VIP Spin Isomers of Water | Very Important Paper

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Separating *Para* and *Ortho* Water**

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Abstract: *Water exists as two nuclear-spin isomers, para and ortho, determined by the overall spin of its two hydrogen nuclei. For isolated water molecules, the conversion between these isomers is forbidden and they act as different molecular species. Yet, these species are not readily separated, and no pure para sample has been produced. Accordingly, little is known about their specific physical and chemical properties, conversion mechanisms, or interactions. The production of isolated samples of both spin isomers is demonstrated in pure beams of para and ortho water in their respective absolute ground state. These single-quantum-state samples are ideal targets for unraveling spin-conversion mechanisms, for precision spectroscopy and fundamental symmetry-breaking studies, and for spin-enhanced applications, for example laboratory astrophysics and astrochemistry or hypersensitized NMR experiments.*

Significant efforts have been undertaken to separate and study the nuclear-spin isomers of water, motivated by their importance in a wide variety of scientific disciplines. This ranges from the astronomical importance of the *para–ortho* ratio,[1–5] to studies of nuclear-spin conversion,[6,7] selection rules and reactive collisions,[8–10] or symmetry breaking.[11] Spin-enriched samples furthermore would allow for hypersensitized NMR experiments by polarization transfer reactions.[12–14] However, unlike other small polyatomic molecules exhibiting spin isomerism, such as fluoromethane or ethylene,[15,16] which were spin-isomerically enriched using the light-induced drift technique,[7] this has not been achieved for water. Separation through selective adsorption on surfaces was reported,[17] but these results remain controversial and could not be reproduced.[18–21] Thus, studies of spin-conversion dynamics in water have been limited to water embedded in rare gas matrices, with relative spin populations modified by the sample temperature.[22] A recent study investigated nuclear-spin conversion in the gas phase and found no spin conversion for water monomers.[23]

Recently, the production of a single spin isomer of water in a magnetic-hexapole-focuser setup was demonstrated.[24] One of the magnetically active spin projections $(m=+1)$ of ground-state *ortho* water was magnetically focused into the interaction volume, while all other spin–projection states were defocused or diverged unaffected by the field. The purity of the produced *ortho* beam was later evaluated as 93%, with simulations suggesting an upper limit for the achievable purity of 97%.[24,25]

Here, we demonstrate experimentally the production of pure samples of both, *para* and *ortho,* water, the latter further separated into its $M=0$ and $M=1$ angular momentum projections, in the gas phase. The produced single quantum states are ideally suited for further experiments on nuclear-spin conversion under collision-free conditions, nuclear-spin-dependent reactivity,[8] trapping of single spin-isomer samples in electromagnetic traps[26] or cold matrices.[25]

Nuclear-spin isomers are different molecular species that arise from the indistinguishability of identical protons, each of which can have its nuclear spin $(i=1/2)$ up $(m_i=+1/2)$ or down $(m_i=-1/2)$. In the case of water the nuclear spins of the two equivalent protons can be combined in four different ways (Figure 1). These combinations are grouped into one antisymmetric and three symmetric nuclear-spin wavefunctions, termed *para* $(I=0)$ and *ortho* $(I=1)$, respectively. The symmetrization postulate (Pauli principle) requires an overall antisymmetric wavefunction with respect to exchange of the two fermionic hydrogen atoms. This constrains the allowed

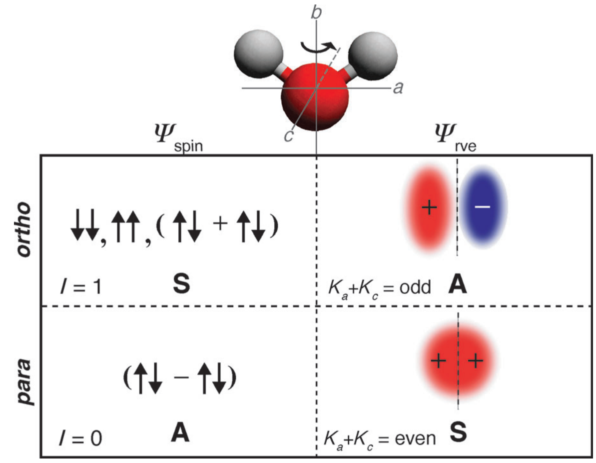

Figure 1. Water spin isomers. The necessity for an overall antisymmetric wavefunction requires that the symmetric (*S*) spin combinations Ψ_{spin} of *ortho* water combine with an antisymmetric (*A*) rovibronic eigenstate Ψ_{rve}, and vice versa for *para* water.

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combinations of rovibronic eigenstates (Ψ_{rve}) with spin configurations (Ψ_{spin}), that is, the product of the two corresponding symmetry species must be antisymmetric regarding this exchange. Under the conditions of a cold molecular beam, all of the molecules reside in the ground electronic and vibrational state, both of which are totally symmetric. Therefore, the restrictions are on the rotational levels corresponding to each spin isomer. Relative abundances are determined by the spin degeneracy for each symmetry.

To spatially separate the spin isomers, we exploit the different rotational states occupied by *para* and *ortho* water and the corresponding differences in their dc Stark effects. The rotational quantum states of the asymmetric rotor, that is, water, can be classified by $J_{K_aK_c}M$, with the total angular momentum quantum number J, the projection labels K_a and K_c onto the molecule-fixed a and c axes as defined in Figure 1, respectively, and the projection quantum number M onto the space-fixed Z axis. In the molecule-fixed coordinate system exchange of the proton spins corresponds to rotation of π about the b axis, which is identical to a rotation of π about a followed by a rotation of π about c. The corresponding symmetry of the rotational wavefunction is the product of the parities, $P=(-1)^{K_a+K_c}$. This leads to *para* water requiring K_a+K_c being even with an absolute ground state of $|0_{00}0\rangle$. For *ortho* K_a+K_c is odd and the ground state is denoted $|1_{01}M\rangle$. The responses of the two absolute ground states to a strong dc electric field are displayed in Figure 2a, showing the non-degeneracy of the *ortho* water M states in the presence of an electric field. The differences in the Stark effect lead to distinct effective dipole moments μ_{eff}, that is, space-fixed dipole moments (Figure 2b).

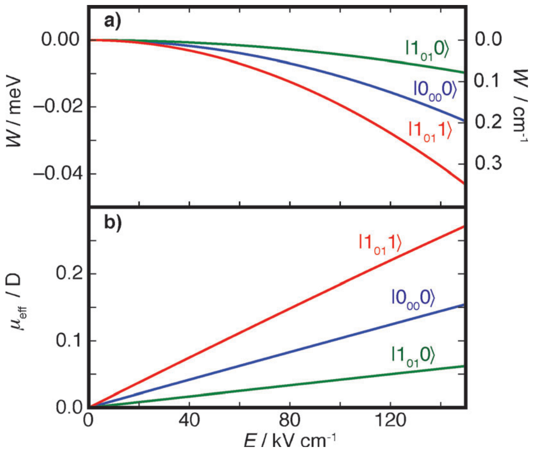

Figure 2. Calculated a) Stark-energy shifts W and b) effective electric dipole moments μ_{eff} for the absolute ground states of *para* and *ortho* water as a function of electric field strength E.

The force experienced by the molecules inside the electric deflection field E is proportional to $\mu_{\text{eff}}\nabla E$.[27] The ground states of both *para* and *ortho* water are strong-field seeking (Figure 2), preventing their separation using electric focusing techniques for weak-field-seeking states.[26] The general applicability of the electrostatic deflection technique to water samples was demonstrated.[28,29] Our combination of the deflection by strong inhomogeneous electric fields with very cold molecular beams allows for the separation of the nuclear-spin states. The quantum-state-resolved detection method allows for their unambiguous assignment. In the current experiment (see the Supporting Information for details), a supersonic molecular beam is used to produce a cold water sample in the gas phase with a rotational temperature of 8 K, corresponding to more than 99% of *para* and more than 96% of *ortho* molecules in their absolute ground state, respectively. The molecular beam is then dispersed perpendicular to its flight direction according to the effective-dipole-moment-to-mass ratio (μ_{eff}/m) using strong inhomogeneous electric fields.[27,30] Water molecules are quantum state selectively ionized by (2+1) resonance-enhanced multiphoton ionization (REMPI); a spectrum is shown in the Supporting Information.

Spatial profiles of the individual quantum states in the molecular beam are shown in Figure 3, with solid lines indicating corresponding trajectory simulations (see Supporting Information for details). In the absence of a deflection field (Figure 3a), the *para* and *ortho* constituents of the beam are mixed and centered around the zero position.

This is confirmed by the REMPI spectrum obtained at this position (Figure 4a). Analysis of the spectrum yields a *para*–

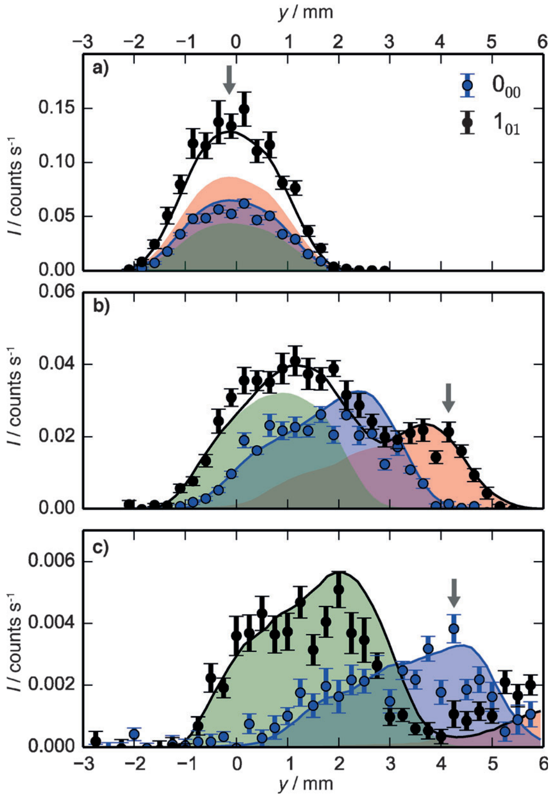

Figure 3. Measured (data points) and simulated (solid lines) spatial profiles for water co-expanded in 40 bar of neon using deflection voltages of a) 0 kV and b) 15 kV. c) Expansion in 15 bar of argon using a deflection voltage of 15 kV. Green and red shading correspond to $M=0$ and $M=1$ levels of the $|1_{01}\rangle$ state, respectively, and blue shading to the $|0_{00}\rangle$. Gray arrows indicate the positions at which the spectra in Figure 4 were collected. Bars correspond to one standard error.

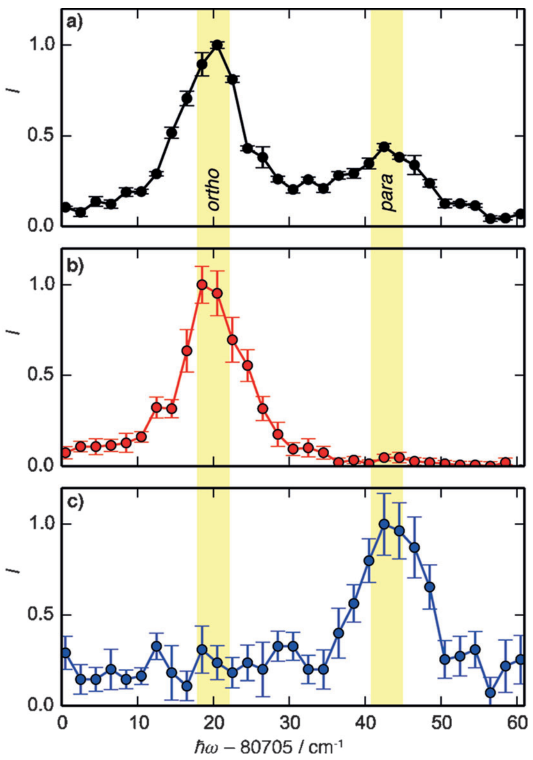

Figure 4. Rotationally resolved 2+1 REMPI spectra showing characteristic transitions for *para* and *ortho* water. a) Undeflected beam with thermal population of both spin states. b) Pure *ortho* ($|1_{01}1\rangle$) sample created in the neon expansion at 15 kV deflection voltage. c) Pure *para* ($|0_{01}0\rangle$) sample created in the argon expansion at 15 kV deflection voltage. Bars correspond to one standard error.

ortho ratio of approximately 1:3, consistent with a conservation of the nuclear-spin temperature through the supersonic expansion. Application of an electric field deflects the beam in the upward direction. The spatial shift depends on the effective dipole moment, and a clear separation of *para* and *ortho* water is observed. At large deflection fields, the spatial profile of *ortho* water bifurcates, corresponding to the splitting of the $M=0$ and $M=1$ components. This is indicated by the green and red shading in Figure 3b and c. Consistent with the calculated Stark curves and effective dipole moments (Figure 2a and b), the $|1_{01}1\rangle$ state experiences the largest deflection and the $|1_{01}0\rangle$ state the least deflection, with the $|0_{00}0\rangle$ *para* state in between. For water co-expanded in neon, application of 15 kV to the deflector creates a region of space, $y>4$ mm, where only the $|1_{01}1\rangle$ state is present and a pure *ortho* sample is obtained. This is confirmed by the REMPI spectrum shown in Figure 4b. The measured purity of the *ortho* beam at this position is 97%, which is primarily limited by background water in the vacuum chamber. Simulations suggest an achievable purity in excess of 99% with the present setup (see the Supporting Information for details).

Further increasing the deflection through the use of a slower molecular beam, seeded in argon, leads to a nearly complete depletion of the $|1_{01}1\rangle$ *ortho* state and the creation of an enriched *para* $|0_{00}0\rangle$ sample (Figure 3c) and confirmed by the REMPI spectrum (Figure 4c). A purity of 74% for *para* water is measured, which simulations indicate would be increased to more than 87% if background water was more efficiently suppressed. Using a setup with two subsequent deflection stages, a purity of more than 96% could be obtained. Furthermore, the slower beam allows the creation of a pure *ortho* sample in the $M=0$ angular momentum projection at a position $-1<y<0$ mm. This position is depleted of all other quantum states in the original beam, and we obtain a more than 99% pure $|1_{01}0\rangle$ sample.

The produced pure molecular beams have densities on the order of 10^8 cm^{-3} and 10^7 cm^{-3} for neon and argon expansions, respectively. The latter is limited by the longer gas-pulse duration and possibly by the inverse seeding effect resulting from argon being heavier than water. Combined with the strong deflection experienced in the slower beam, this leads to molecules colliding with the skimmers or electrodes and not reaching the interaction region anymore. These densities are sufficient for precision spectroscopy or laboratory scattering experiments.[6,7]

The current experiment, at 20 Hz, allows the production of about 10^{13} nuclear-spin-selected molecules, or 1 picoliter, per day. Significantly larger quantities could be produced using higher repetition rates[31] or continuous molecular beams. The current quantities could be sufficient for the production of nuclear-spin-pure surface layers, for instance highly polarizable layers of *ortho* water, if very low spin-relaxation rates can be maintained. The production of pure *para* water might open up possibilities for hypersensitized NMR experiments through polarization transfer by water addition, comparable to *para*-hydrogen induced polarization transfer (PHIP),[12,13] but with wider chemical applicability.

The presented technique for quantum-state separation is generally applicable to polar neutral molecules and allows for the production of single-quantum-state samples, that is, for the separation of nuclear-spin isomers.

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