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NQR frequencies in polycrystalline samples and their correlation with σ and k_i values

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Abstract. NQR frequencies are studied in 6 compounds at 77°K and room temperature. The frequencies of the substituted chlorobenzene derivatives are compared with values calculated using the σ and k values of Hammett and Biedenkapp and Weiss respectively. The poor agreement between observed and calculated values is ascribed to the presence of two or more substituent groups other than chlorine and the consequent interaction between them. The poor agreement with Nagarajan's equation at room temperature is ascribed to the increase in temperature. The σ and k values for the orthobenzamide group are estimated from the observed frequencies as 0·275 and 0·369 respectively.

Keywords. Nuclear quadrupole resonance; polycrystalline samples.

1. Introduction

Using a frequency modulated self-quenching super-regenerative nuclear quadrupole resonance spectrometer chlorine quadrupole resonances have been observed for the first time in six compounds at liquid nitrogen and room temperatures. The frequencies are measured with a 121-b hetrodyne frequency meter. The estimated error in frequency is about ± 100 kHz.

All the compounds were supplied by M/s. K and K Laboratories, USA. The commercial grade samples were further purified by recrystallisation using appropriate solvents. All the compounds are solids at room temperature. The frequencies of all the lines are given in table 1. In four compounds single lines are observed while in the fifth compound two close lying lines are observed at both liquid nitrogen and room temperatures. In the compound 2,4-dichloronaphthol, two close lying lines were observed at room temperature while only a single line is observed at liquid nitrogen temperature indicating a possible phase transition. Detailed temperature variation studies on this compound are being undertaken.

2. Discussion

The observed frequencies of the substituted chlorobenzenes are compared with frequencies calculated empirically from the following equations due to Bray and Barnes (1957), Nagarajan (1962) and Biedenkapp and Weiss (1968).

Table 1. Observed and calculated frequencies of NQR lines.

Compound	Observed frequencies (MHz)		Calculated frequencies (MHz)		
			77°k		Room temperature
	303°k	77°k	σ	k	
2,6-dichlorobenzamide $Cl_2C_6H_3(CONH_2)$	34·42	35·20	—	—	33·804
	34·76	35·78	—	—	
3,5-dichloronitrobenzene $Cl_2C_6H_3(NO_2)$	36·04	36·65	35·935	36·263 ±0·128	35·180
2,6-dinitro-chlorobenzene $(NO_2)_2C_6H_3Cl$	38·14	39·35	38·983	38·887 ±0·174	40·253
3-chloro 4-methoxyaniline $NH_2C_6H_3Cl(OCH_3)$	34·72	35·46	34·773	35·509 ±0·174	31·590
2,4-dichloronaphthol $C_6H_4C_4H(OH)Cl_2$					
Cl (2nd position)	34·69	35·23	—	—	—
Cl (4th position)	34·58				
4,4′-dichloro diphenylsulfide $ClC_6H_4(S)C_6H_4Cl$	34·68	35·41	—	—	—

$$\nu_{77°K} = 1{\cdot}024\ \sigma + 34{\cdot}826 \text{ MHz (Bray and Barnes 1957)} \quad (1)$$

$$\nu_{\text{room temp.}} = 1{\cdot}704\ \sigma + 33{\cdot}335 \text{ MHz (Nagarajan 1962)} \quad (2)$$

$$\nu_{77°K} = \nu_0 + \sum_i k_i \text{ (Biedenkapp and Weiss 1968)} \quad (3)$$

σ_i is the Hammett's parameter while k_i is the parameter introduced by Biedenkapp. Numerical values of these are taken from the papers already cited. The calculated values of the frequencies are indicated in table 1. The agreement between observed and calculated values is not satisfactory either with σ values or with k values and this may be due to the presence of not less than two substituents other than chlorine in any of these compounds. The interaction between the substituent groups has been neglected in both the equations. The presence of NO_2 group may also be a factor for the poor agreement. The agreement between observed and calculated frequencies at room temperature is far more unsatisfactory. However Nagarajan's equation is only an approximate one since it is obtained on the basis of a comparatively fewer observations. Further the equations which should apply at a absolute zero from an ideal point of view become more and more approximate with increasing temperature.

As there is no σ or k value for the benzamide group ($CONH_2$) in the ortho position, these are now estimated from the observed frequency (average over the doublet) in 2,6-dichlorobenzamide. The σ and k values used in the estimation of frequencies are listed in table 2. The values for the benzamide group are indicated by a star.

Table 2. Values of σ and k used in the estimation of frequencies.

Substituent group	σ	k
m-Cl	0·373	0·499±0·035
m-NO_2	0·710	1·069±0·093
o-NO_2	2·030	2·096±0·087
m-NH_2	−0·161	−0·103±0·130
o-OCH_3	0·109	0·917±0·172
o-$NHCOCH_3$	0·320	0·455
o-$CONH_2$	0·275*	0·369*

References

Biedenkapp D and Weiss A 1968 *J. Chem. Phys.* **49** 3933

Bray P J and Barnes R G 1957 *J. Chem. Phys.* **27** 551

Nagarajan V 1962 *Studies on chlorine nuclear quadrupole resonance* Ph.D. Thesis, Andhra University