

Quantum State-Resolved Characterisation of a Magnetically-Focused Beam of Ortho-H₂O

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Abstract

Magnetic focusing of a molecular beam formed from a rotationally-cooled supersonic jet of H₂O seeded in argon is shown to yield water vapour highly enriched in the ortho-H₂O nuclear spin isomer (NSI). Rotationally-resolved resonance-enhanced multi-photon ionisation time-of-flight mass spectrometry demonstrates this methodology enables the preparation of a beam of water molecules enriched to >98 % in the ortho-H₂O NSI, that is having an ortho-to-para ratio (OPR) in excess of 50:1. The flux and quantum-state purity achieved through the methodology described herein could enable heterogeneous chemistry applications including the preparation of a nuclear spin-polarized water adlayers, making nuclear magnetic resonance investigations amenable to surface science studies, as well as laboratory investigations of NSI interconversion mechanisms and rates in ice and at its surface.

Introduction

To this day, spatial quantization, a concept that was coined by Estermann, Gerlach, and Stern¹⁻³ at the dawn of the quantum theory, remains one of the most promising enrichment strategies for the separation of nuclear spin isomers (NSI). Indeed, while chromatographic⁴ and catalytic⁵⁻⁷ conversion methods⁸ are firmly established as the gold standard for the preparation of samples enriched in either ortho-H₂ (i.e., $I = 1$) or para-H₂ (i.e., $I = 0$), they cannot be used in the case of heavier polyatomic molecules (e.g., H₂O) due to the rapid interconversion kinetics at elevated temperatures in the condensed/adsorbed phases.⁹ Laser-based methods¹⁰⁻¹³ have also been shown to be effective strategies for the separation of NSI unfortunately, they yield only modest enrichments and fluxes that preclude most condensed phase applications, such as investigations of heterogeneous chemistry, nuclear magnetic resonance spectroscopy/imaging of water adlayers, and investigations of NSI interconversion mechanisms and rates in ice and at its surfaces, to name but a few. While the last few decades have seen traditional molecular beam techniques evolve into sophisticated

cold molecules manipulations^{14–16} and quantum-state separation methodologies,¹⁷ those that enable intense fluxes and large NSI enrichments (or better, their separation) are proving particularly attractive for these applications. For example, electric deflection^{18–20}/focusing²¹ of a molecular beam afforded significant enrichment to be achieved by enabling the sorting of molecules, from a statistical mixture of NSI rotationally-cooled in a supersonic free jet expansion, according to the strong/weak field seeking character of individual quantum-states resulting from the interaction of the external field with their rotationally-averaged effective electric dipole moments. In the case of H₂O,^{18,19} standard quantum-state resolved characterization of the electrically-deflected “beams” using rotationally-resolved resonance-enhanced multi-photon ionisation time-of-flight mass spectrometry (REMPI-TOF-MS) showed that a purity of up to 74% could be achieved for para-H₂O (in its $J_{\tau M_J} = 0_{00}$ ground state) and between 97% and 100% for ortho-H₂O. One note that electric deflection enables the nine-fold degenerate rotational ground state to be spatially sorted into contributions from the three-fold degenerate $J_{\tau M_J} = 1_{-10}$ state, and the six-fold degenerate $J_{\tau M_J} = 1_{-11}/1_{-1-1}$ states but that the rotational Stark shifts cannot discriminate between the $M_J = \pm 1$ space-fixed projections of J. Nonetheless, using electric deflection as a separation method for the NSI of water enabled the different gas phase bimolecular reaction rates displayed by ortho-H₂O and para-H₂O towards N₂H⁺ ions to be quantified.¹⁹

Magnetic deflection²²/focusing²³ affords a different and complementary preparation strategy enabling the separation of NSI according to their total magnetic moment which, for a rotationally-cooled beam of water molecules, sorts ortho-H₂O and para-H₂O principally according to the projection of their total nuclear magnetic moment, M_I . In contrast with the electric deflection work (which resorted to a pulsed molecular beam),^{18,19} we elected to utilize a continuous molecular beam yielding average fluxes that are a few orders of magnitude higher in intensity. This, combined with spin-based selection afforded by magnetic focusing, makes this methodology particularly well-suited for condensed phase applications where spin-polarised samples of water (or other molecules) are desired, for example, to cre-

ate molecularly-thin magnetically ordered layers. Up to now, separation of the NSI of water by magnetic focusing in a molecular beam was detected indirectly for example, by spatial profiling of the beam using a moving aperture and a mass spectrometer.^{23,24} Alternatively, trapping water molecules from the magnetically-focused beam by embedding them in a growing krypton matrix at cryogenic temperature, where their rotational motion is essentially unhindered, enabled the evolution of their nuclear spin state distributions to be probed using rovibrational spectroscopy.²⁵ While both of these detection techniques suggested a sizable enrichment in ortho-H₂O could be achieved using magnetic focusing, their indirect nature lead to inherent uncertainties when quantifying the nuclear spin isomer composition of the beam. In particular, extracting the isomer composition from beam profiles is plagued with uncertainties due to the beam properties (i.e., velocity and angular distributions, velocity slip) as well as the magnitude of the contribution from the rotational magnetic moment of the water molecules to magnetic focusing, an effect which can however safely be neglected for rotationally cold beams.^{23,24} Depositing molecules from the magnetically-focused beam, and trapping them in a growing rare gas matrix, also has significant drawbacks as nuclear spin isomer interconversion results in an erosion of the enrichment in ortho-H₂O which required extrapolation of the interconversion kinetics backwards to evaluate the initial NSI populations in the beam.²⁵ Furthermore, this procedure cannot take into account any impulsive NSI conversion dynamics that may occur as a result of the collision of water molecules with the matrix upon deposition from the beam, neither can it reveal the occurrence of faster relaxation mechanisms which take place before a significant IR signal can be acquired.²⁵

In this paper, we report the direct determination of the nuclear spin isomer distribution, and the rotational temperature, of water molecules in a magnetically-focused molecular beam also using REMPI-TOF-MS characterisation and compare the merits of this enrichment strategy with those reported for the electric deflection method.^{18,19} Quantum state-resolved imaging of the molecular beam cross sectional spatial profiles reveals that magnetic focusing produces a high flux beam enriched in the ortho-H₂O NSI to a purity comparable to that

achieved by electric deflection.^{18,19} These properties are essential for applications where rapid deposition of spin-polarised molecularly thin layers of water at low temperatures is required, either because NSI interconversion kinetics in the condensed/adsorbed phase may lead to an erosion of the enrichment in NSI, or because spin-lattice relaxation kinetics may result in a decay in sample magnetization.

Experimental methods

The schematics of the apparatus used to prepare water vapour significantly enriched in the ortho-H₂O nuclear spin isomer is presented in Figure 1 (See Supplementary Information for a detailed description of the experimental protocols). Briefly, water molecules are inverse seeded in a continuous supersonic free jet expansion using argon as carrier gas and the resulting rotationally-cooled H₂O beam is skimmed and shone through a hexapolar magnetic lens. As can be gleaned from the simulations in Figure 2, the trajectories of water molecules: a) are unaffected when $M_I = 0$ (i.e., for para-H₂O, as well as ortho-H₂O); b) are defocused when $M_I = +1$ (i.e., for ortho-H₂O); but c) are focused when $M_I = -1$ (i.e., for ortho-H₂O) as these latter experience a restoring force that bends their trajectories back onto the beam axis as a result of their interaction with the strong inhomogeneous hexapolar field afforded by the magnetic lens.^{23,24} Simulations suggest the flux of these latter reaches a maximum at a location ~ 1.5 m downstream from the exit of the magnetic lens (i.e., TOF position 2, Figure 2c).

Results and discussion

Expanded views of the REMPI-TOF-MS spectra of H₂O are presented in Figure 3. The experimental spectrum (black trace), obtained by introducing $1 \cdot 10^{-7}$ Torr of water vapour in the analysis chamber is shown, in Figure 3a, to be in excellent agreement with the simulated spectrum (green trace, calculated using oscillator strengths and band widths reported by

Yang et al.;²⁶ see SI for details) obtained using a rotational temperature, $T_{\text{rot}} = 300$ K, and an ortho-to-para ratio, $\text{OPR} = 3$. The simulated spectrum is decomposed into the individual contributions from the ortho-H₂O (blue shading) and para-H₂O (red shading) nuclear spin isomers thereby revealing the great number of rotational states that are populated at 300 K.

In Figure 3b, simulations (green trace) of the REMPI-TOF-MS spectrum acquired in the molecular beam in absence of magnetic focusing (black trace) demonstrate that efficient rotational cooling is afforded as a result of the supersonic free jet expansion. Fitting the spectrum using $T_{\text{rot}} = 22.0 \pm 0.5$ K yielded an $\text{OPR} = 3.4 \pm 0.3$ that is, no smaller than 3 according to our experimental uncertainty (corresponding to a relative abundance of 75% ortho-H₂O). As the equilibrium OPR is 1.92 at $T = 22$ K, this indicates that nuclear spin interconversion is much less efficient than rotational cooling under our experimental conditions resulting in the nuclear spin isomers populations remaining frozen in their high temperature distribution during the free jet expansion (i.e., retaining an $\text{OPR} = 3$), in agreement with previous observations.^{26–28} Contributions from ortho-H₂O (blue shading) and para-H₂O (red shading) to the simulated spectrum indicate that the majority (i.e., >75%) of water molecules occupy their respective fundamental rotational states at $T_{\text{rot}} = 22$ K (i.e., $J_{K_a K_c} = 1_{01}$ for ortho-H₂O and 0_{00} for para-H₂O). A small but significant contribution due to (rotationally hot) water vapour from the residual background gas ($P_{\text{H}_2\text{O}} \sim 1 \cdot 10^{-10}$ Torr) is also clearly present in the REMPI-TOF-MS spectrum acquired in the molecular beam (Figure 3b; dashed line).

The REMPI-TOF-MS spectrum obtained in the magnetically-focused beam (Figure 3c, obtained in absence of the beam block) indicates that a significant enrichment is already achieved as simulations using $T_{\text{rot}} = 22$ K (i.e., justified by using identical source conditions as in Figure 3b) reveal an $\text{OPR} = 12 \pm 3$, corresponding to a relative abundance of > 90% ortho-H₂O (dashed line: contribution of water from residual background gas). Rotational cooling, arising from the free jet expansion, and magnetic focusing, promoted by the decreased average velocity of H₂O molecules afforded by inverse seeding, are enhanced

as a function of increasing Ar carrier gas backing pressure (See SI for details, Figure S1 and Table S1) accounting for this significant enrichment. The number density of ortho-H₂O in the molecular beam at the focus of the magnetic lens in absence of the beam block was evaluated to be $(5 \pm 1) \cdot 10^7$ ortho-H₂O molecules·cm⁻³ (see SI for details). This figure is slightly greater than the peak density, but more than two orders of magnitude greater than the average density reported previously^{18,19} using electric deflection of water in a pulsed molecular beam, a definite advantage for condensed phase applications. Furthermore, we stress that while the ortho-H₂O beam (peak) densities and state purities afforded by the electric deflection and magnetic focusing methods are comparable, the two methods provide complementary quantum-state selection strategies that should find useful in a broad and diverse array of applications.

Figure 3d demonstrates that further enrichment in ortho-H₂O can be achieved by introducing the beam block in the molecular beam path, at the expense of a 16-25% reduction in flux, as the intensity of the $J_{K_a K_c} = 2_{21} \leftarrow 0_{00}$ transition attributed to para-H₂O now lies well beneath the detection limit afforded by REMPI-TOF-MS while the strong features attributed to ortho-H₂O (i.e., $J_{K_a K_c} = 3_{22} \leftarrow 1_{01}$ and $2_{20} \leftarrow 1_{01}$ transitions; blue shading) are still observed (dashed line: contribution of water from residual background gas). Using $T_{\text{rot}} = 22$ K (i.e., justified by using identical source conditions as in Figure 3b and 3c), simulations reveal an OPR > 50 indicating that the magnetically-focused molecular beam is composed of $>98\%$ ortho-H₂O.

The tightly focused UV laser used for rotationally-resolved REMPI-TOF-MS enables quantum state-resolved spatial profiling of the distribution of ortho-H₂O and para-H₂O throughout the magnetically-focused molecular beam cross section. As displayed in Figure 4a, the beam block casts a shadow that creates a depletion zone at the center of the beam that is visible in both the ortho-H₂O (blue squares: experiment; blue shading: simulations; both of which display contributions from all three nuclear spin states, $M_I = -1, 0,$ and $+1$) and para-H₂O (red circles: experiment; red shading: simulations) spatial beam profiles

at position 1 (Figure 2). The inset to Figure 4a displays the contributions, obtained from the trajectory simulations (Figure 2), from molecules that display both $M_I = 0$ (red dots, arising from either para- H_2O , or ortho- H_2O) as well as $M_I = -1$ (blue dots, arising solely from ortho- H_2O) to the cross sectional distribution in the magnetically-focused molecular beam. Figure 4b shows that, at position 2 (Figure 2), magnetic focusing causes the depleted zone at the center of the beam to be replenished in the ortho- H_2O nuclear spin isomer (blue squares; note that only the $M_I = -1$ state is focused) while the spatial profiles for para- H_2O (red circles) has broadened significantly due to the divergence of the molecular beam (attributed both to the geometrical and transverse velocity effects). The inset to Figure 4b illustrates the effect of the divergence of molecules that are unfocused (red dots; $M_I = 0$) and those that are focused (blue dots; $M_I = -1$) by the magnetic lens as obtained from the trajectory simulations (Figure 2). The increasing breadth of the depletion zone, arising from the shadow cast by the beam block, combined with magnetic focusing of the water molecules having $M_I = -1$, creates a 1 mm diameter wide zone that is highly enriched in ortho- H_2O near the center of the molecular beam with added benefit that the seed gas was removed from the focal region by the beam block.

The intense flux and high spin state purity revealed by this quantum state-resolved characterisation of a magnetically-focused “beam” of ortho- H_2O open up exciting new perspectives for heterogeneous chemistry studies for example, by enabling detailed investigations into the NSI interconversion mechanism and rates of H_2O at surfaces. Previous studies relied on alternative enrichment methods, such as electric focusing, to investigate NH_3 scattering from NH_3 -saturated W(100)²⁹ at 300-650K, or stimulated Raman pumping, to study scattering of vibrationally-excited H_2 from Cu(100) at 400-800K.³⁰ While similar investigations have yet to be reported for water, these reports suggest that heterogeneous NSI interconversion could be ineffective when the surface residence time of the adsorbate (ranging from sub-picosecond for direct scattering, to a few picoseconds for bound-state resonance scattering and up to tens of microseconds for trapping-desorption) is too short for NSI interconversion

to occur. In contrast, observation of extensive interconversion and complete equilibration of the NSI distribution of H₂O were reported for water molecules that have undergone thermal- and photon-induced desorption^{9,31} from ice. This suggests that reduced temperatures, yielding extended surface residence times, as well as intermolecular interactions, can indeed promote NSI interconversion kinetics in the condensed/adsorbed phase. Systematic studies of the competition between desorption and NSI interconversion rates as a function of (metallic, oxide, ice) surface temperature could help fill gaps in our current understanding of these important but complex coupled interfacial kinetics. The high molecular beam densities afforded by the methodology described herein will likely facilitate state-to-state dynamics studies of NSI interconversion (of water, but also other small molecules) at surfaces and thus, provide molecular-level insight into the underlying mechanisms.

Magnetic focusing^{23–25} relies on a different physical principle for the separation of NSI than electric deflection^{18–20} and thus, it provides a complementary enrichment strategy that is uniquely suited for many applications. For example, magnetic focusing would be the preferred technique for optimizing the transfer of spin polarisation from the gas phase to surfaces or to the condensed phase (e.g., inert matrices, ice), en route towards the development of hyperpolarised nuclear magnetic resonance methodologies.²⁴ Indeed, while preliminary observations demonstrated that the large enrichment in the ortho-H₂O NSI, provided by magnetically-focusing a molecular beam of water, can be transferred to inert matrices (i.e., Ar, Kr), it was observed to unfortunately decay on the timescale of minutes to hours (depending on water content, matrix composition and temperature),²⁵ a significant shortcoming that is attributable to NSI interconversion.^{32–34} However, the conversion of ortho-H₂O to para-H₂O is not the relevant criteria for assessing potential hyperpolarised NMR applications; the questions are rather how and where do the spins transfer to the solid/adsorbed phase as well as the magnitude of the T_1 time required for thermodynamic spin equilibrium to be reached.²⁴ Accordingly, ongoing work relying on the methodology described herein is aimed at improving our molecular-level understanding of the processes responsible for the decay in

sample magnetisation and erosion of the NSI enrichment in the adsorbed/condensed phase, as well as the underlying relaxation mechanisms and rates.

Conclusions

A continuous magnetically-focused molecular beam was demonstrated to provide a source of water vapor enriched to up to >92% in the ortho-H₂O NSI with a number density as high as $(5 \pm 1) \cdot 10^7$ molecules·cm⁻³ as measured using REMPI-TOF-MS, allowing the molecular beam flux and flow to be estimated as $J_{\text{H}_2\text{O}} = 3.3 \cdot 10^{12}$ molecules·cm⁻²·s⁻¹ and $(1.0 \pm 0.2) \cdot 10^{11}$ molecules·s⁻¹, respectively. The enrichment can be further increased to >98% when resorting to a beam block, resulting in a decrease in the flux of 16-25%, but allowing to remove contamination from the seed gas. These figures are particularly attractive for condensed phase applications. Indeed, intense fluxes and highly enriched vapors could enable rapid deposition of spin-polarised adlayers before their magnetisation decays due to spin-lattice relaxation processes. The methodology described herein may thus help overcoming this important technological bottleneck to NMR spectroscopic/imaging investigations into interfacial chemical structure and dynamics.²⁴ Elevated fluxes and efficient separation of NSI should also facilitate investigations into the dynamics and rates for heterogeneous NSI interconversion, a process which lead to an erosion of the NSI enrichment when molecules interact with surfaces or condense onto a solid. Thus, the highly enriched intense molecular beam source described herein could help improve our molecular-level understanding of the underlying mechanism, potentially shedding light onto the interpretation of the nuclear spin temperature of interstellar icy bodies.⁹

Supporting Information Available

This supplementary information comprises :

1. Details on the experimental method;
2. Calculation details for the trajectory simulations;
3. Evolution of the rotational temperature and nuclear spin isomer distribution in the magnetically-focused molecular beam of water as a function of the stagnation pressure in the nozzle;
4. Determination of the ionisation zone longitudinal intensity profile;
5. Determination of the number density of water molecules in the molecular beam.

The following files are available free of charge.

- pdf file : Magnetically-focused beam of ortho-water SI.pdf

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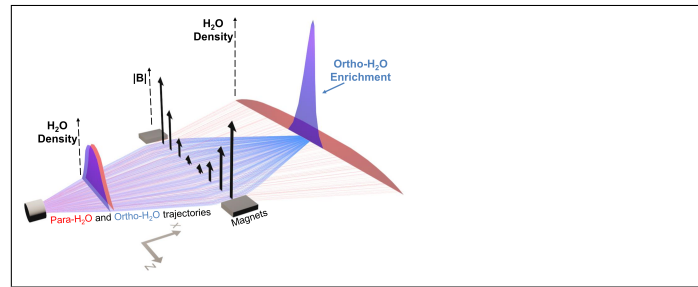
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Graphical TOC Entry



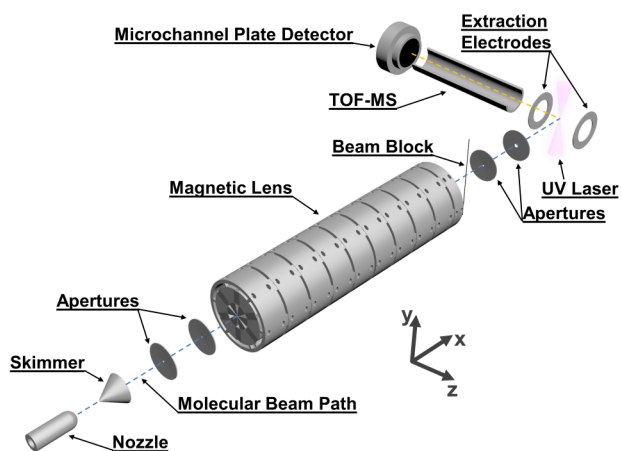


Figure 1: Schematics of the apparatus used for separating the nuclear spin isomers of water, ortho- H_2O and para- H_2O , by magnetic focusing of a continuous molecular beam (see Figure 2). The spectroscopic determination of the rotational temperature and nuclear spin state population distribution of water molecules directly in the magnetically-focused beam (see Figure 3) is reported here using rotationally-resolved resonance-enhanced multi-photon ionisation time-of-flight mass spectrometry (REMPI-TOF-MS) while the cross sectional distribution of ortho- H_2O and para- H_2O is scrutinized using quantum state-resolved spatial profiling (see Figure 4).

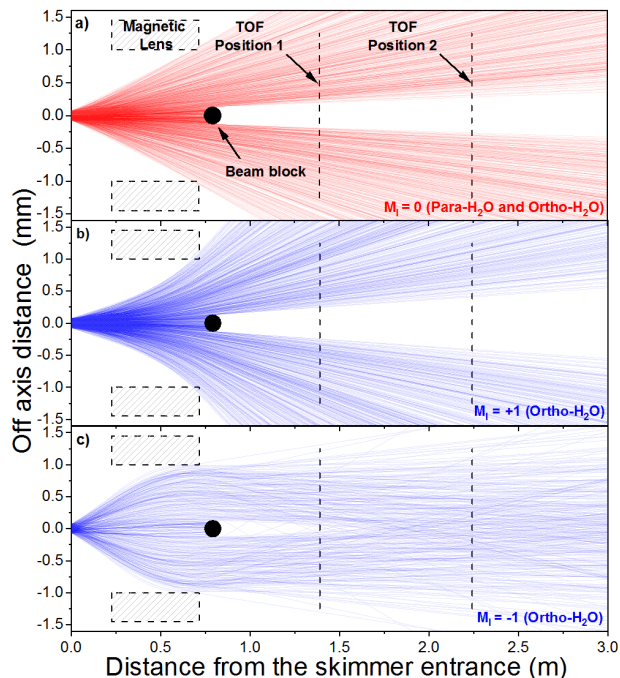


Figure 2: Semi-classical trajectory simulations for the three possible total nuclear spin projections of H_2O , a) for $M_I = 0$, b) for $M_I = +1$, c) for $M_I = -1$, were performed by numerical integration of Newton's equations of motion in the x - z plane using realistic source conditions.²³ Water molecules from a 3:1 statistical mixture of nuclear spin isomers are shown to be sorted spatially according to their total nuclear magnetic moment demonstrating that a significant enrichment in ortho- H_2O is afforded by magnetic focusing. Resorting to a beam block results in further enrichment in ortho- H_2O as on-axis trajectories of para- H_2O nuclear spin isomers are excluded from the focal area of the magnetic lens. TOF positions 1 and 2 (located at 0.65 m and 1.50 m from the exit of the magnetic lens, respectively) indicate the locations at which spatial profiling, using quantum state-resolved REMPI-TOF-MS of the magnetically-focused molecular beam, was performed experimentally (see Figure 4).

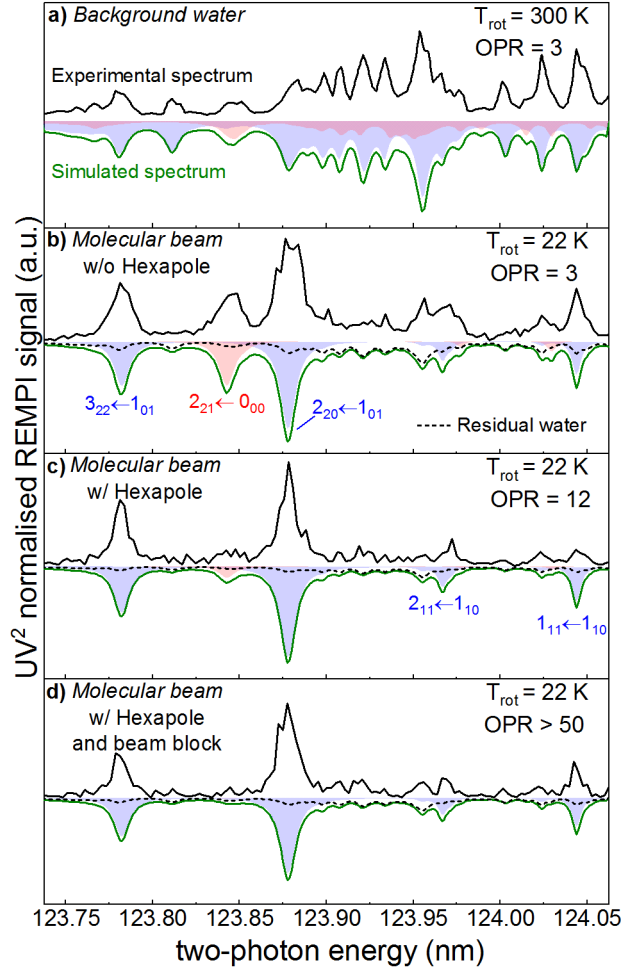


Figure 3: Experimental (black curves) and simulated (green curves; blue and red shadings, highlighting the contributions from ortho-H₂O and para-H₂O, respectively) REMPI-TOF-MS spectra of the rovibronic transitions, labeled using the conventional approximate quantum numbers $J_{K_a K_c}$, near the $\tilde{C}^1B_1 \leftarrow \tilde{X}^1A_1$ band origin in H₂O for: (a) water vapour introduced by backfilling the analysis chamber at $P=1 \cdot 10^{-7}$ Torr. Simulations use $T_{\text{rot}} = 300$ K and $\text{OPR} = 3$; (b) water vapour in the supersonic molecular beam without magnetic focusing. Simulations using $T_{\text{rot}} = 22.0 \pm 0.5$ K reveal $\text{OPR} = 3.4 \pm 0.3$ that is, no smaller than 3 according to our experimental uncertainty; (c) water vapour in the magnetically-focused molecular beam. Simulations using $T_{\text{rot}} = 22$ K reveal an $\text{OPR} = 12 \pm 3$; and (d) water vapour in the magnetically-focused molecular beam in the presence of the beam block. Simulations using $T_{\text{rot}} = 22$ K suggest an $\text{OPR} > 50$. All spectra were acquired near the focus of the magnetic lens namely, at TOF position 2 (see Figure 2).

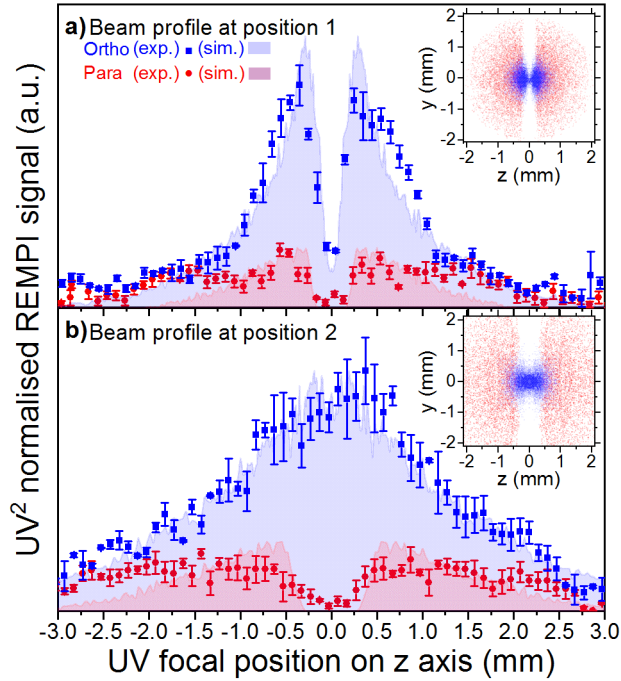


Figure 4: Measured (blue squares: ortho-H₂O probed using the $J_{K_a K_c} = 2_{20} \leftarrow 1_{01}$ transition; red circles: para-H₂O probed using the $J_{K_a K_c} = 2_{21} \leftarrow 0_{00}$ transition) and simulated (ortho-H₂O: blue shading; para-H₂O: red shading) spatial beam profiles of the magnetically-focused molecular beam cross-sectional distribution performed at two different positions namely: (a) at TOF position 1 and (b) at TOF position 2 located at 0.65 m and 1.50 m downstream from the hexapolar magnetic lens, respectively (see Figure 2). Insets displays the spatial distribution obtained from the trajectory simulations of molecules with $M_I = -1$ (i.e., ortho-H₂O; blue dots) and of molecules with $M_I = 0$ (i.e., both ortho-H₂O and para-H₂O; red dots) at TOF positions 1 and 2. Note that the spatial distribution of molecules with $M_I = +1$, that contribute to both the experimental and simulated spatial beam profiles for ortho-H₂O, have been omitted from the inset for clarity.