Dissociation threshold of $H_2{}^{18}O$: Validating *ab initio* calculations by state-selective triple-resonance spectroscopy

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ABSTRACT

We employ state-selective triple-resonance vibrational overtone spectroscopy for a direct measurement of the lowest dissociation energy, D_0, in the $H_2{}^{18}O$ molecule. The measured value of 41 154.22 ± 0.25 cm^{-1} is in an excellent agreement with that, predicted by *ab initio* theoretical calculations. This result validates the computations, adding more confidence to what this theory can predict for water. In addition, we have measured the required for this experiment energy levels of $H_2{}^{18}O$ in the region near 27 000 cm^{-1}, as well as the laser-induced fluorescence (LIF) spectrum of the ^{18}OH isotopologue, for which near 60 electronic transitions have been assigned.

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1. Introduction

Water is a key molecule to our life and a benchmark triatomic for theory. The spectroscopy of different isotopologues of H_2O is well studied due to its importance in a variety of applications [1–4]. For the main isotopologue, $H_2{}^{16}O$, the rovibrational energy levels are known from experiments up to 41 300 cm^{-1} [5], which is slightly above its the lowest dissociation energy of 41 145.92 ± 0.12 cm^{-1} [6,7]. For HDO isotopologue, the energy levels have been determined up to the blue end of the optical region and the lowest dissociation energy (D_0) was measured recently [7]. For other isotopologues, such as D_2O, $H_2{}^{17}O$ and $H_2{}^{18}O$, the limit of the measured energy levels remains near 16 000–18 000 cm^{-1} [1,4] and the accurate dissociation thresholds for these species are unknown.

Just a few years ago, the derivation of a global solution for water molecule was hindered by the lack of the experimental data for molecular states with energy above ~26 000 cm^{-1}. The most recent experimental and theoretical advances have filled the gap between the optical region below this limit and the dissociation threshold [8–13]. The breakthrough in this field came after combining the multi-resonance state-selective laser spectroscopy with accurate *ab initio* calculations [7]. The energy 'ladder' up to above the first dissociation limit was built for $H_2{}^{16}O$ and the most accurate value of D_0 was directly measured for this isotopologue. Dissociation energy of O—H bond in the HDO molecule was also measured using the

same experimental approach. The work on building the HDO levels ladder is currently in progress.

The availability of high precision data for energy levels up to the dissociation limit makes water molecule a unique benchmark triatomic for global variational calculations of light molecules. Currently, for the energy levels of the $H_2{}^{16}O$ molecule below 39 000 cm^{-1} the accuracy of the *ab initio* calculations is only a few cm^{-1}, although around the dissociation limit it drops to 20 cm^{-1}. Achieving a better accuracy is a difficult task, since a large number of calculations are required for constructing a global Born–Oppenheimer potential energy surface (PES), which would include several finer corrections, such as adiabatic, relativistic and quantum-electrodynamical [14,15]. Global PES construction requires calculations of thousands of points in various nuclear configurations. For example, the *ab initio* calculations for the global PES of the $H_3{}^+$ molecular ion were performed with 42 000 geometries [16]. For water, this implies that the highest basis set in *ab initio* calculations can be aug-cc-pV6Z Gaussian, and a complete basis set extrapolation is required for determining a pure Born–Oppenheimer (BO) PES. For determining the dissociation energy, it is necessary to calculate the energies of only two molecular configurations: the ground state geometry of H_2O, E_{gs} (H_2O), and the geometry, where one H atom is far away from OH ($E(H + OH)$), and then use in following equation:

$$D_0 = E(H + OH) - E_{gs}(H_2O). \tag{1}$$

Both *ab initio* energies in (1) are calculated relative to the zero, where all particles in the molecule are far away from each other:

$$E(H + OH) = E_{gs}(H) + E_{gs}(OH). \tag{2}$$

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The energy of the ground state can be calculated from the energy of the minimum configuration E_{min} and the zero point energy E_{zero} as

$$E_{gs} = E_{min} + E_{zero} \qquad (3)$$

The low number of the geometries, required for dissociation energy calculations opens an opportunity for the use of more time consuming *ab initio* methods, then those used for the PES construction. For the calculation of, for instance, E_{min} for H_2O, the basis sets up to aug-cc-pV8Z were used [7]. Incorporation of many 'small' effects into the calculations of the dissociation energy in addition to the BO value results in the *ab initio* value for several water isopologues and different dissociation paths (removal of H or D atom). A conservative estimate suggests ± 8 cm^{-1} for the uncertainty of the calculated dissociation energies. The calculated values contain mass-dependent and mass-independent contributions. The isotopic shifts for different water isotopologues I_a and I_b, calculated as $\delta = D_0(I_a) - D_0(I_b)$, are determined entirely by the mass-dependent contributions and have been calculated more accurately then the D_0 value itself. Calculated mass-dependent terms have been combined with the measured values of D_0 ($H_2^{16}O$ and $HD^{16}O$) to provide the predicted dissociation energies for the other isotopologues of water. Thus calculated, the predicted values have the estimated uncertainty of about 1 cm^{-1}.

The measurements of D_0 in $H_2^{18}O$ has been performed in a similar fashion to the measurements of D_0 in $H_2^{16}O$ [10] and HDO [7] isotopologues of water molecules, which employ a state-selective, triple resonance overtone excitation, combined with photodissociation detection, as described elsewhere [6,8,10,12]. In comparison with these previous measurements, the application of this experimental approach to $H_2^{18}O$ required some preliminary work for determination of certain highly excited rotation-vibrational levels of this isotopologue that have been used as intermediate levels in the excitation, as well as the energy of LIF transitions in ^{18}OH for detecting this fragments. Currently, the energy of only a limited number of ro-vibrational states for the studied isotopologue is known. HITRAN and GEISA databases, for instance, provide the data on the transitions involving levels only below 20 000 cm^{-1}. Although Partridge and Schwenke calculations [17] include vibrational levels as high as (8,0,0) and (8,1,1), these levels are not suitable for our experiment: the first one has insufficient energy, while the second one, due to the one bending mode quantum, is difficult to use for excitation of a significant fraction of molecules. Moreover, no reliable systematic data was available prior to this work for transitions between $A^2\Sigma_{3/2}$ and $X^2\Pi_{3/2}$ electronic states of ^{18}OH hydroxyl radical. Here we report, first, on the measurements and assignment of LIF spectra of ^{18}OH and some ro-vibrational states of the (9,0,0) and (8,0,1) vibrational levels. We then use these new data for the measurements of D_0 in $H_2^{18}O$ and compare the determined value of the dissociation threshold with that, predicted by *ab initio* theory.

2. Experimental

The ^{8}OH radicals were produced by UV photolysis of $H_2^{18}O$ vapor through the $(0,0,0)1_{01} \rightarrow (3,0,1)0_{00} \rightarrow E$ ($E > D_0$) excitation pathway, using two tunable pulsed dye lasers. The wavenumber of the first Nd:YAG pumped dye laser was set to 13 771.65 cm^{-1}, to prepare a good fraction of the irradiated $H_2^{18}O$ molecules to the $(3,0,1) 0_{00}$ intermediate ro-vibrational state, while the second laser was kept at ~280 nm, such that the photon energy of this laser is still below D_0 of water, but the full excitation energy is well above D_0. The UV light at 280 nm was generated by frequency doubling the output of a tunable dye laser, pumped by 6 ns pulses of a Nd:YAG laser, in a KTP crystal. The crystal resides in an

autotracker, which allows automatic adjustment of the crystal position for maximum UV power while tuning wavelength of the dye laser. Similarly, the output of the third laser was frequency doubled and used for spectroscopy of ^{18}OH. We tuned this laser within the 32 000–32 700 cm^{-1} range, while recording the total LIF signal as a function of UV wavenumber.

The energy levels of the (9,0,0) and (8,0,1) vibrational states of $H_2^{18}O$ that we use as gateway states in the triple-resonance excitation of water, have been measured as described elsewhere [8]. Briefly, the first and the second laser pulses were used to promote $H_2^{18}O$ to the vibrational states (3,0,1) and (9,0,0), respectively. The third laser pulse promotes the excited molecules to the electronic repulsive surface, where they promptly fragment. Subsequently, a pulse form the fourth laser detects the appearing ^{18}OH fragments *via* LIF. High selectivity in detecting this isotopologues of hydroxyl makes the experiment insensitive to small contaminations of the isotopically enriched water sample by other than $H_2^{18}O$ isotopologues. Monitoring ^{18}OH fluorescence as a function of the frequency of the second laser pulse, while keeping wavenumbers of all other pulses fixed, generates a photofragment spectrum of an overtone transition from the (9,0,0) state rotational levels to a repulsive state.

In the measurements of D_0 in $H_2^{18}O$ we use three tunable pulsed lasers to access high-lying terminal vibrational levels through sequential excitation of three vibrational overtone transitions. The prepared in a terminal level below the dissociation threshold molecules are promoted further to the repulsive electronic surface by a second photon of the third excitation laser. The subsequent fourth laser pulse detects the appearing photofragments, ^{18}OH, by means of laser-induced fluorescence (LIF). Similar to the previous experiments with the $H_2^{16}O$ and $HD^{16}O$ isotopologues, the dissociation threshold is reached using, subsequently, the (4,0)$^-$0 and (9,0)$^+$0 intermediate vibrational states, denoted in normal mode notations as (3,0,1) and (9,0,0), respectively.

All pump laser beams enter a vacuum chamber on the same side through a fused silica window. These beams have been combined using dichroic mirrors and/or a polarization cube for the orthogonally polarized beams. The LIF probe beam counter-propagates and enters the chamber through a similar window. In all the measurements we use liquid water, isotopically enriched to 90% of $H_2^{18}O$. The water vapor leaks into the vacuum chamber, pumped to 10^{-5} mBar, and is slowly pumped out, such that to maintain a constant pressure of 100 mBar.

Thus measured energies of the $J = 0$, 1, 2, (9,0,0) rotational-vibrational levels in $H_2^{18}O$ molecules and the frequencies of the $A^2\Sigma_{3/2} \leftarrow X^2\Pi_{3/2}$ electronic transitions of the ^{18}OH radical allowed us, finally, to measure photofragment spectra of $H_2^{18}O$ at the energies around the lowest dissociation threshold.

3. Results and discussion

Figure 1 shows the measured LIF spectrum of ^{18}OH. The positions of 65 lines were precisely determined from this spectrum by
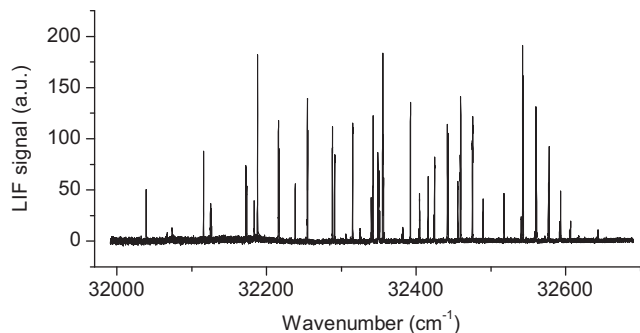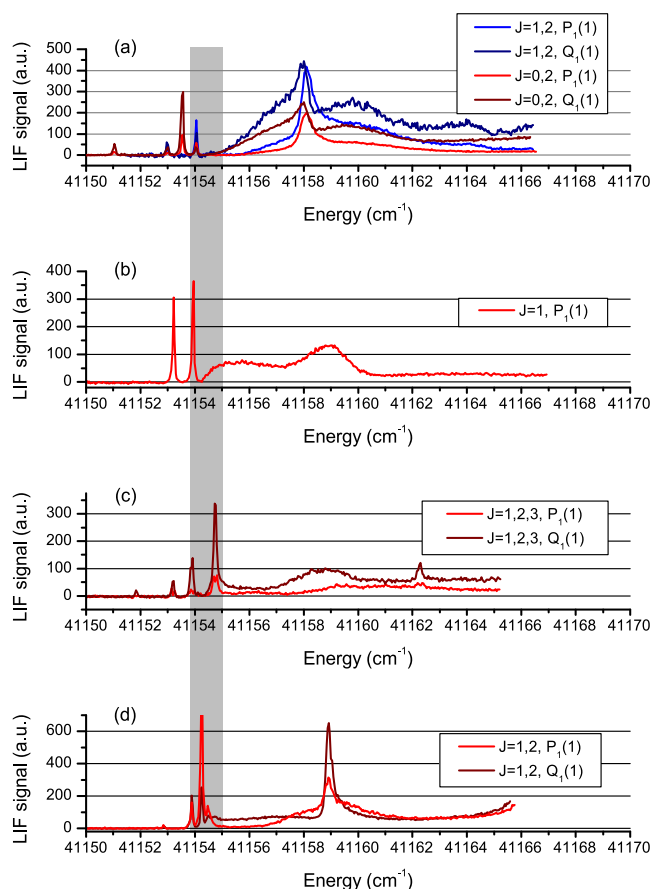

Figure 1. LIF-spectrum of ^{18}OH radicals, created by UV photodissociation of $H_2^{18}O$.

Figure 2. Triple resonance photofragment spectra of $H_2^{18}O$, measured as transitions from different gateway states to upper terminal levels in energy region around the dissociation threshold and plotted in function of total ro-vibrational energy of the molecules. The gateway state are prepared via (a) $(0,0,0)1_{01} \rightarrow (3,0,1)0_{00} \rightarrow (9,0,0)1_{01}$, (b) $(0,0,0)0_{00} \rightarrow (3,0,1)1_{01} \rightarrow (9,0,0)0_{00}$, (c) $(0,0,0)2_{02} \rightarrow (3,0,1)1_{01} \rightarrow (9,0,0)2_{02}$ and (d) $(0,0,0)1_{10} \rightarrow (3,0,1)1_{11} \rightarrow (9,0,0)1_{10}$ pathway. The spectra are measured with parallel (light and dark blue traces in (a)) and orthogonal (all other traces) polarizations of the 2nd and the 3rd excitation lasers. ^{18}OH photofragments are detected via $P_1(1)$ and $Q_1(1)$ LIF transitions. Each trace is labeled by the allowed rotational quantum number J of the terminal states and by the used LIF transition. The gray area shows the approximate positions of the continuous absorption onsets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

fitting them with Gaussian profiles. Ro-vibrational assignment of the observed transitions was done based on a comparison of the measured wavenumbers, obtained from the fit of the experimental data and the known energies of the transitions in ^{16}OH [18]. Quantum numbers have been assigned under the assumption that the difference between the frequencies of the ^{18}OH and ^{16}OH transitions is small, compared with the typical spacing of the lines in the LIF spectrum. This assumption is based on the fact that the reduced masses of the ^{16}OH and ^{18}OH radicals differ only slightly. For example, the evaluated difference for the $Q1(K)$ transitions in the two isotopologues is only $1 \, cm^{-1}$. The measured wavenumbers and the assignment of the $A^2\Sigma_{3/2} \leftarrow X^2\Pi_{3/2}$ electronic transitions in ^{18}OH are given in Table S1 (Supplementary Information). The most intense transitions of ^{18}OH, which we assigned to $Q_1(1)$ and $P_1(1)$ (notations of Ref. [18]), appear at $32\,475.431$ and $32\,441.686 \, cm^{-1}$, respectively. We used these transitions and the energies of their respective lower states in the measurements of high ro-vibrational states of $H_2^{18}O$.

The energy levels of the $(9,0,0)$ and $(8,0,1)$ vibrational states in $H_2^{18}O$ are given in the table S2 (Supplementary Information). Uncertainty of the measured values is of the order of
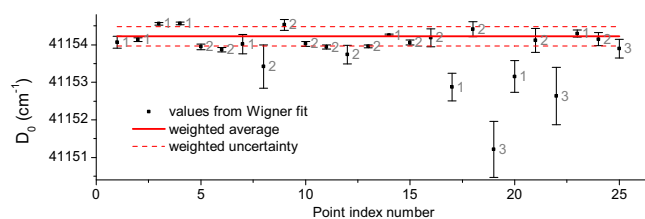
Figure 3. Results of the Wigner function fit to the recordings from Figure 2 in the vicinity of the dissociation threshold. Points show the fitted D_0 value with statistical uncertainty error bars, numbers show J values for the corresponding points, solid line shows weighed average value, dashed lines show weighed uncertainty of the average value.

10^{-2}–$10^{-3} \, cm^{-1}$, and the measured values are in a better than $0.5 \, cm^{-1}$ agreement with the ab initio predictions. These energies have been obtained from our latest ab initio quantum mechanical calculation methods; the details will be published elsewhere.

Figure 2 shows triple resonance excitation spectra of $H_2^{18}O$, measured by using different excitation pathways and plotted in function of the total excitation energy of the molecule. The respective spectra of the transitions originating from different gateway states are shown in the Figures S1–S4 (Supplementary Information). All spectra in Figure 2 exhibit onsets of continuum absorption around $41\,154 \, cm^{-1}$, which correspond to the lowest dissociation energy of the molecules, D_0. In comparison with the similar spectra of the $H_2^{16}O$ and HDO molecules [7,10], the onsets in Figure 2 look less sharp and less intense. We therefore average 5–10 scans for each spectrum in Figure 2 to improve the signal-to-noise ratio of the data. For accurate determination of the onset positions, we use Wigner's threshold low to fit the spectra in the energy range of $2 \, cm^{-1}$ around the onsets using the expression:

$$S(E) = y_0 + A(E - D_0)^{J+1/2} + F_i(a_i, \Delta E_i, C_i, E), \qquad (4)$$

where S is the measured LIF signal, y_0, A and D_0 are the fit parameters, J is the total angular momentum of the dissociating molecule, F_i are Lorentzian functions, which account for resonances within selected total energy interval, and a_i, ΔE_i, C_i are the amplitude, width and center of a corresponding Lorentz function, respectively. We use the function (4) with different number of peaks and by iterating the available J values for each trace. The latter has been required due to the weakness of the onset, which does not allow for distinguishing, for instance, $(E - D_0)^{3/2}$ and $(E - D_0)^{5/2}$ dependencies, especially in the case, when the onset is masked by a resonance. The values of the continuous absorption onsets and their uncertainties calculated from the fits are shown in Figure 3. The average value of D_0 has been calculated taking into account the statistical weight of the each fitted onset, using a reverse square of the uncertainty of the fitted value. This procedure yields the final value of $D_0 = 41\,154.22 \pm 25 \, cm^{-1}$ (one standard deviation), which is in an excellent agreement with the value of $41\,154.2 \, cm^{-1}$, predicted by the ab initio calculations discussed in the introduction. Our experiment therefore validates the theoretical approach, adding confidence for its use in predicting energy levels for one of the most important to our life species – the water molecule.

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Appendix A. Supplementary data

Supplementary data associated with this Letter can be found, in the online version, at doi:10.1016/j.cplett.2015.03.036.

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