) The molecular axis is parallel with the $x$-coordinate.
b) The nuclei in parenthesis are non-bonding.
c) $J_{zz}=J_{yy}$.

couplings ($CH_2F_2$ and 1,1-$C_2H_2F_2$), their signs cannot be explained unless *both* of the SD and OB contributions are included. In *trans*-$C_2H_2F_2$ (Table 3) and $C_2F_2$ (Table 4), the OB term is predominant and negative in sign. In *cis*-$C_2H_2F_2$, the contributions due to the SD and OB terms are very small and almost cancel each other, giving the positive coupling constant due chiefly to the FC term. Although both signs are reported (Ref. g in Table 3), the present calculation favours the positive sign. 2) For the F–F coupling anisotropies, the OB term is most important, although the FSD term is also important. The SD term seems less important. 3) For the C–F couplings, the anisotropy becomes large (in absolute magnitude) by fluorine substitution from $CH_3F$ to $CH_2F_2$ chiefly due to an increase in the OB contribution. The change in the isotropic C–F coupling constants from $CH_3F$ to $CH_2F_2$ cannot be explained without OB contributions.

## Meaning of the Difference in Theoretical and Experimental Values

It has been made clear that the experimentally estimated $^{13}$C–H coupling anisotropies of the methyl derivatives still contain some other effects more important than electronic one.

The experimental value of the coupling anisotropy is calculated from the NMR spectral splitting $(\Delta\nu)_{\mathrm{CH}}$ obtained in a nematic solvent by means of the following formula for the $C_{3v}$-symmetry molecules.[3)]

$$(J_{\mathrm{CH}})_{\mathrm{aniso}} = \{(\Delta\nu)_{\mathrm{CH}}-(J_{\mathrm{CH}})_{\mathrm{iso}}-D_{\mathrm{CH}}\}/(2/3)S_{zz}, \tag{5}$$

where $S_{zz}$ is the orientation parameters of the molecular symmetry axis ($z$-axis) with respect to applied magnetic field and $D_{\mathrm{CH}}$ the anisotropy due to direct coupling. In Table 1, $S_{zz}$ is obtained by assuming that the anisotropies of the indirect H–H couplings are zero.[6,7)] This is justified by Barfield.[11)] Krugh and Bernheim[8a)] examined the effects on the isotropic coupling constant $(J_{\mathrm{CH}})_{\mathrm{iso}}$ due to the solvent change and the solvent phase change from nematic to isotropic phases, and concluded that they would not be major factors influencing the results. Thus, the most important factor should be the effect on $D_{\mathrm{CH}}$, by which the value of the $^{13}$C–H coupling anisotropy sensitively changes through Eq. (5).[8a,14)] In order to obtain the values of $(J_{\mathrm{CH}})_{\mathrm{aniso}}$ given in Table 1, $D_{\mathrm{CH}}$ values were calculated from the $r_0$-structure determined by means of microwave technique in gas phase. However, since the NMR measurements of these molecules were carried out in their solute states in nematic solvents, the $D_{\mathrm{CH}}$ values in Eq. (5) should correspond to this state and method of measurement. If we designate this correction by $\Delta_{\mathrm{M}}$ (M indicates a special molecule), it is given by

$$\Delta_{\mathrm{M}} = \text{[NMR geometry in the solute state in nematic solvent]} - \text{[Microwave geometry in gas phase]} \tag{6}$$

The apparent substituent effect on $(J_{\mathrm{CH}})_{\mathrm{aniso}}$ given in Table 1 is reconsidered as representing the substituent effect essentially on $\Delta_{\mathrm{M}}$.

There are two possible origins of the effect on $\Delta_{\mathrm{M}}$. (a) Molecular (harmonic and anharmonic) vibrations.[7d,8a)] The measured value is approximately $\langle\!\langle 1/r^3\rangle\!\rangle$ in NMR and approximately $\langle\!\langle 1/r^2\rangle\!\rangle$ in microwave spectroscopy.[25a)] $r$ is the internuclear distance and $\langle\!\langle\ \rangle\!\rangle$ denotes the statistical average.[26)] (b) The change in molecular geometry from gas state to solute state in the nematic solvent.[7a,7c)]

First, the effect (a) is examined. If we assume that the orientation parameter $S_{zz}$ is independent of internal molecular vibration,[6)] and that the anisotropy of the indirect H–H coupling constant is negligible, we obtain the following equation from Eq. (5).[27)]

$$(T_{\mathrm{CH}})_{zz} = \frac{(\gamma_{\mathrm{C}}\gamma_{\mathrm{H}}\hbar/2\pi)(\langle r_{\mathrm{HH}}{}^2/r_{\mathrm{CH}}{}^5\rangle-2\langle 1/r_{\mathrm{CH}}{}^3\rangle)+2/3(J_{\mathrm{CH}})_{\mathrm{aniso}}}{(\gamma_{\mathrm{H}}{}^2\hbar/2\pi)\langle 1/r_{\mathrm{HH}}{}^3\rangle} \times (T_{\mathrm{HH}})_{zz} \tag{7}$$

---

[25)] a) J. A. Ibers and D. P. Stevenson, *J. Chem. Phys.*, **28**, 929 (1958). b) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes," Elsevier Pub. Co. N. Y. (1968).

[26)] $\langle\!\langle\ \rangle\!\rangle$ denotes the statistical average in the solute state in a nematic solvent. However, if the molecular potential function in this state does not differ much from that in gas state, we can, to first approximation, use the vibrational average in gas state $<\ >$ in spite of $\langle\!\langle\ \rangle\!\rangle$.

[27)] The dependence of the "true" value of $(J_{\mathrm{CH}})_{\mathrm{aniso}}$ on the molecular vibration is negligible.

where $(T_{\mathrm{CH}})_{zz}$ and $(T_{\mathrm{HH}})_{zz}$ are the observed total anisotropic couplings.

Let us introduce the notation[25a)]

$$r_n = \langle r^n\rangle^{1/n}.$$

As a special case, $r_{-2}$ corresponds approximately to the microwave $r_0$ structure, if we neglect the Coriolis and other terms. Ibers and Stevenson[25a)] gave the expansion of $r_n$ as follows.

$$r_{\pm n} = r_{\mathrm{e}}\left(1+\frac{\langle x\rangle}{r_{\mathrm{e}}}-\frac{(1\mp n)}{2r_{\mathrm{e}}^2}\langle x^2\rangle+\cdots\right), \tag{8}$$

where $r_{\mathrm{e}}$ is the equilibrium distance and $x$ the displacement coordinate ($x=r-r_{\mathrm{e}}$). From Eq. (8), we obtain

$$\begin{aligned} r_{-3} &= r_{-2} - \frac{1}{2}\langle x^2\rangle/r_{\mathrm{e}}+\cdots \\ &\simeq r_0(\mathrm{m.w.}) - \frac{1}{2}\langle x^2\rangle/r_{\mathrm{e}}+\cdots, \end{aligned} \tag{9}$$

which shows that if we use the microwave $r_0$ structure in Eq. (7), the main correction due to molecular vibration comes only from the harmonic one. It should be noted that the value of $r_{-3}$ is always smaller than that of $r_{-2}$. For polyatomic molecules the displacement coordinate $x_i$ is given by a linear combination of the normal coordinates $Q_k$:

$$x_i = \textstyle\sum_k L_{ik}Q_k\,,$$

By virtue of the separability of normal coordinates in the harmonic oscillator treatment, the mean-square amplitude $\langle x_i^2\rangle$ is given by[25b)]

$$\langle x_i^2\rangle = \textstyle\sum_k L_{ik}^2\langle Q_k^2\rangle \tag{10}$$

where $\langle Q_k\rangle^2$ is given by

$$\begin{aligned} \langle Q_k^2\rangle &= \frac{h}{8\pi^2 c\nu_k}\coth\frac{hc\nu_k}{2\kappa T} \\ &\rightarrow \frac{h}{8\pi^2 c\nu_k}\ (T\rightarrow 0;\ \text{zero-point vibration}), \end{aligned} \tag{11}$$

where $\nu_k$ is the wave number given in $\mathrm{cm}^{-1}$, and $T$ the absolute temperature. The values of $L_{ik}$ and $\nu_k$ of methyl halides were summarized by Reichman and Overend, and Russel *et al.*[28)]

We consider the effects of harmonic C–H stretching and H–C–H bending vibrations. By substituting the correction term of Eq. (9) into Eq. (7), the value of the first term ($D_{\mathrm{CH}}$ part) in the numerator becames smaller and that of the denominator larger (both these terms are positive). These corrections make the resulting value of $(J_{\mathrm{CH}})_{\mathrm{aniso}}$ larger than the uncorrected one.[29)] Thus, for $CH_3F$ and $CH_3I$, the effect of harmonic vibration can not explain the difference between theory and experiment. Moreover, it cannot explain the substituent effect on $(J_{\mathrm{CH}})_{\mathrm{aniso}}$ shown in Table 1. In fact, since $\nu_{\mathrm{HCH}}(\nu_2)$ is more sensitive to substitution than $\nu_{\mathrm{CH}}(\nu_1)$, it suffices to consider the correction term to $1/r_{\mathrm{HH}}^3$ in the denominator of Eq. (7). From the observed wave numbers, the correction term is larger in $CH_3I$ than in $CH_3F$. This is contrary to the substituent effect shown in Table 1.

The effect of anharmonicity is not so clear as that of harmonic vibration for lack of experimental constants. However, we could eliminate this effect approximately in the above treatment. Since the apparent anisotropies given in Table 1 are most sensitive to the H–C–H valence angle,[8a,14)] this effect and especially the substituent effect, is not large enough to explain the large change. Thus, we believe that the effect (a) cannot interpret the difference between theory and experiment.

Next, the effect (b) is examined. It should be noted that important chemical and/or physical solvent-solute interactions must exist in the solute state in a nematic solvent. The orientation parameter $S_{zz}$ indicates essentially the strength of interaction. We find an approximate parallelism between the apparent anisotropy (essentially proportional to $\Delta_{\mathrm{M}}$ above) and $S_{zz}$ (Table 1).[14)] Although experiments showing this kind of parallelism are still few[29)] and we cannot stress this finding, it gives a support to the effect (b).

There are further supports: Snyder and Meiboom[30)] found a distortion of molecular geometry in a nematic solvent for neopentane and tetramethylsilane. A similar result was also found for tetramethyltin.[31)] There are X-ray diffraction studies[32a)] showing the geometrical change in condensed phase: Harris and Clayton[32b)] reported a slightly larger C–F bond length of $CF_4$ in liquid state than in gas state. There are some experiments showing the geometrical change from gas phase to molecular crystal phase: The I–As–I valence angle in $AsI_3$ is 100.2°± 0.4° (electron diffraction)[33a)] in gas phase and 102.0°± 0.1° (X-ray)[33b)] in crystal phase. Similar differences are also found for $AsBr_3$,[34)] $SbCl_3$[35)] and $SbI_3$.[36)] Thus, we believe that the effect (b) is the most important origin of $\Delta_{\mathrm{M}}$.

For methyl derivatives, the most probable change in molecular geometry from gas state to the solute state in nematic solvents may be a change in the H–C–H

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28) The values of $\nu_1(a_1)$ and $\nu_2(a_1)$ are respectively 2995 and 1493 $\mathrm{cm}^{-1}$ for $CH_3F$, and 3048 and 1279 $\mathrm{cm}^{-1}$ for $CH_3I$. (S. Reichman and J. Overend, *J. Chem. Phys.*, **48**, 3095 (1968).) Since the matrix $\{L_{ik}^2\}$ is almost diagonal for the totally symmetric $a_1$ vibrations, $\nu_1$ and $\nu_2$ represent approximately the C–H stretching and H–C–H angular displacement frequencies, respectively. The values of $L_{11}^2$ and $L_{22}^2$ are respectively 1.0167 and 1.9251 for $CH_3F$. (J. W. Russell, C. D. Needham, and J. Overend, *J. Chem. Phys.*, **45**, 3383 (1966).)

29) Buckingham, *et al.* studied the structure of 3,3,3-trifluoropropylene dissolved in different nematic solvents at various temperatures (Ref. 7d). Their results show a parallelism between $S_{zz}$ and the molecular structures calculated by neglecting the anisotropies of the indirect F–F couplings.

30) L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, **44**, 4057 (1966).

31) K. Hayamizu and O. Yamamoto, *Symposium on Nuclear Magnetic Resonance*, **8**, 88 (1969) (in Japanese).

32) a) R. F. Kruh, *Chem. Revs.*, **62**, 319 (1962); K. Furukawa, *Rept. Progr. Phys.*, **25**, 395 (1962). b) R. W. Harris and G. T. Clayton, *J. Chem. Phys.*, **45**, 2681 (1966).

33) a) Y. Morino, T. Ukaji, and T. Ito, This Bulletin, **39**, 71 (1966). b) J. Trotter, *Z. Kristallogr.*, **121**, 81 (1965).

34) a) Gas phase; K. Hedberg, *Trans. Am. Cryst. Assocn.*, **2**, 79 (1966). b) Crystal phase; J. Trotter, *Z. Kristallogr.*, **122**, 230 (1966).

35) a) Gas phase; P. Kisliuk, *J. Chem. Phys.*, **22**, 86 (1954). b) Crystal phase; I. Lindqvist and A. Niggli, *J. Inorg. Nucl. Chem.*, **2**, 345 (1956).

36) a) Gas phase; S. M. Swingle, quoted by P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3**, 46 (1950). b) Crystal phase; J. Trotter and T. Zobel, *Z. Kristallogr.*, **123**, 67 (1966).

valnece angle,[14] since it is most sensitive[37] to the value of the apparent anisotropy shown in Table 1, and the energy necessary for the change of this order will easily be compensated[37] by van der Waals forces and other interaction energies.[38]

A fuller examination of the origins of the effect (b) will help us to clarify the relationship between the molecular geometry in a solvent and the nature of solvent-solute interaction.[38]

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## Appendix

Hereafter we abbreviate $2\mathrm{p}_{\alpha\mathrm{A}}$ AO as $\alpha_\mathrm{A}$ ($\alpha=x$, $y$, or $z$), since only the 2p AO's appear in the following equations.

(i) SD term

(a) Level A approximation

$$
\begin{aligned}
(\boldsymbol{K}_{\mathrm{AB}}{}^{(2)})_{\alpha\alpha} = &-(4\beta^2/25)\langle r^{-3}\rangle_\mathrm{A}\langle r^{-3}\rangle_\mathrm{B}\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{vac}}({}^3\Delta E_{i\to j})^{-1} \\
&\times[4(2C_{i\alpha_\mathrm{A}}C_{j\alpha_\mathrm{A}}-\sum_{\delta(\neq\alpha)}{}' C_{i\delta_\mathrm{A}}C_{j\delta_\mathrm{A}})(2C_{i\alpha_\mathrm{B}}C_{j\alpha_\mathrm{B}} \\
&-\sum_{\delta(\neq\alpha)}{}' C_{i\delta_\mathrm{B}}C_{j\delta_\mathrm{B}})+9\sum_{\delta(\neq\alpha)}{}'(C_{i\alpha_\mathrm{A}}C_{j\delta_\mathrm{A}}+C_{i\delta_\mathrm{A}}C_{j\alpha_\mathrm{A}}) \\
&\times(C_{i\delta_\mathrm{B}}C_{j\alpha_\mathrm{B}}+C_{i\alpha_\mathrm{B}}C_{j\delta_\mathrm{B}})]
\end{aligned}
\tag{A·1-a}
$$

$$
\begin{aligned}
\underset{(\alpha\neq\beta)}{(\boldsymbol{K}_{\mathrm{AB}}{}^{(2)})_{\alpha\beta}} = &-(12\beta^2/25)\langle r^{-3}\rangle_\mathrm{A}\langle r^{-3}\rangle_\mathrm{B}\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{vac}}({}^3\Delta E_{i\to j})^{-1} \\
&\times[(4C_{i\alpha_\mathrm{A}}C_{j\alpha_\mathrm{A}}-2\sum_{\delta(\neq\alpha)}{}' C_{i\delta_\mathrm{A}}C_{j\delta_\mathrm{A}})(C_{i\alpha_\mathrm{B}}C_{j\beta_\mathrm{B}}+C_{i\beta_\mathrm{B}}C_{j\alpha_\mathrm{B}}) \\
&+(C_{i\alpha_\mathrm{A}}C_{j\beta_\mathrm{A}}+C_{i\beta_\mathrm{A}}C_{j\alpha_\mathrm{A}})(4C_{i\beta_\mathrm{B}}C_{j\beta_\mathrm{B}}-2\sum_{\delta(\neq\beta)}{}' C_{i\delta_\mathrm{B}}C_{j\delta_\mathrm{B}}) \\
&+3(C_{i\alpha_\mathrm{A}}C_{j\gamma_\mathrm{A}}+C_{i\gamma_\mathrm{A}}C_{j\alpha_\mathrm{A}})(C_{i\beta_\mathrm{B}}C_{j\gamma_\mathrm{B}}+C_{i\gamma_\mathrm{B}}C_{i\beta_\mathrm{B}})]
\end{aligned}
\tag{A·1-b}
$$

(b) Level B approximation

$$
\begin{aligned}
(\boldsymbol{K}_{\mathrm{AB}}{}^{(2)})_{\alpha\alpha} = &(2\beta^2/25)\langle r^{-3}\rangle_\mathrm{A}\langle r^{-3}\rangle_\mathrm{B}({}^3\Delta E)^{-1} \\
&\times[2(4P^2{}_{\alpha_\mathrm{A}\alpha_\mathrm{B}}+P^2{}_{\beta_\mathrm{A}\beta_\mathrm{B}}+P^2{}_{\gamma_\mathrm{A}\gamma_\mathrm{B}}) \\
&+9P_{\alpha_\mathrm{A}\beta_\mathrm{B}}(P_{\beta_\mathrm{A}\beta_\mathrm{B}}+P_{\gamma_\mathrm{A}\gamma_\mathrm{B}})-2(2P^2{}_{\alpha_\mathrm{A}\beta_\mathrm{B}}+2P^2{}_{\alpha_\mathrm{A}\gamma_\mathrm{B}} \\
&+2P^2{}_{\beta_\mathrm{A}\alpha_\mathrm{B}}+2P^2{}_{\gamma_\mathrm{A}\alpha_\mathrm{B}}-P^2{}_{\beta_\mathrm{A}\gamma_\mathrm{B}}-P^2{}_{\gamma_\mathrm{A}\beta_\mathrm{B}}) \\
&+9(P_{\alpha_\mathrm{A}\beta_\mathrm{B}}P_{\beta_\mathrm{A}\alpha_\mathrm{B}}+P_{\alpha_\mathrm{A}\gamma_\mathrm{B}}P_{\gamma_\mathrm{A}\alpha_\mathrm{B}})]
\end{aligned}
\tag{A·2-a}
$$

$$
\begin{aligned}
\underset{(\alpha\neq\beta)}{(\boldsymbol{K}_{\mathrm{AB}}{}^{(2)})_{\alpha\beta}} = &(6\beta^2/25)\langle r^{-3}\rangle_\mathrm{A}\langle r^{-3}\rangle_\mathrm{B}({}^3\Delta E)^{-1} \\
&\times[4(P_{\alpha_\mathrm{A}\alpha_\mathrm{B}}P_{\alpha_\mathrm{A}\beta_\mathrm{B}}+P_{\beta_\mathrm{A}\beta_\mathrm{B}}P_{\alpha_\mathrm{A}\beta_\mathrm{B}} \\
&+3(P_{\alpha_\mathrm{A}\beta_\mathrm{B}}P_{\gamma_\mathrm{A}\gamma_\mathrm{B}}+P_{\alpha_\mathrm{A}\gamma_\mathrm{B}}P_{\gamma_\mathrm{A}\beta_\mathrm{B}}) \\
&-2(P_{\alpha_\mathrm{A}\alpha_\mathrm{B}}P_{\beta_\mathrm{A}\alpha_\mathrm{B}}+P_{\beta_\mathrm{A}\beta_\mathrm{B}}P_{\beta_\mathrm{A}\alpha_\mathrm{B}} \\
&+P_{\alpha_\mathrm{A}\gamma_\mathrm{B}}P_{\beta_\mathrm{A}\gamma_\mathrm{B}}+P_{\gamma_\mathrm{A}\alpha_\mathrm{B}}P_{\gamma_\mathrm{A}\beta_\mathrm{B}})]
\end{aligned}
\tag{A·2-b}
$$

(ii) OB term

Under the one-center integral approximation, the contribution coming from $\mathscr{H}_1{}^{(\mathrm{a})}$ becomes zero, and we have only to consider the contribution coming from $\mathscr{H}_1{}^{(\mathrm{b})}$ (*cf.* Eqs. (1) and (2)).[9]

(a) Level A approximation

$$
\begin{aligned}
(\boldsymbol{K}_{\mathrm{AB}}{}^{(1\mathrm{b})})_{\alpha\alpha} = &16\beta^2\langle r^{-3}\rangle_\mathrm{A}\langle r^{-3}\rangle_\mathrm{B}\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{vac}}({}^1\Delta E_{i\to j})^{-1} \\
&\times(C_{i\gamma_\mathrm{A}}C_{j\beta_\mathrm{A}}-C_{i\beta_\mathrm{A}}C_{j\gamma_\mathrm{A}})\times(C_{i\beta_\mathrm{B}}C_{j\gamma_\mathrm{B}}-C_{i\gamma_\mathrm{B}}C_{j\beta_\mathrm{B}})
\end{aligned}
\tag{A·3-a}
$$

$$
\begin{aligned}
(\boldsymbol{K}_{\mathrm{AB}}{}^{(1\mathrm{b})})_{\alpha\beta} = &16\beta^2\langle r^{-3}\rangle_\mathrm{A}\langle r^{-3}\rangle_\mathrm{B}\sum_{l}^{\mathrm{occ}}\sum_{j}^{\mathrm{vac}}({}^1\Delta E_{i\to j})^{-1} \\
&\times(C_{i\gamma_\mathrm{A}}C_{j\beta_\mathrm{A}}-C_{i\beta_\mathrm{A}}C_{j\gamma_\mathrm{A}})(C_{i\gamma_\mathrm{B}}C_{j\alpha_\mathrm{B}}-C_{i\alpha_\mathrm{B}}C_{j\gamma_\mathrm{B}})
\end{aligned}
\tag{A·3-b}
$$

(b) Level B approximation

$$
\begin{aligned}
(\boldsymbol{K}_{\mathrm{AB}}{}^{(1\mathrm{b})})_{\alpha\alpha} = &8\beta^2\langle r^{-3}\rangle_\mathrm{A}\langle r^{-3}\rangle_\mathrm{B}({}^1\Delta E)^{-1}(P_{\beta_\mathrm{A}\beta_\mathrm{B}}P_{\gamma_\mathrm{A}\gamma_\mathrm{B}} \\
&-P_{\beta_\mathrm{A}\gamma_\mathrm{B}}P_{\gamma_\mathrm{A}\beta_\mathrm{B}})
\end{aligned}
\tag{A·4-a}
$$

$$
\begin{aligned}
(\boldsymbol{K}_{\mathrm{AB}}{}^{(1\mathrm{b})})_{\alpha\beta} = &8\beta^2\langle r^{-3}\rangle_\mathrm{A}\langle r^{-3}\rangle_\mathrm{B}({}^1\Delta E)^{-1}(P_{\beta_\mathrm{A}\gamma_\mathrm{B}}P_{\gamma_\mathrm{A}\alpha_\mathrm{B}} \\
&-P_{\beta_\mathrm{A}\alpha_\mathrm{B}}P_{\beta_\mathrm{A}\gamma_\mathrm{B}})
\end{aligned}
\tag{A·4-b}
$$

Note that, although the tensor due to the FSD term is symmetric, those due to the SD and OB terms are not necessarily symmetric. For the FC contribution, its tensor is diagonal and given by Pople and Santry[16] for both approximations.

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[37] For $\mathrm{CH_3F}$, the increase in the H–C–H angle about 1° is necessary in order to explain the difference between theoretical and experimental values. For $\mathrm{CH_3I}$, it is about 20′. For the molecules for which the values of the $(J_{\mathrm{CH}})_{\mathrm{aniso}}$ in Table 1 are negative, the decrease in the H–C–H angle is necessary (Ref. 14). The energy necessary for the change of this order in the H–C–H angle is less than 20∼30 calories.

[38] Saupe, Englert, and Povh (Ref. 7a, 7c, 7h) studied the molecular geometry of $\mathrm{CH_3CN}$ dissolved in three nematic solvents and observed slight differences in H–C–H angle. They interpreted these differences as due to those of the protonating abilities of these solvents. Englert and Saupe (Ref. 7a) obtained the C–N bond length considerably shorter than its microwave geometry, and they suggested that the change is caused by the solvent-solute interaction such as the interaction of the polar C–N bond with the electric reaction field induced by nematic solvent molecules.