State-resolved spectroscopy of high vibrational levels of water up to the dissociative continuum

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We summarize here our experimental studies of the high rovibrational energy levels of water. The use of double-resonance vibrational overtone excitation followed by energy-selective photofragmentation and laser-induced fluorescence detection of OH fragments allowed us to measure previously inaccessible rovibrational energies above the seventh OH-stretch overtone. Extension of the experimental approach to triple-resonance excitation provides access to rovibrational levels via transitions with significant transition dipole moments (mainly OH-stretch overtones) up to the dissociation threshold of the O–H bond. A collisionally assisted excitation scheme enables us to probe vibrations that are not readily accessible via pure laser excitation. Observation of the continuous absorption onset yields a precise value for the O–H bond dissociation threshold, 41145.94 ± 0.15 cm⁻¹. Finally, we detect long-lived resonances as sharp peaks in spectra above the dissociation threshold.

Keywords: double-resonance spectroscopy; triple-resonance spectroscopy; photofragmentation; dissociation threshold

1. Introduction

This paper summarizes our measurements of the vibrational states of water above approximately 26 000 cm⁻¹ that began in 2005 [4–5]. The initial motivation was to study the absorption of solar radiation by water vapour. Transitions to levels with energies up to approximately 25 500 cm⁻¹ had previously been measured using Fourier transform spectroscopy [6–9]. Emission spectra from sunspots [10] and laboratory confined hot water vapour [11] yielded levels with high rotational quantum numbers. The use of sensitive cavity ringdown spectroscopy [12–14] increased this limit to approximately 26 300 cm⁻¹. However, more than 7 per cent of solar radiation intensity still resides in the remaining near-ultraviolet (UV) region above this value [15].

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While the spectra measured with double- and triple-resonance vibrational overtone excitation followed by photofragment detection yield precise energy levels of water, they do not reflect adequately the cross sections of solar radiation absorption by water vapour in the ground vibrational state. Collaboration with the theory groups of Tennyson, Polyansky and Császár has been essential to bypass this problem. Polyansky and co-workers [16,17] empirically adjusted their high-level \textit{ab initio} potential energy surface (PES) of water to fit the highly excited rovibrational levels that we measured [1]. Later, a new PES that included calculated points at higher energy was generated as a starting point for a newly fitted surface [2]. Quantum chemical calculations on the resulting semi-empirical PES using an \textit{ab initio} dipole moment surface (DMS) [18] should predict well both the positions and the intensities of all rovibrational transitions within the range of validity of the PES and DMS.

Once the computational results with the fitted PES were able to fit the relatively small number of lines in our double-resonance spectra with near-spectroscopic accuracy, it became possible and beneficial to validate the calculations with a more extensive set of measured rovibrational levels. In order to access numerous terminal levels, we introduced a technique that we call collisionally assisted double-resonance overtone spectroscopy (CADROS). This approach allowed full rotational and partial vibrational relaxation of an intermediate level by introducing long delay times between overtone excitation lasers and by increasing the water vapour pressure.

We then went beyond the initial goal of measuring transitions relevant to the absorption of solar radiation by recording the entire set of rovibrational levels that could be reached by dipole-active transitions (mainly OH-stretch overtones) up to the dissociation threshold. Since transitions to vibrations involving nuclear motion along the dissociation coordinate (stretching of a single OH bond) possess a considerable transition dipole moment, we are able to excite to the continuum of states above the dissociation threshold. The position of the continuum onset defines the dissociation threshold with spectroscopic accuracy. Our value, $D_0 = 411 145.94 \pm 0.15 \text{cm}^{-1}$, is 30 times more precise than the previous most accurate result [19]. The dissociation energy of water is one of the most fundamental thermochemical values and has been addressed by a number of other studies, as summarized and analysed in a paper by Ruscic \textit{et al.} [20].

Spectra above $D_0$ reveal both sharp and broad peaks superimposed on continuous absorption. The sharp peaks correspond to long-lived states that are only weakly coupled to the dissociation coordinate. Such states should be accounted for in modelling of dissociation reactions (where they are called quasi-bound states) and association reactions (where they are called scattering resonances). Experimental observation and rigorous characterization of scattering resonances remain challenging objectives in chemical reaction dynamics [21]. Only a few molecular species have been studied in the past by state-selective excitation combined with state-resolved detection of fragments to reveal details of unimolecular reactions [22–27]. Our study contributes to the scarce set of experimentally observed quasi-bound states.

The present review is based on five papers, which we will refer to as papers 1–5 throughout the text. Paper 1 [1] reports the measurement of rovibrational levels up to 34 000 cm$^{-1}$ with our double-resonance approach; paper
2 [2] extends the measured energies of bound states up to the dissociation threshold; paper 3 [3] introduces the CADROS technique and reports additional bound rovibrational levels; paper 4 [4] reports our direct measurement of the dissociation threshold; and paper 5 [5] discusses resonances above the dissociation threshold.

(a) Nomenclature of rovibrational states in water

For low levels of excitation, normal-mode notation is commonly used to denote the vibrational states of water. For the highly excited levels with predominantly stretching excitation, the local-mode approach [28,29] gives a more convenient description [8,30,31]. In our experiments, electric dipole transitions excite molecules in such states, because the transition dipole moment for bend overtones is much smaller than for stretch overtones. For stretch overtones, vibrational energy is effectively localized in a single bond as a result of the large anharmonicity and weak interbond coupling [32]. In local-mode notation [33], \((m,n)^\pm b\), \(m\) and \(n\) represent quanta of stretch localized in each OH bond in symmetric (+) or asymmetric (−) combinations, and \(b\) is the number of quanta of bending vibration. We will refer to \((m,0)^\pm 0\) states as \(v_{\text{str}} = m\) for brevity. Rotational levels of water are labelled using standard asymmetric top notation as \(J_{K_aK_c}\). Most of the labels used to characterize vibration–rotation energy levels are approximate [34]. The only rigorous quantum numbers for water are the rotational angular momentum \(J\), parity \(p = \pm 1\), and the symmetry upon interchanging the two H atoms. This latter causes the spectrum to split into two distinct series based on nuclear-spin statistics.

2. Multiple-resonance photofragment spectroscopy

(a) Excitation and detection schemes

Direct overtone transitions from the ground vibrational state to highly excited vibrational states are extremely weak, since they are forbidden in the harmonic approximation. They become possible owing to anharmonicity of the potential for nuclear motion and/or nonlinearity of the dipole moment dependence on vibrational coordinates. For low overtones, a rule of thumb is that the transition strength drops by an order of magnitude for a unitary increment in the vibrational quantum number difference. Consequently, an exponential increase of laser pulse energy is needed to excite successively higher vibrational overtone transitions of a molecule, which is difficult to achieve in practice. Moreover, high overtone transitions can be in the UV spectral region, where powerful tunable laser sources are not readily available.

We employ double- and triple-resonance vibrational overtone excitation (figure 1) to access high rovibrational states of H₂O in the electronic ground state. The double-resonance scheme has been employed previously by the group of Sinha [35] to measure \(v_{\text{str}} = 8\) levels. We extend this technique to higher vibrational levels and introduce three-photon excitation. A sequence of nanosecond laser pulses (P1–P3) of specific frequencies promotes water molecules to very high vibrational levels via intermediate rovibrational states. This scheme allows orders of magnitude more efficient population of the final upper state compared with

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Figure 1. Energy-level diagram of double- and triple-resonance vibrational overtone excitation (photons P1–P3a) followed by photodissociation (dashed arrows, photons P3b or PP) and OH fragment detection (photon PD). $D_0$ designates the dissociation threshold of the OH bond.

single-photon excitation with similar pulse energy. An overtone transition with a modest change of vibrational quantum number ($\Delta v < 5$) can be saturated by a focused dye laser pulse. Our multiple-resonance overtone excitation schemes consist of two or three such elementary steps in which one half of the molecules are promoted to a higher level in each step. The delay between the excitation steps is 5–10ns, which, at typical pressures of 50–100 $\mu$bar, is short enough to ensure that no relaxation occurs at intermediate levels.

Molecules in the terminal level are detected by vibrationally mediated photodissociation pioneered by Crim and co-workers [36] in their study of $v_{\text{str}} = 4$ in water. A UV/visible photon (photolysis pulse, PP) from another pulsed laser or a second photon from the third excitation laser brings the excited molecules to the repulsive $\tilde{A}^1B_1$ electronic surface. The fourth laser pulse (PD) detects a fraction of OH fragments residing in the ground state ($X^2\Pi_{3/2}$, $e$, $J = 3/2$, $v = 0$) via laser-induced fluorescence (LIF) from the $A^2\Sigma_{3/2}$ electronic state. Photodissociation yields hot OH fragments with a broad rotational distribution because of the excess of energy above the dissociation threshold. In some measurements, we delay the detection pulse (PD) with respect to the photolysis pulse (PP) to allow for rotational relaxation of the hot OH fragments in collisions with room-temperature...
H$_2$O. Monitoring OH fluorescence as a function of the wavenumber of the last overtone excitation laser (P2 or P3), while keeping the wavenumbers of all other lasers fixed, generates a photofragment spectrum of the overtone transition from the intermediate single rovibrational state (gateway state) to a terminal level. Such an action spectrum accurately reflects the transition wavenumber, but the detection scheme may distort its relative intensities.

(b) Experimental implementation

Figure 2 presents a schematic optical layout of our experiments. Two or three tunable laser pulses for double- and triple-resonance overtone excitation schemes, respectively, are generated by dye lasers (Lumonics HD-500 and Lambda-Physik Scanmate) pumped by the second harmonic of Nd:YAG lasers (Spectra-Physics GCR-190, GCR-250). Typically, 60–70 mJ pulses of 6–7 ns duration are produced at 20 Hz repetition rate. For LIF detection of OH fragments, the 3–5 mJ output of Nd:YAG-pumped continuum dye laser is frequency-doubled in a KDP (potassium dihydrogen phosphate) crystal, which is mounted in an autotracker (Inrad, AT-II). The PP results either from tripling (for the $v_{str} = 9$ and lower terminal levels) or doubling (for the terminal levels above $v_{str} = 9$) a fraction of the Nd:YAG fundamental.

All the overtone-pumping laser beams (P1, P2 and P3) are focused to the centre of a vacuum chamber by individual $F = +60$ cm lenses to ensure a correct focal point for distinct laser wavelengths. The first two p-polarized beams are then combined on a dichroic mirror (or on a partially reflecting mirror in the case when
the two wavelengths are nearly identical). The third s-polarized beam is combined with the first two on a polarizing beam-splitter cube. The p-polarized photolysis laser beam (PP) and the UV detection beam (PD) are combined on a dichroic mirror. Counter-propagating with the overtone excitation beams, they enter and leave the chamber through fused silica windows mounted at the Brewster angle to minimize scattering of the detection laser beam inside the chamber. This beam is focused to the centre of the chamber by an \( F = 100 \text{ cm} \) lens and spatially filtered by a 0.5 mm pinhole placed 30 cm after the lens. Light baffles are placed in the side arms of the chamber to further reduce scattered light. All beams are carefully overlapped inside the chamber.

The emitted OH fluorescence photons are collected by a condenser lens in a direction orthogonal to the beam axis and imaged onto a \( 10 \times 1 \text{ mm}^2 \) slit in front of a photomultiplier tube (PMT, EMI 6935QB). A bandpass glass filter (Hoya U-340) placed in front of the PMT suppresses scattered light of the overtone excitation lasers and reduces that from the detection laser, while transmitting most of the red-shifted fluorescence. A small part of each dye laser beam is reflected into a neon-filled hollow cathode optogalvanic lamp for spectral calibration purposes. We tune the first excitation laser to a desired overtone transition by sending it through a water vapour-filled photoacoustic cell. To correct for nonlinearities of the scan in between neon optogalvanic lines, a well-collimated fraction of the beam of the scanned laser passes perpendicular to an air-spaced etalon with \( 1 \text{ cm}^{-1} \) free spectral range; the transmitted signal is detected with a photodiode placed behind the etalon. In the most recent experiments (states above \( 34000 \text{ cm}^{-1} \)), we continuously monitor laser wavenumber with a highly accurate wavemeter (Angstrom WS6).

(c) Analysis of the spectra

The known rotational identity of the originating level, along with rotational assignment of the intermediate state(s) employed [37,38], leaves only a few options for the rotational assignment of the terminal rovibrational states. All excitation steps are governed by rotational selection rules, which strictly determine the change of parity \( P (+1 \leftrightarrow -1) \), change of angular momentum \( J (\Delta J = 0, \pm 1) \) and change of its projection onto the \( z \)-axis in the laboratory frame \( M (\Delta M = 0, \pm 1) \). The strongest A-type and B-type transitions obey the \( \Delta K_a = 0, \Delta K_c = \pm 1 \) and the \( \Delta K_a = \pm 1, \Delta K_c = \pm 1 \) selection rules, respectively. In addition, the total nuclear spin of the two hydrogen atoms, \( I \), does not change upon excitation, allowing transitions only between either ortho \( (I = 1) \) or para \( (I = 0) \) levels of water.

The \( M \) selection rules, which are usually irrelevant to single-laser experiments, bring additional constraints in situations that employ sequential excitation by two linearly polarized laser beams. Parallel polarization of the two beams implies that the same component of the transition dipole moment is involved in two sequential transitions, whereas in the case of orthogonal polarizations, two laser fields interact with different components. Consideration of the transition matrix elements for different components of the dipole moment operator [39] indicates that the \((J = 1) \leftrightarrow (J' = 1) \leftrightarrow (J'' = 0) \) and \((J = 0) \leftrightarrow (J' = 1) \leftrightarrow (J'' = 0) \) two-step transition schemes are forbidden for the parallel and orthogonal polarizations, respectively. A comparison of two spectra

\[ \text{(c) Analysis of the spectra} \]
originating from the same $J' = 1$ gateway state but obtained with different relative polarizations of the excitation lasers makes the identification of vibrational band origins straightforward.

3. Results

(a) Bound rovibrational states above 26000 cm$^{-1}$

The experiments described in this section provided access to the bound vibrational states up to the first dissociation threshold via two or three sequential OH-stretch overtone transitions between single rotational levels. In the double-resonance overtone excitation scheme (figure 1), the photons from the first laser (P1) promotes a fraction of the water vapour molecules in a chosen rotational state to a level that contains four or five vibrational quanta in one of the stretches, $v_{\text{str}} = 4, 5$. In the triple-resonance scheme, only transitions to $v_{\text{str}} = 4$ are employed in the first step. The second excitation laser (P2) subsequently promotes a fraction of these pre-excited molecules to a higher rovibrational level. Terminal levels in the double-resonance experiments contain between 8 and 12 OH-stretch quanta and between 0 and 1 quanta of OH bend. Triple-resonance gateway states contain eight or nine quanta of OH stretch. A third photon (P3a) further excites molecules from the gateway state to a state below the dissociation threshold. A second photon from the third excitation laser (P3b) promotes water molecules in the terminal rovibrational level to the repulsive $\tilde{A}^1B_1$ electronic state, yielding OH and H fragments. In the double-resonance scheme, an additional photolysis laser pulse (PP) was needed: 532 nm for the terminal levels above $v_{\text{str}} = 9$ or 355 nm for lower levels. To increase the detection efficiency, we allowed some collisional relaxation of the hot OH fragments by introducing a 100 ns delay between the last excitation (P3 or PP) and the detection (PD) photons.

Altogether we measured the energies of 551 rovibrational levels of water, which are tabulated in paper 3 [3] (below 34000 cm$^{-1}$) and paper 2 [2] (above 34000 cm$^{-1}$). The assigned rotational states have quantum number $J$ ranging from 0 to 7. These levels come from 67 different vibrational bands whose band origins are given in table 1. The states up to (12,0)$^0$ have been reached via double-resonance excitation; access to the higher ones required three excitation steps.

(b) Collisionally assisted double-resonance spectroscopy

In CADROS-type experiments, we increase the delay $\Delta t$ between P1 and P2 and/or the water vapour pressure to allow for significant rotational relaxation of H$_2$O in the intermediate level. Figure 3 presents the energy-level scheme for rotationally selective double-resonance laser excitation to the (10,0)$^+$ vibrational level of H$_2$O. Excitation of the seventh to eleventh OH-stretch overtones and stretch–bend combination levels (with a single bending quantum) employs similar schemes. The wavelength of the first pulsed laser (P1) is tuned to a rovibrational transition from a single rotational level of the vibrational ground state to an intermediate level that contains four or five vibrational quanta in one of the OH stretches. We scan the frequency of the second laser pulse (P2). When in resonance, P2 promotes molecules from the intermediate state to a rovibrational state containing between eight and 12 stretch quanta and up to one quantum
Table 1. Vibrational band origins for highly excited states of water.

<table>
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<tr>
<th>assignment</th>
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<th>assignment</th>
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<td>(14,0)$^-$0</td>
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<td>(12,1)$^+$0</td>
<td>37 439$^b$</td>
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<td>(12,1)$^-$0</td>
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<td>(9,0)$^-$0</td>
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<td>(13,0)$^+$2</td>
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<td>27 569.8(1)$^b$</td>
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$^a$Experimental accuracy ±0.03 cm$^{-1}$.

$^b$Extrapolated from levels with $J > 0$ (with the uncertainty in parentheses).

of bend. Rotational and, to some extent, vibrational relaxation that takes place within the time interval $\Delta t$ between the pulses P1 and P2 populates a variety of intermediate states from the initially prepared single rovibrational state.

To optimize the signal using this approach, one needs to consider experimental factors that reduce the signal-to-noise ratio, in addition to the inevitable reduction of population in individual intermediate states compared with short-delay measurements. During long time delays, molecules in intermediate states can escape from the region of overlap with the subsequent lasers. This consideration favours higher vapour pressure and shorter delay times at constant

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collisional parameter $p\Delta t$. Quenching of electronically excited OH and consequent loss of detection efficiency at higher pressures favours the opposite. Empirically, we determined that the optimal conditions for the highest collisional parameter are: $\Delta t = 215$ ns and $p = 700$ μbar.

An increase of the collisional parameter, $p\Delta t$, increases relaxation of the initially prepared state up to full rotational thermalization of the excited molecules. At the maximum collisional parameter of our experiment, $p\Delta t = 1.5 \times 10^{-10}$ bar, vibrational relaxation should also be noticeable [40]. A variety of vibrational states, some of which are difficult to access by direct laser excitation (for instance, states with high bending excitation), can be prepared in such a collisional process. However, the second and third photons (P2 and P2a/PP) can reach the repulsive electronic surface only from intermediate vibrational levels with a certain minimum number of stretching quanta. The calculated ground [17] and repulsive [41] surfaces provide a means of identifying such states. Only the transitions from these states can be detected in the photofragment spectra. No additional vibrational states appeared in CADROS spectra.

All the states involved in the same scan have the same nuclear spin, because they are accessed from the same initially prepared spin state (ortho or para). To cover both nuclear species, we obtained pairs of CADROS spectra by pumping

Figure 3. Energy-level diagram for the measurement of the (10,0)$^+$ vibration in H$_2$O. A significant delay $\Delta t$ between the two excitation pulses and an elevated pressure in CADROS experiments ensure collisional rotational relaxation.

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different spin states with the first laser pulse. For instance, a pair of intermediate states \((4,0)^-0\), \(J_{K_aK_c} = 1_{01}\) (ortho) and \((4,0)^+0\), \(J_{K_aK_c} = 1_{11}\) (para) was used to identify 81 upper levels additional to previously measured ones. We used PES12 [1] (PES fitted up to \(v_{\text{str}} = 12\) experimental data) for assignment.

\(c\) Dissociation threshold measurement

Figure 4 illustrates a qualitative change in detection scheme for the rovibrational states above the dissociation threshold. From these states, the molecule dissociates directly on the ground potential surface. For long-lived states, including all those below threshold, a regular triple-resonance scheme with an additional photolysis photon (P3b) from the third laser is applicable. We accessed \((8,0)^+0\) or \((9,0)^+0\) gateway states with a two-step overtone excitation via the \((4,0)^-0\) level.

Figure 5 shows an example of a spectrum originating from a gateway state with nine quanta of OH stretch in a single localized vibration, \((90)^+0\), and with \(J_{K_aK_c} = 1_{01}\). There are sharp laser linewidth-limited (approx. 0.08 cm\(^{-1}\)) peaks on the low-frequency side of the spectrum and a continuous absorption with superimposed broadened peaks starting at 13584.7 cm\(^{-1}\). The sharp peaks correspond to transitions to bound states that subsequently absorb an additional photon and dissociate on the excited electronic surface. The continuous absorption represents...
Figure 5. Photofragment excitation spectrum of transitions from the second intermediate state, prepared via the following pathway: $[27\,561.27\text{ cm}^{-1},(9,0)^+0,1_{01}] \leftarrow [13\,830.94\text{ cm}^{-1},(4,0)^-0,0_{00}] \leftarrow [23.79\text{ cm}^{-1},(0,0)0,1_{01}]$.

direct excitation to the dissociative OH-stretch continuum. This conclusion is supported by an \textit{ab initio} estimation of the state density below the dissociation threshold \cite{42}. Adapting this estimation to the spectrum in figure 5, we take into account that the rotational selection rules allow transitions to only $J=1$ and $J=2$ terminal levels, since the $(J=0) \leftrightarrow (J=1) \leftrightarrow (J=0)$ pathway is forbidden owing to the orthogonal polarizations of the second and third excitation photons in our experiment. The resulting average spacing between the accessible rovibrational states should be 1.5–2.0 cm\(^{-1}\), which agrees with our observation. Any significant spectral broadening should thus originate from the OH-stretch dissociation continuum. The onset of the continuous absorption corresponds to the OH bond dissociation threshold, provided we detect OH fragments in the rovibrational ground state. The total energy of a terminal level is the sum of the rovibrational energy of the first intermediate state in the $(4,0)^-0$ vibrational level and the energies of two subsequent excitation photons (P2) and (P3).

We examined regions of water spectra near the onset of continuous absorption using different gateway states, different relative polarizations of overtone excitation lasers and different detected states of the OH fragments. Conservation of total angular momentum stipulates that there will be a centrifugal barrier for the unimolecular dissociation of rotating molecules. The presence of such a barrier would reduce the intensity of transitions to the states in the continuum lying above the dissociation threshold but below the centrifugal barrier, since we are measuring absorption by detecting dissociation fragments, and this complicates the determination of the dissociation threshold. For this reason, we determine the threshold primarily from the spectrum that contains a transition

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to non-rotating \((J = 0)\) molecules, where this barrier does not exist. The onset of the continuous absorption remains the same, however, in the spectra with \(J = 1\) and 2 terminal levels only, indicating that, for low \(J\), the centrifugal barrier effect is not significant. We detected OH fragments alternatively in the ground state \(X^2\Pi_{3/2, e, J = 3/2, v = 0}\) or in the upper level of the \(\Lambda\) doublet \(X^2\Pi_{3/2, f, J = 3/2, v = 0}\). The energy of the onset does not change provided we shift the energy scale by \(-0.03\) cm\(^{-1}\) to account for the energy of the upper \(\Lambda\)-doublet component. For accurate determination of the continuum onset, we performed numerical deconvolution of the spectrally measured lineshape of the third excitation laser from the experimental spectra. Treated in this way, and combined with the uncertainty in the frequency of lasers P2 and P3, we obtained a value of \(D_0 = 41145.94 \pm 0.15\) cm\(^{-1}\) for the lowest dissociation energy of the OH bond of water from its ground rovibrational state within a 95% confidence level.

\((d)\) Quasi-bound states

In triple-resonance spectra above \(D_0\), we observed both sharp and broad peaks, some of them with a pronounced lineshape asymmetry. These quasi-bound states could correspond to Feshbach resonances [43], in which the extra energy is stored in non-dissociating (bending or the second local stretch) vibrational modes. Another possible origin is shape resonances due to the vibrational states whose non-rotating energies are below dissociation but rotational excitation shifts the levels above the dissociation limit. We performed characterization of observed quasi-bound states by employing selection rules based on rigorous quantum numbers as well as tentative vibrational assignment.

Vibrational characterization of dissociative resonances with quantum numbers is only approximate, since any such state is coupled to a single-stretch dissociative continuum and cannot be rigorously treated as a bound state. Moreover, at high excitation levels, the probability of couplings between different ‘pure’ localized stretches and stretch–bend states increases, scrambling the local-mode representation. However, even an approximate local-mode assignment can be meaningful. Our vibrational characterization of some of the dissociative resonances was based on the comparison of transitions originating from gateway states of different vibrational character, using the known assignment of the employed gateway states \([1,3,13,38,44]\) (N. F. Zobov 2009, private communication) and the assignments of vibrational band origins of several bound states near \(D_0\) \([2]\). Figure 6 compares the spectra of transitions from the same \((9,0)^+0, 1_{01}\) gateway state to states above \(D_0\) measured with parallel and orthogonal relative polarizations of the last two lasers. The full set of measured spectra can be found in paper 5 \([5]\) and its online electronic supplementary material. The accessible states are \(J = 0, 2\) and \(J = 1, 2\) in the upper and lower traces of figure 6, respectively (see the explanation of the \(M\) selection rules in §2.3). The features common to both spectra must therefore belong to transitions to terminal states with \(J = 2\); those that appear only in the upper spectrum or only in the lower spectrum are assigned to \(J = 1\) and \(J = 0\), respectively.

Fits of the observed features to Fano profiles [45] yield the centres, spectral widths \(\Gamma\) and the fitting parameter \(q\) of the observed resonances, listed in the electronic supplementary material for paper 5 \([5]\). The absolute value of \(q\)
Figure 6. Photofragment spectra of transitions from gateway states to energies above the lowest dissociation limit $D_0$ plotted as a function of the total rovibrational energy. The spectra are labelled by the accessible quantum numbers $J$. The gateway state has been prepared by the following transitions: $[27 561.27 \text{ cm}^{-1}, (9,0)^+0, l_{01}] \leftarrow [(4,0)^-0, 0_{00}] \leftarrow [(0,0)^0, 1_{01}]$. The parameters and assignment of peaks A–N are given in table 2.

reflects the deviation of the lineshape from a Lorentzian; the sign of $q$ indicates the direction of the tail of the asymmetric Fano profile. The parameters of the Fano profile contain information on the dissociation dynamics of the water molecule [45], which serve as benchmarks for an accurate theoretical treatment of this process.

The analysis presented in paper 1 [1] revealed a significant coupling between the $(9,0)^+0$ single-stretch state and close-lying states with excitation in both stretch and bend vibrations: $(7,1)^+1$ and $(6,1)^+3$. By using such ‘mixed’ eigenstates of the $v_{\text{str}} = 9$ manifold as gateway levels, we accessed terminal states of different vibrational character, yielding the rich structure in the spectra in figure 6. To characterize the observed transitions, we compared these spectra with those from three ‘pure’ gateway states with vibrational excitation in a single stretch, both stretches, and a single stretch plus a bend vibration [5].

The lowest energy resonance (labelled A in figure 6) appears immediately after $D_0$. Rotational assignment of this resonance to $J = 2$, together with the published assignment of water states just below $D_0$ [2], suggests that its vibrational origin is $(19,0)^\pm0$. 

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Table 2. Quasi-bound states observed in the spectra in figure 6.

<table>
<thead>
<tr>
<th></th>
<th>resonance (cm$^{-1}$)</th>
<th>width $\Gamma$ (cm$^{-1}$)</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>41146.17 ± 0.05</td>
<td>0.43</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>41154.11 ± 0.1</td>
<td>0.35</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>41161.24 ± 0.2</td>
<td>2.40</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>41167.24 ± 0.05</td>
<td>0.60</td>
<td>2</td>
</tr>
<tr>
<td>E</td>
<td>41172.67 ± 0.05</td>
<td>0.21</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>41203.73 ± 0.05</td>
<td>0.22</td>
<td>0</td>
</tr>
<tr>
<td>G</td>
<td>41212.95 ± 0.1</td>
<td>1.03</td>
<td>2</td>
</tr>
<tr>
<td>H</td>
<td>41221.23 ± 0.1</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>41225.99 ± 0.05</td>
<td>0.42</td>
<td>0</td>
</tr>
<tr>
<td>J</td>
<td>41236.45 ± 0.05</td>
<td>0.89</td>
<td>2</td>
</tr>
<tr>
<td>K</td>
<td>41268.09 ± 0.05</td>
<td>0.36</td>
<td>0</td>
</tr>
<tr>
<td>L</td>
<td>41273.03 ± 0.05</td>
<td>0.10</td>
<td>2</td>
</tr>
<tr>
<td>M</td>
<td>41291.93 ± 0.05</td>
<td>0.16</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>41295.77 ± 0.05</td>
<td>0.52</td>
<td>0</td>
</tr>
</tbody>
</table>

The most prominent feature in the upper spectrum in figure 6 is the intense and sharp ($\Gamma = 0.21$ cm$^{-1}$) peak E at 41172.67 cm$^{-1}$, which we assign to a state with $J = 0$. The same peak was observed in transitions from the ‘pure’ gateway state with excitation in both stretches (7,1)$^{+0}$, leading to the conclusion that it originates from the (7,1)$^{+1}$ component of the ‘mixed’ gateway state. Based on this similarity and the estimated energies of pure vibrational states, we suggest (13,1)$^{+2}$ as the most probable vibrational character for the state E. The lifetime of this state determined from its linewidth is approximately 25 ps. Within the spectral range of our measurements, we observed several similarly long-lived Feshbach resonances with lifetimes up to 60 ps (peak L). Such long lifetimes suggest that motion of each stretch and/or bend vibration remains highly localized even at energies above the dissociation limit. The proposed vibrational characterization of the observed resonant states remains tentative. A recent paper [46] extended the theoretical approach, which has been validated at energies below $D_0$ [2], to higher energies. Ab initio accuracy is still not sufficient to reproduce a recognizable pattern of dissociative resonances. The theoretical vibrational assignment differs significantly from ours; the strongest resonances are predicted to have $(m,0)^{\pm}v_2$ character.

4. Conclusions

We employed double- and triple-resonance overtone excitation and photofragment detection schemes to measure energies of very high rovibrational states in H$_2$O. Multiple-step excitation is orders of magnitude more effective in transferring population than a direct single-photon transition. Another advantage of this technique is its extreme selectivity, resulting in simplified spectra originating...
from single rovibrational states. This selectivity is based on the strict selection rules governing the change of rotational, nuclear spin and parity quantum numbers in allowed electric dipole moment transitions of each excitation step. The simplicity of the spectra facilitates assignment in computationally challenging high vibrational energy regions.

Positions of rovibrational levels between 26 000 cm\(^{-1}\) and the first dissociation threshold have been measured. Stretch overtones \((m, 0)\pm 0\) were primarily detected due to the highest transition dipole moment of these states. Two notable exceptions are the \((7,1)^{\pm 1}\) and \((6,1)^{\pm 3}\) states, which borrow oscillator strength from the \((9,0)^{\pm 0}\) state. Our fruitful collaboration with the theory groups of Tennyson, Polyansky and Császár resulted in a significant increase of predictive ability of calculations on empirically fitted \textit{ab initio} PESs. The CADROS approach significantly improved the productivity of double-resonance experiments and allowed the monitoring of transitions from states that are difficult to prepare by laser excitation. Two CADROS spectra alone allowed the determination of 81 new rovibrational levels in the 26 000–34 200 cm\(^{-1}\) energy region. No collisional \textit{ortho–para} spin relaxation in water vapour was detected in the measured CADROS spectra, suggesting that such relaxation is slower than \(6.7 \times 10^{-9}\) bar\(^{-1}\) s\(^{-1}\).

The value of the first dissociation threshold of water, \(D_0 = 41 145.94 \pm 0.15\) cm\(^{-1}\), determined from the onset of the dissociative continuum in triple-resonance spectra, is 30 times more accurate than the previous best result, 41 151 \pm 5 cm\(^{-1}\), and is positioned just on the edge of its error bars [19]. The high accuracy of our measurement also brings an important reduction in the uncertainty of some other thermochemical values. For example, based on the most accurate recommended value for the total atomization energy of water [20], \(\Delta H_{\text{at}} = 76 721 \pm 8\) cm\(^{-1}\), and our accurate \(D_0\) value, one can calculate the dissociation energy \(D_0\) for the hydroxyl radical, OH, to be 35 575 \pm 8 cm\(^{-1}\).

We observed complex spectra above \(D_0\) superimposed on a dissociative continuum displaying asymmetric resonance shapes. The narrow widths of some of these resonances indicate that water molecules may survive for as long as 60 ps in states above the dissociation threshold. Comparison of the measured dissociation spectra allowed us to perform a rigorous assignment of rotational quantum numbers \(J\), nuclear spin and parity, and a tentative vibrational characterization of the observed resonances. A recent \textit{ab initio} study suggests a different assignment for some of the observed vibrational levels, although the accuracy of the calculations is still too low to set an unambiguous correspondence to the measured transitions [46]. Regardless of the exact vibrational assignment, the long-lived quasi-bound states observed here suggest a high degree of localization of the vibrational motion in water, even at energies above \(D_0\) that are comparable with the translational energies of molecules at room temperature. Such resonances may have implications for unimolecular dissociation and for the association reaction stabilized by collisions with a buffer gas. Long-lived activated complexes have a higher probability for stabilization by collisions. Noticeable deviations from Rice–Ramsperger–Kassel–Marcus (RRKM) theory predictions may be expected in the case when resonance states that interact with the same dissociation continuum do not overlap [47], which is true for the observed resonances in water.

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References


