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EPR Spectra and Structure of the Radical Cations of Fluorinated Ethylenes and Propenes

Yoshiteru Itagaki, Masaru Shiotani, Akinori Hasegawa,[*,†] **and Hisao Kawazoe**[††]

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-0046

†Department of Chemistry, Kogakkan University, Ise 516-0016

††Asahi-Garasu Co., Ltd., Yuraku-cho, Chiyoda, Tokyo 100-0006

(Received May 1, 1998)

EPR spectra for the radical cations of a series of fluorinated ethylenes and propenes, generated by irradiation with γ-rays in halocarbon solid matrices, have been observed at low temperature. The spectra consist of a hyperfine structure with a nearly axial symmetry mainly due to fluorine nuclei. For the trifluoro olefin cations, $CF_2{=}CFX^{+\cdot}$ (X = H, CH_3, or CF_3), the experimental spectra were successfully analyzed in terms of the three ^{19}F nuclei with coaxial parallel components. This may strongly suggest a planar structure for the radical cations, similarly to the case of the $CF_2{=}CF_2{}^+$ cation already reported. On the other hand, for mono- and di-fluoro olefin radical cations, it is difficult to conclude the planar structure unequivocally from the experimental ^{19}F and ^1H hf splittings. Thus, the optimized geometry of the radical cations was calculated by an ab initio MO method. In contrast with the ethylene cation and the propene cation, having nonplanar twisted structures, the fluorinated ethylene and propene cations are concluded to have planar structures. Calculations at the INDO levels including the evaluation of interatomic dipole-dipole interactions were done for the geometries of the radical cations optimized by the ab initio method. The calculated results strongly support the EPR spectra observed and assigned to the radical cations.

We have studied the radical cations formed from fluorinated derivatives of unsaturated organic compounds such as benzene,[1,2] pyridine,[3] butadiene,[4] and ethylene.[5] Fluorine substitution in the organic molecules has a significant effect on their geometry and electronic structure.[6] In particular for the benzene derivatives, the structure and the symmetry of the SOMO of the radical cations are affected not only by the number of substitutions by fluorine but also by the position of the substitution.[1,2]

The radical cations of olefins are important intermediates in reactions such as cationic polymerizations[7] and catalytic reactions.[8] They are also interesting from the standpoint of electronic structure. Although the geometrical structures of neutral olefins are planar at the ground electronic state, nonplanar structures in bent-form or in twist-form have been suggested for the radical cations and anions of olefins, by EPR,[9] photo-electron spectroscopy, and theoretical calculations.[10]

One of us (MS) started an experimental EPR study on the ethylene radical cation, $CH_2{=}CH_2{}^+$, to investigate its twisted structure.[11a] The EPR spectrum from a γ-irradiated CCl_2FCCl_2F solution containing C_2H_4 was characterized by an isotropic ^1H hyperfine (hf) splitting of 2.33 mT (for 4H) and was attributed to the radical cation with a torsional angle of 45° about the C–C bond. However, the following spectral attribution was claimed by Fujisawa et al.: They suggested that the spectrum should be attributed to a propagating radical cation of $^+CH_2{-}(CH_2)_n{-}\dot{C}H_2$.[11b] Thus the EPR spectrum of the radical cation was reinvestigated using a neon matrix. The results indicated a value of approximately 0.3 mT for the isotropic ^1H hf splitting.[12a] Lunell and his co-worker calculated the isotropic ^1H hf splitting by an accurate CI study and concluded that the splitting of (−)0.3 mT corresponds to the torsional angle of 28°.[12b] On the other hand, the spectrum for the cation of $CF_2{=}CF_2$ formed in a CCl_3F matrix was observed.[5a] The parallel components of its typical axially symmetric anisotropic hf structure were attributed to four equivalent ^{19}F nuclei, suggesting a planar structure for the cation and an ^{19}F nucleus in a matrix molecule interacting with the cation.[5a]

Toriyama et al. did an EPR study on the cation of propene, $CH_2{=}CH{-}CH_3{}^+$, produced in a CCl_3F matrix and analyzed the spectrum observed at 77 K on the assumption that the rotation of the CH_3 group was hindered.[13] However, using a partially deuterated propene, $CH_3CH{=}CD_2$, we found that the CH_3 group rotates freely even at 77 K.[14] INDO calculations suggested that an energy minimum was found for a configuration with a twist angle of 45°.[14] However, comparing the observed hf splitting of 0.70 mT for the CH proton and the calculated value, it was concluded that the propene cation might interchange between two configurations corresponding to the energy minimum rapidly enough to give the apparent planarity on the EPR time scale because of its low barrier.[14] Furthermore, Toriyama et al. reinvestigated the cation of propene, in addition to a study on a trimethylethylene cation, $(CH_3)_2C{=}CH(CH_3)^+$. Using a twisted model along the C=C bond and the bent structure in the group of

$CHCH_3$ or CH_2 of the cations, they interpreted the observed hf splittings of 0.6 mT for the CH proton of the propene cation as well as a large inequivalence of the two CH_2 proton couplings of 2.35 and 1.1 mT.[15)]

Thus, it is of interest to investigate the cations of a series of fluorinated ethylenes and propenes and compare them with the results of the ethylene and propene cations already reported, because fluorine substitution is expected to have a significant effect on their geometry and electronic structure.

Experimental

Commercially available reagents were used for fluorinated ethylenes (ethenes) and propenes such as 1,1-difluoroethylene ($CF_2{=}CH_2$), 1,1,2-trifluoroethylene ($CF_2{=}CFH$), 2-fluoropropene ($CH_2{=}CFCH_3$), 3,3,3-trifluoropropene ($CH_2{=}CHCF_3$), and hexafluoropropene ($CF_2{=}CFCF_3$). The reagents used as matrices favorable for the formation of cation radicals[16)] are trichlorofluoromethane (CCl_3F), 1,1,2,2-tetrachloro-1,2-difluoroethane (CCl_2FCCl_2F) (F-112), 1,2,2-trichloro-1,1,2-trifluoroethane ($CClF_2CCl_2F$) (F-113), 1,2-dichloro-1,1,2,2-tetrafluoroethane ($CClF_2CClF_2$) (F-114), perfluorocyclohexane (c-C_6F_{12}), and sulfur hexafluoride (SF_6). Solutions containing about 1 mol% of these fluorinated ethylenes or propenes in matrices were prepared in Spectrosil EPR sample tubes on a vacuum line. The samples were irradiated with γ-rays from a ^{60}Co source at 77 K, the typical total absorption dose being about 10 kGy. EPR measurements were done with a JEOL JES-PX-1X X-band spectrometer operating at 100 kHz modulation and at various temperatures from 77 K to the temperature for the decay of the radicals. The field strength was calibrated using a standard sample of Mn^{2+}/MgO. Photobleaching by visible-light was examined at 77 K.

Ab initio calculations were done on a Cray Unicos computer (Nobel) at the IFM, Linköping University in Sweden, with UHF 6-31 G basis sets, using the GAUSSIAN 94 program,[17)] to obtain optimized geometries for the radical cations of the fluorinated ethylenes and propenes. To evaluate theoretical spin densities and isotropic hf couplings for atoms in the radical cations, INDO calculations[18)] were done for the geometries optimized by the ab initio method. Regarding the anisotropic terms of the hf tensors, calculations of interatomic dipole-dipole interaction were done with the INDO spin densities and the ab initio optimized geometries using the program ANALDIP developed by Edlund et al.[19)]

Results and Discussion

EPR Spectra and Their Assignments for the Cations. The $CF_2{=}CH_2^+$ Cation. The EPR spectrum shown in Fig. 1(a) was recorded at 93 K after γ-irradiation of a solid solution containing about 1 mol% $CF_2{=}CH_2$ in CCl_3F at 77 K. Although the spectrum at 77 K is broad, the spectrum at 93 K shows a feature characteristic of an anisotropic hf structure with nearly axial symmetry. A triplet with a large coupling of 10.0 mT and parallel features is attributable to two equivalent ^{19}F nuclei in the CF_2 group of the $CF_2{=}CH_2^+$ cation. A smaller triplet (2.1 mT) appears at the central band. Two interpretations may be possible for the latter triplet. One is that the observed splitting is due to the perpendicular component of two equivalent ^{19}F [; splitting due to ^1H nuclei being unresolved]. The other is that the splitting is due to two ^1H nuclei ; [splitting due to two ^{19}F nuclei being unresolved].

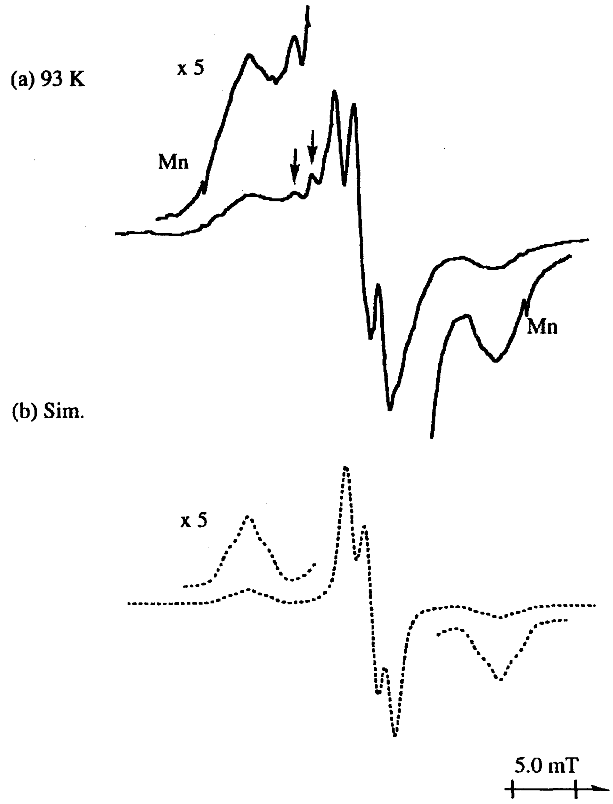

Fig. 1. (a) First-derivative X-band EPR spectrum observed at 93 K after γ-irradiation of a solid solution containing ca. 1 mol% $CF_2{=}CH_2$ in CCl_3F at 77 K, and (b) EPR spectrum simulated for the $CF_2{=}CH_2^+$ cation using the parameters: $g_{\parallel} = 2.002$; $g_{\perp} = 2.004$; $A_{11} = 0.5$, $A_{22} = 0.7$, and $A_{33} = 10.0$ mT for the ^{19}F nuclei; $A_{11} = (-)2.1$, $A_{22} = (-)$-0.3, and $A_{33} = (-)1.5$ mT for the ^1H nuclei; their principal directions corresponding to those obtained from the ANALDIP calculations and shown in Fig. 7. The directions of $g_{\parallel}$, A_{33} for ^1H and A_{33} for ^{19}F are parallel to one another. $\Delta H_{\parallel} = 1.3$ and $\Delta H_{\perp} = 0.9$ mT are used for the line-width. The signals marked with arrows in the observed spectrum (a) may be attributable to the radicals originated from the matrix molecules.

The magnitude of the observed coupling, 2.1 mT, may be reasonable for α-^1H nuclei,[11,20)] and the perpendicular coupling of α-^{19}F nuclei is generally smaller than this value for the π-type radicals.[1—3)] The former cannot, however, be excluded with only this evidence. In the case of the fluorinated benzene cations,[2)] the $A_{\perp}$ values for ^{19}F nuclei were estimated by computer simulation. However, the analysis of the central features of the spectra for fluorinated olefin cations is not as easy as those for the fluorobenzene cations. This may be due to deviation from axial symmetry originating from the increased dipole–dipole interactions between the unpaired electron localized on C=C atoms and the nuclear spins of ^1H and ^{19}F. Therefore, we attempted to evaluate the $A_{\perp}$ values, as a first approximation, for the ^{19}F nuclei using the data for the fluorobenzene cations, on the assumption that the hyperfine couplings for α-^{19}F nuclei of the π-type behave similarly between aromatic and olefinic cations. For ^{19}F couplings in the fluorobenzene cations, the $A_\perp$ values estimated by computer simulation are related to the observed $A_\parallel$ values with a correlation coefficient of $R = 0.74$ as follows:[2)]

$$A_\perp(^{19}\mathrm{F}) = 0.060\,A_\parallel(^{19}\mathrm{F}). \qquad (1)$$

From this equation and the observed $A_\parallel = 10.0$ mT for the $CF_2{=}CH_2^+$ cations, $A_\perp = 0.6$ mT is estimated, and this value is too small compared with the observed coupling of 2.1 mT. Thus, the observed smaller coupling may be assigned to the ^1H nuclei. The observed values from the EPR spectrum are listed in Table 1 together with the isotropic a_iso and anisotropic $2B$ values calculated from the observed $A_\parallel(^{19}\mathrm{F})$ and estimated $A_\perp(^{19}\mathrm{F})$ values.

This assignment was confirmed by comparing the observed spectrum, shown in Fig. 1(a), with the simulation spectrum, shown in Fig. 1(b), calculated taking into account the dipole-dipole interactions, which will be described later.

The spectrum attributable to $CF_2{=}CH_2^+$ in CCl_3F was breached by visible-light illumination at 77 K. A suggested mechanism for the photo-breaching is that the electron, which is liberated from the matrix anion radical, CCl_3F^-, by the illumination, reacts with $CF_2{=}CH_2^+$ to yield $CF_2{=}CH_2$ by a neutralization reaction. This observation is consistent with this spectral assignment to the radical cation. It should be noted that similarly all the fluorinated olefin radical cations studied were decayed by the visible-light illumination.

Observations at elevated temperatures indicate a gradual decrease in the coupling constant of the parallel components, and the spectral lines decay at 140 K before the averaging of the anisotropic hf structure begins. Observation at 4 K was done because the spectrum obtained at 77 K may be due to the cation not in a rigid state but in a mobile state. The spectrum recorded at 4 K is, however, almost the same as that observed at 77 K. Thus, it was concluded that the spectrum at 77 K should be assigned to the radical cation with a rigid limit structure.

In the case of the SF_6 matrix at 77 K, a central triplet obviously appears with a coupling of 1.9 mT, corresponding to 2.1 mT for the CCl_3F matrix. This triplet is attributable to two equivalent protons of the $CF_2{=}CH_2^+$ cation. However, the signals of the parallel components for the cation are obscure for the SF_6 matrix.

The $CF_2{=}CFH^+$ Cation. EPR measurements for the radical cation of $CF_2{=}CFH$ were done with a CCl_3F matrix. The spectrum observed at 77 K is broad, but on annealing at 105 K, the line-width decreases to give poorly resolved

Table 1. EPR Parameters for the Radical Cations of a Series of Fluorinated Ethylenes and Propenes and Related Cations

		T					Hf coupling constant/mT				
Cation	Matrix	K	$g_\parallel$	$g_\perp$	g_iso	Nuclei[a)]	$A_\parallel$	$A_\perp$	a_iso[b)]	$2B$[c)]	Ref.
$CH_2{=}CH_2^+$	Neon	4			2.003	4H			0.3		12a
$CF_2{=}CH_2^+$	CCl_3F	93	2.002	2.004		2F	10.0		3.7	6.3	This work
						2H		2.1	2.1		
$CF_2{=}CFH^+$	CCl_3F	105	2.003			1F (CHF)	22.3		8.3	14.0	This work
						2F (CF_2)	12.1		4.5	7.6	
						1H	1.6		1.6		
						1F in CCl_3F	1.0		0.4	0.6	
	SF_6	77	2.003			1F (CHF)	22.6		8.4	14.2	This work
						2F (CF_2)	11.9		4.4	7.5	
						1H	1.6		1.6		
						1F in SF_6	1.6		0.6	1.0	
$CF_2{=}CF_2^+$	CCl_3F	77	1.9905	1.9903		4F	14.63		5.46	9.17	2
						1F in CCl_3F	1.39				
$CH_2{=}CHCH_3^+$	CCl_3F	77			2.003	1H (CH_2)			2.30		14
						1H (CH_2)			1.20		
						3H (CH_3)			2.40		
						1H (CH)			0.70		
$CH_2{=}CFCH_3^+$	CCl_3F	93	2.003			2H (CH_2)	1.7		1.7		This work
						3H (CH_3)	1.4		1.4		
						1F	13.8		5.1	8.7	
$(CCl_3F)_2^+$	CCl_3F	156	2.005			$2\,^{35}Cl$	9.3				This work
	($CH_2{=}CHCF_3/CCl_3F$)					$2\,^{37}Cl$	7.7				
$CF_2{=}CFCF_3^+$	CCl_3F	77	2.002	2.009		1F (CF)	22.9		8.6	14.3	This work
						2F (CF_2)	11.5		4.3	7.2	
	F-114	77	2.002	2.007		1F (CF)	24.1		9.0	15.1	This work
						2F (CF_2)	11.2		4.2	7.0	
	c-C_6F_{12}	77	2.004	2.007		1F (CF)	23.0		8.6	14.4	This work
						2F (CF)	11.4		4.3	7.1	

a) ^1H for H and ^{19}F for F. b) the approximate values for ^{19}F calculated from the equation $a_\mathrm{iso} = (A_\parallel + 2A_\perp)/3$ on the basis of the relationship of $A_\perp = 0.060A_\parallel$ derived from the data for the ^{19}F couplings of fluorobenzene cations and those for ^1H, having negative signs, obtained on the assumption that the observed couplings are isotropic. c) calculated from $2B = A_\parallel - a_\mathrm{iso}$.

splitting to each of the spectral lines observed at 77 K, as shown in Fig. 2. The parallel components of the spectrum are interpreted in terms of the large splittings of a doublet due to the ^{19}F nucleus in the CFH group and of a 1 : 2 : 1 triplet due to two equivalent ^{19}F nuclei in the CF_2 group in addition to the poorly resolved splittings due to two different doublets with small couplings of 1.0 and 1.6 mT, as shown with the stick diagram in Fig. 2. The double doublet splittings of 1.0 and 1.6 mT were evaluated from the feature of the poorly resolved peaks and shoulders in the observed spectrum. Since only one of the two doublets with the small couplings should be assigned to an ^{1}H nucleus in the cation CF_2=CFH^+, the other may originate from one ^{19}F nucleus in a matrix molecule.[5,21]

Similar experiments were done using an SF_6 matrix. Although the outermost lines of the parallel components attributable to the radical cation are partly masked by signals due to SF_6^- and SF_5 radicals,[22] the inner lines undoubtedly split into a 1 : 2 : 1 triplet with a small spacing of 1.6 mT. The parallel couplings for ^{19}F in the CFH and CF_2 groups for the cation are hardly affected by the difference in the matrix, CCl_3F or SF_6. The 1 : 2 : 1 triplet supports the assignment of the double doublet splittings of 1.0 and 1.6 mT for CCl_3F and means that the couplings of two doublets are almost equal to each other for SF_6. One of them can be assigned to ^{1}H for the cation and the other to additional splitting.

Thus, it may be reasonable to assign one of the two doublets found in the spectra for CF_2=CFH^+ in the CCl_3F and SF_6 matrices to the additional coupling due to the ^{19}F nucleus in a matrix molecule interacting with a delocalized system.[21] Therefore, the doublet giving a coupling of 1.6 mT is assigned to the ^{1}H nucleus in the cation CF_2=CFH^+, and the other doublet, with a coupling of 1.0 mT for the CCl_3F matrix or of 1.6 mT for the SF_6 matrix, is attributed to an ^{19}F nucleus in a matrix molecule interacting with the cation.

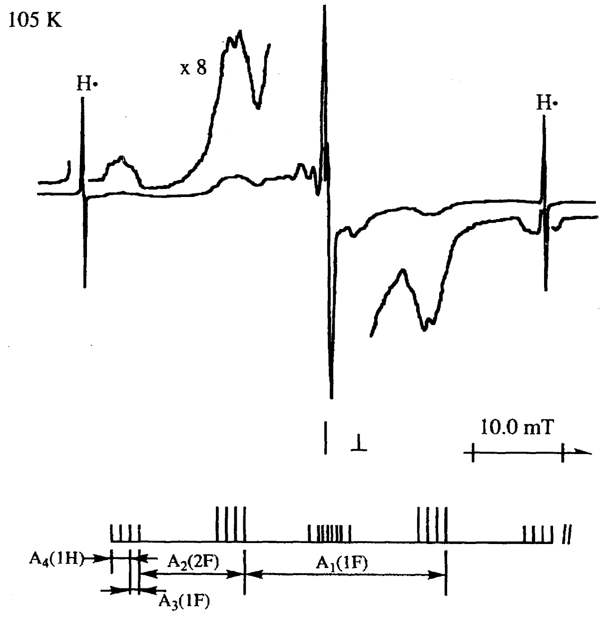

Fig. 2. First-derivative X-band EPR spectrum observed at 105 K after γ-irradiation of a solid solution containing ca. 1 mol% CF_2=CFH in CCl_3F at 77 K, and the stick diagram for CF_2=CFH^+ cation calculated with the parameters listed in Table 1. The intense signals in the central part of the spectrum have been occasionally observed upon the use of the CCl_3F matrix. Thus, they may be the signals for the radicals originated from the matrix molecule or O_2^- generated in the case of insufficient evacuation. Defects formed in quart tubes may also be responsible in this region.

The CH_2=CF–CH_3^+ Cation and the Two Radicals Formed from CH_2=$CFCH_3$. Figure 3 shows the anisotropic EPR spectrum for a CH_2=CF–CH_3^+ cation, observed at 93 K after γ-irradiation of a solid solution containing CH_2=$CFCH_3$ in CCl_3F at 77 K. The parallel components consist of a doublet with a large hf coupling of 13.8 mT due to the ^{19}F nucleus in CH_2=$CFCH_3$ and several lines due to protons. Although the proton splittings are not well-defined, they may be attributable to two types of splittings: one is a triplet of 1.7 mT due to two protons, and the other is a quartet of 1.4 mT due to three equivalent protons, as shown in Table 1.

When the proton hf couplings of CH_2=$CFCH_3^+$ are compared with those of CH_2=$CHCH_3^+$ on the assumption that the proton couplings are also isotropic in the case of CH_2=$CFCH_3^+$, for the protons in the CH_2 groups, they are almost equal to each other, but for those in the CH_3 groups, the coupling for CH_2=$CFCH_3^+$ is about one-half of that for CH_2=$CHCH_3^+$.

When CH_2=CF–CH_3 was irradiated in F-113 and F-114 matrices at 77 K, five well-defined isotropic lines were observed. For the F-113 matrix, a broad signal attributable to the CH_2=CF–CH_3^+ cation appears in addition to these

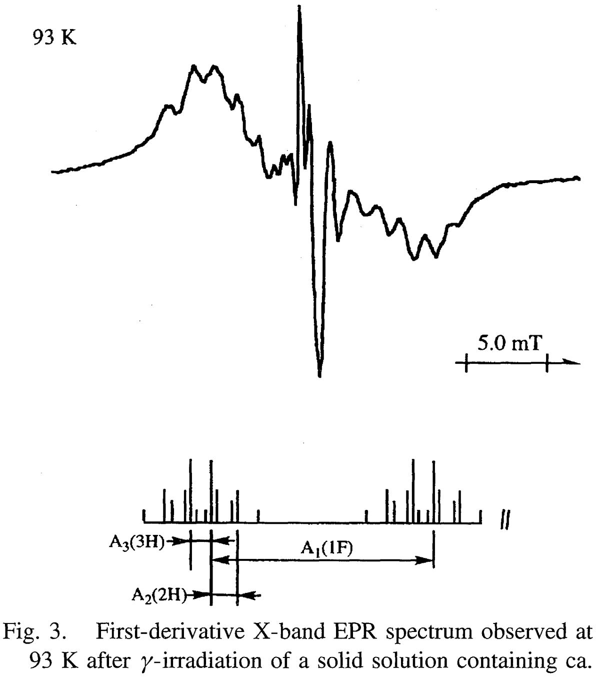

Fig. 3. First-derivative X-band EPR spectrum observed at 93 K after γ-irradiation of a solid solution containing ca. 1 mol% CH_2=$CFCH_3$ in CCl_3F at 77 K, and the stick diagram for CH_2=$CFCH_3^+$ cation calculated with the parameters listed in Table 1. Concerning to the intense signals in the central region, see the caption in Fig. 2.

lines. The five lines are assigned to $CH_2{=}C{=}CH_2^+$ cations because the observed parameters ($g = 2.003$, and $a_{iso}(4H) = 1.4$ mT for F-113 and F-114) coincide with the values reported for $CH_2{=}C{=}CH_2^+$ 23) and they closely resemble those in the spectrum obtained after irradiation of allen, $CH_2{=}C{=}CH_2$, in these matrices. The $CH_2{=}C{=}CH_2^+$ cations in the F-114 matrix were observed even for the measurement of EPR at 4.2 K after irradiation at the same temperature. For the F-114 matrix, the radical cations were observed at the low concentrations of 0.1—1.0 mol% $CH_2{=}CF{-}CH_3$, while only the signals resulting from the matrix molecules were observed at higher concentrations of 10—20 mol%. Thus, the $CH_2{=}C{=}CH_2^+$ cation may be generated not through an ion-molecule reaction but through the release of HF from $CH_2{=}CF{-}CH_3^+$.

The $(CCl_3F)_2^+$ Dimer Cation and Its Precursor, Formed in an Irradiated $CH_2{=}CHCF_3/CCl_3F$ System. The spectrum shown in Fig. 4(a) was obtained at 77 K after irradiation of $CH_2{=}CHCF_3$ in a solid matrix of CCl_3F. In contrast with the spectra for the other cations formed in CCl_3F matrices, this spectrum was not bleached with visible-light. The line-width of the spectrum decreased, but no significant change in the spectrum was observed at 120 K.

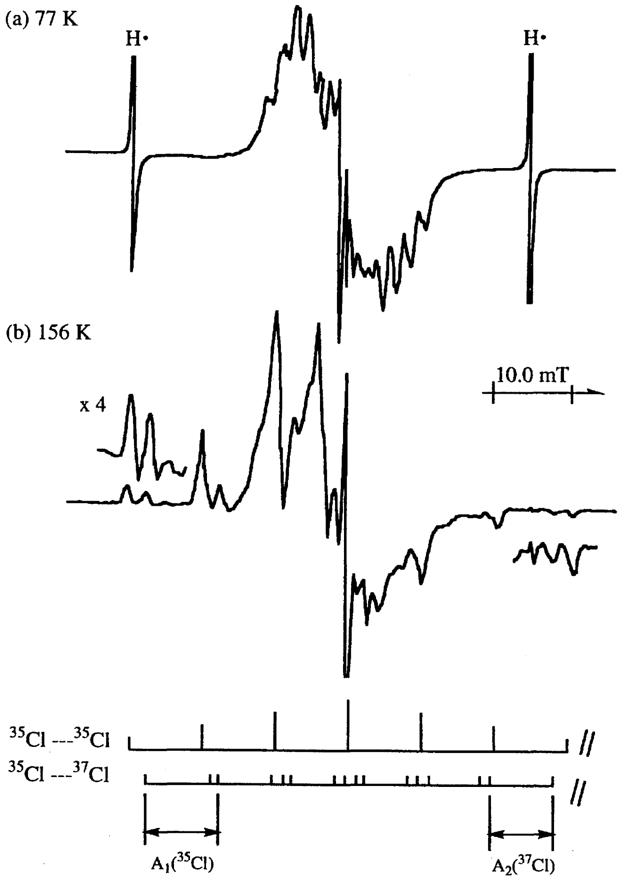

Fig. 4. First-derivative X-band EPR spectra observed at 77 K (a) and 156 K (b) after γ-irradiation of a solid solution containing ca. 1 mol% $CH_2{=}CH{-}CF_3$ in CCl_3F at 77 K, and the stick diagram for a $(CCl_3F)_2^+$ dimer cation calculated with the parameters listed in Table 1.

On annealing at higher temperatures, these spectral lines begin to diminish, and a spectrum with highly anisotropic features takes their place at about 135 K. The spectrum observed at 156 K is shown in Fig. 4(b). The species giving this spectrum is thermally stable until 160 K, corresponding to the melting point of CCl_3F. Note that no significant change occurred in the spectrum (b) upon decreasing the temperature to 77 K, while visible-light illumination at 77 K brought about conversion of spectrum (b) into spectrum (a).

The parallel components in the wing regions of spectrum (b) consist of lines due to three combinations, $^{35}Cl{-}^{35}Cl$, $^{35}Cl{-}^{37}Cl$, and $^{37}Cl{-}^{37}Cl$, made by two equivalent Cl nuclei having two isotopes of ^{35}Cl and ^{37}Cl with the relative natural abundance of about 1 and 1/3, respectively. This spectrum closely resembles that assigned to the dimer cation of the matrix molecules, $(Cl_2FCCl{-}ClCCl_2F)^+$, having one electron shared by the two Cl nuclei, which was observed at 10 K after exposure of a CCl_3F solution containing ethylene oxide to X-rays at 4 K.24) Thus, the observed spectrum is assigned to the dimer cation of the matrix CCl_3F molecules with the parameters given in Table 1. It is curious that although EPR signals of the dimer cation were seen over the temperature range 20—60 K for the CCl_3F–ethylene oxide system, in this system they were observed over the range of 135—160 K and on cooling down to 77 K without photo-bleaching.

The spectrum shown in Fig. 4(a) may be due to a precursor for the dimer cation. Because the spectrum is not photobleached, it may not be a solute cation but the radical cation adduct formed from $CH_2{=}CH{-}CF_3^+$ and CCl_3F molecules, although unfortunately the spectrum was not analyzed.

The $CF_2{=}CF{-}CF_3^+$ Cation. EPR spectra mainly due to the cation of $CF_2{=}CFCF_3$ were obtained using matrices of CCl_3F, $CClF_2CClF_2$, and c-C_6F_{12}. Among them, the most resolved spectrum was observed after irradiation of a solid matrix containing $CF_2{=}CFCF_3$ in $CClF_2CClF_2$ at 77 K, as shown with the solid line in Fig. 5. The spectrum observed after photo-bleaching with visible-light, following γ-irradiation, is shown with a dashed line in Fig. 5. The spectral components that were easily photo-bleached and distinguishable from the signals due to the matrix, marked with ●, may be assigned to the radical cation of $CF_2{=}CFCF_3$. The cation shows a largely anisotropic spectrum. The parallel components are attributable to the ^{19}F in the CF group and two equivalent ^{19}F nuclei in the CF_2 group giving the couplings of 24.1 and 11.2 mT, respectively, as shown in Table 1. As for the perpendicular component, the value of $g_\perp$ was obtained from the central singlet which decayed together with the parallel components by photo-bleaching. Thus obtained perpendicular couplings of these ^{19}F nuclei are too small to be resolved, indicating a radical of the π-type. No splitting due to ^{19}F in the CF_3 group has been observed even for the parallel components. The EPR spectrum and the parameters for this cation resemble those for the $CF_2{=}CHF^+$ cation, excepting that the latter cation has resolved splittings to an ^1H and an additional ^{19}F nuclei.

The formation of the $CF_2{=}CFCF_3^+$ cation could not be detected using matrices other than these three matrices.

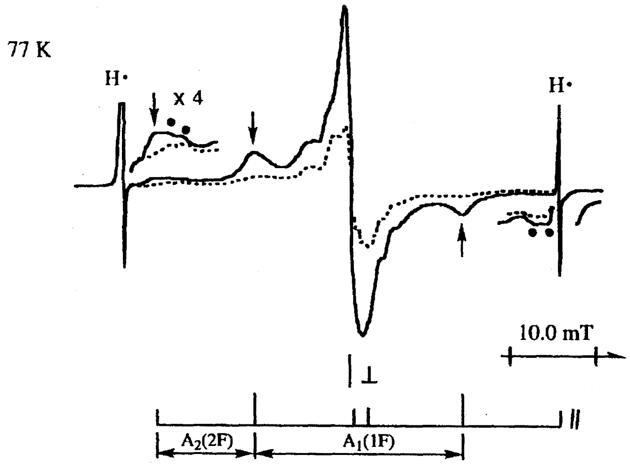

Fig. 5. First-derivative EPR spectra observed at 77 K after irradiation of a solid matrix containing CF_2=$CFCF_3$ in $CClF_2CClF_2$ at 77 K, the spectrum represented by a solid line was observed before photo-bleaching at 77 K and that by a dashed line was observed after photo-bleaching. The bands indicated with ● are attributed to radicals from the matrix molecule and the peaks marked with arrows in the spectrum were assigned to the CF_2=$CFCF_3{}^+$ radical cation.

For the trifluoro olefin cations, CF_2=CFX^+ (X = H, CH_3, or CF_3), the experimental spectra were successfully analyzed in terms of the three ^{19}F nuclei with coaxial parallel components. This suggests that the unpaired electron largely occupies the 2p orbital of each ^{19}F nucleus, which is perpendicular to the molecular plane. Thus, the planar structure was experimentally concluded for the trifluoro olefin radical cations, similarly to the case of the tetrafluoroethylene radical cation.[5a)]

On the other hand, concerning the mono- and di-fluoro olefin radical cation of CH_2=$CFCH_3{}^+$ and CF_2=$CH_2{}^+$, it is difficult to conclude the planar structure unequivocally from the experimental ^{19}F and ^1H hf splittings, although the experimental splittings are characteristic of a p-type radical. We have to add to note that the experimental ^1H hf splittings (1.2 mT to 1.6 mT) are considerably larger than that observed for the twisted ethylene radical cation (0.3 mT for four equivalent protons).[12a)] Thus, theoretical calculations may be essential for the identification of the structure of the radical cations.

Geometries Calculated by ab initio, Spin Densities, and Hf Couplings by INDO. The optimized geometries of these fluorinated olefin cations were derived from ab initio calculations, as shown in Fig. 6. The results showed planar structures for the fluorinated ethylene and propene cations, in contrast with the nonplanar twisted structures for the ethylene and propene cations.[11,12,14—16)] The ethylene and propene cations have twisted structures because of a strong hyperconjugation effect.[10c,15)] However, the planar structures for the fluorinated olefin cations may result from the π electron system stabilized by the participation of the nonbonding π electrons of the fluorines.

INDO calculations were done for the geometries optimized by the ab initio method. Isotropic hf couplings to ^1H and ^{19}F were acquired from the calculated s-spin densities on their nuclei and the atomic hf constants a^0_{iso} adjusted for INDO calculations, 53.986 and 4482.92 mT, respectively.[18)] In Fig. 6, the calculated isotropic couplings are shown in parentheses together with the optimized geometrical parameters. Anisotropic hf coupling, $2B$, to the ^{19}F nuclei can be obtained from the p-spin densities on the nuclei in Fig. 6 and the calculated atomic value, $2B_0 = 108.4$ mT.[25,26)]

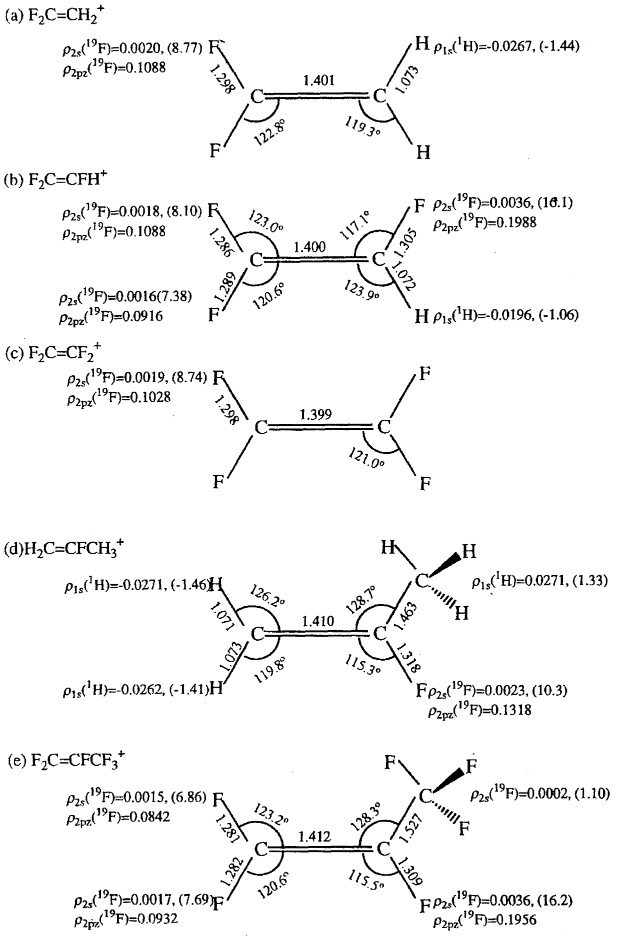

Fig. 6. Optimized geometric structures for the fluorinated ethylene and propene cations, calculated with a GAUSSIAN 94 program at the UHF/6-31G level, together with the calculated spin densities and isotropic hf couplings, a_{iso}, in mT. The isotropic couplings in parentheses were obtained from the s-spin densities calculated by the INDO method for the ab initio optimized structure and from the atomic hf constants a^0_{iso} adjusted for INDO calculations.[18)]

Comparison between the calculated and the observed hf couplings to the ^{19}F nuclei leads us to the conclusion that the calculated couplings are systematically larger than the observed ones for the isotropic and anisotropic couplings. In the case of the fluorinated benzene cations, the observed couplings (Y) were related to the calculated INDO spin densities (X) by the linear function

$$Y = CX, \qquad (2)$$

in both cases of $a_{\text{iso}}(^{19}F)$ and $2B(^{19}F)$, the constants C

being 23.8×10^2 and 72.3 mT for $a_{\mathrm{iso}}(^{19}\mathrm{F})$ and $2B(^{19}\mathrm{F})$, respectively.[2)] When the relationship was applied to these cases, excellent agreement was obtained for both the isotropic and anisotropic ^{19}F couplings. Thus, it is expected that the relationship will be hereafter used for the evaluation of hf couplings to ^{19}F nuclei from the INDO calculations.

However, anisotropy in hf couplings may be generated not only by spin densities in the 2p orbitals on the ^{19}F nuclei but also by interatomic dipole–dipole interactions between the unpaired electron and the nuclear spins of ^{1}H and ^{19}F. Although the dipole–dipole interactions have been neglected for the study on fluorinated benzene cations[1,2)] because of the delocalization of the spin density on benzene rings, the interactions may be more important in the case of olefin cations. Thus, calculations for the anisotropic part of the hf coupling tensor involving this interaction were done at the INDO level, using the ANALDIP program.[19)] For the calculation, the INDO spin densities and the geometrical structure are required as input parameters.[19,20,27)] We used the geometrical structure optimized by the ab initio method and the associated INDO spin densities, shown in Fig. 6. The principal values and the principal directions for the anisotropy of the hf coupling are given in Fig. 7.

For example, let us evaluate the calculated values shown in Figs. 6 and 7 for the $\mathrm{CF_2{=}CH_2^+}$ cation. The calculated anisotropy in the ^{19}F coupling, 9.04 mT, is greater than the observed value, 6.3 mT. The principal directions of the anisotropic hf couplings to the ^{19}F and ^{1}H nuclei lying in the molecular plane are not parallel between the ^{19}F and ^{1}H nuclei. For the spectral simulation done on these bases, we intended to use the results of ANALDIP as much as possible according to the equation:

$$A_{ii} = a_{\mathrm{iso}} + KP_{ii}, \qquad (3)$$

where A_{ii}, a_{iso}, P_{ii}, and K are the principal value used for simulation, the isotropic coupling to be measured, the anisotropic coupling obtained from the ANALDIP calculations, and a constant, respectively, for the ^{1}H and ^{19}F couplings. The principal direction for the A_{ii} value corresponds to that derived from the ANALDIP calculations and is shown in Fig. 7. Thus, the best fit simulation spectrum shown in Fig. 1(b) was obtained for $a_{\mathrm{iso}} = 3.7$ mT and $K = 0.69$ for the ^{19}F coupling and for $a_{\mathrm{iso}} = -1.3$ mT and $K = 0.77$ for the ^{1}H coupling, using the EPR parameters given in the caption of Fig. 7. Being small, the deviation from an axial symmetry for the ^{19}F couplings scarcely affected the simulation spectrum. However, the three different principal values for the ^{1}H couplings played an important role in the simulation. This example may be sufficient to demonstrate that the calculation of dipolar interaction is important for a deeper understanding of the anisotropic hf structure. The ANALDIP calculations also indicate that the $a_{\mathrm{iso}}(^1\mathrm{H})$ values in Table 1, which were obtained on the assumption that the observed ^{1}H couplings are isotropic, are approximate values because the ^{1}H coupling observed in the parallel components corresponds to the intermediate principal value in magnitude and the largest and the smallest values (in the absolute value) appear in the "perpendicular" components.

The isotropic coupling constant, 4482.9 mT, used for the 2s orbital of ^{19}F in INDO calculations was adjusted to an average value from the results obtained for only nine different fluorinated radicals.[18)] Instead of this value, using the value of 23.8×10^2 mT is recommended, being the constant in Eq. 2, for the INDO calculations based on the ab initio geometry. The value was evaluated from the accumulation of fifteen results for fluorinated benzene cations and seven results for these olefin cations.

As for the dipole–dipole interaction, the dipolar integrals are evaluated using the analytical expression for Slater-type

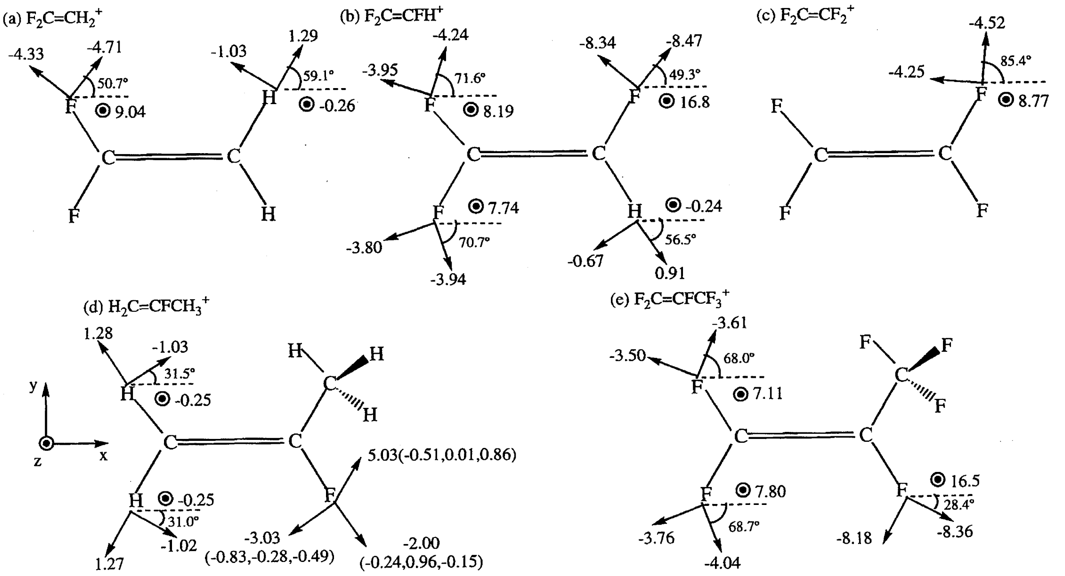

Fig. 7. The principal values (mT) and directions for anisotropic hf tensors calculated based on INDO spin densities using the ANALDIP program for interatomic dipole–dipole interaction. As for (d), the direction cosines of the axes are given in parentheses by the x, y, z coordination system shown in Fig. 7(d).

orbitals with effective nuclear charges according to Slater's rules.[19] The ANALDIP program gives intermediate calculated $2B$ values to the ^{19}F nuclei between those obtained from $2B_0 = 108.4$ mT calculated by the SCF method[25] and those from $2B_0 = 72.3$ mT for Eq. 2 obtained experimentally from the fluorinated benzene and olefin cations.

It is generally expected that the matrix used can affect more or less the electronic or geometrical structure of the radical cation stabilized in it. However, it has been reported that the matrix effects are generally small for the similar p-type radical cations studied so far.[16,28] In this study, the calculated hf splittings agree rather well with the experimental ones. This strongly suggests that in this case, too, the matrix contributes only as a perturbation to the structures of the radical cations.

The assignment of the EPR spectra for a series of the fluorinated olefin cations is strongly supported by these calculation results. In the order of $CF_2{=}CH_2^+$, $CF_2{=}CFH^+$, and $CF_2{=}CF_2^+$, the magnitude of the observed isotropic and anisotropic hf couplings to the ^{19}F nuclei in the CF_2 groups systematically increases with the number of F nuclei in the group of the counterpart of the CF_2 group. For the σ electrons system, the ^{19}F coupling is expected to decrease with the substitution of H atoms in a CH_2 group by F atoms because fluorine has a high electronegativity. On the other hand, for the π electrons, the coupling is expected to increase by the "back donation" effect of the fluorine which behaves as a π donor.[29,30] The observed systematic increase in ^{19}F couplings in the CF_2 groups in that order of cations indicates that the "back donation" effect dominates in these π-type radical cations. It may be also of interest to note that the spin density distributions in the $CF_2{=}CFH^+$ and $CF_2{=}CF{-}CF_3^+$ cations are almost equal, which means that the CF_3 group is ineffective for the electronic structure of the cation. In contrast with the fact that two largely different hf couplings were observed for the ^{1}H nuclei in the CH_2 group of the $CH_2{=}CH{-}CH_3^+$ cation, the two hf couplings are scarcely distinguished for the ^{1}H nuclei in the CH_2 group of the $CH_2{=}CF{-}CH_3^+$ cation from the experiments as well as the calculation. This may arise from the difference in the structure of the cations: the nonplanar structure for $CH_2{=}CH{-}CH_3^+$ and the planar structure for $CH_2{=}CF{-}CH_3^+$.

We thank Prof. Anders Lund for his help in using the ANALDIP program and the IFM, Linköping University, for the use of the computer. This study was partially supported by a Grant-in-Aid for Science Research No. 0824105 from the Ministry of Education, Science, Sports and Culture.

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