Noncoincidence Effects of Dimethyl Carbonate in Binary Mixtures Probed by Raman Spectroscopy: Experimental and DFT Calculations

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Supporting Information

ABSTRACT: The components of isotropic Raman and anisotropic Raman for dimethyl carbonate (DMC) dispersed in cyclohexane and acetone at different volume fractions were recorded separately. The noncoincidence effects (NCE) of the $\nu(C=O)$ stretching mode were calculated accordingly. The NCE values ($\Delta\nu_{\text{NCE}}$) of the $\nu(C=O)$ versus DMC volume fractions in the DMC/C$_6$H$_{12}$ mixtures exhibits a convex (upward) curvature pattern, while the $\Delta\nu_{\text{NCE}}$ vs concentration in the DMC/CH$_3$COCH$_3$ mixtures exhibits a concave (downward) curvature. These different NCE behaviors in the different binary mixtures may arise from the solvent-induced aggregation character. Thus, monomer and dimer structures of DMC were optimized and the vibration spectra were obtained using density functional theory (DFT) calculations. An aggregation model was suggested to expound the DMC’s characteristic NCE behavior and concentration effect. We found that the theoretical spectra from DFT/polarizable continuum model calculation based on the aggregation model is in accordance with our experimental data. Solvent-dependent experiments show the $\Delta\nu_{\text{NCE}}$ values increase with the decrease of the solvent dielectric constant under the identical volume fractions.

INTRODUCTION

Most of the reactions take place in the liquid phase in the form of mixtures, and various molecular interactions like solute–solute, solute–solvent, and solvent–solvent interactions are present in the solution. The competition between these interactions plays a crucial role in determining ground-state and transition-state structures, reaction pathway and kinetics, activation energy, etc. For a binary solute–solvent solution, the dilution process of the solution results in three effects, i.e., breaking of the solute aggregation structure, changes in absolute Raman cross section, vibrational line full width at half-maximum, and the value of noncoincidence effects. Of course, solvents can also cause more profound effects, such as solubility, equilibrium geometry structure, and aggregation behavior in their ground state. In this paper, we report the intermolecular interaction between solute–solute C=O vibration coupling and solute–solvent interaction of dimethyl carbonate (DMC) and their competition behavior in different concentrations or in various solvents by Raman spectroscopy. Based on the density functional theory (DFT) calculations and the isotropic and anisotropic Raman spectra assignment, we know that the interactions that are taking place between dimethyl carbonate and the solvent mainly come from the C=O group of dimethyl carbonate. Experiments show that the NCE of C=O stretch mode is a particularly meaningful index to intermolecular interactions, including transition dipole–transition dipole coupling (TD–TD) and van der Waals force, and demonstrate that isotropic Raman and anisotropic Raman
spectroscopy techniques provide dynamic molecular pictures of the competition between solute–solute and solute–solvent interactions with different concentrations and different solvents.

**RESULTS AND DISCUSSION**

The vibrational spectra have been calculated for DMC using DFT to assign and describe the molecular spectra obtained by Fourier transform infrared (FT-IR) and FT-Raman. Figure 1 shows the comparison among the FT-IR, FT-Raman, and micro-Raman spectra. Table 1 displays the DFT calculated vibrational wavenumbers with B3LYP-D3/6-311G(d,p) basis set, corresponding to the experimental vibrational frequencies obtained by FT-Raman and FT-IR accordingly. The corresponding data between the DFT calculated vibrational frequencies and the experimental vibrational frequencies is in good agreement. The dashed lines in Figure 1 illustrate the correlation of the vibrational frequencies in FT-IR to the corresponding frequencies in FT-Raman and micro-Raman, respectively. The noticeable frequency difference (17 cm⁻¹ frequency difference) of the C=O stretch mode obtained from the FT-Raman spectrum and FT-IR measurements is one key character of the noncoincidence effect. The C=O vibration TD–TD interaction may account for this noncoincidence effect. The TD–TD interaction organized the DMC in a short- or long-range orientation order; we proposed one aggregated dimer model, and the corresponding DFT calculations based on the DMC monomer and the proposed dimer structure had been carried out to manifest the rationality of the model. The comparison between these data and the isotropic and anisotropic Raman spectra at different concentrations will be discussed later.

Full conformational optimization for the DMC was performed to establish the most stable molecule structure as the initial geometry for further calculations. The polarizable continuum model (PCM) solvent model at the B3LYP-D3/6-311G(d,p) level of theory was applied to calculate the vibrational spectra of the DMC monomer and dimer dispersed in C₆H₁₂. Figure 2 demonstrates the calculated most stable structures of the monomer and dimer of DMC. The dimer geometry adopted a face-to-face, head-to-tail antiparallel pattern with intermolecular weak interaction. The as-calculated theoretical vibrational frequencies, their corresponding depolarization ratios, the assignment of experimental Raman and IR spectra, and the ZPE-corrected total energy of the monomer and dimer are given in Table 1. TD–TD interactions drive molecules to reorientate their alignment, reduce the molecular potential energy, and gain the most stable conformation. From Table 1 and Figure 2, we observe that the TD–TD coupling of a neighbor C=O stretching modes from the dimer differentiates the interaction in two ways. One interaction is synchronous and the second is asynchronous, which leads to a discrepancy in the C=O vibrational frequency and depolarization ratio. The synchronous C=O stretching frequency lies below the asynchronous one.

The DMC dimer has 24 atoms and produces 66 normal modes of vibration, in which 60 normal modes arise from the synchronous and asynchronous coupling between these two neighbor molecules and 6 normal modes come from the relative translation and rotation of these two neighbor molecules. The assignment and description of the experimental Raman and IR frequencies for monomer and dimer structures are listed in Table 1. Synchronous and asynchronous vibration patterns produce differences in vibrational wavenumbers; the value of these differences depend on the strength of interaction between neighbor molecules. The intermolecular interactions between different parts of the neighbor molecules have different strengths. The computed frequencies in Table 1 show that the intermolecular coupling in the dimer structure breaks the degeneracy of the individual vibrational level; however, only few interaction pairs split distinctly. These splits may still beyond the Raman resolution limits. Thanks to the prominent difference in the depolarization ratio of coupled C=O stretching pairs, we can take advantage of these differences to preferentially collect parallel and perpendicular polarized Raman spectra separately. With the parallel and perpendicular polarized Raman spectra, we can get the isotropic and anisotropic components of Raman spectra using the equation.

\[
I_{iso}(v) = I_{VV}(v) - \frac{4}{3}I_{VH}(v)
\]

\[
I_{aniso}(v) = I_{VH}(v)
\]

where \(I_{VV}(v)\) and \(I_{VH}(v)\) are experimentally collected Raman intensities of the polarized and depolarized Raman components, respectively, and \(v\) is the frequency in cm⁻¹. For the detailed meaning of \(VV\) and \(VH\), please see the Experimental and Computational Methods section.

Due to the significant difference in the depolarization ratio, this collected parallel or perpendicular polarized spectra preferentially get the relative small \(\rho\) component or large \(\rho\) of the C=O stretching pairs, respectively; these two \(\rho\) components for the C=O stretching pairs have different frequencies and, thus, present the noncoincidence effects of these two components, that is the so-called NCE phenomenon. In other words, only the interaction pairs with a distinct difference simultaneously in the vibrational frequency and depolarization ratio present the NCE phenomenon. By screening the DFT computed data in Table 1, only C=O vibration mode satisfies these terms. Figure 3 shows the isotropic and anisotropic components of Raman spectra of DMC for \(\nu_s(C=O)\) vibration. The isotropic component frequency at 1750.2 cm⁻¹ was ascribed to the computed...
frequency at 1793 cm\(^{-1}\). The anisotropic component at 1754.5 cm\(^{-1}\) was assigned to the calculated frequency at 1815 cm\(^{-1}\). Their corresponding depolarization ratios are 0.12 and 0.30. The frequencies calculated using the dimer model are consistent with the experimentally observed isotropic Raman and anisotropic Raman spectra.

Noncoincidence effects always come with the concentration effect. Figure 3 illustrates the polarized Raman spectra (isotropic and anisotropic parts) of DMC at various volume fractions in the DMC/C\(_6\)H\(_{12}\) mixture. It demonstrates that when the DMC concentration decreases, both of the polarized Raman frequencies of C==O stretch, including the isotropic and anisotropic Raman frequencies, increase. The NCE value (that is, \(\Delta V_{\text{NCE}} = v_{\text{aniso}} - v_{\text{iso}}\)) is 4.3 cm\(^{-1}\) for DMC, while it reduces to 1.9 cm\(^{-1}\) for DMC at \(\Phi_A = 0.4\) in the DMC/C\(_6\)H\(_{12}\) mixture. To explore the relationship between the changes in the frequency and the volume fraction, both the C==O stretching frequencies of the isotropic and anisotropic Raman spectra in six volume fractions, 0.900, 0.800, 0.700, 0.600, 0.500, 0.400 in the binary mixture (DMC + C\(_6\)H\(_{12}\)), as well as in pure DMC are abstracted from Figure 3, which were drawn as a function of concentration, as shown in Figure 4. The \(\Delta V_{\text{NCE}}\) will eventually becomes 0 at an extreme concentration \(\Phi_A\). The Raman frequencies of both components increase with the decrease of solute concentrations. Especially, the isotropic \(\nu\) (C==O) frequencies for neat DMC and \(\Phi_A\) (DMC in C\(_6\)H\(_{12}\)) of 0.400 are 1750.2 and 1754.0 cm\(^{-1}\), respectively. That is to say, the wavenumbers of isotropic C==O stretching become blue-shifted by 3.8 cm\(^{-1}\) from the highest to the lowest concentration of DMC, while other vibrational bands remain the same. The NCE value, that is, \(\Delta V_{\text{NCE}} = v_{\text{aniso}} - v_{\text{iso}}\) can be calculated from Figure 4 and is plotted with volume fractions in C\(_6\)H\(_{12}\), as shown in Figure 5. The \(\Delta V_{\text{NCE}}\) for the C==O stretching mode decreases upon dilution with C\(_6\)H\(_{12}\) from 4.30 cm\(^{-1}\) in neat DMC to 1.90 cm\(^{-1}\) at \(\Phi_A\) (DMC in C\(_6\)H\(_{12}\)) of 0.400. The change of \(\Delta V_{\text{NCE}}\) with dilution is due to the decrease in the TD--TD interaction. For the variation of isotropic and anisotropic Raman peak frequencies of C==O

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**Table 1. B3LYP-D3/6-311G(d,p) Computed Frequency, Depolarization Ratio, ZPE-Corrected Total Energy of the DMC Monomer and Dimer**

| modes | freq. | D. ratio | freq. | D. ratio | Raman | IR | descriptions |
|-------|-------|----------|-------|----------|-------|----|--------------|
| \(\nu_1\) | 3159  | 0.68     | 3166/3166 | 0.68/0.68 | H–C–H asymmetric stretch |
| \(\nu_2\) | 3153  | 0.62     | 3160/3160 | 0.68/0.68 | H–C–H asymmetric stretch |
| \(\nu_3\) | 3126  | 0.75     | 3144/3144 | 0.72/0.72 | H–C–H asymmetric stretch |
| \(\nu_4\) | 3122  | 0.75     | 3143/3143 | 0.74/0.74 | H–C–H asymmetric stretch |
| \(\nu_5\) | 3050  | 0.01     | 3061/3061 | 0.01/0.01 | H–C–H symmetric stretch |
| \(\nu_6\) | 3046  | 0.01     | 3059/3059 | 0.05/0.04 | H–C–H symmetric stretch |
| \(\nu_7\) | 1825  | 0.23     | 1815/1793 | 0.30/0.12 | 1753 | 1736 | C==O stretch |
| \(\nu_8\) | 1500  | 0.73     | 1507/1506 | 0.73/0.74 | H–C–H scissor |
| \(\nu_9\) | 1494  | 0.75     | 1503/1450 | 0.73/0.74 | H–C–H scissor |
| \(\nu_{10}\) | 1492 | 0.73     | 1497/1492 | 0.75/0.73 | H–C–H scissor |
| \(\nu_{11}\) | 1487 | 0.75     | 1488/1486 | 0.67/0.72 | H–C–H scissor |
| \(\nu_{12}\) | 1480 | 0.75     | 1486/1481 | 0.72/0.73 | H–C–H scissor |
| \(\nu_{13}\) | 1469 | 0.74     | 1468/1464 | 0.68/0.69 | 1460 | 1458 | H–C–H wag |
| \(\nu_{14}\) | 1275 | 0.48     | 1296/1272 | 0.62/0.55 | O–C–O stretch |
| \(\nu_{15}\) | 1213 | 0.43     | 1224/1221 | 0.46/0.50 | O–C–H wag |
| \(\nu_{16}\) | 1193 | 0.75     | 1203/1199 | 0.75/0.75 | O–C–H wag |
| \(\nu_{17}\) | 1178 | 0.75     | 1185/1185 | 0.72/0.72 | O–C–H wag |
| \(\nu_{18}\) | 1174 | 0.75     | 1176/1175 | 0.73/0.73 | C==O out-of-plane bend |
| \(\nu_{19}\) | 1110 | 0.55     | 1114/1114 | 0.53/0.53 | C==O out-of-plane bend |
| \(\nu_{20}\) | 1038 | 0.65     | 1040/1038 | 0.70/0.70 | C==O out-of-plane bend |
| \(\nu_{21}\) | 869  | 0.14     | 878/876  | 0.11/0.11 | O–C–H wag |
| \(\nu_{22}\) | 789  | 0.75     | 800/783  | 0.60/0.20 | O–C–H wag |
| \(\nu_{23}\) | 641  | 0.47     | 644/642  | 0.44/0.43 | CH3 rocking |
| \(\nu_{24}\) | 580  | 0.58     | 582/581  | 0.58/0.58 | CH3 rocking |
| \(\nu_{25}\) | 353  | 0.13     | 352/351  | 0.12/0.12 | CH3 rocking |
| \(\nu_{26}\) | 244  | 0.71     | 254/250  | 0.75/0.74 | CH3 rocking |
| \(\nu_{27}\) | 216  | 0.75     | 216/216  | 0.75/0.75 | CH3 rocking |
| \(\nu_{28}\) | 161  | 0.75     | 173/170  | 0.72/0.72 | CH3 rocking |
| \(\nu_{29}\) | 141  | 0.75     | 161/155  | 0.75/0.74 | CH3 rocking |
| \(\nu_{30}\) | 110  | 0.75     | 135/133  | 0.65/0.68 | CH3 rocking |
| \(\nu_{31}\) | 98   | 0.91     | 99/91    | 0.69/0.68 | CH3 rocking |
| \(\nu_{32}\) | 78   | 0.63     | 78/63    | 0.72/0.71 | relative translation |
| \(\nu_{33}\) | 43   | 0.28     | 43/28    | 0.73/0.75 | relative translation |

ZPE-corrected total energy (kJ/mol): 
- \(\nu\) monomer: \(\Delta E = HF(dimer) - 2HF(monomer) = -75.46\) kmol
- \(\nu\) dimer: \(HF = -20741474.10\)

Remarks: In the dimer, there are synchronous and asynchronous vibrational modes and the synchronous vibrational frequency is less than the asynchronous vibrational frequency.
stretching mode with volume fractions from 0.1 to 1, see the Supporting Information, S1.

The noncoincidence phenomenon between isotropic and anisotropic Raman spectra of the C=O mode in DMC implies that there may exist C=O coupling that degenerated the C=O vibration frequency by dipole−dipole interactions. Dipole−dipole coupling inclines to array the molecules to lower its total energy. During the dilution process, the emergence of a large number of solvent molecules isolate the reference molecules and weaken the dipole−dipole interaction, till the C=O coupling between the solute molecules breaks. In consideration of the low energy barrier (75.46 kJ/mol) between the DMC monomer and dimer from DFT calculations, it is easy to transform from dimer to monomer, and vice versa. During the dilution process, the DMC-aggregated dimer structure gradually separates and breaks into monomers; accordingly, the pattern of Raman spectra gradually switches from the dimer feature to the monomer feature. By scrutinizing the calculated frequencies for dimers in Table 1, only ν(C=O) coupling pairs present distinct vibrational frequency difference; moreover, their vibration frequencies (1815/1793 cm⁻¹) are all lower than that of the monomer (1825 cm⁻¹). These computed results are in accordance with the experimental data that we observed in Figure 3, that is, the frequency of C=O stretching blue-shifted upon the dilution process (dimer transforms to monomers) and simultaneously the peak sharpens and become symmetric. The value of ΔνNCE gets smaller and smaller upon dilution.

Until now, all positive and negative ΔνNCE cases have been reported, which depend on the orientation of the dipoles by TD−TD interactions. For the case of DMC, the ΔνNCE is positive and it takes on the antiparallel side-by-side interaction of the intermolecular C=O dipoles, which is shown in Figure 2. It is well known that the NCE phenomenon is a spectroscopic manifestation of the existence of the resonant intermolecular dipole−dipole coupling by the TD−TD interaction.28,29 This coupling results in the degeneration in energy of resonant dipole oscillators by assuming a short-range orientational order.21,28,30 The property and value of ΔνNCE depend on the pattern of short-range orientation and the strength of the TD−TD interaction. The Born−Oppenheimer approximation and all quantum chemistry state that the electric

Figure 2. B3LYP-D3/6-311G(d,p) computed geometry of DMC and its aggregates.

Figure 3. ν(C=O) vibration isotropic and anisotropic parts of the Raman spectra in the region 1710−1830 cm⁻¹ for DMC and six other volume fractions of DMC, 0.900, 0.800, 0.700, 0.600, 0.500, and 0.400 in the binary mixture (DMC + C₆H₁₂).

Figure 4. Variation of isotropic and anisotropic Raman peak frequencies of the C=O stretching mode of DMC as a function of solute volume fractions (DMC + C₆H₁₂).

Figure 5. Variation of NCE of C=O stretching mode of DMC as a function of solute volume fractions (DMC + C₆H₁₂).

Table 1, only ν(C=O) coupling pairs present distinct vibrational frequency difference; moreover, their vibration frequencies (1815/1793 cm⁻¹) are all lower than that of the monomer (1825 cm⁻¹). These computed results are in accordance with the experimental data that we observed in Figure 3, that is, the frequency of C=O stretching blue-shifted upon the dilution process (dimer transforms to monomers) and simultaneously the peak sharpens and become symmetric. The value of ΔνNCE gets smaller and smaller upon dilution.

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dipole moment remains constant at different concentrations. However, the fluctuation of the concentration of the reference molecules changes the relative alignment of the coupling dipoles. The decrease of the concentration leads to a weakening of the coupling between resonant dipole oscillators and results in the decrease of the value of $\Delta \nu_{\text{NCE}}$.

To investigate the dependence of NCE behavior on the solvents properties, especially on polarity of the solvents, the NCE measurements were extended to polar solvents such as CH$_3$COCH$_3$ and a thorough comparison was made between these two different polarity solvent data.

Similarly, we carried out the concentration dependence experiments also. The measured $\nu_{\text{iso}}$ and $\nu_{\text{aniso}}$ components of the C$=$O stretching mode vs volume fractions in DMC/CH$_3$COCH$_3$ mixtures are plotted and shown in Figure 6. From this, we learn that the $\nu_{\text{iso}}$ of C$=$O stretching (isotropic Raman frequency) increases with the dilution of DMC in DMC/CH$_3$COCH$_3$ mixtures, whereas the $\nu_{\text{aniso}}$ component decreases with the dilution of DMC. The fitted curve of DMC in DMC/CH$_3$COCH$_3$ mixtures displays a downward (concave) curvature feature, contrary to the upward (convex) fitted curve obtained for nonpolar solvents, as shown in Figure 4.

By drawing the values of $\nu_{\text{iso}}$ and $\nu_{\text{aniso}}$ components of C$=$O stretching, shown in Figure 6, we can calculate the $\Delta \nu_{\text{NCE}}$ values, which are shown in Figure 7. Figure 7 clearly shows that the fitted curve of $\Delta \nu_{\text{NCE}}$ vs volume fractions in DMC/CH$_3$COCH$_3$ mixtures presents a downward (concave) curvature feature. On the contrary, as shown in Figure 5, the upward (convex) curvature was obtained for the relationship of $\Delta \nu_{\text{NCE}}$ vs volume fractions in DMC/C$_6$H$_{12}$ mixtures. These results are the same as the rule found for acetone.$^{31}$ Moreover, this rule has been manifested by further MD simulations. They ascribed the phenomenon to the decrease (or the increase) of the dimer structure of DMC in the DMC/C$_6$H$_{12}$ mixture may account for the shift of peak frequencies.

Figures 5 and 7 show that the character of $\Delta \nu_{\text{NCE}}$ behavior largely depends on the relative dipole moment of the solute to the solvent. To further know the effect of dipole moment on $\Delta \nu_{\text{NCE}}$, a series of solvents with different static dielectric constants were chosen to prepare the same concentration of DMC ($\Phi_A = 0.5$) and their isotropic and anisotropic Raman spectra of DMC ($\Phi_A = 0.5$) were collected, as shown in Figure 8. The $\Delta \nu_{\text{NCE}}$ vs $\Phi_A$ is illustrated in Figure 9, which shows that under the same volume fraction the $\Delta \nu_{\text{NCE}}$ increases with the decrease of the solvent dielectric constant, which is in good agreement with Logan’s theory.$^{32}$ Within this theory, the character shown in Figure 10 could be expected, that is, a downward (convex) curvature for a lower-polarity solvent and an upward (concave) curvature for a higher-polarity solvent.

To get further evidence on this property rule and strengthen the rationality of the dimer model, DFT calculations in association with the polarizable continuum model (PCM) at the hybrid B3LYP-D3 levels of theory with the 6-311G(d,p) basis set have been carried out to obtain the DMC dimer...
structure using the Gaussian 09 program. The results are shown in Table 2, wherein the C=O vibrational frequencies, the corresponding depolarization ratios, and the Δν_{NCE} of DMC in a variety of solvents are listed in detail. The calculations show that with the decrease of the solvent dielectric constant the Δν_{NCE} increases. This result is based on our proposed dimer model and is consistent with the conclusion drawn from Figure 9, which further manifests the rationality of our proposed dimer model.

In an extremely diluted solution, the Δν_{NCE} will vanish; this is independent from the solvent. In sum, our solvent-dependent experiment shows that, in a given concentration, the value of NCE increases with the decrease of the solvent dielectric constant. By extending this rule to the whole concentration, a upward (convex) fitted curve for a lower-polarity solvent and a downward (concave) fitted curve for a higher-polarity solvent could be expected, which conform to the conclusion reported by many scientists.31,33

All our experimental spectra and dimer model-based computational calculations show a satisfactory relationship between the NCE character and the resonant dipolar coupling as well as the solute to solvent polarity in mixtures at molecular resolution.

| solvents             | dielectric constant (ε) | dipole moments (μ)/D | freq.     | D. ratio | NCE/cm⁻¹ |
|----------------------|-------------------------|----------------------|-----------|----------|-----------|
| CH₃COCH₃             | 20.70                    | 2.91                 | 1789/1773 | 0.11/0.13 | 16        |
| CHCl₃                | 4.81                     | *                    | 1799/1781 | 0.74/0.12 | 18        |
| CCl₄                 | 2.24                     | 0                    | 1811/1789 | 0.21/0.12 | 22        |
| C₆H₁₂                | 2.02                     | 0                    | 1812/1790 | 0.24/0.12 | 22        |
| dimethyl carbonate   | 3.09                     | 0.91                 | 1827/1802 | 0.46/0.12 | 25        |

“Asterisk (*) indicates undetermined values.

### CONCLUSIONS

Experimental Raman and IR spectroscopy techniques in association with DFT/PCM calculations have been applied to investigate the NCE phenomenon of the ν(C=O) band of DMC in the liquid mixture. The Δν_{NCE} of the ν(C=O) stretching vs volume fraction exhibits a downward (concave) fitted curve and an upward (convex) fitted curve in the DMC/CH₃COCH₃ and DMC/C₆H₁₂ mixtures, respectively. The order of the dielectric constant accounts for this phenomenon, ε(CH₃COCH₃) > ε(DMC) > ε(C₆H₁₂). A solvent having a larger dielectric constant can easily destroy the aggregate structure (short-range dimer structure) of DMC in the mixtures. To explain this phenomenon, a dimer model was proposed and the vibrational frequencies have been computed for both the monomer and dimer; NCE concentration effects can be explained by the transformation between dimer and monomer forms. During the dilution process, the DMC gradually transformed from a dimer form to a monomer form, corresponding to the blue shift of the ν(C=O) vibrational frequencies. The solvent-dependent properties of the NCE phenomenon can also be explained using the dimer model. The experiment shows that the Δν_{NCE} increases with the decrease of the solvent dielectric constant. The DFT calculations based on the dimer model give a consistent picture with the experimental results. Our dimer model provides a satisfactory explanation of the NCE phenomenon, concentration dependence properties, and solvent dependence properties.

### EXPERIMENTAL AND COMPUTATIONAL METHODS

The experimental setup of Raman spectroscopy has been reported in the literature with modifications.9,36 Briefly, the experimental apparatus consists of a triple monochromator (TriVista TR557, Princeton Instruments) equipped with an argon ion laser (Coherent, CVI MELLES GRIOT) as a source of excitation light at 488 nm (75 mW output) and with a liquid nitrogen-cooled CCD array (Princeton Instruments Inc.) allowing a wavenumber coverage of 1089 cm⁻¹ and a spectral resolution (the instrumental apparatus function, FWHM) of 2.0 cm⁻¹. The accuracy in the measurement (the physical matrix pixel of the CCD camera) of the band positions was 0.45 cm⁻¹. Raman spectra were collected for DMC at the concentration ranging from 40 to 100% in the DMC/C₆H₁₂ mixture. A 488 nm laser was used to produce the Raman scattering signals, and a backscattering geometry was applied to collect the Raman-scattered light. The polarized Raman measurements were carried out using a polarizer and an analyzer in the VV and VH polarization configurations. First, using a polarizer by vertically (V) polarizing the exciting laser

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**Figure 9.** Variation of NCE of C=O stretching mode of DMC as a function of solvent dielectric constant.

**Figure 10.** Scheme for calculated rule and the expected curves of NCE vs concentration.
DFT calculations are based on a Gaussian program. The FT-IR spectra were obtained with 2 cm\(^{-1}\) resolution using an FT-IR spectrometer (Thermo Nicolet avatar 370, Thermo Fisher Nicolet). The FT-Raman spectra were obtained with an FT-Raman spectrometer at 1064 nm excitation (Thermo Nicolet 960, Thermo Fisher Nicolet).

Computational density functional theory (DFT) helps to better understand the characteristic thermally stable structure of the molecule. Herein, DFT calculations at the B3LYP-D3/6-311G(d,p) level of theory were carried out to optimize the structure and for the calculation of vibrational frequencies. DFT calculations are based on a Gaussian program.\(^1\)

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00175.

Variation of isotropic and anisotropic Raman peak frequencies of C=O stretching mode with volume fractions from 0.1 to 1 (PDF)

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Notes

The authors declare no competing financial interest.

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