Electronic Supplementary Information for:

Ultrashort-laser-pulse-induced thermal lensing in pure H_2O and a NaCl-H_2O solution

Yi-Ci Li,[1] Yu-Ting Kuo,[1] Po-Yuan Huang,[1] Cheng-I Lee[2], and Tai-Huei Wei[1,*]

[1]*Department of Physics, National Chung Cheng University, Min-Hsiung, Chia-Yi 621, Taiwan*
[2]*Department of Life Science, National Chung Cheng University, Min-Hsiung, Chia-Yi 621, Taiwan*

*Author to whom correspondence should be addressed;

E-mail: twei@ccu.edu.tw (T.H.W.).

Tel.: +886-5-272-0411 (ext. 66324) (T.H.W.); Fax: +886-5-272-0587 (T.H.W.).

In this **Electronic Supplementary Information** (**ESI**), we present our review of conclusive work and on-going tasks of thermal and mass diffusions occurring in various binary systems. Specifically, we show the commonly used experimental techniques, the experimental results relevant to our study, the binary systems exhibiting sign changes of the Soret coefficients (S_T's) with mass fractions, the microscopic approaches to simulate the behaviors of thermal and mass diffusions, and the artifacts induced by inert dyes and convection. In all, this review helps us to determine the crucial tasks to be dealt with in our future *Z*-scan study of both diffusions induced in NaCl-H_2O (see the **Main Text**) and other binary systems.

In contrast to *Z*-scan, the conventional thermal diffusion forced Rayleigh scattering technique, a transient holographic grating technique dubbed TDFRS, proposed by Pohl et al. in the 1970s [1] can only measure the magnitudes of the thermal coefficients (D_θ's), the mass diffusion coefficients (D_{md}'s) and S_T's of individual constituents in binary systems. However, after Kohler introduced the optical heterodyne detection (OHD) scheme in TDFRS in the 1990s [2–5], a modified version of TDFRS, referred to as OHD-TDFRS, was established and proved capable of measuring the signs, in addition to the magnitudes, of D_θ's, D_{md}'s and S_T's [6]. With this technique, many reliable results of various binary systems, e.g., liquid mixtures, polymer solutions and colloidal suspensions [7–11], have been first obtained [5, 12]. In addition, sign changes of S_T's with the mass fractions have been observed in certain binary systems with water as a constituent, e.g., poly (ethylene oxide) (PEO) in an ethanol-water mixture [13, 14, 15], colloidal boehmite rods in an ethanol-water mixture, ethanol-water and methanol-water solutions [6, 16]. Note that the ethanol-water mixture is regarded as a composite component in both PEO-ethanol-water and colloidal boehmite-ethanol-water solutions.

To more fully understand the OHD-TDFRS results of binary small-molecule liquids at the molecular level, molecular dynamics (MD) simulation methods developed based on irreversible thermodynamics and non-equilibrium statistical mechanics have been used to compute S_T's to be compared with the ones obtained by quantitatively fitting the experimental results [17–21]. When S_T's depend on the ratios of masses, sizes and moments of inertias of individual molecules of the constituents as well as their inter-molecular interaction strength [17, 22], the sign changes of S_T's with mass fractions in aqueous solutions are primarily due to the strong and very directional hydrogen-bonding interactions between individual molecules of water and other constituents [16, 23, 24]. This suggests that in-depth study of the inter-molecular interaction helps to clarify the properties of water interface with other constituents of the binary solutions. Furthermore, we expect that it even helps to explain vapor-solution interfacial tensions [25]. In particular, the study of aqueous solutions of biological molecules is of great practical importance [see the Introduction Sec. (Sec. I), **Main Text**].

When visible continuous light was commonly used in OHD-TDFRS to investigate thermal and mass diffusions induced in transparent binary systems, inert dyes were commonly added to the

systems to enhance the absorption. For example, quinizarin was added to aniline-cyclohexane [18], benzene-cyclohexane [22], carbon tetrachloride solutions of carbon tetrabromide, tetraethylsilane and di-tert-butylsilane [26], polystyrene calibration standards-ethyl acetate [3], polystyrene calibration standards-toluene [4], toluene-(n-hexane) [2, 27], polystyrene-toluene [28], and alkane-benzene [29]; alizarin was added to ethanol-water [27]; basantol yellow 215 was added to PEO-ethanol-water [14, 15]; basantol yellow was added to aqueous solutions of acetone and DMSO [30]. Since the added inert dyes may participate in the diffusions appreciably, special attention needs to be paid to rule out their influence [27].

Besides OHD-TDFRS, diffusion cells [31−33] and the thermal lens methods (including *Z*-scan) [34−37] have also been used to measure S_T′s. However, a database for reliable D_θ′s, D_{md}′s and S_T′s measured by these techniques is still small up to now. As compared with OHD-TDFRS in Ref. [34], the thermal lens methods have the advantage of ease of operation. This is because, in the operation of OHD-TDFRS, the grating induced by the two writing beams needs to be shifted along the grating vector over a few half-wavelengths with a step width of a fraction of a half-wavelength. To fulfill this requirement, the phase difference between the two writing beams needs to be changed over a few times of π and tracked with an accuracy considerably higher than π [2−5]. When a phase change between the two writing beams enables heterodyne signal detection, it inevitably demands higher equipment costs than *Z*-scan.

On the other hand, thermal lens methods have the disadvantage of higher sensitivity to convection-induced artifact [34]. This issue concerns the characteristic convection time τ_{con} in comparison to the mass diffusion time constant τ_{md} and the approaches to lengthen τ_{con} or to weaken convection. Given that the beam radius at the sample position (54 μm) for the thermal lens methods used in Ref. [34] is considerably larger than the typical fringe spacing (5.1 μm) of the grating in OHD-TDFRS (see e.g. Ref. [4]), τ_{md} for the thermal lens methods [$(54\ \mu m)^2/4D_{md}$] is longer than that for the typical OHD-TDFRS [$(5.1\ \mu m)^2/D_{md}$] by ~28 times. Assuming that the samples used in both techniques are of equal thickness L, τ_{con} for the thermal lens methods ($54\ \mu m/v_{con}$ with v_{con} being the convection speed) is longer than that for OHD-TDFRS ($5.1\ \mu m/v_{con}$) by ~11 times. This indicates that convection-induced artifact is more likely to set in before the diffusion signal detected by the thermal lens methods turns stationary. In other words, convection-induced artifact is less likely to be removed from the diffusion signal detected by the thermal lens methods. Knowing that v_{con} is proportional to L^2 for our NaCl-H_2O sample (L=1 mm) with Grashof number less than one and that the thermal lens methods are less sensitive to the diffusion signal than OHD-TDFRS [34], L for the thermal lens methods can hardly be made smaller (in order to lengthen τ_{con}) than that for OHD-TDFRS. This further indicates that convection-induced artifact detected by the thermal lens methods is harder to remove than that detected by OHD-TDFRS. As to weakening of convection, a feasible approach is to turn the optical axes for OHD-TDFRS and the axis for the thermal lens methods

normal to the optical table [38]. This helps to weaken or even eliminate convection by reducing the Rayleigh number to approach or even meet the critical Rayleigh number.

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