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Laser-induced selective alignment of water spin isomers

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We consider laser alignment of ortho and para spin isomers of water molecules by using strong and short off-resonance laser pulses. A single pulse is found to create a distinct transient alignment and antialignment of the isomeric species. We suggest selective alignment of one isomeric species (leaving the other species randomly aligned) by a pair of two laser pulses.

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I. INTRODUCTION

According to quantum mechanics, a molecule that contains two identical atoms whose nuclei have nonzero spins can exist in the form of spin isomers. In particular, a water molecule exists in one of the two spin isomers, ortho or para with parallel or antiparallel proton spins, respectively. The ortho-para conversion is highly improbable in the gas phase [1]. Water isomer separation (or their ratio measurement) can be of great importance in medicine, biology, chemistry, magnetic resonance imaging, etc. Measurement of the para-to-ortho ratio was used to estimate the formation temperature of molecules in space [2]. A method for mixture enrichment in one of the water isomers was reported using selective adsorption onto various surfaces [3], although some of these results were hardly reproducible. Recently, Andreev *et al.* [4] discussed an expected difference in the response of the ortho and para forms of water to a nonuniform dc electric field near solid surfaces, which may lead to isomers separation. We are currently exploring an alternative route to ortho and para separation based on selective field-free alignment and antialignment of water isomers by short nonresonant laser pulses (for a review on field-free alignment, see [5]). By alignment we mean the angular localization of a molecular axis along the laser polarization direction, while antialignment assumes localization of the same molecular axis in the plane perpendicular to the laser polarization. Although previous experimental studies on dissociative fragmentation by relatively long laser pulses have not found alignment of water molecules [6], we show that a sizable alignment can be achieved in an ultrashort regime. The selective alignment was recently experimentally demonstrated in a mixture of ortho and para modifications of linear molecules ($^{15}N_2$ considered as an example) [7]. Here we consider selective alignment for bent triatomic molecules like water. The paper is organized as follows. We briefly discuss the classification of the states of the ortho and para water molecules in Sec. II. The interaction of the water molecules with the laser field is considered in Sec. III. The results are presented in Sec. IV and briefly summarized in Sec. V. In the Appendix, we give a detailed description of the rotational wave functions of the ortho and para water isomers.

II. CLASSIFICATION OF THE EIGENSTATES OF THE WATER MOLECULE

The water molecule wave function is given by

$$|\Psi\rangle = |\Psi_{\mathrm{rot}}\rangle|\Psi_{\mathrm{spin}}\rangle|\Psi_{\mathrm{vib}}\rangle|\Psi_{\mathrm{ele}}\rangle, \tag{1}$$

where $|\Psi_{\mathrm{rot}}\rangle$, $|\Psi_{\mathrm{spin}}\rangle$, $|\Psi_{\mathrm{vib}}\rangle$, and $|\Psi_{\mathrm{ele}}\rangle$ are rotational, nuclear spin, vibrational, and electronic wave functions, respectively. The water molecule eigenstates are classified using the $C_{2v}(M)$ molecular symmetry (MS) group [1], i.e., using the irreducible representations A_1, A_2, B_1, B_2. We provide the group operations as well as its character table in the Appendix. According to the Pauli exclusion principle, the total wave function should change its sign after permutation of the hydrogen nuclei. Since we consider $|\Psi_{\mathrm{vib}}\rangle$ and $|\Psi_{\mathrm{ele}}\rangle$ in the ground state [which is symmetric with respect to the $C_{2v}(M)$ operations], only $|\Psi_{\mathrm{rot}}\rangle$ and $|\Psi_{\mathrm{spin}}\rangle$ are effected by the operations. The rotational part of the water molecule Hamiltonian is presented by the rigid rotor model,

$$\hat{H} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c}, \tag{2}$$

where $\hat{J}$ is the angular momentum operator, (a,b,c) are the molecule's principal axes, and I_a, I_b, I_c are the corresponding moments of inertia ($I_a < I_b < I_c$). Rotational states of A_1 and A_2 symmetries do not change sign as a result of permutation and belong to the para states (with antiparallel spins), while the states of B_1 and B_2 symmetries correspond to the ortho states. Further information about the water molecule eigenstates classification is given in the Appendix.

III. INTERACTION OF THE WATER MOLECULES WITH LASER FIELD

We consider the alignment process based on interaction with short off-resonance laser pulses that induce molecular polarization, interact with it, and excite rotational wave packets. The interaction of the water molecule (shown in Fig. 1) with the laser pulse is given by [8],

$$H_{\mathrm{int}} = -\frac{1}{4}\sum_{\rho,\rho'} \varepsilon_\rho(t)\alpha_{\rho,\rho'}\varepsilon_{\rho'}(t), \tag{3}$$

where the ρ index denotes the space-fixed Cartesian coordinates, ε_ρ is the laser pulse envelope component, and α is the polarizability tensor.

For linearly polarized fields oriented in the laboratory Z direction, the interaction term is reduced to

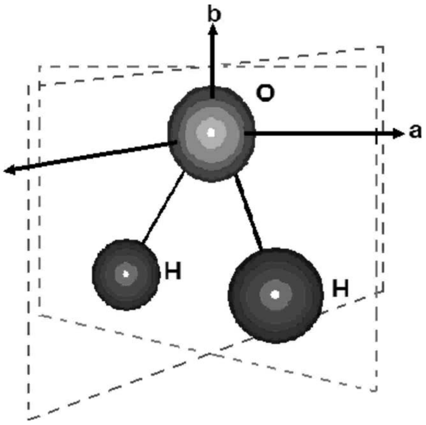

FIG. 1. The water molecule geometry. The axes are the principal axes of the molecule, *a*, *b*, and *c* (*a* and *b* are in the molecular plane, and *c* is perpendicular to it). The principal moments of inertia are $I_a=1.025\times10^{-47}$ kg m^2, $I_b=1.921\times10^{-47}$ kg m^2, and $I_c=2.946\times10^{-47}$ kg m^2 (note that $I_c=I_a+I_b$ according to [9]).

$$H_{\mathrm{ind}} = -\frac{\varepsilon^2(t)}{4}[\alpha^{ab}\cos^2\theta + \alpha^{cb}\sin^2\theta\sin^2\chi]$$
$$= -\frac{\varepsilon^2(t)}{4}\left\{\frac{\alpha^{ab}+\alpha^{ac}}{3}D^2_{00}(\hat{R}) - \frac{\alpha^{cb}}{\sqrt{6}}[D^2_{02}(\hat{R})+D^2_{0-2}(\hat{R})]\right\}. \qquad (4)$$

The Euler angles θ and χ, as well as the principal axes of the molecule (a,b,c), appear in Fig. 2, which presents the coordinates used in this work. In Eq. (4), $\alpha^{ab}=\alpha_{aa}-\alpha_{bb}$, etc., D^J_{mk} are the rotational matrices [10], and $\hat{R}\equiv(\theta,\phi,\chi)$.

In the case of a symmetric top molecule (i.e., when $\alpha_{xx}=\alpha_{yy}=\alpha_\perp$ and $\alpha_{zz}=\alpha_\parallel$), the Hamiltonian is reduced to the well known form $H_{\mathrm{ind}}=-\frac{1}{4}\varepsilon^2(t)\Delta\alpha\cos^2\theta$, where $\Delta\alpha=\alpha_\parallel-\alpha_\perp$. In the case of water, the polarizability tensor components are $\alpha_{aa}=1.528$ Å^3, $\alpha_{bb}=1.468$ Å^3, and $\alpha_{cc}=1.415$ Å^3 [11].

Given an initial rotational eigenstate of the asymmetric water molecule, we are interested in the field-free evolution of the rotational subsystem after an excitation by a laser pulse that is short compared to the typical rotational periods of the water molecule. Using the impulsive approximation, we consider only the contribution from the interaction term to the Schrödinger equation during the pulse,

$$\{\gamma_1 D^2_{00} + \gamma_2[D^2_{02}+D^2_{0-2}]\}\Psi = i\hbar\frac{d\Psi}{dt}, \qquad (5)$$

where γ_1 and γ_2 are found from Eq. (4).

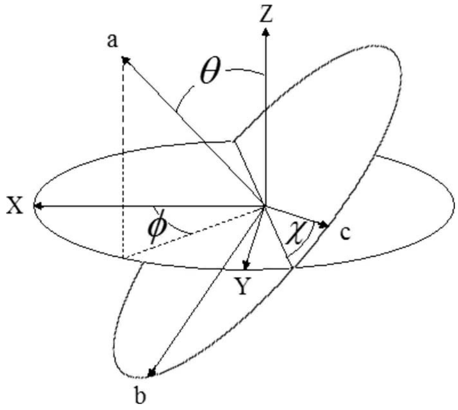

FIG. 2. The coordinate system. (X,Y,Z) are the space fixed laboratory axes, (a,b,c) are the body fixed principal axes, and (θ,ϕ,χ) are the Euler angles which define the body orientation in space with respect to the space fixed coordinates.

Solving Eq. (5), we obtain the relation between the states before and after the pulse,

$$\Psi(t=0^+) = \exp\left\{\frac{1}{i}\{\beta_1 D^2_{00} + \beta_2[D^2_{02}+D^2_{0-2}]\}\right\}\Psi(t=0^-), \qquad (6)$$

where $\beta_{1,2}=(1/\hbar)\int\gamma_{1,2}dt$.

In order to find $\Psi(t=0^+)$, we introduce an artificial parameter ξ that will be assigned the value $\xi=1$ at the end of the calculations,

$$\Psi_\xi = \exp\left\{\frac{1}{i}\{\beta_1 D^2_{00} + \beta_2[D^2_{02}+D^2_{0-2}]\}\xi\right\}\Psi(t=0^-). \qquad (7)$$

We express Ψ_ξ in terms of the water molecule eigenstates,

$$\Psi_\xi = \sum_{J,\tau} c^+_{J,\tau}|J,\tau,m\rangle, \qquad (8)$$

where J is the angular momentum quantum number and m is the quantum number of the angular momentum projected on the laboratory Z axis. For the chosen laser field polarization, m is a conserved quantum number. This allows us to consider the excitation of the states with a different initial m value separately. Index τ (which is assigned the values $-J,\ldots,+J$) numerates various $2J+1$ eigenstates arranged from the lowest energy $(\tau=-J)$ to the highest energy $(\tau=+J)$.

Then we take a derivative of both sides of Eq. (7) with respect to ξ, apply the bra $\langle J',\tau',m|$ from the left, and obtain a set of differential equations,

$$\dot{c}^+_{J'\tau'} = \frac{1}{i}\sum_{J,\tau} c^+_{J,\tau}\{\beta_1\langle J'\tau'm|D^2_{00}|J\tau m\rangle + \beta_2\langle J'\tau'm|D^2_{02}|J\tau m\rangle$$
$$+ \beta_2\langle J'\tau'm|D^2_{0-2}|J\tau m\rangle\}, \qquad (9)$$

where $\dot{c}\equiv dc/d\xi$.

Since $\Psi_{\xi=0}=\Psi(t=0^-)$ and $\Psi_{\xi=1}=\Psi(t=0^+)$ [Eq. (7)], we solve numerically this set of equations from $\xi=0$ to 1, and find $\Psi(t=0^+)$.

The post-pulse field-free propagation of the created rotational wave packet is calculated as

$$\Psi(t) = \sum_{J,\tau} c^+_{J,\tau}\exp\left\{-i\frac{E^{J\tau}}{\hbar}t\right\}|J,\tau,m\rangle, \qquad (10)$$

where $E^{J\tau}$ is the eigenvalue corresponding to the eigenstate $|J,\tau,m\rangle$. We calculate the matrix elements in Eq. (9) by expressing the water molecule eigenstates using the basis of the symmetric rotor: $|J,k,m\rangle$ (J and m are defined as before, and k is the quantum number of the angular momentum projected on the rotor symmetry axis), and using the following relations:

$$\langle Jkm|D^2_{0s}|J'k'm\rangle = (-1)^{k'+m}\sqrt{(2J+1)(2J'+1)}\begin{pmatrix} j & 2 & j' \\ m & 0 & -m \end{pmatrix} \times \begin{pmatrix} j & 2 & j' \\ k & s & -k' \end{pmatrix}. \tag{11}$$

Here $s=0, \pm 2$, and $\left(\begin{smallmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{smallmatrix}\right)$ is the 3-j symbol, related to the Clebsch-Gordan coefficient by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3}(2j_3+1)^{-1/2} \times \langle j_1 m_1 j_2 m_2 | j_3 - m_3\rangle. \tag{12}$$

The nonzero matrix elements from Eq. (11) satisfy the following selection rules: $|J-2| \leqslant J' \leqslant J+2$ and $k'=k, k\pm 2$.

In order to evaluate the values of $\beta_{1,2}$, we consider the following pulse shape: $\varepsilon^2(t)=\varepsilon_0^2 \exp\{\frac{-t^2}{2\sigma^2}\}$. Considering the maximal pulse intensity to be $I=3\times 10^{13}$ W/cm^2 and duration $\sigma=20$ fs, we evaluate ε_0 as $\varepsilon_0=1.5\times 10^{10}$ V/m and obtain $\beta_1=-0.174$ and $\beta_2=-0.065$.

In order to calculate the alignment factor $\langle\cos^2\theta\rangle$ at temperature T, one has to perform thermal averaging,

$$\langle\cos^2\theta\rangle_T(t) = \sum_{J,\tau,m} \frac{\exp\{-E^{J\tau}/k_B T\}}{Q_{\mathrm{rot}}} \langle\cos^2\theta\rangle_{J\tau m}(t). \tag{13}$$

Here Q_{rot} is the rotational partition function, k_B is Boltzmann's constant, $\langle\rangle_T$ denotes the quantum thermal average over the molecular ensemble, and the indexes J, τ, m denote the initial rotational state $|J,\tau,m\rangle$ of a molecule in the ensemble. The quantum average is calculated using

$$\langle\cos^2\theta\rangle_{J\tau m}(t) = \langle\Psi(t)|\cos^2\theta|\Psi(t)\rangle, \tag{14}$$

where $\Psi(t)$ is found by solving Eqs. (8)–(10) with the initial state $\Psi(t=0^-)=|J,\tau,m\rangle$. The right-hand side in Eq. (14) can be easily calculated using the relation

$$\cos^2\theta = \frac{2D^2_{00}(\hat{R})+1}{3}. \tag{15}$$

It is natural to consider the alignment of the para and ortho water molecules separately, since the laser pulse does not mix the para and ortho rotational states, i.e., if one considers an initial para rotational state and applies the pulse, only para rotational states are excited. The same holds for ortho rotational states. This is because the interaction term H_{ind} in Eq. (4) includes

$$D^2_{00}(\hat{R}) \propto \langle\hat{R}|J=2,k=0,m=0\rangle,$$

$$D^2_{02}(\hat{R}) + D^2_{0-2}(\hat{R}) \propto \langle\hat{R}|2,2,0\rangle + \langle\hat{R}|2,-2,0\rangle, \tag{16}$$

which [according to Eq. (A2) in the Appendix] have A_1 symmetry. In order to have a transition from a para to ortho state, the following matrix element should not necessarily vanish: $\langle\mathrm{para}|H_{\mathrm{ind}}|\mathrm{ortho}\rangle$. Since the interaction term has a symmetry $\Gamma_{\mathrm{ind}}=A_1$, the para state has $\Gamma_{\mathrm{para}}=A_1$ or A_2 symmetries, and the ortho has $\Gamma_{\mathrm{ortho}}=B_1$ or B_2; a direct product of the symmetries $\Gamma_{\mathrm{para}}\times\Gamma_{\mathrm{ind}}\times\Gamma_{\mathrm{ortho}}$ never contains A_1 and, therefore, necessarily $\langle\mathrm{para}|V_{\mathrm{ind}}|\mathrm{ortho}\rangle=0$ (forbidden transition). Thus, the transitions between para and ortho states are forbidden and the sum in Eq. (13) includes either initial para states or initial ortho states separately.

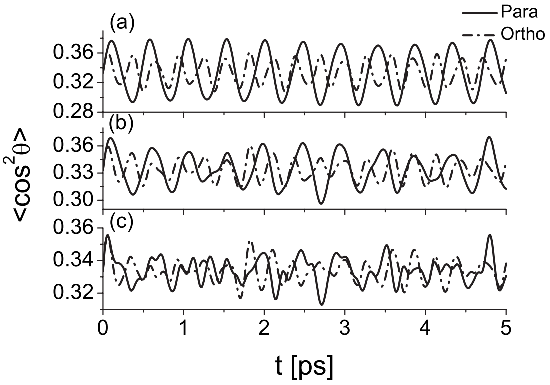

FIG. 3. Alignment factor as a function of time after the laser pulse excitation. Different dynamics of the ortho and para isomers is revealed during the free evolution of rotational wave packets. Graphs (a), (b), and (c) correspond to the temperature of 10, 30, and 70 K, respectively. The alignment and antialignment peaks are noticeably reduced in (c) due to temperature effects.

IV. RESULTS

Applying a linearly polarized 3×10^{13} W/cm^2, 20 fs laser pulse, we expect the molecular highest polarizability axis (i.e., the a axis in Fig. 1) to be aligned along the laser field polarization shortly after the pulse. Since the pulse is short compared to the typical rotational periods of the water molecule, it is considered as a δ pulse. The calculated alignment factor $\langle\cos^2\theta\rangle_T$ [Eq. (13)] is plotted in Fig. 3 as a function of time at temperatures of 10, 30, and 70 K.

We notice that the alignment and antialignment peaks are moderate even at low temperature, which is due to relatively small differences between the polarizability components. As the temperature is increased, the alignment and antialignment peaks are further reduced. It is clearly seen that the ortho and para rotational wave packets evolve differently after the application of the pulse, and transient moments of simultaneous alignment and antialignment for the two species can be found. For instance, at $t=2$ ps, the para molecules are aligned while the ortho molecules become antialigned. Naturally, the rotational energies of both ortho and para molecules are increased as the result of the pulse. Further selective control of the isomers can be achieved by applying an additional pulse (of the same intensity and duration, for simplicity) at $t=1.9$ ps, when the ortho and para molecules are on the way of becoming antialigned and aligned, respectively. At this time, the alignment factors of both isomers are close to each other, and are a bit larger than 1/3. The dynamics of the alignment factor after the second pulse is shown in Fig. 4 (again for temperatures of 10, 30, and 70 K). It depicts selective alignment (and antialignment) of the para molecules, while leaving the ortho modifications

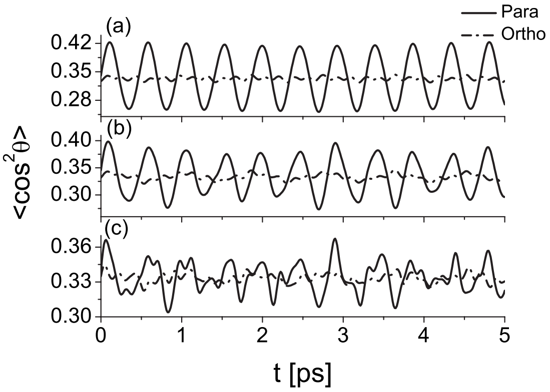

FIG. 4. Alignment factor versus time after the second pulse. (a) Temperature $T=10$ K. While the transient alignment of the para molecules is increased, the ortho alignment is reduced, and the ortho molecules become almost isotropically distributed. (b),(c) Temperature $T=30$ and 70 K, respectively.

more or less isotropically distributed. Moreover, the total rotational energy of the ortho and para molecules is affected in a different way by the second pulse. While the rotational energy of the para molecules is further increased, the energy of the ortho molecules is reduced as the result of the action of the second pulse. Again, we observe that the effect is reduced as the temperature is increased.

V. CONCLUSIONS

We considered interaction of the water molecules with strong and short off-resonant laser pulses and analyzed dynamics of rotational wave packets of ortho and para spin isomers of water. We showed that these two forms of the water molecules experience distinct series of transient alignment and antialignment events, which leads to the angular separation of an initially isotropic mixture of nuclear spin modifications. Moreover, we showed that by applying a second, properly delayed laser pulse it is possible to suppress the rotational energy of one isomeric species, and leave it in a more or less isotropic state. In contrast, the other species will experience an enhanced series of transient alignments and antialignments. Such a selective alignment establishes grounds for the actual separation of ortho and para water isomers via interaction with additional spatially inhomogeneous static or time-dependent fields. This is a subject of our ongoing research.

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APPENDIX-ROTATIONAL WAVE-FUNCTION CLASSIFICATION

TABLE I. The character table of the $C_{2v}(M)$ MS group. E is the identity operator, (12) is the permutation of the hydrogen nuclei operator, E^* is the inversion operator (both for the nuclei and electron coordinates), and $(12)^*$ is the combination $(12)E^*$. The effect of the MS group on the rotational eigenstates is equivalent to the effect of the operations of the molecular rotation group D_2 (i.e., $R^0, R_b^\pi, R_c^\pi, R_a^\pi$) on the rotational eigenstates.

$C_{2v}(M)$ Rotation	E R^0	(12) R_b^π	E^* R_c^π	$(12)^*$ R_a^π
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	−1	1
B_2	1	−1	1	−1

The eigenstates of the water molecule are classified using the $C_{2v}(M)$ molecular symmetry (MS) group [1]. Considering the water molecule eigenstate [Eq. (1)], we define the nuclei rotational and vibrational, as well as electronic degrees of freedom as a rovibronic eigenstate. We denote the rovibronic eigenstate symmetry as Γ_{rve} (within the MS group) and the nuclear spin state symmetry as Γ_{ns} (within the MS group). The water nuclear spin states are divided into either $S=0$ or 1 nuclear spin states, denoted as para or ortho, respectively. The Pauli principle imposes symmetry limitations on the valid basis functions for expressing the internal molecular wave function, Φ_{int} (the entire molecular wave function, without the translational degrees of freedom). A rovibronic state having Γ_{rve} symmetry can only be combined with a nuclear spin state having Γ_{ns} symmetry if the product of the two symmetries is an allowed symmetry for Φ_{int}. In this appendix, we review the symmetries of the rotational eigenstates, and identify each rotational eigenstate as para or ortho.

We start by examination of the symmetry of the internal wave function, Φ_{int}. The character table of the MS group is given in Table I. The group operations are E, (12), E^*, and $(12)^*$, where E is the identity operator, (12) is the permutation of the hydrogen nuclei operator, E^* is the inversion operator (both for the nuclei and electron coordinates), and $(12)^*$ is the combination $(12)E^*$. In Table I, only the symmetries B_2 (positive parity with respect to inversion) and B_1 (negative parity with respect to inversion) change sign under the operation (12) (i.e., the permutation of the two hydrogen nuclei, which are fermions). Therefore, they are the only allowed symmetries of the internal wave function.

Next, we classify the nuclear spin wave function. There are two possible spin functions for $s=1/2$ proton spin: $\alpha=|\frac{1}{2},\frac{1}{2}\rangle$ and $\beta=|\frac{1}{2},-\frac{1}{2}\rangle$, where α and β correspond to spin-up and spin-down states, respectively. There are four possible spin configurations,

$$\alpha\alpha=\Phi_{\mathrm{ns}}^{(1)}, \quad m=1,$$

$$\alpha\beta=\Phi_{\mathrm{ns}}^{(2)}; \quad \beta\alpha=\Phi_{\mathrm{ns}}^{(3)}, \quad m=0,$$

$$\beta\beta=\Phi_{\mathrm{ns}}^{(4)}, \quad m=-1. \tag{A1}$$

One should bear in mind that the spin functions are invariant to E^*, and also for them $(12)^*=(12)$. $\Phi_{\mathrm{ns}}^{(1)}$ and $\Phi_{\mathrm{ns}}^{(4)}$ are invariant to the group operations and have symmetry A_1 (see

TABLE II. The symmetries of the rovibronic eigenstates appear in the left column. The right column displays the possible symmetries of the internal eigenstates. The middle column presents the corresponding nuclear spin symmetries such that $\Gamma_{\mathrm{rve}} \otimes \Gamma_{\mathrm{ns}} \supset \Gamma_{\mathrm{int}}$. Γ_{ns} can be either B_2 or $3A_1$. The dash indicates that no appropriate Γ_{ns} exists for the combination of symmetries in the first and the third columns.

Γ_{rve}	Γ_{ns}	Γ_{int}
A_1	B_2;–	B_2;B_1
A_2	–;B_2	B_2;B_1
B_1	–;$3A_1$	B_2;B_1
B_2	$3A_1$;–	B_2;B_1

Table I). The characters of $\Phi_{\mathrm{ns}}^{(2)}$ and $\Phi_{\mathrm{ns}}^{(3)}$ (which transform together) are 2,0,2,0 [for $E,(12),E^*,(12)^*$, respectively], i.e., $\Phi_{\mathrm{ns}}^{(2)}$ and $\Phi_{\mathrm{ns}}^{(3)}$ generate the representation $A_1 \oplus B_2$. The four nuclear spin wave functions, therefore, generate the representation $\Gamma_{\mathrm{ns}} = 3A_1 \oplus B_2$.

As the next step, we classify each rotational eigenstate. It turns out that the effect of the MS group on the rotational eigenstates is equivalent to the effect of the operations of the molecular rotation group D_2 (i.e., $R^0, R_b^\pi, R_c^\pi, R_a^\pi$) on the rotational eigenstates (see Table I). E or R^0 is the identity operation. (12) (permutation of the two hydrogen nuclei) is a rotation about b by π (see Fig. 1), which we denote as R_b^π. E^* is rotation about c by π, i.e., R_c^π. Finally, $(12)^*$ is a rotation about a by π, i.e., R_a^π. The operations are given by [1]

$$R_a^\beta |J,k,m\rangle = e^{ik\beta}|J,k,m\rangle,$$

$$R_\alpha^\pi |J,k,m\rangle = (-1)^J e^{-2ik\alpha}|J,-k,m\rangle, \qquad \text{(A2)}$$

where $\alpha = 0, \pi/2$ for b and c, respectively. Using Eq. (A2) for each eigenstate, one can find the characters of the group operators operating on the eigenstate, compare them to Table I, and identify the symmetry of the eigenstate. The results are given in Table III (presented here only for $J=0$, 1, 2, and 3).

We assume the vibrational and electronic subsystems to be in the ground state (that has A_1 symmetry). The overall rovibronic symmetry is therefore determined by the rotational symmetry.

One may form a valid basis wave function for expressing Φ_{int} by combining a rovibronic state having a Γ_{rve} symmetry and a nuclear spin state having a Γ_{ns} symmetry, in such a way that the product of these two contains Γ_{int} ($\Gamma_{\mathrm{rve}} \otimes \Gamma_{\mathrm{ns}} \supset \Gamma_{\mathrm{int}}$, where Γ_{int} is an allowed symmetry for Φ_{int}). A detailed list of rovibronic symmetries and their corresponding spin symmetries is given in Table II.

TABLE III. Para and ortho wave functions (here presented only up to $J=3$) identification. The water asymmetric rotor eigenstates are $|J,\tau,m\rangle$, where J is the angular momentum quantum number ($J=0,1,2,\ldots$), and m is the quantum number of the angular momentum projected on the laboratory Z axis (since there exists no preferred direction in space, we choose here $m=0$ without loss of generality). Index τ numerates various $2J+1$ eigenstates arranged from lowest energy ($\tau=-J$) to highest energy ($\tau=+J$). The table displays also the symmetry of the rotational eigenstates.

Para(P) or ortho(O)	Symmetry	J	τ
P	A_1	0	0
O	B_1	1	−1
P	A_2	1	0
O	B_2	1	1
P	A_1	2	−2
O	B_2	2	−1
P	A_2	2	0
O	B_1	2	1
P	A_1	2	2
O	B_1	3	−3
P	A_2	3	−2
O	B_2	3	−1
P	A_1	3	0
O	B_1	3	1
P	A_2	3	2
O	B_2	3	3

From Table II one can relate the A_1 and A_2 rovibrational wave functions with $S=0$ nuclei spin, i.e., para water (the antisymmetric $S=0$ wave function has a B_2 symmetry). Similarly, the B_1 and B_2 rovibrational wave functions are related with the $S=1$ nuclei spin, i.e., ortho water (the symmetric $S=1$ wave functions generate the representation $3A_1$). The statistical weight is therefore clear from the table: there are three times more ortho species than para species (75% of the water is ortho and 25% is para).

Finally, Table III identifies the eigenstates of water molecules as para or ortho for various values of J and τ.

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