^{19}F Nuclear Quadrupole Coupling in some Halomethanes *

M. Frank, F. Gubitz, W. Ittner, W. Kreische, A. Labahn, B. Röseler, and G. Weeske

Physikalisches Institut der Universität Erlangen-Nürnberg, Erwin-Rommel-Str. 1,
D-8520 Erlangen, West Germany

Z. Naturforsch. **41 a,** 171–174 (1986); received Spetember 23, 1985

The ^{19}F quadrupole coupling constants in CF_4, CHF_3, $CClF_3$ and $CHClF_2$ are reported. The measurements were carried out temperature dependent using the time differential perturbed angular distribution method (TDPAD). The temperature dependence can be satisfactorily described in the framework of the Bayer-Kushida theory. A simple model is used to explain the appearance of H–F and Cl–F coupling constants in $CHF_3/CHClF_2$ and $CClF_3$, respectively.

Introduction

Due to the vanishing quadrupole moment of the ^{19}F ground state, fluorine compounds have for a long time not been included in the discussion of nuclear quadrupole coupling in compounds containing halogen atoms. But if an excited nuclear state with a non-zero quadrupole moment is used, the quadrupole interaction of ^{19}F can be observed during the lifetime of this excited level. In the experiment the $5/2^+$-state was populated via a ^{19}F (p, p′) ^{19}F* reaction, using 5 MeV protons from the Erlangen Tandem accelerator. Now, with the time differential perturbed angular distribution method, many systematic investigations of the quadrupole interaction at the fluorine site could be done [1–3]. To compare fluorine quadrupole coupling data with other halogen data, e.g. ^{35}Cl, by Townes and Dailey analysis, the electric field gradient (EFG) in the fluorine atom must be known [4]. Therefore measurements in solid fluorine have been done [5]. It has been shown that the coupling constant in solid fluorine must be a very good approximation for the atomic coupling constant. Nuclear quadrupole interaction in simple fluorides is a matter of interest in theoretical physics, too. An irregular trend in coupling constants, experimentally found, has been calculated with a SCCEH (Self-Consistent Charge Extended Hückel-)method by Mishra et al. [6].

In this paper we report the ^{19}F coupling constants in some methanehalogen-derivates and their dependence on temperature.

Experimental

During the lifetime τ of an excited level an extranuclear electric field gradient (EFG) can interact with the nuclear quadrupole moment. The interaction leads to a perturbation of the angular distribution of the emitted γ-rays. This causes a characteristic modulation of the exponential decay of the excited nuclear state. The time dependent angular distribution of the $(5/2)^+$-level can be written as

$$W(\theta, t) = 1 + A_{22}\, G_{22}(t)\, P_2(\cos\theta)\,.$$

G_{22} is the time depending perturbation factor, A_{22} depends on spin and multipolarity of the levels involved and on the nuclear alignment produced by the beam. For static randomly oriented interactions the perturbation function $G_{22}(t)$ is given by

$$G_{22}(t) = s_{20}(\eta) + \sum s_{2n}(\eta)\, \exp(-n\,\delta t)\, \cos(n\,\omega(\eta)\, t)\,.$$

The asymmetry parameter η is defined as usual, the term δ takes into account a possible Lorentzian spread in the interaction frequency.

In our experiments the second excited level at 197 keV of ^{19}F was used. It was populated via the ^{19}F (p, p′) ^{19}F* reaction with a 5 MeV pulsed proton beam of 2 μsec repetition period at the Erlangen Tandem accelerator.

---

* Presented at the VIIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

Reprint requests to Prof. W. Kreische, Physikalisches Institut der Universität Erlangen-Nürnberg, Erwin-Rommel-Straße 1, D-8520 Erlangen.

The γ-rays of the decaying 197 keV level were detected under angles of 90° and 180° relative to the incident proton beam and started a time to pulse height converter which was stopped by the following proton pulse. The recorded counting rates $N(90°)$ and $N(180°)$ were reduced after background correction according to

$$R(t) = \frac{N(180°, t) - N(90°, t)}{N(180°, t) + 2N(90°, t)}.$$

This ratio is equal to $A_{22}G_{22}$ within the experimental error.

Temperature dependent measurements were performed using a closed-cycle He-refrigerator which allowed to cover the temperature range from 17 K up to the melting point of the compounds. The target substances, all gaseous under normal conditions, were directly passed into the target vacuum and frozen down on a target finger mounted at the refrigerator. After every gas inlet the target had to be warmed up to about 60 K for approximately 15 minutes and then cooled down again to the desired temperature.

Results and Discussion

The nuclear quadrupole interaction has been determined in CF_4, $CClF_3$, CHF_3 and $CHClF_2$ in the temperature range from 17 K to about 70 K. In all the compounds the typical interaction of about

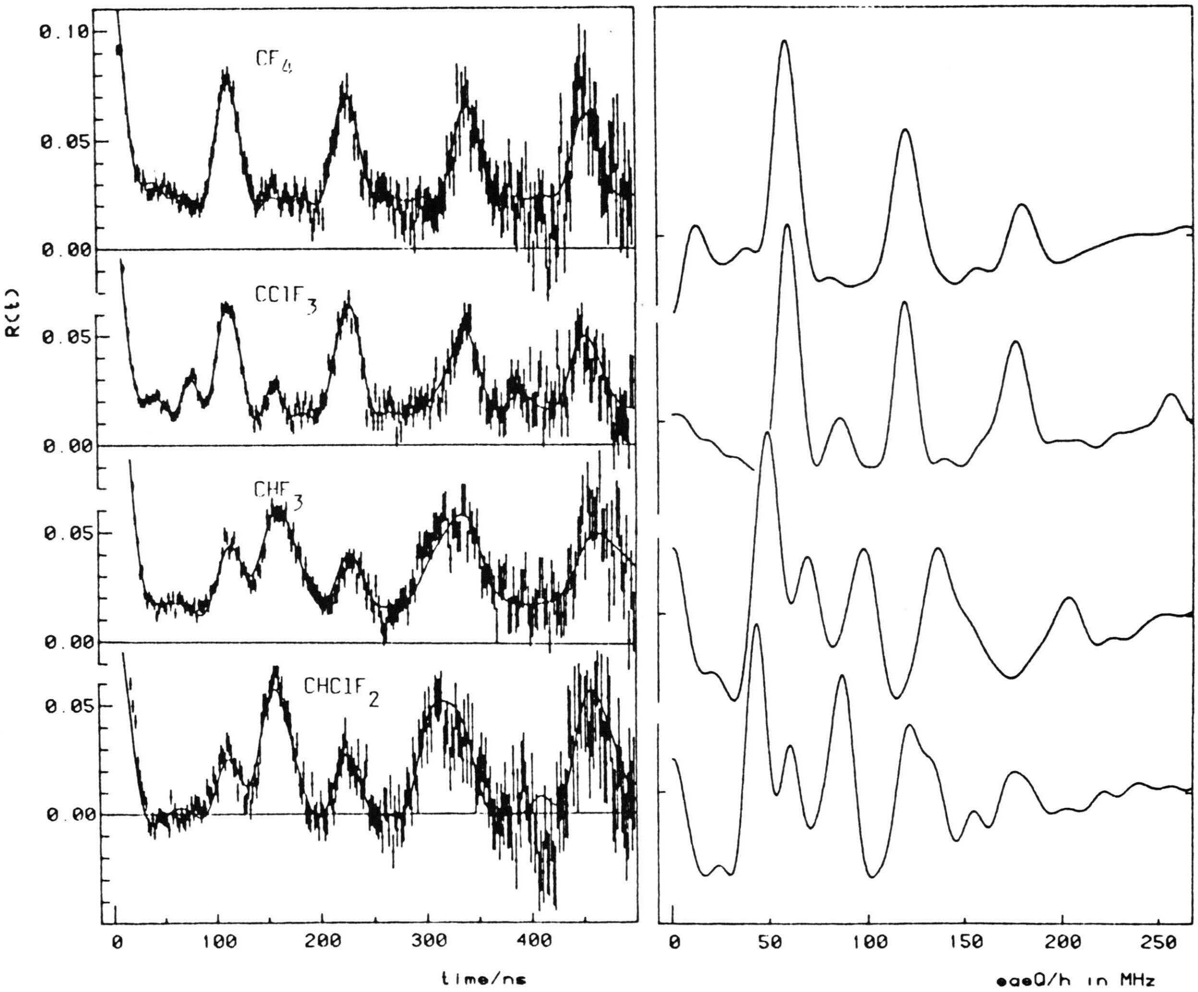

Fig. 1. Time spectra and corresponding fourier spectra of the substances under investigation at about 20 K.

60 Mc due to the C−F bond could be observed [7]. This coupling constant is the only expected one. But in addition to the C−F frequency others appear with remarkable amplitude. Figure 1 shows the time and fourier spectra of the compounds. In CF_4 a frequency of 127 Mc, the fluorine coupling constant appears at low temperatures. In $CClF_3$ the Cl−F frequency of 85 Mc can be observed, and in CHF_3 and $CHClF_2$ the H−F coupling constant appears with even higher amplitude than the expected C−F frequency. The following model provides a possible explanation for the appearing EFG's.

An excited fluorine nucleus, produced by the incident protons, recoils through the target. At the end of its way there are several possibilities for the probe nucleus:

i) A fluorine atom in the compound is hit by the recoil nucleus and replaced by it; the expected coupling constant due to a C−F bond can be observed (Figure 2a).

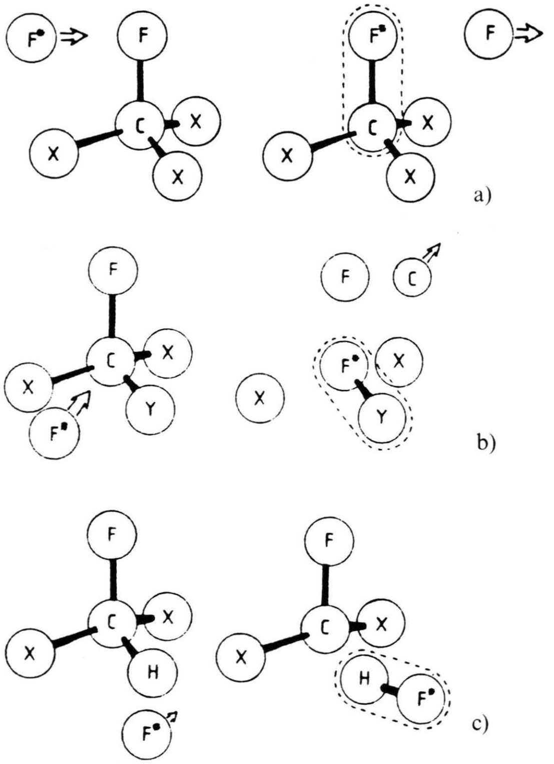

Fig. 2. A simple model explaining the different EFG's: a) The "regular" EFG can be observed. b) A new bond is formed out of the fragments − the bond with the highest electronegativity difference appears. c) Another possibility of HF formation.

ii) The central atom in the compound is hit and thrown out by the recoil nucleus. Thereby the molecule is destroyed, but the excited probe nucleus can form a new bond with the remaining fragments. Many results show that electronegativity must play a great role, too, because the bond with the highest difference in electronegativity appears (Figure 2b).

iii) The extreme affinity of fluorine to form HF out of compounds containing hydrogen might be the reason for a second possibility of HF formation with the excited probe nucleus. If the probe nucleus comes to rest near the hydrogen atom of a hydrogen containing compound it can tear H out of its bond and form HF (Figure 2c).

It is obvious that the coupling constants of F_2 or ClF can be observed with a certain probability in our measurements.

By studying the quadrupole coupling constant over a wide temperature range one can observe that ν_Q decreases with increasing temperature. It is well known that torsional motions in the molecule are responsible for a shift to lower frequencies. This can be described by the theory of Bayer and Kushida [8, 9], where the temperature dependence is explained by

$$\nu_Q(T) = \nu_Q 1 - \frac{3h}{8\pi^2\theta\nu_T}\,\frac{1}{2} + \left(\exp\left\{\frac{h\nu_T}{kT}\right\} - 1\right)^{-1}.$$

This formula was least-squares fitted to the experimental data. One thus gets the moment of inertia θ, the frequency of the torsional motion ν_T and the coupling constant at OK. The results together with a summary of the experimental data are listed in the Table 1. Our data indicate that the C−F coupling constant is lowered by about 1 Mc if the target compound containes hydrogen. The high electronegativity of fluorine might be the reason for a different charge distribution in these compounds. CF_4 seems to be an exception in this considerations. The coupling constant at OK is clearly lower than expected, and the small temperature dependence of this coupling constant shows that there are only very small torsional motions in solid CF_4. Furthermore a different temperature dependence of the coupling constant attributed to the same bond can be observed in different compounds. More detailed investigations will be necessary both to verify the lowered C−F coupling constant and the different tempera-

Table 1.

Subst.	T (K)	$\nu_{Q,I}$ (Mc)	$A_{22,I}$ (%)	$\nu_{Q,II}$ (%)	$A_{22,II}$ (%)	Remarks
CF_4	0	58.71 (02)	–	–	–	Fit
	10	59.6 (1)	6.7 (1)	128.0 (5)	1.0 (1)	Ref. [2]
	18.9	58.61 (10)	5.32 (16)			
	31.5	58.59 (08)	4.97 (11)			
	40.1	58.55 (10)	4.10 (13)			
	53.0	58.55 (08)	5.42 (21)			
	60.1	58.15 (18)	2.84 (16)			
	69.0	55.09 (46)	3.55 (90)			
$CClF_3$	0	60.59	–	85.95	–	Fit
	20.0	59.88 (08)	4.84 (12)	86.14 (38)	1.22 (12)	
	30.1	58.95 (15)	3.20 (22)	85.30 (72)	1.24 (28)	
	40.0	58.59 (15)	3.88 (25)	85.05 (37)	2.38 (23)	
	48.3	58.05 (36)	2.99 (28)	85.44 (1.2)	2.46 (30)	
CHF_3	0	59.40	–	42.86	–	Fit
	25.0	58.72 (20)	3.61 (32)	41.73 (13)	6.93 (55)	
	40.0	59.79 (61)	1.82 (45)	40.23 (23)	7.50 (74)	
	52.0	56.16 (87)	0.74 (14)	39.18 (24)	5.31 (63)	
	67.0	55.31 (1.3)	0.30 (11)	38.24 (11)	5.48 (74)	
	77.9	54.72 (32)	0.98 (37)	37.72 (35)	4.86 (93)	
$CHClF_2$	0	59.27	–	42.87	–	Fit
	20.0	59.26 (16)	2.94 (21)	42.75 (09)	6.23 (43)	
	29.1	59.20 (24)	2.49 (27)	42.63 (15)	5.75 (37)	
	40.4	59.13 (38)	2.14 (31)	42.03 (15)	5.56 (36)	
	57.0	59.27 (38)	0.79 (15)	41.21 (08)	4.43 (36)	
	73.0	58.10 (98)	2.31 (75)	42.18 (18)	6.29 (73)	

ture dependences of the coupling constants due to the same bond. A lowered ν_Q in the C–F coupling constant in hydrogen containing halogenmethane-derivatives could be a useful hint about the electron distribution in those compounds.

Acknowledgement

This work was supported by the Bundesministerium für Forschung und Technologie and the Deutsche Forschungsgemeinschaft.

[1] H. Barfuß, G. Böhnlein, H. Hohenstein, W. Kreische, M. Meinhold, H. Niedrig, and K. Reuter, J. Mol. Struct. **58,** 503 (1980).

[2] H. Barfuß, G. Böhnlein, F. Gubitz, W. Kreische, and B. Röseler, Hyp. Int. **15/16,** 901 (1983).

[3] H. Barfuß, G. Böhnlein, F. Gubitz, W. Kreische, and B. Röseler, Hyp. Int. **15/16,** 911 (1983).

[4] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17,** 782 (1949).

[5] H. Barfuß, G. Böhnlein, G. Gradl, H. Hohenstein, W. Kreische, H. Niedrig, A. Reimer, and B. Röseler, Phys. Lett. **90 A,** 33 (1982).

[6] K. C. Mishra, A. Coker, P. Kelires, S. K. Mishra, T. P. Das, W. Kreische, G. Böhnlein, H. Barfuß, and K. Bonde Nielsen, Hyp. Int. **15/16,** 907 (1983).

[7] H. Barfuß, G. Böhnlein, G. Gradl, H. Hohenstein, W. Kreische, H. Niedrig, and A. Reimer, J. Chem. Phys. **76,** 5103 (1982).

[8] H. Bayer, Z. Phys. **130,** 227 (1951).

[9] T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104,** 1364 (1956).