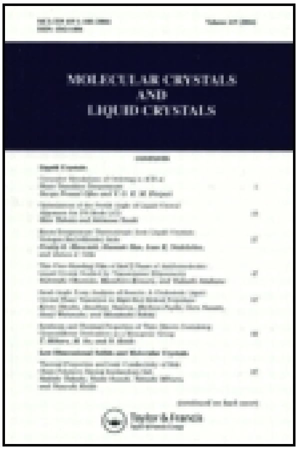

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Mechanism of Q(C≡N) Band Broadening in Condensed State of Alkoxycyanobiphenyles

V. Krasnoholovets [a], I. Khakimov [a], G. Puchkovskaya [a] & E. Gabrusenoks [b]

[a] Institute of Physics, National Academy of Sciences, Prospect Nauky 46, UA-252650, Kyïv, 22, Ukraine

[b] Institute of Solid State Physics, Riga University, 256000, Riga, Latvia

Version of record first published: 24 Sep 2006

To cite this article: V. Krasnoholovets, I. Khakimov, G. Puchkovskaya & E. Gabrusenoks (2000): Mechanism of Q(C≡N) Band Broadening in Condensed State of Alkoxycyanobiphenyles, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 348:1, 101-109

To link to this article: http://dx.doi.org/10.1080/10587250008024799

Mol. Cryst. Liq. Cryst., Vol. 348, pp. 101-109
Reprints available directly from the publisher
Photocopying permitted by license only

Mechanism of Q(C≡N) Band Broadening in Condensed State of Alkoxycyano-biphenyles

V. KRASNOHOLOVETS[a*], I. KHAKIMOV[a], G. PUCHKOVSKAYA[a] and E. GABRUSENOKS[b]

[a]*Institute of Physics, National Academy of Sciences, Prospect Nauky 46, UA-252650, Kyïv 22, Ukraine and* [b]*Institute of Solid State Physics, Riga University, 256000, Riga, Latvia*

(Received October 01, 1997; In final form July 16, 1999)

In the present paper the spectral-structural-phase correlations in a series of the 4-cyano-4′-*n*-alkoxybiphenyles ($n = 3 - 8$) are studied. The analysis of Q(C≡N) band behaviour in the solid crystal (SC), liquid crystal (LC), isotropic liquid (IL) and hexane solution is carried out. The mechanism of intradimer energy transfer which explains the Q(C≡N) band breadth in the LC and IL phases is proposed.

Keywords: liquid crystals; vibrational spectra; phase transitions; dimer-dimer interaction; energy transfer

1. INTRODUCTION

It is the matter of fact that for the majority of liquid crystals the types of mesogenic phases are defined by peculiarities of molecular packing in the solid crystalline phase for the majority of liquid crystals [1,2]. It is interesting to study structural rearrangements, in particular, the nearest surrounding of molecules at the transitions from the solid crystalline phase (SC) to liquid crystal (LC), isotropic liquid (IL) and solution in a homologous series of mesogenes. Unfortunately the structural data on different phases only for a few liquid crystals and only for separated terms of the homologous series are available.

Vibrational spectroscopy methods are known to be very sensitive to the reconstruction of a local environment, to change in the molecular structure and to the

---

* Correspondence author.

peculiarities of molecular dynamics in different phase states. The study of vibrational band parameters (frequency, half-width and intensity) in a wide temperature range can be done quite easily and quickly by utilizing modern spectrometers whose resolving power is sufficiently high. Having found spectral-structural-phase correlations for some homologues one may apply them to the analysis of other terms of the homologous series.

In the present paper we investigate the vibrational spectra of 4-cyano-4′-*n*-alkoxybiphenyls (*n*OCB) homologues, that are widely used in the industry. The physical and chemical properties of *n*OCB series and the crystalline structure of the first five terms of the homologous series [3,4] as well as the structure of LC phases [4,5] found by means of X-ray scattering have previously been defined. The IR and Raman spectra in different phase states of some terms of the series have been measured for different phase states in papers [6–10]. Our preceding works [11,12] have been dedicated to the experimental study of IR spectra of the *n*OCB ($n = 3 - 8$) in the temperature region from 100 to 450 K and analyzed normal vibrations of different conformers. Thermodynamic properties of different phases have been examined by means of both the differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods.

It has been found [7–10,13] that parameters of the Q(C≡N) stretching vibration band are sensitive to changes in the *n*OCB phase state. Indeed, the IR spectrum of 7OCB contains [8] the doublet (2243 and 2232 cm^{-1}) which characterizes the SC I phase, the doublet (2239 and 2231 cm^{-1}) which characterizes the SC II phase and the singlet (2237 cm^{-1}) with a shoulder at 2230 cm^{-1} that describes the SC III phase. In the IR spectrum of 8OCB [7] the maximum at 2235 cm^{-1} corresponds to the SC I phase, the doublet (2236 and 2228 cm^{-1}) depicts the SC II phase and the maximum at 2239 cm^{-1} with a shoulder in the shortwave range fixes the SC III phase. The Raman spectrum of the CS phase of 8OCB displays [10] the intensive band with the maximum at 2227.6 (±0.8) cm^{-1} and a shoulder at 2218 (±1.1) cm^{-1}. Unfortunately no spectral data for short homologues are available.

In similar compounds, for example, acetonitrile, the frequency of the Q(C≡N) band and its width change with the environment: in nonpolar solvents the frequency of the maximum reaches the highest magnitude and the bandwidth is the narrowest one; in polar solvents the associates formation becomes possible [15] owing to the dipole-dipole interaction of the C≡N polar group ($\mu = 4.05$ D [14]) with polar groups of solvent molecules.

The comparative study of the contribution of various broadening mechanisms of the Q(C≡N) band in the Raman spectra of SC, LC and IL phases of *n*OCB [6] has shown that the main contribution to vibrational relaxation depends on dephasing [10].

The aim of the present paper is to determine the spectral-structural-phase correlations in a series of the *n*OCB molecules and to propose a mechanism which could explain the broadening of the Q(C≡N) band in the LC and IL phases.

2. EXPERIMENTAL

This paper presents the detailed analysis of the Q(C≡N) band parameters in the IR and Raman spectra for the *n*OCB ($n = 3 - 8$) in the SC, LC, IL phases and the hexane solution. The IR spectra have been measured by the UR-20 spectrophotometer with resolution of 2–3 cm^{-1}. The Raman spectra have been measured by the Spex Ramanlog with resolution of 2 cm^{-1} and the Spectra Physics 165–8 laser ($\lambda_{excit} = 514$ nm). For both the IR and Raman studies the SC samples were prepared from the melt by slow cooling (1 K/min). The samples were placed between KBr plates (the IR study) and in a glass capillary (the Raman study). The temperature dependence of the IR spectra has been measured by the high temperature cell and the FIS-3 temperature stabilization system with the temperature control accuracy ± 0.5 K. For the Raman measurement a special quartz cell was constructed. The temperature has been raised by the automatic thermocontroller with the accuracy ± 0.5 K. The Raman spectra have been studied with the IBM PC XT, Intel-80286 utilizing the Spectra Calc program (Florida Atlantic University, Dr. Medina). Since the width of the Q(C≡N) band has varied in the range from 5 to 12 cm^{-1}, the value of the split spectral width $\Delta\nu = 2$ cm^{-1}has not been taken into account.

3. RESULTS AND DISCUSSION

Broadening of the Q(C≡N) band at melting and the shift of the band maximum towards low frequencies in the Raman spectra of the considered homologues of *n*OCB has been observed. The fragments of the Raman spectra of 3OCB and 5OCB in the SC, LC and IL phases appear in Fig. 1. It is seen that the spectra of both compounds are similar. Fig. 2 shows the temperature dependence of the maximum location and half-width of the band (in the regime of heating and cooling). At the SC → LC and LC → IL transitions, the maximum shifts from 2236 cm^{-1} to 2228 cm^{-1} and the half-width of the band increases from 4–5 cm^{-1} (SC) to 8–10 cm^{-1}(LC) and to 10 cm^{-1} (IL) for 3OCB, and from 4–5 cm^{-1} (SC) to 8 cm^{-1} (LC) and to 12 cm^{-1} (IL) for 5OCB.

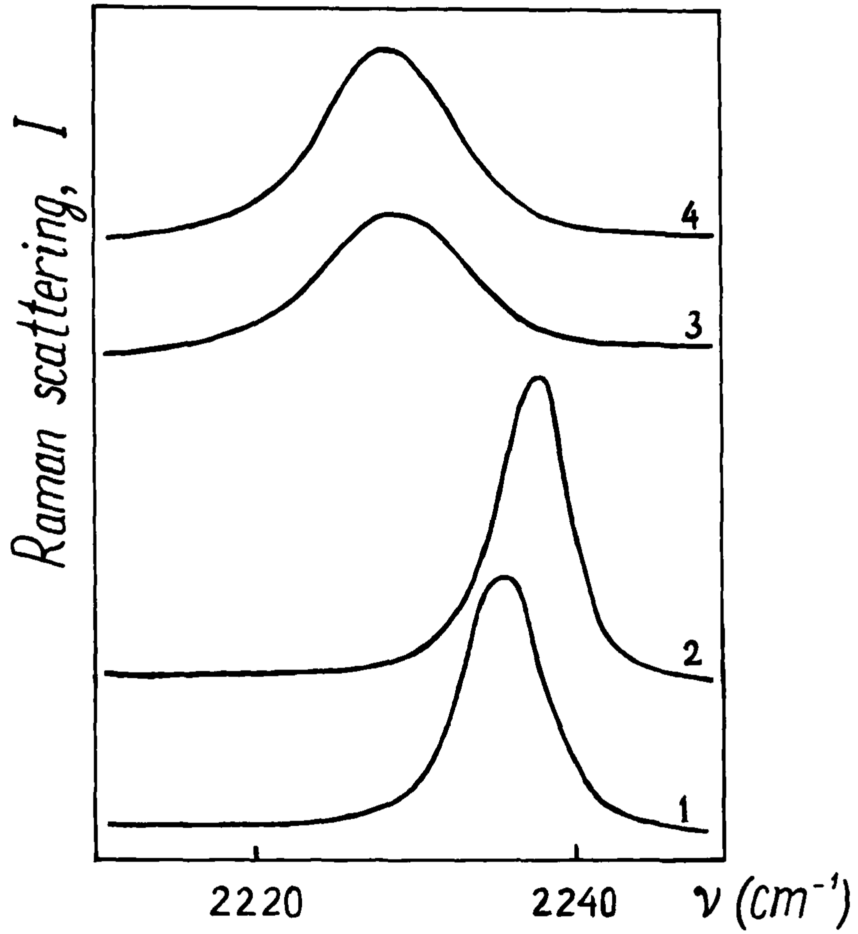

FIGURE 1 Raman spectra of 3OCB and 5OCB at the different phases. (1) the SC, 3OCB; (2) the SC, 5OCB; (3) the IL and nematic LC, 3OCB; (4) the IL and nematic LC, 5OCB

Let us consider the reason of the above changes. As follows from the X-ray analysis of *n*OCB, the crystalline structures of the first five first terms of the homologous series ($n = 1 - 5$) vary [3,4]. The arrangement of molecules in the SC depends on the length of the alkyl radical. In the *n*OCB crystals with $n = 3, 5$ the phenyl rings of the molecules have arranged one over the other. It has been shown by means of low-angle X-ray scattering in papers [4,5] that the molecules of *n*OCB with $n = 5, 6, 8$ in the LC and IL phases form dimers with an antiparallel packing. The position of the Q(C≡N) band maximum in the Raman spectrum

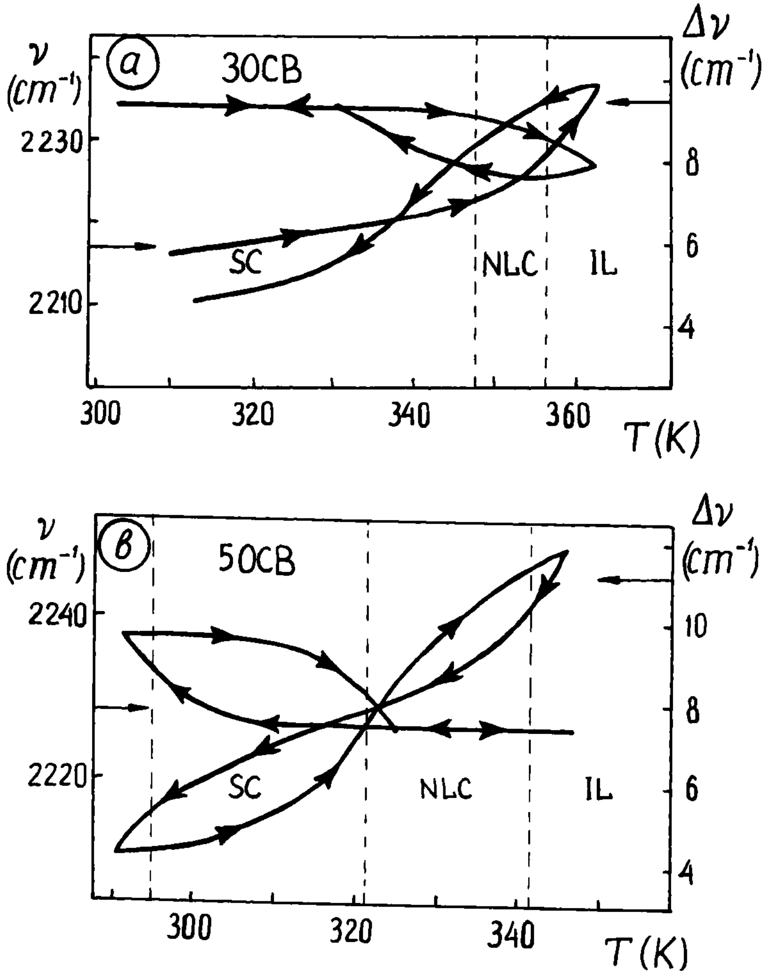

FIGURE 2 The temperature dependence of the position and half-width of the Q(C≡N) band

and the correlation functions of reorientational motion in IL and LC have been described in papers [10,13]. The correlation function has a reorientational component, but it has been caused only by the vibrational relaxation owing to dephasing processes [10]. Special attention has been paid in works [9,13] to broadening mechanisms of the Q(C≡N) band in the IL and LC phases.

The transition moment of the C≡N stretching vibration is located in the direction of the long axis of the molecule, so that the molecule reorientations on this axis do not make contribution to the broadening of the band. Contributions from the reorientations with respect to the other two axes is negligible as it was shown [10] by means of the correlation function analysis of Raman bands. Paper [9] examines the three most possible mechanisms of vibrational relaxation – the dipole-dipole induced transitions, vibrational energy resonance transitions and vibrational dephasing. However it was noted that for all the *n*OCB molecules, these mechanisms make a small contribution to the bandwidth, and another broadening mechanism – the intramolecular energy transfer – has been suggested.

Nevertheless as pointed out above it has been elucidated that the bipolar molecules *n*OCB in the LC and IL phases formed stable dimers with the coupling energy $\Delta E_{dd} > k_B T$ [4,5]. The structure of this type allows us to suggest a new mechanism of energy exchange, namely the mechanism of intradimer energy transfer.

We have investigated the Q(C≡N) IR band of the samples of the *n*OCB ($n = 3 - 8$) in the SC, LC and IL phases and *n*-hexane solution in an effort to test the above mechanism. When melting, the shift of the Q(C≡N) band from 2232 cm^{-1} to 2226 cm^{-1} in the LC phase, has been observed in the IR spectra of 3OCB and 5OCB. The latter frequency is the same in the LC and IL phases. For all *n*OCB under studied the bandwidth $\Delta\nu_{1/2}$ is equal to 10 ± 0.5 cm^{-1} in both phases. In the *n*-hexane solution the maximum of the band is located at 2228 cm^{-1} and the bandwidth is halved, $\Delta\nu_{1/2} = 5 \pm 0.3$ cm^{-1}.

In this connection, it is interesting to point out the result of paper [15] which examined the behavior of the Q(C≡N) band of acetonitrile solved in CCl_4 with addition of polar phosphine derivatives. It has been found that in the composite Q(C≡N) band, two components could be distinguished when the concentration of phosphinoxyde increases. The first component (2256 cm^{-1}) corresponds to the free monomer of acetonitrile and the other (2253 cm^{-1}) corresponds to the acetonitrile – phosphinoxyde complexes. The complex formation is claimed [15] to be the result of dipole-dipole interaction which reduces to the weakening of the C≡N bond (the frequency lowered by 3 cm^{-1}) and the broadening of the Q(C≡N) IR band from $\Delta\nu_{1/2} = 7$ cm^{-1}, typical for a free acetonitrile molecule to $\Delta\nu_{1/2} = 10$ cm^{-1} for the complex.

Let us consider the following mechanism of intradimer energy transfer. The *n*OCB molecules are extended and each molecule is characterized by a significant dipole moment directed along the long axis. The presence of the conjugate system in the molecule (the C≡N) group, phenil rings and C-O group) should lead to the shift of the electronic cloud from the O atom to the N one. Hence the negative charge is located at the N atom and the positive charge, at the O atom. The distance between $N^-$and O^+ in the isolated OCB molecule is equal to 1.35 nm [16]. Molecules in the dimer arrange one above the other in such a way that their dipoles are antiparallel and compensate each other. In this case the C≡N bond of one molecule is found in the immediate vicinity of the C-O bond of the other molecule.

Now let us study the Raman spectrum of the C≡N bond utilizing the donor-acceptor model of the vibrational energy transfer [18]. If the C≡N bond is considered as a donor, then the nearest C-O bond of a neighboring molecule should manifest itself as an acceptor for electrons. In this model the time T_2 of transversal relaxation of a vibration in the donor is connected with the broadening $\delta\nu$ of spectral band by the relation

$$1/T_2 = 2\pi\delta\nu. \tag{1}$$

In the dipole-dipole approximation the interaction between these two bonds separated by a distance R (the average distance between the long axes of molecules in the dimer) is equal to

$$M_{\mathrm{da}} = |\vec{p}_{\mathrm{d}}| \cdot |\vec{p}_{\mathrm{a}}|/R^3 \tag{2}$$

where $|\vec{p}_{\mathrm{d}}|$ and $|\vec{p}_{\mathrm{a}}|$ are the transition dipole moments of the donor (C≡N) and acceptor (C-O) bond respectively. The matrix elements $|\vec{p}_{\mathrm{d}}|$ and $|\vec{p}_{\mathrm{a}}|$ are expressed in terms of the corresponding oscillator forces $f_{\mathrm{d,a}}$

$$p_i^2 = (\hbar c^2/2m_i d_i)f_i \tag{3}$$

here m_i is the reduced mass of donor (i = d) or acceptor (i = a). The time τ_i of oscillator excitation, i.e. time of longitudinal relaxation, is connected with the corresponding oscillator forces f_i:

$$\tau_i = \frac{m_i c^3}{e^2\omega_i^2}\frac{1}{f_i}. \tag{4}$$

The probability of energy transfer per unit of time, i.e. the rate of energy transfer, is determined according to the expression

$$W = \frac{2|M_{\mathrm{d,a}}|^2 T_2/\hbar}{1 + (T_2\Delta E/\hbar)^2} \tag{5}$$

where ΔE is the difference between the energies of vibrational levels of the donor and acceptor. Hence the dimensionless parameter defining the probability of vibrational excitation transfer from the donor to the acceptor is $W\tau_{\mathrm{d}}$. Setting $W\tau_{\mathrm{d}}$= 1 and utilizing expressions from (1) to (5) we obtain the equation for the definition of additional broadening $\delta\nu$ of the Q(C≡N) band at a frequency ν due to the donor-acceptor interaction of the C≡N and C-O bonds in the dimer:

$$\left(\frac{c}{\omega R^2}\right)^3 \frac{p_{\mathrm{a}}^2}{h\delta\nu[1 + \Delta E/h\delta\nu]} = 1. \tag{6}$$

In Eq. (6) we known that $R \simeq 0.5$ nm; $\omega = 2\pi\cdot c\cdot 2228$ cm^{-1} (where c is the velocity of light) as follow from our Raman and IR spectral data of the C≡N bond; the difference between the energies of vibrational levels of the C≡N and C-O bonds is $\Delta E = c\cdot 988$ cm^{-1} (the frequency of ν(C-O) band is equal to 1240 cm^{-1}). So, there is only one fitting parameter, p_a, but we may choose the value $p_a = 0.7$ D that corresponds to the C-O bond dipole [11]. Substituting all these parameters into Eq. (6) we find the value $\delta\nu \approx 5$ cm^{-1}. The result agrees with the observation, that is, the calculated value of δν correlates with the experimental Q(C≡N) band broadening – the difference of band-width of IR spectra in the liquid state and in the solution of *n*-hexane.

Thus in the case of *n*OCB associated molecules in the liquid phase, the broadening of absorption/scattering band of the C≡N bond correlates quite well with the two-level donor-acceptor approach.

4. CONCLUSION

As is obvious from the structural data, the creation of the dimers requires the shift of *n*OCB molecules in the crystal by the length of the C-O bond (≃ 0.136 nm) with melting. *n*OCB molecules in the SC phase are characterized by the dispersional interaction. However, in the LC and IL phases the rearrengement of *n*OCB molecules has to occur: the C≡N group of one molecule is located over the C-O group of the other molecule and the dipole momenta of the two *n*OCB molecules should be really compensated.

So the dimer formation becomes energetically favorable in the LC and IL phases. Nevertheless in the non-polar hexane solution the dimers dissociate into isolated molecules and therefore the narrowing of Q(C≡N) band by 5 cm^{-1} takes place. A correlation of changes in the Q(C≡N) band spectral parameters (the frequency and band-width) in the nearest surrounding is observed. This means the narrowing Q(C≡N) band at the transition from the LC and IL phases to the solution (i.e., transition: dimer → monomer) one can explain in the framework of the mechanism of intradimer energy transfer that we propose in this work.

In the SC the *n*OCB molecules do not join in dimers and the width of the Q(C≡N) band is equal to 5 cm^{-1} in the Raman spectum. The width of the Q(C≡N) band in the IR spectrum of the SC film is equal to 10 cm^{-1}. Therefore in this case one should invoke other mechanisms of the broadening which are based on collective excitations in a crystal and effects of the scattering, absorption and reflection of the incident radiation by particles.

References

1. J.D. Bernal and D. Crowfoot, *Trans. Faraday. Soc.*, **29**, 1032 (1933).
2. R.F. Braiyan, *Zhur. strukt. khimii*, **23**, 1154 (1982) (in Russian).

3. L. Walz, H. Paulus and W. Haase, *Z. Kristallogr.*, **180**, 97 (1987).
4. P. Mandal and S. Paul, *Mol. Cryst. Liq. Cryst.*, **131**, 223 (1985).
5. A.J. Leaddetter, R.M. Richardson and C.N. Collinq, *J. Phys.* (Fr.), **36**, L69 (1975).
6. N. Kirov and P. Simova, *Vibrational Spectroscopy of Liquid Crystals*, Bulgarian Academy of Science, Sofia, 1984.
7. S.C. Jain, S.A. Agnihotry and V.G. Bride, *Mol. Cryst. Liq. Cryst.*, **88**, 281 (1982).
8. S.C. Jain, S.A. Agnihotry, S. Chandra and V.G. Dride, *Mol. Cryst. Liq. Cryst.*, **104**, 161 (1984).
9. B.J. Bulkin and K. Brezinsky, *J. Chem. Phys.*, **69**, 15 (1978).
10. B.J. Bulkin, K. Brezinsky and T. Kennelly, *Mol. Cryst. Liq. Cryst.*, **55**, 53 (1979).
11. L.M. Babkov, N.I. Davydova, G.A. Puchkovskaya and I.N. Khakimov, *Zh. Struk. Khimii*, **34**, 105 (1993) (in Russian).
12. L.M. Babkov, I.N. Khakimov, A.P. Polischuk, G.A. Puchkovskaya et al., *J. Mol. Struct.*, **296**, 29 (1993).
13. W.G. Rothschild, *J. Chem. Phys.*, **65**, 455 (1976).
14. B.I. Minkin, O.A. Osipov and Yu.A. Zhdanov, *Dipole Moments in Organic Chemistry*, Khimiya, Leningrad, 1968 (in Russian).
15. E.V. Ryl'tsev, I.E. Boldeskul, N.F. Pavlenko, Yu.P. Egorov and V.P. Akkerman, *Zh. Priklad. Spektroskop.*, **16**, 513 (1972) (in Russian).
16. P.E. Cladis, R.K. Bodardus and D. Adsen, *Phys. Rev. A*, **18** 2292 (1978).
17. B. Bhattacharjec, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.*, **89**, 181 (1982).
18. V.M. Agranovich and M.D. Galanin, *Energy Transfer of Electron Excitation in Condensed Media*, Nauka, Moskow, 1978, pp. 26, 126 (in Russian).
19. G.P. Buyan, I.I. Kondilenko, V.E. Pogorelov, *Optika i Spektroskop.* **27**, 248 (1969) (in Russian).