eq 5 and 6, we obtain the numbers in the last column of Table I.

It may be seen that the agreement between the experimental and the theoretical susceptibilities is quite satisfactory except for the molecules mesitylene and 1,1-diphenylethylene which we excluded from the parameter fitting. Still, for these two molecules the difference between the experimental and theoretical susceptibilities is less than 5%, which is within the possible experimental error.

Theoretical Study of the Fluorine–Fluorine Nuclear Spin Coupling Constants. I. The Importance of Orbital and Spin Dipolar Terms

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Abstract: The indirect F–F coupling constants of various fluorine-containing compounds are studied theoretically. All the contributions to the F–F couplings are examined by using INDO-MO's and the sum-over-states perturbation method. For F–F couplings, the orbital (OB) and spin dipolar (SD) terms are very important and sometimes make decisive contributions over the Fermi contact (FC) term. By the inclusion of the OB and SD terms, the experimental signs of geminal F–F couplings and trans F–F couplings for fluoro olefins are reproduced. Both the OB and SD terms become small in magnitude for F–F couplings separated by more than four bonds and the FC term becomes significant. Surprisingly large long-range couplings originate from the FC term through the transitions of the F–F antibonding σ orbitals to the corresponding bonding orbitals, for the s-cis conformations of FC=CC=CF (a) and FCCCF (b). These large long-range couplings are named as "fragment couplings" through the quantum chemical considerations.

The theory of the indirect nuclear spin–spin coupling constant is based on the original work of Ramsey.[1] For light nuclei, the indirect nuclear spin-spin coupling constant originates from three electron-nucleus interaction hamiltonians; they are the orbital (OB), spin dipolar (SD), and Fermi contact (FC) terms. The OB term represents the interaction between the nuclear spin and the induced dipole moment due to the orbital motion of electrons, and the SD and FC terms represent respectively the dipole–dipole and Fermi contact interactions between nuclear spin and electron spin.

Among these mechanisms, the FC term was found to be predominant for the proton couplings originally by Ramsey and Purcell,[1] and most of the latter theoretical studies[2–4] based only on this term have been successful in the explanation of proton couplings. However, uncritical extension of this treatment to the couplings between other nuclear pairs is very dangerous.[2,3a,5,6] Indeed, in a previous study,[7] we found extraordinarily large contributions of the OB and SD terms to the F–F coupling constants of some fluorine-containing compounds.

Many experimental values of F–F coupling constants have now accumulated, and interestingly the observed trends of the F–F coupling constants are far different from those seen in the H–H coupling constants. In order to explain these tendencies, Sederholm[8] advanced the concept of the "through space" couplings, although many criticisms[9] have thrown on this concept. Our view is that part of the experimental complexity of the F–F coupling constants may be due to the importance of the OB and SD term in addition to the FC term.

At present, extensive theoretical studies of the F–F coupling constants seem to be very limited, compared with those of the proton couplings, and moreover it seems that no satisfactory rule has yet been developed to provide a unified explanation of the experimental trends of the F–F couplings. Thus, in this series of papers, we will present a systematic theoretical study of the F–F coupling constants. All the mechanisms are considered by using the INDO-MO's[10] and the sum-over-states perturbation theory.

In the first paper, we examine the relative importance of the FC, SD, and OB mechanisms for the F–F couplings in various chemical situations. They are the geminal, vicinal, and long-range couplings in various fluoroalkanes, -alkenes, and -cycloalkanes. Then, we advance to explain the observed trends of the F–F couplings from the above point of view. They are the signs of the coupling constants, the substituent effects, through space couplings, near-zero couplings, etc.

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[1] (a) N. F. Ramsey and E. M. Purcell, *Phys. Rev.*, **85**, 143 (1952); (b) N. F. Ramsey, *ibid.*, **91**, 303 (1953).

[2] H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

[3] (a) M. Karplus, *ibid.*, **30**, 11 (1959); (b) H. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, **31**, 1278 (1959).

[4] M. J. Stephens, *Proc. Roy. Soc., Ser. A*, **243**, 274 (1957).

[5] J. A. Pople, *Mol. Phys.*, **1**, 216 (1958).

[6] J. N. Murell, P. E. Stevenson, and G. T. Jones, *ibid.*, **12**, 265 (1967).

[7] H. Nakatsuji, I. Morishima, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **44**, 2010 (1971).

[8] (a) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); (b) S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964).

[9] (a) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 133 (1964); (b) N. Boden, J. Feeney, and L. H. Sutcliffe, *J. Chem. Soc.*, 3482 (1965).

[10] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

Angular dependences of the fluorine couplings will be the content of the next paper.

Theoretical Background

In this section, we give a short summary of the theoretical background relevant to the later discussions. By applying a molecular orbital theory to the original Ramsey's perturbation formula,[1b] Pople and Santry[11] obtained tractable expressions for the FC, OB, and SD terms. In the LCAO-MO approximation, and by retaining only the one-center integrals, the diagonal element of the coupling tensor of these three mechanisms becomes as follows

(i) FC term

$$J_{\mathrm{AB}} = -(\hbar\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}/2\pi)(256\pi^2/9)\beta^2 S_{\mathrm{A}}{}^2(0)S_{\mathrm{B}}{}^2(0) \times \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}} ({}^3\Delta E_{i\to j})^{-1} C_{i\mathrm{S_A}}C_{j\mathrm{S_A}}C_{i\mathrm{S_B}}C_{j\mathrm{S_B}}$$

(ii) OB term

$$(J_{\mathrm{AB}})_{\alpha\alpha} = (\hbar\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}/2\pi)16\beta^2\langle r^{-3}\rangle_{\mathrm{A}}\langle r^{-3}\rangle_{\mathrm{B}} \times \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}} ({}^1\Delta E_{i\to j})^{-1}(C_{i\gamma_{\mathrm{A}}}C_{j\beta_{\mathrm{A}}} - C_{i\beta_{\mathrm{A}}}C_{j\gamma_{\mathrm{A}}}) \times (C_{i\beta_{\mathrm{B}}}C_{j\gamma_{\mathrm{B}}} - C_{i\gamma_{\mathrm{B}}}C_{j\beta_{\mathrm{B}}})$$

(iii) SD term

$$(J_{\mathrm{AB}})_{\alpha\alpha} = -(\hbar\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}/2\pi)(4\beta^2/25)\langle r^{-3}\rangle_{\mathrm{A}}\langle r^{-3}\rangle_{\mathrm{B}} \times \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}} ({}^3\Delta E_{i\to j})^{-1}[4(2C_{i\alpha_{\mathrm{A}}}C_{j\alpha_{\mathrm{A}}} - \sum_{\delta\neq\alpha}{}' C_{i\delta_{\mathrm{A}}}C_{j\delta_{\mathrm{A}}}) \times (2C_{i\alpha_{\mathrm{B}}}C_{j\alpha_{\mathrm{B}}} - \sum_{\delta\neq\alpha}{}' C_{i\delta_{\mathrm{B}}}C_{j\delta_{\mathrm{B}}}) + 9\sum_{\delta\neq\alpha}{}'(C_{i\alpha_{\mathrm{A}}}C_{j\delta_{\mathrm{A}}} + C_{i\delta_{\mathrm{A}}}C_{j\alpha_{\mathrm{A}}}) \times (C_{i\delta_{\mathrm{B}}}C_{j\alpha_{\mathrm{B}}} + C_{i\alpha_{\mathrm{B}}}C_{j\delta_{\mathrm{B}}})]$$

where α_{A} denotes the $2\mathrm{p}_\alpha$ ($\alpha = x, y,$ or z) AO of atom A, $S_{\mathrm{A}}{}^2(0)$ the density of the valence s AO at the nucleus A, and $\langle r^{-3}\rangle_{\mathrm{A}}$ the mean values of r^{-3} for the 2p AO of atom A. The values for these one-center integrals are often treated as parameters to be determined to fit the experimental data. In the present calculation, we paid attention mainly to the mechanisms in the F–F coupling constants. So we employed the values of these one-center integrals obtained for isolated atoms not treated as parameters. The values are $S_{\mathrm{F}}{}^2(0)S_{\mathrm{F}}{}^2(0) = 143.185$ au and $\langle r^{-3}\rangle_{\mathrm{F}}\langle r^{-3}\rangle_{\mathrm{F}} = 56.942$ au.[12] The basic MO's used in the calculations are the INDO-MO's of Pople, *et al.*[10]

In the above equations, first note that the FC term originates from the induced interactions between valence s electrons of the atoms A and B, while the OB and SD terms come from the interactions between the 2p electrons of atoms A and B. Moreover, the $\alpha\alpha$ element of the OB term represents the induced interaction between the $2\mathrm{p}_\beta$ and $2\mathrm{p}_\gamma$ electrons of atoms A and B and the SD term is complicated. Thus, the behaviors of the OB and SD terms are expected to be far different from that of the FC term, where all the diagonal elements are equal.

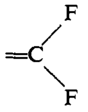
Note also that in the above sum-over-states perturbation treatment, the excited states are constructed from the virtual orbitals in an INDO-MO treatment. However, in the INDO-MO method, the transition energies ${}^1\Delta E_{i\to j}$ and ${}^3\Delta E_{i\to j}$ are usually calculated too large, resulting rather small values of the calculated coupling constants (see Tables I–IX). An improvement of this defect may be achieved by using the finite perturbation method, which is equivalent to the coupled Hartree–Fock perturbation method. As shown by Pople, McIver, and Ostlund[13] for FC contributions and by the present authors[14] for all the contributions, the coupling constants calculated by the finite perturbation method are almost always larger than those calculated by the sum-over-states perturbation method. Theoretical reasoning of this was given recently by Ditchfield, *et al.*[15]

Results and Discussions

In this section we discuss the F–F coupling constants of various fluoroalkanes, -alkenes, and -cycloalkanes. The molecular geometries used in the calculations were cited from the Sutton's table.[16] In the following paragraphs, we discuss the general trends of the F–F couplings in the order of the geminal (Tables I and II), vicinal (Tables IV–VII), and long-range (Tables VIII and IX) couplings.

(i) Geminal F–F Couplings. The calculated geminal F–F coupling constants are summarized in Tables I and II. Table I gives the calculated couplings for fluorines attached to the unsaturated carbons and Table II for fluorines attached to the saturated carbons and ring carbons. Examination of these tables reveals some regular features of the geminal F–F coupling constants. First, both the OB and SD terms make significant contributions as well as the FC term for all the couplings given in Tables I and II. Second, although the sign of

Table I. Calculated Geminal Coupling Constants (Hz) for Fluorines Attached to Unsaturated Carbons



Compound	FC	SD	OB	Total	Exptl
1, $CH_2{=}CF_2$	−24.0	25.7	19.6	20.9	(+)36.4[a]
2, $CHF{=}CF_2$	−15.0	29.9	44.4	59.3	(+)87[b]
3, $CF_2{=}CF_2$	−29.9	31.7	63.9	65.8	
4, $CF_3CF{=}CF_2$	−2.1	24.5	12.2	34.6	(+)57[b]
5, $CF(CN){=}CF_2$	−20.4	22.2	19.9	21.6	(+)27[c]
6, $CF_2{=}CHCH{=}CF_2$					
s-trans	−11.5	20.9	20.4	29.7	(+)36.6[d]
s-cis	−6.7	21.2	14.9	29.4	
7, $CF_2{=}CFCF{=}CF_2$					
s-trans	−10.0	21.5	26.9	38.3	(+)50.74[e,f]
s-cis	−22.1	21.4	21.9	21.2	

[a] G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 226 (1963). [b] See ref 19a and 24. [c] See ref 24. [d] See ref 30. [e] See ref 31. [f] The carbon skeleton of this compound is suggested to be nonplanar. See ref 32.

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(11) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(12) J. A. Morton, *Chem. Rev.*, **64**, 453 (1964).

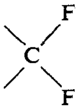
(13) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968).

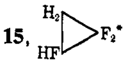
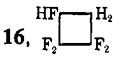
(14) H. Nakatsuji, K. Hirao, H. Kato, and T. Yonezawa, *Chem. Phys. Lett.*, **6**, 541 (1970); K. Hirao, H. Nakatsuji, H. Kato, and T. Yonezawa, to be published.

(15) R. Ditchfield, N. S. Ostlund, J. N. Murell, and M. A. Turpin, *Mol. Phys.*, **18**, 433 (1970).

(16) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11 (1958); *Suppl.*, No. **18** (1965).

Table II. Calculated Geminal Coupling Constants (Hz) for Fluorines Attached to Saturated Carbons and Ring Compounds



Compound	FC	SD	OB	Total	Exptl
8, CH_2F_2	−103.9	36.4	76.9	9.2	
9, CH_3CF_3	−26.5	27.0	24.9	25.0	
10, CH_2FCHF_2	−22.9	31.8	57.4	66.3	
11, CH_2FCF_3	−42.2	26.0	28.4	12.2	
12, $CF_3CF_2CH_2F$ A B					(+)150–270[a]
$J_{AA'}$	−26.5	25.6	26.4	25.5	
$J_{BB'}$	−51.8	32.7	64.1	45.0	
13, $CF_3CF_2CF_3$ A B					
$J_{AA'}$	−15.6	24.5	30.6	39.5	
$J_{BB'}$	−37.8	36.7	84.4	83.2	
4, $CF_2{=}CFCF_3$*	−49.3	23.0	30.8	4.5	
14, $CF{\equiv}CCF_3$	−6.5	25.7	27.0	46.3	
15, 	−17.2	31.5	57.7	72.1	(+)150.5–155.0[b]
16,  A B					
$J_{AA'}$	−11.3	28.5	63.3	80.5	(+)202–230[c]
$J_{BB'}$	−5.0	27.9	61.5	84.4	

[a] These values are J_{FF}^{gem} obtained for several substituted ethanes. [b] These values are J_{FF}^{gem} obtained for halogenated trifluorocyclopropanes. See ref 20. [c] These values are J_{FF}^{gem} obtained for substituted tetrafluorocyclobutanes: W. D. Phillips, *J. Chem. Phys.*, **25**, 949 (1956).

the FC contribution is negative,[17] those of the OB and SD terms are positive, and, consequently, the sign of the resultant coupling constants is positive. This is true without exception for all the couplings given in Tables I and II.

Experimentally, Evans, Manatt, and Ellman[18] have established the sign to be positive for a number of *gem*-fluorines attached to the saturated carbons. Moreover, for the fluorines attached to unsaturated carbons[19] and ring carbons,[20] there are some experimental reasons to believe their couplings to be positive in sign. Clearly, these facts cannot be explained without OB and SD terms. This is direct evidence of the importance of the OB and SD terms in geminal F–F coupling constants.

In order to examine the electronic origin of these coupling mechanisms, all the diagonal elements of the F–F coupling tensors are given in Table III for perfluoroethylenes. The *x* axis of the coupling tensor is chosen to be parallel with the C–C bond. The molecular plane lies on the *xy* plane. Let us first examine the SD terms. Referring to Tables I and II, note that the values of the SD contribution are almost constant and lie in the range of 20.9 ∼ 36.7 Hz for all the F–F pairs studied here. These SD terms are determined chiefly by the excitation of one of the lone-pair electrons into the C–F antibonding σ orbitals ($n \rightarrow \sigma^*$). Since both of these two orbitals are localized approximately in the CF_2 region, the constancy of the calculated SD contribution may be understood. Furthermore, this suggests that the SD contribution to the geminal F–F coupling constants is rather insensitive to the substituents X in the XCF_2 system. This is seen in Tables I and II. On the other hand, for the OB term, the contributions vary considerably from 12.2 to 84.4 Hz. Table III shows that the OB term is determined as a result of partial cancellation of three large values. Namely, the positive contribution from the *zz* element is dominant and always surpasses the negative but appreciable contributions from the *xx* and *yy* elements. Furthermore, the dominant *zz* element comes chiefly from the $n \rightarrow \sigma^*$ transition. The minor but appreciable *xx* and *yy* elements are determined mainly by the transition from n orbitals to the C–F antibonding π orbitals ($n \rightarrow \pi^*$). Since both the n and σ^* orbitals are of a local character in the CF_2 region, the primary feature of the OB term such as the sign and the order of magnitude is common to all the geminal couplings. As to the secondary feature (*e.g.*, substituent effects, structural change, etc.), all the effects on the *xx*, *yy*, and *zz* elements become important in this case and moreover, as seen from Table III, these effects seem to accumulate. That is, with replacing a proton atom on the 2 position of the 1,1-difluorovinyl system by a fluorine atom (from $CF_2{=}CH_2$ (**1**) to $CF_2{=}CF_2$ (**3**)), all the elements of the OB terms increase in magnitude, resulting in 19.6 Hz for $CF_2{=}CH_2$ (**1**) and 63.9 Hz for $CF_2{=}CF_2$ (**3**). This trend is also found between $CF_2{=}CHCH{=}CF_2$ (**6**) and $CF_2{=}CFCF{=}CF_2$ (**7**). For the FC term, the

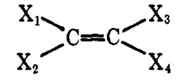
[17] By the finite perturbation treatment, we obtained[14] the positive sign for the FC term in geminal F–F couplings for $CF_2{=}CF_2$ (**3**) and CH_2F_2 (**8**). Moreover, Santry, *et al.*, have reported the positive sign for FC term in geminal couplings for CHF_3 and C_2HF_5 by using the finite perturbation method: A. C. Blizzard and D. P. Santry, *Chem. Commun.*, 87 (1970).

[18] (a) D. F. Evans, *Discuss. Faraday Soc.*, **34**, 139 (1962); (b) S. L. Manatt and D. D. Ellman, *J. Amer. Chem. Soc.*, **84**, 1305 (1962); (c) D. F. Evans, S. L. Manatt, and D. D. Ellman, *ibid.*, **85**, 238 (1963).

[19] (a) D. F. Evans, *Mol. Phys.*, **5**, 183 (1962); (b) D. D. Ellman and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **12**, 23 (1964).

[20] K. L. Williamson and K. Braman, *J. Amer. Chem. Soc.*, **89**, 6183 (1967).

Table III. Calculated F–F Coupling Constant Tensors (Hz) for Some Fluoro Olefins



						SD[a]			OB[a]		
J	X$_1$	X$_2$	X$_3$	X$_4$	FC	xx	yy	zz	xx	yy	zz	Total
J_{12}^{gem}	F	F	H	H	−24.3	29.4	51.0 (25.7)	−3.4	−79.0	−36.3 (19.6)	174.0	20.9
	F	F	H	F	−15.0	33.1	54.2 (29.9)	2.3	−42.0	−29.8 (44.4)	205.1	59.3
	F	F	F	F	−29.9	35.8	55.4 (31.7)	3.9	−31.4	−22.6 (63.9)	245.8	65.8
J_{14}^{trans}	F	H	H	F	13.4	9.2	7.7 (4.2)	−4.2	−92.7	−118.2 (−72.9)	−7.7	−55.2
	F	H	F	F	−11.9	8.6	5.5 (3.1)	−4.9	−77.4	−104.1 (−65.5)	−14.9	−74.3
	F	F	F	F	−3.3	10.2	6.8 (3.9)	−5.4	−76.4	−108.6 (−67.2)	−16.7	−66.7
J_{13}^{cis}	F	H	F	H	49.0	−1.0	−6.5 (1.2)	11.2	−54.2	11.9 (0.9)	39.7	49.4
	F	H	F	F	13.4	0.8	−2.3 (2.8)	9.8	−41.5	32.3 (−7.3)	−12.7	8.9
	F	F	F	F	7.2	3.1	−0.3 (4.4)	10.5	−18.3	38.3 (6.9)	0.9	4.2

[a] The value in parentheses is the contribution to J, $\frac{1}{3}(J_{xx} + J_{yy} + J_{zz})$.

values vary considerably (−2.1 (**4**) ~ −103.9 (**8**) Hz), although they are always negative. These values are determined by $\sigma \rightarrow \sigma^*$ transitions, which have local character since $2s_F$ energies are far below those of the $2p_F$ orbitals. However, since they are the result of a much more complicated cancellation of a number of large values than with proton couplings, it is difficult to systematize the calculated results.

To conclude the electronic aspects of the geminal F–F couplings, the $n \rightarrow \sigma^*$ transitions determine the SD term and the sign and the order of magnitude of the OB term. The FC term is determined by the approximately local $\sigma \rightarrow \sigma^*$ transitions. Consequently the primary features of the geminal F–F couplings depend in general on the local electronic structure within a fragment CF_2. This is the reason for the similar tendencies of all the geminal couplings in saturated, unsaturated, and ring compounds listed in Tables I and II, regardless of the multiplicity of the adjacent C–C bond and of the valence F–C–F angles. For the secondary effects, such as substituent effects, the experimental geminal F–F couplings vary over a wide range of values[21] in a rather complicated manner. This is explained as follows. As mentioned above, the OB and FC terms are rather sensitive to substituent effects, while the SD term is insensitive. Therefore, the different substituent effects on the FC and OB terms contribute simultaneously to the geminal couplings, and then the resultant substituent effects on the geminal couplings become much more complicated than those seen in the proton couplings.

Last note that although the values of the geminal F–F couplings are usually large, several authors[22] pointed out experimentally the existence of very small values. No satisfactory explanation of this has yet been offered. However, as seen for CH_2F_2 (**8**) and $CF_2{=}CFCF_3$ (**4**), the relatively large negative FC contributions are cancelled out by the positive SD and OB contributions, resulting in small geminal couplings. Thus, these low values are caused mainly by the cancellation of three terms having almost equal magnitude but opposite sign. Obviously this can never be explained by a theory considering only the FC term.

(ii) Trans F–F Couplings for Fluoro Olefins. Table IV summarizes the results on the F–F coupling constants obtained for trans-fluorinated olefins FC=CF, which show that the OB term makes the principal contribution and the FC and SD terms make negligibly small contributions except $CF_2{=}CFCN$ (**5**), for which the FC contribution is also significant. The calculated results are all too low except (**5**) in comparison with the experimental data. This is due to the too large values of transition energies ${}^{1,3}\Delta E_{i \rightarrow j}$ obtained by the INDO method. However, our calculation indicates trans F–F couplings to be negative in sign without exception. This trend agrees with the experimental data.[23] The calculated negative sign is not due to the FC contribution but mainly due to the OB contribution. Therefore if only the FC term is considered, the correct signs are not reproduced. This is good evidence of the importance of the OB term in the trans F–F couplings in fluoro olefins.

The principal transitions to give these large OB terms are $n \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$. Moreover, among these transitions, the most important ones are those from the highest occupied π orbital to the σ^* orbitals. Indeed the effect of the π electron is very important. In Table V, we have summarized the F–F couplings for 1,2-difluoroethane (**18**), *trans*-1,2-difluoroethylene (**17**), and difluoroacetylene (**19**). The OB term for **18**, which does not have π electrons, is small in magnitude. While in **19**, the same trends are found as in fluoro olefins, that is, the OB term makes the decisive contribution and its sign is negative. Thus, the OB term accounts for the major difference between saturated and unsaturated vicinal F–F couplings.

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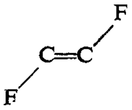
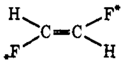
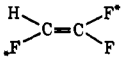
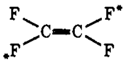
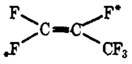
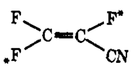
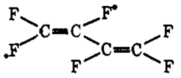
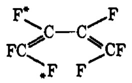
(21) C. G. Moreland and W. S. Brey, *J. Chem. Phys.*, **45**, 803 (1966).

(22) (a) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta*, **17**, 968 (1961); (b) K. C. Ramey and W. S. Brey Jr., *J. Chem. Phys.*, **40**, 2349 (1964); (c) J. D. Swalen and C. A. Reilly, *ibid.*, **34**, 2122 (1961).

(23) (a) Y. Kanazawa, J. D. Baldeschwieler, and N. C. Craig, *J. Mol. Spectrosc.*, 16, 325 (1965); (b) M. Fukuyama, *Tokyo Kogyo Shikensho Hokoku*, **61**, 129 (1966).

Table IV. Calculated Trans F–F Coupling Constants (Hz) for Some Fluoro Olefins



	Compound	FC	SD	OB	Total	Exptl
17		13.4	4.2	−72.9	−55.2	−124.8[a,b]
2		−11.9	3.1	−65.5	−74.3	(−)119[c]
3		−3.3	3.9	−67.2	−66.7	
4		9.4	4.4	−47.0	−33.3	(−)120.2[d]
5		−65.1	1.0	−58.0	−122.1	(−)118[e]
7		−3.8	2.7	−40.8	−41.5	(−)118.57[f]
		−3.9	3.2	−41.8	−42.5	

[a] G. W. Flynn, M. Matsushima, and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 2295 (1963). [b] See ref 23a. [c] See ref 19a and 24. [d] See ref 19a and 22c. [e] See ref 24. [f] See ref *e* and *f* in Table I.

Table V. Calculated F–F Coupling Constants (Hz) for 1,2-Difluoroethane,[a] *trans*-1,2-Difluoroethylene, and Difluoroacetylene

Compound	FC	SD	OB	Total
18, CH_2FCH_2F	11.9	8.8	0.3	21.0
17, CHF=CHF	13.4	4.2	−72.9	−55.2
19, CF≡CF	17.7	−12.9	−90.2	−85.4

[a] The coupling constants in s-trans conformation are listed.

(iii) Cis F–F Couplings for Fluoro Olefins. Table VI gives the results on cis-fluorinated olefins FC=CF. All of the three terms, the FC, SD, and OB terms, are small in magnitude except for *cis*-1,2-difluoroethylene (**20**) and CF_2=CFCN (**5**), and their signs are not uniform except the SD term which is always positive. For compounds **20** and **5** the FC terms are relatively large and positive. On the other hand, for **7** the OB contributions are appreciable and negative. As seen from Table III, the OB contribution to *cis*-fluoro olefins is the result of cancellation of three rather large elements (*xx*, *yy*, and *zz*).

Experimentally Baldeschwieler, *et al.*,[23a] reported a negative sign for **20**. On the other hand, Fukuyama[23b] determined a positive sign for the same compound from analysis of the spectra of a mixture of *cis*- and *trans*-1,2-difluoroethylene. Our calculation favors the positive sign for this coupling. It is difficult to predict the sign for cis F–F couplings since the present calculations indicate positive signs for compounds **20**, **2**, **3**, and **5** but negative signs for compounds **4** and **7**.

In the present calculation, no dominant mechanism (the FC and/or OB terms are rather important) is found for the cis F–F couplings and the calculated results are determined by the cancellation of the three rather small terms of nonuniform sign. But it is difficult to generalize this since the calculated results are not in good agreement with experimental data.

Comparing the geminal, trans, and cis F–F coupling constants for fluoro olefins listed in Tables I, IV, and VI, some generalizations can be derived. (1) Trans coupling is much larger in magnitude than cis in all the calculated cases. That is, the calculation reproduces the experimentally known trans/cis ratio approximately. (2) Geminal coupling is also larger than cis but less than trans coupling except CF_2=CFCN (**5**). These trends agree well with experimentally known ones.[24] The former trend is due to the OB term which makes principal contribution to trans couplings and the latter originates mainly from the OB and SD terms. Note that both trends are not due to the FC term, which is the dominant term in proton couplings. This is the essential difference between proton and fluorine couplings.

(iv) Vicinal F–F Couplings across the C–C Single Bond. Table VII summarizes the results of the F–F coupling constants obtained for vicinal fluorines attached to a C–C single bond. For perfluoroethanes, J_{AV} are the mean values of the three energetically favored isomeric conformations, $J_{AV} = {}^1/_3\,(2J_{\text{gauche}} + J_{\text{s-trans}})$, and J_{AV} for CF_3 are the mean values of the three methyl fluorine atoms. The three terms (the FC, SD, and OB) in these F–F couplings are comparable but small in magnitude, but their signs are not uniform. Experimentally, Evans[18] determined the relative sign of F–F coupling constants in substituted ethanes and found that in all cases, vicinal couplings are opposite in sign to geminal couplings. Therefore the sign of the vicinal couplings for fluoroethanes is presumably negative. However, the s-cis and s-

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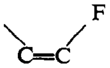
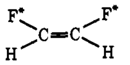
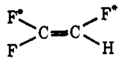
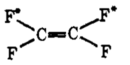
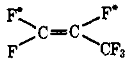
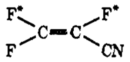
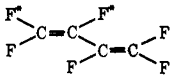
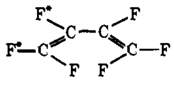
(24) H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, 24, 479 (1956).

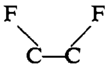
Table VI. Calculated Cis F–F Coupling Constants (Hz) for Some Fluoro Olefins

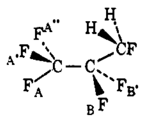
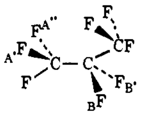
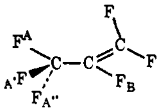


	Compound	FC	SD	OB	Total	Exptl
20		49.0	1.2	−2.6	47.6	(±)18.7[a]
2		13.4	2.8	−7.3	8.9	(+)33[b]
3		−7.2	4.4	6.9	4.2	
4		−9.6	4.1	−5.1	−10.5	(+)40.3[c]
5		31.9	4.2	2.9	39.1	(+)35[d]
7		0.6	2.1	−12.7	−10.0	(+)31.91[e]
		−6.0	1.5	−12.6	−17.1	

[a] See ref 23. [b] See ref 19a and 24. [c] See ref 19a and 22c. [d] See ref 24. [e] See ref *e* and *f* in Table I.

Table VII. Calculated Vicinal F–F Coupling Constants (Hz) across the C–C Single Bond[a]



Compound	*J*	FC	SD	OB	Total	Exptl
CH_2FCH_2F **18**	$J_{\text{s-cis}}$	20.4	0.5	11.0	31.9	
	J_{gauche}	−1.4	−0.3	−2.6	−4.2	(−)10.9[b]
	$J_{\text{s-trans}}$	11.9	8.8	0.3	21.0	(−)30[b]
	J_{AV}	3.0	2.7	−1.6	4.2	
CH_2FCHF_2 **10**	$J_{\text{s-cis}}$	10.6	1.7	12.1	24.4	
	J_{gauche}[c]	1.2	−0.4	2.4	3.2	(−)13.7[b]
	J'_{gauche}[c]	−6.7	−0.6	−3.0	−10.3	
	$J_{\text{s-trans}}$	−6.7	7.2	3.6	4.1	(−)5.2[b]
	J_{AV}	−4.1	2.1	1.0	−1.0	
CH_2FCF_3 **11**	$J_{\text{s-cis}}$	13.6	1.9	11.4	26.9	
	J_{gauche}	4.2	−0.9	0.9	4.2	
	$J_{\text{s-trans}}$	−6.7	6.9	0.5	0.7	
	J_{AV}	0.6	1.7	0.8	3.0	(−)15.5[d]
 **12**	J_{AB}	1.3	−0.6	1.2	1.9	
	$J_{\text{A'B}}$	−4.4	−0.3	−0.1	−4.8	
	$J_{\text{A''B}}$	5.0	6.4	2.7	14.1	
	J_{AV}	0.6	1.8	1.3	3.7	
	J_{BC}	1.8	−0.2	−0.7	0.8	(−)15.2[e]
 **13**	J_{AB}	−4.2	−0.1	−2.5	−6.8	
	$J_{\text{A'B}}$	2.2	−0.3	−1.3	0.6	
	$J_{\text{A''B}}$	10.0	5.6	−0.1	15.5	
	J_{AV}	2.7	1.7	−1.3	3.1	
 **4**	J_{AB}	−19.5	7.4	2.5	−9.6	
	$J_{\text{A'B}}$	−5.2	−1.3	2.8	−3.7	
	J_{AV}	−10.0	1.6	2.7	−5.7	(−)13.2[f]

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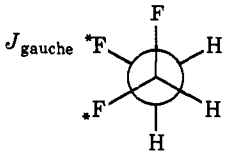
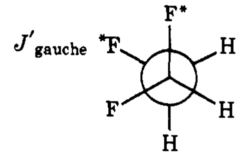
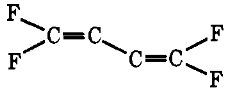
[a] J_{AV} for fluoroethanes is the averaged value of the three energetically favored isomeric conformations, $J_{\text{AV}} = {}^1/_3(2J_{\text{gauche}} + J_{\text{s-trans}})$. J_{AV} for $-CF_3$ is the mean value of the three fluorine atoms. [b] J_{gauche} and J'_{gauche} correspond to the couplings for the following conformations:

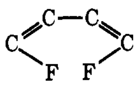


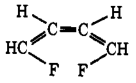
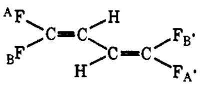
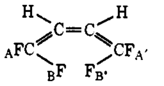
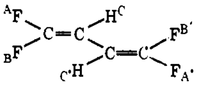
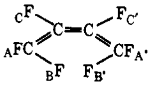


[c] Private communication from Professor R. J. Abraham. [d] D. D. Elleman, L. C. Brown, and D. Williams, *J. Mol. Spectrosc.*, **7**, 307 (1961). [e] D. D. Elleman, L. C. Brown, and D. Williams, *ibid.*, **7**, 322 (1961). [f] See ref 22c.

Table VIII. Calculated Five-Bond F–F Coupling Constants (Hz) for Some Fluorobutadienes





	Compound	J	FC	SD	OB	Total	Exptl
21			168.2	0.7	−2.8	166.1	
6		$J_{AA'}$	7.8	4.0	7.1	18.9	
		$J_{BB'}$	10.1	2.0	−0.4	11.7	
		$J_{AB'}$	3.8	1.3	0.4	5.5	$J_{AA'}$ = (+)35.7[a]
		$J_{AA'}$	5.6	2.2	−0.8	7.0	$J_{BB'}$ = (+)4.8[a] or
		$J_{BB'}$	221.4	−0.8	−3.7	217.0	$J_{AA'}$ = (+)4.8[a]
		$J_{AB'}$	−5.9	1.8	−1.8	−5.9	$J_{BB'}$ = (+)35.7[a]
7		$J_{AA'}$	3.4	4.2	5.6	13.3	
		$J_{BB'}$	−1.2	1.9	−1.1	−0.4	$J_{AA'}$ = (+)4.80[b]
		$J_{AB'}$	5.8	1.3	1.1	8.2	$J_{BB'}$ = (+)11.31[b] $J_{AB'}$ = (+)2.45[b]
		$J_{AA'}$	0.5	1.6	−0.8	1.3	
		$J_{BB'}$	176.9	0.9	−5.0	172.8	
		$J_{AB'}$	−7.9	2.0	−4.6	−10.5	

[a] See ref 30. [b] See ref *e* and *f* in Table I.

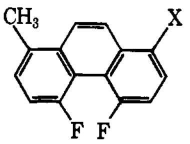
trans couplings in the CF_2–CF_2 fragment in perfluorocyclobutanes and cyclobutenes have been shown experimentally to be large and opposite in sign to each other.[25] Moreover, these two vicinal couplings in the CF_2–CF_2 fragment of perfluorobutane also have different signs.[26] Thus, we can expect that the same phenomena may occur even in perfluoroethane. That is, although the signs of the rotational averages of the vicinal couplings in perfluoroethanes are negative, those of the s-trans and gauche couplings may be opposite to each other, and, in certain cases, the F–F vicinal couplings may have positive signs. Unfortunately it is difficult to predict the signs of these couplings from the present calculations since they are near zero in magnitude and the three terms are not uniform in sign.

Experimentally, the coupling constant between vicinal fluorines across a C–C single bond has been reported[27] to be near zero (near-zero couplings). These couplings are smaller than the F–F couplings across two C–C single bonds. This anomaly may be a consequence of cancellation of the three (the FC, SD, and OB) contributions of nonuniform signs and, in part, attributed to the averaging effects due to the internal rotation about C–C single bond. Note that for 1,2-difluoroethane (**18**, Table VII), the calculated coupling of $J_{\text{gauche}} = -4.2$ and $J_{\text{s-trans}} = 21$ Hz results a low average of $J_V = 4.2$ Hz.

Note last in Table VII that the vicinal couplings between fluorines in the s-trans position have a relatively large SD term. On the other hand, the OB contributions are relatively large in the s-cis position. These observations suggest that both SD and OB terms of vicinal F–F couplings are dependent in a regular manner on the rotational angle. These angular dependences will be reported in more detail in the next paper of this series.

(v) Long-Range Five-Bond F–F Couplings for Fluorobutadienes. In Table VIII, we have summarized the calculated long-range five-bond F–F coupling constants in some fluoro-1,3-butadienes. Note that the F–F coupling constants ($J_{BB'}$) between the fluorines at the 1 and 4 positions of *s-cis*-fluorobutadienes (**21**, **6**, **7**) have extraordinarily large positive values, which originate from the FC term. Indeed, it exceeds in magnitude all the other two-, three-, and four-bond F–F couplings calculated in this paper.

Experimentally, Servis[28] has reported that the F–F coupling constants between fluorines at the 4 and 5 positions of 1-substituted 4,5-difluoro-8-methylphenanthrenes (**23**) are extraordinarily large. In the present



23

$^5J = 167 \sim 170$ Hz

X = $-CH_2Br$, $-CH_2OH$, $-CO_2Et$, $-NH_2$

model calculations the values calculated for compounds **21** and **7** agree fairly well with those found for difluorophenanthrenes. Moreover, the present calculations show that these are positive in sign and arise predominantly from the FC mechanism.

In the valence-bond treatment, the wave function for *s-cis*-difluorobutadiene is given by a linear combination of the following canonical structures illustrated as where $^S\Psi_0$ is the ground-state wave function and $^T\Psi_E$ the triplet excited-state one. Since these large values are determined by the excitation from the antibonding σ orbitals of the F···F pair to the corresponding bonding σ orbitals, these are expected to arise chiefly from

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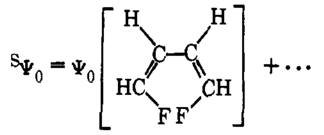
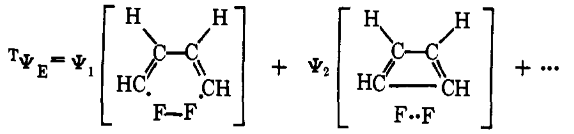
[25] R. K. Harris and V. J. Robinson, *J. Magn. Resonance*, 1, 362 (1969).

[26] R. K. Harris and C. M. Woodman, *J. Mol. Spectrosc.*, 26, 432 (1968).

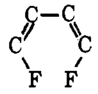
[27] A. Saika and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 78, 4818 (1956).

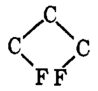
[28] K. L. Servis and K. Fang, *ibid.*, 90, 6712 (1968).

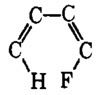


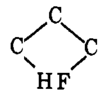


the Fermi-induced interaction between ${}^{S}\Psi_0$ and ${}^{T}\Psi_E$. It should be emphasized that such interaction becomes significant only at short internuclear distances where direct bonding may become possible in ${}^{T}\Psi_E$. The internuclear distance $F_B\cdots F_{B'}$ for *s-cis*-fluorobutadienes used in this calculation is 1.82 Å while that of the free F_2 molecule is *ca.* 1.42 Å. Thus Ψ_1 $\dot{C}{=}CC{=}\dot{C}$ F–F may become stable. Moreover, generally speaking, a similar phenomenon is expected to occur for the X–Y coupling in XC=CC=CY if the fragment X–Y becomes stable in ${}^{T}\Psi_E$. This phenomenon appears also in XCCCY as seen in the next paragraph. Thus, these long-range coupling phenomena may be named "fragment couplings," which are also found in

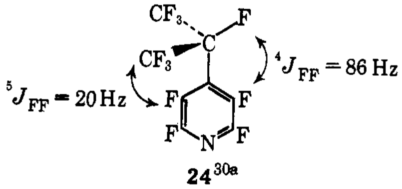

a


b

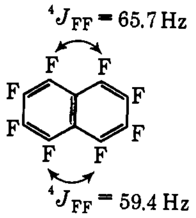

c


d

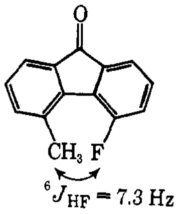
In fact, large coupling constants are found experimentally[29] for



24[30a]



25[30b]



26[30c]

in addition to J_{FF} for compound **23**.

The above mechanism of "fragment coupling" is an important part of the so-called "through space" coupling, advanced by Sederholm.[7] In the fragment coupling mechanism, the direct orbital overlap in the X–Y fragment, which is strongly antibonding in the ground-state configuration ${}^{S}\Psi_0$, but bonding in ${}^{T}\Psi_E$, becomes important. However, a simple distance *vs.* F–F coupling correlation, advocated in the "through space" mechanism by Sederholm,[7a] is questionable in the light of the above discussions. The fragment couplings are closely related to the nature of the X–Y fragment. The "fragment coupling" mechanism presented here is essentially the more quantum chemical concept. These points will be discussed more fully in the succeeding paper of this series.

Experimental long-range five-bond couplings have been reported in these fluorobutadienes. Servis and Roberts reported[30] for 1,1,4,4-tetrafluoro-1,3-butadiene (**6**) that the magnitude and the signs of $J_{AA'}$ and $J_{BB'}$ were +35.7 and +4.8 Hz. Calculated couplings are $J_{AA'} = +18.9$ and $J_{BB'} = +11.7$ Hz for the stable s-trans conformation. Note that the three contributions to $J_{AA'}$ have the same positive sign and the OB term is relatively large for a five-bond coupling. Thus, the resultant $J_{AA'}$ may have a relatively large positive value. The five-bond couplings of hexafluoro-1,3-butadiene (**7**) were determined by Manatt, *et al.*,[31] as $J_{AA'} = +4.80$, $J_{BB'} = +11.31$ Hz. Calculated coupling constants for this compound are similar to those for tetrafluorobutadiene. More recently, it has been suggested[32] from the study of photoelectron and optical spectra that the carbon skeleton of **7** is nonplanar. Therefore a simple comparison of calculated values for planar models with the observed ones may not be valid. Note, however, that if **7** exists completely in the s-trans conformation, the trend in magnitude reproduced by this calculation ($J_{AA'} = +13.3$, $J_{BB'} = -0.4$ Hz) does not coincide with the one determined by experiment. Further studies including a dihedral angle dependence of five-bond couplings will be reported in the next paper.

(vi) Long-Range Four-Bond F–F Couplings. Table IX gives the results of long-range F–F coupling constants across four bonds in saturated and unsaturated fluoro compounds. As can be seen from this table, the OB and SD contributions are small and the FC term is the dominant origin for this long-range coupling. Particularly, for the F–F couplings in the structural fragment b of compound **22**, fairly large FC contribution (−74.9 Hz) exists. This coupling may originate from the "fragment coupling" mechanism discussed in the previous section. Note, however, that in this case the sign is negative.

In general, four-bond couplings are larger in magnitude than vicinal couplings listed in Table VII. This relationship also agrees with the experimental data. That is, the observed coupling constants involving fluorines do not always decrease monotonically with an increasing number of bonds separating the interacting fluorines. This tendency originates from the FC term.

From double resonance techniques for some halogen-substituted fluoropropanes, Evans, *et al.*,[18c] have reported that four-bond coupling has a sign different from vicinal coupling. For hexafluoropropene, Evans[19a] found that the sign of four-bond couplings is opposite to that of vicinal couplings. From these data, Evans assumed the sign of four-bond couplings to be positive. However, as suggested previously, the sign of vicinal coupling across the C–C single bond is not always uniform. Therefore, it does seem impossible to say generally that four-bond couplings have positive signs. In fact, the present calculation produces positive signs for compound **12** but negative signs for other compounds.

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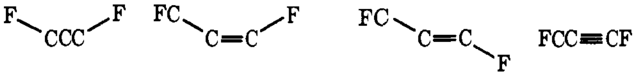
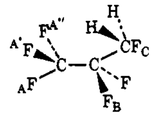
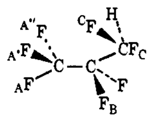
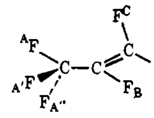
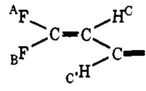
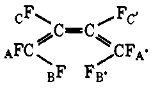
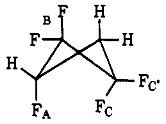
Table IX. Calculated Four-Bond F–F Coupling Constants (Hz)[a]



Compound	J	FC	SD	OB	Total	Exptl
12 	J_{AC}	29.8	2.7	−2.0	30.5	
	$J_{A'C}$	10.8	0.0	0.6	11.4	
	J_{AV}	17.1	0.9	−0.3	17.7	(+)7.9[b]
22 	J_{AC}	23.0	1.8	−1.3	23.5	
	$J_{A'C}$	28.7	−0.4	1.3	29.5	
	$J_{A''C}$	−11.4	0.2	0.7	−10.5	
	$J_{AC'}$	7.6	0.0	−0.0	7.6	
	$J_{A'C'}$	−74.9	−0.7	−0.3	−75.8	
	$J_{A''C'}$	−9.8	−0.1	0.8	−9.1	
4 	J_{AC}	−27.4	−0.4	−0.8	−27.0	
	$J_{A'C}$	−25.2	0.4	−2.0	−26.8	
	$J_{AV}^{\mathrm{cis\ F-CF_3}}$	−25.9	0.1	−1.6	−27.4	(+)22.0[c]
	J_{AD}	−7.4	0.0	−1.3	−8.7	
	$J_{A'D}$	19.8	−1.2	−1.7	16.9	
	$J_{AV}^{\mathrm{trans\ F-CF_3}}$	10.8	−0.8	−1.6	8.4	(+)8.7[c]
14 $CF\equiv CCF_3$		2.4	−2.8	1.1	0.7	
7 	$J_{AC'}$	−1.2	−0.8	−1.3	−3.3	
	$J_{BC'}$	−5.4	−0.6	0.5	−5.4	
	$J_{AC'}$	2.9	3.5	−8.0	−1.7	$J_{AC'}$ = (+)2.41[d]
	$J_{BC'}$	−3.9	−0.7	1.1	−3.5	$J_{BC'}$ = (+)14.19[d]
16 	J_{AC}	−21.6	−0.7	1.0	−21.2	
	$J_{AC'}$	−0.6	−0.0	0.8	0.2	

[a] J_{AV} is the mean value of three fluorine atoms. [b] See ref *e* in Table VII. [c] See ref 19a and 22c. [d] See ref *e* and *f* in Table I.

The relative magnitude between cis and trans F–CF_3 couplings in fluoroalkenes is suggested experimentally as[22c,24]

$$|J_{F-CF_3}{}^{cis}| > |J_{F-CF_3}{}^{trans}|$$

This relationship is also reproduced in hexafluoropropene (**4**). While these two couplings have previously been assumed to have the same sign,[19a] the calculated values are opposite in sign.

Summary and Conclusions

In this paper, we have been concerned mainly with the mechanisms in the F–F coupling constants. The theoretical method applied here has been proved useful for predicting experimental trends, although it is not quantitatively satisfactory. The calculations indicate that the OB and SD terms are very important origins of F–F coupling constants, especially for the geminal and trans F–F couplings in fluoro olefins. This is in marked contrast to the results established for proton couplings. The SD term makes an important contribution only to geminal couplings and it is worth noticing that both the SD and OB terms become small in magnitude for the long-range F–F couplings apart by more than four bonds. By inclusion of both the OB and SD terms, it has been found possible to explain several important features of experimental F–F coupling constants.

(1) All three terms make significant contribution to geminal couplings, causing the substituent effect to become complicated for geminal couplings. The sign is negative for the FC term but positive for the OB and SD terms. Since the three terms have similar magnitudes, geminal couplings are positive. The geminal coupling depends only on the structural fragment of CF_2 since the lone-pair electrons play an important role in the SD and OB terms. Consequently these trends are common in fluoroalkanes, -alkenes, and ring compounds.

(2) The OB term makes predominant contribution to trans couplings in fluoro olefins and the sign is negative. This OB term is determined mostly by the transitions from the highest occupied π orbital to the σ^* orbitals.

(3) For cis F–F couplings in fluoro olefins, the calculations indicate that no dominant contributions exist and the results are determined by the cancellation of the three rather small values of nonuniform signs.

(4) For vicinal couplings across the C–C single bond, the three terms are comparable in magnitude and not uniform in sign; for s-trans couplings, both the FC and SD terms are important while for s-cis and the FC and OB terms are important. It is not possible to predict the signs of these couplings from the present calculation since the three terms are near zero and not uniform in sign.

(5) The FC term makes the dominant contribution to the long-range couplings separated more than four bonds and the other terms become negligibly small. Especially for the s-cis conformation of the fluorobuta-

dienes (a), a surprisingly large five-bond coupling originates from the FC term through the transitions from the F···F antibonding σ orbitals to the corresponding bonding ones. From a valence-bond consideration, this kind of long-range coupling mechanism, called a "fragment coupling" mechanism here, is expected to appear generally in the X–Y coupling in XC=CC=CY and XCCCY, if the fragment X–Y in the above configuration is stable.

A more detailed examination of the angular dependence of F–F couplings would be of value and is one of the problems left unanswered in this paper. Further investigation in this respect has been completed and the results will be published subsequently.

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Application of Thermodynamic Measurements of Polyelectrolyte Solutions for the Prediction of Ion-Exchange Selectivity[1a]

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Abstract: A thermodynamic calculation of the modified selectivity coefficient, K_{AC}, has been made employing the Gibbs–Donnan equation for the exchange of several trace divalent ions and trace sodium ion with macro divalent ion in cross-linked polystyrenesulfonate ion-exchange resins. Evaluation of activity coefficient ratios of the exchanging ions in the resin phase was accomplished using the Gibbs–Duhem equation and osmotic coefficients of polystyrenesulfonates. The osmotic free energy of the exchange reaction was estimated using polystyrenesulfonate osmotic coefficients and ionic partial molal volumes. Calculated modified selectivity coefficients for divalent–divalent ion exchange in general agree with experimentally determined values. Significant discrepancies were found between calculated and experimental selectivities for trace sodium–divalent ion exchange at high resin-phase concentrations. The theoretical treatment of polyelectrolytes by Manning has been used to explain this result.

Ion-exchange equilibria have been extensively studied in recent years[2a] with numerous methods proposed for the interpretation of observed ion-exchange selectivity values.[2b-15] The Donnan membrane model of the ion-exchange process has been found to be particularly useful for this purpose. Thermodynamic expressions obtained from this model lead to the relationship[12]

$$RT \ln K_A = \pi(z_2 \bar{V}_1 - z_1 \bar{V}_2) \qquad (1a)$$

where K_A is the activity product ratio at equilibrium for the ion-exchange reaction, π is the swelling pressure of the resin, $\bar{V}_1$ and $\bar{V}_2$ are the partial molal volumes of the exchanging ions within the resin phase, and z_1 and z_2 are the charges on ions 1 and 2, respectively. For a symmetrical ion-exchange reaction eq 1 can be written

$$RT \ln K_A = \pi(\bar{V}_1 - \bar{V}_2) \qquad (1b)$$

The ion-exchange reaction that occurs in the resin and solution phases when a trace divalent ion, M_1^{2+}, exchanges with a divalent ion, M_2^{2+}, may be expressed as

$$[M(ClO_4)_2]_1 + \overline{[M(ClO_4, PSS)_2]_2} \rightleftharpoons \overline{[M(ClO_4,PSS)_2]_1} + [M(ClO_4)_2]_2 \qquad (2)$$

where

$$\overline{[M_2{}^{2+}]} = \overline{[ClO_4^-]} + \overline{[PSS^-]} \cong \overline{PSS^-}$$

neglecting trace metal ion concentration since $\overline{[PSS^-]} \gg \overline{[ClO_4^-]}$. Species within a squared bracket represent molal concentration. The bar over a symbol refers to the resin phase. The selectivity terms, distribution coefficient, K_D, selectivity coefficient, K_{EX}, and modified selectivity coefficient, K_{AC}, that are used to express the data are defined as

$$K_D = \overline{[M_1{}^{2+}]}/[M_1{}^{2+}] \qquad (3)$$

$$K_{EX} = \overline{[M_1{}^{2+}]}[M_2{}^{2+}]/[M_2{}^{2+}]\cdot\overline{[M_2{}^{2+}]} \qquad (4)$$

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(1) (a) Presented in part at The Symposium on the Physical and Colloid Chemistry of Ion Exchangers, during the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970. (b) Visiting Professor, Chemistry Department, McGill University, 1970–1971, Montreal, Quebec, Canada.

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