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Optical activity measurements at long wavelengths in the blue phases of highly chiral liquid crystals

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A recent calculation of the optical activity in the blue phases using Landau–de Gennes theory predicts the wavelength dependence

$$\phi/d = A_2/\lambda^2 - A_4/\lambda^4,$$

where ϕ/d is the optical activity, λ is the wavelength (assumed to be much greater than the pitch), and A_2 and A_4 are coefficients which depend on the structure of the blue phases. Measurements of the optical activity between 0·78 and 1·1 μm in all three blue phases of the CE2/7S5 system confirm this relationship. For certain values of A_2 and A_4 the optical activity passes through zero within the range of wavelength investigated. The values of A_2 and A_4, however, vary in a way which cannot be explained by the theory. The data suggest that fluctuations in the order parameters, which are not considered in the theory, are large in the blue phases of these highly chiral systems.

1. Introduction

The blue phases which occur in some chiral liquid crystals just below the transition to the isotropic liquid are an example of stable liquid-crystalline phases containing a lattice of singular points. The lattice in two of these phases, BP I and BP II, possesses cubic symmetry, whereas a third phase, BP III, seems to be amorphous. The cubic and amorphous structures are optically isotropic but, like cholesteric liquid crystals, the blue phases are optically active and reflect circularly polarized light. The number of blue phases present and the temperature range over which they are stable generally increase as the chirality of the liquid crystal increases [1].

Free energy calculations of the Landau–de Gennes type show that phases with cubic symmetry can be stable if the chirality is high and the temperature is just below the isotropic transition temperature [2]. A great deal of experimental work has been done on the blue phases, with most directed to (*a*) investigating the symmetry of the phases, (*b*) measuring the lattice constant of the cubic structures, or (*c*) observing effects due to electric fields. However, the Landau–de Gennes calculations also provide quantitative information concerning the various order parameters necessary to specify the blue phase structures, but very few experiments have been performed which provide this type of information [3, 4]. Theoretical work by Bensimon *et al.*, using similar ideas, predicts how the optical activity of the blue phases depends on their structure [5]. This calculation involves these same order parameters and has never been tested.

Here we report optical activity measurements taken in three blue phases. In order to test the theory of Bensimon *et al.*, the measurements were carried out at long wavelengths in highly chiral liquid crystals. The data agree qualitatively with the theory, and provide quantitative information on coefficients which depend on the order parameters. However, close analysis reveals that important differences between the theory and the data are present. It is argued that fluctuations in the order parameters, which are not taken into account by the theory, are responsible for these differences. These fluctuations appear to be very strong, especially in BP III.

2. Theory

In Landau–de Gennes free energy calculations, the anisotropic part of the dielectric tensor, ε_{ij}, is the order parameter which is used to represent the long range orientational order. Since it is a symmetric tensor with zero trace, it can be represented in terms of five independent modes or basis tensors. The $m = 0$ mode is nematic-like, the $m = 1$ mode describes a conical spiral where two principal axes rotate around the spiral axis making an angle of 45°, and the $m = 2$ mode is a planar spiral mode where two principal axes rotate around a spiral axis making an angle of 90°. The $m = -1$ and $m = -2$ modes are similar to the $m = 1$ and $m = 2$ modes, respectively, but the axes rotate in the opposite direction. The blues phases involve structures for which ε_{ij} has a spatial variation representative of a certain symmetry group. Therefore, these structures can be represented by a set of wavevectors for which the average amplitude of ε_{ij} is non-zero. In most of the blue phase structures considered, this set of wavevectors possesses cubic symmetry.

With this as the starting point, Bensimon *et al.* then consider the optical activity tensor for these structures, correct to second order in k/q, where $\mathbf{k}$ is the wavevector of the light propagating through the phase and $\mathbf{q}$ is a wavevector of the structure. By averaging over all possible orientations, a result for the optical activity in a polycrystalline sample is obtained

$$\phi/d = A_2/\lambda^2 - A_4/\lambda^4, \tag{1}$$

where

$$A_2 = \frac{\pi^2}{3\varepsilon_0}\sum_i N_i(\varepsilon_1^2 - \varepsilon_{-1}^2)_i\left(\frac{2\pi}{q_i}\right) \tag{2}$$

and

$$A_4 = \frac{\pi^2}{3\varepsilon_0}\sum_i \varepsilon_0 N_i[2(\varepsilon_1^2 - \varepsilon_{-1}^2)_i + \tfrac{53}{15}(\varepsilon_2^2 - \varepsilon_{-2}^2)_i]\left(\frac{2\pi}{q_i}\right)^3. \tag{3}$$

Here ϕ/d is the optical activity, λ is the wavelength of the light in the sample, ε_0 is the average dielectric constant, N_i is a number representing the multiplicity associated with the ith wavevector, and q_i is the equilibrium wavevector. $(\varepsilon_m)_i$ is the amplitude of the Fourier component corresponding to the mth mode of the ith wavevector.

This result for the optical activity has a number of direct implications. For example, the cholesteric structure with a single twist can be represented using one wavevector and only a combination of the $m = 0$ and $m = 2$ modes. This means that the optical activity of a polycrystalline sample in the cholesteric phase should have a $1/\lambda^4$ dependence, since $A_2 = 0$. The blue phases, on the other hand, are represented by many wavevectors and a combination of modes which includes the $m = 1$ mode. The optical activity of a polycrystalline blue phase sample should therefore have a much more complicated wavelength dependence, with competing $1/\lambda^2$ and $1/\lambda^4$ terms.

3. Experimental method

In order to keep the value of k/q as small possible, highly chiral liquid crystals were used and measurements of the optical activity were taken at long wavelengths. The samples were mixtures of the chiral liquid crystal 4″-(2-methylbutyphenyl)-4′-(2-methylbutyl)-4-biphenylcarboxylate (CE2) and the non-chiral liquid crystal 4-*n*-pentylbenzenethio-4′-*n*-heptyloxybenzoate ($\bar{7}$S5). The $\bar{7}$S5 was obtained from the

Liquid Crystal Institute at Kent State University [6] and the CE2 was purchased from B.D.H. Chemicals. This system shows very high chirality, with the cholesteric pitch ranging from about 0·25 to approximately 0·1 μm as the concentration of CE2 increases from 40 to 100 wt % [7]. The 40 wt % CE2 sample possesses three blue phases, but BP II disappears around 45 wt % CE2, so higher concentrations possess only BP I and BP III.

The rotating analyser system for measuring the optical activity and the temperature control system for the sample (1 cm path length) have been described previously [8]. To allow variation of the wavelength, a 1000 W xenon lamp and a monochromator were used instead of the He–Ne laser. The bandpass of the monochrometer was set at 4 nm and the wavelength was varied from 0·78 to 1·1 μm. The value of k/q therefore ranged from 0·07 for 1·1 μm light in the 100 wt % CE2 sample to 0·32 for 0·78 μm light in the 40 wt % CE2 sample. Data were obtained over this wavelength range at various temperatures for all blue phases in the 40, 60, 80 and 100 wt % CE2 mixtures. Similar measurements were made in the isotropic phase immediately above the BP III–isotropic transition.

Because the CE2 molecules are chiral, there is a small molecular contribution to the optical activity which must be subtracted in order to obtain the optical activity for the structure alone. The molecular contribution was measured by raising the temperature 30–40°C above the isotropic transition temperature and taking optical activity data over the same wavelength range. Previous measurements of the optical activity in the isotropic phase of this system show that the pretransitional effects are very small this far above the transition [8]. These data were then subtracted from the measurements taken in the blue phases. It should be pointed out that both CE2 and $\bar{7}$S5 have weak absorption bands in this wavelength region. These absorption bands do show up as very small but noticeable anomalous regions in the optical activity spectra. However, these anomalous regions disappear after the spectra, taken high in the isotropic phase, are subtracted from the blue phase spectra.

4. Experimental results

Representative spectra (after subtraction) are displayed in figures 1–4, together with the best least-squares fits to equation (1). A positive optical activity indicates that

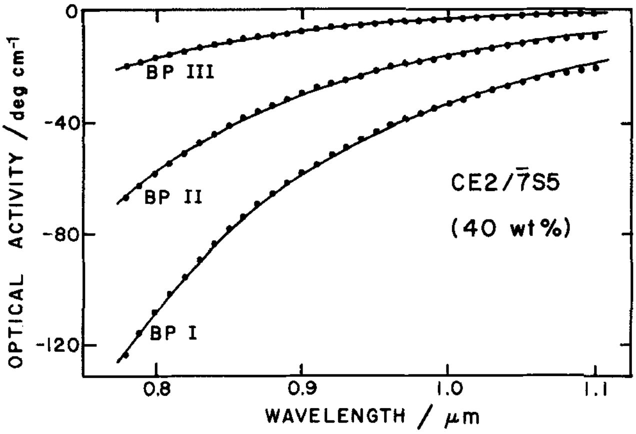

Figure 1. Optical activity spectra for three temperatures in the mixture containing 40 wt % CE2. The lines are least-squares fits to equation (1).

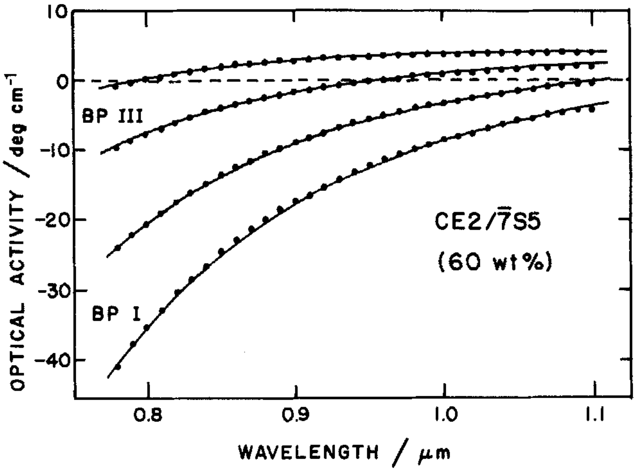

Figure 2. Optical activity spectra for four temperatures in the mixture containing 60 wt % CE2. The lines are least-squares fits to equation (1).

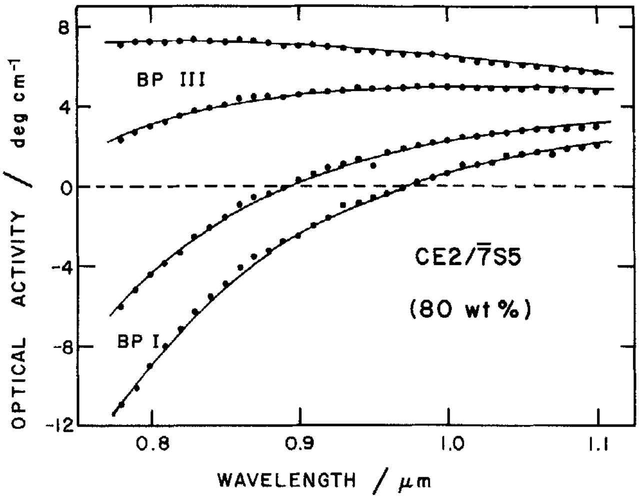

Figure 3. Optical activity spectra for four temperatures in the mixture containing 80 wt % CE2. The lines are least-squares fits to equation (1).

the direction of polarization rotated clockwise for an observer looking back along the beam. In describing these spectra, the wavelength at which the optical activity crosses zero, $\lambda_0 = (A_4/A_2)^{1/2}$, is a useful quantity. In the 40 wt % CE2 sample λ_0 is greater than the range of wavelengths studied, so the spectra monotonically approach zero from the negative side. As the concentration of CE2 (and therefore the chirality) increases, λ_0 decreases and the optical activity passes through zero at some wavelength between 0·78 and 1·1 μm. As is evident from some of the BP III spectra, λ_0 falls below the wavelength region investigated in some of the mixtures with the highest chirality. These spectra show a maximum on the positive side, followed by an asymptotic decrease toward zero.

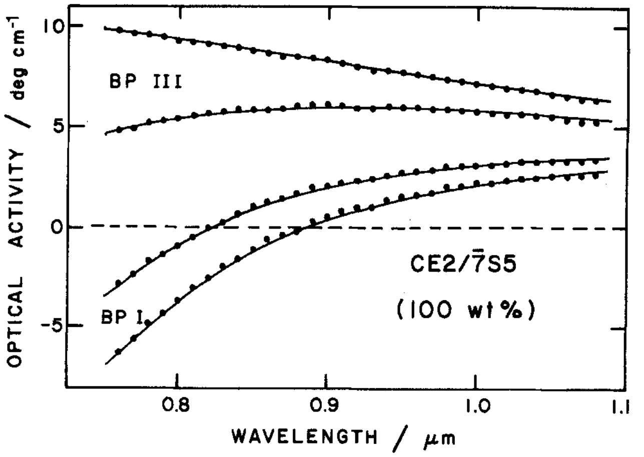

Figure 4. Optical activity spectra for four temperatures in pure CE2. The lines are least-squares fits to equation (1).

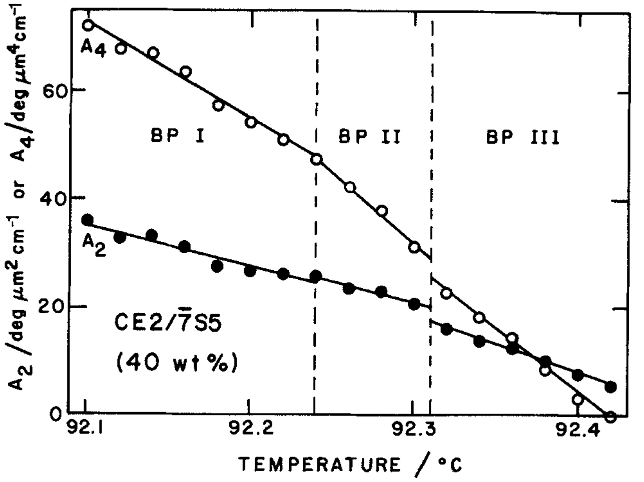

Figure 5. Dependence of the coefficients in equation (1) on temperature in the mixture containing 40 wt % CE2. The lines are linear least-squares fits to the data in each phase.

The values of A_2 and A_4 obtained from the least-square fits to equation (1) are plotted versus temperature in figures 5–8. The transitions between the blue phases are usually evident as a discontinuity. Least-squares linear fits to the data have been included in figures 5–8 to show these discontinuities. Notice that A_4 decreases relative to A_2 as the chirality increases.

The transition from BP III to the isotropic liquid is evident from a change in the temperature dependence of A_2. This is shown in detail for the 100 wt % CE2 sample in figure 9. Also of interest is the observation that A_4 passes through zero in the vicinity of the transition. In fact, for all four mixtures the temperature at which the linear least-squares fit to the BP III A_4 data passes through zero equals the transition temperature as determined by the A_2 data, to within experimental uncertainty. This

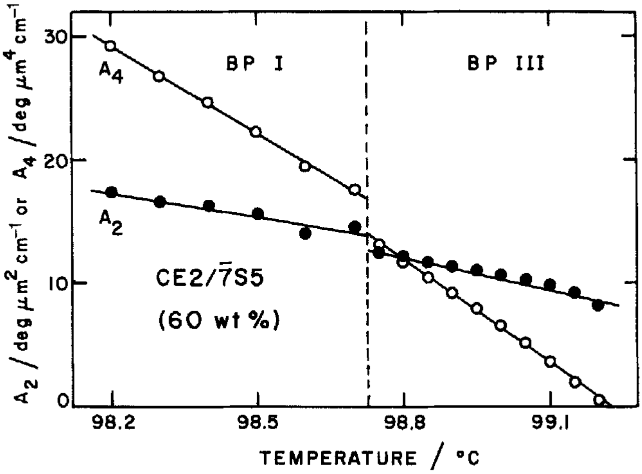

Figure 6. Dependence of the coefficients in equation (1) on temperature in the mixture containing 60 wt % CE2. The lines are linear least-squares fits to the data in each phase.

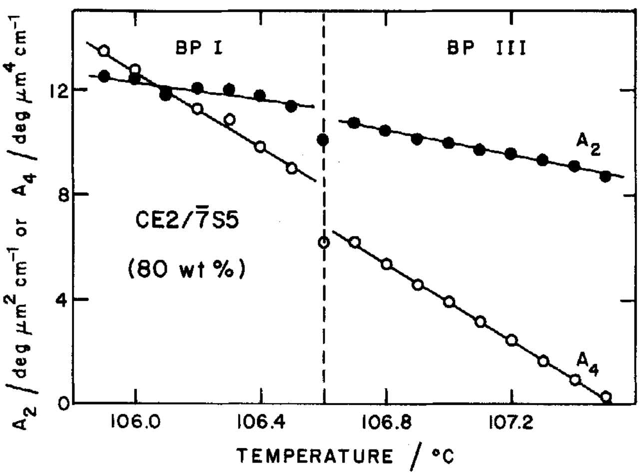

Figure 7. Dependence of the coefficients in equation (1) on temperature in the mixture containing 80 wt % CE2. The lines are linear least-squares fits to the data in each phase.

uncertainty ranges from 0·02 K in the 40 wt % CE2 mixture to 0·2 K in the 100 wt % CE2 mixture.

5. Discussion

As is evident from the results, the data follow the theoretical relationship fairly well. As far as the temperature dependence of the factors A_2 and A_4 is concerned, for two reasons they are expected to decrease as the temperature is increased. First, the amplitude of the Fourier components probably decrease as the temperature increases. Secondly, since q decreases as the temperature increases in these mixtures, equations (2) and (3) also predict that this should cause A_2 and A_4 to decrease. Since A_2 depends on q_i^{-1} and A_4 depends on q_i^{-3}, A_4 should decrease more rapidly than A_2. This is indeed the case. To check whether the data actually follow these functional relationships,

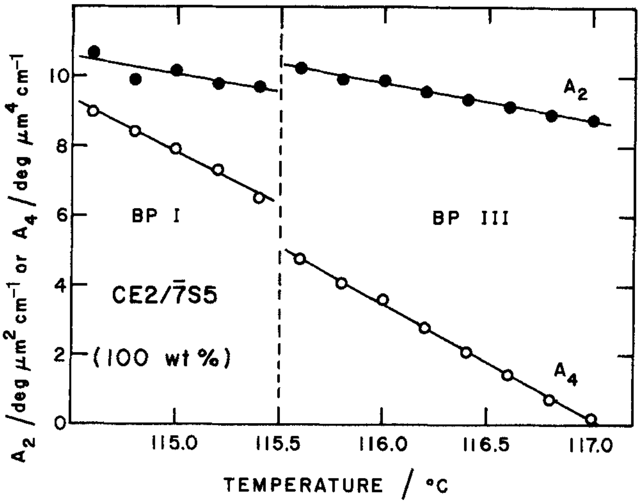

Figure 8. Dependence of the coefficients in equation (1) on temperature in pure CE2. The lines are linear least-squares fits to the data in each phase.

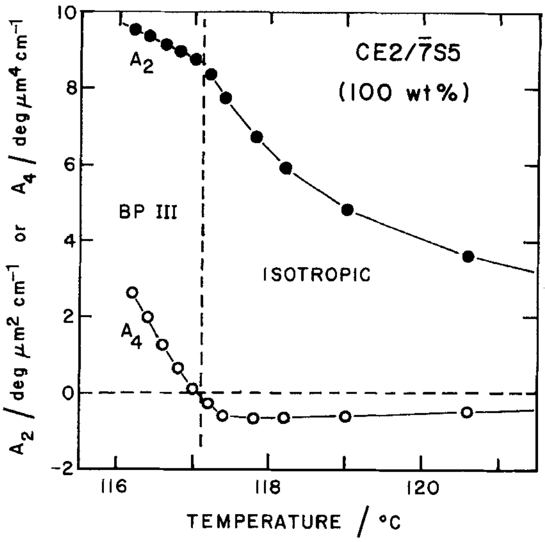

Figure 9. Dependence of the coefficients in equation (1) on temperature in the vicinity of the BP III–isotropic transition in pure CE2. The lines have been added to aid the eye.

values for $A_2 q_0$ and $A_4 q_0^3$ were calculated for all four mixtures at certain points in the phase diagram. q_0 is the chirality of the cholesteric phase, so the wavevectors in a blue phase should be proportional to q_0. According to the theory, these calculated values for any one blue phase should be constant from one mixture to the next, provided the Fourier component amplitudes in the mixtures remain the same.

The results are presented in tables 1 and 2. Notice that the values for $A_2 q_0$ are fairly constant for BP I, both near the cholesteric phase and near the transition to either BP II or BP III. This is not true for the values in BP III near the isotropic transition. In addition, the values for $A_4 q_0^3$ are not constant even in BP I. Although some of this

Table 1. Values of A_2q_0 at three points in the phase diagram for four mixtures of CE2/7S5.

	A_2q_0/degrees		
wt % CE2	Ch–BP I	BP I–BP II/BP III	BP III–I
40	0·18	0·13	0·03
60	0·13	0·11	0·06
80	0·12	0·11	0·08
100	0·13	0·12	0·11

Table 2. Values of $A_4q_0^3$ at two points in the phase diagram for four mixtures of CE2/7S5.

	$A_4q_0^3$/degrees	
wt % CE2	Ch–BP I	BP -BP II/BP III
40	920	610
60	1200	710
80	1200	820
100	1800	1300

variation could be explained by higher Fourier component amplitudes in the more chiral mixtures, it is difficult to imagine the factor of 2 or 3, which is necessary to explain these results, resulting from such an effect. Thus, all aspects of the data cannot be accounted for within the theory.

Since the wavevectors become larger and the Fourier amplitudes most likely decrease at the transition to BP III from either BP I or BP II, we expect A_2 and A_4 to decrease at these transitions. This is true for A_4 but not for A_2. A_2 does decrease at the BP I–BP III transition in the 60 wt % CE2 mixture and perhaps in the 80 wt % CE2 mixture, but it increases in the 100 wt % CE2 sample. Such an increase cannot be explained in the context of the theory.

Finally, the theoretical coefficients A_2 and A_4 must always be positive. The fact that A_4 passes through zero is therefore quite unexpected. Such behaviour might be explained by the fact that in the isotropic phase, where the optical activity is due only to fluctuations, A_4 is negative. If fluctuations in the order parameters are also present in the blue phases, it may be that these tend to decrease the value of A_4. Whether there is significance in the fact that the transition occurs in the region where A_4 equals zero remains an open question.

The behaviour of A_2 also seems to imply that fluctuations in the order parameters are important in the blue phases. As can be seen in figure 9, A_2 is positive in the isotropic phase, but more importantly, there is little discontinuity in its value at the BP III–isotropic transition. The fact that A_2 is of similar magnitude in both BP III and the isotropic phase introduces the possibility that much of its value in BP III is due to order parameter fluctuations. If the fluctuations in the order parameters become more important the higher the chirality is, this could explain why A_2q_0 increases as the chirality increases.

6. Conclusion

Measurement of the optical activity at long wavelengths in highly chiral liquid crystals is a useful method to investigate blue phases. The data from such measurements both confirm some of the important theoretical ideas and raise significant questions concerning the role of order parameter fluctuations, which are not taken into account by the theory. Further work into the importance of fluctuations (especially in BP III), both theoretical and experimental, is certainly needed. Whether fluctuations are important for the stability of BP III or whether the fact that A_4 goes to zero at the isotropic phase transition is theoretically important are two interesting questions.

Our measurements in the isotropic phase also raise crucial questions concerning the calculation of optical activity due to pretransitional fluctuations. We intend to report on these results in the near future.

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References

[1] Recent reviews include: Belyakov, V. A., and Dmitrienko, V. E., 1985, *Usp.fiz. Nauk*, **146**, 369 (1985, *Soviet Phys. Usp.*, **28**, 535). Stegemeyer, H., Blumel, Th., Hiltrop, K., Onusseit, H., and Porsch, F., 1986, *Liq. Crystals*, **1**, 3. Cladis, P. E., 1987, *Theory and Applications of Liquid Crystals*, edited by J. L. Ericksen and D. Kinderlehrer (Springer-Verlag), p. 73.

[2] Grebel, H., Hornreich, R. M., and Shtrikman, S., 1983, *Phys. Rev.* A, **28**, 1114; 1984, *Ibid.* **30**, 3264.

[3] Gorman, J. W., Jr, and Crooker, P. P., 1985, *Phys. Rev.* A, **31**, 910.

[4] Marcus, M., 1982, *Phys. Rev.* A, **25**, 2276.

[5] Bensimon, D., Domany, E., and Shtrikman, S., 1983, *Phys. Rev.* A, **28**, 427.

[6] Neubert, M. E., Organic Synthesis and Purification Group, Liquid Crystal Institute, Kent State University.

[7] Miller, J. D., Battle, P. R., Collings, P. J., Yang, D. K., and Crooker, P. P., 1987, *Phys. Rev.* A, **35**, 3959.

[8] Battle, P. R., Miller, J. D., and Collings, P. J., 1987, *Phys. Rev.* A, **36**, 369.