Effect of isotope substitution in binary liquids with Thermal-Lens spectroscopy

CrossMark

Indrajit Bhattacharyya [1], Pardeep Kumar, Debabrata Goswami *

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

A B S T R A C T

Effect of isotope substitution from the modulation of Thermal-Lens (TL) signals in binary liquid mixtures is explored using femtosecond pump–probe mode-mismatched Z-scan TL spectroscopy. Binary solutions of water and heavy water with pure methanol at various concentrations are used for the study, where pure methanol acts as the TL marker across the different samples. The TL signal is found to be effectively modulated by isotope substitution under the experimental conditions, indicating that TL signal depends on hydrogen bonding.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of isotopes [1], Deuterium isotopic substitution [2] has had significant applications in chemical, physical, biological and environmental sciences [3–7]. Many researchers have used this particular technique to study the mechanism of reaction dynamics, site specific biological processes and geometric changes in molecular systems including liquids, biological macromolecules, crystalline solids, etc. through anharmonicity of the zero point vibrations [8–10]. Soper et al. has shown that deuterium substitution effectively changes the hydrogen bond parameters [7]. Though a series of theoretical and experimental studies have been performed to explore the effect of isotope substitution on different samples, a sensitive optical technique to study this effect is yet to emerge. We found that Thermal-Lens (TL) spectroscopy is a very sensitive and useful optical tool, which can probe a significant modulation in TL signals resulting from the isotopic substitution in binary liquid mixtures.

TL spectroscopy was first reported in 1965 [11]. Since then this field was rapidly developed and improvised in such a way that it gradually became a powerful spectroscopic tool and has found several applications in molecular and solid-state spectroscopy [12–14]. Dual beam TL spectroscopy [15] under mode matched and mode-mismatched condition [16–21] provides a lot of useful information about the sample under study. Several authors have also measured TL-signals by using two-color pump–probe Z-scan technique [22–29]. Thus TL technique gradually became very popular among the spectroscopists because of its sensitivity and experimental simplicity.

The TL technique measures the distortion of the probe beam wave-front induced by the heat generated in the sample due to the non-radiative relaxation of the photo-excited molecules when the pump beam is on. Our experiment uses high repetition rate femtosecond laser pulses, which provide high enough peak powers for non-linear TL studies at fairly low average powers without any sample damage. In fact, within error-bars, the effective stationary TL from such high repetition rate femtosecond laser is similar to that generated from a CW laser [30]. Moreover, the instantaneous thermal effect of individual pulses produces a cumulative thermal effect, which is found to be very effective in measuring the TL signals in highly volatile liquids, such as methanol. The magnitude of the induced thermal lens is measured from the change in transmittance of the probe beam in the presence (versus the absence) of the pump beam through a small aperture located at the far field.

Due to unusual behavior, the study of physical and chemical properties of binary liquid mixtures has found considerable attention and has potential applications in solution theory and molecular dynamics [22,28,29,31]. In our present work, we use water (H_2O), heavy water (D_2O) as well as their individual mixtures with methanol (CH_3OH) at different ratios to prepare the binary liquid samples. In each case, we measure the TL signals at different compositions of the binary mixtures by ultrafast two-color Thermal-Lens Pump–probe mode-mismatched Z-scan technique and observe an effective modulation of Thermal Lens (TL) signal. Our attempt is to probe how the change in intramolecular H-bonding due to isotope substitution results in an effective modulation of TL signals at different compositions of the binary mixtures.

* Corresponding author. Fax: +91 512 259 7554.
 E-mail address: dgoswami@iitk.ac.in (D. Goswami).
[1] Present address: International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan.
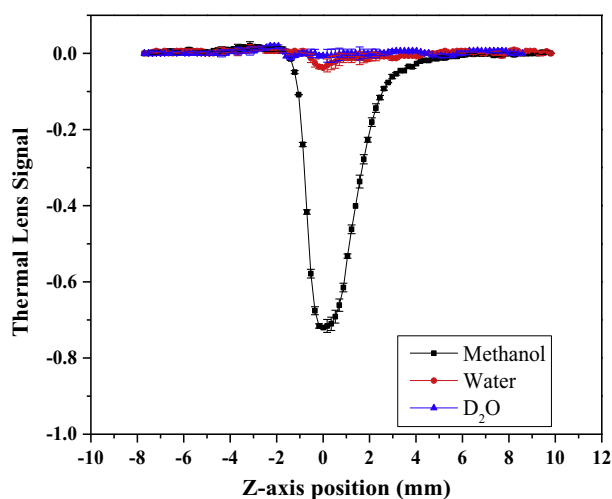
2. Experiment

We use mode-mismatched two-color TL pump–probe Z-scan technique to measure the Thermal-Lens (TL) signals in the binary mixtures. The details description of the experimental set-up is provided in our previous article [22]. Briefly, we use a 50 MHz train of femtosecond collinear laser pulses from a mode-locked Er-doped fiber laser (Femtolite, IMRA Inc.) at 1560 nm and 780 nm as the respective pump and probe beams. In order to measure the TL signal from each of the binary liquid samples, we focused the pump and the probe beams into the sample and measured the probe beam (780 nm) transmittance in presence of the thermal pump beam (1560 nm) through a 60% closed aperture at far field by using an amplified silicon photodetector (Thorlabs: PDA 100A-EC). In our particular study, since the pump and probe beams have different divergences and were focused into the sample by using a single non-achromatic lens, the resulting TL setup had a mode-mismatched geometry. Mode-mismatched Z-scan technique is a preferred approach to measuring TL signals as it is more sensitive in comparison to the mode-matched condition [16]. Moreover, the mode-mismatched technique directly measures the maximum TL that is formed at the focal point of the pump beam.

Since methanol shows significant TL signal compared to the other two solvents under the experimental condition (Figure 1), methanol is treated as the TL marker sample and the binary mixtures of water and heavy water with methanol at different compositions are prepared by varying the volume fraction of methanol from 0 to 1. For each individual binary mixture, the closed aperture Z-scan trace is recorded and the TL signal is eventually measured at each Z-position of the sample. Since we measure the TL signals under mode-mismatched condition, the maximum TL signal is formed at the focal point of the 1560 nm in each of the cases. The magnitude of TL signal is plotted against the volume fraction of methanol for both the cases of water and heavy water to show the modulation of TL signals with the change of mixture composition in each case.

3. Results and discussion

The vibrational combination states of the hydroxyl group (–OH) in methanol get coupled to the femtosecond laser pulses, which results in the non-resonant saturation absorption at 1560 nm [23].
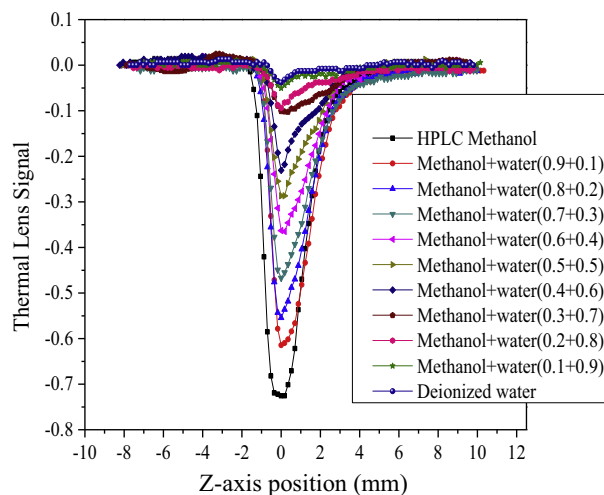
The absorption of 1560 nm pulses followed by the nonradiative relaxation of the excited molecules produce transient TL signal at longer time scale. The amplitude of the TL signal for each of the individual pure samples as well as the binary mixtures is calculated from the closed aperture Z-scan traces obtained experimentally as:

$$S(\lambda_e) = \frac{T_a(\lambda_e) - T_{a0}}{T_{a0}} \tag{1}$$

where $T_a(\lambda_e)$ and T_{a0} are the respective probe beam transmittances through the aperture in the presence and in the absence of the pump beam [32].

The variation of the TL signals as a function of sample position for each of the pure samples is shown in Figure 1, where we also show the associated error-bars for every experimental point through repeated measurements. Since errors due to laser fluctuations are below one percent [22], we find that the maximum error is 2% in the TL values presented in the graphs. In spite of the strong absorption around 1560 nm for water, methanol shows the maximum TL signal among all the components (methanol, water and heavy water) studied under the experimental condition and thus is used as our thermal lens marker. In Figure 2, we show the variation of the TL signal for each particular composition of methanol–water binary liquid mixtures (as a representative one). The maximum TL signal appears at $Z = 0$ (mode-mismatched condition) i.e., at the focal point of 1560 nm pump beam. We calculate the magnitude of TL signal for all the binary liquids mixtures (Figures 3 and 4) as $|S(\lambda_e, Z = 0)| = \frac{T_a(\lambda_e, Z = 0) - T_{a0}(Z = 0)}{T_{a0}(Z = 0)}$, where $T_a(\lambda_e, Z = 0)$ and $T_{a0}(Z = 0)$ are the respective probe beam transmittance through the far field aperture in the presence and absence of the pump beam at the focal point of the 1560 nm [22]. Data in Figures 3 and 4 are calculated on the basis of our repeated experimental measurements, which also shows the maximum possible error of 2% in our experiments.

Phenomenologically, the magnitude of TL signal in pure samples depends on physical parameters, such as, the absorption coefficient, the thermal expansion coefficient, thermal conductivity, thermo-optic coefficient of the sample [16,22]. Using this identical concept, we calculate different physical parameters and the amplitude of TL signal considering ideal intermolecular interaction between the mixture components in both of the series of binary solutions. The mismatch between experimentally measured and

Figure 1. Thermal-Lens signal for different Z-positions in the case of methanol, water and D$_2$O including the experimental error-bars from repeated experiments: Comparative signal for each of the solvents show the TL trend as: Methanol ≫ Water > D$_2$O.

Figure 2. Variation of TL signal as a function of sample position for methanol–water binary mixtures at different compositions, where the volume fraction of methanol and water change from 0 to 1 and from 1 to 0, respectively.
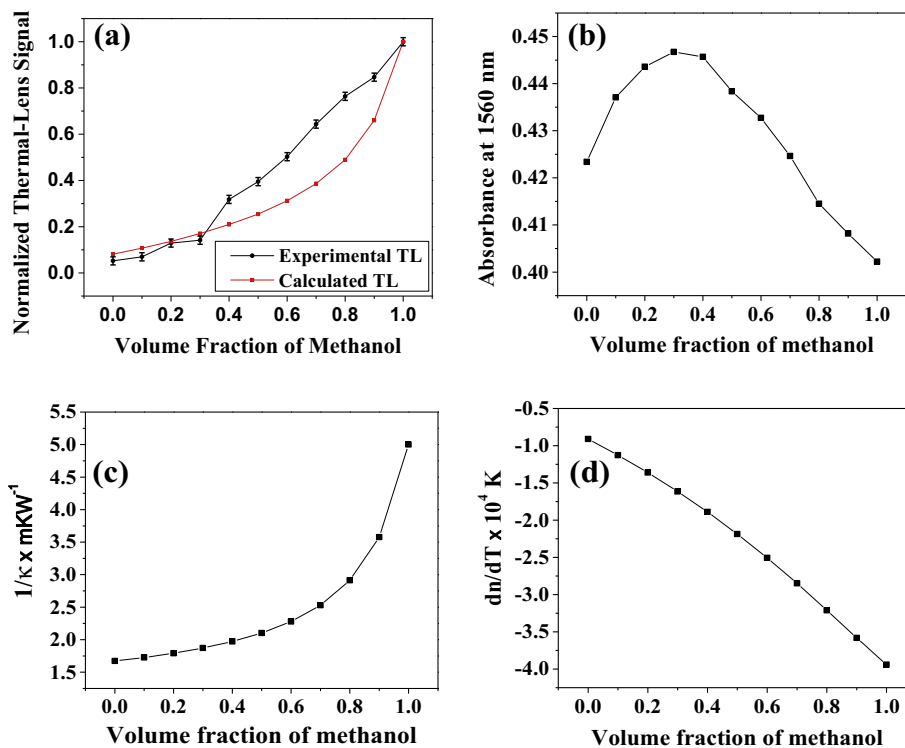
Figure 3. (a) Variation of TL signal (including the maximum error-bars for the experimental case), (b) measured absorption at 1560 nm, (c) reciprocal of thermal conductivity ($1/\kappa$) and (d) the thermo-optic coefficient (dn/dT) at different compositions of methanol–H_2O binary mixtures, where the volume fraction of methanol changes from 0 to 1 and the volume fraction of H_2O changes from 1 to 0.
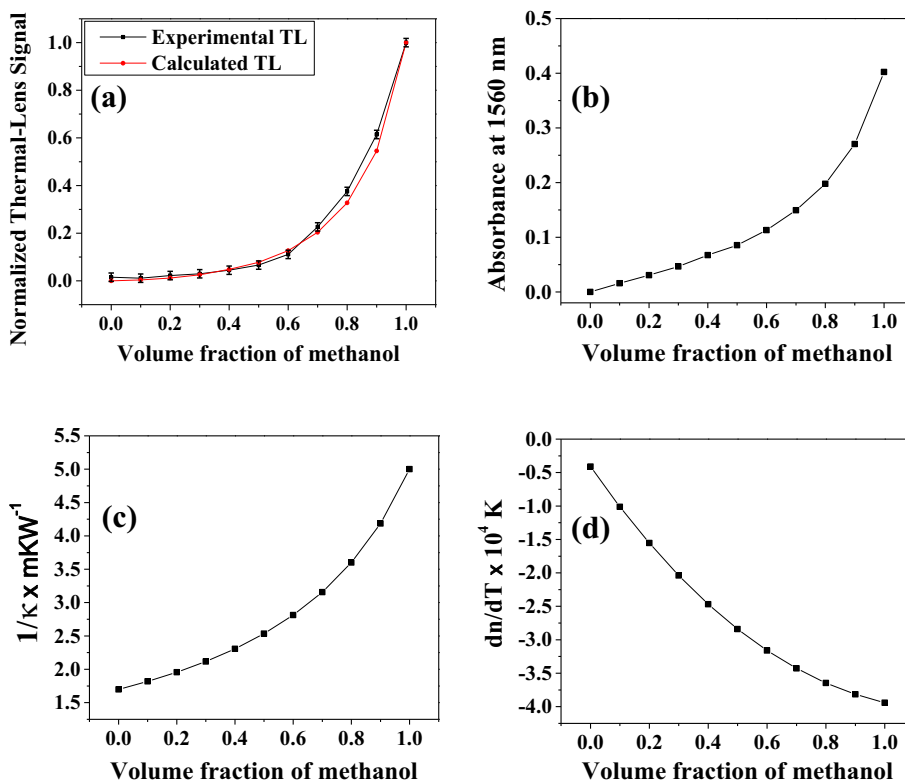
Figure 4. (a) Variation of TL signal (including the maximum error-bars for the experimental case), (b) measured absorption at 1560 nm, (c) reciprocal of thermal conductivity ($1/\kappa$) and (d) the thermo-optic coefficient (dn/dT) at different compositions of methanol–heavy water binary mixtures, where the volume fraction of methanol changes from 0 to 1 and the volume fraction of heavy water changes from 1 to 0.

theoretically calculated TL signal trends in the present study supports our previous observation [22], where the deviation is explained in terms of the change of the molecular properties, such as the intermolecular interaction between the two components of the binary solution.

Theoretically calculated and experimentally measured TL signal trends for different binary mixture concentrations of methanol in water is shown in Figure 3a. Water shows stronger hydrogen bonding as well as higher dipolar interaction as compared to that of methanol. The linear absorption of each of the methanol–water binary mixtures with increasing methanol concentration (Figure 3b) were measured experimentally using the commercial UV/Vis/NIR spectrometer (Perkin–Elmer Lambda 900) using a 1 mm quartz cuvette. We find that though both water and methanol absorb at 1560 nm, pure water absorbs more strongly than methanol and the binary mixture of methanol in water at certain methanol volume fractions have even higher absorptions. Thus the absorption in the binary mixture goes through a maximum at ~30% volume fraction of methanol in water mixture at 1560 nm and thereafter the absorption reduces rapidly with further increase in its methanol volume fraction (Figure 3b). On the contrary, due to higher thermal conductivity and lower thermo-optic coefficient (as predicted from Figure 3c and d, respectively), water shows negligible TL signal as compared to methanol under experimental conditions. The stronger H-bonding in water accounts for the effective modulation of the intermolecular interaction, which results in a significant deviation of the experimentally measured TL signals from those calculated theoretically in case of the methanol water binary solution series (Figure 3a).

However, in the case of methanol and heavy water (D_2O) mixture case, the calculated TL signal for the series matches surprisingly well with the experimental TL signal (Figure 4a). To apprehend this difference in behavior, we start by noting that unlike pure water, heavy water does not have any absorption at 1560 nm under the experimental conditions. This becomes very clear from the absorbance profile of the methanol–heavy water binary mixtures (Figure 4b), where the absorbance simply increases as the volume fraction of methanol gradually approaches to 1. The change of the thermal conductivity and thermo-optic coefficient across the binary mixtures for methanol–heavy water case has also been shown in Figure 4c and d, respectively. Overall, the heavy water has weaker H-bonding as compared to that in water and thus could not produce any significant modulation in the intermolecular interaction, which in turn did not lead to an effective deviation in the trend of experimentally measured TL signals of methanol-heavy water binary solutions (Figure 4a) unlike the methanol–water binary mixtures (Figure 3a).

Under Born–Oppenheimer approximation, the dispersion interaction and equilibrium dipole moment are independent of the isotope substitution. Clough et al. have shown that there is slight change in the dipole using Stark effect [33]. In 2008, Soper et al. have shown that the hydrogen bond length in D_2O is longer and hence weaker compared to that of water [7], which also supports our experimental results. In our experiment, deuteration results in comparatively longer and hence weaker H-bond, which in turn, does not affect intermolecular interaction in binary mixtures compared to the case of methanol–water mixtures. Consequently, the modulation in TL signals in case of methanol–D_2O binary samples are significantly less compared to the case of methanol–water mixtures, where it is noticeably higher and results in a considerable deviation in the experimentally measured TL signals from that calculated theoretically. Thus we probe the modulation of TL signals

resulting from the deuteration substitution effect. The result indicates that the change in H-bonding resulting from the isotope effect induces a change in the intermolecular interaction and thus the TL signal trend gets modulated under experimental condition.

4. Conclusion

The isotope substitution effect on TL signal in binary liquid mixtures is explored by using two-color pump–probe mode-mismatched Thermal-Lens Z-scan technique. We use the heavy water and normal water mixed them individually with methanol to prepare the binary liquid samples. We find that the isotopic substitution greatly affect the TL signal and subsequently propose that under the Born–Oppenheimer approximation, dispersion interaction would not change. Since the hydrogen bond parameters change due to isotope substitution, it is the change in hydrogen bond which greatly affects the intermolecular interaction and thus modulates TL signal under the experimental condition.

References

[1] T.S. Moore, T.F. Winmill, J. Chem. Soc. 101 (1912) 1635.
[2] H.C. Urey, F.G. Brickwedde, G.M. Murphy, Phys. Rev. 39 (1932) 164.
[3] C.E. Hinkle, A.B. McCoy, J. Phys. Chem. A 116 (2012) 4687.
[4] J.M. Lopez delAmo, U. Fink, B.J. Reif, Biomol. NMR 48 (2010) 203.
[5] S. Ullah, W. Zhang, P.E. Hansen, J. Mol. Struct. 976 (2010) 377.
[6] I. Vigano et al., Geochim. Cosmochim. Acta 74 (2010) 3865.
[7] A.K. Soper, C.J. Benmore, Phys. Rev. Lett. 101 (2008) 065502.
[8] S.Y. Park, D.J. Jang, Phys. Chem. Chem. Phys. 14 (2012) 8885.
[9] Y. Ikabata, Y. Imamura, H. Nakai, J. Phys. Chem. A 115 (2011) 1433.
[10] C.N.R. Rao, J. Chem. Soc., Faraday Trans. 71 (1975) 980.
[11] J.P. Gordon, R.C.C. Leite, R.S. Moore, S.P.S. Porto, J.R. Whinnery, J. Appl. Phys. 36 (1965) 3.
[12] N.G.C. Astrath et al., Appl. Phys. Lett. 95 (2009) 191902.
[13] N.G.C. Astrath et al., Opt. Lett. 33 (2008) 1464.
[14] C. Jacinto, T. Catunda, D. Jaque, J. Garcia-Sole, A.A. Kaminskii, J. Appl. Phys. 101 (2007) 023113.
[15] R.L. Swofford, J.A. Morreil, J. Appl. Phys. 49 (1978) 3667.
[16] A. Marcano, C. Loper, N. Melikechi, J. Opt. Soc. Am. B 19 (2002) 119.
[17] A. Marcano, N. Melikechi, Appl. Spectrosc. 61 (2007) 659.
[18] J.A. Sampaio, S. Gama, M.L. Baesso, T. Catunda, J. Non-Cryst. Solids 351 (2005) 1594.
[19] S.M. Lima, J.A. Sampaio, T. Catunda, A.C. Bento, L.C.M. Miranda, M.L. Baesso, J. Non-Cryst. Solids 273 (2000) 215.
[20] S.M. Lima, T. Catunda, R. Lebullenger, A.C. Hernandes, M.L. Baesso, A.C. Bento, L.C.M. Miranda, Phys. Rev. B 60 (1999) 15173.
[21] M.L. Baesso et al., Phys. Rev. B 57 (1998) 10545.
[22] I. Bhattacharyya, P. Kumar, D. Goswami, J. Phys. Chem. B 115 (2011) 262.
[23] I. Bhattacharyya, S. Priyadarshi, D. Goswami, Chem. Phys. Lett. 469 (2009) 104.
[24] D. Goswami, Opt. Commun. 261 (2006) 158.
[25] J. Wang, M. Sheik-Bahae, A.A. Said, D.J. Hagan, E.W. Van Stryland, J. Opt. Soc. Am. B 11 (1994) 1009.
[26] M. Sheik-Bahae, A.A. Said, T. Wei, D.J. Hagan, E.W.J. Van Stryland, Quantum Electron. 26 (1990) 760.
[27] M. Sheik-Bahae, A.A. Said, E.W. Van Stryland, Opt. Lett. 14 (1989) 955.
[28] N.G.C. Astrath, C. Jacinto, T. Catunda, S.M. Lima, F.G. Gandra, M.J.V. Bell, V. Anjos, Phys. Rev. B 71 (2005) 2.
[29] S. Gupte, A. Marcano, R.D. Pradhan, C.F. Desai, N. Melikechi, J. Appl. Phys. 89 (2001) 4939.
[30] S.M. Mian, S.B. McGee, N. Melikechi, Opt. Commun. 207 (2002) 339.
[31] S. Gupta, S. Rafiq, M. Kundu, P. Sen, J. Phys. Chem. B 116 (2012) 1345.
[32] J. Hung, A. Marcano, J. Castillo, J. González, V. Piscitelli, A. Reyes, A. Fernández, Chem. Phys. Lett. 386 (2004) 206.
[33] S.A. Clough, Y. Beers, G.P. Klein, L.S. Rothman, J. Chem. Phys. 59 (1973) 2254.