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^{13}C NMR spectral assignments for nematic liquid crystals by 2D chemical shift γ -encoding NMR

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Abstract

A novel method to accomplish ^{13}C NMR spectral assignments for nematic liquid crystals is proposed. The two-dimensional (2D) isotropic/anisotropic chemical shift correlation spectrum is observed in which the anisotropic shift parameters are represented as sharp lines by γ -encoding. The ^{13}C spectral assignments can be made from the 2D spectrum with the aid of the ^{13}C isotropic shift assignments for the same compound in the isotropic liquid state. The experiments were performed on *p*-methoxybenzilidene-*p*-*n*-butylaniline. © 2002 Elsevier Science (USA). All rights reserved.

Keywords: Liquid crystal; Spectral assignment; γ -Encoding; ^{13}C NMR; Off-magic-angle spinning

1. Introduction

^{13}C NMR spectral assignments for nematic liquid crystals are sometimes difficult due to the presence of anisotropic interactions, which cause shifts in peak positions [1]. Each peak in the ^{13}C spectrum of a liquid crystal should have the corresponding peak in the ^{13}C spectrum of the same molecule in the isotropic liquid state and vice versa. When one obtains the one-to-one peak correspondences between the two phases, one can accomplish the spectral assignments for the liquid crystal with the aid of those for its isotropic liquid, which can be prepared by raising the temperature above the nematic–isotropic transition point or by solving the liquid crystal into a solvent. To obtain the one-to-one correspondences, several devised methods were proposed [2–7], which are based on the manipulation of the director orientation, as described below. Using variable angle spinning [2–4] or mixed liquid crystals having diamagnetic anisotropies with signs opposite to each other [5], one can obtain the spectra for several director orientations, from which one can deduce the one-to-one

correspondences. However, it is sometimes difficult to obtain the one-to-one correspondences due to overlap of the peaks. Motor-driven reorientation of the liquid crystalline director [6,7] gives two-dimensional (2D) anisotropic/anisotropic chemical shift correlation spectra between two distinct orientations, in which overlapped peaks in complex 1D spectra may be two-dimensionally separated. Temperature-jump 2D NMR [8,9], stopping rotation [10], and switching angle sample spinning [11] can also provide 2D correlation spectra that are useful for spectral assignments. However, these experiments need special equipment.

In this paper, we propose a novel method to obtain a 2D isotropic/anisotropic ^{13}C chemical shift correlation spectrum of a nematic liquid crystal. Recently, we proposed some γ -encoded sequences and γ -encoding transformation of the free induction decay (FID) [12,13] to obtain γ -encoded spectra of uniaxially oriented material, which show sharp peaks at the positions σ_2 ; on the other hand, off-magic-angle spinning (OMAS) represents sharp peaks at $\bar{\sigma}$, where σ_2 and $\bar{\sigma}$ are different linear combinations of the chemical shift anisotropy (CSA) principal values, as described below. Using one of the γ -encoding methods at an OMAS condition, the 2D anisotropic/anisotropic chemical shift correlation spectrum can be observed, representing the γ -encoded spectrum in one dimension and the OMAS spectrum in

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the other dimension [12]. We show that this 2D correlation spectrum can be transformed into the 2D isotropic/anisotropic chemical shift correlation spectrum by a simple numerical procedure. Thus, the spectral assignments for the nematic liquid crystal are made from the 2D correlations with the aid of assignments for its isotropic liquid.

2. Theory

We consider an isolated ^{13}C spin in a nematic liquid crystal under sample spinning, assuming that both the chemical shift tensor and the magnetic susceptibility tensor are axially symmetric around the director. When a nematic liquid crystal with positive (negative) magnetic susceptibility anisotropy $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ is spun in the magnetic field with the spinning axis inclined from the magnetic field direction by an angle larger (smaller) than the magic angle θ_m , the directors are distributed in planes perpendicular to the spinning axis [3,14,15]. Under this condition, the principal axis system (PAS) of the chemical shift tensor is uniformly distributed around the spinning axis. Thus, this sample composes a uniaxially oriented system with the symmetry axis parallel to the spinning axis. In the following, we assume that this condition is satisfied.

We define the director-fixed frame with the z^{dir} and x^{dir} axes parallel to the director and spinning axes, respectively, the rotor-fixed frame with the z^{rot} axis parallel to the spinning axis, and the laboratory frame with the z^{lab} axis parallel to the magnetic field direction. The transformation from the director-fixed frame to the rotor-fixed frame is expressed by the Euler angles $(0, \pi/2, \gamma)$, for which we use Rose's definition [16]. The angle γ represents the orientation of the director around the z^{rot} axis and is uniformly distributed from 0 to 2π . The transformation from the rotor-fixed frame to the laboratory frame is described by $(\omega_r t, \theta, 0)$, where ω_r is the angular velocity of sample spinning, and θ is the angle between the z^{rot} and z^{lab} axes. The time-dependent resonance frequency of a ^{13}C spin packet under ^1H decoupling is written as [12,17]

$$\omega(\gamma, t) = \omega_0[\bar{\sigma} + \sigma_2 \cos 2(\omega_r t + \gamma + \delta)] \quad (1)$$

with

$$\sigma_2 = \frac{1}{2} |\sigma_{\parallel} - \sigma_{\perp}| \sin^2 \theta, \quad (2)$$

$$\bar{\sigma} = \sigma^{\text{iso}} - \frac{1}{3} P_2(\cos \theta)(\sigma_{\parallel} - \sigma_{\perp}), \quad (3)$$

$$\sigma^{\text{iso}} = \frac{2\sigma_{\perp} + \sigma_{\parallel}}{3}, \quad (4)$$

$$\delta = \begin{cases} 0 & \text{for } \sigma_{\parallel} - \sigma_{\perp} > 0, \\ \pi/2 & \text{for } \sigma_{\parallel} - \sigma_{\perp} < 0, \end{cases} \quad (5)$$

where σ_{\parallel} and σ_{\perp} are the chemical shift tensor components parallel and perpendicular to the director, respectively. The line broadening due to the γ dependence of the resonance frequency $\omega(\gamma, t)$ is removed by sample spinning and the center band appears at $\bar{\sigma}$.

Recently, we reported that the high resolution spectrum peaked at $\mu\sigma_2$ can be obtained for uniaxially oriented material by chemical shift γ -encoding under sample spinning with the symmetry axis parallel to the spinning axis [12], where μ is the scaling factor given in reference [12] for several pulse sequences. We can obtain the 2D anisotropic/anisotropic chemical shift correlation spectrum peaked at $(\mu\sigma_2, \bar{\sigma})$ for a uniaxially oriented sample: one of the proposed γ -encoding methods is applied during the t_1 period, and the OMAS spectrum is observed in the t_2 period. Since $(\sigma_{\parallel} - \sigma_{\perp}) \sin^2 \theta/2$ is equal to σ_2 or $-\sigma_2$, we obtain the 2D anisotropic/anisotropic chemical shift correlation $(\mu(\sigma_{\parallel} - \sigma_{\perp}) \sin^2 \theta/2, \bar{\sigma})$ spectrum by symmetrizing the $(\mu\sigma_2, \bar{\sigma})$ spectrum with respect to the $\sigma_2 = 0$ axis. This 2D correlation spectrum, however, includes the false peak for the wrong sign of $\sigma_{\parallel} - \sigma_{\perp}$: when the peak at $(-\mu|\sigma_{\parallel} - \sigma_{\perp}| \sin^2 \theta/2, \bar{\sigma})$ is true, the peak at $(\mu|\sigma_{\parallel} - \sigma_{\perp}| \sin^2 \theta/2, \bar{\sigma})$ is false and vice versa. Considering the fact that the spectrum of the liquid crystal under static conditions is peaked at $\sigma^{\text{sta}} = \sigma_{\parallel}$ for positive $\Delta\chi$ and at $\sigma^{\text{sta}} = \sigma_{\perp}$ for negative $\Delta\chi$ [1], one can understand that the 2D isotropic/anisotropic chemical shift correlation spectrum which is peaked at $(\sigma^{\text{iso}}, \sigma^{\text{sta}})$ can be obtained from the 2D correlation $(\mu(\sigma_{\parallel} - \sigma_{\perp}) \sin^2 \theta/2, \bar{\sigma})$ spectrum using a linear transformation:

$$\begin{pmatrix} \sigma^{\text{iso}} \\ \sigma^{\text{sta}} \end{pmatrix} = \begin{pmatrix} \frac{3\cos^2\theta-1}{3\mu\sin^2\theta} & 1 \\ \frac{\cos^2\theta+1}{\mu\sin^2\theta} & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2}\mu(\sigma_{\parallel} - \sigma_{\perp}) \sin^2 \theta \\ \bar{\sigma} \end{pmatrix} \quad (6)$$

for positive $\Delta\chi$ and

$$\begin{pmatrix} \sigma^{\text{iso}} \\ \sigma^{\text{sta}} \end{pmatrix} = \begin{pmatrix} \frac{3\cos^2\theta-1}{3\mu\sin^2\theta} & 1 \\ -\frac{1}{\mu} & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2}\mu(\sigma_{\parallel} - \sigma_{\perp}) \sin^2 \theta \\ \bar{\sigma} \end{pmatrix} \quad (7)$$

for negative $\Delta\chi$. The true and false peaks appear equidistantly from the point $(\bar{\sigma}, \bar{\sigma})$, on the line passing the point and parallel to the vector $\vec{v} = (\cos^2 \theta - 1/3, \cos^2 \theta + 1)$ for positive $\Delta\chi$ and $\vec{v} = (\cos^2 \theta - 1/3, \cos^2 \theta - 1)$ for negative $\Delta\chi$. Since the angle θ is set to an angle larger (smaller) than θ_m for positive (negative) $\Delta\chi$, Eq. (6) (Eq. (7)) shows that the peak for positive $\sigma_{\parallel} - \sigma_{\perp}$ appears in the region $\sigma^{\text{sta}} > \sigma^{\text{iso}}$ ($\sigma^{\text{sta}} < \sigma^{\text{iso}}$) and that for negative $\sigma_{\parallel} - \sigma_{\perp}$ appears in $\sigma^{\text{sta}} < \sigma^{\text{iso}}$ ($\sigma^{\text{sta}} > \sigma^{\text{iso}}$).

We can distinguish between the true and false peaks by comparing the 2D correlation $(\sigma^{\text{iso}}, \sigma^{\text{sta}})$ spectrum with both the 1D spectra of the nonspinning liquid crystal and those of its isotropic liquid: the true peak at $(\sigma^{\text{iso}}, \sigma^{\text{sta}})$ in the 2D correlation spectrum should have the corresponding peaks at σ^{sta} and σ^{iso} in the 1D spectra of the liquid crystal and those of its isotropic liquid, respectively, and the false peak does not. Thus,

we can obtain the one-to-one peak correspondences between the spectra of the static liquid crystal and those of its isotropic liquid. We can also identify the true peak by making the 2D experiment at a different angle θ : the position of the true peak does not depend on the angle θ , while that of the false peak does depend on θ .

3. Experimental

A uniaxial nematic liquid crystal of *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA), which has positive $\Delta\chi$ [18], was obtained from Tokyo Kasei, and was used without further purification. Liquid crystal MBBA was directly filled in a 5 mm o.d. rotor, which was capped with tight Teflon spacers near the liquid N₂ temperature. A 9 mm sample length shorter than the sample coil length of 14 mm was used to reduce the rf-field inhomogeneity.

The NMR experiments were performed on a Chemagnetics CMX-300 spectrometer under a magnetic field of 7.1 T. The sample temperature was controlled at 301 K within a fluctuation of 1° by a Chemagnetics REX-C1000 variable temperature unit. We adjusted an angle θ by comparing the CSA powder pattern of the carbonyl carbon in *L*-alanine under OMAS conditions with that for the static sample. The length of composite inversion pulses was set to 40 μ s, corresponding to an rf-field strength of 25 kHz. CW ¹H decoupling during the t_1 period and TPPM ¹H decoupling [19] during the acquisition were used. The ¹H rf-field strength was set at a low level of 33–50 kHz for CW decoupling and 33–

34 kHz for TPPM decoupling to avoid the sample heating [20] during ¹³C pulse intervals, while it was increased to 51–77 kHz for CW decoupling during ¹³C irradiation to avoid ¹H–¹³C recoupling [21]. Cross-polarization with a contact time of 2–5 ms was employed.

2D INADEQUATE experiments [22,23] for the 70 wt% CDCl₃ solution of MBBA were made at ambient temperature, using a JEOL Lambda 500 spectrometer operating at 125 MHz for ¹³C.

4. Results and discussion

First, spectral assignments for the CDCl₃ solution of MBBA were accomplished by 2D INADEQUATE experiments. The δ - γ - β - α -4 linkage and the 4-3-2-1 and 7-1'-2'-3'-4' linkages were deduced from the spectra shown in Fig. 1a and b, respectively, with the aid of the 1D ¹³C ¹J_{CH}-split spectrum (not shown), by which the knowledge of the proton numbers attached to the ends of the individual linkages was acquired. The assignments agree with partial assignments reported in the spectral database system SDBS [24], but disagree with the result of a hetero-COSY experiment [5], in which the cross-peaks via ³J_{CH} were mistaken for those via ²J_{CH} [25].

The 2D ($\sigma^{\text{iso}}, \sigma^{\text{sta}}$) ¹³C spectrum of liquid crystal MBBA was obtained as follows. The composite inversion pulse train (CIPT) [12] consisting of four composite inversion pulses within the one-rotor period under phase cycling (X, X, -X, -X, -X, -X, X, X) was applied in the

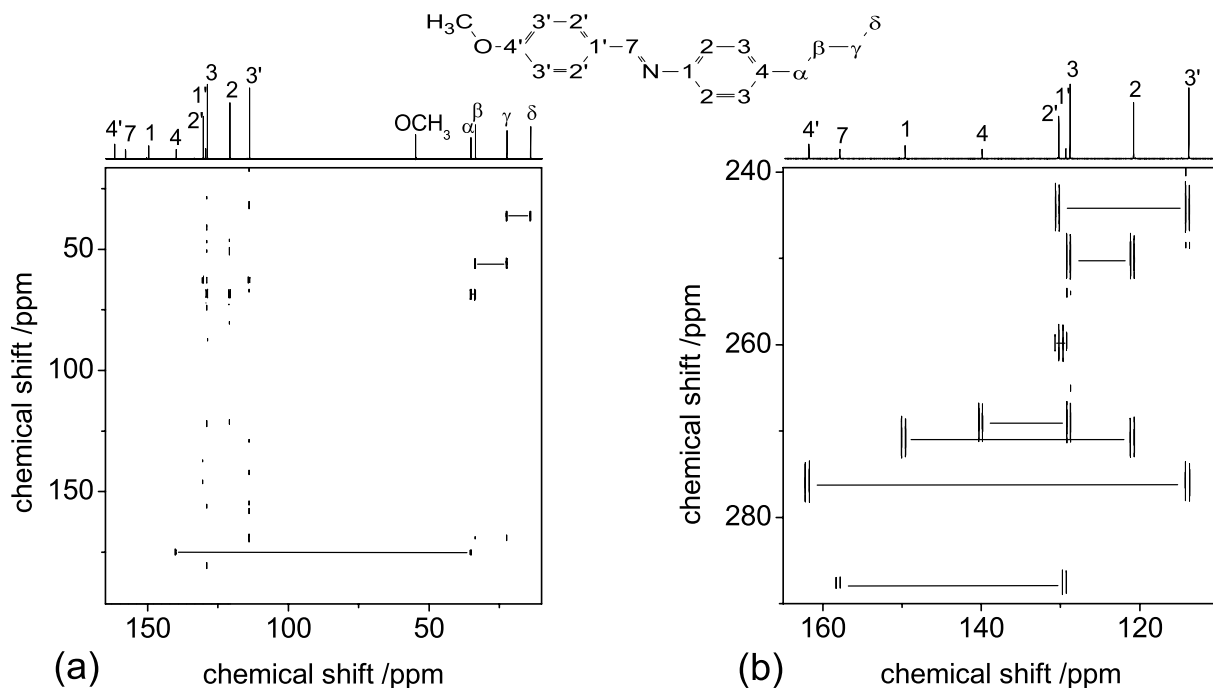


Fig. 1. ¹³C NMR spectra of MBBA/CDCl₃. Upper traces: ¹H-decoupled. 2D spectra: INADEQUATE spectra observed with $\tau = 7.1$ ms (corresponding to $J_{CC} = 35$ Hz) (a) and $\tau = 4.2$ ms (corresponding to $J_{CC} = 60$ Hz) (b).

t_1 period, and the FID in the t_1 period was transformed to the γ -encoded spectrum by γ -encoding transformation [12,13]. In the t_2 period, the OMAS signal was recorded. CIPT is somewhat sensitive to the resonance offset so that the rf-field should be applied within ± 2 kHz from $\bar{\sigma}$ [12]. To fulfill this condition, we observed the 2D spectrum by dividing it into the following two regions: the aliphatic region from 10 to 60 ppm and the aromatic region from 100 to 220 ppm. The experiments were performed at $\theta = 90^\circ$ and 63° for each region. The 2D $(\sigma_2, \bar{\sigma})$ spectra thus obtained were converted to the 2D $(\sigma^{\text{iso}}, \sigma^{\text{sta}})$ spectra using Eq. (6). The results for the aromatic and aliphatic regions are shown in Figs. 2 and 3, respectively. The 1D spectra of the isotropic solution and those of the static liquid crystal are also shown in each figure.

We have theoretically shown that in the 2D $(\sigma^{\text{iso}}, \sigma^{\text{sta}})$ spectrum the true and false peaks appear on the straight line parallel to the vector $\vec{v} = (\cos^2 \theta - 1/3, \cos^2 \theta + 1)$ and passing the point $(\sigma^{\text{iso}}, \sigma^{\text{sta}}) = (\bar{\sigma}, \bar{\sigma})$, being equidistant from the point on both sides, and that the true peak connects a peak in the solution spectrum to that in the liquid crystal spectrum. Pairs of true and false peaks can be found using the above geometrical features, and only one peak (true peak) of the pair connects peaks between the two 1D spectra. Thus, we can assign the individual peaks in the liquid crystal spectrum to the carbons of the

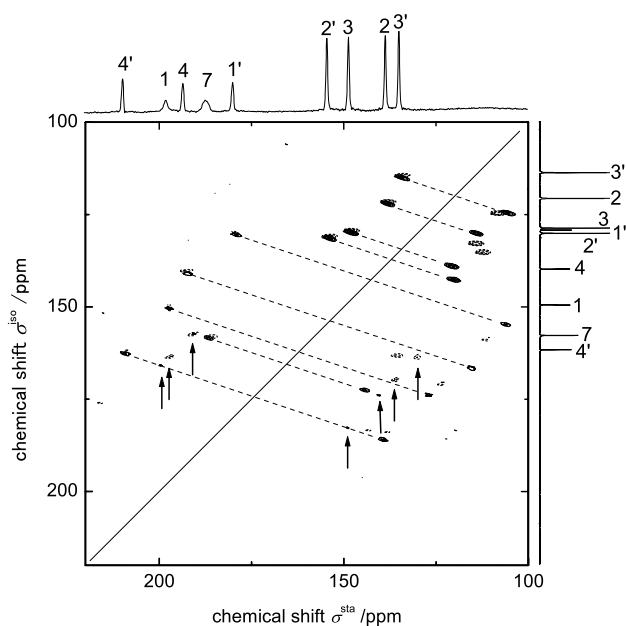


Fig. 2. ^{13}C NMR spectra for the aromatic part of MBBA. Upper trace: static liquid crystal. Right trace: CDCl_3 solution. 2D spectrum: the 2D isotropic/anisotropic chemical shift correlation spectrum observed at $\theta = 90^\circ$ with $\omega_r/2\pi = 2200$ Hz (solid line) and that at $\theta = 63^\circ$ with $\omega_r/2\pi = 1770$ Hz (dotted line). The solid arrows indicate peaks caused by cycling sidebands [27]. The spectral assignments for the isotropic solution were made by INADEQUATE experiments (Fig. 1) and those for the liquid crystal were obtained from the 2D correlation spectra (see text).

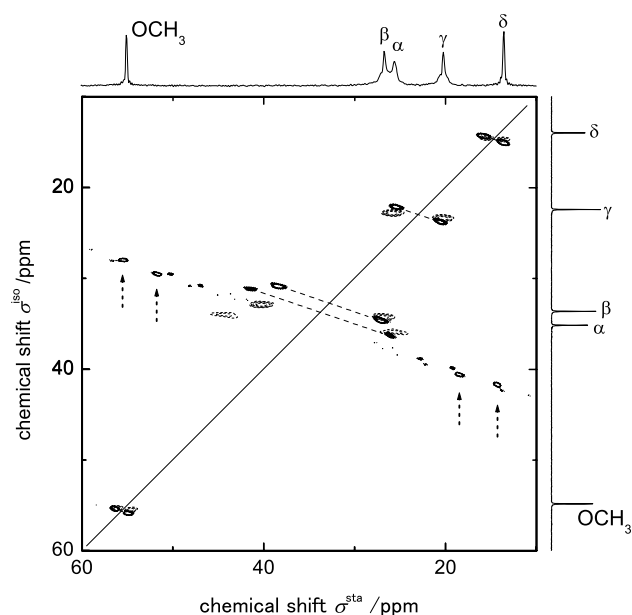


Fig. 3. ^{13}C NMR spectra for the aliphatic part of liquid crystal MBBA. The 2D isotropic/anisotropic chemical shift correlation spectrum observed under OMAS conditions at $\theta = 90^\circ$ with $\omega_r/2\pi = 2200$ Hz (solid line) and at $\theta = 63^\circ$ with $\omega_r/2\pi = 2120$ Hz (dotted line). The dotted arrows indicate the DC noise. The others are the same as in Fig. 2.

liquid crystal molecule, if the resonance assignments of the solution spectrum have been accomplished. In Figs. 2 and 3, each pair of true and false peaks is shown by connecting the peaks by a broken line parallel to the vector $(-1/3, 1)$ for the 2D spectra obtained at $\theta = 90^\circ$; the paired peaks are equidistant from the diagonal solid line of $\sigma^{\text{iso}} = \sigma^{\text{sta}}$. As an example, let us consider the pair of peak (125, 105) ppm and peak (115, 135) ppm. The former peak corresponds to no peaks in the 1D spectrum of either the liquid crystal or the solution, while the latter has the corresponding peaks in both 1D spectra. Therefore, the latter peak is the true peak, and the peak at 135 ppm in the 1D liquid crystal spectrum is assigned to carbon 3'. In the same way, such one-to-one correspondence was found for all the other carbons, and the spectral assignments were made for the liquid crystal of MBBA, as shown in the upper traces of Figs. 2 and 3. The present spectral assignments for liquid crystal MBBA agree with those previously accomplished using some selectively ^2H and ^{15}N labeled samples [26]. The present method enables us to accomplish the spectral assignments for nematic liquid crystals using a ^{13}C naturally abundant sample, that is, without necessity of such elaborate sample preparation.

In addition to the true and false peaks, some more peaks appear in Fig. 2, which are ascribed to cycling sidebands [27]: in the t_1 period, the signals were observed every rotation period $2\pi/\omega_r$ shorter than the cycle time $4\pi/\omega_r$ of CIPT with the phase cycling scheme of (X, X, -X, -X, -X, -X, X, X), to extend the spectral width. When $\mu\sigma_2$ is close to $\omega_r/4\pi$, i.e., when a peak appears near

a cycling sideband, the intensity of the cycling sideband increases [28], as shown by the peak of carbon 7. However, the intensities of the other cycling sidebands are reasonably weak, and therefore do not hinder the analysis.

Overlapping the 2D spectra observed at $\theta = 90^\circ$ and 63° , we can also discriminate the true and false peaks as described in Theory: the overlapped peaks are true and the others are false. In a complex system, it might be difficult to choose the true peaks from a single 2D correlation spectrum and the two 1D spectra, because of overlap of peaks in the 1D spectra. The 2D spectrum observed at a different angle θ would help us to choose the true peaks even in a complex spectrum, since peaks overlapped in the 1D spectra may be separated in the 2D spectrum. However, one should pay attention to the fact that overlap of peaks in the two 2D spectra may occur even for a false peak accidentally or because of small anisotropy.

In the above analysis, we used the 2D correlation spectra of $(\sigma^{\text{iso}}, \sigma^{\text{sta}})$ to obtain the one-to-one peak correspondences between the spectra of the static liquid crystal and its isotropic solution. It should be noted that other representations of the 2D correlation spectrum such as $(\sigma^{\text{iso}}, \bar{\sigma})$ and $(\sigma_{\parallel} - \sigma_{\perp}, \bar{\sigma})$, which are easily obtained by transformation similar to that shown in Eq. (6) or Eq. (7), may be more convenient for some purpose other than $(\sigma^{\text{iso}}, \sigma^{\text{sta}})$. For example, the $(\sigma_{\parallel} - \sigma_{\perp}, \sigma^{\text{iso}})$ representation is suitable for the determination of the $\sigma_{\parallel} - \sigma_{\perp}$ values.

The present method provides a powerful procedure to obtain spectral assignments for nematic liquid crystals. As far as the homogeneous orientation of directors is preserved under OMAS conditions, the present method can be applied to any uniaxial liquid crystals, which include not only the nematic liquid crystals but also the smectic liquid crystals in the uniaxial phase.

Acknowledgments

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