Nonlinear rotational spectroscopy and many-body interactions in water molecules

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Abstract:

Because of their central importance in chemistry and biology, water molecules have been the subject of decades of intense spectroscopic investigations. Rotational spectroscopy of water vapor has yielded detailed information about the structure and dynamics of isolated water molecules as well as stable water dimers and clusters\textsuperscript{1,2}. Nonlinear rotational spectroscopy in the terahertz regime has been developed recently to investigate rotational dynamics of linear and symmetric-top molecules whose rotational energy levels are regularly spaced\textsuperscript{3-5}, but it has not previously been applied to water or other lower-symmetry molecules with irregular rotational energy levels. Here we report the use of a recently developed extension of rotational spectroscopy, two-dimensional terahertz spectroscopy, to observe high-order rotational coherences and correlations between rotational transitions that could not be seen previously. The results show significant many-body interactions between water molecules, directly revealing the presence of previously unseen metastable water complexes with lifetimes of ~ 100 ps or longer. Our work opens the door to detailed study of intermolecular interactions that give rise to rotational correlations in water molecules specifically and in asymmetric-top molecules (the majority of natural molecular species) generally through multi-dimensional terahertz spectroscopy.
Main Text:

Water has attracted extensive spectroscopic interest because of its critical implications for theoretical and applied sciences. Water shows anomalous properties because of complicated fluxional hydrogen-bond networks and has been investigated by Raman and infrared spectroscopy, sum frequency spectroscopy, optical Kerr effect spectroscopy, vibration-rotation-tunneling spectroscopy, and recently by two-dimensional (2D) infrared spectroscopy and 2D Raman-terahertz (THz) spectroscopy. In the gas phase, water is also of utmost importance for atmospheric science, astrophysics, combustion research, and fundamental chemistry and physics. Although the pure rotational spectrum of water vapor has been well known for decades, nonlinear THz spectroscopy of water rotational dynamics has not been previously reported. Nonlinear rotational spectroscopy in the microwave spectral range is well established, but because of the small mass and moments of inertia of water, most of its rotational transition frequencies lie in the terahertz frequency range (see Fig. 1). Nonlinear THz rotational spectroscopy was first reported only recently, and two-dimensional (2D) THz rotational spectroscopy more recently still. As in 2D spectroscopy of vibrational, electronic, and other degrees of freedom, 2D rotational spectroscopy may reveal correlations between rotational states, many-body effects, and distinct multiple-field interactions that cannot be observed by linear spectroscopy. The large water dipole moment, manifest in strong atmospheric absorption in the THz window, and the existence of water dimers and larger clusters with complex structures and dynamics, suggest that 2D spectroscopy of water could generate important insights that have thus far been elusive.

2D THz rotational spectroscopy has not been extended previously to water or any asymmetric-top molecules although such molecules, whose rotational spectra are complex because all three of their moments of inertia are unequal, are the majority of natural molecular species. Unlike a linear or symmetric top molecule, in which the spectral transitions between successive total rotational angular momentum levels denoted by quantum number \( J \) are spaced by even-integer multiples of a common factor, the rotational constant \( B \), the asymmetric nature of water molecules leads to irregularly-spaced rotational energy levels, described approximately by quantum numbers \( J, K_a, \) and \( K_c \) that indicate total angular momentum and its symmetry-axis projections in the symmetric top limiting cases. The spectrum of water vapor shows many transitions, with \( \Delta J = -1, 0, +1 \) (P, Q, and R branches) all allowed and, for each, changes \( \Delta K_a = \pm 1, \Delta K_c = \pm 1 \) as well. The large centrifugal distortion of water and the distinct rotational states occupied by its spin isomers (even-symmetry for para, odd-symmetry for ortho) further complicate its rotational spectrum.

A typical THz time-domain free-induction decay (FID) signal from water vapor at ambient conditions, induced by a weak single-cycle THz pulse, is shown in Fig. 1e. The irregular oscillations arise from more than 15 transitions (Fig. 1d) that contribute significantly to the water vapor absorption spectrum in the 0.1-2 THz region.

The 2D THz experimental setup is illustrated schematically in Fig. 1f and described further (Methods). Briefly, two variably time-delayed THz pulses are focused on the water vapor sample in a gas cell at about 60°C and 150 Torr pressure. The induced THz signal is detected in an electro-optic crystal by a variably delayed optical readout pulse, the polarization rotation of which reveals the signal field temporal profile. The signal is collected at a 1 kHz repetition rate, with a total data acquisition time of 2-3 days as both time delays are swept. Fourier transformation (FT) of the signal as a function of both time delays yields the 2D spectra (Figs. 2 and 3). In order to resolve
closely spaced peaks near 1.0 THz, separate measurements with long delay times (up to 300 ps) are recorded (Fig. 2g).

Figure 2 shows the experimental 2D THz rotational spectra. The spectra mainly consist of non-rephasing (NR) (Figs. 2a-c) and photon echo or rephasing (R) (Figs. 2d-f) parts. Many nonlinear spectral peaks appear along the $f_{\text{pump}} = \pm f_{\text{probe}}$ diagonals. These peaks can be understood in terms of a two-level system model and the Feynman diagram in Fig. 2i. The first field interaction from the first pulse induces a coherence between the rotational states $|0\rangle$ and $|1\rangle$, described by the density matrix element $|1\rangle\langle 0|$; the successive two interactions from the second pulse can convert the coherence first into a population state, $|1\rangle\langle 1\rangle$, and then into the coherence, $|1\rangle\langle 0\rangle$, which radiates at the same frequency as the first. For example, the rotational states $|1_{01}\rangle$ and $|1_{10}\rangle$ denoted as $|0\rangle$ and $|1\rangle$, respectively, give rise to the diagonal peak in position ($f_{\text{probe}} = 0.558$ THz, $f_{\text{pump}} = 0.558$ THz). The third field interaction may alternatively convert the population $|1\rangle\langle 1\rangle$ into a new coherent superposition, $|2\rangle\langle 1\rangle$, which radiates at a new frequency, leading to off-diagonal or cross peaks, such as the one at ($f_{\text{probe}} = 1.23$ THz, $f_{\text{pump}} = 0.75$ THz) (Fig. 2b, Feynman diagram (b) in Fig. 2j) that results from the three levels, $|2_{02}\rangle$, $|2_{11}\rangle$, and $|2_{20}\rangle$.

Some diagonal peaks between 0.5 and 0.8 THz, which stem from coherences of an extremely small amount of gaseous acetonitrile residue from previous experiments (Figs. 2a and d), appear but do not significantly affect the 2D spectra of the water molecules except for the resonance associated with the $|J = 30\rangle \rightarrow |J' = 29\rangle$ transition at 0.552 THz in acetonitrile which interferes with that of the $|1_{01}\rangle \rightarrow |1_{10}\rangle$ transition in water, leading to slightly split double-peaks at ($f_{\text{probe}} = 0.558$ THz, $f_{\text{pump}} = 0.558$ THz) (Fig. 2a). The 2D THz spectra show no cross-peaks at mixed frequencies that belong to both water and acetonitrile molecules nor between para- and ortho-water molecules, indicating that distinct constituent species and different nuclear spin isomers of the same molecular source generate independent spectra, similar to the behavior of alkali-metal atoms in 2D electronic spectra. We note that far weaker peaks than those from acetonitrile, due to water dimers, also appear. Their analysis requires careful subtraction of the acetonitrile peaks and consideration of signal levels far weaker than those of interest in this paper, and will be presented in a separate publication.

Sum-frequency signals (SFs) and difference-frequency signals (DFs) appear, arising from ladder-type (Fig. 2j, diagram (e)) and V-type (Fig. 2k) transitions, respectively. The SFs (Figs. 2c and f) are two-quantum (2Q) signals in which two successive field interactions from the first THz pulse generate a 2Q coherence $|2\rangle\langle 0|$, followed by a third interaction from the second pulse, which produces a radiating coherence $|2\rangle\langle 1|$ or $|1\rangle\langle 0|$ whose amplitude and/or phase oscillate at the $|2\rangle\langle 0|$ coherence frequency as the inter-pulse time delay $\tau$ is varied, thereby revealing the 2Q frequency in the FT with respect to $\tau$ as well as the radiating signal coherence frequency in the FT with respect to $t$. A representative example of this type of coherence is the peak at ($f_{\text{probe}} = 1.23$ THz, $f_{\text{pump}} = 1.98$ THz) in Fig. 2c. DFs can be observed specifically in a so-called V-type system consisting of the three ortho water states, $|0\rangle = |1_{01}\rangle$, $|1\rangle = |1_{10}\rangle$, and $|2\rangle = |2_{12}\rangle$ (Figs. 1d, 2h and 2k diagram (d)). The excited rotational states $|1\rangle$ and $|2\rangle$ share the same ground state $|0\rangle$, and the transition between the two excited states is forbidden by the selection rule ($\Delta K_c = \pm 1$, $\Delta K_t = \pm 1$). The DFs come from the coherence $|1\rangle\langle 2|$ induced by two interactions from the first THz pulse, applied in succession starting with the initial population state $|0\rangle\langle 0|$. This is also a 2Q coherence, and although (just like the SF 2Q coherence $|2\rangle\langle 0|$) it is not radiative and therefore
cannot be observed in a conventional linear spectrum, the $|1\rangle \leftrightarrow |2\rangle$ coherence becomes observable in 2D spectroscopy through the third field interaction, from the second THz pulse, which projects onto either of the coherences $|1\rangle \langle 0|$ or $|0\rangle \langle 2|$, which radiate at frequencies of $f_{\text{probe}} = 0.558$ THz and 1.670 THz, respectively.

Based on the energy levels of individual water molecules, no 2Q resonant peak is anticipated near $(f_{\text{probe}} = 0.753$ THz, $f_{\text{pump}} = 1.506$ THz) along the line $f_{\text{pump}} = 2f_{\text{probe}}$, since the $|2_{\text{Q2}}\rangle \rightarrow |2_{\text{Q1}}\rangle$ transition at 0.753 THz is not followed by a second transition at the same frequency. Surprisingly, a strong 2Q signal appears at $f_{\text{probe}} = 0.753$ THz as shown in Fig. 3a. In addition, 2Q off-diagonal features with discrete peaks extend downward from both of the 2Q diagonal peaks at $f_{\text{probe}} = 0.558$ THz and $f_{\text{probe}} = 0.753$ THz. These features can be explained by the collective resonances induced by many-body interactions in water molecules, similar to effects observed in 2D electronic spectra of atomic vapors$^{40,41}$ and quantum wells$^{35}$. For example, three molecules with identical two-level systems can create an eight-level system with a ground state, three singly excited states, three doubly excited states, and one triply excited state (Fig. 3b). Dipole-dipole interactions among the water molecules could split the singly and doubly excited-state energies and could create correlations between the successive transitions, yielding the 2Q diagonal and 2Q off-diagonal peaks as well as the three-quantum (3Q) signal, shown in Fig. 3a.

Owing to the much smaller shifts measured here (~20 GHz) compared to the binding energy value (~21 kJ/mol $\approx 5.3\times10^4$ GHz) of a true hydrogen-bonded water dimer$^{33}$, we attribute the 2Q and 3Q features to the transient formation of metastable water complexes$^{32}$. A lower limit of ~100 ps for the lifetime of the metastable complexes can be estimated from the linewidths of the 2Q off-diagonal peaks along the pump axis. This value is equal to our maximum time delay between the two THz pump pulses and is therefore instrumentally limited. Note that at the experimental pressure of 150 Torr, the mean free time between molecular collisions is about 1.1 ns, so weakly interacting complexes can persist for longer than 100 ps without being destroyed by collisions with other molecules. 2D spectroscopy permits direct access to the metastable complexes, which may represent the precursor states on the path toward forming true bound dimers.

Another possible source for 2Q and 3Q signals is the radiative interaction$^4$ in which the emitted THz field resulting from the interaction of the incident THz field with one molecule can subsequently serve as the excitation field for another molecule. However, this radiative interaction does not generate molecular excited states different from those that exist in individual water molecules, and thus makes no contribution to the 2Q off-diagonal peaks. A rough estimate indicates that more than 50% of the 2Q diagonal peak intensities arises from many-body interactions, assuming that the 2Q diagonal and off-diagonal peaks share a similar contribution from collective resonances. To confirm the distinct sources of the 2Q off-diagonal and diagonal peaks, we analyzed the observed ratio between them at two sample temperatures. Figure 4d shows that the intensity ratio of 2Q off-diagonal peaks to 2Q diagonal peaks increases by a factor of about 7 when the temperature is increased from room temperature (21°C) to 60°C, which increases the water vapor pressure from 18 Torr to 150 Torr, i.e. by a factor of 8.3. Since the number density of weakly bound water complexes that could contribute to the 2Q off-diagonal peaks increases with temperature much faster than that of water molecules$^{32}$, this result supports our conclusion that the 2Q off-diagonal peaks originate from metastable water complexes, almost surely predominantly molecule-pairs. Further confirmation is provided by comparisons between the 2Q off-diagonal
peaks and diagonal or off-diagonal peaks in the rephasing or non-rephasing spectra, which give similar results (Fig. S18). Simulation data (Figs. 4a and b) reproduce well the experimental results (see supplementary information for simulation details). Additional higher-order signals from non-interacting water molecules do not significantly contribute to the 2Q and 3Q signals since they are one or two orders of magnitude smaller than those from the dominant many-body interactions (Figs. 3c, 4e, and supplementary information). Some features in the simulated 2D spectra (for example, peaks labelled as (e) and (e’) in Fig. 4c) arise from nonlinear interactions with weak water transitions. Figure 4c shows the energy-level and Feynman diagrams associated with the 0.380 THz transition. These features are too weak to be extracted in the present experiment.

Nonlinear 2D rotational spectra of water vapor have shown rephasing (photon echo), non-rephasing, and multiple-quantum signals that arise from different field-induced pathways between rotational states and have directly revealed many-body effects that are associated with transient metastable complexes. Our work paves the way for systematic study of intricate intermolecular interactions and energy transfer mechanisms that give rise to correlations between otherwise unrelated rotational transitions. Many experimental refinements are possible, including the introduction of a third THz pulse\textsuperscript{43,44}, which would enable measurements at variable population times and that may yield the lifetimes of transient complexes, distinct from the dephasing times reported here. Considerable reduction in data acquisition time may be possible by incorporating single-shot spectroscopy methods to eliminate the need for one of the variable delays\textsuperscript{45-47} or through high-resolution multidimensional spectroscopy with frequency combs\textsuperscript{39}, which have been generated and used for linear spectroscopy of water vapor at THz frequencies\textsuperscript{48}. Multidimensional THz rotational spectroscopy holds promise for many applications including measurement of enantiomeric excess\textsuperscript{18,19}, molecular cluster identification and characterization, and coherent manipulation of molecular orientation.

**Methods**

**Sample preparation**

A capped storage vessel (25ml, Chemglass Life Sciences) with a sidearm served as a liquid water container. About 5 ml liquid water was pipetted into the storage vessel at room temperature. The sidearm of the vessel was connected to a stainless steel transfer line (approximately 50 cm long), the other end of which was linked to a gas cell with a 1.25 cm path length. Three valves were equipped to adjust the gas flow. Liquid water in the storage vessel was frozen into ice using liquid nitrogen, following a vacuum pumping process to eliminate air in the storage vessel, the transfer line, and the gas cell before ice melted.

The storage vessel was then sealed by the cap and immersed in a warm water bath heated by a hotplate. The temperature was stabilized at approximate 60°C to avoid water condensation. A temperature-controllable silicone heating tape (Cole-Parmer) was wrapped around the system in order to maintain a stable temperature (copper wires were also used at local turning points for the same purpose). By slightly unscrewing the cap of the storage vessel, water vapor was allowed to slowly diffuse into the gas cell via the transfer line. A few minutes was allowed for the gas pressure to equilibrate (approximately 150 Torr at 60°C). The gas cell was then sealed and moved into the experimental setup while the heating tape was still attached and turned on until the experiment was completed.

**THz time-domain spectroscopy (THz-TDS)**
A typical THz-TDS system was used to record the temporal profile of water vapor from ambient air at room temperature (Fig. S1). A mode locked Ti: Sapphire oscillator (78 MHz rep rate, 150 mW average power, 800 nm central wavelength, < 100 fs pulse duration) was used to pump a DC biased photoconductive antenna (PCA) made of low-temperature-grown gallium arsenide (LT-GaAs). The generated single-cycle THz field (~1 ps, 0.1-5 THz spectrum) was collected by four 90-degree off-axis parabolic mirrors and detected by another PCA. A small portion of the femtosecond laser beam was split and sent into an optical delay line, attenuated, and used to read out the THz field profile. The THz field amplitude was proportional to the time-averaged photocurrent, and detected by a lock-in amplifier. The coherent nature of the detection ensures a high signal-noise ratio on the order of $1.0 \times 10^4$.

**2D THz spectroscopy**

Two Ti:Sapphire amplifier systems (Coherent, 1 kHz repetition rate, 800 nm central wavelength) were used in our experiments. One delivered 35-fs pulses and had an output power of 7 W; the other delivered 100-fs pulses and had 3.5 W output power. Using either system, 95% of the output power was divided into two equal parts with time delays between them controlled by a mechanical delay stage. Both parts were directed into the same lithium niobate (LN) crystal to generate two time-delayed, collinearly propagating THz pulses by the tilted-pulse-front technique. The generated THz pulses (Fig. S2) were collected by four 90-degree off-axis parabolic mirrors, and focused on the gas sample in the gas cell. The remaining 5% laser output was attenuated, routed into a third path to read out the THz signals by EO sampling in a 2 mm ZnTe crystal. Dry air was used to purge the experimental setup to avoid THz absorption by water vapor from ambient air. The two THz electric field amplitudes were 440 kV/cm and 290 kV/cm using the 35-fs laser system, and 300 kV/cm and 350 kV/cm using the 100 fs laser system.

**Differential chopping technique**

Differential chopping was employed to separate nonlinear THz signals from strong linear signals (Figs. S3-S4). Two optical choppers were placed in the two optical paths to modulate the optical pulses used for THz generation. One chopper was operating at 500-Hz frequency, the other at 250 Hz. Each chopper was put in one optical path. Within four sequential laser shots, THz pulses from both paths 1 and 2 denoted as $E_{12}$, only from path 1 denoted as $E_1$, only from path 2 denoted as $E_2$, and none denoted as $E_{BG}$ were produced, respectively. The two choppers and the laser were synced to a data acquisition card (National Instruments) that was used to measure the signal out of EO sampling. Each data point was averaged over 100 laser shots in order to achieve a signal-noise ratio of around 5000. The total acquisition time period for a complete 2D scan was roughly 2.5 days.

**Data availability:** All data are available in the main text and the supplementary information, and are available from the corresponding author on reasonable request.

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**Supplementary Information:**
- Supplementary Text
- Figs. S1 to S18
- Tables S1 to S4
- Supplementary References
Fig. 1. Overview of the experiment. a, Water molecule in the lab frame, showing the dipole moment $\mu$ at an angle $\theta$ from the $Z$ axis (THz polarization direction). b, Water molecule in the molecule-fixed frame with the three moments of inertia $I_a$, $I_b$, and $I_c$ along the corresponding axes. c, Relative population distribution as a function of the $J$ rotational quantum number. Inset shows the relative population distribution within the state $J=2$. d, Rotational energy levels of para-H$_2$O and ortho-H$_2$O molecules. Red arrows illustrate rotational transitions involved in this work. e, Measured THz free-induction decay (top) and Fourier transform (bottom) showing rotational transitions (marked by dashed vertical lines) of water vapor in ambient air. f, Schematic illustration of the 2D THz experimental setup. Linear THz spectra (in e) are measured with only one THz pump pulse.
Fig. 2. 2D rotational spectra of water vapor. a to c, Non-rephasing (NR) 2D rotational spectrum. d to f, Rephasing (R) 2D rotational spectrum. g, Spectra recorded with extended time delays (to 300 ps) in order to resolve closely spaced peaks. The two cross peaks at \( f_{probe} = 1.098 \) THz, \( f_{pump} = -1.165 \) THz and \( f_{probe} = 1.165 \) THz, \( f_{pump} = -1.098 \) THz labelled in g arise from rotational coherences among levels \(|3_{03}\rangle, |3_{12}\rangle, \) and \(|3_{21}\rangle\). h, Close-up view of three peaks. i, Two-level system diagram. j, Three-level system diagram. k, V-type system diagram. All 2D spectra are based on the same color bar. Continuous, evenly-spaced features in gray dashed boxes (in a, b, and d) arise from acetonitrile residue in the gas cell, and they do not significantly affect the nonlinear signals of water vapor. Representative peaks are labelled ((a), (b), (c), (d), (e) and (f)) and their Feynman diagrams are listed. All other 2D signals can be interpreted in a similar manner.
Fig. 3. Many-body interaction in water vapor. a, 2Q spectra near (\(f_{\text{probe}} = 0.558 \text{ THz}, f_{\text{pump}} = 1.115 \text{ THz}\)) (Left) and (\(f_{\text{probe}} = 0.753 \text{ THz}, f_{\text{pump}} = 1.506 \text{ THz}\)) (Middle) and 3Q spectrum near (\(f_{\text{probe}} = 0.558 \text{ THz}, f_{\text{pump}} = 1.673 \text{ THz}\)) (Right). (a1 and a2) 2Q diagonal peaks. (b1, c1, and b2) 2Q off-diagonal features. (d1, e1, c2, and d2) are side peaks arising from distinct coherence pathways. b, Energy ladder and Feynman diagrams of many-body interactions. The ground state (\(|g\rangle\)), the three singly-excited states (\(|e'e\rangle\)), the three doubly-excited states (\(|e''e\rangle\)), and the triply-excited state (\(|e'''e\rangle\)) are illustrated. Energy level splittings (denoted as \(\Delta\)) could occur in any level. c, V-type energy ladder and other possible coherence pathways contributing to the 2Q (left panel in Fig. 3a) and 3Q features.
**Fig. 4. Simulation results.**

a. Simulated NR (Top) and R (Bottom) spectra. No intermolecular interactions are included. Peaks in blue and red circles are magnified by 5 and 50, respectively.

b. Simulated 2Q and 3Q spectra with many-body interactions. The weak interactions in the simulation are sufficient to allow 2Q and 3Q signals to appear but not enough to induce significant energy shifts, leading to only diagonal peaks in b. The pump-probe (PP), 1Q, 2Q (magnified by 10), and 3Q (magnified by 50) signals are illustrated.

c. Rotational couplings involving weak water transitions. Weak peaks (e) and (e’) are related to the transition $3_{21} \leftrightarrow 4_{14}$, the intensity of which is too weak to be observed in the present experiment.

d. Ratio of 2Q off-diagonal peaks to the 2Q diagonal peaks vs temperature. Red circles and blue squares are data near ($f_{\text{probe}} = 0.558 \text{THz}$, $f_{\text{pump}} = 1.115 \text{THz}$) and ($f_{\text{probe}} = 0.753 \text{THz}$, $f_{\text{pump}} = 1.506 \text{THz}$), respectively. The strong increase in the ratios with temperature suggests that 2Q off-diagonal features originate from (metastable) water complexes.

e. Ratios of 2Q and 3Q diagonal peaks to the corresponding 1Q diagonal peaks. Red circles and squares indicate experimental data. Points in blue and black are simulated results without many-body interactions when THz fields are 300 kV/cm and 900 kV/cm. Since the simulation conditions are similar to those in the experiments except for the absence of intermolecular interactions, the much smaller 2Q and 3Q signal amplitudes (blue and black) in the simulation than the experimental signals (red) indicate that weak nonlinear signals (e.g. those in Fig. 3c) from non-interacting water molecules are not contributing significantly to 2Q and 3Q features.
Supplementary Information for

Nonlinear rotational spectroscopy and many-body interactions in water molecules

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Simulation details

Coordinate system

Before we discuss any simulation details, it is beneficial to clarify the relevant coordinate systems (Fig. S5). The excitation THz field is defined in the space-fixed frame (X, Y, Z). For a linearly polarized THz field, the polarization vector is assigned along the +Z axis without any loss of generality.

Hamiltonian

A quantum mechanical rotational system is governed by the rotational Hamiltonian \( H(t) \), which consists of a field independent Hamiltonian \( H_0 \), and a field-molecule interaction term \( H_1(t) \),

\[
H(t) = H_0 + H_1(t) \tag{S.1}
\]

where \( H(t) \) is the total rotational Hamiltonian.

The field-free term is

\[
H_0 = AJ_a^2 + BJ_b^2 + CJ_c^2 \tag{S.2}
\]

where \( A, B, \) and \( C \) are three rotational constants inversely proportional to the three components of moment of inertia along \( a-, b- \) and \( c- \) axes, respectively (\( J_a, J_b, \) and \( J_c \) are the three components of the total angular momentum \( J \)).

If we choose the following coordinate identifications:

\[
a \leftrightarrow z, b \leftrightarrow x, c \leftrightarrow y \tag{S.3}
\]

Accordingly,

\[
H_0 = AJ_z^2 + BJ_x^2 + CJ_y^2 \tag{S.4}
\]

The matrix elements, for example in the basis set of the symmetric top

\[
\langle JKM | H_0 | J'K'M' \rangle \tag{S.5}
\]

has been evaluated in textbook\(^1\). The other part of the total Hamiltonian is dictated by the field-dipole interaction,

\[
H_1(t) = -\mu \cdot E_{THZ}(t) \tag{S.6}
\]

which can be expressed in the language of irreducible spherical tensor operator as follows\(^1\),

\[
H_1(t) = - \sum_{p=-1}^{1} (-1)^p T_p^0(\mu)T_p^0(E_{THZ}(t)) \tag{S.7}
\]

Evaluation of matrix elements

In the Cartesian coordinate system (space-fixed frame), we know the components of the THz field,

\[
E_{THZ}(t) = (E_X, E_Y, E_Z) = (0,0, E_{THZ}(t)) \tag{S.8}
\]
\[
T_0^i(E) = E_z = E_{\text{THz}}(t) \\
T_{\pm 1}^i(E) = \frac{-i(E_x \mp iE_y)}{\sqrt{2}} = 0
\] (S.9)

On the other hand, the tensor components of the permanent dipole vector are given in the molecule-fixed frame in a similar manner,

\[
\mu = (\mu_x, \mu_y, \mu_z) = (\mu_a, \mu_b, \mu_c) \\
T_0^{(1)}(\mu) = \mu_z = 0 \\
T_{\pm 1}^{(1)}(\mu) = \mp (\mu_x \pm i\mu_y) = \mp \mu_b \mp \mu_c \\
\frac{\sqrt{2}}{\sqrt{2}}
\] (S.10)

(S.11)

In order to evaluate the field-molecule interaction \( H_1(t) \), a coordinate transformation is needed. If we transform the dipole moment from molecule-fixed frame into space-fixed frame, that is

\[
T_0^{(1)}(\mu) \mid_{\text{space}} = \sum_{q=1}^{1} D_{0q}^{(1)*} T_q^{(1)}(\mu) \mid_{\text{molecule}} = \frac{\mu}{\sqrt{2}} (D_{0,1}^{(1)} - D_{0,1}^{(1)*})
\]

\[
T_1^{(1)}(\mu) \mid_{\text{space}} = \sum_{q=1}^{1} D_{1q}^{(1)*} T_q^{(1)}(\mu) \mid_{\text{molecule}} = \frac{\mu}{\sqrt{2}} (D_{1,1}^{(1)} - D_{1,1}^{(1)*})
\]

\[
T_{-1}^{(1)}(\mu) \mid_{\text{space}} = \sum_{q=1}^{1} D_{-1q}^{(1)*} T_q^{(1)}(\mu) \mid_{\text{molecule}} = \frac{\mu}{\sqrt{2}} (D_{-1,1}^{(1)} - D_{-1,1}^{(1)*})
\]

then \( H_1(t) \) is ready to be evaluated in that both the dipole moment and the excitation THz field are in the same frame (in this case, space-fixed frame).

The matrix element of \( H_1(t) \) in the basis set of the symmetric top wavefunction \( |JKM\rangle \) is given as

\[
\langle JKM \mid H_1(t) \mid J'K'M'\rangle \\
= -\mu_b E_{\text{THz}}(t) \langle JKM \mid \frac{1}{\sqrt{2}} (D_{0,1}^{(1)} - D_{0,1}^{(1)*}) \mid J'K'M'\rangle \\
= -\frac{\mu_b E_{\text{THz}}(t)}{\sqrt{2}} (-1)^{M-K} [(2J+1)(2J'+1)]^{1/2} \times \\
\begin{pmatrix}
  J & 1 & J' \\
-1 & -1 & K'
\end{pmatrix} \begin{pmatrix}
  J & 1 & J' \\
-1 & -1 & K'
\end{pmatrix}^{-1} \begin{pmatrix}
  J & 1 & J' \\
-1 & -1 & K'
\end{pmatrix} \begin{pmatrix}
  J & 1 & J' \\
-1 & -1 & K'
\end{pmatrix}
\]

(S.13)

where \( D \) is a rank (1) Wigner rotational matrix, and \((\cdots)\) is a 3-j symbol\(^1\). The nonvanishing condition is

\[
\Delta M = 0; \Delta J = 0, \pm 1; \Delta K = \pm 1
\]

(S.14)

The following relation is used in the calculation,
\[
\left\langle J\Omega M \mid D_{pq}^{k\gamma}(\omega) \mid J'\Omega'M' \right\rangle \\
= (-1)^{M-\Omega}[2J+1](2J'+1)^{3/2} \times \left( \begin{array}{ccc} J & k & J' \\ -\Omega & q & \Omega' \end{array} \right) \left( \begin{array}{ccc} J & k & J' \\ -M & P & M' \end{array} \right)
\]  

(S.15)

The Wigner 3-j symbol is evaluated numerically by the Racah formula. Alternatively, the matrix element can also be expressed in the basis set of the asymmetric-top wavefunction \(\mid JK_aK_eM \rangle \geq \mid J\tau M \rangle\). Expanding \(\mid J\tau M \rangle\) as a linear combination of the symmetric-top wavefunction, one obtains

\[
\mid J'\tau' M \rangle = \sum_{K'} a_{K'}^{J'} \mid J'K'M' \rangle
\]

(S.16)

Inserting the identity operator, we find,

\[
\left\langle J\tau M \mid H_1(t) \mid J'\tau' M' \right\rangle \\
= \left\langle JK_aK_eM \mid -\mu_p E_{TH_1}(t) \cos \theta_p \mid J'K_e'K_a'M' \right\rangle \\
= \sum_{K''} \sum_{K'''} (a_{K''}^J)^* \left\langle JKM \mid H_1(t) \mid J'K'M' \right\rangle (a_{K'}^{J'} )
\]

(S.17)

Therefore,

\[
\left\langle J\tau M \mid H_1(t) \mid J'\tau' M' \right\rangle \\
= \left( \begin{array}{ccc} a_{K_1(1)}^J & \left\langle JK \mid H_1 \mid J'K' \right\rangle_{11} & \cdots & \left\langle JK \mid H_1 \mid J'K' \right\rangle_{1n} \\ a_{K_2(2)}^J & \left\langle JK \mid H_1 \mid J'K' \right\rangle_{21} & \cdots & \left\langle JK \mid H_1 \mid J'K' \right\rangle_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{K_n(n)}^J & \left\langle JK \mid H_1 \mid J'K' \right\rangle_{n1} & \cdots & \left\langle JK \mid H_1 \mid J'K' \right\rangle_{nn} \end{array} \right) \left( \begin{array}{c} a_{K_1(1)}^{J'} \\ a_{K_2(2)}^{J'} \\ \vdots \\ a_{K_n(n)}^{J'} \end{array} \right)
\]

(S.18)

The nonvanishing condition is the same as above. A typical implementation of the density matrix has been illustrated (Fig. S6) below.

Time evolution

At the condition of thermal equilibrium, the initial density matrix is

\[
\rho(0) = \frac{e^{-\beta H_0}}{Tr(e^{-\beta H_0})}
\]

\[
\beta = \frac{1}{k_B T}
\]

(S.19)
or simply by

\[ \rho(0) = \sum_i P_i |\psi_i\rangle\langle\psi_i| \]  

(S.20)

where \( P_i \) is the statistical probability of the system in the normalized pure state \(|\psi_i\rangle\),

\[ \sum_i P_i = 1 \]  

(S.21)

The system evolution is described by the well-known Liouville-von Neumann equation,

\[ \frac{d\rho(t)}{dt} = -\frac{i}{\hbar} \left[ \rho(t), H(t) \right] \]  

(S.22)

the time-dependent density matrix can be calculated by the time propagation operator,

\[ \rho(t) = e^{-\frac{H(t)}{\hbar}} \rho(0) e^{\frac{H(t)}{\hbar}} \]  

(S.23)

Orientation calculation and THz field representation

The ensemble averaged orientation is,

\[ \langle\cos \theta\rangle(t) = Tr[\rho(t)\cos \theta] \]  

(S.24)

And the nonlinear orientation factor\(^2\),

\[ \langle\cos \theta(\tau,t)\rangle_{NL} = \langle\cos \theta(\tau,t)\rangle_{12} - \langle\cos \theta(\tau,t)\rangle_{1} - \langle\cos \theta(\tau,t)\rangle_{2} - \langle\cos \theta(\tau,t)\rangle_{BG} \]  

(S.25)

where 12 denotes both THz fields are on, 1 denotes only THz field 1 is on, 2 denotes only THz field 2 is on, and BG denotes both THz fields are off (see Fig. S4). Note that the orientation angle \( \theta \) here is understood as the angle between THz field polarization (along +Z axis) and the molecular dipole moment (along \( b \) axis), so that \( \theta = \theta_{\text{space}}^{\text{molecule}} \), which can be further evaluated by the Wigner rotational matrix,

\[ \theta = \theta_{\text{space}}^{\text{molecule}} = \frac{1}{\sqrt{2}} (D_{0,-1}^{(1)*} - D_{0,1}^{(1)*}) \]  

(S.26)

A THz field pulse is characterized by a Gaussian-envelope modulated sine or cosine wave with a center frequency \( \omega_0 \).

\[ E_{\text{THz}}(t) = E_i e^{-t^2/\tau^2} \cos(\omega_0 t + \phi_1) \]  

(S.27)

Two pulses with a time delay are described by,

\[ E_{\text{THz}}(t) = E_1 e^{-t^2/\tau^2} \cos(\omega_0 t + \phi_1) + E_2 e^{-(t+\delta t)^2/\tau^2} \cos(\omega_0 (t + \delta t) + \phi_2) \]  

(S.28)

For the sake of simplicity, the initial phases are set to zero, \( \phi_1 = \phi_2 = 0 \).

Watson’s reduced Hamiltonian
Centrifugal distortion has to be taken into consideration in order to accurately find the positions of rotational transition lines. The non-rigidity causes significant spectral line shifts, on the order of 1% of the line frequencies, and needs to be accounted for to avoid misassignments of the spectral lines. The line positions can be calculated with around 0.1% accuracy (absolute error on the order of 1 GHz) with the centrifugal distortion taken into account (Fig. S7-S10).

One approach to including centrifugal distortion is Watson’s reduced Hamiltonian. This approach is based on a perturbative treatment to high order, and is extensively used although it inherently diverges\(^3\). Watson’s reduced Hamiltonian, up to the 6\(^{th}\) order, is sufficient to address our concern. The total Hamiltonian is written as\(^4,5\),

\[
H = H_r + H_d^{(4)} + H_d^{(6)}
\]  

(S.29)

where the unperturbed (2\(^{nd}\) order) term is

\[
H_r = \frac{1}{2} (B + C) J^2 + \left[ A - \frac{1}{2} (B + C) \right] (J_z^2 - b_p J_z^2)
\]  

(S.30)

The 4\(^{th}\) order term is given as

\[
H_d^{(4)} = -\Delta J J^4 - \Delta_{jk} J^2 J_z^2 - \Delta_k J_z^4 - 2\delta J J_z^2 J_\perp^2 - \delta_k (J_z^2 J_z^2 + J_\perp^2 J_\perp^2)
\]  

(S.31)

And the 6\(^{th}\) order term,

\[
H_d^{(6)} = H_{fj} J^6 + H_{jk} J^4 J_z^2 + \\
H_{kj} J_z^4 J_z^2 + H_k J_z^6 + 2h_j J^4 J_z^2 + h_{jk} (J_z^2 J_z^2 + J_\perp^2 J_\perp^2) + h_k (J_z^4 J_z^2 + J_\perp^4 J_\perp^2)
\]  

(S.32)

with

\[
b_p = \frac{C - B}{2A - B - C}
\]  

(S.33)

The rotational constants used in this work are listed (Table S1).

In order to implement the calculation of matrix elements of the angular moment operator, we follow the method in textbooks\(^1\) using commutation rules and matrix multiplication. Matrix elements of the angular momentum operator through 6\(^{th}\) order are evaluated and listed below (Tables S3 and S4).

Qualitative simulation of many-body interactions between water molecules

We model water intermolecular interactions qualitatively by treating an individual transition as a two-level quantum system and considering three nearby molecules. The three two-level systems yield together a four-level system via intermolecular interactions such as dipole-dipole interactions among the molecules (Fig. S13). The singly-excited and doubly-excited energy levels are degenerate, each consisting of three energy levels. The small energy shifts induced by many-body interactions are not shown in the figure. Combined three-level and multiple-level pictures can be interpreted in a similar way. A small energy shift of the combined energy levels is needed to break
the symmetry of the combined states so that emission signals from distinct pathways do not completely cancel each other\textsuperscript{6-8}.

In order to understand the many-body interactions among water molecules, a qualitative simulation is developed. The orientation simulation follows the time propagation mechanism described above, with a new Hamiltonian in which the interactions give rise to perturbation terms represented by off-diagonal elements (labelled as \(a\) in Fig. S14). Diagonalization gives a set of new eigenenergies. Generally, the coupling strength is very small (\(a \ll \hbar \omega\)) and a multi-level quantum system with an approximately equal energy spacing \(\hbar \omega\) between neighboring, non-degenerate energy levels is created by many-body interactions. Note that the coupling elements (the assignments of \(a\) are not necessarily the same as shown in Fig. S14). Different arrangements of the coupling elements produce similar energy levels.

Up to 6 combined energy levels have been included in the simulation. The transition frequency is specifically chosen as 0.558 THz (the first ortho-type transition \(I_{10} \leftrightarrow I_{11}\) ) in water. 2Q and 3Q peaks with respect to 0.753 THz transition can be implemented in a similar way. The transition dipole matrix is set as that of a linear or prolate symmetric-top molecule in which only coherences between distinct J states are taken into account. A quantitative and accurate simulation of both diagonal and off-diagonal features may require a complete knowledge of the intermolecular interaction and the newly formed Hamiltonian.

**Supplementary Text**

**Rotational energy levels of water molecules**

The population distribution of rotational states at the condition of thermal equilibrium follows the Boltzmann distribution\textsuperscript{5} (Fig. S11)

\[
\text{Population} \propto (2J + 1) e^{-E_{rot}/k_BT}\]

(S.34)

where the factor \((2J + 1)\) is introduced due to the \(M\) sublevel degeneracy. As a result, at or not far from ambient temperature, most of the rotational population stays in low \(J\) states. The majority of the rotational population is under \(J = 10\) at room temperature, and this value is used as a cut-off number to simplify the simulation. We note that (i) the population distribution within a single \(J\) state is not uniform (Fig. S11), in contrast to linear or symmetric-top molecules; (ii) any two successive para (ortho) rotational states are always separated by an ortho (para) state, leading to no adjacent rotational states with the same nuclear spin configuration within one specific \(J\) quantum state.

The rotational energy levels of a quantum-mechanical rigid rotor are given by

\[
H_0 = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} = AJ_a^2 + BJ_b^2 + CJ_c^2
\]

(S.35)

where \(A, B,\) and \(C\) (\(A \geq B \geq C\)) are three rotational constants, each of which is inversely proportional to \(I_a, I_b,\) and \(I_c\) \((I_a \leq I_b \leq I_c)\), the three components of the moment of inertia. For water, the values are listed with other related rotational constants below (Table S1).
For a linear polar molecule (e.g. OCS), \( I_a = 0; I_b = I_c \), and \( A = \infty; B = C \). The energy levels are solely determined by one rotational constant \( B \), and no angular momentum occurs along the molecular axis (the direction of the permanent dipole moment) because a torque cannot exist along the molecular axis. A (prolate) symmetric top\(^2\) (e.g. CH\(_3\)CN), satisfying \( I_a < I_b < I_c \), and \( A > B > C \), has a slightly complicated rotational energy level structure described by introducing a new quantum number \( K \), giving the projection of angular momentum onto the molecular axis. Fortunately, the selection rule requires that \( \Delta J = \pm 1; \Delta K = 0 \), thus reducing the energy level structure into multiple blocks distinguished by \( K \) values. Within each energy level block, a symmetric top resembles a linear molecule.

When one moves to a small asymmetric-top molecule, especially with a large asymmetry (e.g. water), the three principle moments of inertia are all unequal, as are the rotational constants (\( I_a < I_b < I_c \), and \( A > B > C \)), leading to an extremely irregular rotational energy level structure\(^4,5\). The transition energy values are not multiples of a fundamental frequency\(^2\) any more. And there is no simple pattern describing the various absorption peaks (Fig. S12).

Selection rules

The rotational selection rules for the water molecule is given (for linearly polarized THz fields) by\(^4,5\)

\[
\begin{align*}
\Delta M &= 0, \\
\Delta J &= 0, \pm 1, \\
\Delta K_a &= \pm 1, \pm 3, \ldots \\
\Delta K_c &= \pm 1, \pm 3, \ldots 
\end{align*}
\]  
(S.36)

Therefore, rotational transitions of water molecules involve not only those within one specific \( J \) state (only \( K \) quantum number is changing, Q-branch) but also between distinct \( J \) states (both \( J \) and \( K \) are changing, P-/R-branches). In addition, many weak transition lines from \( \Delta K = \pm 3 \) also contribute to the final spectrum.

Wavefunctions of an asymmetric top

The wavefunctions of an asymmetric top are generally given as linear combinations of symmetric-top wavefunctions,

\[
|J\tau K_aK_cM\rangle = \sum_{K=-J}^{J} a_K(JK_aK_c)JKLM\rangle
\]  
(S.37)

Two pseudo-quantum numbers \( K_a, K_c \), or their difference \( \tau \), are introduced to characterize the wavefunction of an asymmetric top. One can choose either \( |JK_aK_cM\rangle \) or \( |JKLM\rangle \) as the basis set to construct the Hamiltonian matrix although the latter is only exact for symmetric tops.

Spin statistics

Water naturally exists as a mixture of two nuclear-spin species, para and ortho, which are determined by the total spin of the two hydrogen nuclei. For total spin \( I = 0 \), water is para, and \( K_a + K_c \) is even; for total spin \( I = 1 \), water is ortho, and \( K_a + K_c \) is odd. No transition between
ortho and para is allowed, separating the water energy levels into two parts (Fig. S12). Different nuclear spin statistical weights for para- and ortho- transitions strongly affect transition line strengths.

Centrifugal distortion

Because the water molecule is very light, its rotational constants are notably large compared to most others. For example, the rotational constant $B$ of water molecule is 70 times larger than that of OCS and 47 times larger than CH$_3$CN. As a consequence, water molecule shows an extraordinarily large centrifugal distortion effect even when the angular momentum quantum number $J$ is very small (e.g. $J < 5$), since the product of the rotational constant and the square of the angular momentum component (e.g. $BJ^2$) contributes to the Hamiltonian$^{4,5}$. This non-rigid behavior shifts the absorption and emission spectra and further affects the rotational spectrum.

Mixing and collision

For our nonlinear 2D THz measurements, a gas cell was used. We discovered afterward that a small amount of the previous sample, gaseous acetonitrile, was adsorbed onto the aluminum surface of the gas cell. Although no couplings between water molecule and acetonitrile were found (a similar case has been reported where no coupling occurs between atoms of different rubidium isotopes$^7$), a diagonal peak splitting around 0.557 THz is clearly observed. This is formed by the coincidence and interference of two third-order coherent processes: one in the water molecule with the $1_{01} \leftrightarrow 1_{10}$ coherence, and the other in acetonitrile with $J = 29 \leftrightarrow 30$.

At the typical relative humidity of 40% in our lab, there is about 10 Torr water vapor in the ambient air, and one can make full use of the water vapor for the linear THz absorption measurement (Fig. S1). Frequent collisions with nitrogen and oxygen molecules in the air broadens the linewidths to roughly twice those of pure water vapor.

Radiative interaction

One possible contribution to the two-quantum peaks is radiative interaction$^9$. After the main THz pulse interacts with one water molecule, the emitted THz field from this molecule will subsequently excite another water molecule, and the cascaded two-step excitation can also create two-quantum diagonal peaks. Similarly, three-quantum diagonal peaks can be generated involving radiative interactions among three water molecules or many-body interactions between two nearby molecules and radiative interactions with a third molecule. Radiative interactions cannot yield energy shifts away from simple sums of the separate transition energies, so such shifts provide clear signatures of many-body interactions.

Field dependences and Feynman diagrams for selected spectral peaks

Feynman diagrams of many spectral peaks of water molecules can be identified and assigned based on previous experimental results and analyses$^{2,10}$, especially the diagonal peaks and off-diagonal peaks not far away from the diagonal. Other off-diagonal peaks arise from either 2Q or 3Q coherences (See Figs. 2 and 3). The 2D water rotational spectra from both simulations and experimental data reveal the complexity of the 2Q and 3Q signals, because they can occur due to three distinct origins: (i) many-body interactions; (ii) radiative interactions; and (iii) nonlinear responses of individual water molecules. Since the simulation conditions are similar to those in the experiments, the much smaller 2Q and 3Q signal amplitudes (blue and black signals in Fig. 4e)
than the experimental signals (red signals in Fig. 4c) reveal that weak nonlinear responses (Fig. 3c, Fig. S16, 17) from non-interacting water molecules are not contributing significantly to 2Q and 3Q features. (i) and (ii) together are estimated to have a dominant contribution (>90%) to the overall multiple-quantum signals, while (iii) has a small contribution (<10%). Signals from (iii) are overlapped and merged with the strong 2Q/3Q signals in the NR spectra, but some nonlinear responses from (iii) can be observed in the R spectra (Fig. 2h), offering another approach to estimating the contributions of distinct origins of the 2Q/3Q signals and giving the same results. In addition, both NR and R contributions from (iii) can be captured in the simulation (without many-body interactions) (Fig. 4a).

Simulated field dependences of several selected spectral peaks are shown (Fig. S16). As expected, peaks (P2-P6) show a third-order dependence on THz field strength in the moderate THz field regime. P1, overlapped with the 2Q signal, is fifth-order on the THz field amplitude, because no corresponding third-order responses can be assigned to it. In particular, one cannot connect the coherences |2><1| and |1><0| by one single interaction between THz fields and water molecules in the V-type energy ladder diagram (Fig. S17). However, its counterpart in the R spectra (i.e. P3 in Fig. S16) is third-order since one THz excitation process can connect |1><2| and |1><0| on the bra side of the Feynman diagram.

As a consequence, only two peaks in our measurement belong to fifth-order signals, namely, (a) 3Q signal (Fig. 3a) and (b) the fifth-order signal discussed above which is overlapped with the 2Q signal (Fig. 3c and P1 in Fig. S16). The rest of the 2D spectral peaks are all third-order signals.

Note that different excitation pathways in the Feynman diagram (for example, the two distinct excitation pathways |0><0| → |1><0| → |1><2| (B (1) in Fig. S17) and |0><0| → |0><2| → |1><2| (b (2) in Fig. S17) could be distinguished through the use of three pulses to temporally separate each of the field interactions temporally, revealing the first coherence frequency from the first interaction in addition to the second and third field interactions, the variable delays of which reveal the 2Q coherence11,12.
Fig. S1. Measured THz spectrum of water vapor in ambient air. a, The time domain signal is obtained by a typical THz time-domain spectroscopy (THz-TDS) system in which photoconductive antennae (PCA) are used for THz generation and detection as described in the text. The trailing oscillation after the main THz peak in the top panel stems from THz emission (i.e. the rotational free-induction decay) from water vapor in the ambient air. b, Fourier transform of the time domain signal (including both the main peak and the trailing oscillation) reveals the rotational absorption peaks.
**Fig. S2. Typical profile of a single-cycle THz electric field.** The single-cycle THz field profile shown in this figure was generated in a lithium niobate crystal by the tilted-pulse-front technique. 

**a,** The time domain signal in the top panel includes the THz main peak around 0 ps and the trailing oscillation from water vapor emission. Double reflections from the gas cell window and optics in the setup appear beyond 20 ps and are excluded. **b,** FT spectrum from top panel, in which only the main THz peak is taken into account (zero-padding was added after the first large THz cycle.)
Fig. S3. Mechanism of differential chopping detection. The laser is run at a 1 kHz repetition rate (red). Chopper 1 (green) is operated at a 500 Hz frequency while the other chopper 2 (blue) is at 250 Hz. The signal sequence shown here consists of a background signal ($E_{BG}$), an “only THz 1 on” signal ($E_1$), an “only THz 2 on” signal ($E_2$), and a “both THz 1 and 2 on” signal ($E_{12}$). The nonlinear signal can be obtained by subtraction: $E_{NL} = E_{12} - E_1 - E_2$. 
Fig. S4. Typical linear and nonlinear signals in the experiment. a, THz time-domain signals with only THz 1 (blue) and only THz 2 (magenta) on, respectively. b, THz signals when both THz 1 and 2 are on. The nonlinear THz signal (red) is obtained by subtraction of both $E_1$ and $E_2$ from $E_{12}$, namely $E_{NL} = E_{12} - E_1 - E_2$. The background noise can also be subtracted when necessary. The nonlinear signal is magnified by a factor of 10 for the sake of clarity.
**Fig. S5. Coordinate system assignment.** a, THz field is polarized along the Z direction in the space-fixed frame (X, Y, Z). b, Ball-stick model of a water molecule with its principle axes (a, b, c). The permanent dipole moment of water is along its principle b-axis. c, Orientation angle is identified as the intersection angle between the THz field polarization vector (along Z-axis in the space-fixed frame) and the dipole moment vector (along b-axis in the molecule-fixed frame). The identification of the principle axes (a, b, c) with molecule-fixed coordinates (x, y, z) is indicated in b.
**Fig. S6. Density matrix format of the rotational Hamiltonian.** Each column and row holds one specific rotational state denoted as $|JK>$ ($M$ quantum number is omitted for simplicity). Diagonal matrix elements (red star) are the population states. Off-diagonal matrix elements (green cross) are the coherence states. Matrix elements belonging to the same $J$ quantum number are encompassed by a blue square. When implemented in the eigen-states of an asymmetric top $|JKr>$ or $|J\tau>$, the density matrix basically remains the same structure except that $K$ in the figure is replaced by $\tau = K_a - K_r$. The $M$ quantum number is omitted for simplicity.
Fig. S7. Simulation of linear THz spectroscopy of water molecules. a, Simulated THz free-induction decay from water molecules. The maximum $J$ quantum number was set at 15. $M$ states considered here are those with $|M| \leq 4$. Temperature $T = 100$ K. The THz field strength was set at 300 kV/cm. b, FT spectrum from the time domain signal.
Fig. S8. Simulated 2D THz signals in the time domain. The maximum $J$ quantum number was set at 15. $M$ states considered were those with $|M| \leq 4$. Temperature was set at 100 K. Both THz field strengths were set at 300 kV/cm. The step size for the inter-pulse pump axis was 0.25 ps, and that for the probe axis was 0.1 ps. The similar features along both time scales correspond to diagonal peaks in the 2D spectrum. The pronounced periodicity of 1.3 ps (along both axes) corresponds to the strongest diagonal peaks in the spectra, at 0.75 THz (apparent in the measured spectra of Fig. 2 and the simulated spectra of Fig. 4). The features that start at $t_{\text{probe}} \approx 0$ at any time along the $t_{\text{pump}}$ axis, i.e. signals that begin immediately after the two pulses, correspond to non-rephasing signals. The signals (clearest for the 1.3 ps periodic feature) that are at their approximate maxima along the diagonal correspond to rephasing (photon echo) signals, i.e. they reach their maxima (neglecting dephasing) at a time delay $t_{\text{probe}}$ equal to the delay $t_{\text{pump}}$ between the THz pump pulses.
Fig. S9. Centrifugal distortion effect on transition line positions. a, Comparison between calculated line positions with and without centrifugal distortion (CD). b, Enlargement of the top panel in the region (1.65-1.95 THz). Deviations as large as 10 GHz are observed between experimentally observed transition frequencies and those calculated when no centrifugal distortion is taken into account (red line). Watson’s reduced Hamiltonian has been employed to account for centrifugal distortion so that the deviation is reduced to around 1 GHz (blue line).
Fig. S10. Experimental and simulated water THz spectra. a. Measured THz spectrum of water vapor at 60ºC pumped by a THz pulse generated in a lithium niobate crystal. b, Simulated water spectrum using Watson’s reduced Hamiltonian. The transitions above 1.5 THz are enlarged by a factor of 10 in both panels. Dashed black lines indicate the positions of observed rotational transition lines of water vapor in ambient air by a photoconductive antenna detection. Large oscillations of a in the frequency intervals (0.558 THz, 0.753 THz) and (0.753 THz, 0.989 THz) are from double reflections in the setup and reduced by a factor of 0.1, causing a slight distortion at the edges of peaks at 0.558 THz, 0.753 THz, and 0.989 THz.
Fig. S11. Calculated population distribution of water molecules at room temperature. (Top) Relative population in each $J$ (0-4) state is indicated. Orange and blue denote para and ortho water rotational states, respectively. The rotational states $J_{K_aK_c}$ are indicated. (Bottom) Relative population in each state up to $J = 8$. The largest populations occur at $J = 2$ and $J = 3$ when treating all rotational states sharing the same $J$ quantum number as a whole.
Fig. S12. Energy-level diagram of water rotational states. Rotational energy levels are divided into two parts: para-type (left side, in black) where the total nuclear spin of the two hydrogen atoms is 0, and ortho-type (right side, in blue) where the total nuclear spin is 1. Red arrows indicate allowed transitions between 0.5 THz and 1.8 THz observed in this work. Black arrows indicate other possible transitions either lower than 0.5 THz or higher than 1.8 THz. Two transitions below 2 THz, with frequencies of 1.798 THz (6_{25} \leftrightarrow 6_{24} and 7_{25} \leftrightarrow 7_{34}) and 1.871 THz (5_{23} \leftrightarrow 5_{32}) are associated with higher-energy rotational states than those shown here.
Fig. S13. Diagram of the formation of a four-level system in water molecules. Three two-level quantum systems of three individual water molecules generate a four-level quantum system via intermolecular interactions such as dipole-dipole interactions among water molecules. The singly-excited and doubly-excited energy levels are three-fold degenerate in the absence of interactions but non-degenerate when interactions are taken into account.
**Fig. S14. Diagram of Hamiltonian under many-body interactions.** (Top) The rotational Hamiltonian under many-body interactions is subject to the impact of perturbation terms, acting as off-diagonal elements (labelled as $a$). (Bottom) Hamiltonian diagonalization gives eigen-energy levels. Note that the coupling elements are not necessarily the same as shown in this figure. Different coupling elements will produce similar splittings among the levels that are three-fold degenerate in the absence of interactions.
**Fig. S15. Estimation of the lifetime of possible metastable water dimers.** The 2Q diagonal, off-diagonal peaks and 3Q peaks are replotted in a, and their spectral slices along the $f_{\text{pump}}$-axis are shown in b, respectively. Peak positions are listed as: A1 (1.064 THz), A2 (1.077 THz), A3 (1.090 THz), A4 (1.101 THz), A5 (1.113 THz), A6 (1.450 THz), A7 (1.464 THz), A8 (1.476 THz), A9 (1.505 THz), and A10 (1.676 THz). The estimated linewidths for the main peaks (A5, A9, and A10) are 18 GHz, 28 GHz, and 14 GHz, giving dephasing times of 55.6 ps, 35.7 ps, and 71.4 ps, respectively. The 2Q off-diagonal peaks (A1-A4, A6-A8) have an averaged linewidth of ~10 GHz, yielding a dephasing time of ~100 ps. No 3Q off-diagonal features are observed in the present measurements.
**Fig. S16. Field dependence of selected spectral peaks in the simulation.** Peaks (P1-P6) are selected to show their peak intensities and field dependence fittings. In the weak to moderate THz field range, P2-P6 show third-order responses, whereas P1 is fifth-order.
Fig. S17. Possible Feynman diagrams for selected peaks. **a.** V-type energy ladder with defined energy level labels. The transition between rotational states $|1\rangle$ and $|2\rangle$ is forbidden. **b, c,** Four possible Feynman pathways for P3 (as shown in Fig. S16). **c,** Nine possible Feynman pathways for P1 (as shown in Fig. S16).
Fig. S18. Ratio of diagonal and off-diagonal rephasing and non-rephasing peak intensities to diagonal 2Q peak intensities. Black circles and green squares indicate the ratios with respect to the diagonal 2Q peak at (0.558 THz, 1.12 THz) at room temperature (21°C) and at 60°C, respectively. For example, the data of Peak 1 is the ratio of the diagonal NR peak (0.989 THz, 0.989 THz) to the 2Q peak at (0.558 THz, 1.12 THz). All these peak intensities increase at the higher temperature due to the increase in water vapor pressure, but their relative intensities (given by the plotted ratios) do not change significantly, as expected for signals that all depend linearly on the water concentration. The ratios with respect to the other diagonal 2Q peak at (0.753 THz, 1.506 THz) yield the same conclusion. In contrast, Fig. 4d shows that the off-diagonal 2Q peak intensities increase far more than the diagonal 2Q peak intensities (and based on the present figure, far more than the NR and R peak intensities) at the higher temperature, as expected for signals from metastable molecular complexes such as weakly bound molecular pairs whose concentration scales quadratically with the water concentration. The positions of the diagonal and off-diagonal peaks selected for the plot above are as follows: Peak 1 (0.989 THz, 0.989 THz); Peak 2 (1.098 THz, 1.098 THz); Peak 3 (1.165 THz, 1.165 THz); Peak 4 (1.208 THz, 1.208 THz); Peak 5 (1.229 THz, 1.229 THz); Peak 6 (0.753 THz, 1.229 THz); Peak 7 (1.229 THz, 0.753 THz); Peak 8 (0.753 THz, -0.558 THz); Peak 9 (1.229 THz, -0.753 THz); and Peak 10 (0.753 THz, -1.229 THz), where the first (second) coordinate value is the probe (pump) frequency.
| Rotational constants | Values ( GHz) |
|----------------------|--------------|
| $A$                  | 835.83910    |
| $B$                  | 435.347353   |
| $C$                  | 278.139826   |
| $\Delta_j$          | $3.758280 \times 10^{-2}$ |
| $\Delta_{jk}$       | $-1.73361 \times 10^{-1}$ |
| $\Delta_k$          | $9.742470 \times 10^{-1}$ |
| $\delta_j$          | $1.521950 \times 10^{-2}$ |
| $\delta_k$          | $3.96461 \times 10^{-2}$ |
| $H$                  | $1.6284 \times 10^{-5}$ |
| $H$                  | $-5.2534 \times 10^{-5}$ |
| $H$                  | $-5.42802 \times 10^{-4}$ |
| $H$                  | $3.84436 \times 10^{-3}$ |
| $h_j$                | $8.1611 \times 10^{-6}$ |
| $h_{jk}$             | $-2.5607 \times 10^{-5}$ |
| $h_k$                | $9.4784 \times 10^{-4}$ |

**Table S1. Rotational constants of water molecules used in this work.** Rotational constants of water rotational states are listed for the implementation of Watson’s reduced Hamiltonian. Parameter values are taken from references$^{4,5}$. 
| Line number | Para/Ortho type | Observed freq (THz) | Simulated freq (THz) | Obs-Sim (THz) | Transition assignment |
|-------------|----------------|---------------------|---------------------|--------------|----------------------|
| 1           | Ortho          | 0.5574              | 0.5576              | -0.0002      | 101 ↔ 110           |
| 2           | Para           | 0.7525              | 0.7523              | 0.0002       | 202 ↔ 211           |
| 3           | Para           | 0.9883              | 0.9885              | -0.0002      | 111 ↔ 202           |
| 4           | Ortho          | 1.098               | 1.098               | 0            | 303 ↔ 312           |
| 5           | Para           | 1.114               | 1.114               | 0            | 000 ↔ 111           |
| 6           | Ortho          | 1.165               | 1.163               | 0.002        | 312 ↔ 321           |
| 7           | Para           | 1.209               | 1.208               | 0.001        | 413 ↔ 422           |
| 8           | Para           | 1.229               | 1.229               | 0            | 211 ↔ 220           |
| 9           | Ortho          | 1.412               | 1.411               | 0.001        | 514 ↔ 523           |
| 10          | Para           | 1.603               | 1.602               | 0.001        | 404 ↔ 413           |
| 11          | Ortho          | 1.657               | 1.650               | -0.003       | 212 ↔ 221           |
| 12          | Ortho          | 1.679               | 1.670               | 0.009        | 101 ↔ 212           |
| 13          | Ortho          | 1.725               | 1.717               | 0.008        | 212 ↔ 303           |
| 14          | Para           | 1.766               | 1.764               | 0.002        | 624 ↔ 633           |
| 15          | Ortho          | 1.796               | 1.795               | 0.001        | 725 ↔ 734           |
|             | Para           |                     |                     |              | 615 ↔ 624           |
| 16          | Ortho          | 1.870               | 1.867               | 0.003        | 523 ↔ 532           |
| 17          | Para           | 1.920               | 1.920               | 0            | 313 ↔ 322           |

**Table S2. Pure rotational transition lines of water vapor.** Both observed and simulated pure rotational transition lines from the present work are listed. The typical deviation between observation and simulation is approximately 1 GHz.
| Matrix elements | Results (given J, K, M) |
|-----------------|-------------------------|
| \(\langle JKM | J, K \pm 1, M \rangle\) | \(\frac{1}{2} [(J + 1) - K(K \pm 1)]^{1/2}\) |
| \(\langle JKM | J, K \pm 1, M \rangle\) | \(\pm \frac{i}{2} [(J + 1) - K(K \pm 1)]^{1/2}\) |
| \(\langle JKM | J, K \rangle\) | \(K\) |
| \(\langle JKM | J^2 | JKM \rangle\) | \(J(J + 1)\) |
| \(\langle JKM | J_y^2 | JKM \rangle\) | \(\frac{1}{2} [J(J + 1) - K^2]\) |
| \(\langle JKM | J_x^2 | JKM \rangle\) | \(\frac{1}{2} [J(J + 1) - K^2]\) |
| \(\langle JKM | J_z^2 | JKM \rangle\) | \(K^2\) |
| \(\langle JKM | J^2 | J, K \pm 2, M \rangle\) | \(\frac{1}{2} [J(J + 1) - K(K \pm 1)]^{1/2}[J(J + 1) - (K \pm 1)(K \pm 2)]^{1/2}\) |
| \(\langle JKM | J^4 | JKM \rangle\) | \([J(J + 1)]^2\) |
| \(\langle JKM | J_y^2 J_z | JKM \rangle\) | \(J(J + 1)K^2\) |
| \(\langle JKM | J_z^4 | JKM \rangle\) | \(K^4\) |
| \(\langle JKM | J^2 J_y^2 | J, K \pm 2, M \rangle\) | \(J(J + 1) \cdot \frac{1}{2} [(J + 1)(K + 1)]^{1/2}[J(J + 1) - (K \pm 1)(K \pm 2)]^{1/2}\) |
| \(\langle JKM | J_y^2 J_z^2 | J, K \pm 2, M \rangle\) | \(K^2 \cdot \frac{1}{2} [(J + 1) - K(K \pm 1)]^{1/2}[J(J + 1) - (K \pm 1)(K \pm 2)]^{1/2}\) |
| \(\langle JKM | J_z^2 J_x^2 | J, K \pm 2, M \rangle\) | \((K \pm 2)^2 \cdot \frac{1}{2} [(J + 1) - K(K \pm 1)]^{1/2}[J(J + 1) - (K \pm 1)(K \pm 2)]^{1/2}\) |

Table S3. Calculated matrix elements of the rotational Hamiltonian up to the 4th order. Matrix elements of the angular momentum operator up to 4th order employed in this work are evaluated and listed here\(^1\).
### Matrix elements

| Matrix elements | Results (given J, K, M) |
|-----------------|--------------------------|
| \( \langle JKM | \mathbf{A} | JKM \rangle \) | \([J(J+1)]^3\) |
| \( \langle JKM | \mathbf{A}^2 | JKM \rangle \) | \([J(J+1)]^2 K^2\) |
| \( \langle JKM | \mathbf{A}^4 | JKM \rangle \) | \([J(J+1)]K^4\) |
| \( \langle JKM | \mathbf{A}^6 | JKM \rangle \) | \(K^6\) |
| \( \langle JKM | \mathbf{B} J^2 \mathbf{J} J^2 | J, K \pm 2, M \rangle \) | \([J(J+1)]^2 \frac{1}{2} [J(J+1) - K(K \pm 1)]^{1/2} [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2}\) |
| \( \langle JKM | \mathbf{B} J^2 J^2 \mathbf{J} | J, K \pm 2, M \rangle \) | \([J(J+1)]K^2 \cdot \frac{1}{2} [J(J+1) - K(K \pm 1)]^{1/2} [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2}\) |
| \( \langle JKM | \mathbf{B} J^2 J^2 \mathbf{J} J^2 | J, K \pm 2, M \rangle \) | \([J(J+1)](K \pm 2)^2 \cdot \frac{1}{2} [J(J+1) - K(K \pm 1)]^{1/2} [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2}\) |
| \( \langle JKM | \mathbf{B} J^2 J^2 \mathbf{J} | J, K \pm 2, M \rangle \) | \([J(J+1)](K \pm 1)^2 \cdot \frac{1}{2} [J(J+1) - K(K \pm 1)]^{1/2} [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2}\) |
| \( \langle JKM | \mathbf{B} J^2 J^2 \mathbf{J} J^2 | J, K \pm 2, M \rangle \) | \((K \pm 2)^4 \cdot \frac{1}{2} [J(J+1) - K(K \pm 1)]^{1/2} [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2}\) |

**Table S4. Calculated matrix elements of the rotational Hamiltonian of the 6th order.** Matrix elements of the angular momentum operator of 6th order are evaluated and listed\(^1\).
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