

REMARKS ON REORIENTATION OF CH₃OH MOLECULES IN THE β -QUINOL CLATHRATE

BY M. MASSALSKA-ARODŹ

Institute of Nuclear Physics, Cracow*

(Received April 8, 1977)

On basis of the dielectric measurements two weakly hindered motions of the methanol molecule enclosed in β -quinol clathrate are proposed: the reorientation of the whole molecule and the intramolecular O-H group rotation.

The results of the dielectric and the IR profile measurements for CH₃OH molecules in the β -quinol clathrate (HQ) presented in [1] confirmed the earlier information [2, 3] about the large rotational freedom of the methanol molecules enclosed in HQ cages. The dielectric measurements were made in [1] for the polycrystalline samples in the microwave frequencies region from 2.54 GHz to 37.6 GHz in temperature covered range 120 K — 290 K. The results of these investigations are presented in the form of the Cole-Cole diagrams in Fig. 1. Through the four points for lower frequencies one can draw the Debye semicircle. The corresponding dipole relaxation process is interpreted as related to the reorientation of the whole CH₃OH molecule round the axis perpendicular to the C-O bond. The correlation times τ_1^D for this process are presented in Table I. The activation energy obtained from the Arrhenius equation is (1.25 ± 0.3) kcal/mole. The temperature-change analysis of the IR band profile was made in [1] for the C-O stretching absorption band at 1022 cm^{-1} . The correlation times τ_1^R obtained in this way and the dielectric results τ_1^D differ by the factor of 3-5 only. The activation barrier acquired from the temperature change of τ_1^R is (1.5 ± 0.5) kcal/mole.

Further analysis of the results of the dielectric GHz-measurements is made in order to facilitate the understanding of the methanol molecule behaviour in the HQ cage.

Using the Onsager equation [4] for the dielectric increment $\epsilon'_0 - \epsilon'_\infty$ extrapolated from the Debye semicircle (in the temperature range 130 K — 200 K) we can calculate the value of the dipole moment responsible for the observed relaxation process. The (1.3 ± 0.2) D value obtained is in good agreement with the value of $\mu = 1.3$ D which was assumed in [3] for a proper estimation of the transition temperature $T_c = 67$ K interpreted

* Address: Instytut Fizyki Jądrowej, Radzikowskiego 152, 31-342 Kraków, Poland.

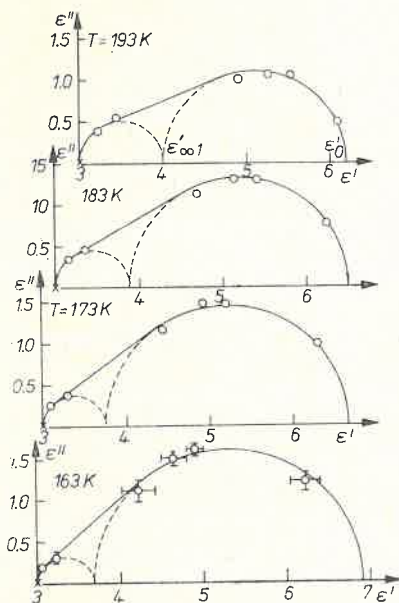


Fig. 1. Cole-Cole plots for β -quinol clathrate with the methanol molecules in four chosen temperatures 163 K, 173 K, 183 K, 193 K (dotted curve arbitrarily joins the measurement points, dashed curve indicates two dispersion regions extrapolated by the Debye equation. The electric permittivity for the β -quinol with empty cages is signified by the asterisks)

TABLE I

Temperature T (K)	Correlation time (ps)	
	τ_1^D	τ_1^{OH}
143	57.8 ± 15	
153	41.0 ± 13	13.2 ± 5.0
163	32.9 ± 10	11.0 ± 5.0
173	25.9 ± 9	10.0 ± 5.0
183	22.4 ± 9	9.15 ± 4.0
193	17.9 ± 10	8.37 ± 3.0

as associated with the freezing of the methanol molecule rotation in the HQ cage. Taking into account the above statement and the suggestions from the structural investigations [5] and from the dielectric kHz-measurements for a monocrystalline sample [3] we propose placing the molecule in the HQ cage as is shown in Fig.2. Then, the projection of the methanol molecule dipole moment on the c -axis of the clathrate crystal lattice equals $1.28 \cdot D$. Now the reorientations of the CH_3OH molecule around the S axis would not require the cage deformation. This is consistent with the small activation barrier value ΔH .

The clear Debye character of the main reorientational process, stated earlier, indicates the existence of the additional higher-frequency process which we associate with the intramolecular O—H group rotation in the methanol. The additional dielectric dispersion can

also be illustrated by the Debye semicircle. The correlation times τ_1^{OH} estimated for this process are presented in Table I. The τ_1^{OH} temperature dependence leads to the activation barrier (0.62 ± 0.3) kcal/mole. The same value can be obtained from the temperature broadening of the O–H stretching absorption band of the methanol molecule in the HQ

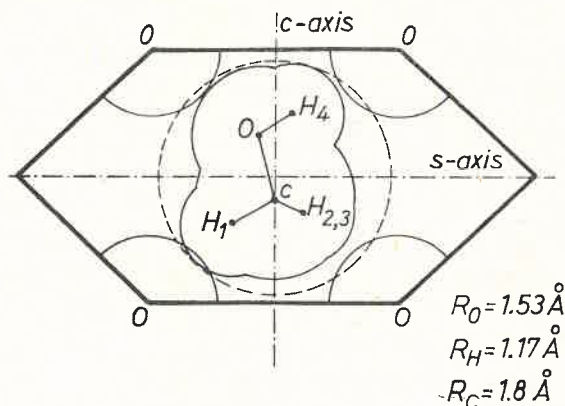


Fig. 2. CH_3OH molecule in β -quinol clathrate cage. The cutting plane of the cage goes through the c - and s -axes of the clathrate elementary cell. (Van der Waals radius for the hydrogen atom R_H , oxygen atom R_O and carbon atom R_C are marked. S is the probable rotational axis of the methanol molecule)

cage [6]. Neither the correlation times τ_1^{OH} nor the activation barrier values differ much from the analogical parameters typical for the O–H intramolecular rotation of various alcohols in the dilute solutions [7].

The two motions of the methanol molecule in the HQ cage have small activation barrier energy. The values of the correlation time τ_1^{D} and τ_1^{OH} (in the ps range) do not differ much. At higher temperatures, above 200 K, the separation of the two Debye dielectric relaxation regions is impossible. Thus, the methanol molecule behaviour in the HQ cage can be regarded as a complex, weakly hindered movement. The rotational jumps of the OH group round the C–O bond axis occur during slower C–O bond reorientations. Besides, it is probable that this intramolecular rotation is facilitated by insignificant displacements of the methanol molecule in not too loose HQ cage.

The author is grateful to Professor Dr. J. A. Janik and to Dr. S. Urban for suggesting this work and for stimulating discussions.

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