

## Supporting Information

### Controlled Chemistry via Contactless Manipulation and Merging of Droplets in an Acoustic Levitator

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#### Contents

Acoustic Radiation Pressure for a Modulated Standing Wave.

Tables S1 to S8.

Figures S1 to S14.

Supporting Text:

A. Non-Reactive Mixing of Ethanol and Water

B. Aqueous Acetic Acid and Sodium Hydroxycarbonate Reaction

C. Merging of a Solid Particle and a Liquid Droplet: Water Droplet and a Copper Sulfate crystal  
Movies S1 - S4.

Supporting References

### Acoustic radiation pressure for a modulated standing wave

The total pressure,  $P$ , is the sum of the ambient pressure,  $P_0$ , and the acoustic pressure,  $p$ :

$$P = P_0 + p \quad (S1)$$

For a standing wave, the acoustic pressure  $p$  and the particle velocities,  $v$ , can be written as <sup>1</sup>:

$$p = A \sin k_z z \sin \omega_c t \quad (S2)$$

$$v = \frac{A}{\rho_0 c_0} \cos k_z z \cos \omega_c t \quad (S3)$$

where  $A$  is the pressure amplitude,  $\rho_0$  is the ambient density,  $c_0$  is the speed of sound,  $k_z$  is the wavenumber along the central axis of the levitator, and  $\omega_c$  the angular frequency of the standing wave.

To induce oscillations in the droplet, the voltage of the carrier wave is amplitude modulated by a low-frequency voltage output from a signal generator. The voltage  $V_a$  applied to the ultrasonic transducer is given by:

$$V_a = V_c (1 + m \sin \omega_m t) \sin \omega_c t \quad (S4)$$

where  $V_c$  is the voltage amplitude of the carrier wave oscillating at the angular frequency  $\omega_c$  of the unmodulated ultrasonic standing wave ( $\omega_c/2\pi = 58$  kHz),  $\omega_m$  is the angular frequency of the modulation voltage and has typical values in the range of  $20 \lesssim \omega_m/2\pi \lesssim 40$  Hz, and  $m$  is the modulation index (See Figure 1). For the linear operation of the piezoelectric transducer, where the displacement  $\propto$  applied voltage  $V_a$ , the acoustic pressure  $p$  is proportional to  $V_a$ . Owing to the modulation, equations (S2) and (S3) therefore become:

$$p = A \sin k_z z \sin \omega_c t (1 + m \sin \omega_m t) \quad (S5)$$

$$v = \frac{A}{\rho_0 c_0} \cos k_z z \cos \omega_c t (1 + m \sin \omega_m t) \quad (S6)$$

The mean excess pressure,  $\langle P - P_0 \rangle$ , or equivalently the acoustic radiation pressure,  $P_r$ , is given by:<sup>1</sup>

$$\langle P - P_0 \rangle = \frac{1}{2\rho_0 c_0^2} \langle p^2 \rangle - \frac{1}{2} \rho_0 \langle v^2 \rangle = \langle V \rangle - \langle K \rangle \quad (S7)$$

where  $\langle V \rangle$  is the time-averaged potential energy density,  $\langle p^2 \rangle / 2\rho_0 c_0^2$ , and  $\langle K \rangle$  is the time-averaged kinetic energy density,  $\rho_0 \langle v^2 \rangle / 2$ . Substituting equations (S5) and (S6) into equation (S7), evaluating the time-average over one period of the ultrasonic wave,  $2\pi/\omega_c$ , and making the accurate approximation that  $\sin \omega_m t$  is constant over the one period ( $\omega_c/\omega_m \approx 2000$ ) gives:

$$P_r(z, t) = \frac{A^2}{4\rho_0 c_0^2} (\sin^2 k_z z - \cos^2 k_z z) (1 + 2m \sin \omega_m t + m^2 \sin^2 \omega_m t) \quad (S8)$$

Thus, the amplitude modulation produces a time-independent pressure that levitates the droplet, and a time-varying pressure with the frequencies of  $\omega_m$  and  $2\omega_m$ . The modulation index  $m$  is typically  $\ll 1$ , and so the last term on the right-hand side of equation (S8) is usually much smaller than the other terms. Finally, we can therefore write:

$$P_r(z, t) \approx -\frac{A^2}{4\rho_0 c_0^2} \cos 2k_z z (1 + 2m \sin \omega_m t) \quad (S9)$$

## Supporting Tables

Table S1. Q-branch wavenumbers and vibrational mode assignments for bands a\*–d\* in the FTIR spectra of the nitric acid droplet (see Figure 4).

| Band | Q-branch wavenumber (cm <sup>-1</sup> ) | Q-branch Ref. wavenumber (cm <sup>-1</sup> ) <sup>a)</sup> | Number (symmetry) | Vibrational mode <sup>†</sup>  |
|------|-----------------------------------------|------------------------------------------------------------|-------------------|--------------------------------|
| a*   | 3551.1 ± 0.1                            | 3550.0                                                     | $\nu_1(A')$       | $\nu(\text{OH})$               |
| b*   | 1711.8 ± 0.1                            | 1711.8                                                     | $\nu_2(A')$       | $\nu_{\text{as}}(\text{NO}_2)$ |
| c*   | 1325.15 ± 0.04                          | 1324.9                                                     | $\nu_4(A')$       | $\nu_s(\text{NO}_2)$           |
| d*   | 878.5 ± 0.1                             | 878.6                                                      | $\nu_5(A')$       | ONO angle deformation          |

<sup>†</sup> $\nu$  denotes stretch; s, symmetric; and as, antisymmetric.

<sup>a)</sup>Ref.<sup>2</sup>.

Table S2. Vibrational mode assignments for the new bands (a)–(n) in the FTIR spectra produced by merging a [BMIM][DCA] droplet and a nitric acid droplet (see Figure 4).

| Band | Centre wavenumber <sup>††</sup> (cm <sup>-1</sup> ) | Molecule                     | Ref. band centre (cm <sup>-1</sup> ) | Number (symmetry)                       | Vibrational mode <sup>†</sup>  |
|------|-----------------------------------------------------|------------------------------|--------------------------------------|-----------------------------------------|--------------------------------|
| a    | 3715                                                | CO <sub>2</sub>              | 3714.8 <sup>a)</sup>                 | $\nu_1(\sigma_g^+) + \nu_3(\sigma_u^+)$ | combination band               |
| b    | 3612                                                | CO <sub>2</sub>              | 3612.8 <sup>a)</sup>                 | $\nu_1(\sigma_g^+) + \nu_3(\sigma_u^+)$ | combination band               |
| c    | 3480                                                | N <sub>2</sub> O             | 3480.8 <sup>b)</sup>                 | $\nu_1(\sigma^+) + \nu_3(\sigma^+)$     | combination band               |
| d    | 3364                                                | N <sub>2</sub> O             | 3364.0 <sup>b)</sup>                 | $2\nu_2(\pi) + \nu_3(\sigma^+)$         | combination band               |
| e    | 2797                                                | N <sub>2</sub> O             | 2798.3 <sup>b)</sup>                 | $\nu_2(\pi) + \nu_3(\sigma^+)$          | combination band               |
| f    | 2562                                                | N <sub>2</sub> O             | 2563.3 <sup>b)</sup>                 | $2\nu_1(\sigma^+)$                      | combination band               |
| g    | 2461                                                | N <sub>2</sub> O             | 2462.0 <sup>b)</sup>                 | $\nu_1(\sigma^+) + 2\nu_2(\pi)$         | combination band               |
| h    | 2349                                                | CO <sub>2</sub>              | 2349.1 <sup>a)</sup>                 | $\nu_3(\sigma_u^+)$                     | $\nu_{\text{as}}(\text{CO}_2)$ |
| i    | 2223                                                | N <sub>2</sub> O             | 2223.8 <sup>b)</sup>                 | $\nu_3(\sigma^+)$                       | $\nu(\text{NN})$               |
| j    | 1377                                                |                              |                                      |                                         |                                |
| k    | 1355                                                | NO <sub>3</sub> <sup>-</sup> | 1356.2 <sup>d)</sup>                 | $\nu_3(e')$                             | $\nu(\text{NO}_3)$ (tentative) |
| l    | 1285                                                | N <sub>2</sub> O             | 1284.9 <sup>b)</sup>                 | $\nu_1(\sigma^+)$                       | $\nu(\text{NO})$               |
| m    | 668                                                 | CO <sub>2</sub>              | 667.4 <sup>a)</sup>                  | $\nu_2(\pi_u)$                          | $\delta(\text{CO}_2)$          |
| n    | 589                                                 | N <sub>2</sub> O             | 589 <sup>c)</sup>                    | $\nu_2(\pi)$                            | $\delta(\text{N}_2\text{O})$   |

<sup>†</sup> $\nu$  denotes stretch;  $\delta$ , bend; and as, antisymmetric.

<sup>††</sup>Uncertainties less than 1 cm<sup>-1</sup>.

<sup>a)</sup>Ref.<sup>3</sup>, <sup>b)</sup>Ref.<sup>4</sup>, <sup>c)</sup>Ref.<sup>5</sup>, <sup>d)</sup>Ref.<sup>6</sup>.

Table S3. Wavenumbers and vibrational mode assignments for peaks in the Raman spectra of the 70% nitric acid and 30% water droplet (see Figure 5).

| Peak | Wavenumber (cm <sup>-1</sup> ) | Molecule or ion                      | Ref. wavenumber (cm <sup>-1</sup> ) | Number (symmetry)          | Vibrational mode <sup>†</sup> |
|------|--------------------------------|--------------------------------------|-------------------------------------|----------------------------|-------------------------------|
| a*   | ≈3700-2900                     | HNO <sub>3</sub><br>H <sub>2</sub> O | 3550.0 <sup>a)</sup>                | $\nu_1(A')$                | $\nu(OH)$                     |
| b*   | 1649 ± 1                       | NO <sub>3</sub> <sup>-</sup> (aq)    | 1648 <sup>b)</sup>                  | (A')                       | 2 x $\delta$ out-of-plane     |
| c*   | 1440 ± 1                       | NO <sub>3</sub> <sup>-</sup> (aq)    | 1430 <sup>b)</sup>                  | $\nu_3(E')$                | $\nu_{as}(NO_3^-)$            |
| d*   | 1305 ± 1                       | HNO <sub>3</sub>                     | 1304 <sup>b)</sup>                  | $\nu_4(A')$ A <sub>1</sub> | $\nu_s(NO_2)$                 |
| e*   | 1043 ± 1                       | NO <sub>3</sub> <sup>-</sup> (aq)    | 1046 <sup>b)</sup>                  | $\nu_1(A')$                | $\nu_s(NO_3^-)$               |
| f*   | 960 ± 1                        | HNO <sub>3</sub>                     | 955 <sup>b)</sup>                   | $\nu_5(A')$ A <sub>1</sub> | $\nu(N-OH)$                   |
| g*   | 705 ± 1                        | NO <sub>3</sub> <sup>-</sup> (aq)    | 720 <sup>b)</sup>                   | $\nu_4(E')$                | $\delta_4(O-N-O)$             |
| h*   | 682 ± 1                        | HNO <sub>3</sub>                     | 688 <sup>b)</sup>                   | $\nu_6(A')$ A <sub>1</sub> | $\delta(O-N-O)_{sc}$          |
| i*   | 641 ± 1                        | HNO <sub>3</sub>                     | 640 <sup>b)</sup>                   | $\nu_7(A')$ B <sub>1</sub> | $\delta(O-N-O)_r$             |

<sup>†</sup> $\nu$  denotes stretch;  $\delta$ , bend; s, symmetric; and as, antisymmetric.

<sup>a)</sup>Ref.<sup>2</sup>, <sup>b)</sup>Ref.<sup>7</sup>.

Table S4. Vibrational mode assignments for the observed peaks in the Raman spectra of [BMIM][DCA] (see Figure 5). The letters a) - q) correspond to the [BMIM]<sup>+</sup> peak labels in Figure 5, and  $\nu_4$  -  $\nu_9$  are the vibrational mode numbers of the [DCA]<sup>-</sup> anion.

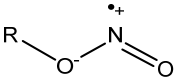
| Peak            | Present measured wavenumbers (cm <sup>-1</sup> ) | Ref. wavenumbers (cm <sup>-1</sup> ) | Vibrational mode assignments <sup>†</sup>                                                                                        |
|-----------------|--------------------------------------------------|--------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|
| a               | 3432 ± 2                                         |                                      |                                                                                                                                  |
| b               | 3165 ± 1                                         | 3173 <sup>a)</sup>                   | $\nu(\text{C4-H, C5-H})$ in-phase                                                                                                |
| c               | 3142 ± 5                                         | 3157 <sup>a)</sup>                   | $\nu(\text{C4-H, C5-H})$ out-of-phase                                                                                            |
| d               | 3111 ± 1                                         | 3112 <sup>a)</sup>                   | $\nu(\text{C2-H})$                                                                                                               |
| e               | 3000 ± 5                                         | 3001 <sup>a)</sup>                   | $\nu_{\text{as}}[\text{CH}_3(\text{Me})]$                                                                                        |
| f               | 2962 ± 1                                         | 2969 <sup>a)</sup>                   | $\nu_{\text{as}}(\text{CH}_2, \text{CH}_3)$                                                                                      |
| g               | 2937 ± 1                                         | 2942 <sup>a)</sup>                   | $\nu_{\text{as}}(\text{CH}_2, \text{CH}_3)$                                                                                      |
| h               | 2914 ± 1                                         | 2917 <sup>a)</sup>                   | $\nu_{\text{s}}[\text{CH}_3(\text{Me})]$                                                                                         |
| i               | 2876 ± 1                                         | 2877 <sup>a)</sup>                   | $\nu_{\text{s}}(\text{CH}_2)$<br>$\nu_{\text{s}}[\text{CH}_3(\text{Bu})]$                                                        |
| j               | 2835 ± 2                                         | 2840 <sup>a)</sup>                   | $\nu_{\text{s}}(\text{CH}_2)$                                                                                                    |
| k               | 2740 ± 1                                         |                                      | Combination band                                                                                                                 |
| $\nu_6 + \nu_7$ | 2236 ± 1                                         | 2228 <sup>b)</sup>                   | Fermi enhanced $\nu_{\text{s}}(\text{N-C}) + \nu_{\text{as}}(\text{N-C})$ combination band                                       |
| $\nu_9$         | 2192 ± 1                                         | 2192 <sup>c)</sup>                   | $\nu_{\text{s}}(\text{C}\equiv\text{N})$ ( $A_1$ )                                                                               |
| $\nu_8$         | 2134 ± 1                                         | 2133 <sup>c)</sup>                   | $\nu_{\text{as}}(\text{C}\equiv\text{N})$ ( $B_2$ )                                                                              |
| l               | 1573 ± 1                                         | 1568 <sup>a)</sup>                   | $\nu(\text{C}=\text{C})$<br>$\nu_{\text{as}}(\text{N1C2N3}), r(\text{C2H})$                                                      |
| m               | 1457 ± 1                                         | 1464 <sup>a)</sup>                   | $\delta_{\text{s}}(\text{CH}_3)$<br>$\delta_{\text{as}}[\text{CH}_3(\text{Me})]$                                                 |
| n               | 1448 ± 1                                         | 1448 <sup>a)</sup>                   | $\delta_{\text{as}}[\text{CH}_3(\text{Bu})]$<br>$\delta_{\text{s}}(\text{CH}_2)$<br>$\delta_{\text{as}}[\text{CH}_3(\text{Me})]$ |
| o               | 1422 ± 1                                         | 1421 <sup>a)</sup>                   | $\delta_{\text{s}}[\text{CH}_3(\text{Me})]$<br>$\delta(\text{CH}_2), \nu_{\text{ring}}$                                          |
| p               | 1392 ± 1                                         | 1391 <sup>a)</sup>                   | $w(\text{CH}_2)$<br>$\nu_{\text{as}}(\text{C2N1C5})$                                                                             |
| q               | 1341 ± 1                                         | 1342 <sup>a)</sup>                   | $\nu(\text{N-Bu, N-Me, breathing})$                                                                                              |
| r               | 1312 ± 1                                         | 1311 <sup>a)</sup>                   | $w(\text{CH}_2)$                                                                                                                 |
| $\nu_7$         |                                                  | 1309 <sup>c)</sup>                   | $\nu_{\text{as}}(\text{N-C})$ ( $B_2$ )                                                                                          |
| s               | 1281 ± 2                                         | 1286 <sup>a)</sup>                   | $r(\text{C-H}), t(\text{CH}_2)$                                                                                                  |
| t               | 1254 ± 2                                         | 1254 <sup>a)</sup>                   | $t(\text{CH}_2), r(\text{C2-H})$                                                                                                 |
| u               | 1213 ± 1                                         | 1212 <sup>a)</sup>                   | $t(\text{CH}_2), r(\text{C2-H})$                                                                                                 |
| v               | 1170 ± 2                                         | 1173 <sup>a)</sup>                   | $\nu(\text{N-Bu, N-Me}), r(\text{C-H})$                                                                                          |
| w               | 1115 ± 1                                         | 1117 <sup>a)</sup>                   | $r(\text{CH}_3), r[\text{CH}_3(\text{Bu})]$                                                                                      |
| x               | 1088 ± 1                                         | 1093 <sup>a)</sup>                   | $r(\text{C-H})$<br>$\nu(\text{C-C})$                                                                                             |
| y               | 1052 ± 1                                         | 1057 <sup>a)</sup>                   | $\nu(\text{C-C})$                                                                                                                |

|                     |          |                                                                               |                                                                             |
|---------------------|----------|-------------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| <u>z</u>            | 1023 ± 1 | 1022-1036 <sup>a)</sup><br>1015-1020 <sup>a)</sup><br>(theoretical<br>values) | $\delta_{\text{ring}}$<br>breathing, $\nu(\text{N-Bu, N-Me})$               |
| <u>a</u>            | 974 ± 2  | 976 <sup>a)</sup>                                                             | $\nu_{\text{as}}(\text{C-C})$                                               |
| <u>b</u>            | 944 ± 3  | 951 <sup>a)</sup>                                                             | $r[\text{CH}_3(\text{Bu}), \text{CH}_2]$<br>$\gamma(\text{C2-H})$           |
| <u>c</u><br>$\nu_6$ | 905 ± 1  | 907 <sup>a)</sup><br>904 <sup>c)</sup>                                        | $\nu(\text{C-C})$<br>$\nu_{\text{s}}(\text{N-C}) (\text{A}_1)$              |
| <u>d</u>            | 881 ± 1  | 884 <sup>a)</sup>                                                             | $\nu(\text{C-C})$                                                           |
| <u>e</u>            | 823 ± 1  | 825 <sup>a)</sup>                                                             | $\gamma(\text{C4-H, C5-H})$<br>$\nu_{\text{s}}(\text{C-C-C})$               |
| <u>f</u>            | 804 ± 2  | 810 <sup>a)</sup>                                                             | $\nu_{\text{s}}(\text{C-C-C})$                                              |
| <u>g</u>            | 755 ± 2  | 765 <sup>a)</sup>                                                             | $r(\text{CH}_2)$                                                            |
| <u>h</u>            | 736 ± 2  | 734 <sup>a)</sup>                                                             | $r(\text{CH}_2)$<br>$\gamma(\text{C4-H, C5-H})$<br>$\nu(\text{N-Me, N-Bu})$ |
| <u>i</u>            | 690 ± 20 | 699 <sup>a)</sup>                                                             | $\nu(\text{N-Me, N-Bu})$                                                    |
| $\nu_5$             | 662 ± 1  | 666 <sup>c)</sup>                                                             | $\delta(\text{CNC}) (\text{A}_1)$                                           |
| <u>j</u>            | 650 ± 10 | 658 <sup>a)</sup>                                                             | $\nu(\text{N-Me, N-Bu})$                                                    |
| <u>k</u>            | 619 ± 1  | 624 <sup>a)</sup>                                                             | $\gamma(\text{N-Bu}), \text{ring puckering}$                                |
| <u>l</u>            | 598 ± 2  | 601 <sup>a)</sup>                                                             | $\delta(\text{N1-C2-N3})$                                                   |
| $\nu_4$             | 536 ± 1  | 524 <sup>c)</sup>                                                             | $\gamma_{\text{s}}(\text{N-C}\equiv\text{N}) (\text{A}_2)$                  |
| <u>m</u>            | 505 ± 2  | 501 <sup>a)</sup>                                                             | $\delta(\text{N-C-C, C-C-C})$                                               |
| <u>n</u>            | 470 ± 4  | 473 <sup>a)</sup>                                                             | $\delta(\text{N-C-C, C-C-C})$                                               |
| <u>o</u>            | 427 ± 4  | 435 <sup>a)</sup>                                                             | $r(\text{N-Bu, N-Me})$<br>$\delta(\text{N-C-C, C-C-C})$                     |
| <u>p</u>            | 408 ± 2  | 415 <sup>a)</sup>                                                             | $r(\text{N-Bu, N-Me})$                                                      |
| <u>q</u>            | 322 ± 1  | 325 <sup>a)</sup>                                                             | $\delta(\text{C-C-C})$                                                      |

<sup>†</sup> $\nu$  denotes stretch;  $\delta$ , bend; w, wagging; t, twisting; r, rocking;  $\gamma$ , out-of-plane; s, symmetrical; as, antisymmetrical; Me, methyl group; and Bu, butyl group.

<sup>a)</sup>Ref.<sup>8</sup>, <sup>b)</sup>Ref.<sup>9</sup>, <sup>c)</sup>Ref.<sup>10</sup>.

Table S5. Wavenumbers and vibrational mode assignments for the new peaks (1) - (4) in the Raman spectrum produced by merging a [BMIM][DCA] and a nitric acid droplet (see Figure 5).

| Peak        | Merged droplet measured wavenumber (cm <sup>-1</sup> ) | Functional group or molecule                                                                                                                       | Region (cm <sup>-1</sup> )    | Vibrational mode assignments <sup>a)</sup>                                                                                              |
|-------------|--------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| 1           | 2260 ± 2                                               | -C≡N                                                                                                                                               | 2240-2260                     | C≡N str. (tentative)                                                                                                                    |
| 2<br>3<br>4 | 1693 ± 1<br>1661 ± 2<br>1631 ± 2                       | Organic nitrites, <i>trans</i> -form<br><br>Carbonyl group<br>C=O | 1680-1650 vs<br><br>1850-1550 | N=O str.<br>primary ~ 1675cm <sup>-1</sup> ,<br>secondary ~ 1665cm <sup>-1</sup> ,<br>tertiary ~ 1625cm <sup>-1</sup> .<br><br>C=O str. |

<sup>a)</sup>Ref. <sup>11</sup>

## Supporting Figures

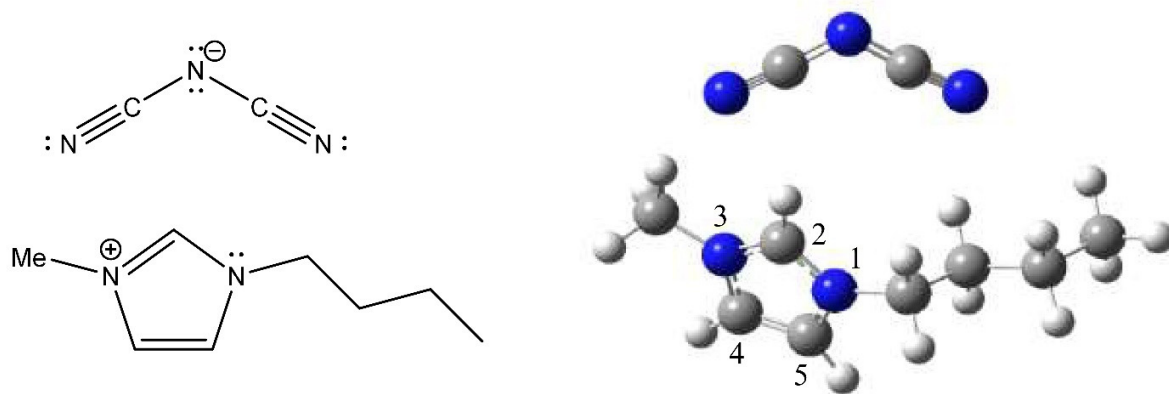


Figure S1. Left: Structure of [BMIM][DCA] showing the [DCA]<sup>-</sup> anion and the positions of the methyl (–CH<sub>3</sub>) and butyl (–C<sub>4</sub>H<sub>9</sub>) functional groups on the imidazolium ring (C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>). Right: Optimized structure of [BMIM][DCA] displaying the numbering convention for the positions of the atoms in the imidazolium as used in Table S4.



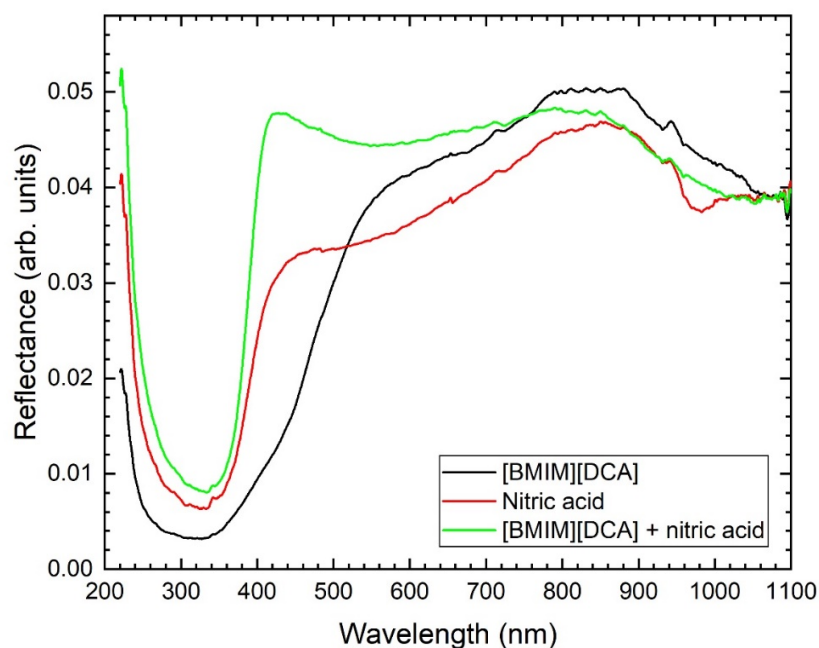


Figure S2. UV-visible reflectance spectra the [BMIM][DCA] droplet, the nitric acid droplet, and the droplet of [BMIM][DCA] merged with nitric acid corresponding to Figure 3. Each of the three samples has strong absorption bands from 200 nm to 400 nm. For [BMIM][DCA], the region of high absorption extends to longer wavelengths into the violet-green region from 400 nm to 560 nm. After merging, there is a significant increase in the reflectance (or reduction in the absorption) in the violet to green region, so that the reflectance is approximately constant across the visible range from 400 nm to 700 nm, which is a consequence of the appearance of the white precipitate. Full interpretation of the UV-visible spectra will require calculation of electronic spectra for the [BMIM][DCA] and the white precipitate.

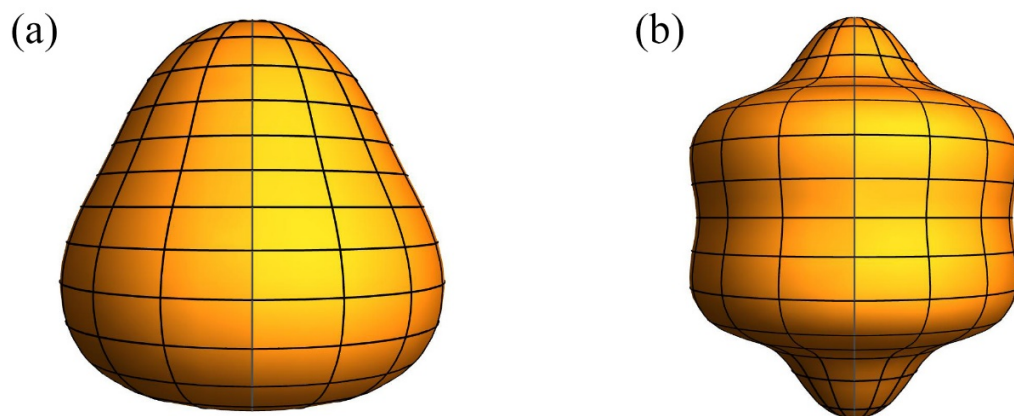


Figure S3. Axisymmetric vibrational modes with (a)  $l = 3$  and (b)  $l = 6$  [equation (4)].

## Supporting Text

### A. Non-Reactive Mixing of Ethanol and Water

To demonstrate the feasibility of the merging technique, we levitated and merged droplets of water and ethanol. Photographs of a  $2.0\text{ mm} \times 1.3\text{ mm}$  ethanol droplet levitated above a  $2.5\text{ mm} \times 1.5\text{ mm}$  water droplet and the  $3.0 \times 2.0\text{ mm}$  merged droplet are shown in Figure S4. A film of the merging process is shown in Movie S2. Raman spectra of the ethanol, water, and merged droplets are presented in Figure S5. Clearly, the Raman spectrum following the coalescence is the sum of the separate Raman spectra of ethanol and water thus demonstrating that the two droplets have merged. The vibrational modes for the ethanol peaks a - q and the water peaks a\* - c\* are assigned in Table S6 and agree with literature values of ethanol<sup>12, 13</sup> and water,<sup>14</sup> respectively. Briefly, the water peaks a\* - c\* arise from O-H stretches, whereas the ethanol peaks a - q can be linked to the symmetric and antisymmetric stretches of the methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2$ ) groups. In the merged spectrum, the O-H stretching fundamental vibrational modes of ethanol are hidden by the O-H fundamental modes of the water molecule. The corresponding FTIR and UV-visible spectra of the ethanol droplet, water droplet, and merged droplet are shown in Figures S6 and S7, respectively.

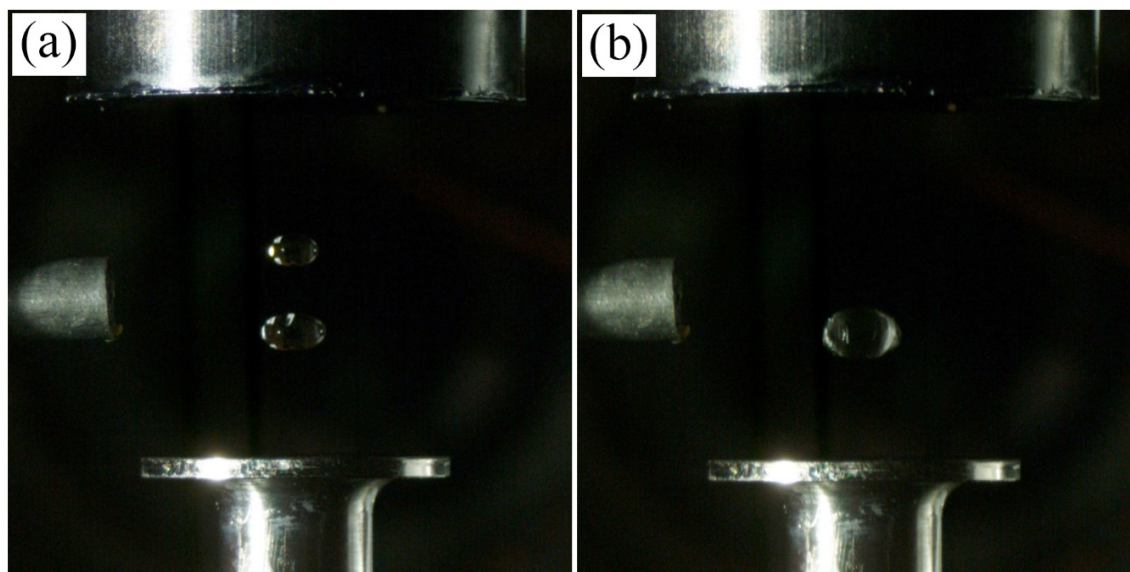


Figure S4. Photographs of (a) an ethanol droplet levitated above a water droplet and (b) the merged droplet.

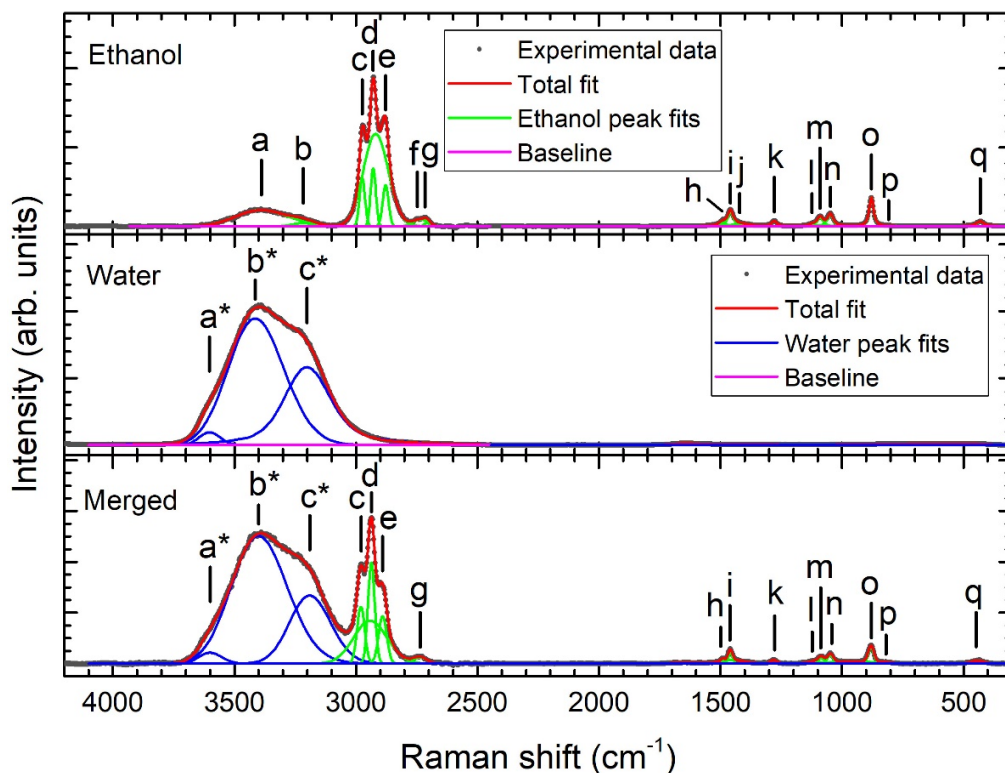


Figure S5. Raman spectra of the ethanol droplet, water droplet, and merged droplet. The wavenumbers and vibrational mode assignments for the labelled peaks are presented in Table S6.

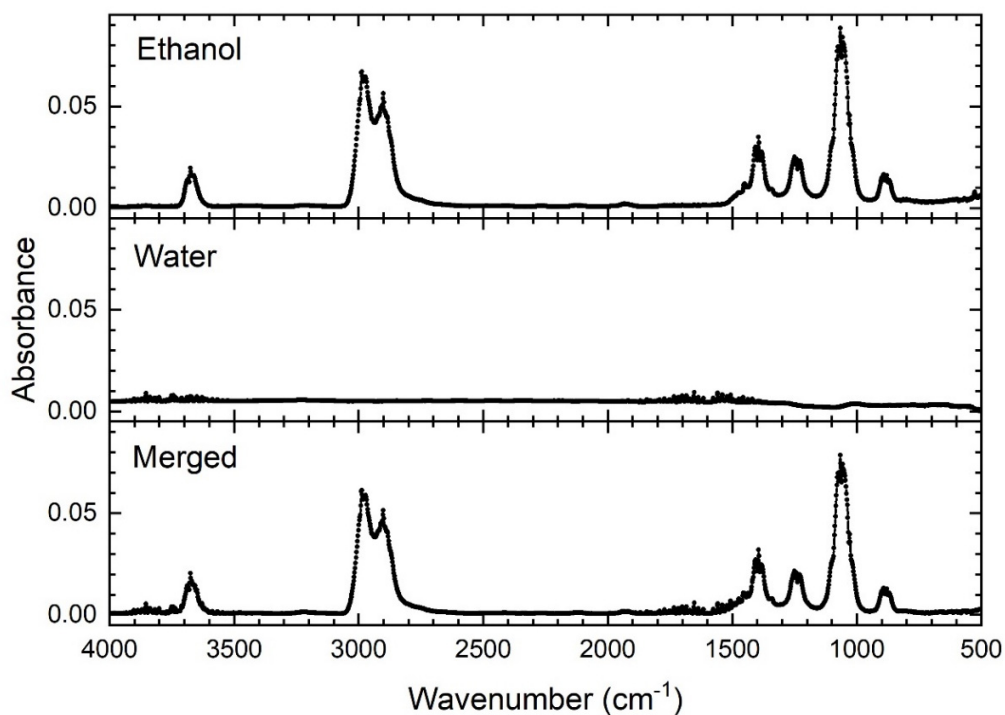


Figure S6. FTIR spectra of the ethanol droplet, water droplet, and merged droplet shown in Figure S4.

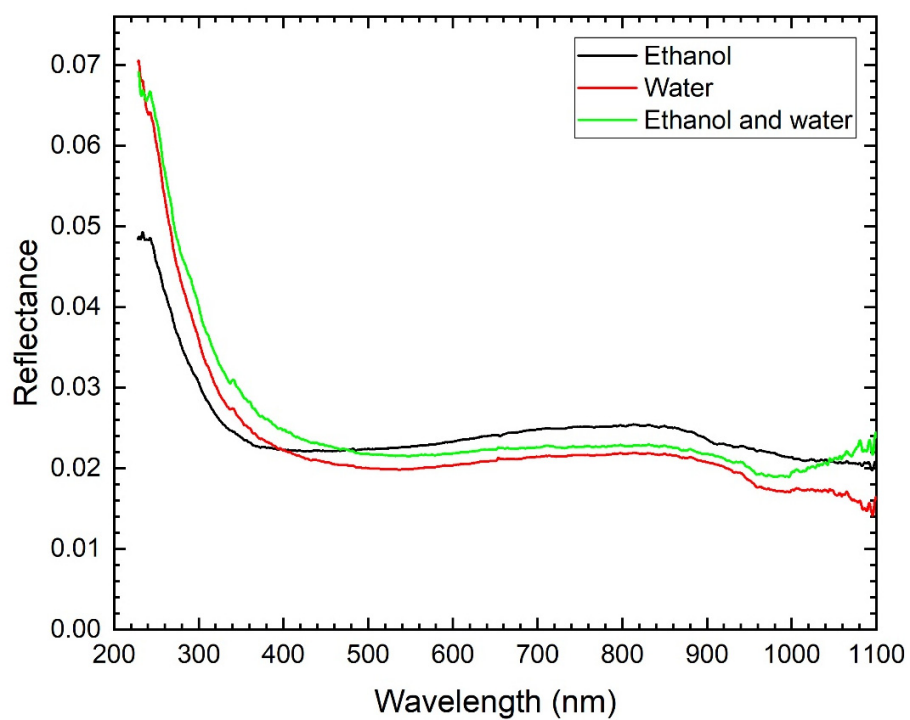


Figure S7. UV-visible spectra of the ethanol droplet, water droplet, and merged droplet shown in Figure S4.

Table S6. Wavenumbers and vibrational mode assignments for peaks in the Raman spectra of the (i) ethanol, (ii) water, and (iii) merged droplets shown in Figure S5.

(i)

| Peak | Wavenumber<br>(cm <sup>-1</sup> ) | Ref.<br>wavenumber*<br>(cm <sup>-1</sup> )   | Vibrational<br>mode <sup>†</sup>                                                                      |
|------|-----------------------------------|----------------------------------------------|-------------------------------------------------------------------------------------------------------|
| a    | 3389 ± 2                          | 3393 <sup>a)</sup>                           | $\nu_1(A')$ $\nu(\text{OH})$                                                                          |
| b    | 3217 ± 3                          | 3220 <sup>a)</sup>                           | $\nu_1(A')$ $\nu(\text{OH})$                                                                          |
| c    | 2974 ± 1                          | 2973 <sup>b)</sup>                           | $\nu_{\text{as}}(\text{CH}_3)$<br>$\nu(\text{gauche-CH}_2)$ in-plane                                  |
| d    | 2929 ± 1                          | 2930 <sup>b)</sup>                           | $\nu_{\text{s}}(\text{CH}_3)$<br>$\nu_{\text{as}}(\text{trans-CH}_2)$<br>FR(CH <sub>2</sub> )         |
| e    | 2878 ± 1                          | 2876 <sup>b)</sup>                           | FR(CH <sub>3</sub> )<br>$\nu_{\text{s}}(\text{trans-CH}_2)$<br>$\nu(\text{gauche-CH}_2)$ out-of-plane |
| f    | 2748 ± 1                          | 2770 <sup>c)</sup>                           | Overtone                                                                                              |
| g    | 2715 ± 1                          | 2730 <sup>c)</sup>                           | Overtone                                                                                              |
| h    | 1492 ± 1                          | 1490.2 <sup>d)</sup>                         | $\delta(\text{CH}_2)$                                                                                 |
| i    | 1459 ± 1                          | 1463.5 <sup>d)</sup><br>1445.8 <sup>d)</sup> | $\delta_{\text{a}}(\text{CH}_3)$<br>$\delta_{\text{a}}(\text{CH}_3)$ A''                              |
| j    | 1422 ± 7                          | 1411.7 <sup>d)</sup>                         | w(CH <sub>2</sub> )                                                                                   |
| k    | 1278 ± 1                          | 1274.8 <sup>d)</sup><br>1256.3 <sup>d)</sup> | tw(CH <sub>2</sub> ) A''<br>$\delta(\text{OH})$                                                       |
| l    | 1123 ± 2                          | 1139.9 <sup>d)</sup>                         | r(CH <sub>2</sub> )+r(CH <sub>3</sub> ) A''                                                           |
| m    | 1090 ± 1                          | 1090.7 <sup>d)</sup>                         | $\nu(\text{CCO})$ +r(CH <sub>3</sub> )                                                                |
| n    | 1048 ± 1                          | 1027.7 <sup>d)</sup>                         | $\nu(\text{CCO})$ +r(CH <sub>3</sub> )                                                                |
| o    | 879 ± 1                           | 887.6 <sup>d)</sup>                          | $\nu(\text{CCO})$                                                                                     |
| p    | 808 ± 1                           | 812 <sup>d)</sup>                            | r(CH <sub>2</sub> )+r(CH <sub>3</sub> ) A''                                                           |
| q    | 431 ± 1                           | 422 <sup>c)</sup>                            | $\delta(\text{CCO})$                                                                                  |

(ii)

| Peak | Wavenumber<br>(cm <sup>-1</sup> ) | Ref.<br>wavenumber*<br>(cm <sup>-1</sup> ) | Vibrational<br>mode <sup>†</sup> |
|------|-----------------------------------|--------------------------------------------|----------------------------------|
| a*   | 3602 ± 1                          | 3628 <sup>a)</sup>                         | $\nu_1(A')$ $\nu(\text{OH})$     |
| b*   | 3414 ± 1                          | 3393 <sup>a)</sup>                         | $\nu_1(A')$ $\nu(\text{OH})$     |
| c*   | 3201 ± 1                          | 3220 <sup>a)</sup>                         | $\nu_1(A')$ $\nu(\text{OH})$     |

(iii)

| Peak | Wavenumber<br>(cm <sup>-1</sup> ) | Ref.<br>wavenumber*<br>(cm <sup>-1</sup> )   | Vibrational<br>mode <sup>†</sup>                                                             |
|------|-----------------------------------|----------------------------------------------|----------------------------------------------------------------------------------------------|
| a*   | 3600 ± 3                          | 3628 <sup>a)</sup>                           | $\nu_1(A')$ $\nu(\text{OH})$                                                                 |
| b*   | 3401 ± 2                          | 3393 <sup>a)</sup>                           | $\nu_1(A')$ $\nu(\text{OH})$                                                                 |
| c*   | 3190 ± 2                          | 3220 <sup>a)</sup>                           | $\nu_1(A')$ $\nu(\text{OH})$                                                                 |
| c    | 2979 ± 1                          | 2973 <sup>b)</sup>                           | $\nu_{\text{as}}(\text{CH}_3)$<br>$\nu(\text{gauche-CH}_2)$ in-plane                         |
| d    | 2936 ± 1                          | 2930 <sup>b)</sup>                           | $\nu_s(\text{CH}_3)$<br>$\nu_{\text{as}}(\text{trans-CH}_2)$<br>FR(CH <sub>2</sub> )         |
| e    | 2890 ± 1                          | 2876 <sup>b)</sup>                           | FR(CH <sub>3</sub> )<br>$\nu_s(\text{trans-CH}_2)$<br>$\nu(\text{gauche-CH}_2)$ out-of-plane |
| g    | 2735 ± 2                          | 2730 <sup>c)</sup>                           | Overtone                                                                                     |
| h    | 1481 ± 1                          | 1490.2 <sup>d)</sup>                         | $\delta(\text{CH}_2)$                                                                        |
| i    | 1450 ± 1<br>1445 ± 2              | 1463.5 <sup>d)</sup><br>1445.8 <sup>d)</sup> | $\delta_a(\text{CH}_3)$<br>$\delta_a(\text{CH}_3)$ A"                                        |
| j    |                                   | 1411.7 <sup>d)</sup>                         | w(CH <sub>2</sub> )                                                                          |
| k    | 1272 ± 1                          | 1274.8 <sup>d)</sup><br>1256.3 <sup>d)</sup> | tw(CH <sub>2</sub> ) A"<br>$\delta(\text{OH})$                                               |
| l    | 1105 ± 9                          | 1139.9 <sup>d)</sup>                         | r(CH <sub>2</sub> )+r(CH <sub>3</sub> ) A"                                                   |
| m    | 1077 ± 1                          | 1090.7 <sup>d)</sup>                         | $\nu(\text{CCO})$ +r(CH <sub>3</sub> )                                                       |
| n    | 1040 ± 1                          | 1027.7 <sup>d)</sup>                         | $\nu(\text{CCO})$ +r(CH <sub>3</sub> )                                                       |
| o    | 874 ± 1                           | 887.6 <sup>d)</sup>                          | $\nu(\text{CCO})$                                                                            |
| p    | 819 ± 3                           | 812 <sup>d)</sup>                            | r(CH <sub>2</sub> )+r(CH <sub>3</sub> ) A"                                                   |
| q    | 442 ± 1                           | 422 <sup>c)</sup>                            | $\delta(\text{CCO})$                                                                         |

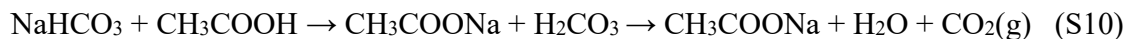
<sup>†</sup> $\nu$  denotes stretch;  $\delta$ , bend; w, wag; r, rock; tw, twist; FR, Fermi resonance; s, symmetric; and as, antisymmetric.

<sup>a)</sup>Ref.<sup>14</sup>, <sup>b)</sup>Ref.<sup>12</sup>, <sup>c)</sup>Ref.<sup>13</sup>, <sup>d)</sup>Ref.<sup>15</sup>.



## B. Aqueous Acetic Acid and Sodium Hydroxycarbonate Reaction

As a benchmark of a reactive system, we investigated the acid-base reaction between acetic acid ( $\text{CH}_3\text{COOH}$ ) and sodium hydroxycarbonate ( $\text{NaHCO}_3$ ) in aqueous solution, which forms sodium acetate ( $\text{CH}_3\text{COONa}$ ), carbon dioxide ( $\text{CO}_2$ ), and water ( $\text{H}_2\text{O}$ ) via a carbonic acid ( $\text{H}_2\text{CO}_3$ ) intermediate:



Photographs and a film illustrating the three main stages of the experiment are presented in Figure S8 and Movie S3, respectively. First, a  $2.0 \text{ mm} \times 1.3 \text{ mm}$  droplet of aqueous acetic acid (10%  $\text{CH}_3\text{COOH}$  by vol.) was levitated above a  $2.1 \text{ mm} \times 1.5 \pm 0.1 \text{ mm}$  droplet of saturated, aqueous sodium hydroxycarbonate solution (9.6%  $\text{NaHCO}_3$  by wt.). Second, after merging, the carbon dioxide bubbles caused the droplet to enlarge significantly to  $3.4 \text{ mm} \times 2.6 \text{ mm}$ , which is only slightly below the limit of the acoustic trapping potential. Finally, the carbon dioxide bubbles escaped to leave a  $2.8 \text{ mm} \times 2.1 \text{ mm}$  droplet containing the newly formed sodium acetate in aqueous solution. The gas bubbles released into the volume surrounding the droplet were probed by FTIR spectroscopy. In the resulting FTIR spectra shown in Figure S9, carbon dioxide bands are observed with centre wavenumbers of  $2,349 \text{ cm}^{-1}$  and  $668 \text{ cm}^{-1}$  corresponding to the  $\nu_3(\sigma_u^+)$  asymmetric stretching mode and the  $\nu_2(\pi_u)$  bending mode of  $\text{CO}_2$ , respectively.<sup>3, 5</sup>

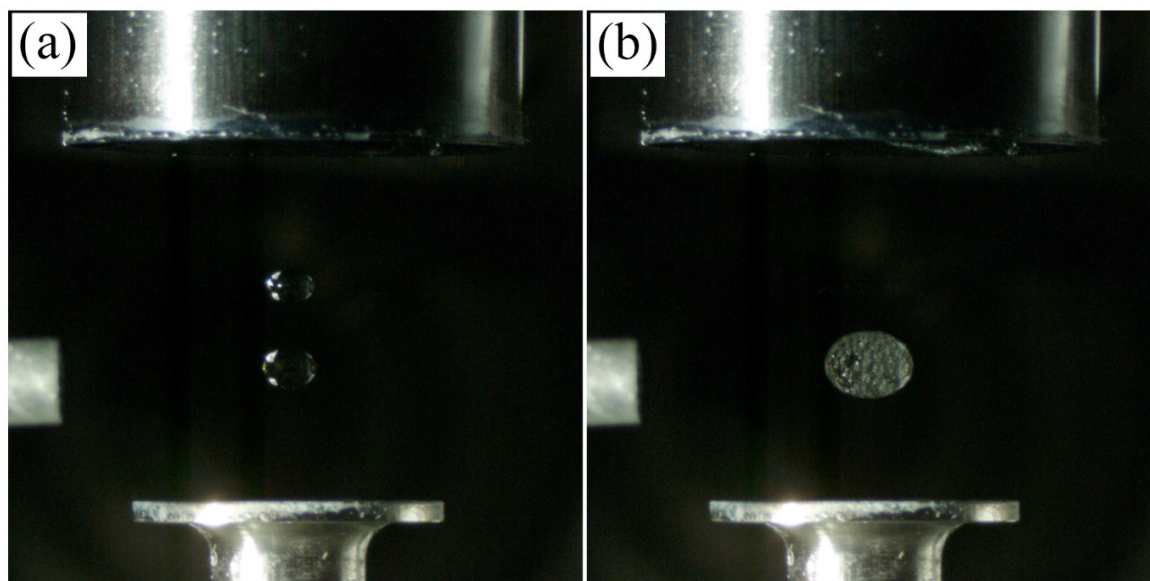


Figure S8. (a) a 10% acetic acid and 90% water droplet levitated above a droplet of sodium hydroxycarbonate-water solution and (b) the enlarged droplet containing carbon dioxide bubbles formed after the two droplets coalesced.



Raman spectra of the aqueous acetic acid, aqueous sodium hydroxycarbonate, and merged droplets are shown in Figure S10. The vibrational modes corresponding to the peaks in each of the three spectra are assigned in Table S7. The acetic acid spectrum was interpreted by comparison with the 18 Raman and infrared active, normal vibrational modes of the  $\text{CH}_3\text{COOH}$  molecule in aqueous solution;<sup>16</sup> whereas the sodium acetate spectrum was assigned based on the 15 normal modes of the  $\text{CH}_3\text{COO}^-$  ion.<sup>16</sup> For sodium hydroxycarbonate in aqueous solution, the Raman spectrum was explained by reference to the nine normal modes of the  $\text{HCO}_3^-$  ion.<sup>17</sup> The correspondence between the present and reference wavenumbers for the acetic acid, sodium hydroxycarbonate, and sodium acetate permits the unambiguous assignment of the vibrational modes for each droplet, and the few minor differences can be attributed to variations in the positions and intensities of the Raman bands with changes in the concentration of the solute.<sup>16, 17</sup> As the two droplets coalesced, a new peak (g) appeared in the merged Raman spectrum at  $927\text{ cm}^{-1}$ , which is assigned to the  $\nu_8(\text{A}')$  C-C stretching mode of the acetate anion ( $\text{CH}_3\text{COO}^-$ ) product. Simultaneously, the peak at  $1,017\text{ cm}^{-1}$  produced by the  $\nu_5(\text{A}')$  C-OH stretching mode of the hydroxycarbonate anion ( $\text{HCO}_3^-$ ) reactant (corresponding to peak (h) the middle panel) vanished. Similarly, the peak at  $927\text{ cm}^{-1}$  linked to the  $\nu_{10}(\text{A}')$  C-C stretching mode of the acetic acid reactant (corresponding to peak (k) in the top panel) reduced although, in contrast to the sodium hydroxycarbonate, retained a significant amplitude following completion of the reaction. Thus, all the sodium hydroxycarbonate (or limiting reactant) reacted with the acetic acid to produce sodium acetate via reaction (S10), although small quantities of unreacted acetic acid (or excess reactant) remained.

The UV-visible spectra of the droplets are shown in Figure S11. Each droplet before and after the merging is mostly composed of water; therefore, the characteristic shape of the water reflectance spectrum dominates. For the acetic acid sample, however, a broad absorption band occurs at wavelengths below 250 nm. This band is produced by the  $\pi^* 1^1\text{A}'' \leftarrow n_o 1^1\text{A}'$  transition of the carbonyl moiety of acetic acid for which the onset of the absorption occurs close to 250 nm.<sup>18</sup> The presence of this UV absorption band for the merged droplet confirms that excess acetic acid remains and supports the findings of the Raman spectroscopy.

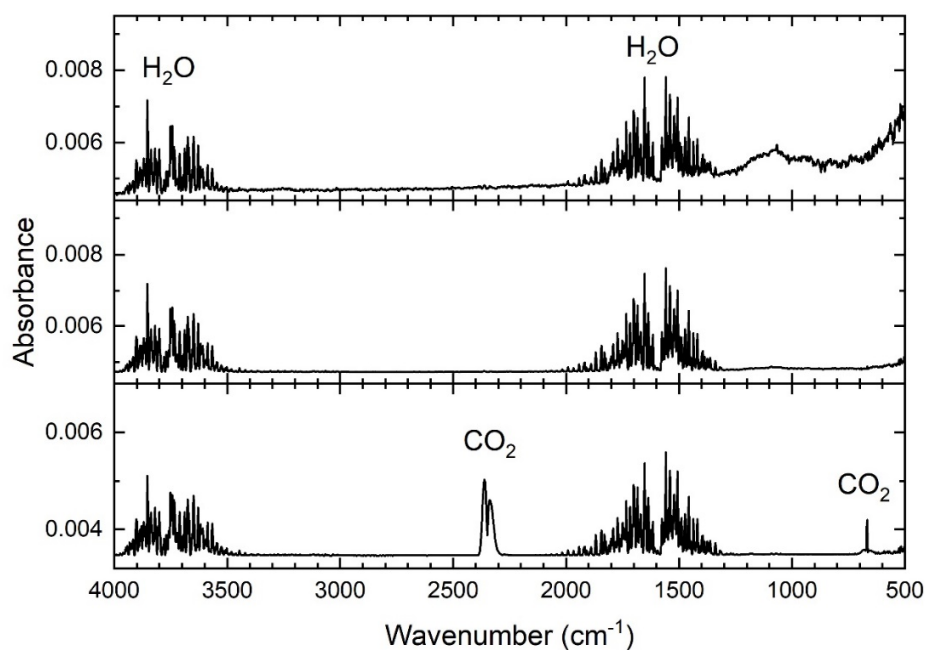


Figure S9. FTIR spectra of the 10% acetic acid and 90% water droplet (top panel), the droplet of water-sodium hydroxycarbonate solution (middle panel), and the merged droplet (bottom panel) corresponding to Figure S8. The carbon dioxide peaks produced by the bubbles visible in Figure S8b are labelled together with the spectral regions of the water lines.

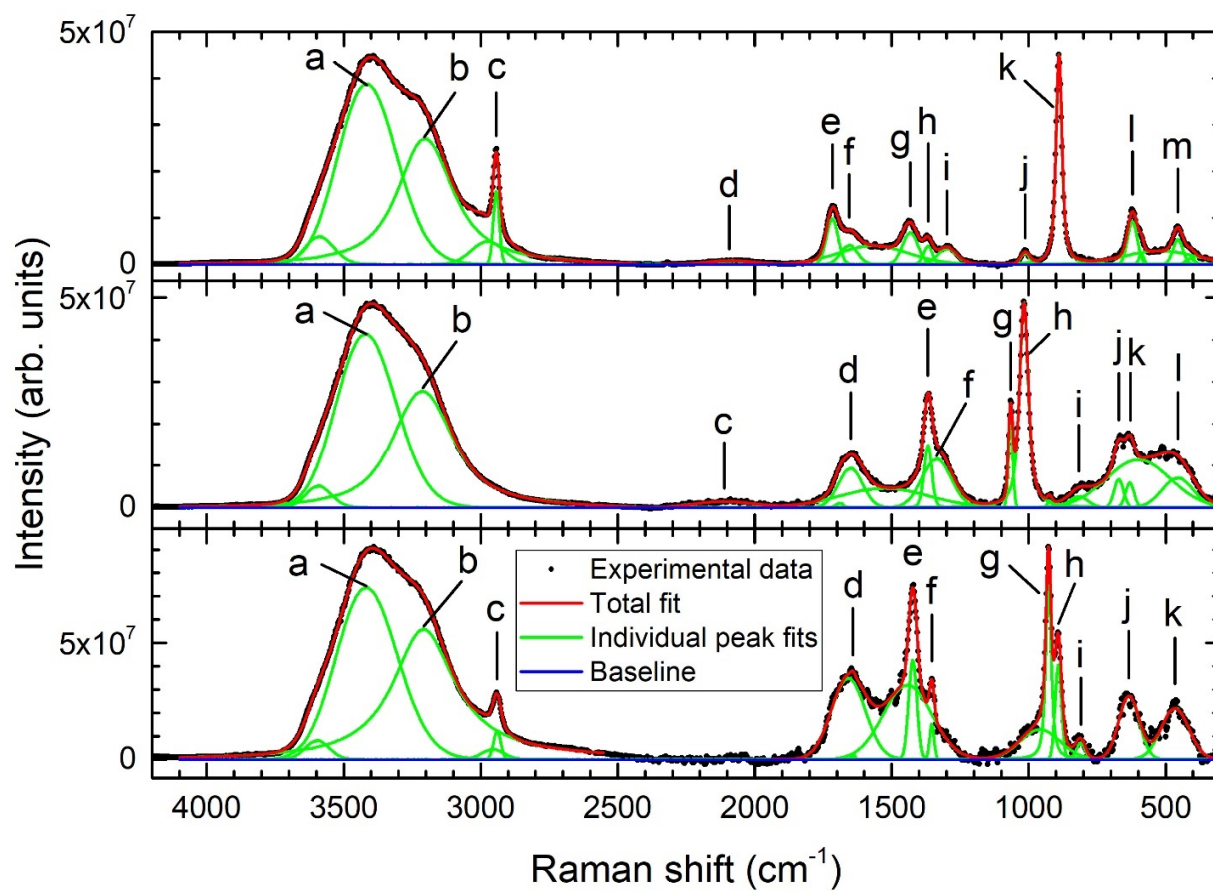


Figure S10. Raman spectra of 10% acetic acid and 90% water (top panel), water-sodium hydroxycarbonate solution (middle panel), and the merged droplet (bottom panel). The wavenumbers and vibrational mode assignments for the prominent peaks are presented in Table S7.

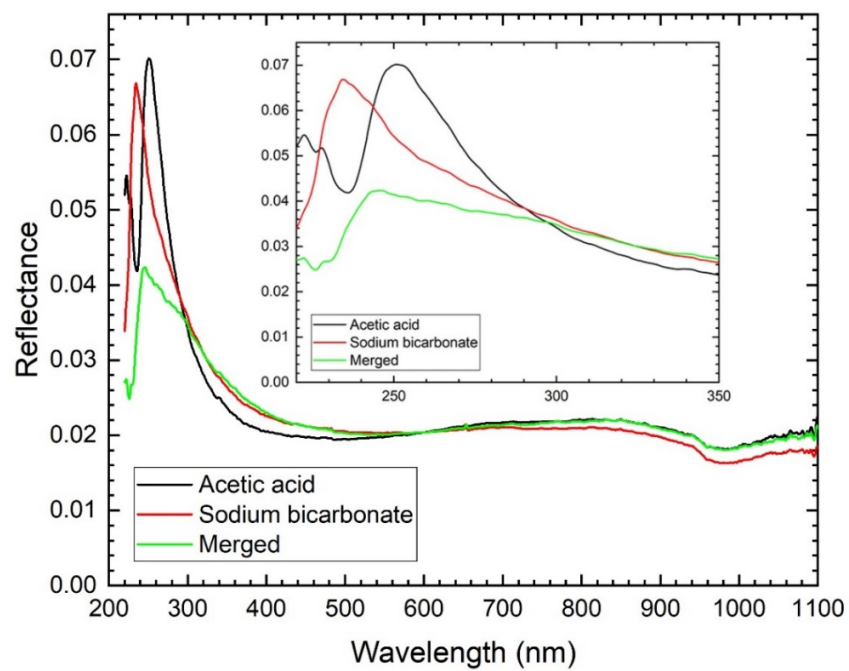


Figure S11. UV-visible reflectance spectra of the 10% acetic acid and 90% water droplet, the droplet of water-sodium hydroxycarbonate solution, and the merged droplet corresponding to Figure S8.

Table S7. Wavenumbers and vibrational mode assignments for peaks in the Raman spectra of i) 10% acetic acid and 90% water, ii) water-sodium hydroxycarbonate solution, and iii) the merged droplet shown in Figure S10.

i)

| Peak | Wavenumber (cm <sup>-1</sup> ) | Molecule                  | Ref. wavenumber* (cm <sup>-1</sup> )     | Number (symmetry)              | Vibrational mode <sup>†</sup>             |
|------|--------------------------------|---------------------------|------------------------------------------|--------------------------------|-------------------------------------------|
| a    | 3416 ± 1                       | H <sub>2</sub> O          | 3393 <sup>a)</sup>                       | $\nu_1(A')$                    | $\nu(OH)$                                 |
| b    | 3203 ± 1                       | H <sub>2</sub> O          | 3220 <sup>a)</sup>                       | $\nu_1(A')$                    | $\nu(OH)$                                 |
| c    | 2943 ± 1                       | CH <sub>3</sub> COOH (aq) | 2944 <sup>b)</sup>                       | $\nu_3(A')$                    | $\nu(CH_3)$                               |
| d    | 2093 ± 6                       | H <sub>2</sub> O          |                                          |                                |                                           |
| e    | 1716 ± 1                       | CH <sub>3</sub> COOH (aq) | 1712.5 <sup>b)</sup>                     | $\nu_4(A')$                    | $\nu(C=O)$                                |
| f    | 1655 ± 2                       | H <sub>2</sub> O          | 1641 <sup>a)</sup>                       | $\nu_2(A')$                    | $\delta(OH)$                              |
| g    | 1432 ± 1                       | CH <sub>3</sub> COOH (aq) | 1438 <sup>b)</sup><br>1417 <sup>b)</sup> | $\nu_{14}(A'')$<br>$\nu_5(A')$ | $\delta_{as}(HCH_2)$<br>$\delta_s(HCH_2)$ |
| h    | 1367 ± 1                       | CH <sub>3</sub> COOH (aq) | 1364 <sup>b)</sup>                       | $\nu_7(A')$                    | $\nu(C-O) + \delta(COH) + \delta(CH_3)$   |
| i    | 1298 ± 1                       | CH <sub>3</sub> COOH (aq) | 1296 <sup>b)</sup>                       | $\nu_8(A')$                    | $\delta(C-O-H)$                           |
| j    | 1013 ± 1                       | CH <sub>3</sub> COOH (aq) | 1017 <sup>b)</sup>                       | $\nu_9(A')$                    | $\gamma_s(CH_3)$                          |
| k    | 889 ± 1                        | CH <sub>3</sub> COOH (aq) | 893 <sup>b)</sup>                        | $\nu_{10}(A')$                 | $\nu(C-C)$                                |
| l    | 621 ± 1                        | CH <sub>3</sub> COOH (aq) | 627.5 <sup>b)</sup>                      | $\nu_{16}(A'')$                | $\tau(OH)$                                |
| m    | 455 ± 1                        | CH <sub>3</sub> COOH (aq) | 460.5 <sup>b)</sup>                      | $\nu_{12}(A')$                 | $\delta(C-C-O)$ in-plane                  |

ii)

| Peak | Wavenumber (cm <sup>-1</sup> ) | Molecule                                    | Ref. wavenumber* (cm <sup>-1</sup> )     | Number (symmetry)          | Vibrational mode <sup>†</sup>  |
|------|--------------------------------|---------------------------------------------|------------------------------------------|----------------------------|--------------------------------|
| a    | 3420 ± 1                       | NaHCO <sub>3</sub> (aq)<br>H <sub>2</sub> O | 3390 <sup>c)</sup><br>3393 <sup>a)</sup> | $\nu_1(A')$<br>$\nu_1(A')$ | $\nu(OH)$<br>$\nu(OH)$         |
| b    | 3213 ± 2                       | H <sub>2</sub> O                            | 3220 <sup>a)</sup>                       | $\nu_1(A')$                | $\nu(OH)$                      |
| c    | 2111 ± 9                       | H <sub>2</sub> O                            |                                          |                            |                                |
| d    | 1650 ± 2                       | H <sub>2</sub> O<br>NaHCO <sub>3</sub> (aq) | 1641 <sup>a)</sup><br>1630 <sup>d)</sup> | $\nu_2(A')$<br>$\nu_2(A')$ | $\delta(OH)$<br>$\nu_{as}(CO)$ |
| e    | 1367 ± 1                       | NaHCO <sub>3</sub> (aq)                     | 1360 <sup>d)</sup>                       | $\nu_3(A')$                | $\nu_s(CO)$                    |
| f    | 1336 ± 1                       | NaHCO <sub>3</sub> (aq)                     | 1302 <sup>d)</sup>                       | $\nu_4(A')$                | $\delta(HOC)$                  |
| g    | 1066 ± 1                       |                                             |                                          |                            |                                |
| h    | 1017 ± 1                       | NaHCO <sub>3</sub> (aq)                     | 1017 <sup>d)</sup>                       | $\nu_5(A')$                | $\nu(C-OH)$                    |
| i    | 817 ± 3                        | H <sub>2</sub> O<br>NaHCO <sub>3</sub> (aq) | 795 <sup>a)</sup><br>841 <sup>d)</sup>   | $B_1$<br>$\nu_8(A'')$      | Librational<br>$\gamma(CO_2)$  |
| j    | 671 ± 2                        | NaHCO <sub>3</sub> (aq)                     | 672 <sup>d)</sup>                        | $\nu_6(A')$                | $\delta(CO_2)$                 |
| k    | 631 ± 2                        | NaHCO <sub>3</sub> (aq)                     | 632 <sup>d)</sup>                        | $\nu_7(A')$                | $w(OC-(OH))$                   |
| l    | 456 ± 2                        | H <sub>2</sub> O                            | 430 <sup>a)</sup>                        | $A_2$                      | Librational                    |

iii)

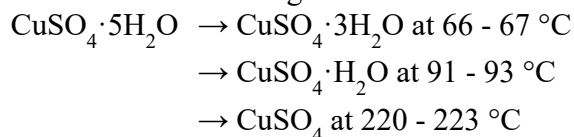
| Peak | Wavenumber<br>(cm <sup>-1</sup> ) | Molecule                                                            | Ref.<br>wavenumber*<br>(cm <sup>-1</sup> )                       | Number<br>(symmetry)                                                | Vibrational mode <sup>†</sup>                                                   |
|------|-----------------------------------|---------------------------------------------------------------------|------------------------------------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------------------|
| a    | 3418 ± 1                          | H <sub>2</sub> O                                                    | 3393 <sup>a)</sup>                                               | ν <sub>1</sub> (A')                                                 | ν(OH)                                                                           |
| b    | 3208 ± 1                          | H <sub>2</sub> O                                                    | 3220 <sup>a)</sup>                                               | ν <sub>1</sub> (A')                                                 | ν(OH)                                                                           |
| c    | 2940 ± 1                          | NaCH <sub>3</sub> CO <sub>2</sub> (aq)<br>CH <sub>3</sub> COOH (aq) | 2935.5 <sup>b)</sup><br>2944 <sup>b)</sup>                       | ν <sub>2</sub> (A')<br>ν <sub>3</sub> (A')                          | ν <sub>s</sub> (CH <sub>3</sub> )<br>ν(CH <sub>3</sub> )                        |
| d    | 1641 ± 5                          | H <sub>2</sub> O                                                    | 1641 <sup>b)</sup>                                               | ν <sub>2</sub> (A')                                                 | δ(OH)                                                                           |
| e    | 1423 ± 1                          | NaCH <sub>3</sub> CO <sub>2</sub> (aq)                              | 1440 <sup>b)</sup><br>1426 <sup>b)</sup><br>1413.5 <sup>b)</sup> | ν <sub>4</sub> (A')<br>ν <sub>12</sub> (A'')<br>ν <sub>5</sub> (A') | δ(CH <sub>2</sub> )<br>δ(CH <sub>2</sub> )<br>ν <sub>s</sub> (CO <sub>2</sub> ) |
| f    | 1353 ± 1                          | NaCH <sub>3</sub> CO <sub>2</sub> (aq)                              | 1347.6 <sup>b)</sup>                                             | ν <sub>6</sub> (A')                                                 | δ(CH <sub>3</sub> )                                                             |
| g    | 927 ± 1                           | NaCH <sub>3</sub> CO <sub>2</sub> (aq)                              | 928.4 <sup>b)</sup>                                              | ν <sub>8</sub> (A')                                                 | ν(C-C)                                                                          |
| h    | 891 ± 1                           | CH <sub>3</sub> COOH (aq)                                           | 893 <sup>b)</sup>                                                | ν <sub>10</sub> (A')                                                | ν(C-C)                                                                          |
| i    | 810 ± 2                           | H <sub>2</sub> O                                                    | 795 <sup>a)</sup>                                                | B <sub>1</sub>                                                      | Librational                                                                     |
| j    | 634 ± 1                           | NaCH <sub>3</sub> CO <sub>2</sub> (aq)                              | 654.2 <sup>b)</sup><br>620.7 <sup>b)</sup>                       | ν <sub>9</sub> (A')<br>ν <sub>14</sub> (A'')                        | δ(CO <sub>2</sub> )<br>r(CO <sub>2</sub> )                                      |
| k    | 466 ± 2                           | NaCH <sub>3</sub> CO <sub>2</sub> (aq)<br>H <sub>2</sub> O          | 474 <sup>b)</sup><br>430 <sup>a)</sup>                           | ν <sub>10</sub> (A')<br>A <sub>2</sub>                              | r(CO <sub>2</sub> )<br>Librational                                              |

<sup>†</sup>ν denotes stretch; δ, bend; w, wag; τ, torsion; r, rock; γ, out-of-plane; s, symmetric; and as, antisymmetric.

<sup>a)</sup>Ref.<sup>14</sup>, <sup>b)</sup>Ref.<sup>16</sup>, <sup>c)</sup>Ref.<sup>19</sup>, <sup>d)</sup>Ref.<sup>17</sup>.

### C. Merging of a solid particle and a liquid droplet: Water droplet and a copper sulfate crystal

To demonstrate the feasibility of merging a solid particle and a liquid droplet using the present method, we studied the coalescence of a copper sulfate crystal and a water droplet. The experiment also illustrates the capability of our apparatus to dehydrate the merged samples, and the colour changes following the dehydration of copper (II) sulfate are ideal to show how UV-visible spectrometer system can discern chemical changes. Photographs of the four steps in the experiment are presented in Figure S12. A film of the merging process is shown in Movie S4. First, a blue copper sulfate pentahydrate crystal ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) is levitated above a water droplet with dimensions of  $2.8 \text{ mm} \times 1.2 \text{ mm}$  and  $2.1 \times 1.6 \text{ mm}$ , respectively. Second, the crystal and droplet are merged and, over a period of a few minutes, the crystal dissolves in the water to form water-copper sulfate solution with a dimension of  $2.7 \text{ mm} \times 1.6 \text{ mm}$ . Third, the droplet of the solution evaporates in the anhydrous argon atmosphere to reform the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  crystals. Finally, the blue pentahydrate crystal is dehydrated by heating with a carbon dioxide laser thereby producing a white copper sulfate crystal. Raman spectra of the water-copper sulfate solution, the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  crystal produced following the evaporation, and the white dehydrated copper sulfate crystal are shown in Figure S13. The wavenumbers and vibrational mode assignments for the prominent, labelled peaks in the Raman spectra for the three stages are compiled in Table S8. The solvation in water and the thermal decomposition of copper sulfate pentahydrate are well understood. Copper sulfate dissolves in water to give the aqueous ion,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ .<sup>20</sup> When heated,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  loses water in three stages at well-defined temperatures:<sup>21</sup>



Each dehydration step has been studied by thermo-Raman spectroscopy and the vibrational modes of each molecule assigned.<sup>21, 22</sup> Briefly, the structures in the high Raman-shift region above approximately  $3000 \text{ cm}^{-1}$  are produced by O-H stretches of the  $\text{H}_2\text{O}$  molecules within the hydrated crystal, whereas the peaks below  $1200 \text{ cm}^{-1}$  are attributed to the  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  symmetric stretching modes of  $\text{SO}_4^{2-}$ . In Figure S13, the reduction in amplitude of the O-H peaks relative to the  $\text{SO}_4^{2-}$  peaks provides clear evidence for dehydration. The Raman spectrum for each hydration state is distinct and so can be used as a “fingerprint” to determine the water content,  $n$ , of the  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  molecules, where  $n = 5, 3, 1$ , or  $0$ . As Table S8(ii) shows, the blue crystal photographed in Figure S12c is in the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  hydration state. The wavenumbers for the Raman peaks of the white crystal correspond closely to the values for  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  (see Table S8(iii)), although the peak at  $1010 \text{ cm}^{-1}$  suggests that some  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  remains.

In Figure S14, we present the corresponding UV-visible reflectance spectra of the water droplet, water-copper sulfate solution,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  crystal, and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  crystal. The dehydration of copper (II) sulfate has been studied by diffuse reflectance spectroscopy in the  $300 \text{ nm}$  to  $1000 \text{ nm}$  wavelength range.<sup>23</sup> In contrast to the monotonic decrease in the reflectance for water as the wavelength increases, absorption bands occur for the copper-sulfate containing samples that change with the hydration state. First, as the water-copper sulfate solution is progressively dehydrated, the  $\text{Cu}(3d \text{ } t_{2g} - 3d \text{ } e_g)$  absorption maximum<sup>23</sup> shifts from approximately  $650 \text{ nm}$  to  $800 \text{ nm}$  and the width of the absorption band reduces. The red shift and narrowing of the d-d band correlates with change of sample colour from blue to white. Second, a broad, relatively weak absorption band appears at around  $500 \text{ nm}$  for the  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . Third, strong absorption is evident

in the UV region, which shifts to longer wavelengths as the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  transforms into  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . Further details and possible band assignments are discussed in Ref.<sup>23</sup>.

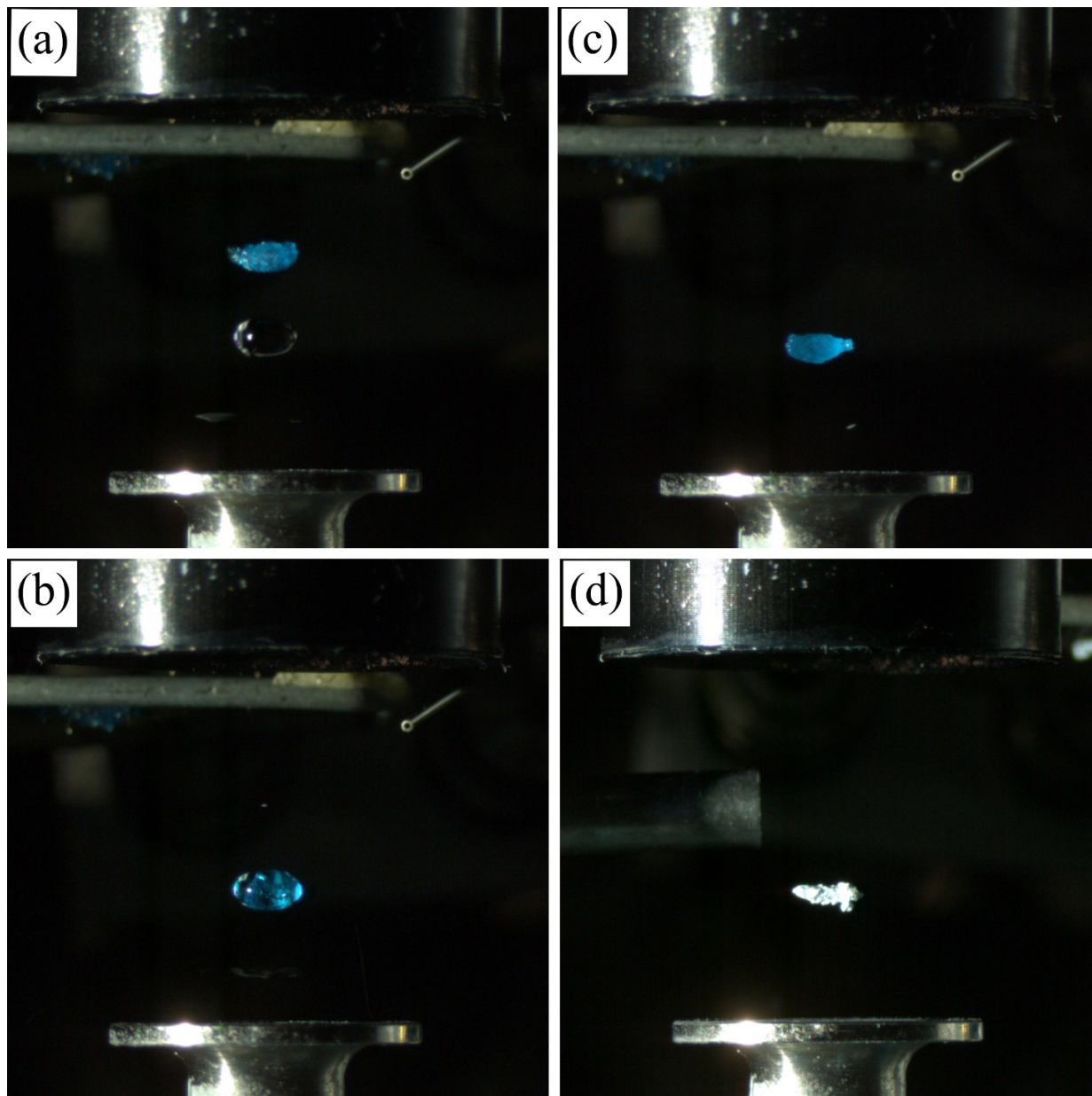


Figure S12. Photographs of (a) a copper sulfate crystal ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and water droplet levitated in adjacent pressure minima, (b) a droplet of water-copper sulfate solution formed after the crystal and droplet in (a) merged, (c) a  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  crystal produced after the droplet in (b) evaporated in the dry argon atmosphere, and (d) the white copper sulfate ( $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ) crystal made by dehydrating the blue crystal in (c) using a carbon dioxide laser



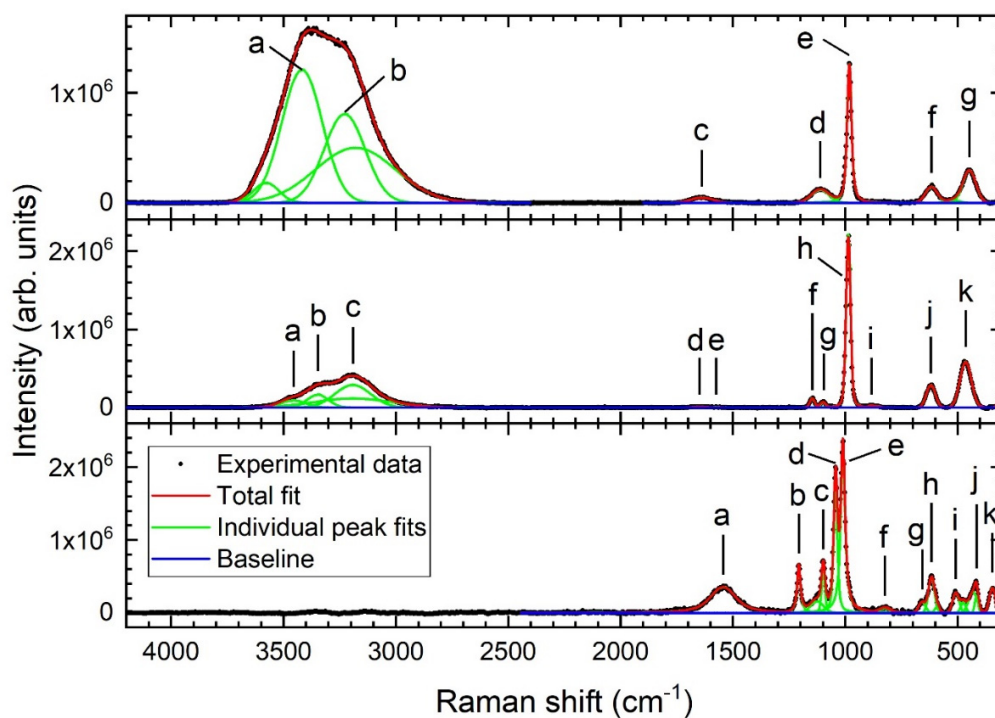


Figure S13. Raman spectra of water-copper sulfate solution (top panel),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (middle panel), and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  (bottom panel) corresponding to the photographs (b), (c), and (d) in Figure S12, respectively. The wavenumbers and vibrational mode assignments for the prominent peaks are presented in Table S8.

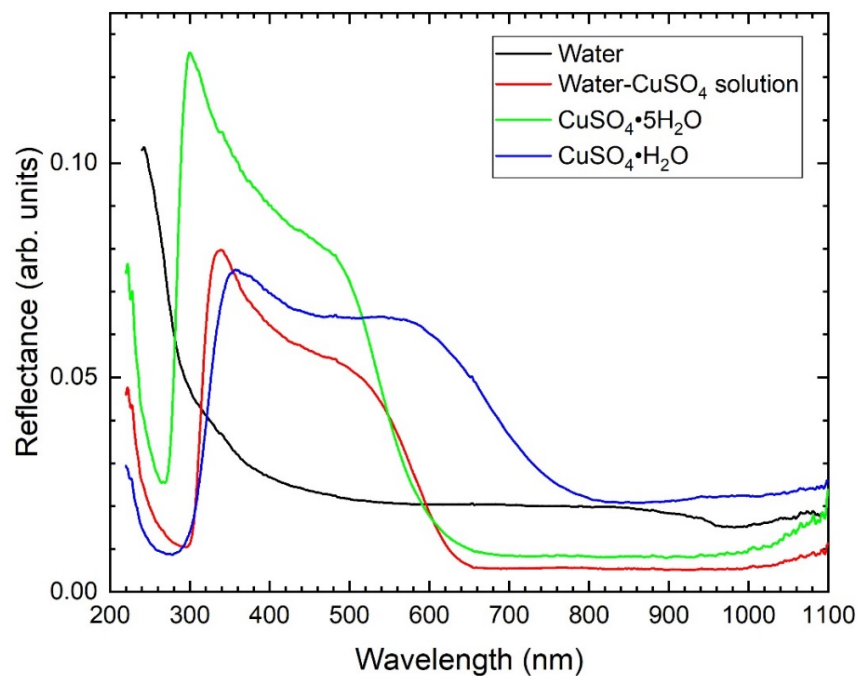


Figure S14. UV-visible reflectance spectra of water, water-copper sulfate solution,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ .

Table S8. Wavenumbers and vibrational mode assignments for prominent peaks in the Raman spectra of the (i) water-copper sulfate solution, (ii) blue copper-sulfate crystals, and (iii) white copper-sulfate crystals shown in Figure S12.

(i)

| Peak | Water-CuSO <sub>4</sub> solution wavenumber (cm <sup>-1</sup> ) | Ref. wavenumber* (cm <sup>-1</sup> )     | Ref. hydration state <sup>†</sup>    | Vibrational mode                                          |
|------|-----------------------------------------------------------------|------------------------------------------|--------------------------------------|-----------------------------------------------------------|
| a    | 3417 ± 2                                                        | 3477 <sup>a)</sup>                       | CuSO <sub>4</sub> •5H <sub>2</sub> O | O-H stretch                                               |
| b    | 3228 ± 3                                                        | 3201 <sup>a)</sup>                       | CuSO <sub>4</sub> •5H <sub>2</sub> O | O-H stretch                                               |
| c    | 1638 ± 3                                                        |                                          |                                      | No assignment                                             |
| d    | 1112 ± 1                                                        | 1144 <sup>a)</sup><br>1094 <sup>a)</sup> | CuSO <sub>4</sub> •5H <sub>2</sub> O | v <sub>3</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| e    | 982 ± 1                                                         | 986 <sup>a)</sup>                        | CuSO <sub>4</sub> •5H <sub>2</sub> O | v <sub>1</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| f    | 616 ± 1                                                         | 617 <sup>a)</sup>                        | CuSO <sub>4</sub> •5H <sub>2</sub> O | v <sub>4</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| g    | 448 ± 1                                                         | 462 <sup>a)</sup>                        | CuSO <sub>4</sub> •5H <sub>2</sub> O | v <sub>2</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |

<sup>†</sup>Used CuSO<sub>4</sub>•5H<sub>2</sub>O in absence of Raman spectra and assignments for water-CuSO<sub>4</sub> solution.

(ii)

| Peak | Blue-crystal wavenumber (cm <sup>-1</sup> ) | Ref. wavenumber* (cm <sup>-1</sup> ) | Ref. hydration state                 | Vibrational mode                                          |
|------|---------------------------------------------|--------------------------------------|--------------------------------------|-----------------------------------------------------------|
| a    | 3456 ± 4                                    | 3477 <sup>a)</sup>                   | CuSO <sub>4</sub> •5H <sub>2</sub> O | O-H str.                                                  |
| b    | 3347 ± 2                                    | 3342 <sup>a)</sup>                   | CuSO <sub>4</sub> •5H <sub>2</sub> O | O-H str.                                                  |
| c    | 3191 ± 2                                    | 3201 <sup>a)</sup>                   | CuSO <sub>4</sub> •5H <sub>2</sub> O | O-H str.                                                  |
| d    | 1650 ± 3                                    |                                      |                                      |                                                           |
| e    | 1574 ± 6                                    |                                      |                                      |                                                           |
| f    | 1147 ± 2                                    | 1144 <sup>a)</sup>                   | CuSO <sub>4</sub> •5H <sub>2</sub> O | v <sub>3</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| g    | 1099 ± 3                                    | 1094 <sup>a)</sup>                   |                                      |                                                           |
| h    | 986 ± 1                                     | 986 <sup>a)</sup>                    | CuSO <sub>4</sub> •5H <sub>2</sub> O | v <sub>1</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| i    | 884 ± 1                                     |                                      |                                      |                                                           |
| j    | 619 ± 1                                     | 617 <sup>a)</sup>                    | CuSO <sub>4</sub> •5H <sub>2</sub> O | v <sub>4</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| k    | 464 ± 1                                     | 462 <sup>a)</sup>                    | CuSO <sub>4</sub> •5H <sub>2</sub> O | v <sub>2</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |

(iii)

| Peak | White-crystal<br>wavenumber<br>(cm <sup>-1</sup> ) | Ref.<br>wavenumber*<br>(cm <sup>-1</sup> ) | Ref.<br>hydration<br>state           | Vibrational mode                                          |
|------|----------------------------------------------------|--------------------------------------------|--------------------------------------|-----------------------------------------------------------|
| a    | 1543 ± 1                                           |                                            |                                      |                                                           |
| b    | 1206 ± 1                                           | 1206 <sup>b)</sup>                         | CuSO <sub>4</sub> •H <sub>2</sub> O  | v <sub>3</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| c    | 1098 ± 1                                           | 1097 <sup>b)</sup>                         |                                      | doublet                                                   |
| d    | 1043 ± 1                                           | 1044 <sup>b)</sup>                         | CuSO <sub>4</sub> •H <sub>2</sub> O  | v <sub>1</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| e    | 1010 ± 1                                           | 1019 <sup>b)</sup>                         |                                      | doublet                                                   |
| e    | 1010 ± 1                                           | 1009 <sup>b)</sup>                         | CuSO <sub>4</sub> •3H <sub>2</sub> O | v <sub>1</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| f    | 825 ± 3                                            |                                            |                                      |                                                           |
| g    | 658 ± 2                                            | 670 <sup>b)</sup>                          | CuSO <sub>4</sub> •H <sub>2</sub> O  | v <sub>4</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| h    | 616 ± 2                                            | 622 <sup>b)</sup>                          |                                      | doublet                                                   |
| i    | 508 ± 2                                            | 512 <sup>b)</sup>                          | CuSO <sub>4</sub> •H <sub>2</sub> O  | v <sub>2</sub> (SO <sub>4</sub> <sup>2-</sup> ) sym. str. |
| j    | 416 ± 1                                            | 426 <sup>b)</sup>                          |                                      | doublet                                                   |
| k    | 345 ± 1                                            | 348 <sup>a)</sup>                          | CuSO <sub>4</sub> •H <sub>2</sub> O  | lattice mode                                              |

<sup>a)</sup>Ref.<sup>22</sup>, <sup>b)</sup>Ref.<sup>21</sup>

## **Supporting Videos**

### **Movie S1**

A video showing the merging of a nitric acid droplet and a [BMIM][DCA] droplet.

### **Movie S2**

A video showing the merging of an ethanol droplet and a water droplet.

### **Movie S3**

A video showing the merging of an aqueous acetic acid droplet and a droplet of saturated, aqueous sodium hydroxycarbonate solution.

### **Movie S4**

A video showing the merging of a copper sulfate crystal ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and water droplet.

## Supporting References

- (1) Hamilton, M. F.; Blackstock, D. T., *Nonlinear acoustics*. Academic Press: San Diego, CA, 1998; p xviii, 455 p.
- (2) McGraw, G. E.; Bernitt, D. L.; Hisatsune, I. C., Vibrational spectra of isotopic nitric acids. *J. Chem. Phys.* **1965**, *42*, 237-244.
- (3) Miller, C. E.; Brown, L. R., Near infrared spectroscopy of carbon dioxide I.  $^{16}\text{O}^{12}\text{C}^{16}\text{O}$  line positions. *J. Mol. Spectrosc.* **2004**, *228*, 329-354.
- (4) Toth, R. A., Line strengths ( $900\text{--}3600\text{ cm}^{-1}$ ), self-broadened linewidths, and frequency shifts ( $1800\text{--}2360\text{ cm}^{-1}$ ) of  $\text{N}_2\text{O}$ . *Appl. Optics* **1993**, *32*, 7326-7365.
- (5) Rothman, L. S.; Jacquemart, D.; Barbe, A.; Benner, D. C.; Birk, M.; Brown, L. R.; Carleer, M. R.; Chackerian, C.; Chance, K.; Coudert, L. H.; Dana, V.; Devi, V. M.; Flaud, J. M.; Gamache, R. R.; Goldman, A.; Hartmann, J. M.; Jucks, K. W.; Maki, A. G.; Mandin, J. Y.; Massie, S. T.; Orphal, J.; Perrin, A.; Rinsland, C. P.; Smith, M. A. H.; Tennyson, J.; Tolchenov, R. N.; Toth, R. A.; Vander Auwera, J.; Varanasi, P.; Wagner, G., The HITRAN 2004 molecular spectroscopic database. *J. Quant. Spectrosc. Ra.* **2005**, *96*, 139-204.
- (6) Forney, D.; Thompson, W. E.; Jacox, M. E., The vibrational spectra of molecular ions isolated in solid neon. XI.  $\text{NO}_2^+$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ . *J. Chem. Phys.* **1993**, *99*, 7393-7403.
- (7) Minogue, N.; Riordan, E.; Sodeau, J. R., Raman spectroscopy as a probe of low-temperature ionic speciation in nitric and sulfuric acid stratospheric mimic systems. *J. Phys. Chem. A* **2003**, *107*, 4436-4444.
- (8) Katsyuba, S. A.; Zvereva, E. E.; Vidis, A.; Dyson, P. J., Application of density functional theory and vibrational spectroscopy toward the rational design of ionic liquids. *J. Phys. Chem. A* **2007**, *111*, 352-370.
- (9) Paschoal, V. H.; Faria, L. F. O.; Ribeiro, M. C. C., Vibrational spectroscopy of ionic liquids. *Chem. Rev.* **2017**, *117*, 7053-7112.
- (10) Kiefer, J.; Noack, K.; Penna, T. C.; Ribeiro, M. C. C.; Weber, H.; Kirchner, B., Vibrational signatures of anionic cyano groups in imidazolium ionic liquids. *Vib. Spectrosc.* **2017**, *91*, 141-146.
- (11) Socrates, G., *Infrared and Raman characteristic group frequencies : tables and charts*. 3rd ed.; Wiley: Chichester ; New York, 2001; p xv, 347 p.
- (12) Wang, L.; Ishiyama, T.; Morita, A., Theoretical investigation of C-H vibrational spectroscopy. 2. Unified assignment method of IR, Raman, and sum frequency generation spectra of ethanol. *J. Phys. Chem. A* **2017**, *121*, 6701-6712.
- (13) Durig, J. R.; Bucy, W. E.; Wurrey, C. J.; Carreira, L. A., Raman spectra of gases. XVI. Torsional transitions in ethanol and ethanethiol. *J. Phys. Chem. A* **1975**, *79*, 988-993.
- (14) Carey, D. M.; Korenowski, G. M., Measurement of the Raman spectrum of liquid water. *J. Chem. Phys.* **1998**, *108*, 2669-2675.
- (15) Coussan, S.; Bouteiller, Y.; Perchard, J. P.; Zheng, W. Q., Rotational isomerism of ethanol and matrix isolation infrared spectroscopy. *J. Phys. Chem. A* **1998**, *102*, 5789-5793.
- (16) Rudolph, W. W.; Fischer, D.; Irmer, G., Vibrational spectroscopic studies and DFT calculations on  $\text{NaCH}_3\text{CO}_2(\text{aq})$  and  $\text{CH}_3\text{COOH}(\text{aq})$ . *Dalton T.* **2014**, *43*, 3174-3185.
- (17) Davis, A. R.; Oliver, B. G., A vibrational-spectroscopic study of the species present in the  $\text{CO}_2\text{--H}_2\text{O}$  system. *J. Solution Chem.* **1972**, *1*, 329-339.

- (18) Limao-Vieira, P.; Giuliani, A.; Delwiche, J.; Parafita, R.; Mota, R.; Duflot, D.; Flament, J. P.; Drage, E.; Cahillane, P.; Mason, N. J.; Hoffmann, S. V.; Hubin-Franskin, M. J., Acetic acid electronic state spectroscopy by high-resolution vacuum ultraviolet photo-absorption, electron impact, He(I) photoelectron spectroscopy and ab initio calculations. *Chem. Phys.* **2006**, *324*, 339-349.
- (19) Bernitt, D. L.; Hartman, K. O.; Hisatsune, I. C., Infrared spectra of isotopic bicarbonate monomer ions. *J. Chem. Phys.* **1965**, *42*, 3553-3558.
- (20) Wiberg, E.; Wiberg, N.; Holleman, A. F., *Inorganic chemistry*. 1st English ed.; Academic Press: San Diego, 2001; p xxxix, 1884 p.
- (21) Widjaja, E.; Chong, H. H.; Tjahjono, M., Use of thermo-Raman spectroscopy and chemometric analysis to identify dehydration steps of hydrated inorganic samples - application to copper sulfate pentahydrate. *J. Raman Spectrosc.* **2010**, *41*, 181-186.
- (22) Chang, H.; Huang, P. J., Dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  studied by thermo-Raman spectroscopy. *J. Chin. Chem. Soc.-Taip* **1998**, *45*, 59-66.
- (23) Nagase, K.; Yokobayashi, H., Spectrophotometric and thermal analytical studies on the dehydration of copper(II) sulfate and its double salts. *Thermochim. Acta* **1978**, *23*, 283- 291.