Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Intramolecular Ultrasonic Relaxation of Nematic Liquid Crystals far below the Transition Temperature

S. Nagai [a] [b] , P. Martinoty [b] , S. Candau [b] & R. Zana [c]

[a] Laboratoire d'Acoustique Moléculaire, Université Louis Pasteur, 4, rue Blaise Pascal, 67070, STRASBOURG, Cedex

[b] National Research Laboratory of Metrolgoy, Itabashi, Tokyo, Japan

[c] Centre de Recherches sur les Macromolécules, 6, rue Boussingault, 67083, STRASBOURG, Cedex

Version of record first published: 29 Aug 2007.

To cite this article: S. Nagai , P. Martinoty , S. Candau & R. Zana (1975): The Intramolecular Ultrasonic Relaxation of Nematic Liquid Crystals far below the Transition Temperature, Molecular Crystals and Liquid Crystals, 31:3-4, 243-252

To link to this article: http://dx.doi.org/10.1080/15421407508082876

Mol. Cryst. Liq. Cryst., 1975, Vol. 31, pp. 243–252

Printed in Holland

The Intramolecular Ultrasonic Relaxation of Nematic Liquid Crystals far below the Transition Temperature

S. NAGAI†, P. MARTINOTY, S. CANDAU

Laboratoire d'Acoustique Moléculaire, Université Louis Pasteur, 4, rue Blaise Pascal,
67070 STRASBOURG Cedex

and

R. ZANA

Centre de Recherches sur les Macromolécules, 6, rue Boussingault,
67083 STRASBOURG Cedex

(*Received June 3, 1975*)

Ultrasonic attenuation has been investigated in a 2 : 1 molar mixture of *p*-methoxy *p'*-*n*-butylazoxybenzene and *p*-methoxy *p'*-methylazoxybenzene and *p*-*p'*-*n*-dihexyl-azoxybenzene as a function of temperature and frequency. The relaxation far below the nematic-isotropic transition temperature was satisfactorily fitted to a single relaxation process.

This process is attributed to the trans-gauche rotational isomerism of the end chains of liquid crystals. The values obtained for enthalpy parameters are in good agreement with those of normal paraffins but there is a marked difference in the entropy parameters.

INTRODUCTION

There are many experimental and theoretical works on the ultrasonic attenuation of nematic liquid crystals.[1] Most of them, however, are concerned with the behaviour near the nematic-isotropic transition. On the other hand, far below the transition temperature, ultrasonic relaxation has been observed on MBBA (*p*-methoxybenzylidene *p'*-*n*-butylaniline).[1] This relaxation has been tentatively assigned[2] to the perturbation of the equilibrium between cis and trans rotational isomers of methoxy end group by analogy with esters and vinyl ethers,[3] where delocalization of Π-electron

---

† On leave from National Research Laboratory of Metrology, Itabashi, Tokyo, Japan.

imparts to C—C bond, a partial double bond character and leads to a rotational barrier.

In another model proposed by Jähnig[4] the relaxation is attributed to the equilibrium between the trans and gauche isomers of the *n*-butyl group at the other end of the molecule of MBBA.

Liquid crystal molecules are characterized structurally with rigid phenyl rings plus flexible end groups and usually exhibit larger ultrasonic attenuation than ordinary liquids. Hence from the view point of structural generality, it is plausible to attribute this large attenuation to the motion of end groups. Recent Raman[5,6] and calorimetric[7] works provide evidence of the existence of several conformations in the nematic phase. For MBBA, the predominant effect on the ultrasonic attenuation is a critical one. It is not easy to distinguish this relaxation process from another one.

Therefore, in an earlier study,[8] the authors have investigated MBAB (*p*-methoxy *p'*-*n*-butylazoxybenzene) which has the same end groups as MBBA, but shows a larger mesomorphic temperature range (16–76°C).

A relaxational ultrasonic absorption was observed, which could be fitted to the Eq. 1 which characterizes a single relaxation process:

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_r)^2} + B \tag{1}$$

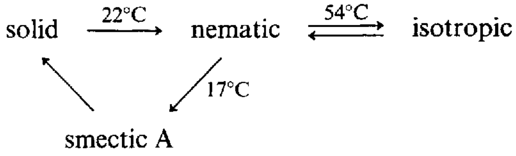
$$f_r = \frac{k_B T}{2\pi h} \exp(-\Delta H^*/RT) \exp(\Delta S^*/R) \tag{2}$$

In Eq. 1, A and B are constants, f_r is the relaxation frequency and α the absorption coefficient. Using the Eq. 2, the activation enthalpy ΔH^* and the activation entropy ΔS^* were found to be 3 Kcal/mole and −11 cal/mole/°K, respectively. However a clear cut assignment as to which end group is responsible of the above process could not be made.

The aim of this paper is to report results on the ultrasonic attenuation of two azoxybenzene derivatives which have permitted us to give an unequivocal answer to this problem.

Experimental

The investigated samples are Merck V (a 2:1 molar mixture of MBAB and MMAB (*p*-methoxy *p'*-methyl azoxybenzene) and DHAB (*p.p'*-*n*-dihexyl azoxybenzene). Merck V was purchased from E. Merck and Co and used without further purification. Its nematic temperature range is −5 ~ 75°C. DHAB was obtained from the "Laboratoire de Chimie Organique de l'Ecole Nationale Supérieure de Chimie de Strasbourg". This substance presents the following transition temperatures.



The chemical formulae of the liquid crystals to be discussed in this work are shown in Figure 1.

The ultrasonic attenuation measurements were carried out in the frequency range 2–155 MHz. The swept acoustical interferometry technique[9]

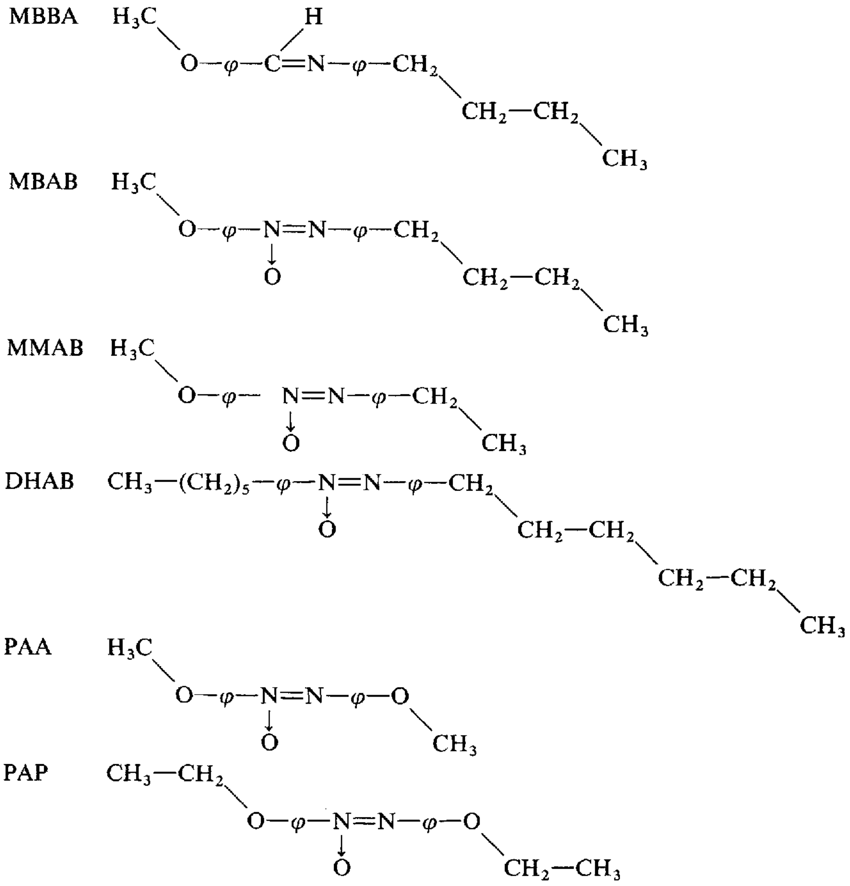


FIGURE 1 Molecules of liquid crystals. The end chains are represented in the all trans conformations.

was used at 2 MHz. The cell consists of two 3 MHz quartz and a brass-made liquid container with three screws to adjust the parallelism. The distance between two quartz is about 7 mm. The half-width of the resonant curve from the receiving quartz was measured with a spectrum analyzer. The standard pulse technique was used for the other frequencies. A 1,285 MHz quartz was driven at 3.9, 6.5, 9.1, 11.7 MHz, and a 5 MHz quartz was used at 5.2, 15, 25, 35, 45, 65, 85, 115, 155 MHz. The temperature of the cells was regulated to better than $\pm 1/15$°C.

All measurements reported here have been performed in unoriented samples.

Elucidation of the intramolecular mechanism

Low frequency values of the quantity α/f^2 of the investigated liquid crystals are plotted in Figure 2 together with those of several other liquid crystals.[10–12] The critical phenomena are characterized by the increase of the attenuation with increasing temperature. However for materials having a wide mesomorphic temperature range, the sign of the temperature coefficient of the attenuation changes far below the transition temperature. This behaviour

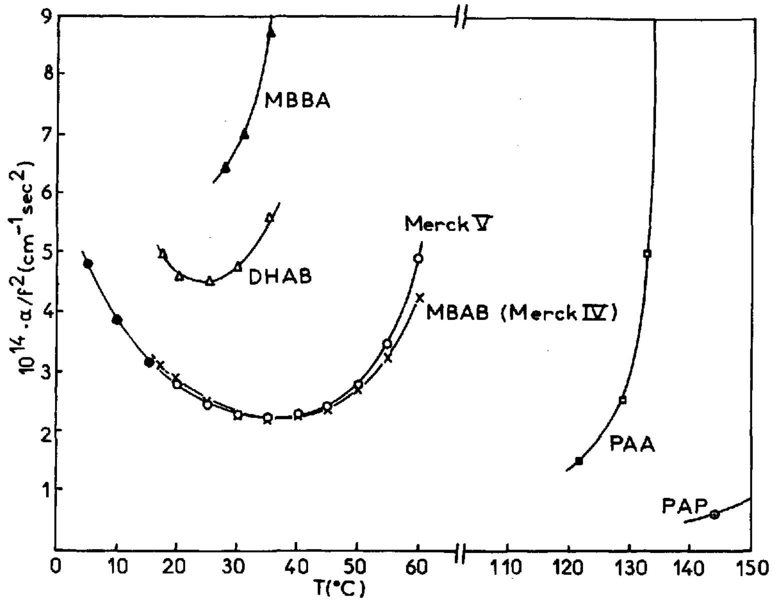


FIGURE 2 The ultrasonic attenuation as a function of temperature
Merck V (● $f = 4$ MHz. ○ $f = 2$ MHz)
MBAB (× $f = 2$ MHz). DHAB (△ $f = 2$ MHz)
PAA (□ $f = 2$ MHz).[10] (■ $f = 5$ MHz)[11]
PAP (⊙ $f = 3$ MHz).[11] MBBA (▲ $f = 3$ MHz).[12]

indicates the presence of another dissipative process which cannot be attributed to shear viscosity because of the magnitude of the observed effect. This contribution, that we assign to intramolecular processes arising in the end groups, decreases with temperature and must be very small at high temperature whichever the end groups responsible of the effect. Indeed, materials having a high transition temperature like PAA (p. azoxyanizole) or PAP (paraazoxy phenetole) exhibit quite small ultrasonic attenuation at temperatures far below the transition temperature (see Figure 2).

For the three investigated azoxybenzene derivatives (MBAB, DHAB, Merck V) the critical attenuation begins to be significant from about $T_c - T = 30°\text{C}$. In considering MBBA, which is only nematic between 22 ~ 45°C, it is easily seen that it is difficult to get information on the intramolecular process.

An important conclusion can be stressed from the data obtained in DHAB, where there is no alkoxy end group. In the low temperature range this compound shows an attenuation about twice larger than MBAB. Accordingly, the possibility can be eliminated that the observed relaxation is due to trans-cis isomers of the alkoxy end group.

Kinetic parameters

The data of Merck V which shows the greatest nematic range among the listed liquid crystals were fitted to Eq. 1 by a least square method. The values of α/f^2 at 20°C are shown in Figure 3. They are satisfactorily described with a

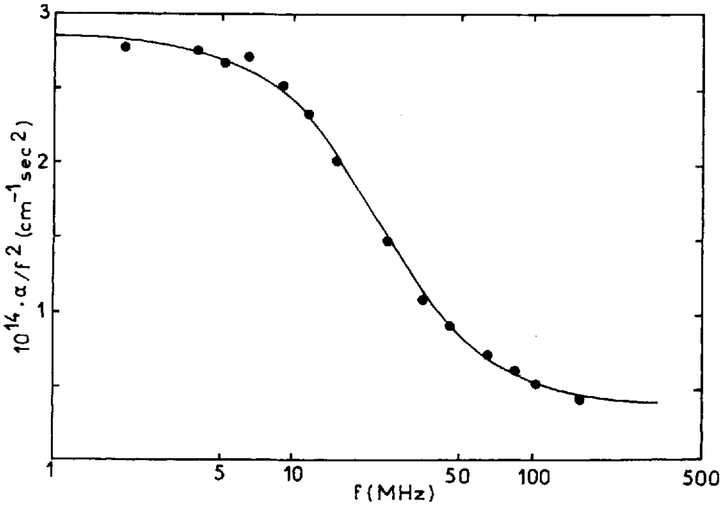


FIGURE 3 Plot of α/f^2 against f for Merck V. $T = 20°\text{C}$.
● : experimental data. The full line has been fitted to Eq. 1.

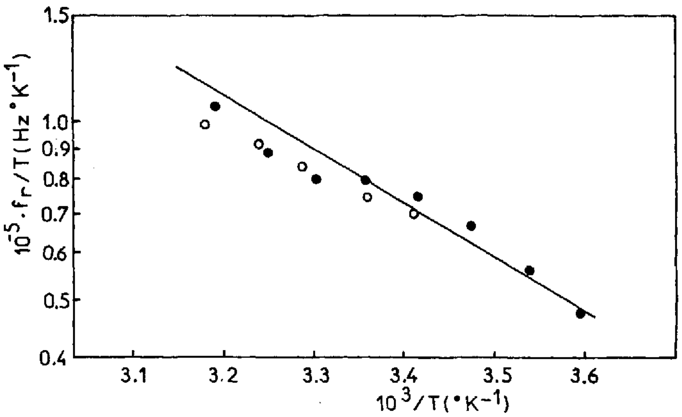


FIGURE 4 Plot of $\log(f_r/T)$ against $10^3/T$
●: Merck V; ○: MBAB.[8]

single relaxation. Plotting $\log(f_r/T)$ against $10^3/T$ in Figure 4 yields the activation enthalpy and entropy as

$$\Delta H^* = 3.5 \text{ Kcal/mole}$$

$$\Delta S^* = -10 \text{ cal/mole/°K}.$$

These values are very close to those of MBAB. A detailed examination of Figure 4 reveals a deviation from linearity. This might suggest that at higher temperature (25 ~ 40°C), the critical relaxation already contributes to the ultrasonic attenuation. Nevertheless we have not attempted to fit the data with a sum of two relaxation terms, because even at higher temperature the results could still be fitted by Eq. 1 within the experimental accuracy. *n*-Butane and *n*-pentane, which show trans-gauche transitions, have activation enthalpies equal to 3.4 and 3.9 Kcal/mole[9,13] respectively. These values are consistent with that of Merck V. This supports the validity of the trans-gauche mechanism. Further confirmation is provided by the fact that DHAB with two hexyl groups shows greater attenuation than MBAB.

If the trans-gauche mechanism is accepted, then MMAB should show no relaxation. Under this condition, the attenuation of Merck V would be expected to decrease considerably, compared with MBAB, while in fact Merck V gives only slightly smaller attenuation in the low temperature range. However, one knows that for highly concentrated solutions the attenuation is not proportional to concentration of the active specie. For instance a weak dependence of the attenuation on concentration has been observed in alcanes by

Piercy and Rao.[13] These authors found that the attenuation of 43.5 mole % solution of *n*-pentane in propane is identical to that of pure *n*-pentane and the attenuation of 25.6 mole % solution decreases by about 30%. A similar effect may be operative in Merck V.

On the other hand, the relaxation frequency of Merck V is very close to MBAB. This behaviour is typical of an intramolecular relaxation.

If we now compare data relative to Merck V and alcanes, one remarks that the relaxation frequency of Merck V at room temperature is about the same as the one of *n*-butane or *n*-pentane at −120°C, that is 15–20 MHz.[3] This indicates that the activation free energy ΔG^* of liquid crystals at room temperature is similar to that of normal paraffins at −120°C. As the activation enthalpy ΔH^* is unchanged, one must conclude that it is the activation entropy ΔS^* which is essentially affected by the orientational order. This fact will be discussed later.

MBBA exhibits greater attenuation than MBAB. In the case of MBBA the predominant critical phenomena makes it impossible to study the internal relaxation. A correct comparison for the internal relaxation should be carried out in the region of a negative temperature coefficient of α/f^2, but the attenuation of MBBA increases continuously with increasing temperature, in the mesomorphic range.

Thermodynamic equilibrium parameters

The thermodynamic equilibrium parameters can be obtained from the analysis of the temperature dependence of $\mu'_{\max}$, maximum value of the relaxational attenuation per wavelength. The plot of $\mu'_{\max}$ versus $10^3/T$ is given in Figure 5.

$\mu'_{\max}$ obeys the equation

$$\frac{2\mu'_{\max}}{\pi} = \frac{c^2 T\theta^2}{C_p^2}\left(1 - \frac{\Delta V_0}{V\theta}\frac{C_p}{\Delta H_0}\right)^2 \delta C_p \tag{3}$$

$$\delta C_p = R\left(\frac{\Delta H_0}{RT}\right)^2 \frac{\exp(-\Delta G_0/RT)}{(1+\exp(-\Delta G_0/RT))^2} \tag{4}$$

$$\Delta G_0 = \Delta H_0 - T\Delta S_0$$

δC_p is the relaxational heat capacity, C_p, the specific heat capacity, θ the thermal expansion coefficient, c the sound velocity, V the molar volume. ΔG_0, ΔH_0, ΔS_0 and ΔV_0 are the differences in free energy, enthalpy, entropy and volume respectively, associated with the trans-gauche reaction. According to Eq. 3, $\mu'_{\max}$ is not a simple function of temperature. In order to determine the enthalpy difference between two conformations, from an

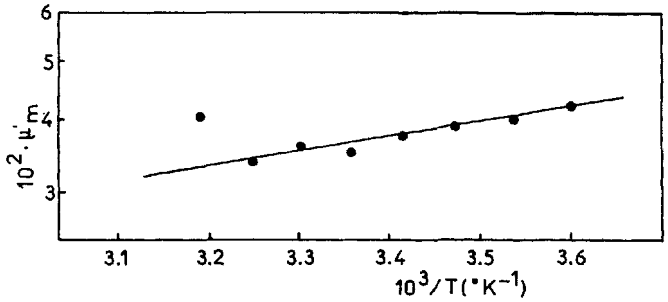


FIGURE 5 The temperature dependence of $\mu'_{\max}$ for Merck V.

analysis of experimental results, it is usually assumed that $\exp(-\Delta G_0(RT)$ $\ll 1$, which reduces Eq. 4 to:

$$\delta C_p = R\left(\frac{\Delta H_0}{RT}\right)^2 \exp\left(-\frac{\Delta H_0}{RT}\right)\exp\left(\frac{\Delta S_0}{R}\right) \tag{5}$$

Then, ΔH_0 can be approximately obtained from the slope of the plot of $\log(\mu'_{\max}\, T/c^2)$ against $10^3/T$. There is however no a priori reasons that the preceeding assumption holds in the case of liquid crystals. Nevertheless, if we plot $\log(\mu'_{\max}\, T/c^2)$ versus $10^3/T$ for Merck V sample (Figure 6) one indeed obtains a straight line with a small negative slope which yields $\Delta H_0 \sim 0.4$ Kcal/mole. This value of ΔH_0 is close to the values 0.8 and 0.5 Kcal/mole found for *n*-butane and *n*-pentane.[15,16]

In order to ensure self-consistency between this quite small value of ΔH_0 and the assumption $\exp(-\Delta G_0/TR) \ll 1$, $|\Delta S_0|$ must necessarily be non negligible. (The calculations yield $\Delta S_0 < -5$ cal/mole/°K.)[3] This last point

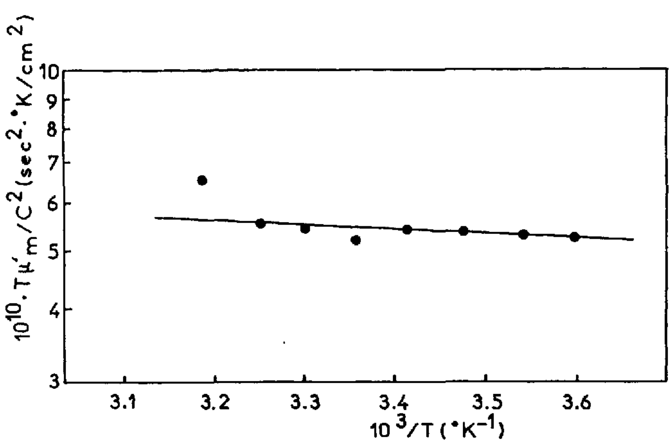


FIGURE 6 Plot of $\log(T\mu'_{\max}/c^2)$ against $10^3/T$ for Merck V.

is supported by the close agreement between the values of $\mu'_{\max}$ for Merck V at room temperature (~ 3.5–$4\ 10^{-2}$) and those of normal paraffins at -120°C ($3.8\ 10^{-2}$ and $2.4\ 10^{-2}$ for *n*-butane and *n*-pentane).[13] We are then led to the same conclusions for both kinetic and equilibrium parameters, that is the enthalpy factors are about the same for liquid crystals and normal paraffins but entropy factors are smaller for the former compound.

CONCLUSION

It has been experimentally shown that the ultrasonic relaxation far below the transition temperature is due to the trans-gauche isomerism of end groups.

The temperature dependence of the relaxation frequency yields an activation enthalpy ΔH^* close to those of normal paraffins but a much smaller activation entropy ΔS^*.

The analysis of equilibrium thermodynamic parameters is much more difficult to handle because of the number of the involved parameters. However from the comparison between values of $\mu'_{\max}$ for pure paraffins and Merck V, as well as the temperature dependence of $\mu'_{\max}$ one can state that the enthalpy difference between trans and gauche conformations is the same for both materials, the entropy difference being quite smaller in the case of liquid crystal. These changes in the entropy parameters illustrate the fact that the end chains of liquid crystals at room temperature are similar to the paraffinic chains at -120°C. This is presumably related with the considerable ordering of the end chains of liquid crystals.[17] Recent Raman work[5] indicates that the fusion of the end chains is not complete in the nematic phase and the transition to the isotropic phase causes the disorientation of the end chains. At low temperature the conformation of paraffinic chains might be to some extent in an ordered state. It is noteworthy that even at room temperature adsorbed layers of long chains of *n*-hydrocarbon derivatives are ordered in all trans conformations as they are in bulk crystals.[18]

Acknowledgements

The authors wish to thank Dr. B. Michels for much encouragement during the course of this work and for the generous use of his equipment. They also wish to thank Dr. C. Mioskowski for kindly providing DHAB.

References

1. For reviews, see S. Candau and P. Martinoty in the International School of Physics *Enrico Fermi* (1974), earlier papers quoted therein.
2. P. Martinoty, Thesis, Strasbourg, (France) (1972), unpublished.
3. A. J. Matheson, *Molecular Acoustics*, J. Wiley and Sons.

4. F. Jähnig, *Chem. Phys. Letters*, **23**, 262 (1973).
5. C. Destrade and H. Gasparoux, *J. Phys.*, **36**, L-105 (1975).
6. J. M. Schnur, *Mol. Cryst. Liq. Cryst.*, **23**, 155 (1973).
7. W. R. Young, I. Haller, and A. Avirm, *Mol. Cryst. Liq. Cryst.*, **13**, 357 (1971).
8. S. Candau, P. Martinoty, and R. Zana, *J. Phys.*, **86**, L-13 (1975).
9. F. Eggers and Th. Funk, *Rev. Sci. Instrum.*, **44**, 969 (1973).
10. W. A. Hoyer and A. W. Nolle, *J. Chem. Phys.*, **24**, 803 (1956).
11. K. A. Kemp and S. V. Letcher, *Phys. Rev. Letters*, **27**, 1634 (1971).
12. D. Eden, C. W. Garland, and R. C. Williamson, *J. Chem. Phys.*, **58**, 1861 (1973).
13. J. E. Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967).
14. See for instance: J. Lamb, Proceed. of the International School of Physics, *Enrico Fermi*, Academic Press (1963).
15. G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 704 (1948).
16. N. Sheppard and G. J. Szasz, *J. Chem. Phys.*, **17**, 86 (1949).
17. S. Marcelja, *J. Chem. Phys.*, **60**, 3599 (1974).
18. C. L. Sutula and L. S. Bartell, *J. Phys. Chem.*, **66**, 1010 (1962).