Theory of Nuclear Quadrupole Interactions in Solid Fluoromethanes with Implanted $^{19}F^*$ Nuclei. Coupling of HF^* and Host Molecule *

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Z. Naturforsch. **51a**, 565–571 (1996); received March 8, 1996

The Quadrupole Coupling Constant e^2qQ and Asymmetry Parameter η of fluorine for fluorine-substitute methane compounds are calculated using the Hartree-Fock Roothaan procedure. Our results are compared with experimental data from measurements by the Time Differential Perturbed Angular Distribution (TDPAD) technique using excited $^{19}F^*$ (spin 5/2) nuclei. The theoretical e^2qQ's for the $^{19}F^*$ nuclei in the fluoromethanes are in good agreement with experimental results. For CH_2F_2 and $CHClF_2$ molecules, where finite η are expected from symmetry considerations, our results for η are small, 0.12 and 0.05 respectively, in agreement with experimental observation. Besides the $^{19}F^*$ coupling constants associated with the C–F bonds in fluoromethanes, additional interesting NQI parameters, close to those in solid hydrogen fluoride, are observed in the TDPAD measurements. It is demonstrated through investigations of the total energies and electric field gradients that these additional NQI parameters for the fluoromethanes can be explained by a HF^* molecule hydrogen-bonded through the hydrogen to a fluorine atom in the host molecular systems. This complexing of an ionic molecule to the host molecules in organic solids containing strongly electronegative atoms is expected to be a general feature in both implantation and conventional techniques.

Key words: Nuclear Quadrupole Interaction, $^{19}F^*$ (nuclear excited state), Fluoromethane, Hartree-Fock Calculation, Hydrogen Bonding.

1. Introduction

The development of Time Differential Perturbed Angular Distribution (TDPAD) [1–3] and Beta Decay Nuclear Magnetic Resonance (β-NMR) [4] allows the study of the Nuclear Quadrupole Interaction (NQI) of fluorine, which is not possible by conventional magnetic resonance techniques since the ^{19}F nucleus in its ground state has no quadrupole moment. In the TDPAD experiment on a fluorine compound one excites the ^{19}F nucleus to its state $^{19}F^*$ with spin $I = 5/2$ and studies the anisotropy of its gamma ray emission. In the β-NMR technique [4] one observes the asymmetry in the β-decay of ^{20}F ($I = 2$), produced by irradiation of ^{19}F by polarized neutrons. In both techniques the anisotropy of the γ or β emission is influenced by the NQI of the fluorine nuclei. The observed NQI's provide information on the electron distribution and associated properties at the sites of the fluorine atoms. In the TDPAD experiment [3], the results of which are compared with our theoretical results the $^{19}F^*$ nuclei are produced by the $^{19}F\,(p\,p')\,^{19}F^*$ reaction outside the host material. They are then implanted in the host molecules, replacing the ^{19}F nuclei in the latter. The $^{19}F^*$ nuclei emit γ-radiation during the decay to the ground state. The intensity of the decay pattern is modulated in time due to the NQI of the $^{19}F^*$ nuclei with the surrounding electronic environment, thus allowing for a determination of the NQI parameters.

In the present work we have carried out first-principle Hartree-Fock calculations of the quadrupole coupling constant (e^2qQ) and asymmetry parameter (η) of the fluoromethanes $CH_{4-n}F_n$ ($n = 1, 2, 3$), and of $CHClF_2$ as an example involving fluorine in a mixed halogen derivative. The understanding of an observed frequency comparable to that observed in the TDPAD experiments on solid hydrogen fluoride (HF) [5] is also a subject of our investigation. For this purpose, our investigation includes the analysis of a complex involving the HF^* molecule and of a fluoromethane molecule.

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* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23–28, 1995.

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0932-0784 / 96 / 0500-0565 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

Section II explains briefly the procedure employed for the Hartree-Fock calculation of the electronic structure of the molecular systems involved and the associated $^{19}F^*$ quadrupole coupling constants. In Sect. III we present our results their comparison with experiment and discussions. Finally, in Sect. IV we present conclusions and possible improvements that can be made in the future.

2. Procedure

The self-consistent field Hartree-Fock procedure [6, 7] was applied for our electronic structure calculations using the available Gaussian 86 and 92 programs [8]. In these programs each molecular orbital is taken as a linear combination of atomic orbitals, and the atomic orbitals in turn are taken as linear combinations of Gaussian orbitals. The use of a Gaussian basis set simplifies [9] the evaluation of the multi-center integrals which occur in the Hartree-Fock procedure. The Gaussian based Hartree-Fock procedure is described extensively in the literature [8], including our earlier publications [7, 11] on $^{19}F^*$ systems, and will therefore not be discussed here.

Nuclear quadrupole interactions are characterized [7, 11, 12] by the quadrupole coupling constant $e^2 q Q$ and the asymmetry parameter η in the principal axes of the electric field gradient tensor at the nucleus. Once the molecular wave functions ψ_μ for the occupied states are obtained from the Hartree-Fock procedure, the components V_{ij} ($i, j = 1, 2, 3$ corresponding to x, y, and z axes) of the electric field gradient tensor can be obtained from the relation [7]

$$V_{ij} = e\,[\textstyle\sum_n' \xi_n (3\, r_{in} r_{jn} - r^2 \delta_{ij})/r_n^5 - \sum_\mu \int \psi_\mu (3\, r_i r_j - r^2 \delta_{ij})/r^5 \,\mathrm{d}\tau]\,, \qquad (1)$$

where $\boldsymbol{r}_\mathbf{n}$ is the position vector of the nucleus n with respect to the nucleus under study, r_{in} and r_{jn} are its components, $e\,\xi_n$ is the nuclear charge on the nth nucleus, $\boldsymbol{r}$ the radius vector of an electron with respect to the nucleus under study and r_i are its components. The first term on the right hand side of (1) represents the contribution of the nuclear charges to the field-gradient tensor and the second term denotes the electronic contribution. The maximum component (labeled as the ZZ-component) of the electric field gradient tensor in its diagonalised form in the principal axis system is denoted as eq. The asymmetry parameter η is defined by

$$\eta = (V_{xx} - V_{yy})/V_{zz}\,, \qquad (2)$$

the X, Y, Z axes in the principal axis system being based on the convention

$$|V_{zz}| > |V_{yy}| > |V_{zz}|\,.$$

For the nuclear quadrupole moment Q of $^{19}F^*$ the value 0.072×10^{-24} cm^2 from [11] is used. A number of different atomic orbital basis sets was used in the Hartree-Fock calculation in order to test the convergence of the calculated electric field gradient (EFG) tensor with respect to the size of the basis set. The used basis sets were 6-31G, D95 and 6-311G [13]. The influence of polarization effects [14] involving the mixing of s and p orbitals on all the atomic sites due to the potentials of neighboring atoms are included in the chosen basis sets which have significant numbers of s and p functions. To study in addition the influence of mixing of p and d orbitals on the EFG at the $^{19}F^*$ nucleus, one and two d-orbitals were added to the 6-31G basis set as in earlier work on fluorobenzenes [7]. The effects of adding diffuse p-orbitals to the basis set [7] were also examined.

3. Results and Discussion

The systems studied in this work were CH_3F, CH_2F_2 and $CHClF_2$. As mentioned in Section I, the purpose of this study was two-fold. The first was to study the values of $e^2 q Q$ and η and the trends in them for the $^{19}F^*$ in these molecules. The second was to attempt to understand the origin of the additional resonance at a lower frequency observed in the TDPAD spectra in a number of these systems similar to that found for $^{19}F^*$ in solid HF. Considering first the $^{19}F^*$ in the host molecular systems, we studied the dependence of the NQI parameters on the basis sets by choosing three such sets of varying flexibility for our investigations, namely 6-31G, 6-311G and D95 [13]. Though there were some variations in $e^2 q Q$ for these three choices, the differences were not substantial, indicating satisfactory convergence. In Table 1 we have presented the results for the three basis sets. To study the polarization effects due to mixing of d orbitals with the p orbitals, we examined the influence of adding one and two d-like basis orbitals to the 6-31G basis set [7]. This led to about a ten percent decrease in $e^2 q Q$, which is in the opposite direction in terms of agreement with experiment, similar to the behavior found in fluorobenzene [7]. As has been discussed there, the introduction of one or two *d*-functions may not always be sufficient for studying such polarization effects. It would be helpful in the future to use more extensive and specific sets of *d*-type Gaussian functions which represent 3d and higher atomic *d* orbitals to examine this effect accurately. Additionally, we have studied the importance of many-body pair correlation effects [15] on the electric field gradient at the $^{19}F^*$ nucleus using second order many-body perturbation theory and the empty states from Hartree-Fock calculations as excited states, applying the subroutine MP2 from the Gaussian 92 set of programs [8]. For all four molecules, the many-body contribution to the field-gradient by this procedure was found to be only about five percent of the result from Hartree-Fock calculations. In view of this, we shall assume that many-body effects are not significant in general in this class of covalently bonded systems and will not consider them any further.

It is interesting to compare the trends in the $^{19}F^*$ coupling constants for the fluorine atom in the host fluoromethane as one increases the number of hydrogens substituting for fluorine. Considering CH_3F and CHF_3, the theoretical values are nearly the same, while the experimental values show a small decrease of 1 MHz in going from CH_3F to CHF_3. From the consideration that there is increasing competition for electron acquisition between the three fluorines in the case of the latter molecule, one would expect a decrease in ionic character of the C-F bond relative to CH_3F and therefore an increase in the $^{19}F^*$ coupling constant, according to the Townes and Dailey relation [16]. The opposite trend is observed experimentally. It thus appears that, in contrast to the corresponding chlorine compounds [11, 17], consideration of the variations in ionic character alone is not sufficient to explain the trends of small and significant variations in the present cases. Other factors include, for instance, differences in the radial characters of the atomic orbitals for the fluorine and carbon in CHF_3 and CH_3F. These differences could lead to both different bonding strengths between carbon and fluorine atoms in the two molecules and in the expectation value $\langle 1/r^3 \rangle$ for the atomic *p*-orbitals of the fluorine atoms in these molecules. These effects could counteract the influence of the difference in the ionic characters of the two molecules, the latter effect being thought to cause the main variations in the field-gradient in Townes and Dailey theory [16].

It is also interesting to compare the $^{19}F^*$ quadrupole coupling constant in $CHClF_2$ with those in CHF_3 and CH_2F_2. Considering first the pair, CHF_3 and $CHClF_2$, from Townes and Dailey theory, one would expect a smaller $^{19}F^*$ quadrupole coupling constant in the latter molecule. This is because chlorine is less electronegative than fluorine and substitution of chlorine for a fluorine in CHF_3 would tend to increase the ionic character of the C-F bonds. Again the opposite trend is observed from experiment and from our first principle investigations. It is interesting, however, that for the pair CH_2F_2 and $CHClF_2$ the Townes and Dailey prediction for the trend in the $^{19}F^*$ coupling constant is in the same direction as that from our theoretical results in Table 1. It would be helpful to have experimental results for CH_2F_2 to observe the experimental trend in going to $CHClF_2$. In summary, the results in Table 1 indicate that for the fluoroderivatives of methane it is not possible in general to explain experimental trends in $^{19}F^*$ quadrupole coupling constants by the Townes and Dailey theory, while first-principle Hartree-Fock theory can explain the experimental results.

We turn next to the origin of the resonances that have been observed in the neighborhood of 40 MHz as compared to those around 60 MHz that are associated with the $^{19}F^*$ belonging to the fluoromethanes which have just been discussed. A plausible model that has been suggested for the occurrence of the 40 MHz signal is the following [18]. In the process of implantation of the excited $^{19}F^*$ nucleus in the solid fluoromethanes, the $CH_{4-n}F_n$ molecule could be broken up into fragments. A fragment involving a hydrogen atom could then combine with the fluorine atom projectile and form a HF^* molecule containing the excited $^{19}F^*$ nucleus. The $^{19}F^*$ quadrupole coupling constant in a free HF^* molecule has been calculated

Table 1. Nuclear quadrupole interaction parameters for $^{19}F^*$ in fluoromethanes.

Molecular	e^2qQ in MHz for 6-31G basis	e^2qQ in MHz for 6-311G basis	e^2qQ in MHz for D95 basis	Experimental values of e^2qQ in MHz	Calculated values of η [a]
CH_3F	55.7	59	55	59.8	0
CH_2F_2	53.9	58	55.5	not avail.	0.12
CHF_3	54.6	59	57.5	58.7	0
$CHClF_2$	56.6	60.6	58.7	59.3	0.05

[a] No experimental values of η are available.

by the Hartree-Fock procedure to be 52.9 MHz [19]. In solid HF*, two coupling constants have been found experimentally, namely 40.0 MHz and 33.0 MHz [5]. The latter coupling constant has been explained by carrying out Hartree-Fock calculations [19] on sizable clusters involving HF* molecules in the crystals which are hydrogen-bonded to each other. The coupling constant of 40.0 MHz has been explained as arising from a fragment involving two or three HF molecules formed during the implantation process. In both cases, the hydrogen-bonding reduces the $^{19}F^*$ coupling constant substantially from the value for the free molecule. It therefore seems worthwhile to explore if the additional $^{19}F^*$ NQI parameters in the fluoromethanes involving coupling constants [3] in the neighborhood of 40 MHz could be explained by a HF* molecule bonded to the $CH_{4-n}F_n$ molecules. We have carried out such an analysis to study both whether one can get a stable bonding of HF to a $CH_{4-n}F_n$ molecule and also if for such a stably bonded state one can explain the observed $^{19}F^*$ NQI parameters.

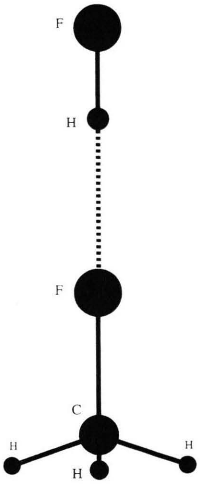

Fig. 1 a. F atom of the host molecule hydrogen bonded to H atom of the HF* molecule.

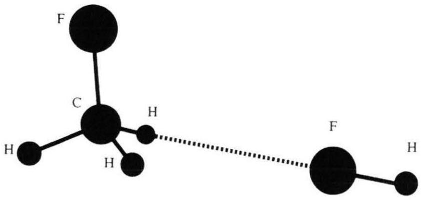

Fig. 1 b. H atom of the host molecule hydrogen bonded to the F atom of the HF*.

We started our analysis by investigating structures of the type shown in Figs. 1 a and 1 b using CH_3F as an example. In Fig. 1 a, the HF* molecule is considered to be attached through hydrogen-bonding between the fluorine of CH_3F and the hydrogen in HF*. In Fig. 1 b, on the other hand, the attachment of HF* is considered to occur through hydrogen bonding of the fluorine atom in HF* to a hydrogen atom in CH_3F. In both these structures we considered the HF* to be located along a straight line associated with a C-X bond with X corresponding either to the F or H atoms of CH_3F through which the hydrogen-bonding occurs. The binding energies for the HF molecule in each case was calculated using the relation

$$E = E(CH_{4-n}F_n) + E(HF) - E(CH_{4-n}F_n;\ HF) \qquad (3)$$

with E representing the total energies of the systems in parenthesis, the last system in (3) representing the complexes involving $CH_{4-n}F_n$ and HF in Figs. 1 a and 1 b. Using the Hartree-Fock procedure to obtain the total energies of the isolated and complexed systems in (3), the binding energy for the (CH_3F; HF) complex in Fig. 1 a was found to be 0.3503 eV with the minimum energy at a separation of 1.75 Å between the hydrogen atom of HF* and the fluorine atom of CH_3F that are hydrogen bonded. For Fig. 1 b, where the hydrogen-bonded fluorine belongs to the HF molecule in contrast to the situation in Fig. 1 a, the corresponding binding energies and H-F separation are − 0.0092 eV and 2.85 Å. These results indicate that the complex in Fig. 1 b is unstable while that in Fig. 1 a is stable. The difference in stabilities of the two structures can perhaps be understood physically as follows: The hydrogen atom in HF molecule is expected to carry a larger positive charge than a hydrogen atom in CH_3F due to the stronger ionic character of the H-F bond in HF as compared to the C-H bond in CH_3F. This is a consequence of the greater electronegativity difference between hydrogen and fluorine atoms as compared to that between carbon and hydrogen. Indeed, our electronic structure calculations show that the charges on the hydrogen atoms in the two cases, using Mulliken approximation, are 0.49 and 0.16 for HF and CH_3F respectively. The charges on the fluorine atoms for HF and CH_3F are −0.49 and −0.46, respectively, the small difference being understandable from considerations of the small differences in the electronegativities of hydrogen and fluorine and of carbon and fluorine. From these charges and the distances between the hydrogen bonded H-F pairs in the two cases, the electrostatic interaction between the H and F atoms is expected to be stronger for Fig. 1a than for Fig. 1b, thus leading to the lower total energy for the complex in the former case and a stronger binding energy from (3).

We have also carried out this same type of analysis for HF* bonded to CH_2F_2, CHF_3 and $CHClF_2$. The $^{19}F^*$ quadrupole coupling constant in the neighborhood of 40 MHz has been observed [3] for the latter two compounds and while it has not so far been observed for CH_2F_2, efforts are under way to locate it. For all three compounds, again the structures of the type in Fig. 1a for CH_3F with hydrogen from HF* hydrogen-bonded to an F-atom were found to be the stable ones.

Table 2 lists both the observed [3] additional e^2qQ for $^{19}F^*$ in the four compounds CH_3F, CH_2F_2, CHF_3, and $CHClF_2$, as well as the theoretical values from the present work associated with the hydrogen-bonded HF* in Figure 1a. There is satisfactory agreement between the calculated e^2qQ in Table 2 and experiment in the three systems in which experimental data are available, in that they are substantially smaller than the host $^{19}F^*$ quadrupole coupling constants, indicating the adequacy of the model in Fig. 1a. Quantitatively, the experimental results are about 15 to 20 percent smaller than the theoretical ones. In looking for reasons for this overestimate, a likely source appears to be the Van der Waals interaction between the HF* molecule and fluoromethanes which has not been considered. Thus the dipole-dipole component of the Van der Waals interaction [15, 20] leads to dipole polarizations at the atomic sites. Since the molecular orbitals have primarily *p*-character at the fluorine site in HF*, the dipole polarization would be expected to lead to an increase of *s* character at the fluorine atom and reduction in *p* character, which would be expected to lead to a reduction in the field-gradient at the $^{19}F^*$ site and improve agreement with experiment. A quantitative study of the Van der Waals effect would involve an extensive many-body calculation on the fluoromethane-HF* complex. Such a calculation would be rather time consuming because of the number of electrons involved and the need for a very extensive variational basis set for obtaining the excited states involved in a many-body perturbation theory calculation [15]. This is especially true because Van der Waals interaction between atoms is known to involve substantial excitations to a number of higher atomic states which would have to be included, especially for the fluorine and hydrogen atoms that are hydrogen-bonded. It would, however, be helpful in the future to calculate the influence of the Van der Waals effect for the complex of HF* for at least one fluoromethane, to judge its importance.

Table 2. Nuclear quadrupole coupling constant for $^{19}F^*$ associated with HF molecules hydrogen-bonded to fluoromethanes.

Molecule	Theoretical values of e^2qQ for $^{19}F^*$ in HF* bonded to fluoromethanes	Additional experimentally observed e^2qQ for $^{19}F^*$ in fluoromethanes
CH_3F	48	44.3
CH_2F_2	48.9	–
CHF_3	50.6	41.7
$CHClF_2$	49.6	42.8

To add to the flexibility of the search for the location of the HF* molecule attached to the fluoromethane, we have studied the dependence of the energy of the CH_3F-HF^* complexes on the angle of orientation θ of the HF* molecule with respect to the direction of the CF bond to which it is attached. The energy dependence as a function of θ turns out to be rather weak, and a shallow minimum was found for $\theta = 112.6°$. The physical reason for the minimum at this value of θ instead of $\theta = 0°$, with HF* aligned along the CF direction as in Fig. 1a, is difficult to find. One possibility is that there may be some weak but significant covalent or ionic interaction between the fluorine atom in HF* and the hydrogen atoms of CHF_3, the bending of the HF* molecule representing a tendency to maximize this interaction. This latter interaction is expected to be weak for both the covalent and ionic mechanisms, explaining the insensitiveness of the energy dependence that we have found as a function of θ. The weakness of the covalent mechanism is a consequence of the relatively large distances between the fluorine in HF* and the hydrogens of CH_3F. For the ionic mechanism, both these large distances and the relatively small charges on the hydrogen atoms in CH_3F would be responsible for the weakness of the interaction.

The $^{19}F^*$ quadrupole coupling constant for the bent configuration in CH_3F-HF, corresponding to $\theta = 112.6°$, was calculated to be 48.0 MHz, very slightly different from the value in Table 2 for the straight configuration for HF* attached to CH_3F. The asymmetry parameter η for the bent configuration was found to be small but non-vanishing, namely $\eta = 0.03$, as would be expected because the symmetry about the $^{19}F^*$ nucleus is lower than the three-fold symmetry for the straight configuration. Unfortunately, the calculated value of η is well within the range of experimental error and so one cannot verify its non-vanishing nature. The small difference between the calculated values of e^2qQ for the bent and straight configurations indicate that it is mainly the interaction between the hydrogen atom of the HF* molecule and the nearest fluorine atom of the host fluoromethane which determines the departure of the electron distribution in HF* from that for the free HF* molecule. The Van der Waals effect suggested earlier for the straight configuration is expected to be similar and comparable in importance for the bent configuration, reducing the theoretical e^2qQ and leading to closer agreement with the experimental result (Table 2). The smallness of the difference observed in the total energies of the straight and bent complexes also supports the primary importance of the interaction between HF* and the F in CH_3F to which it is bonded. One expects this conclusion to be applicable to the cases of the other hydrofluoromethanes in Table 2, the binding of HF* leading to the reduction in the theoretical results for e^2qQ with respect to that for free HF*, in the proper direction for agreement with experiment. This conclusion from, the present work is thus in agreement with that found [19] in the case of solid hydrogen fluoride.

In summary, the present investigations on the origin of the additional e^2qQ of about 40.0 MHz observed in the fluoromethane systems demonstrate that it is associated with a HF* complexed to the host molecule through H-bonding, a result that would be expected for other organic compounds in which $^{19}F^*$ is implanted experimentally. The very small difference in hydrogen-bonding energy for straight and bent configurations makes it difficult to decide which is the more likely system. Further, the small value of η makes it difficult to measure, and thus one cannot arrive at a definitive decision in this respect from experiment. The very substantial difference in e^2qQ from that for a free HF* molecule found both from experiment and the theoretical work reported here on fluoromethane-HF* complexes provides support for the occurrence of hydrogen bonding between hydrogen in HF* and the fluorine atoms of the fluoromethanes. It would be very helpful to verify the conclusions regarding the complexing of HF* molecule to the host fluoromethane through the study of electron distribution in the complex by other techniques besides TDPAD. Unfortunately, the small concentration of the complexes involving HF and the host compounds would make it difficult to apply the NMR technique to study the ^{19}F (nuclear ground state with $I = 1/2$) chemical shift [21, 22] for the fluorine in HF or indirect spin-spin interaction [21, 22] of ^{19}F with the proton. We hope that some other techniques can be devised in the future to study the influence on the electron distribution in the HF and host fluoromethane molecules.

Conclusion

It is shown that Hartree-Fock-Roothaan calculations on the fluoromethanes CHF_3, CH_2F_2, CH_3F and $CHClF_2$ can explain the observed quadrupole interaction, obtained by TDPAD measurements, of the excited $^{19}F^*$ nuclei with spin $I = 5/2$ in the host molecules. It is also shown that HF* molecules, expected to be produced in the process of the implantation of $^{19}F^*$, can be complexed with the host molecules through hydrogen-bonding between the hydrogen in the HF* molecule and fluorine atoms in the host molecules. The hydrogen bonding substantially reduces the calculated $^{19}F^*$ e^2qQ's for the complexed HF* molecule from the value for free HF* molecule, in the direction of agreement with the observed $^{19}F^*$ e^2qQ's in TDPAD measurements [3], which are close to that for solid hydrogen fluoride. The present calculations include the effect of covalent and ionic interactions between the HF* molecule and the host fluoromethanes. It is suggested that the relatively small but significant remaining gaps between the experimental and theoretical values for the additional e^2qQ's for these systems can be understood through the influence of the Van der Waals interaction between the HF* molecule and the host fluoromethane molecules. It is hoped that the validity of this suggestion can be tested in the future through first principle investigation of the Van der Waals interaction in the HF*-fluoromethane complexes. This feature of complexing of HF molecules, and indeed of all relatively ionic molecules, to fluoromethanes is expected to be applicable to other related hydrocarbons containing highly electronegative atoms like fluorine and oxygen. It will be helpful to examine this expectation by TDPAD measurements [3] in other hydrocarbons.

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