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1 **Raman Spectroscopy of Isotopic Water Diffusion in Ultra-Viscous, Glassy and**
2 **Gel States in Aerosol Using Optical Tweezers**

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6 **Abstract**

7 The formation of ultra-viscous, glassy and amorphous gel states in aqueous aerosol following the
8 loss of water results in non-equilibrium dynamics due to the extended timescales for diffusive
9 mixing. Existing techniques for measuring water diffusion using isotopic exchange are limited by
10 contact of samples with the substrate, and methods applied to infer diffusion coefficients from
11 mass transport in levitated droplets requires analysis using complex coupled differential equations
12 to derive diffusion coefficients. We present a new technique that combines contactless levitation
13 using aerosol optical tweezers with isotopic exchange (D_2O/H_2O) to measure the water diffusion
14 coefficient over a broad range ($D_w \sim 10^{-12} - 10^{-17} \text{ m}^2 \text{ s}^{-1}$) in viscous organic liquids (citric acid,
15 sucrose and shikimic acid) and inorganic gels (magnesium sulfate, $MgSO_4$). For the organic liquids
16 in binary and ternary mixtures, D_w depends on relative humidity and follows a simple
17 compositional Vignes relationship. In $MgSO_4$ droplets, water diffusivity decreases sharply with
18 water activity and is consistent with predictions from percolation theory. These measurements
19 show that combining micron-sized particle levitation (a contactless measurement with rapid mixing
20 times) with an established probe of water diffusion, D_w can be simply and directly quantified for
21 amorphous and glassy states that are inaccessible to existing methods.

22

23 Introduction

24 The amount of water associated with an aqueous solution determines its physical characteristics,
25 such as density and viscosity. On drying, the loss of water leads to discrete phase transitions such
26 as crystallization, or continuous changes leading to the formation of highly concentrated
27 metastable amorphous states.¹ Amorphous states can exhibit very high viscosity relative to
28 aqueous solutions, leading to slow diffusion and altered chemical kinetics.²⁻⁴ The formation of
29 amorphous states is enhanced in nanometer and micron-sized aerosol due to the lack of
30 heterogeneous surfaces that act as nucleation sites for crystallization. Fully understanding the role
31 of aerosol in the atmosphere, for instance, requires understanding how high viscosity and slow
32 diffusion couple with reactive gas uptake and chemical processing. However, a key challenge
33 remains in measuring the diffusive properties and viscosity in highly concentrated aqueous
34 solutions.

35 Quantifying viscosity in liquids is straightforward using bulk methods, such as a rheometry and
36 flow-based techniques.^{5,6} Aerosol particle methods have also been developed using coagulation,²
37 impaction⁷ or fluorescence imaging⁸ to measure viscosity. The Stokes-Einstein (S-E) relationship
38 provides a means of relating viscosity measurements to the diffusivity of solution constituents.
39 Unfortunately, S-E has been shown to be unreliable for estimating water diffusion coefficients
40 (D_w) in viscous media due to the ability of smaller water molecules to percolate through channels
41 in the viscous matrix.^{2,9,10}

42 Measurements of diffusion in highly viscous media are challenging. NMR-based methods are not
43 applicable for slow diffusion, with lower limits in the region of $\sim 10^{-12} \text{ m}^2 \text{ s}^{-1}$, although rotational
44 diffusion may be resolved to lower values.¹¹ Other methods using the timescales for water transport
45 have enabled indirect estimates of water diffusion in aqueous solutions of maltose, sucrose, citric
46 acid, magnesium sulfate and shikimic acid.¹²⁻¹⁷ These aerosol-based methods measure the change
47 in size and light scattering intensity during evaporation or condensation of water following changes
48 in relative humidity (RH). These data are then analyzed by mass transport models and the best D_w
49 is determined. A technique reported by Price and coworkers,^{3,18} based on the approach of Zhu et
50 al.,¹⁹ uses Raman microscopy to measure radially-resolved isotopic exchange rates (at a fixed
51 water content) for a cylinder of solution held between glass slides. By comparing the isotope
52 concentration as a function of both position and time to predictions from a solution to Fick's

53 Second Law of diffusion, a single best fit value of D_w is obtained. Isotopic tracer methods have
54 also been applied to droplets on glass cover slides.²⁰ Due to the relatively large sample sizes (up
55 to a few hundred microns), measurements of isotopic exchange for low D_w ($10^{-14} - 10^{-16} \text{ m}^2 \text{ s}^{-1}$)
56 typically require tens to hundreds of hours. Thus, maintaining stable experimental conditions (RH,
57 temperature) over these long timescales can be challenging. In contrast, droplet measurements
58 employ much smaller sample sizes (up to tens of microns) allowing equivalent measurements to
59 be conducted over much shorter timescales (minutes to hours).

60 The isotopic tracer method of Price et al. and the mass transport method of Zobrist et al. have been
61 applied to sucrose solutions, a common benchmark for new methods of exploring diffusion
62 limitations.^{3,12} However, there remains some disagreement between the two methods, particularly
63 at low water content where D_w is on the order of $10^{-15} \text{ m}^2 \text{ s}^{-1}$. Studies using parameterizations of
64 D_w in sucrose to explain mass transport data from droplets held in optical traps have reported closer
65 agreement to models when using the values of Zobrist.²¹ This suggests that there are additional
66 factors that must be considered or better characterized in order to relate D_w between these
67 techniques. For instance, when concentration gradients (strictly chemical potential gradients) are
68 present, the mutual diffusion coefficient determines the rate of mass transfer. To accurately model
69 this process, knowledge of the solution activity of diffusing species, as well as the concentration
70 dependence of D_w , is required. During isotopic exchange, however, the concentration gradients
71 arise from the relative isotope concentrations, and the self-diffusion coefficient is the determining
72 factor. Under the assumption that the diffusive properties of H_2O and D_2O are identical, a single
73 value of D_w may be applied to understand the isotopic exchange process, simplifying the analysis
74 and providing a more fundamental quantity describing diffusion.

75 In this work, we combine the benefits of single particle levitation (fast mixing timescales,
76 contactless measurements) with an isotopic exchange technique to measure D_w . First, we measure
77 D_w in sucrose solution droplets, benchmarking our results with established techniques. We present
78 measurements of D_w in citric acid (CA) and shikimic acid, both explored in studies examining the
79 role of viscosity in reactive uptake kinetics.^{4,22} We discuss mixed organic particles of sucrose and
80 citric acid, quantifying D_w as a function of mass fraction. Finally, we report new measurements of
81 D_w in magnesium sulfate, a challenging system since crystallization prevents such measurements
82 in macroscopic samples at low RH. In the absence of crystallization, MgSO_4 transitions into a two-

83 phase gel, resulting in slow mass transport as water diffusion only occurs through pores in the solid
84 network of the inorganic salt.

85 **Experimental**

86 The work described here used a commercially available Aerosol Optical Tweezer (AOT-100 Biral)
87 for contactless levitation of single droplets of 3 - 6 μm in radius. We modified the environmental
88 control system to allow for rapid exchange of the gas phase humidity source between H_2O and
89 D_2O (Figure 1) and monitored the progression of the droplet composition using Raman
90 spectroscopy. A model using the solution to Fick's Second Law describing diffusion in a sphere
91 was used to analyze the data by varying D_w to achieve the best fit to both the D_2O and H_2O datasets
92 (Figure 2A). D_w are reported with an error of $\pm 50\%$, reflecting the uncertainty in fits to the data,
93 the difference between the self-diffusion coefficients of D_2O and H_2O (reported to be in the range
94 10 - 25%),³ and the variability in RH ($\pm 1\%$). The absolute uncertainty in the RH is reported as
95 $\pm 2\%$ to reflect the accuracy of the RH probes (Honeywell HIH-4602C).

96 *Single particle confinement*

97 In a typical optical tweezers measurement, a solution is aerosolized using an ultrasonic nebulizer
98 and introduced into the laser trapping chamber, where a single droplet is confined and enlarged by
99 coalescence with further droplets in the plume. The chamber is subsequently sealed and a
100 humidified nitrogen flow is introduced to equilibrate the chamber and droplet at a known RH. A
101 schematic of the optical tweezers arrangements is shown in Figure 1. The size and refractive index
102 of the droplet are determined in real-time from the wavelength position of cavity enhanced
103 resonances in the droplet, detected using Raman spectroscopy, using the proprietary Biral and
104 University of Bristol sizing software (LARA 2.0) incorporating the algorithms of Preston and
105 Reid.²³ Using this technique, the theoretical limits on the precision to which the radius and
106 refractive index may be determined are, respectively, 1 nm and 0.05%. Experimentally,
107 measurements typically have an uncertainty of ± 5 nm in radius and ± 0.001 in refractive index. The
108 spontaneous Raman signals arising for the O-H stretch (at wavelength 638 - 660 nm), the C-H
109 stretch (at wavelength 627 - 634 nm), the vinylic C=H stretch (at wavelength 634 - 637 nm) and
110 O-D stretch (at wavelength 607 - 620 nm), are observable (see, for example, the inset of Figure
111 2A) and may be used to quantify the relative abundance species in the droplet.²⁴ For isotopic

112 exchange, the water supply generating the RH in the chamber was switched to D₂O, and the Raman
113 bands corresponding to H₂O and D₂O were monitored over time (Figure 2A).

114 *H₂O/D₂O Exchange*

115 In order to ensure rapid exchange of the gas phase environment in the AOT chamber with D₂O
116 vapor at a constant RH, a three-way valve system was used (Figure 1). Following cell equilibration
117 at the measurement RH with water vapor, the gas flow was deflected away from the cell through
118 an exhaust port, allowing a second valve to deflect the flow to a D₂O bubbler without influencing
119 the droplet stability. The RH of the D₂O flow was allowed to stabilize at the value from the H₂O
120 flow, after which the gas flow was redirected back into the chamber. The total time for the switch
121 procedure is around 1-2 minutes and the chamber response time is on the order of 10's seconds.
122 The main limitation in the response of the droplet to a change in the water isotope is the time
123 required for the liquid deposited on surfaces within the cell to fully exchange. Until this occurs,
124 the gas phase composition is a varying mixture of D₂O and H₂O vapor. From calibration
125 measurements done on NaCl and LiCl solution droplets at variable humidity, the timescale for this
126 to occur is around 20 – 60 s. It was noted for solutions that retain less water but exhibit rapid
127 diffusive mixing in the particle phase that exchange occurs on a more rapid timescale. These
128 calibration data allow us to estimate a limit of detection of the technique to diffusion coefficients
129 less than approximately 10⁻¹³ m² s⁻¹.

130 *Diffusion Theory and Raman Spectroscopy*

131 In order to derive the water diffusion coefficient, D_w , from the timescale for isotopic exchange, a
132 solution to Fick's Second Law of diffusion is used:²⁵

$$133 \quad \frac{C}{C_0} = 1 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{a} \exp \left[\frac{-D_w n^2 \pi^2 t}{a^2} \right]$$

134 where C/C_0 is the fractional concentration of D₂O in the particle during a H₂O to D₂O transition,
135 a is the particle radius, r is the radial distance from the center of the droplet, and t is the time. For
136 a sphere of uniform composition, this solution is used to resolve the time and positional
137 dependence of the droplet isotopic composition during an isotopic exchange step. The model
138 predicts that the surface region rapidly exchanges, while the time for increasing depths to exchange
139 is much longer. Thus, a volume-averaged composition shows a sharp change initially,

140 corresponding to the outer layers of the particle exchanging rapidly, followed by a slower approach
141 to complete the exchange. This was clearly observed in the experiments conducted by Price et al.
142 where the radial composition across a liquid cylinder was measured as a function of time.³ In the
143 AOT, however, the spectroscopic information relates to a radially-averaged composition across
144 the particle depth. This arises due to the laser irradiance, I_0 , and beam cross-section, S , terms in
145 the Raman intensity (N_R) as formulated by Signorell and Reid:²⁶

$$146 \quad N_R = \frac{\partial\sigma}{\partial\Omega}(\Delta\Omega) \frac{I_0}{h\nu} NSL$$

147 with Raman scattering cross-section $\partial\sigma/\partial\Omega$, solid angle $\Delta\Omega$, incident light frequency ν , molecular
148 number concentration N , and interaction length L . In a droplet conceptually broken into radial
149 shells of equal thickness, denoted with the index i , the focused laser beam in the AOT requires the
150 laser irradiance incident on a shell to scale with its surface area, A_i , and the total laser power, P ,
151 thus, giving:

$$152 \quad [N_R]_i \propto \frac{P}{A_i} \times N_i \times A_i \times L_i$$

153 The beam cross-section incident on each shell also scales with the surface area, and these terms
154 cancel out, leading N_R to vary as a function of radial shell thickness, concentration and total laser
155 power. Thus, each radial shell contributes to the total signal weighted by its thickness and
156 concentration, and the scattering intensity measured experimentally corresponds to radially-
157 averaged concentration. Accounting for this by determining a radially-averaged composition from
158 the diffusion model leads to excellent agreement between the shape of the predicted isotope
159 kinetics and the experimental observations. To illustrate the difference, both radial and volume
160 averages are shown in Figure 2B. The volume averaged approach does not replicate the shape of
161 the observed dependence for any value of diffusion coefficient, while the radial approach exhibits
162 excellent agreement. To our knowledge, this is the first time the spontaneous Raman intensity from
163 droplets in an optical tweezers has been used to quantify composition in particles that exhibit a
164 gradient in the radial dimension. Previous work has assumed well mixed particles, where
165 assumptions of radial versus volume averaging become irrelevant.

166 **Results and Discussion**

167 *Water diffusion in binary solution droplets*

168 The isotopic exchange method was applied to sucrose solution droplets with radii in the range 4-5
169 μm , and D_w as a function of RH is shown in Figure 3A. These results are compared to
170 parameterizations reported by Price et al. and Zobrist et al., and the Stokes-Einstein predictions
171 using the viscosity data reported by Power et al.^{2,3,12} Our results are in closer agreement with the
172 isotopic exchange measurements of Price et al. than those reported by Zobrist et al. using mass
173 transport methods. The predictions using S-E fall many orders of magnitude below the
174 measurements and further highlight the limitations of S-E for predicting the diffusion of small
175 molecules in viscous media. The large difference in mobility between water and sucrose due to
176 their molecular size contributes to the breakdown of S-E.

177 Measurements of water diffusion were made in CA solutions (Figure 3B) and, while D_w is larger
178 than for sucrose at a given RH, the prediction by S-E from the viscosity data provided by Reid and
179 coworkers²⁷ are in much closer agreement (although the discrepancy remains greater than an order
180 of magnitude). Given that S-E fails to capture the behavior of water diffusion in sucrose solutions,
181 the improved predictive power for water diffusion in CA solution may arise from the smaller
182 difference in molecular radius between the organic and water. Water diffusion in CA was explored
183 by Lienhard et al., at temperatures $<281\text{ K}$, using an optical model based on Mie theory coupled
184 with evaporation and condensation measurements, and parameterized as a function of temperature
185 and mole fraction of water.¹³ The prediction at 293 K is shown in Figure 3B and fails to reproduce
186 the observations reported here. The optical technique of Lienhard has also been applied to shikimic
187 acid solution droplets by Steimer et al.¹⁵ We observe here values of D_w which are 5 – 10 times
188 smaller than those determined by Steimer et al. (Figure 3C), the discrepancy potentially arising
189 from the complications associated with measuring and interpreting mutual diffusion, as discussed
190 earlier.

191 A Vignes-type fit is commonly used to parameterize the relationship between composition and
192 diffusion coefficient:

193
$$D_w = D_{w,w}^0 (\alpha x_w) \cdot D_{w,org}^0 (1 - \alpha x_w)$$

194 where $D_{w,org}^0$, and $D_{w,w}^0$ are the diffusion coefficient of water in pure organic and in pure water,
195 respectively. x_w is the mole fraction of water, and α is akin to an activity coefficient. Practically

196 any measured dependence could be well described by this relationship given the number of fit
197 parameters usually included in α , which varies as a function of mole fraction of water and
198 temperature. Using the water activity – mole fraction parameterization of Norrish et al.²⁸ (shown
199 by Power et al.² to be most appropriate) for sucrose and E-AIM for CA,²⁹ Vignes curves were fit
200 to the data in two ways. First, by simply assuming $\alpha = 1$ and then allowing $D_{w,org}^0$ to vary, and
201 second, using a functional form (simplified compared to that used by Lienhard et al. due to the
202 fixed temperature of these measurements) of α given by:

$$203 \quad \ln(\alpha) = A(1 - x_w)^3$$

204 and allowing the constant, A, and $D_{w,org}^0$ to vary. These fits are shown in Figure 3A and 3B and
205 both yield a reasonable description of the data, with the $\alpha(x_w)$ method, as expected given the
206 additional fit parameters, performing better.

207 *Water diffusion in ternary solutions*

208 To probe the applicability of the simple Vignes formulation in more complex systems, mixtures
209 of CA and sucrose were investigated in 3:1, 2:1 and 1:1 molar ratios (Figure 4). It is apparent that
210 D_w scales between the limitation cases of the binary solution of citric acid and sucrose, and by
211 plotting the dependence of $\log(D_w)$ with mass fraction, a linear relationship is clearly observed at
212 a given RH (Figure X). Thus, the values of $\log(D_{w,CA}^0)$ and $\log(D_{w,suc}^0)$ established from the binary
213 solutions were scaled linearly using the mass fraction. In order to estimate the mole fraction of
214 water in the ternary solutions, the Zdanovskii-Stokes-Robinson relationship was applied using the
215 dependence of x_w on RH in the binary solutions. Using these data, the Vignes equation was used
216 to estimate the diffusion coefficient for the mixtures, using $\alpha = 1$. There is close agreement between
217 data and prediction despite the simplicity of the relationship and assumptions of ideality. It may
218 be the case that the opposing non-ideality effects in the limiting cases of the binary solutions cancel
219 out in the ternary system. Thus, one might expect complex mixtures to exhibit a relatively simple
220 dependence of D_w on composition and, for application in atmospheric modelling, such a simple
221 dependence is desirable.

222 *Gel formation in inorganic solutions*

223 While ultra-viscous and glassy states are encountered with some organic solutions, inorganic salts
224 typically crystallize at low RH forming distinct solid phases (i.e. efflorescence). An alternative to

225 this process is the formation of a micro-gel – a two phase amorphous state where saturated aqueous
 226 solution and a solid network coexist. Magnesium sulfate is one example of a gel forming salt, as
 227 the divalent ions allow an inorganic network to develop. Water transport becomes limited by slow
 228 percolation through pores in the network. In macroscopic bulk samples, efflorescence or localized
 229 gel formation readily occurs, making measurements of water diffusion challenging. However, in a
 230 contactless technique, the gel phase forms readily, and water transport limitations can be
 231 observed.^{20,30}

232 The dependence of D_w on RH in $MgSO_4$ solution droplets was measured, as shown in Figure 5.
 233 These data exhibit a much stronger decrease in D_w as a function of RH than the organic systems.
 234 While data at higher RH is not accessible to this technique, Price et al. report values down to an
 235 RH of 60%, and combined with our data suggest a rapid onset of diffusion limitations at an RH in
 236 the range 30 – 45%, consistent with a previously reported range of 30 – 55%. A recent study by
 237 Leng et al.¹⁴ report values of D_w at 30%, 20% and 0% using a pulsed RH technique on droplets
 238 deposited on cover slides. At 30%, there is excellent agreement with our data. At lower RH's we
 239 observe diffusion to be slower (by a factor of $\sim 5x$). This may be a consequence of radial
 240 inhomogeneity in droplets during the pulsed RH procedure, leading to measurements that report
 241 an average value of D_w for a droplet with large compositional gradients. The AOT data we report
 242 corresponds to fully equilibrated particles at the measurement RH, and so provides a measurement
 243 of D_w for a sample of uniform composition.

244 The form of the dependence of D_w on RH during gel formation closely resembles predicted
 245 behavior from percolation theory for a mixed system with two different diffusion coefficients^{31,32}.
 246 Percolation theory treats a system as packed hard spheres (the pores) in a matrix (the solid), with
 247 two limiting diffusion coefficients describing water transport in the solid inorganic matrix, D_s , and
 248 the liquid pores, D_p . The overall D_w is predicted to be:³¹

$$249 \quad D_w = \left[D'_p + D'_s + \left\{ (D'_p + D'_s)^2 + 2(Z - 2)D_p D_s \right\}^{\frac{1}{2}} \right] / (Z - 2)$$

$$250 \quad D'_p = D_p \left(\frac{ZV_p}{2f} - 1 \right)$$

251

$$D'_s = D_s \left(\frac{Z}{2} \left\{ 1 - \frac{V_p}{f} \right\} - 1 \right)$$

252 where Z is the coordination number, f is the packing fraction, and V_p is the volume fraction of the
 253 pores. By extrapolating the hygroscopicity data of Ha et al. to 0% RH,³³ it was determined that the
 254 gel phase consists of $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$. For $\text{RH} > 0$, the solid phase and a saturated aqueous phase
 255 coexist. Thus, not all of the MgSO_4 is bound in the solid phase. To account for this, D_p was taken
 256 from the slowest aqueous diffusion constant measured by Price et al. prior to gel formation (2×10^{-11}
 257 $\text{m}^2 \text{s}^{-1}$). The mole fraction of MgSO_4 in the liquid in the pores was assumed to be 0.067; the
 258 saturation concentration of MgSO_4 in water. V_p was estimated from the hygroscopicity data, while
 259 f and Z were allowed to vary to best replicate the data. The best approximation of the data to
 260 percolation theory is shown in Figure 5 using $f = 0.85$ and $Z = 4$. The model exhibits a strong
 261 dependence on these parameters (Figure 5B) and, while their physical interpretation in the MgSO_4
 262 gel is somewhat unclear, the distinct functional form of D_w vs. RH is reproduced by the theory. By
 263 applying the concepts of percolation theory, the onset of gel formation and the sharp fall in D_w
 264 may be ascribed to the development of the solid portion of the gel throughout the whole droplet.
 265 This leads to a state where aqueous channels through the droplet become diminishingly small and
 266 diffusion through the solid phase becomes the limiting step.

267 **Conclusions**

268 In summary, we highlight the unique advantages of the droplet-based isotopic tracer method for
 269 measurements of diffusion coefficients. Firstly, the simplicity of the system allows values of D_w
 270 to be determined with very little computation, eliminating assumptions relating to concentration
 271 and viscosity gradients. Secondly, compared to the liquid disc method of Price et al., the timescales
 272 for equilibration are much shorter, allowing access to measurements of D_w down to $\sim 10^{-17} \text{m}^2 \text{s}^{-1}$
 273 in a single day, which would otherwise take weeks. Thirdly, by eliminating any surfaces, samples
 274 that exhibit contact efflorescence may be studied, having significant advantages for atmospheric
 275 samples, which routinely exist in highly supersaturated states. We have demonstrated excellent
 276 agreement to previous methods of measuring diffusion via isotopic exchange and have shown the
 277 applicability of a simple Vignes relationship for complex mixtures. However, we observe a
 278 significant discrepancy between diffusion measurements made using mass transport and those
 279 made using isotopic exchange. Such observations may reveal complexities associated with

280 modelling mass transport in viscous aerosol that have not yet been fully resolved. The resolution
281 of gel formation in magnesium sulfate highlights the potential utility of the technique in identifying
282 phase behavior that leads to abrupt changes in water mobility (e.g. hydrophobic phase separation).
283 Further applications of this technique will explore the changing role of water diffusion during
284 chemical transformation, providing valuable insight into the influence of oxidative aging in
285 determining diffusive properties of atmospheric aerosol, and the role of diffusion in regulating the
286 rate of chemical change.

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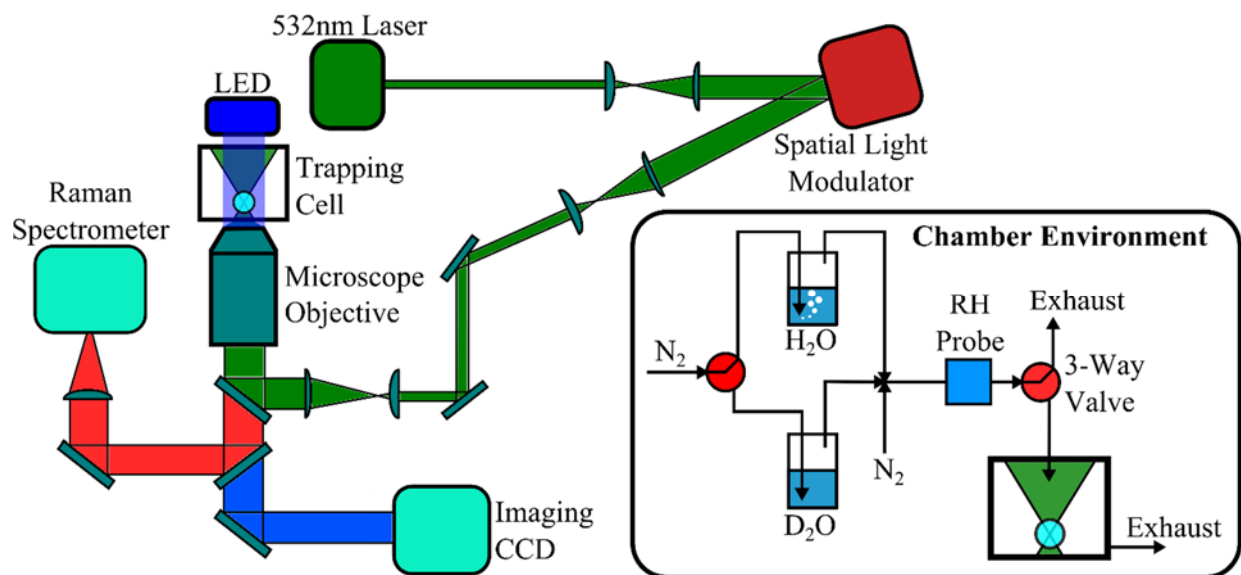
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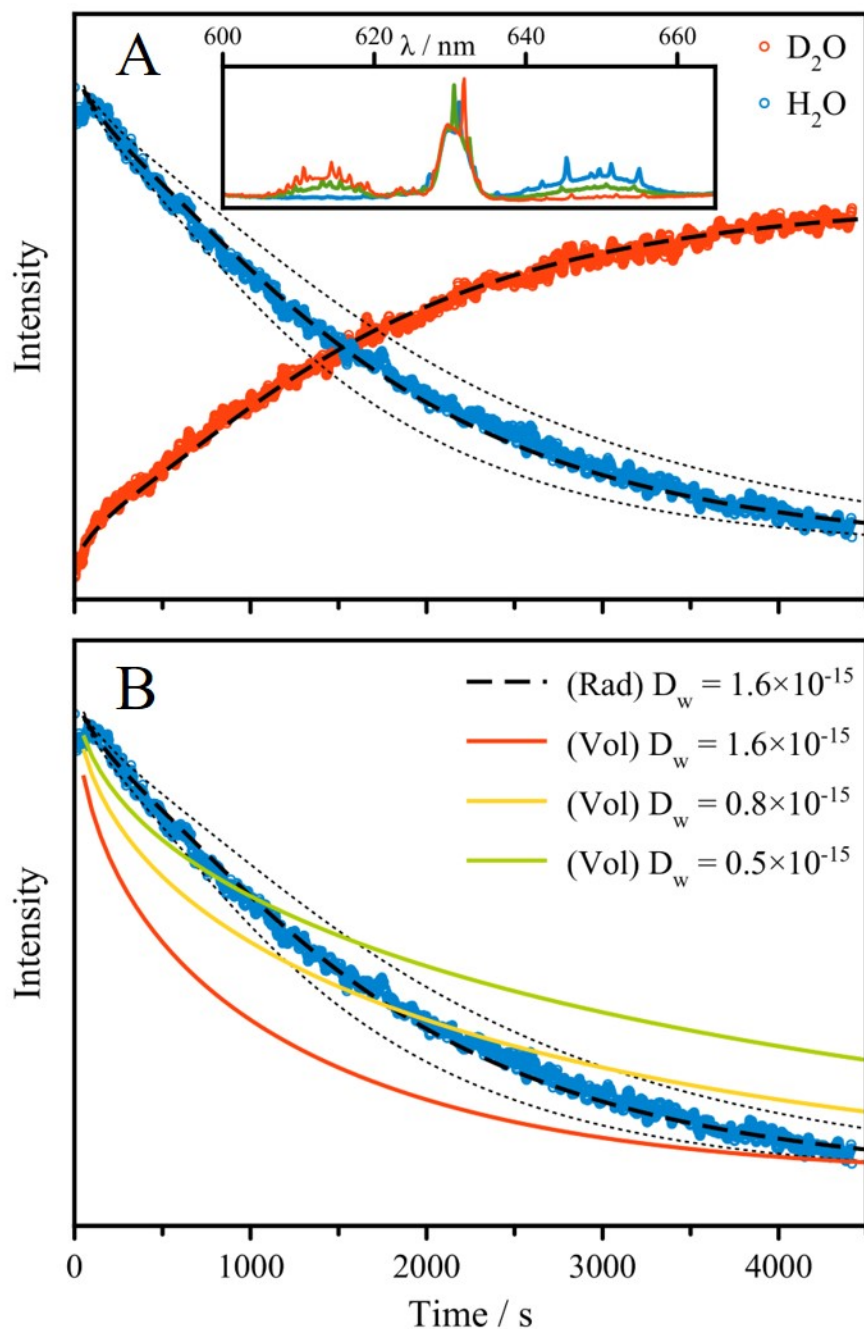


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387 **Figure 1:** Standard optical tweezers (Biral AOT 100) arrangement and (inset) the valve system
 388 used to initiate the exchange between D₂O and H₂O.

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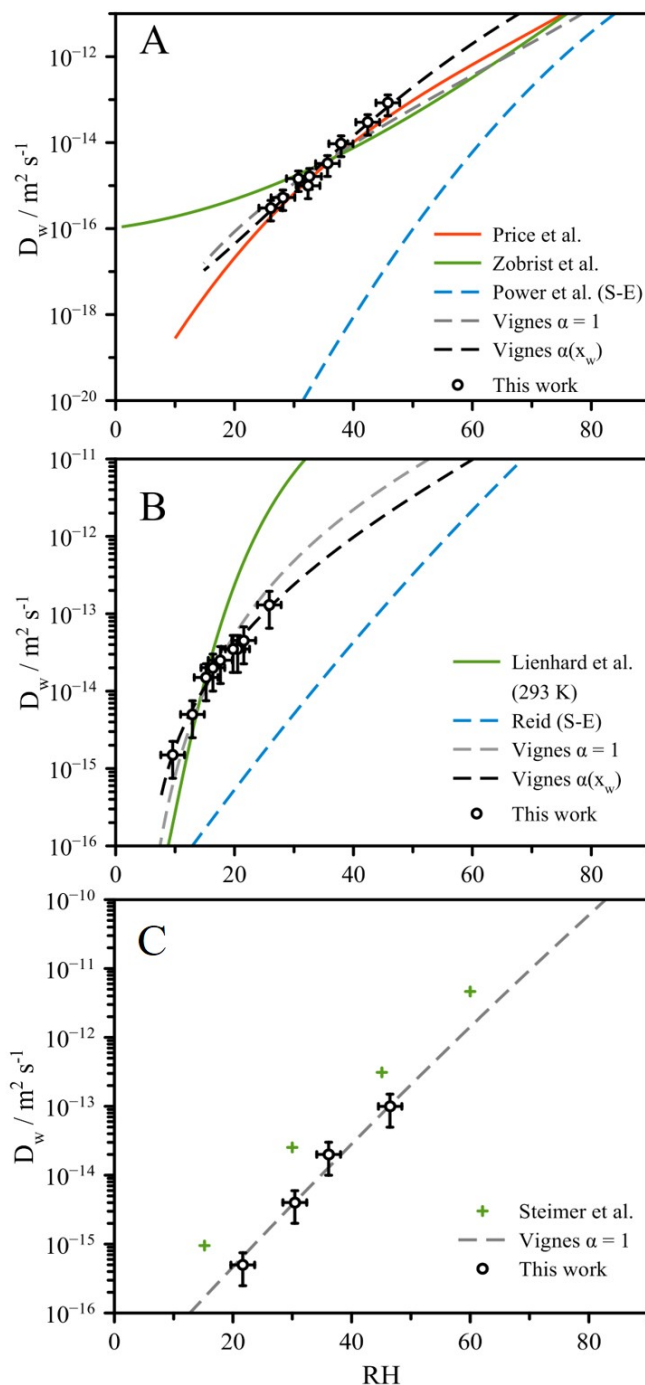
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392 **Figure 2:** (A) Raman band intensity corresponding to H_2O and D_2O stretching vibrations during
 393 isotopic exchange in a $4.8 \mu m$ sucrose droplet at 32% RH. Black dash lines indicate model with D
 394 $= 1.6 \times 10^{-15} m^2 s^{-1}$ with a $\pm 20\%$ variation indicated by the dashed lines. (Inset) Full Raman
 395 spectrum prior to (blue), during (green) and after (red) the exchange. (B) Radially-averaged
 396 composition (dashed lines) and volume-averaged composition (solid lines) simulations for a
 397 sucrose droplet at 32% RH. Diffusion coefficients are indicated in $m^2 s^{-1}$. The dotted lines
 398 represents a $\pm 20\%$ uncertainty in D_w used in the simulation for the radially-averaged case.

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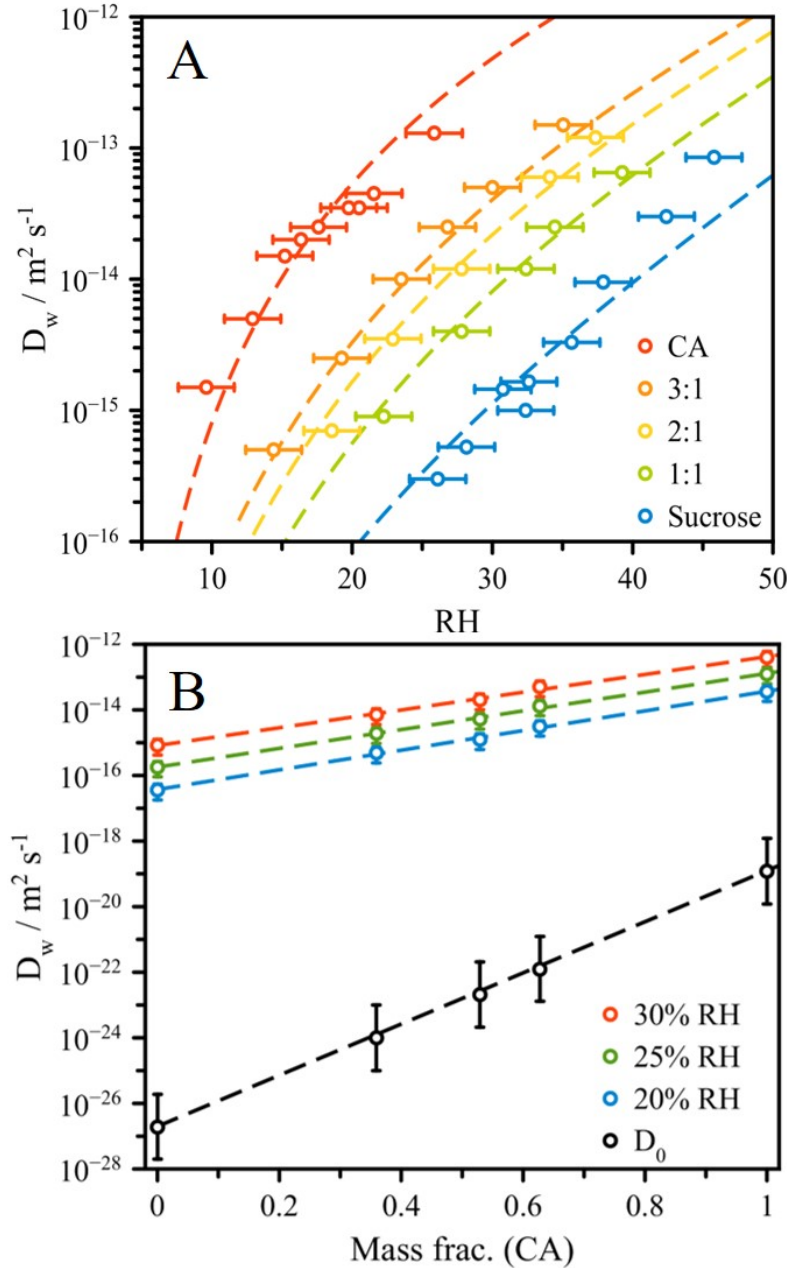
401 **Figure 3:** (A) D_w as a function of RH for sucrose droplets compared to diffusion measurements
 402 derived from mass transport (Zobrist et al.¹²), isotopic exchange on a cover slide (Price et al.³),
 403 and estimates using Stokes-Einstein viscosity (Power et al.²). The Vignes fits are shown for $\alpha = 1$
 404 and $\alpha(x_w)$ as described in the text. (B) D_w as a function of RH for CA droplets compared to the
 405 mass transport / optical approach of Lienhard,¹³ and estimates using the S-E prediction on the
 406 viscosity data of Reid and coworkers.²⁷ Vignes fits shown as described in (A). (C) D_w in shikimic
 407 acid as a function of RH compared to the data reported by Steimer et al. using the mass

408 transport/optical approach of Lienhard.^{13,15} The Vignes fit uses the thermodynamic data of
409 Steimer et al. and $\alpha = 1$ is assumed.

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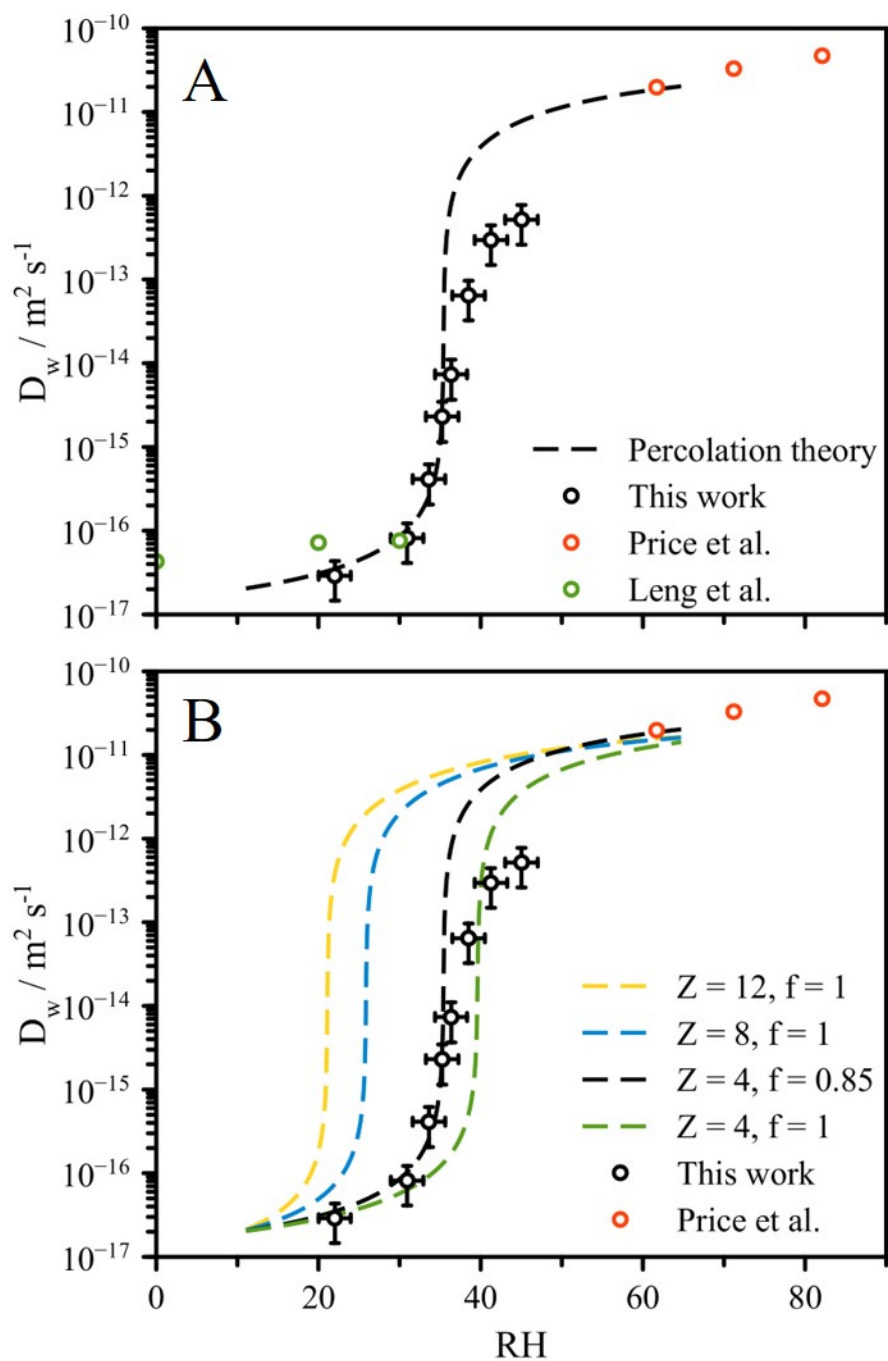
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414 **Figure 4:** (A) D_w for molar ratio mixtures of citric acid and sucrose as a function of RH. The
 415 Vignes predictions with $\alpha = 1$ and assuming a linear relationship for $\log(D_w^{0,\text{mix}})$ with mass fraction
 416 of CA. (B) Water diffusion coefficient in mixtures of CA and sucrose at the specified RH. D_w vs
 417 RH curves were interpolated to infer a value of D_w at the same RH for each dataset. Colored dash
 418 lines represent linear fits. Black dash line represents a linear fit between the values of $\log(D_0)$ for
 419 pure CA and sucrose determined from the Vignes fits with $\alpha = 1$, while the black points represent
 420 D_0 fit separately for each dataset, using individual Vignes fits (with $\alpha = 1$) for each mixture. The
 421 uncertainty in D_0 is an order of magnitude.

422



423

424 **Figure 5:** (A) D_w as a function of RH for magnesium sulfate. Gel formation is indicated by the
 425 rapid decrease of D_w , as predicted by percolation theory (as described in the text and SI). The
 426 isotopic exchange values of Price et al.³ and those determined using the pulsed RH method of Leng
 427 et al.¹⁴ are also shown. (B) A comparison of the percolation theory predictions for a range of values
 428 of coordination number (Z) and packing fraction (f).

429