2D Raman-THz spectroscopy of binary CHBr$_3$-MeOH solvent mixture

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Hybrid two-dimensional (2D) Raman-terahertz spectroscopy is used to measure the interactions between two solvents pair in the binary CHBr$_3$-MeOH mixture in the frequency range of 1-7 THz. Changes in the cross peak signature are monitored, originating from the coupling of an intramolecular bending mode of CHBr$_3$ to the collective intermolecular degrees of freedom of the mixture. The appearance of a new cross peak in the 2D spectrum measured for solvent mixture with MeOH molar fraction of 0.3 indicates a coupling to a new set of low-frequency modes formed due to the hydrogen bond interactions between the two solvents. This interpretation is supported by the measurement of the CHBr$_3$-CS$_2$ binary solvent mixture as well as by 1D absorption measurements of neat MeOH.

I. INTRODUCTION

Over the course of recent years, there has been significant progress in the development of time-resolved multidimensional spectroscopy techniques in the low-frequency part of the electromagnetic spectrum. Following the well-established multidimensional techniques in infrared regimes, their low-frequency counterpart is aiming to access detailed structural information through spectral densities residing below 10 THz (1 THz = 33 cm$^{-1}$), where the rotational transition of molecules in the gas phase, strong transition in the semiconductor solids, and intra/intermolecular vibrational motion of the liquid phase can be found.

The first attempts to study the inhomogeneous nature of the low-frequency transitions in liquids were inspired by the concept of 2D Raman spectroscopy, which was proposed by Tanimura and Mukamel in 1993\cite{1}. 2D Raman spectroscopy allows observing microscopic molecular dynamics through the change of the polarizability of the sample in response to the sequence of five electronically off-resonant excitations\cite{2}. Despite the tremendous experimental challenges associated with the realization of the fifth-order nonlinear technique, signals from simple organic liquids such as CS$_2$ and formamide were successfully measured\cite{3,4}. Recently, a single pulse 2D Raman technique developed by Silberberg and coworkers was implemented to overcome the most significant experimental obstacle in the form of parasitic low-order cascading process\cite{5} and demonstrated the ability to measure intramolecular coupling of simple halogenated liquids\cite{6}. Steady progress in the generation and manipulation of strong THz fields\cite{7} stimulated the development of alternative spectroscopic path toward low-frequency multidimensional spectroscopy – third-order 2D THz spectroscopy\cite{8} which probes multipoint correlation function of the nuclear dipole moment of low-frequency transitions. 2D THz spectroscopy was successfully realized on molecules in a gas phase\cite{9,10} and semiconductor solids\cite{11}, however, the still rather limited available energies and bandwidth of THz pulses, and the experimental limitation in generation and recombination of multiple THz pulses, have not allowed yet the realization of such experiments in liquids, where transition dipoles of the low-frequency modes are extremely small.

In an attempt to circumvent the experimental limitation of the “pure” techniques mentioned above, 2D Raman and 2D THz spectroscopy, hybrid methods, which combine indirect optical and direct THz excitation in a single experiment, were proposed and realized experimentally for various systems, including molecular liquid\cite{12,13} and semiconductor solids\cite{14}, Bonn and coworkers combined THz, mid-IR, and visible pulses to measure couplings between the high and low-frequency modes in liquid water\cite{15} Blake and co-workers have introduced 2D THz Raman spectroscopy with the THz-THz-Raman (TTR) pulse sequence to study halogenated liquids\cite{16,17}.

At the same time in our group, an alternative hybrid method denoted 2D Raman-THz spectroscopy with the Raman-THz-THz pulse sequence (RTT) has been under steady development\cite{18}. 2D Raman-THz spectroscopy allows to interrogate the low-frequency vibrational modes of liquids consecutively through impulsive (nonlinear) Raman and direct (linear) THz excitation, providing equivalent information accessible by conventional third-order echo-based spectroscopies\cite{19,20}. By measuring the extent of the emitted echo signals, the approach demonstrated the ability to report on the inhomogeneity of low-frequency intermolecular modes of liquid water\cite{21} and aqueous salt solutions, providing a glance into the correlation between macroscopic viscosity and structuring of hydrogen-bond networks on the molecular level\cite{22}. In further work, we were able to disentangle the contribution of nuclear quantum effects to water’s structure in different water isotopologues\cite{23}.

We also applied 2D Raman-THz spectroscopy to a series of halogenated organic molecules, liquid bromofom and iodoform\cite{24}. This study was inspired by the work of Blake and co-workers on similar halogenated systems with THz-THz-Raman (TTR) pulse sequence mentioned earlier\cite{18,19,25}, to see whether RTT pulse sequence can provide complementary information on these molecules. The most recent interpretation of the TTR signals by Blake and coworkers suggested that the observed signal stems from the instantaneous excitation of intramolecular vi-
brations through a two-photon absorption process by a pair of strong THz fields (sum-frequency excitation pathway). This explanation is consistent with the interpretation of the THz-Kerr effect observed earlier for similar liquids. Our RTT pulse sequence lacks the strong initial THz process required for that process. Concurrently, we suggested that the RTT response originates from a different coherence pathway, initiated by a Raman induced excitation of intramolecular modes, and followed by a weak THz interaction that switches coherences from intra to intermolecular modes through two-quantum process revealing a cross peak between these two degrees of freedom.

In the present paper, we like to test this interpretation further by measuring 2D Raman-THz spectra for a binary bromoform-methanol (CHBr$_3$-MeOH) solvent mixture, which is more complex with respect to its intermolecular response. To that end, we monitor changes in the cross peaks signature originating from the coupling of intramolecular symmetric bending mode of CHBr$_3$ at $v_3=6.7$ THz with the broad intermolecular band at about 1.6 THz as a function of the MeOH concentration in the CHBr$_3$-MeOH mixture.

It is well known that various excess thermodynamic properties such as the molar heat of mixing ($H^E$), molar excess Gibbs free energy ($G^E$), and excess volumes of mixing ($V^E$) for binary solvent systems of $n$-alcohols with CHCl$_3$ and CHBr$_3$ show significant deviation from ideal behavior. For example, $V^E$ for the CHBr$_3$-MeOH solvent mixture is constantly negative throughout the entire mole fraction range, indicating that there are specific interactions between alcohol chains and CHBr$_3$, which result in the volume decrease (negative $V^E$). They overweight positive $V^E$ factors such as the steric repulsion between the alcohol alkyl chains and the bulky Br atom, and the rupture of the MeOH hydrogen bond networks upon dilution with CHBr$_3$. It was proposed that the hydrogen bond donating ability of CHBr$_3$ (the H atom) and the hydrogen bond accepting properties of MeOH (the O atom) are primarily responsible for the formation of networks of hydrogen bond clusters in CHBr$_3$-MeOH binary system. Further UV-Vis studies with various solvatochromic probe molecules in CHCl$_3$-MeOH mixture provided clear evidence that both molecules interact through hydrogen bond networks. In the current study, we measure that interaction via a cross peak between a intramolecular mode of CHBr$_3$ and the intermolecular networking modes of the binary mixture directly in the low-frequency THz spectral range.

II. METHODS

The experimental set-up for 2D Raman–THz spectroscopy was essentially the same as described in detail before albeit based on a different laser system. In brief, the output of a Yb-doped fiber laser/amplifier system (short-pulse Tangerine, Amplitude Systems, France) with a central wavelength of 1030 nm, pulse duration of 150 fs, and repetition rate of 10 KHz was split into THz and Raman branches. The THz pulses were generated via optical rectification by focusing 7 μJ of the fundamental amplifier output into a 100 μm thick (110) GaP crystal, which generated weak but broadband THz pulses with a near single-cycle shape and a bandwidth that extends to $\sim 7$ THz. The THz pulse was focused on the sample by a custom made elliptical mirror with $2f = 83$ mm and the emitted signal was subsequently detected with an equivalent GaP crystal via electro-optic sampling with enhanced sensitivity. Raman pulses with a central wavelength of 860 nm and energy of 5 μJ were produced in an OPA (Twin STARZZ, Fastlight, France) pumped from the second harmonic of the Tangerine system.

Delay $t_1$ between the Raman pump and the THz pulse was controlled by a step-scan motor (Physics Instruments, M-405.DG), while sampling delay $t_2$ was scanned contentiously by a fast-scanning motor (Physics Instruments, V-408). The sample was contained in the static cuvette made of two thin sapphire windows (UQG optics) separated by a 300 μm Teflon spacer. A low-pass filter with a cutoff frequency of 7 THz as well as Gaussian apodization has been applied to all data. The averaging time varied from 5h for the pure CHBr$_3$ sample up to 80h for the X$_{MeOH} = 0.3$ sample.

In contrast to our previous work we undersampled data along the Raman axis by a factor of 2. This reduced the signal acquisition times by the same factor, which became crucial when the much smaller signals from CHBr$_3$-MeOH mixtures are measured. There are two intramolecular vibrational modes (asymmetric $v_5=4.7$ THz and symmetric $v_3=6.7$ THz C-Br bending modes) giving rise to two cross peaks in the 2D Raman-THz spectrum due to the coupling to the intermolecular modes of CHBr$_3$. The $v_3$ mode tends to provide much stronger cross peaks signals, despite the fact that it is placed on the edge of the detection bandwidth of our 2D spectrometer. Under-sampling along the Raman axis results in the “folding” of the 6.7 THz mode into the rephasing part of the 2D spectra and inherent separation of that signal from the weak contribution of the $v_5$ mode. This folding is justified by the fact that the rephasing part of the signal is significantly suppressed by the specific shape of the instrument response function (IRF) in our experiment (for a detailed discussion see). In all representations of 2D spectra, the data are folded back into the non-rephasing quadrant.

III. RESULTS AND DISCUSSION

We start in Figures 1 and 2 with neat CHBr$_3$, which we have also investigated in our previous works but has been measured again for a consistent comparison with the subsequent dilution series. Figure 1 shows its
2D Raman-THz signal in the Raman-THz-THz quadrant measured beyond the pulse overlap region ($t_1 > 0.7$ ps). The vibrational signal was isolated from rotational contributions, which originate from the alignment of the CHBr$_3$ molecules along the polarization direction of the strong Raman pulse, by subtracting a single-exponential fit along each $t_1$ cut. There is a very long-lived oscillatory signal along the $t_1$ direction (Raman to THz delay), extending significantly beyond our measurement window, while the signal decays significantly faster along $t_2$ axis (THz to THz delay). It appears to be a rephasing signal with the fringes inclined along the diagonal, but that is an artifact from the undersampled acquisition along $t_1$ (see Methods). Figure 1 depicts the signal obtained for the CHBr$_3$-MeOH binary solvent mixture with the highest MeOH molar fraction $X_{MeOH}=0.3$ used in this work. Two main differences can be noticed upon MeOH dilution: a significant decrease in signal size (more than a factor of 5) and additional beating of the oscillatory signal along the THz ($t_2$) axis with a nodal line around $t_2 = 0.25$ ps. Both effects will be quantified and discussed in detail below.

Figure 2 shows the absolute value of the 2D Fourier transformation of the data in Figure 1, revealing a single cross peak with the $f_1$ frequency matching exactly the $v_3$ symmetric bending mode of CHBr$_3$. Along the $f_2$ axis, it shows a broad band peaking at around 3.3 THz, as is evident from the cut in Figure 2, blue line. As discussed in great details in our previous publication,[19] the convolution of the molecular response with the IRF significantly distorts position, shape, and amplitude of the observed peaks in the 2D spectrum. In order to decipher the real frequency position of the observed cross peaks, one needs to reconstruct the IRF by taking into consideration temporal shapes of THz and Raman pulses, and subsequently perform a deconvolution by dividing the measured response through IRF in the frequency domain. Figure 2, red line shows the result of that procedure, with the cross peak shifted downwards significantly along the $f_2$ axis, now peaking at 1.5 THz, where collective intermolecular motions of CHBr$_3$ and many other polar liquids can be found.[33,34]

Figures 3a-c show the absolute value 2D spectra obtained for a series of CHBr$_3$-MeOH mixtures with $X_{MeOH} = 0.1, 0.2, \text{ and } 0.3$ mole fraction of MeOH. Figure 3a depicts the 2D spectrum obtained for a solution with 0.3 mole fraction of CS$_2$ in CHBr$_3$, which was measured as a control. Comparison with the reference data of neat CHBr$_3$ (Figure 2a) shows that the addition of MeOH with 0.1 and 0.2 mole fraction (Figures 2b and b) does not significantly affect the shape of the cross peak. The only significant difference is the reduction in signal size upon addition of MeOH. However, for the $X_{MeOH} = 0.3$ (Figure 3c), along with a further reduction of signal size, there is a significant change in the cross peak line-shape, which splits into two portions and becomes significantly broader. That substructure is the result of the beating discussed in the context of the time-domain data of Figure 1. On the other hand, the control measurement of a binary mixture with 0.3 mole fraction of CS$_2$ does not show any significant change in the cross peak line-shape.

Figure 4a confirms that observation on a more quantitative level, depicting spectral cuts at $f_1=6.7$ THz along the $f_2$ axis for all five aforementioned measurements. The

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**FIG. 1:** Experimental 2D Raman-THz data for a) neat CHBr$_3$ and b) CHBr$_3$-MeOH binary mixture with $X_{MeOH} = 0.3$.

**FIG. 2:** a) Absolute value of the 2D Fourier transform for the neat CHBr$_3$ signal in Figure 1a. (b) 1D vertical cut through the 2D spectrum at $f_1 = 6.7$ THz (blue line), together with the deconvoluted data (red line) obtained by dividing through the IRF slice (black dashed line). The regions with unreliable deconvolution are shaded out.
FIG. 3: Absolute value 2D spectra of a series of CHBr₃-MeOH binary mixtures with a) XMeOH = 0.1, b) XMeOH = 0.2, and c) XMeOH = 0.3 molar fractions. (d) Absolute value 2D spectrum of the control CHBr₃-CS₂ binary mixture with XC₅S₂ = 0.3.

FIG. 4: a) Comparison of vertical cuts corresponding to f₁ = 6.7 THz for neat CHBr₃ (blue), XMeOH = 0.1 (red), XMeOH = 0.2 (magenta), XMeOH = 0.3 (green), and XC₅S₂ = 0.3 (black dashed). b) Comparison between absorption spectrum of MeOH (black line) and deconvoluted vertical cut of XMeOH = 0.3 measurement at f₁ = 6.7 THz. The regions with unreliable deconvolution are shaded out.

The fact that the frequency of the shoulder in the deconvoluted 2D Raman-THz response falls very close to the intermolecular vibration of MeOH provides evidence for the interaction between the two solvents, indicating that the intramolecular bending mode of CHBr₃ is weakly coupled to the intramolecular hydrogen bond motion of MeOH. This claim can be supported further by considering the signal obtained from the control CHBr₃-CS₂ binary mixture (Figure 3d). Similarly to the CHBr₃-MeOH mixture, CHBr₃ and CS₂ are fully miscible for all
FIG. 5: 2D Raman-THz size dependence on CHBr₃ dilution. Measured signal vs. MeOH mole fraction (blue circles). Expected square concentration dependence (black crosses). Measured signal size for the control measurement with X₃CS₂ = 0.3 (red square).

mole fractions. However, unlike MeOH, CS₂ lacks the ability to form any hydrogen bond with CHBr₃ and thus can be considered a simple dilution agent. Figure 3b shows that the line-shape of the cross peak remains intact upon the addition of CS₂, indicating that splitting observed in Figure 3a for XMeOH = 0.3 mixture is not related to CHBr₃ dilution but originates from the interactions between the two solvents.

Additional indirect evidence for non-ideal behaviour is derived when examining the dependence of the signal size of the 2D response as a function of concentration of MeOH, which is significant. By the time the molar content of MeOH reaches 0.3, the signal is decreased by a factor 5, significantly limiting our ability to measure CHBr₃-MeOH systems beyond this composition. This behavior is illustrated in Figure 5, where signal size, scaled with the transmitted THz field and normalized to the maximum signal obtained for a neat CHBr₃ sample, is plotted against MeOH fraction in the mixture. The signal decreases much faster than the square of concentration (black line), which would be expected in the case of a simple dilution. It is worth noticing that when MeOH is replaced with CS₂ (red square), this trivial concentration dependence is indeed observed. We believe that the “missing” signal in the XMeOH = 0.3 sample is an indication of the significant disruption of the long-range interaction in CHBr₃ on account of the formation of new intermolecular interaction in the CHBr₃-MeOH binary solvent.

IV. CONCLUSION

The combination of experimental findings presented here, namely, the split of the ν₃ cross peak into two contributions in the XMeOH = 0.3 sample, the close correspondence of one of these cross peaks with the linear MeOH spectrum, and the non-ideal signal size dependence on MeOH concentration, provide new insights into the structure and dynamics of binary solvent mixtures. A deeper understanding of these effects will require molecular dynamics simulations, in connection with procedures to calculate the 2D-Raman THz response. Furthermore, the double peak structure of the cross peak, or correspondingly, the beating of the time-domain data in the t₂-direction, emphasize that the response is not instantaneous in the THz dimension in our RTT pulse sequence, unlike for the TTR pulse sequence. The demonstrated sensitivity of 2D Raman-THz spectroscopy toward low-frequency intra/intermolecular vibrational couplings can be utilized further to study structural characteristics of hydrogen bond network forming systems.

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References:

(1) Hamm, P.; Zanni, M. T. Concepts and methods of 2D infrared spectroscopy; Cambridge University Press: Cambridge, 2011.
(2) Tanimura, Y.; Mukamel, S. Two-dimensional femtosecond vibrational spectroscopy of liquids. J. Chem. Phys. 1993, 99, 9496–9511.
(3) Kubarych, K. J.; Milne, C. J.; Miller, R. J. D. Fifth-order two-dimensional Raman spectroscopy: a new direct probe of the liquid state. Int. Rev. Phys. Chem. 2003, 22, 497–532.
(4) Kaufman, L. J.; Heo, J.; Ziegler, L. D.; Fleming, G. R. Heterodyne-detected fifth-order nonresonant Raman scattering from room temperature CS₂. Phys. Rev. Lett. 2002, 88, 207402.
(5) Li, Y. L.; Huang, L.; Miller, R. J. D.; Hasegawa, T.; Tanimura, Y. Two-dimensional fifth-order Raman spectroscopy of liquid formamide: Experiment and theory. J. Chem. Phys. 2008, 128, 234507.
(6) Frostig, H.; Bayer, T.; Dudovich, N.; Eldar, Y. C.; Silberberg, Y. Single-beam spectrally controlled two-dimensional Raman spectroscopy. Nat. Photonics 2015, 9, 339–343.
(7) Hurwitz, I.; Raanan, D.; Ren, L.; Frostig, H.; Oulevey, P.; Bruner, B. D.; Dudovich, N.; Silberberg, Y. Single beam low frequency 2D Raman spectroscopy. Opt. Express 2020, 28, 3803–3810.
(8) Hwang, H. Y.; Fleischer, S.; Brandt, N. C.; Jr., B. G. P.; Liu, M.; Fan, K.; Sternbach, A.; Zhang, X.; Averitt, R. D.; Nelson, K. A. A review of non-linear tera-
hertz spectroscopy with ultrashort tabletop-laser pulses. J. Mod. Opt. 2015, 62, 1447–1479.

9. Elsesser, T.; Woerner, M. Concepts and Applications of Nonlinear Terahertz Spectroscopy; Morgan & Claypool Publishers, 2019.

10. Fleischer, S.; Field, R. W.; Nelson, K. A. Commensurate Two-Quantum Coherences Induced by Time-Delayed THz Fields. Phys. Rev. Lett. 2012, 109, 126603.

11. Lu, J.; Zhang, Y.; Hwang, H. Y.; Ofori-Okai, B. K.; Fleischer, S.; Nelson, K. A. Nonlinear two-dimensional terahertz photon echo and rotational spectroscopy in the gas phase. Proc. Natl. Acad. Sci. U. S. A. 2016, 113, 11800–11805.

12. Kuehn, W.; Reimann, K.; Woerner, M.; Elsesser, T.; Hey, R.; Schade, U. Strong Correlation of Electronic and Lattice Excitations in GaAs/AlGaAs Semiconductor Quantum Wells Revealed by Two-Dimensional Terahertz Spectroscopy. Phys. Rev. Lett. 2011, 107, 067401.

13. Savolainen, J.; Ahmed, S.; Hamm, P. Two-dimensional Raman-terahertz spectroscopy of water. Proc. Natl. Acad. Sci. U. S. A. 2013, 110, 20402–20407.

14. Finneran, I. A.; Welsch, R.; Alldì, M. A.; Miller, T. F.; Blake, G. A. Coherent two-dimensional terahertz-terahertz-Raman spectroscopy. Proc. Natl. Acad. Sci. U. S. A. 2016, 113, 6857–6861.

15. Finneran, I. A.; Welsch, R.; Alldì, M. A.; Miller, T. F.; Blake, G. A. 2D THz-THz-Raman Photon-Echo Spectroscopy of Molecular Vibrations in Liquid Bromoform. J. Phys. Chem. Lett. 2017, 8, 4640–4644.

16. Shalit, A.; Ahmed, S.; Savolainen, J.; Hamm, P. Terahertz echoes reveal the inhomogeneity of aqueous salt solutions. Nat. Chem. 2017, 9, 273–278.

17. Grecko, M.; Hasegawa, T.; D’Angelo, F.; Ito, H.; Turchinovich, D.; Nagata, Y.; Bonn, M. Coupling between intra- and intermolecular motions in liquid water revealed by two-dimensional terahertz-infrared-visible spectroscopy. Nat. Commun. 2018, 9, 885.

18. Berger, A.; Ciardi, G.; Sidler, D.; Hamn, P.; Shalit, A. Impact of nuclear quantum effects on the structural inhomogeneity of liquid water. Proc. Natl. Acad. Sci. U. S. A. 2019, 116, 2458–2463.

19. Ciardi, G.; Berger, A.; Hamn, P.; Shalit, A. Signatures of Intra- and Intermolecular Vibrational Coupling in Halogenated Liquids Revealed by Two-Dimensional Raman-Terahertz Spectroscopy. J. Phys. Chem. Lett. 2019, 10, 4463–4468.

20. Johnson, C. L.; Knighton, B. E.; Johnson, J. A. Distinguishing Nonlinear Terahertz Excitation Pathways with Two-Dimensional Spectroscopy. Phys. Rev. Lett. 2019, 122, 073901.

21. Hamn, P.; Savolainen, J. Two-dimensional Raman-terahertz spectroscopy of water: Theory. J. Chem. Phys. 2012, 136, 094516.

22. Hamn, P.; Shalit, A. Perspective: Echoes in 2D-Raman-THz spectroscopy. J. Chem. Phys. 2017, 146, 130901.

23. Mead, G.; Lin, H.-W.; Magdau, I.-B.; Miller, T. F.; Blake, G. A. Sum-Frequency Signals in 2D-Terahertz-Terahertz-Raman Spectroscopy. J. Phys. Chem. B 2020, 0, Accepted.

24. Alldì, M. A.; Finneran, I. A.; Blake, G. A. Nonlinear terahertz coherent excitation of vibrational modes of liquids. J. Chem. Phys. 2015, 143, 234204.

25. Hoffmann, M. C.; Brandt, N. C.; Hwang, H. Y.; Yeh, K.-L.; Nelson, K. A. Terahertz Kerr effect. Appl. Phys. Lett. 2009, 95.

26. Sajadi, M.; Wolf, M.; Kamprath, T. Transient birefringence of liquids induced by terahertz electric-field torque on permanent molecular dipoles. Nat. Commun. 2017, 8, 14963.

27. Kamprath, T.; Campen, R. K.; Wolf, M.; Sajadi, M. The Nature of the Dielectric Response of Methanol Revealed by the Terahertz Kerr Effect. J. Phys. Chem. Lett. 2018, 9, 1279–1283.

28. Singh, P. P.; Sharma, B. R.; Sidhu, K. S. Thermodynamics of bromoform + methanol mixtures. Aust. J. Chem. 1978, 31, 1419–1423.

29. Singh, P. P.; Sharma, B. R.; Sidhu, K. S. Excess volumes of chloroform and bromoform mixtures with some n-alcohols at 303.15K. Can. J. Chem. 1978, 56, 2128–2127.

30. Gupta, S.; Rafiq, S.; Kundu, M.; Sen, P. Origin of Strong Synergism in Weakly Perturbed Binary Solvent System: A Case Study of Primary Alcohols and Chlorinated Methanes. J. Phys. Chem. B 2012, 116, 1345–1355.

31. Gupta, S.; Rafiq, S.; Sen, P. Dynamics of Solvent Response in Methanol-Chloroform Binary Solvent Mixture: A Case of Synergistic Solvation. J. Phys. Chem. B 2015, 119, 3135–3141.

32. Ahmed, S.; Savolainen, J.; Hamn, P. Detectivity enhancement in THz electrooptic sampling. Rev. Sci. Instrum. 2014, 85, 013114.

33. Davies, M.; Pardoe, G. W. F.; Chamberlain, J. E.; Gebbie, H. A. Character of absorption in far infra-red by polar molecules in liquid state. Trans. Faraday Soc. 1968, 64, 847–860.

34. Afar, M.; Hasted, J.; Zafar, M.; Chamberlain, J. Absorption bands in liquid chloroform and bromoform. Chem. Phys. Lett. 1975, 36, 69 – 72.

35. Sarkar, S.; Saha, D.; Banerjee, S.; Mukherjee, A.; Mandal, P. Broadband terahertz dielectric spectroscopy of alcohols. Chem. Phys. Lett. 2017, 678, 65 – 71.

36. Garberoglio, G.; Vallauri, R. Instantaneous normal mode analysis of liquid methanol. J. Chem. Phys. 2001, 115, 395.

37. Woods, K. N.; Wiedemann, H. The influence of chain dynamics on the far-infrared spectrum of liquid methanol-water mixtures. J. Chem. Phys. 2005, 123, 134507.

38. Hasegawa, T.; Tanimura, Y. Calculating fifth-order Raman signals for various molecular liquids by equilibrium and nonequilibrium hybrid molecular dynamics simulation algorithms. J. Chem. Phys. 2006, 125, 074512.

39. Ito, H.; Hasegawa, T.; Tanimura, Y. Calculating two-dimensional THz-Raman-THz and Raman-THz-THz signals for various molecular liquids: The samplers. J. Chem. Phys. 2014, 141, 124503.

40. Hamn, P. 2D-Raman-THz spectroscopy: A sensitive test of polarizable water models. J. Chem. Phys. 2014, 141, 184201.

41. Magdau, I. B.; Mead, G. J.; Blake, G. A.; Miller, T. F. Interpretation of the THz-THz-Raman Spectrum of Bromoform. J. Phys. Chem. A 2019, 123, 7278–7287.