^{35}Cl NQR Spectroscopy on Salts and Molecular Compounds of Trichloroacetic Acid*

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The temperature dependence of salts $M^{(I)}H(Cl_3CCOO)_2$ and molecular compounds of trichloroacetic acid with amines and benzaldehydes, TCA · X, was studied,

The data fit rather well to the known dependence of the mean frequency shift $\Delta\langle\nu(^{35}Cl)\rangle$ on the pk_a difference of X with respect to TCA. A linear relation is observed between the bleaching out temperature T_b of the ^{35}Cl NQR lines and $\Delta\langle\nu(^{35}Cl)\rangle$ for $M^{(I)}H(Cl_3CCOO)_2$ and for TCA · X, X = benzaldehydes.

Introduction

It is well-known, that trichloroacetic acid (TCA), Cl_3CCOOH, forms molecular compounds $(TCA)_nX_m$, where X is a hydrogen bond accepting molecule. ^{35}Cl NQR is a sensitive method to study such systems besides the fact that the chlorine atoms in $(TCA)_nX_m$ are quite remote from the hydrogen bond forming position as shown by Biedenkapp and Weiss [1]. The formation of the molecular complex – in most cases a 1:1 complex TCA · X – may be due to very weak hydrogen bonds $Cl_3CCOOH\cdots X$ in a case like TCA · acetophenone on the one hand. On the other hand very strong interactions may lead to proton transfer and thereby to formation of salt $(TCA)^{\ominus}X^{\oplus}$ as in the system TCA · triethylamine (Poleshchuk et al. [2]).

As expected for the monobasic acid TCA, in most cases a 1:1 complex is formed. However, other stoichometries can be found for instance in salts $M^{(I)}H(Cl_3CCOO)_2$ or with twobasic molecules such as 1,4-dioxane or 2,6-dimethyl-γ-pyrone [1].

Another interesting observation is, that in solids TCA · X very often three ^{35}Cl NQR lines are observed at $T = 77$ K, which shows that the three Cl-atoms of the group $-CCl_3$ are crystallographically inequivalent.

Furthermore, due to rotational motions of the group $-CCl_3$ the ^{35}Cl NQR signals bleach out at temperatures far below the melting point (T_b = bleaching out temperature). Such a temperature T_b is found for many organic compounds incorporating a group $-CCl_3$ [3], and Hashimoto [4] has discussed the observation of bleaching out in detail by classifying the compounds with $-CCl_3$ groups into an R-type (reorientation restricted) and an F-type (free reorientation). The disappearance of the ^{35}Cl NQR signals of the $-CCl_3$ group, due to reorientational motions, is clearly seen in 1-Cl-4-$CCl_3(C_6H_4)$ (m.p. = 297 K). For this compound the ^{35}Cl NQR signals of the $-CCl_3$ group disappear at $T \approx 250$ K, whereas the ring bonded chlorines give an NQR signal up to the melting point [5]. Such a behaviour is also observed for a number of ring chlorinated trichloroacetanilides [6].

Pietrzak et al. [7] have rationalized a number of ^{35}Cl NQR spectra of TCA · X by considering the deviation of the mean ^{35}Cl NQR frequencies of the $-CCl_3$ group from the mean frequency found for TCA itself

$$\Delta\langle\nu(^{35}Cl)\rangle = \frac{1}{3}\left(\sum_{i=1}^{3}\nu_i(^{35}Cl)_{TCA\cdot X}\right) - \frac{1}{3}\left(\sum_{i=1}^{3}\nu_i(^{35}Cl)_{TCA}\right). \quad (1)$$

The first term in (1) is the mean ^{35}Cl NQR resonance frequency of the $-CCl_3$ group in the compound TCA · X, and the second term belongs to pure trichloroacetic acid. The reference temperature is 77 K and appropriate weighting has to be done if some of the ^{35}Cl NQR lines of TCA · X coincide.

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It was shown that a plot of $\Delta \langle \nu(^{35}\mathrm{Cl}) \rangle$ against the difference of the pk_a value of X and TCA,

$$\Delta pk_a = (pk_a)_{\mathrm{Base}} - (pk_a)_{\mathrm{TCA}} \quad (2)$$

rationalizes the experimental data very well and the function

$$\Delta \langle \nu(^{35}\mathrm{Cl}) \rangle = f(\Delta pk_a) \quad (3)$$

is a smooth sigmoidal curve.

In the following we report about a series of ^{35}Cl NQR measurements on compounds TCA · X; some of them have been done some time ago [8]. Furthermore, it will be shown that by determination of T_b from a measurement of the line width $\Delta\nu(^{35}\mathrm{Cl})$ as a function of temperature a qualitative relation between $\Delta \langle \nu \rangle$ and T_b is found for certain groups of compounds TCA · X. From the half widths $\Delta\nu = f(T)$ a rough estimate of the activation energy for the hindered rotation of the group $-CCl_3$ is possible.

Experimental

The compounds were prepared from purified TCA (purification by dissolving the hygroscopic TCA in CCl_4, filtration, drying with Na_2SO_4 for more than 5 h, filtration, and destillation of the solvent) and the components X (purified by destillation). Several ways of synthesis were applied:

S1 (mixing the compounds at 25 °C or higher and cooling the thereby produced melt until crystallisation arises; undercooling is quite common); S2 (TCA and X are dissolved separately in CCl_4 and the solution of TCA is slowly added to the solution of X); S3 (TCA is dissolved in H_2O and either X or a solution of X in H_2O is slowly added); S4 (a solution of TCA and the metal carbonate in H_2O is prepared; crystals are obtained by slow evaporation). In Table 1 the way of synthesis, colour of the compound and crystal habitus are given.

The ^{35}Cl NQR spectra were measured at 77 K by use of a DECCA superregenerative spectrometer. The signal to noise ratio, S/N was in all cases $\geqq 10$ (recorder, time constant 10 s). The measurements of $\nu = f(T)$ and $\Delta\nu = f(T)$ were done with a pulse spectrometer and Fourier transform, pulse length (90°) 6–10 μs, pulse sequence $\geqq 20$ ms (dependent from the line width), number of pulses $\geqq 500$ (to reach a S/N > 20 in all cases, except measurement near T_b). The temperature at the sample site was produced by a flow and temperature regulated gas stream and determined by thermocouples to ± 0.6 K.

Table 1. Some properties of the compounds TCA · X.

Compound	Synthesis	m.p.[a] [°C]	Colour	Habitus	Remarks
TCA · Aniline	S3[b], S2	145 [9] 143 (D)	white	plates	well developed crystals
TCA · N-Methylaniline	S3[c]	96 (D)	white	needles	well developed crystals
TCA · N,N-Diethylaniline	S3	− 7	white	needles	
TCA · Triethylamine	S2		white	needles	
TCA · Benzaldehyde	S1	7			
TCA · o-Chlorobenzaldehyde	S1	16			
TCA · 2,4-Dichlorobenzaldehyde	S1	29			
TCA · o-Ethoxybenzaldehyde	S1	26			
TCA · o-Hydroxybenzaldehyde	S1	3			
TCA · o-Methylbenzaldehyde	S1	38	white		
TCA · p-Methylbenzaldehyde	S1		white		
TCA · m-Nitrobenzaldehyde	S1	11			
TCA · 2,4,6-Trimethylbenzaldehyde	S1	29	yellowish		
$(Cl_3CCOO)_2RbH$	S4		colourless	prism	well developed crystals
$(Cl_3CCOO)_2TlH$	S4		colourless	prism	well developed crystals

[a] (D): under decomposition.
[b] [10] describes TCA · Aniline with 1 H_2O of crystallisation. By chemical analysis we found (element/calc. for TCA · Aniline/exp.): C/37.46/37.1; H/3.1/2.9; N/5.46/5.37; the compound is free of H_2O.
[c] Chemical analysis: C/39.96/39.88; H/3.73/3.72; N/5.18/5.16.

Results

In the Figs. 1–4 the temperature dependence of $\nu(^{35}Cl)$ in the compounds TCA · X is shown. Included are the compounds $(Cl_3CCOO)_2HRb$ and $(Cl_3CCOO)_2HTl$ for which the 77 K results have been given already [1]. In addition, in Figs. 1 and 2 the corresponding half widths $\Delta\nu$ are given, too. There is little use to analyze the data $\nu(^{35}Cl) = f(T)$. However, for further use they are rationalized

Table 2. Temperature dependence of the ^{35}Cl NQR in molecular compounds or salts incorporating trichloroacetic acid, TCA. $\nu = f(T)$; $\nu = \sum a_i T^i$; $\Delta T = T_1 \ldots T_2$ = temperature range of observation.

Substance		a_0 / MHz	$a_1 \cdot 10^3$ / MHz · K^{-1}	$a_2 \cdot 10^6$ / MHz · K^{-2}	$a_3 \cdot 10^9$ / MHz · K^{-3}	a_{-1} / MHz · K	T_1 / K	T_2 / K
TCA · Aniline	ν_1	39.7860	−8.4360	−7.473		−17.673	77	124
	ν_2	36.9769	17.8593	−87.238		55.613	77	129
	ν_3	37.6701	5.8021	−40.147		23.630	77	124
TCA · N-Methyl-aniline	ν_1	38.8481	−1.5858	−16.742		7.864	77	170
	ν_2	38.2003	−0.3493	−11.786		5.796	77	177
	ν_3	38.1330	−1.2651	−17.030		11.631	77	170
TCA · Benz-aldehyde	ν_1	40.5432	−2.0074	−6.828			77	236
	ν_2	39.5265	−0.3706	−10.192		12.027	77	264
	ν_3	39.6865	−3.7640	8.208	−31.173		77	264
TCA · o-Chloro-benzaldehyde	ν_1	40.4746	−1.5328	−13.464			77	231
	ν_2	40.5392	−7.3494			−15.508	77	159
	ν_3	40.0249	−5.9144	11.997	−53.681	–	77	231
	ν_4	35.7439	0.0992	−11.375		10.612	77	287
TCA · 2,4-Dichlor-benzaldehyde [a]	ν_1	40.4725	−2.5858	−5.389			77	214
	ν_2	40.0453	−1.9824	−5.323			77	214
	ν_3	39.8067	−2.2525	−7.301			77	214
	ν_4	36.2692	−6.3338	40.578	−175.273		77	302
	ν_5	35.5269	−2.6390	16.758	−80.077		77	302
TCA · o-Ethoxy-benzaldehyde [b]	ν_1	40.1418	−3.3043	3.697	−31.718		77	233
	ν_2	39.9914	−3.8419	3.703	−35.236		77	233
TCA · o-Hydroxy-benzaldehyde	ν_1	39.6880	3.6126	−23.739		36.360	77	199
	ν_2	40.3247	−2.9332	−6.328			77	199
	ν_3	39.7760	−2.9933	−6.139			77	199
TCA · o-Methyl-benzaldehyde [b]	ν_1	40.0114	0.8590	−17.114		11.245	77	246
	ν_2	39.5784	0.2536	−17.248		12.060	77	246
TCA · p-Methyl-benzaldehyde	ν_1	47.4496	−71.0169	169.643		−228.129	77	110
	ν_2	45.0136	−33.3808	−42.582		−188.549	77	110
	ν_3	49.5333	−102.8601	293.751		−298.321	77	106
	ν_4	59.7356	−216.4474	711.331		−603.805	77	106
	ν_5	70.7357	−335.9330	1145.048		−945.992	77	106
	ν_6	38.4049	28.6699	−233.328		−6.344	77	110
TCA · m-Nitro-benzaldehyde	ν_1	40.5876	−3.3188	2.272	−24.600		77	215
	ν_2	40.6337	−4.1341	5.650	−33.452		77	215
	ν_3	40.7556	−5.5625	12.630	−53.689		77	199
	ν_4	40.3693	−2.4532	−10.432			77	199
	ν_5	39.8632	−1.2387	−9.478			77	215
	ν_6	39.7937	−2.2822	−10.176			77	199
TCA · 2,4,6-Tri-methylbenz-aldehyde	ν_1	39.2983	7.4654	−37.952		40.620	77	221
	ν_2	39.2227	2.9371	−24.247		24.505	77	221
	ν_3	39.2520	2.1008	−20.495		15.172	77	221
$(Cl_3CCOO)_2RbH$	ν_1	40.9747	−6.7985	−5.642		−17.979	77	203
	ν_2	40.2408	−8.7777	−2.781		−24.673	77	203
	ν_3	39.7027	−4.7336	−2.591		−15.703	77	203
$(Cl_3CCOO)_2TlH$	ν_1	40.0352	−2.5807	−8.614		2.902	77	227
	ν_2	39.2256	−1.7250	−11.871		5.954	77	220
	ν_3	39.1153	−0.7742	−8.462		3.036	77	229

[a] $\frac{a_4 \cdot 10^9}{\text{MHz} \cdot \text{K}^{-4}}$: 0.230466 ($\nu_4$); 0.109238 ($\nu_5$). – [b] Two coinciding lines.

Table 3. Selected ^{35}Cl NQR frequencies of compounds TCA · X.

Substance	$\frac{\nu}{\text{MHz}}$ (T = 77 K)			$\frac{\langle\nu\rangle}{\text{MHz}}$	$\frac{\Delta\langle\nu\rangle}{\text{MHz}}$	$\frac{\nu}{\text{MHz}}\left(\frac{T_b}{\text{K}}\right)$			pk_a	Δpk_a
Trichloroacetic acid (TCA)	40.236	40.159	39.964	40.120	0.0				0.63	0
TCA · Aniline	38.861	38.555	38.184	38.533	−1.587	38.481(124.1)	38.261(128.7)	37.961(124.3)	4.63	4.0
TCA · N-Methylaniline	38.729	38.179	38.086	38.331	−1.789	38.138(170.2)	37.802(177.1)	37.492(170.2)	4.85	4.22
TCA · N,N-Diethylaniline	39.056	38.376	38.088	38.507	−1.613				6.61	5.98
TCA · Triethylamine[a]	38.415	38.355	37.798	38.189	−1.931				10.87	10.24
TCA · Benzaldehyde	40.353	39.593	39.431	39.792	−0.328	39.688(236.0)	38.770(263.8)	38.694(263.8)	−7.1	−7.73
TCA · o-Chlorobenzaldehyde	40.275	39.771	39.614	39.887	−0.233	39.407(231.0)	39.272(159.3)	38.637(231.0)		
	35.882					34.878(286.6)				
TCA · 2,4-Dichlorobenzaldehyde	40.234	39.863	39.593	39.900	−0.220	39.670(213.7)	39.375(213.7)	38.987(213.7)		
	35.948	35.390				35.152(302.0)	34.964(302.0)			
TCA · o-Ethoxybenzaldehyde	39.894	39.701[b]		39.765	−0.355	39.165(233.3)	38.846(233.3)			
TCA · o-Hydroxybenzaldehyde	40.297	40.064	39.510	39.957	−0.163	39.652(199.0)	39.487(199.0)	38.936(199.0)		
TCA · o-Methylbenzaldehyde	40.121	39.651[b]		39.808	−0.312	39.221(246.1)	38.636(245.9)		−6.5	−7.13
TCA · p-Methylbenzaldehyde	40.031	39.750	39.486	39.540	−0.580	39.620(109.8)	39.123(109.8)	39.126(105.5)	−6.32	−6.95
	39.448	39.376	39.151			39.094(105.5)	39.076(105.5)	38.681(109.8)		
TCA · m-Nitrobenzaldehyde	40.332	40.332	40.375	40.072	−0.048	39.733(215.4)	39.672(215.4)	39.721(199.5)		
	40.121	39.714	39.560			39.460(199.5)	39.154(215.4)	38.928(199.5)		
TCA · 2,4,6-Trimethylbenzaldehyde	40.176	39.624	39.491	39.764	−0.356	39.273(221.2)	38.788(221.2)	38.788(221.2)	−4.7	−5.33
$(Cl_3CCOO)_2RbH$	40.187	39.226	39.121	39.511	−0.609	39.277(203.0)	38.221(203.0)	38.567(202.9)		
$(Cl_3CCOO)_2TlH$	39.824	39.099	39.044	39.322	−0.798	39.021(226.8)	38.236(229.0)	38.505(229.1)		

[a] pk_a-value taken from [2]. – [b] Two coinciding lines.

according to

$$\nu(^{35}\text{Cl}) = \sum_i a_i T^i . \qquad (4)$$

The coefficients a_i are given in Table 2. In Table 3 we list the ^{35}Cl frequencies of TCA · X at T = 77 K and $T = T_b$.

Discussion

As pointed out by Pietrzak et al. [7] the Δpk_a dependence of the mean frequency shift $\Delta\langle\nu(^{35}\text{Cl})\rangle$ follows a sigmoidal curve. In Fig. 5 this curve is shown including newer literature data and

Fig. 1. Temperature dependence of the ^{35}Cl NQR frequencies (upper part) and half width $\Delta\nu$ (lower part) as a function of temperature for the compounds TCA · o-Methylbenzaldehyde (□); $(Cl_3CCOO)_2RbH$ (▲); and $(Cl_3CCOO)_2TlH$ (●).

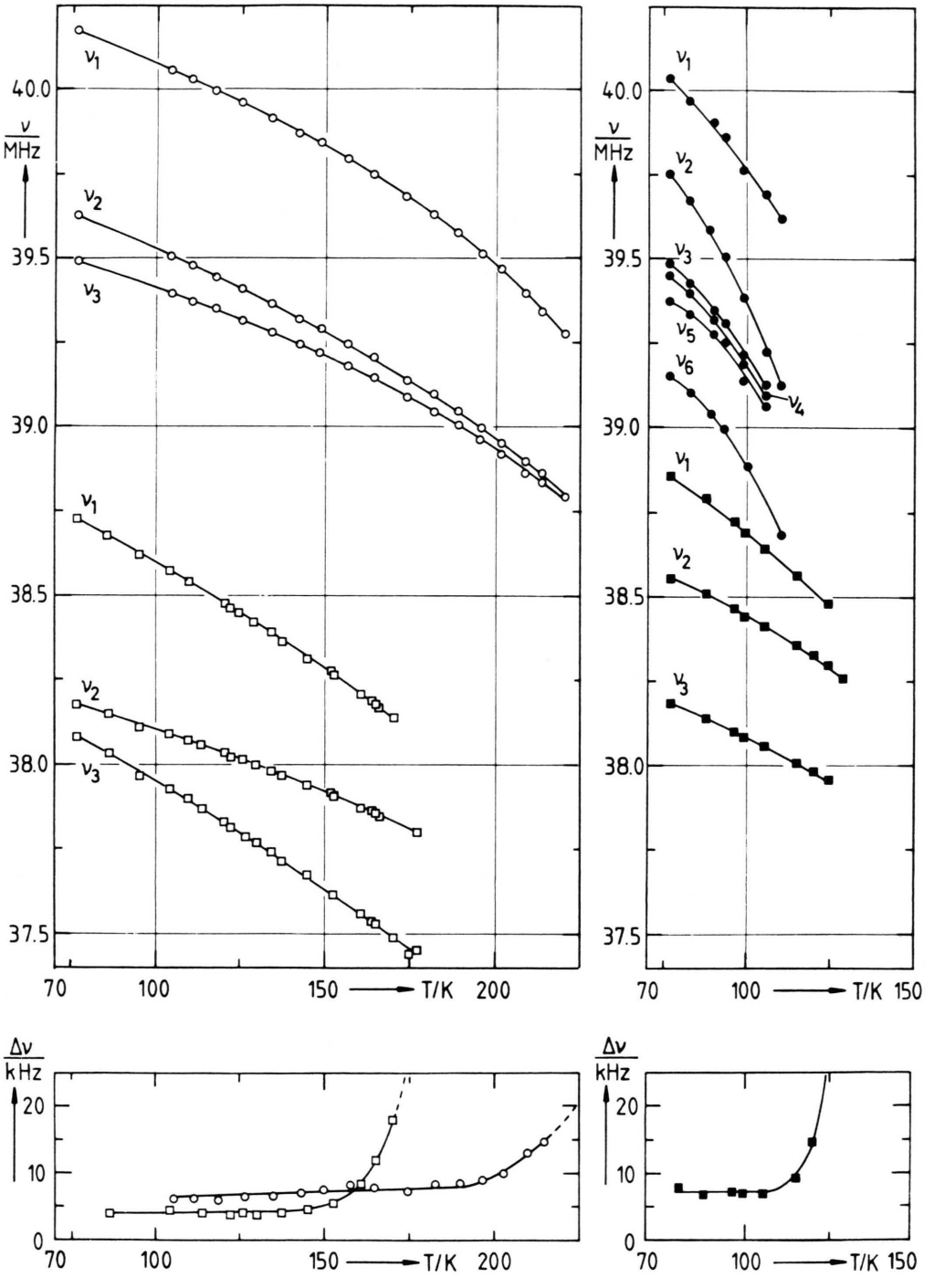

Fig. 2. Temperature dependence of the ^{35}Cl NQR frequencies (upper part) and half width $\Delta\nu$ (lower part) as a function of temperature for the compounds TCA · 2,4,6-Trimethylbenzaldehyde (○); TCA · N-Methylaniline (□); TCA · p-Methylaniline (●); and TCA · Aniline (■).

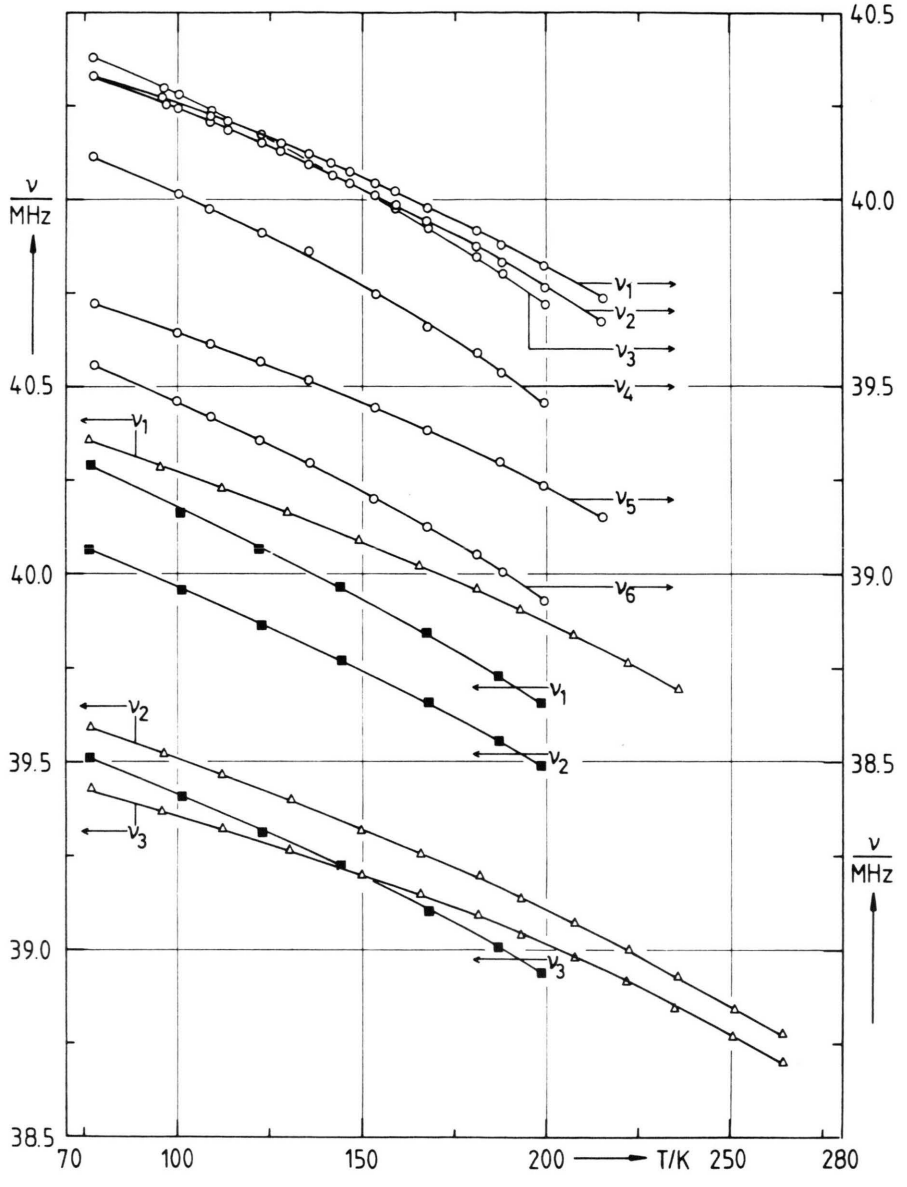

Fig. 3. Temperature dependence of the ^{35}Cl NQR frequencies as a function of temperature for the compounds TCA · m-Nitrobenzaldehyde (○); TCA · Benzaldehyde (△); and TCA · Hydroxybenzaldehyde (■).

data reported here. There is no doubt that the shape found is due to the charge transfer from TCA to X, which depends on Δpk_a [12] and which is reflected on the electron distribution at the sites of the TCA chlorines.

There is an appreciable scattering of the experimental values around the curve drawn in Fig. 5, and there are several reasons for this scattering:

a) Besides the small errors in measuring $\nu(^{35}\mathrm{Cl})$, which are completely uninteresting within the scale of Fig. 5, there is a fairly large error in determining pk_a of the base X and literature data scatter widely.

b) Intermolecular interactions have some influence on $\nu(^{35}\mathrm{Cl})$ of TCA · X (Crystal field effect).

c) 77 K may not be a true reduced temperature particularly for such complexes as TCA · 4-(CH_3)-

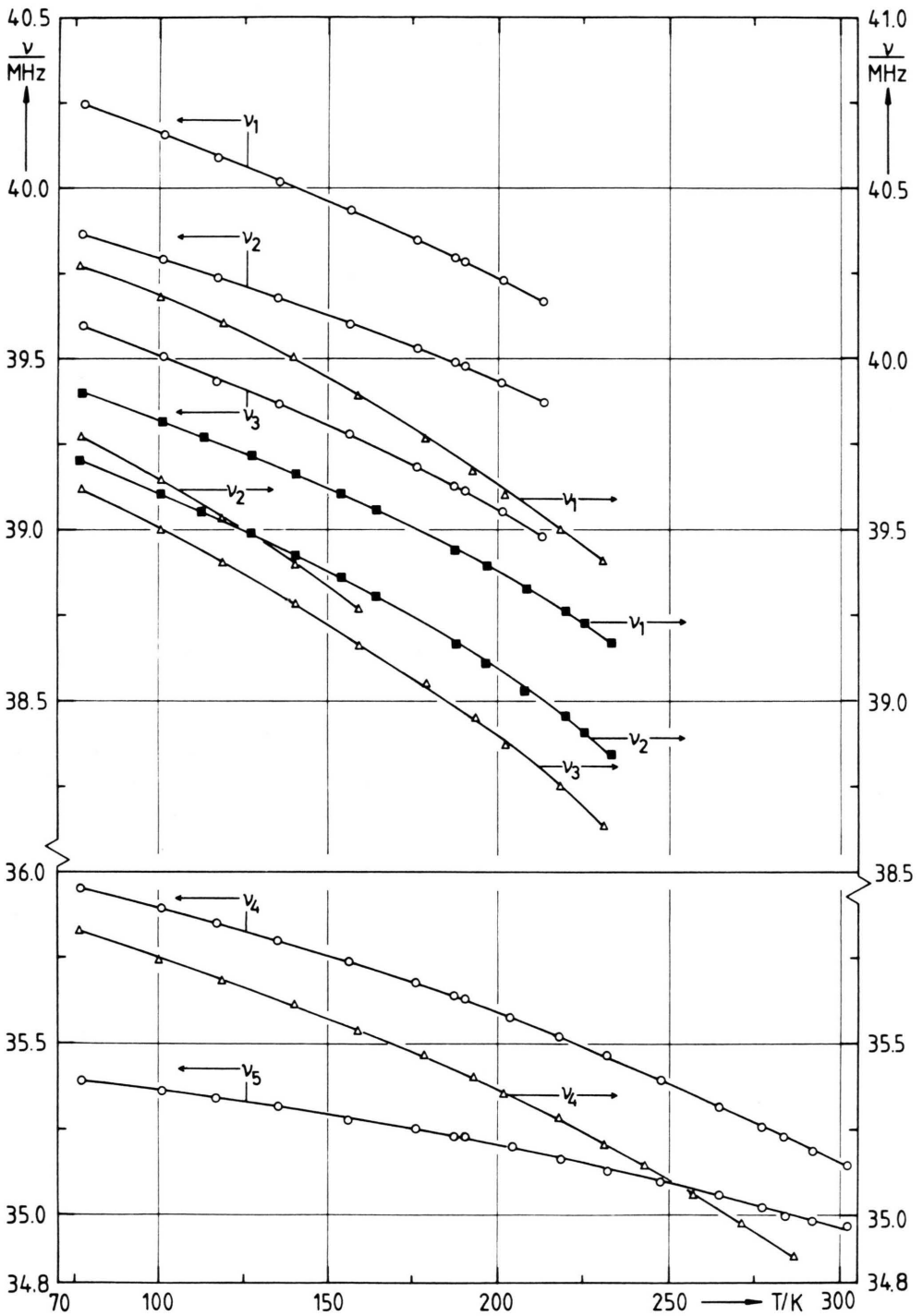

Fig. 4. Temperature dependence of the ^{35}Cl NQR frequencies as a function of temperature for the compounds TCA · 2,4-Dichlorobenzaldehyde (○); TCA · o-Chlorobenzaldehyde (△); and TCA · o-Ethoxybenzaldehyde (■).

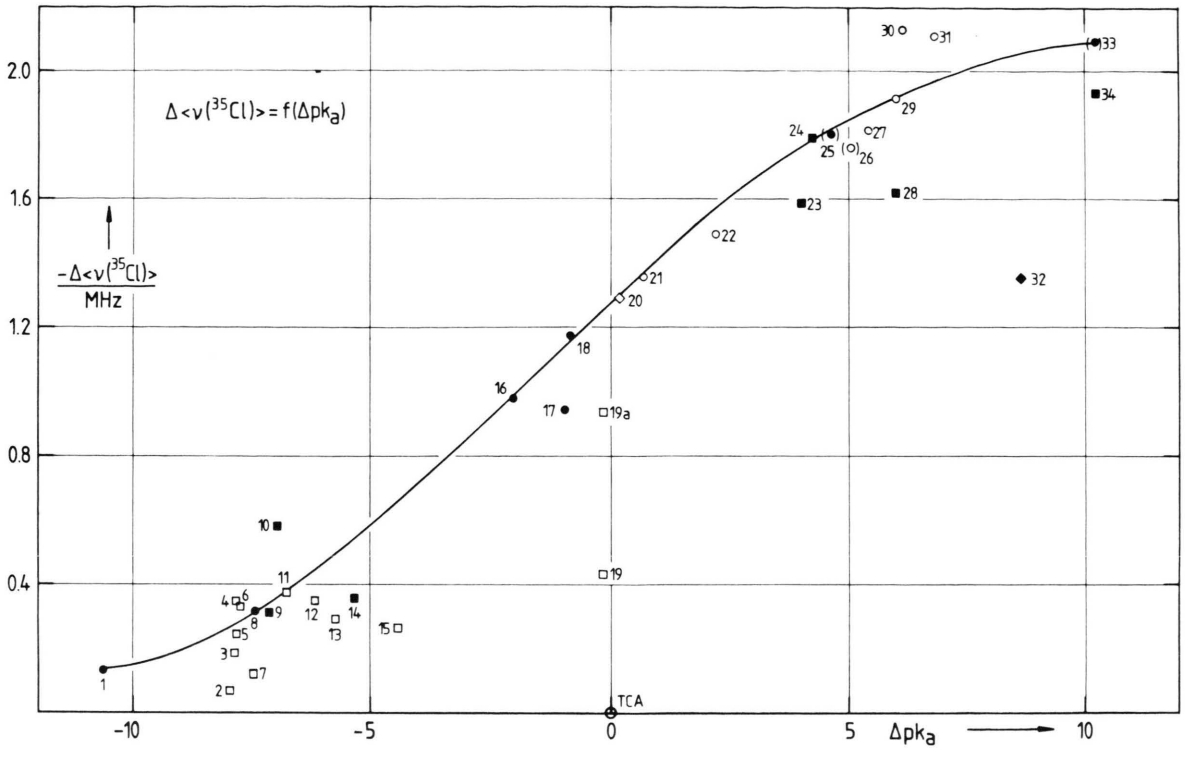

Fig. 5. Mean frequency shift $\Delta\langle\nu(^{35}\mathrm{Cl})\rangle$ in the compounds TCA · X as a function of Δpk_a (see Eqs.(1) and (2)). The molecules correspond to different X. 1: Acetonitrile; 2: o-Toluic acid; 3: Benzoic acid; 4: Acetone; 5: m-Toluic acid; 6: Benzaldehyde; 7: Phenol; 8: Cyclohexanone; 9: o-Methylbenzaldehyde; 10: p-Methylbenzaldehyde; 11: Acetophenone; 12: Anisaldehyde; 13: Ethyl acetate; 14: 2,4,6-Trimethylbenzaldehyde; 15: tert-Butyl alcohol; 16: Acetamide; 17: α-Pyrrolidine; 18: Dimethylacetamide; 19: 2,6-Dimethyl-γ-pyrone; 19a: TCA · 2,6-Dimethyl-γ-pyrone; 20: Pyridine-N-oxide; 21: 4-Methylpyridine-N-oxide; 22: 3-Bromopyridine; 23: Aniline; 24: N-Methylaniline; 25: Pyridine; 26: 4-Methylquinoline; 27: 4-Methylpyridine; 28: N,N-Diethylaniline; 29: 2,4-Dimethylpyridine; 30: 2,6-Dimethylpyridine; 31: 2,4,6-Trimethylpyridine; 32: Ammonia; 33: Triethylamine [2] 34: Triethylamine. References: □ [1]; ● [2]; ○ [7]; ◇ [10]; ◆ [11]; ■ this paper.

1-(CHO)C_6H_4 or TCA · $C_6H_5NH_2$ complexes for which T_b is below 150 K. According to this argument the measured $\Delta\langle\nu\rangle$ is most probably high. Then the point 23 in Fig. 5 (TCA · $C_6H_5NH_2$) is shifted in the wrong direction but point 10 (TCA · p-methylbenzaldehyde) is shifted in the right one.

To our opinion a), that is the uncertainity in the determination of pk_a (or the incompatibility of pk_a data measured by different methods) has higest weight in the discussion of errors.

The hydrogen bond for systems with small $\Delta\langle\nu\rangle$ such as TCA · CH_3CN, TCA · $(CH_3)_2CO$, TCA · C_6H_5CHO etc. may be formulated as shown in Figure 6a. Strong hydrogen bonds as formed by TCA itself we find in the middle of the curve of Figure 5. An example is TCA · pyridine-N-oxide with O ··· O distances as short as 241 pm [13], see Fig. 6b, and finally large $\Delta\langle\nu\rangle$ correspond to a complete proton transfer (Figure 6c).

All intermediate situations should be verified by going along the curve $\Delta\langle\nu\rangle = f(\Delta pk_a)$. With increasing proton transfer corresponding charge transfer will raise the electron density at the TCA molecule until the negative ion $Cl_3CCOO^{\ominus}$ is reached. The thereby increased negative charge at the Cl-atoms of the $-CCl_3$ group increases the ionic character of the bond C−Cl and lowers the ^{35}Cl NQR frequencies. $d(\Delta\langle\nu\rangle)/d(\Delta pk_a)$ at $\Delta pk_a = 0$ gives a maximum, which in turn means that small changes in Δpk_a and/or in distance O−H ··· O or O−H ··· N create large charge shifts and thereby

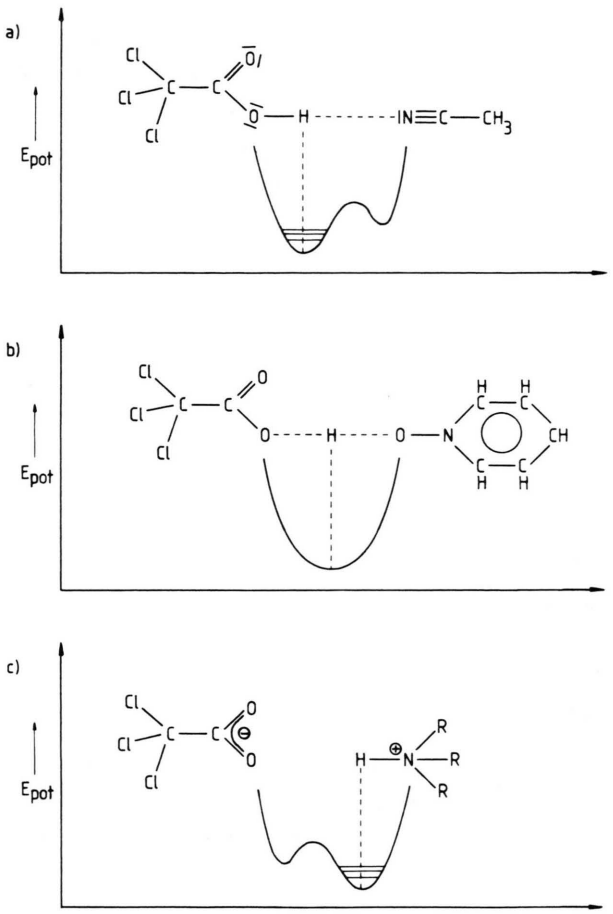

Fig. 6. Potential function for the proton in TCA · X compounds. The bases are weak (a), medium (b) and strong (c).

large changes in $\Delta\langle\nu\rangle$. This was proved by Stankowski [14] through the investigation of $d(\Delta\langle\nu\rangle)/dp$ in systems $C_6Cl_5OH \cdot X$.

As long as the crystal structures of most of the compounds TCA · X are unknown there is little room for speculation about the onset of hindered rotations of the group $-CCl_3$.

However, by plotting $\Delta\langle\nu\rangle$ as a function of T_b, two curves have been found, one for X = benzaldehydes and one for the acid salts $M^{(I)}H(Cl_3CCOO)_2$. There is no doubt that the mean frequency shift is a linear function of T_b (Figure 7). It should be mentioned that TCA · $(2,4,6\text{-}(CH_3)_3C_6H_2CHO)$ did not fit the linear relation $\Delta\langle\nu\rangle = a + bT_b$.

We have estimated the activation energy for the $-CCl_3$ group rotation. The values found are comparable with data from literature. Thy are listed in Table 4. Due to the lack of crystal structure deter-

Table 4. Activation energies E_a for the $-CCl_3$ group rotation of TCA · X and related compounds ([a] this paper).

Compound	E_a / kJ mol^{-1}	Literature
Cl_3CCOOH	16.8	[3]
Chloral hydrate	36.9	[15]
4-Cl-1-$CCl_3(C_6H_4)$	45.7	[5]
TCA · $C_6H_5NH_2$	14.3	[a]
TCA · $C_6H_5NHCH_3$	21.9	[a]
TCA · 2-$CH_3(C_6H_4)CHO$	8.3	[a]
TCA · 2,4,6-$(CH)_3(C_6H_2)CHO$	10.7	[a]
$(Cl_3CCOO)_2RbH$	23.8	[a]
$(Cl_3CCOO)_2TlH$	41.6	[a]

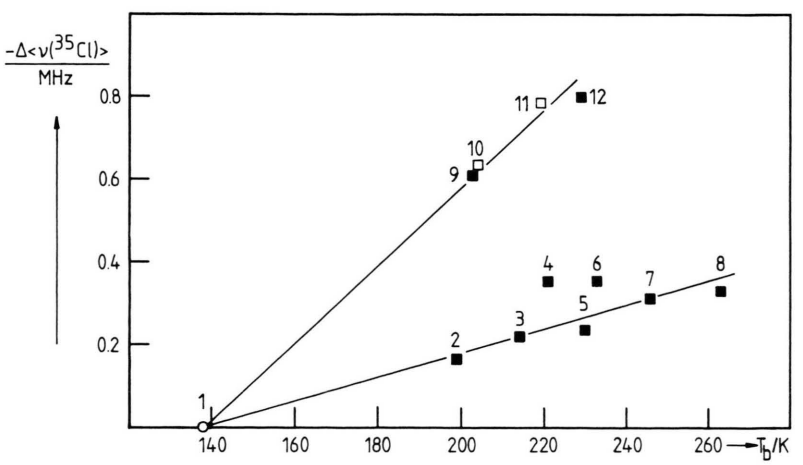

Fig. 7. Correlation of the mean frequency shift $\Delta\langle\nu(^{35}Cl)\rangle$ with the bleaching out temperature T_b.
1: TCA, 2: TCA · o-Hydroxybenzaldehyde; 3: TCA · 2,4-Dichlorobenzaldehyde; 4: TCA · 2,4,6-Trimethylbenzaldehyde; 5: TCA · o-Chlorobenzaldehyde; 6: TCA · o-Ethoxybenzaldehyde; 7: TCA · o-Methylbenzaldehyde; 8: TCA · Benzaldehyde; 9: $(Cl_3CCOO)_2RbH$; 10: $(Cl_3CCOO)_2NH_4H$; 11: $(Cl_3CCOO)_2KH$; 12: $Cl_3CCOO)_2TlH$.
Compounds with more than three resonance frequencies are excluded. References: □ [1]; ○ [3]; ■ this paper.

minations, no comparison with thermal amplitudes from X-ray diffraction is possible.

By temperature dependent single crystal Zeeman split ^{35}Cl NQR and ^{2}H NMR spectroscopy a chance may come up to find out more about the empirical relations of $\Delta \langle \nu(^{35}\mathrm{Cl}) \rangle = f(T_b)$ and $\Delta \langle \nu(^{35}\mathrm{Cl}) \rangle = f(\Delta pk_a)$.

Such a study may also give some information on the crystal field effects on the shifts of the ^{35}Cl NQR frequencies in compounds TCA · X [16].

There is an argument against the explanation: Bleaching out of ^{35}Cl NQR in CCl_3 groups ↔ hindered rotations (reorientations).

From rotational motions of the group around its 3-fold axis one expects a strong averaging of the ^{35}Cl EFG's with increasing temperature as one approaches the bleaching out temperature T_b. A large $\lim_{T \to T_b} |\mathrm{d}^2\nu(^{35}\mathrm{Cl})/\mathrm{d}T^2|$ should be observed. This is not the case for several compounds TCA · X discussed here. T_1 measurements of the ^{35}Cl NQR may be helpful to solve the problem.

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