Precision spectra of $A^2\Sigma^+, v' = 0 \leftrightarrow X^2\Pi_{3/2}, v'' = 0, J'' = 3/2$ transitions in $^{16}$OH and $^{16}$OD

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We report absolute optical frequencies of electronic transitions from the $X^2\Pi_{3/2}, v'' = 0, J'' = 3/2$ rovibronic ground state to the 12 lowest levels of the $A^2\Sigma^+, v' = 0$ vibronic state in $^{16}$OH, as well as to the 16 lowest levels of the same vibronic state in $^{16}$OD. The absolute frequencies of these transitions have been determined with a relative uncertainty of a few parts in $10^{11}$, representing a ~1000-fold improvement over previous measurements. To reach this level of precision, an optical frequency comb has been used to transfer the stability of a narrow-linewidth I$_2$-stabilized reference laser onto the 308-nm spectroscopy laser. The comb is also used to compare the optical frequency of the spectroscopy laser to an atomic clock reference, providing absolute accuracy. Measurements have been carried out on OH/OD molecules in a highly-collimated molecular beam, reducing possible pressure shifts and minimizing Doppler broadening. Systematic shifts due to retroreflection quality, the Zeeman effect, and the ac Stark effect have been considered during the analysis of the measured spectra; particularly in the case of the OD isotopologue, these effects can result in shifts of the fitted line positions of as much as 300 kHz. The transition frequencies extracted in the analysis were also used to determine spectroscopic constants for the $A^2\Sigma^+, v' = 0$ vibronic state. The constants fitted in this work differ significantly from those reported in previous works that measured the $A \leftrightarrow X$ transitions, resulting in typical deviations of the predicted optical transition frequencies of ~150 MHz, but they generally agree quite well with the constants determined using hyperfine-resolved measurements of splittings within the A state.

The hydroxyl radical, OH, is a prototypical open-shell diatomic molecule that is important in a variety of fields, including atmospheric chemistry [1], interstellar chemistry [2], crossed-beam molecular collision studies [3], and Stark deceleration [4]. In laboratory studies, OH is commonly detected with rotational state selectivity by measuring laser-induced fluorescence from ultraviolet $A^2\Sigma^+ \rightarrow X^2\Pi$ transitions. More-recently, a sensitive detection scheme based on 1+1’ resonance-enhanced multiphoton ionization (REMPI) was demonstrated which also makes use of $A \leftarrow X$ excitation as a first step [5]. Previous studies have determined the absolute frequencies of the $A \leftrightarrow X$ transitions with an uncertainty of approximately 0.005 cm$^{-1}$ (150 MHz) [6-8]. This level of accuracy is quite sufficient for excitation with commonly-used frequency-doubled pulsed dye lasers, which typically have a bandwidth on the order of 0.1 cm$^{-1}$, but for driving the transitions with a continuous-wave (cw) laser with a linewidth on the order of 1 MHz or less, the transition frequencies must be known much more exactly.

In this work, we present high-precision measurements of the $A^2\Sigma^+, v' = 0 \leftrightarrow X^2\Pi_{3/2}, v'' = 0, J'' = 3/2$ transitions in $^{16}$OH and $^{16}$OD. Using a frequency-doubled cw dye laser which is stabilized and monitored with the help of an optical frequency comb, we have measured transitions to the 12 lowest levels of the $A^2\Sigma^+, v' = 0$ vibronic state of $^{16}$OH and to the 16 lowest $A$ levels in $^{16}$OD with an experimental uncertainty of a few tens of kHz, or a few parts in $10^{11}$ relative uncertainty. These measurements have enabled us to determine spectroscopic constants such as the $A^2\Sigma^+, v' = 0$ band origin and the rotational constant $B$ with orders of magnitude higher precision than previously possible.

I. EXPERIMENTAL SETUP

The experimental setup can be roughly divided into two major components: a precision laser system, which is used in this work to generate a frequency-stable, narrow-linewidth cw beam with a wavelength near 308 nm whose absolute frequency is known relative to atomic clock references, and a molecular beam apparatus for producing packets of rotationally-cold OH radicals in vacuum and detecting the fluorescence induced by the spectroscopy laser.

A. Precision laser system

A schematic diagram of the precision laser system is shown in figure 1. The foundation of the laser system is a short-term frequency reference based on a 1064-nm cw neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Coherent Mephisto 1000 NE), part of which is frequency doubled to 532 nm using a periodically-poled lithium niobate (PPLN) waveguide (NTT Electronics). Using a similar apparatus to that described by Dörringshof et al. [9], the laser’s optical frequency is stabilized to the $a_{10}$ component of the R(56) 32–0 transition in molecular iodine (I$_2$) using saturated absorption spec-
FIG. 1. Schematic overview of the precision laser system used to produce a tunable, narrow-linewidth 308-nm cw beam for spectroscopy of the low-lying $A-X$ transitions in OH/OD. The optical frequency of the UV source is stabilized to an $I_2$-referenced 1064/532-nm laser using an optical frequency comb as a transfer oscillator. The comb is also used to monitor the laser’s optical frequency relative to a local rubidium oscillator and a global navigation satellite system (GNSS) receiver, providing a record of its absolute optical frequency during the measurement.

An optical frequency comb is then stabilized to this optical frequency reference. The comb is based on a Ti:Sapphire femtosecond oscillator with a $\sim$1-GHz repetition rate (Taccor-6 from Laser Quantum) which is broadened to cover the spectral region from 1100 to 500 nm using a photonic crystal fiber module (NKT Femtowhite 800). The two degrees of freedom that determine the absolute frequency of every comb mode (commonly defined in terms of the repetition rate $f_r$ and the carrier-envelope offset frequency $f_0$ [10]) are stabilized to the iodine frequency reference using the combination of an optical beatnote between the comb and the 1064-nm beam and a beatnote between the comb and the 532-nm beam. Specifically, a pair of phase-locked loops ensure that one mode of the comb has an optical frequency exactly 100 MHz lower than the 1064-nm beam and that another comb mode is exactly 200 MHz lower in frequency than the 532-nm beam. These constraints force $f_0$ to be zero and result in a direct link between $f_r$ and $f_{532}$ given by

$$f_r = \frac{f_{532} - 200 \text{ MHz}}{2n},$$

where $n$ is an integer describing the number of comb modes between the 1064-nm and 532-nm frequencies. For the measurements shown in this paper, $n$ is either 281 630 (as shown in figure 1) or 281 631, resulting in a repetition rate of 1 000 000 006.1 Hz or 999 996 455.3 Hz, respectively. While the exact value of $f_r$ can vary over time, due to slight drifts of the iodine-locked optical reference, absolute accuracy is nonetheless achieved by recording the comb’s repetition rate on deadtime-free frequency counter. The counter is referenced to a rubidium oscillator (PRS10 from Stanford Research Systems) which is stabilized against long-term drifts using a pulse-per-second (PPS) signal from a global navigation satellite system (GNSS) receiver (PolaRx4TR PRO from Septentrio). The GNSS receiver also records data that can be used to reconstruct the phase error of the rubidium oscillator relative to GNSS time, enabling further post-correction of the frequency offset; for the precision of the current measurements, however, this extra step was not found to be necessary. Radio-frequency (rf) reference signals for stabilizing the various beatnotes are also derived from the rubidium oscillator, so any beatnote frequencies specified in this work (such as the “200 MHz” in equation 1) are defined relative to this reference.

The 308-nm spectroscopy laser is based on a tunable cw dye laser operating at 616 nm (Matisse 2 DR from Sirah GmbH) which is subsequently converted to 308 nm through second-harmonic generation (SHG) using a beta barium borate (BBO) crystal in an enhancement cavity (WaveTrain 2 from Sirah). The optical frequency of the dye laser is compared to the frequency comb using an optical beat note and stabilized with a tunable frequency offset (specified using a computer-controlled rf generator) to the nearest comb mode using a feedback loop that controls piezo mirrors on the dye laser’s cavity. To scan over each transition, the frequency of the rf generator is adjusted in 100 kHz steps over a typical span of between 16 and 25 MHz. Unfortunately, it is not possible to stabilize the dye laser’s optical frequency at every offset frequency between 0 and $f_r/2$: if the beatnote frequency is too low, there is ambiguity as to whether the laser’s frequency is higher or lower than the comb mode, and if it is too high, there is ambiguity between the beatnote with comb mode below and with the comb mode above the laser’s frequency. While the full range of beatnote frequencies could theoretically, with our 1-GHz comb, span from 0 to $\sim$500 MHz, the feedback loops can only operate properly when the offset frequency is between 50 MHz and 450 MHz. If the comb were only stabilized at the repetition rate corresponding to $n = 281 630$ (from equation 1), measuring certain transitions would require scans that, at least partially, overlap with the dead zones. Fortunately, all of the transitions that fall into dead zones for $n = 281 630$ end up with more favorable offset frequencies.
for $n = 281 \, 631$, so all transitions presented in this work could be measured using one of these two comb repetition rates.

**B. Molecular beam**

Figure 2 shows a schematic diagram of the molecular beam apparatus used in the experiment. The OH/OD molecules in the molecular beam are produced through photodissociation of (deuterated) nitric acid with an ArF excimer laser in a xenon-seeded pulsed supersonic molecular beam. Approximately 625 mm downstream, the molecules are excited by the 308-nm spectroscopy laser, emitting fluorescence which is detected by a photomultiplier tube (PMT). Near its source, the spectroscopy laser passes through a reflective attenuator (AT) and a 0.8-mm pinhole (PH), after which it travels approximately 2 m through free space, diverted only by flat mirrors. Immediately before entering the vacuum chamber, the laser is collimated by a 2-m focal length lens (L), and after exciting the chamber on the other side is retroreflected by a flat mirror (M). The retroreflected beam returns through the pinhole, reflects off the attenuator, and is detected on a photodiode (PD). By maximizing the intensity of the beam reaching the photodiode, the residual angle between the counterpropagating beams is minimized.

The expanding molecular beam passes through a 4-mm skimmer into a second differentially-pumped chamber containing the traveling-wave Stark decelerator described in [12]. This decelerator has a 4-mm wide circular profile and is approximately 480 mm long. For the current experiments, the decelerator electrodes are simply grounded, which results in a narrow transverse velocity spread in the molecular beam ($\sim 2.5 \, \text{m/s full width at half maximum}$) and ensures a negligibly-small electric field strength in the spectroscopy region at the expense of molecular density. After passing through the decelerator, the molecules interact with the 308-nm spectroscopy laser, producing fluorescence which is collected with a 50-mm fused silica lens and directed onto an on-axis photomultiplier tube (PMT, model 9829QSB from ET Enterprises). To reduce the intensity of the light from the photodissociation pulse that reaches the PMT, a UG5 color filter has been inserted just behind the collection lens and a UG11 filter directly in front of the PMT. The gain of the PMT is also suppressed for a 20-µs interval around the excimer laser pulse by switching the photocathode to a more positive potential than the first dynode.

The 308-nm laser originates from a small waist in the BBO crystal and travels approximately 2.3 meters before reaching the Brewster window at the entrance of the vacuum chamber. Immediately before entering the chamber, the beam is collimated with a 2-m focal length lens, resulting in an approximately 0.8 mm $\times$ 1.0 mm wide beam in the spectroscopy region. Inside the chamber, a total of four 5-mm circular light baffles (two before the spectroscopy region and two after) help to shield stray light from the photomultiplier. The beam exits the vacuum chamber through a second Brewster window and is retroreflected along the same path. Exciting the molecules using two beams exactly anti-parallel to one another helps to eliminate residual Doppler shifts due to a non-zero average velocity of the molecules along the propagation axis of the laser. To help ensure the retroreflected beam is as anti-parallel to the original beam as possible, a 0.8-mm circular aperture is placed approximately 27 cm after the source waist, or about 2 m before the collimating lens. The retroreflection is then adjusted in order to maximize the fraction of the returning beam that passes through the original aperture. Using this technique, we estimate that the offset between the outgoing and returning beams at the aperture can be reduced.
Measurements of individual transitions in OH and transition clusters in OD were carried out by scanning the frequency offset between the 616-nm laser and the nearest mode of the frequency comb in 100-kHz steps and recording the resulting fluorescence with a photomultiplier tube. At each frequency, the analog signal at the anode of the photomultiplier (with a 100-kΩ load to ground) was recorded on a digital oscilloscope from 1.0 to 3.8 ms after the excimer pulse with a resolution of 2 μs; measurements were averaged over 50 shots at a repetition rate of 10 Hz. A single scan results in a two-dimensional matrix of fluorescence intensity versus laser frequency and time delay after the excitation pulse. Scans over a single transition were repeated consecutively between 4 and 30 times, depending on the signal-to-noise ratio of a single measurement.

The resulting two-dimensional matrices from the repeated scans were then averaged into a single matrix. Since the frequencies in each scan correspond to fixed offsets from the nearest comb mode, these must first be converted to absolute frequencies using the formula

\[ f_{abs} = 2(nf_r + fb_n), \]

where \( n \) is an integer determined through frequency measurements with a wavemeter, \( fb_n \) is the beatnote frequency, and \( f_r \) is approximated as the average frequency of the comb’s repetition rate over the scan. This approximation preserves the 200-kHz spacing between individual lines in the frequency scan, but due to small drifts of the reference laser frequency from one scan to the next, each scan has a slightly different frequency offset. To account for these offsets, scans after first were shifted slightly in frequency, using linear interpolation between laser frequencies at each time delay, to match the offset in the first scan.

An example of the resulting averaged matrix, as well as a cut-through at a single laser frequency, are shown in figure 3. In addition to fluorescence from the packet of molecules (arriving at ~1.84 ms), there are background contributions at early times due to fluorescence resulting from the excimer pulse and a steady-state background due to scattering of the spectroscopy laser. To remove these background contributions, the entire time trace at each frequency is fit independently to a model containing 7 parameters: two for an exponential decay, two for a linear trend of the baseline (which likely contains one or more exponential decays with a long time constant), and three (amplitude, position, and width) for a Gaussian profile to describe the packet of molecules. The amplitude fitted to the Gaussian profile is then used to represent the fluorescence intensity at that frequency.

Figure 4 shows typical fluorescence intensity versus laser frequency curves for a single transition in OH and a single transition cluster in OD. For OH, all hyperfine transitions were separated by much more than the measured linewidth, so a single transition to each accessible \( A \)-state level, generally the strongest transition from the \( J'' = 3/2, \Omega'' = 3/2 \) ground state, was measured. With OD, however, most transitions were blended, due to a smaller ground-state hyperfine splitting, and it was necessary to scan over all allowed transitions from the multiple ground-state hyperfine levels to each excited-state hyperfine level. Fortunately, the ground-state splittings are quite well known (see section IV B), which simplified the subsequent analysis. Each transition or transition...
cluster was measured at least twice, on separate days, to ensure the measurements are reproducible.

III. SYSTEMATIC EFFECTS

In order to extract the line positions from these measurements, we must first account for possible systematic shifts to the observed line positions. In this section, we discuss what we consider to be the three largest systematic error sources in this experiment: the quality of the retroreflection of the spectroscopy laser, Zeeman shifts, and ac Stark shifts. While OH and OD are both equally affected by retroreflection quality, the effects of Zeeman and ac Stark shifts are larger in OD, due to its smaller hyperfine splittings.

A. Retroreflection quality

The transitions being measured are subject to Doppler shifts due to the motion of individual molecules along the spectroscopy laser’s propagation direction. While the laser’s propagation direction should, in principle, be perpendicular to the molecular beam, an error as small as 100 µrad (0.006°) would result in a shift of the measured transition frequency of 110 kHz. Such systematic Doppler shifts can be largely mitigated by retroreflecting the spectroscopy laser. For perfect retroreflection (i.e. a reflected beam that has the same intensity and profile as the original beam and is exactly anti-parallel), any systematic Doppler shifts for molecules excited by the outgoing beam will have the opposite sign in molecules excited by the retroreflected beam. If the reflected beam is not exactly anti-parallel, however, a small residual Doppler shift can remain.

As stated in section IB, a 0.8-mm aperture was placed near the laser source, and the pointing of the retroreflected beam was adjusted for maximum retransmission through the aperture. Including the effect of the 2-m collimation lens, an offset between the outgoing and returning beams at this aperture of 0.1 mm would correspond to an angle of 40 µrad between the two beams in the spectroscopy region, leading to a ~23-kHz shift of the measured transition frequency if the offset is along the direction of the molecular beam. Based on the sensitivity of the retroreflected signal to small transverse adjustments of the aperture position, as well as the precision with which we can reproducibly adjust the pointing of the mirrors along the beamline, the 0.1 mm and 40 µrad values were found to be reasonable estimates of the reproducibility of the retroreflection. Over the course of each measurement, the pointing was frequently reoptimized, leading to the magnitude and sign of this residual error to be continually randomized. Additionally, only offsets along the molecular beam direction result in a shift. Based on this, we estimate the overall contribution of pointing differences between the outgoing and returning beams to the measured transition frequencies to be less than 10 kHz.

A mismatch between the intensities of the outgoing and retroreflected beams can also potentially induce a shift in the measured transition frequencies. The returning beam must necessarily have a lower intensity than the outgoing beam due to losses in the retroreflection mirror and Brewster window. If the returning beam excites a different velocity class from the outgoing beam, the stronger weighting of excitation by the outgoing beam will result in a net shift. While the losses at the Brewster window are likely negligible, the retroreflection mirror in our setup has a UV-enhanced aluminum coating, which has a reflectance of only about 93% at 308 nm. To mitigate the influence of this effect, we measured select transitions both with and without the retroreflection beam and adjusted the angle of the spectroscopy laser such that no significant difference could be observed in the transition frequencies. After performing this alignment step, we estimate that the additional error contributed by the amplitude mismatch is less than 5 kHz and therefore assign an overall uncertainty due to retroreflection quality of 10 kHz.

B. Zeeman shifts

All measurements were conducted in the ambient magnetic field present in the laboratory, with no active compensation. Using Hall-effect probes (HMMT-6J04-VR and HMNA-1904-VR from Lake Shore Cryotronics), the field strength in the spectroscopy region was measured to be 74 µT in the vertical direction, 14 µT along the spectroscopy laser’s propagation direction, and 2 µT in the horizontal direction perpendicular to the spectroscopy laser. Since the laser’s polarization is horizontal, the magnetic field is almost exactly perpendicular to the laser’s polarization axis. The field measurements were carried out with a vented vacuum chamber through an open CF40 flange. To determine whether the turbulent molecular pumps and other devices that are running during the experiment affect the field, we measured the field at a fixed point just outside the chamber both with the pumps off and the pumps on and found no measurable change.

Since the magnetic field is, to good approximation, perpendicular to the laser polarization, the transitions observed are those with \( \Delta M_F = \pm 1 \). In the limit of a small magnetic field, the shifts of the \( \Delta M_F = +1 \) transitions would be equal and opposite to those of the \( \Delta M_F = -1 \) transitions, and the blended line would show no net shift. For larger shifts, however, the states can mix with other hyperfine components, resulting both in a deviation from the linear Zeeman shift and a change of the transition strength. Since one of the states will be shifted closer to the other hyperfine component while the other will be shifted further away, a non-zero net shift can appear.

To account for effect of the magnetic field, we made use...
of an effective Hamiltonian model computed by the pro-
gram PGOPHER \cite{13} to predict the expected spectrum. The zero-field parameters for the preliminary model were
determined by first estimating approximate line positions
through Gaussian fits of the measured spectra, ignoring
the Zeeman shifts, and then fitting the zero-field param-
eters to these line positions; the absolute line positions
predicted by this fit were within 300 kHz of the final
line positions. Zeeman terms were then included in the
Hamiltonian assuming a 75-μT magnetic field perpen-
dicular to the laser polarization and magnetic g-factors
of $g_l = 1$ for the orbital angular momentum in the elec-
tronic ground state, $g_S = 2.002$ for the electron spin, and
$g_r = 0$ for the rotational angular momentum. The mea-
sured traces were then fit to the calculated spectra using a
frequency offset, scaling factor, baseline offset, and, in the
case of OD, relative intensities of the blended hyperfine
components as free parameters. By combining the fit-
ted frequency offsets with the line positions predicted by
the preliminary fit, the zero-field transition frequencies
could be extrapolated. For OH, the difference between
the line positions extracted with this method and those
extracted with a simple Gaussian fit was quite small, at
most 12 kHz, but for OD, deviations as large as 280 kHz
(when compared to a multi-Gaussian fit) were observed.

C. AC Stark shifts

To estimate the shifts of the measured transition fre-
cuencies caused by the ac Stark effect, we consider the
coupling between a state involved in the transition being
measured and each of the nearby off-resonant hyperfine
state due to the spectroscopy laser’s time-varying (“al-
ternating current” or ac) electric field. For simplicity,
we ignore couplings due to other external fields and use
a two-state model (i.e. consider one perturbing state at
a time). Invoking the rotating-wave approximation and
assuming the coupling strength is much less than the
tuning results in a shift of the eigenenergies of

$$\Delta E = \pm \frac{I \mu_0 c^2}{2(E_A - E_X - h\nu)},$$

where $I$ is the laser intensity (power per unit area), $\mu_0 c$
is the impedance of free space (approximately 377 Ω); $\mu$
is the transition dipole moment of the perturbing transi-
tion, $E_A - E_X$ is the energy of the perturbing transition,
and $\nu$ is the photon energy of the ac field (which is
assumed to be on resonance with the transition being
measured). The prefactor is positive for the upper state
and negative for the lower state.

While the $M_F$ levels are degenerate in the absence of
an external field, the transition dipole moments depend
on the the $M_F$ quantum numbers and thus lead to a
breaking of this degeneracy. This dependence can be
expressed using the Wigner-Eckart theorem:

$$|\langle FM_F|T^1_q(\vec{\mu})|F'M_F\rangle|^2 \quad = \quad \left(\begin{array}{cc} F & 1 \\ -M_F & 0 \end{array}\right) \left(\begin{array}{cc} F' & 0 \\ 0 & M_F \end{array}\right) \left(\begin{array}{cc} F & 0 \\ 0 & M_F \end{array}\right)^2.$$  \hspace{1cm} (4)

This equation implicitly assumes a linearly polarized
laser field that defines the $M_F$ quantization axis. The square of the amplitude of the reduced matrix element,
$|\langle FM_F|T^1_q(\vec{\mu})|F'\rangle|^2$, can be calculated with the help of
PGOPHER \cite{13}. Specifically, if “HohlLondon” is chosen for
the “IntensityUnits” parameter and the correct value
is assigned to the “Strength” parameter of the $A - X$
transition moment, the “Strength” calculated for the in-
dividual transitions will correspond to $|\langle FM_F|T^1_q(\vec{\mu})|F'\rangle|^2$.
Based on the 688-ns lifetime for the $v' = 0, N' = 0$
excited state measured by German \cite{14}, the $A - X$
“Strength” parameter is determined to be

$$|\langle A, v' = 0|T^1_{q=\pm 1}(\vec{\mu})|X, v'' = 0\rangle|^2 = 0.2612 \text{D}^2.$$  \hspace{1cm} (5)

Because the ac Stark shift breaks the degeneracy be-
tween $M_F$ levels, we approximate the effective shift as
the $M_F$-state dependent shift weighted by the transition
strength. The weighted average of the $M_F$-dependent 3-j
symbol in equation (4) is given by

$$\sum_{M_F} \left(\begin{array}{cc} F'' & 1 \\ -M_F & 0 \end{array}\right)^2 \left(\begin{array}{cc} F & 1 \\ -M_F & 0 \end{array}\right)^2$$

$$\sum_{M_F} \left(\begin{array}{cc} F'' & 1 \\ -M_F & 0 \end{array}\right)^2 \left(\begin{array}{cc} F & 1 \\ -M_F & 0 \end{array}\right)^2
= \left\{ \begin{array}{cccc} 1 & 0 & 1 \\ F'' & F' & F \end{array} \right\} + 2 \left\{ \begin{array}{cccc} 1 & 0 & 1 \\ 0 & 1 & 0 \end{array} \right\}.$$  \hspace{1cm} (6)

Here, $F$ applies to the perturbing state (i.e. the state not
involved in the transition currently being measured), $F'$
to the state being perturbed, and $F''$ to the other state
in the transition. The $F$ and $F''$ labels apply to levels in
the same electronic state, while $F'$ corresponds to a level
in the other electronic state.

Combining equations (3) and (6) with the reduced matrix
elements and transitions frequencies calculated using
PGOPHER, we are able to estimate the expected ac
Stark shifts. For OH, these shifts are completely negli-
gible at our level of precision: the largest shift for all tran-
sitions could no longer be avoided, due to the blend-
ing of the measured transitions. The largest line-position
shifts are estimated to be $-9.4 \text{ kHz}$ at 1 mW/mm² (for $N' = 0$, $J' = 1/2$, $F' = 1/2 \leftarrow e, F'' = 1/2$), and based on the laser intensities used in the experiments, shifts as large as $23 \text{ kHz}$ could be expected. Since it was not feasible to include these shifts in the line-position fits directly, we instead estimated an extra contribution to the line position uncertainty by computing the product of the largest line position shift in each cluster and the highest laser intensity with which the cluster was measured.

### IV. ANALYSIS

#### A. Zero-field line positions

The zero-field transition frequencies resulting from the fits described in section III B are summarized in Table I for OH and Table II for OD. All transitions originate from the $X^2 \Pi_{3/2}, v'' = 0$, $J'' = 3/2$ rovibronic ground state. The $p''$ and $F''$ columns indicate the ground-state parity and $F$ quantum number, respectively, while the $N'$, $J'$, and $F'$ columns indicate the excited-state $(A^2 \Sigma^+, v' = 0)$ quantum numbers. One standard deviation statistical uncertainties are indicated, in units of the last digit, next to the frequency, and deviations between the observed and calculated (see section IV B) transition frequencies are shown in the last column. Due to multiple blended transitions being fit simultaneously, all transitions in OD are shown as if they originated from an $F'' = 1/2$ level, even if this transition would be forbidden by angular momentum selection rules.

#### B. Effective Hamiltonian fit

The measured transitions were fit to an effective molecular Hamiltonian by varying the $A$-state parameters to minimize the root mean square residuals. The effective Hamiltonian used in this work follows, where possible, the linear molecule terms of the 1994 IUPAC recommendation for fine and hyperfine structure parameters [15], and the quantum numbers follow the 1997 IUPAC recommendation on notations and conventions in molecular spectroscopy [16]. The rotational part of the Hamiltonian (which is not defined in the IUPAC recommendations) follows the $N^2$ convention, i.e.

\[
\hat{H}_\text{rot} = B \hat{N}^2 - D \hat{N}^4 + H \hat{N}^6 + L \hat{N}^8 + M \hat{N}^{10} + P \hat{N}^{12} + Q \hat{N}^{14}.
\]

Centrifugal distortion terms are similarly described in terms of anti-commutators with powers of $\hat{N}$. For example, the spin-orbit Hamiltonian, including centrifugal distortion terms, is given by

\[
\hat{H}_\text{so} = A[\hat{N}^2, \Lambda \Sigma]_+ + A_D[\hat{N}^4, \Lambda \Sigma]_+ + A_H[\hat{N}^6, \Lambda \Sigma]_+ + \cdots
\]

The fitting procedures were carried out using PGOPHER [13], whose definitions of the spectroscopic constants generally match those described above.

To model the structure of the $X^2 \Pi_{3/2}, v'' = 0$ ground state, we rely on the comprehensive global fit carried out by B. J. Drouin [17], which distills the large body of microwave, pure rotational, and rovibrational spectroscopy that has been carried out on the various isotopologues of OH into a single set of Dunham parameters. For our analysis, it was more convenient to convert the Dunham parameters to two separate parameter sets that describe a single vibronic state of each isotopologue, as summarized in Table III. All transitions measured originate from the various $A$-doublet and hyperfine components of the $N'' = 3/2$, $J'' = 3/2$ rotational state. For OH, the model yields a term value of the absolute ground state ($e$, $F'' = 1$) of $-589 504.229 \text{ MHz}$, with the other levels $53.171 \text{ MHz}$ ($e$, $F'' = 2$), $1665.402 \text{ MHz}$ ($f$, $F'' = 1$), and $1720.530 \text{ MHz}$ ($f$, $F'' = 2$) higher in energy. For OD, the term value of the absolute ground state ($e$, $F'' = 1/2$) is $-1250 744.792 \text{ MHz}$, with the other levels $7.112 \text{ MHz}$ ($e$, $F'' = 3/2$), $19.229 \text{ MHz}$ ($e$, $F'' = 5/2$), $310.143 \text{ MHz}$ ($f$, $F'' = 1/2$), $317.320 \text{ MHz}$ ($f$, $F'' = 3/2$), and $329.591 \text{ MHz}$ ($f$, $F'' = 5/2$) higher.

### Table I. Measured transition frequencies for OH.

| $p''$ | $F''$ | $N'$ | $J'$ | $F'$ | Frequency [MHz] | $O - C$ [kHz] |
|-------|-------|------|------|------|----------------|----------------|
| 1     | 1     | 0    | 1/2  | 0    | 972.543.544.509(28) | 2              |
| 2     | 2     | 0    | 1/2  | 1    | 972.544.263.408(23) | −6             |
| 3     | 3     | 1    | 1/2  | 1    | 973.552.523.087(20) | 2              |
| 4     | 4     | 1    | 1/2  | 0    | 973.552.777.983(25) | −2             |
| 5     | 5     | 1    | 3/2  | 1    | 973.562.502.971(20) | 2              |
| 6     | 6     | 2    | 3/2  | 2    | 973.562.933.797(27) | 11             |
| 7     | 7     | 2    | 3/2  | 2    | 975.583.190.510(91) | 10             |
| 8     | 8     | 2    | 3/2  | 1    | 975.583.518.551(31) | −19            |
| 9     | 9     | 1    | 5/2  | 2    | 975.600.025.281(27) | 2              |
| 10    | 10    | 2    | 5/2  | 3    | 975.600.407.630(73) | 29             |
| 11    | 11    | 2    | 5/2  | 3    | 978.623.067.785(31) | −12            |
| 12    | 12    | 3    | 5/2  | 2    | 978.623.423.607(22) | 7              |

### Table II. Measured transition frequencies for OD.

| $p''$ | $F''$ | $N'$ | $J'$ | $F'$ | Frequency [MHz] | $O - C$ [kHz] |
|-------|-------|------|------|------|----------------|----------------|
| 1     | 1/2   | 0    | 1/2  | 0    | 975.191.515.238(45) | −30            |
| 2     | 1/2   | 0    | 1/2  | 1    | 975.191.328.951(23) | 7              |
| 3     | 1/2   | 1    | 1/2  | 1    | 975.729.510.744(17) | −1             |
| 4     | 1/2   | 1    | 1/2  | 2    | 975.729.554.332(74) | 34             |
| 5     | 1/2   | 1    | 3/2  | 1    | 975.734.851.195(42) | 44             |
| 6     | 1/2   | 1    | 3/2  | 2    | 975.734.909.692(47) | −61            |
| 7     | 1/2   | 1    | 3/2  | 3    | 975.735.004.075(21) | 1              |
| 8     | 1/2   | 2    | 3/2  | 5    | 976.811.945.283(35) | −13            |
| 9     | 1/2   | 2    | 3/2  | 3    | 976.811.996.638(37) | 12             |
| 10    | 1/2   | 2    | 3/2  | 1    | 976.812.027.966(64) | 294            |
| 11    | 1/2   | 2    | 3/2  | 2    | 978.820.927.100(43) | 23             |
| 12    | 1/2   | 2    | 5/2  | 2    | 978.820.984.312(36) | −54            |
| 13    | 1/2   | 2    | 5/2  | 2    | 978.821.062.952(21) | 14             |
| 14    | 1/2   | 2    | 5/2  | 2    | 978.834.704.049(25) | 35             |
| 15    | 1/2   | 2    | 5/2  | 2    | 978.834.756.836(33) | −25            |
| 16    | 1/2   | 2    | 5/2  | 3    | 978.834.794.761(38) | −45            |

* Observation excluded from effective Hamiltonian fit
The previous best values of the $A - X$ transition frequencies in OH and OD come from Stark et al. [8], as well as from two earlier papers by Coxon [6,7]. Additionally, for OH, ter Meulen et al. [18] have measured several of the $A$-state spin-rotation splittings with high precision using microwave double-resonance spectroscopy, and for OD, numerous authors have measured the $A$-state hyperfine splittings [19-21]. Since we have only been able to measure transitions to the lowest rotational states, we have augmented our effective Hamiltonian fits with information from these previous works, which include transitions to higher rotational levels. In particular, we have fixed the values for $H$, $L$, $M$, and $\gamma_H$ to those given by Coxon [7] for OH and those given by Stark et al. [8] for OD. For OH, we have combined our 12 measurements with the 8 given by ter Meulen et al. [18] into a single global fit, and for OD, we have included the $A$-state hyperfine splittings measured by Carter et al. [20], as well as those measured by Xin et al. [21].

While all OH transitions measured in this work (as well as all transitions from ter Meulen et al.) were included in the effective Hamiltonian fit, three OD splittings were excluded as outliers (residuals of more than 3$\sigma$). These splittings are transition #10 from this work, $N = 3, J = 7/2, F' = 9/2 \leftrightarrow F'' = 7/2$ from Carter et al., and $N = 1, J = 3/2, F' = 3/2 \leftrightarrow F'' = 1/2$ from Xin et al. There is no indication that any of these anomalies are the result of a deviation between the actual splittings and the effective Hamiltonian model, since the splittings in other data sets that involve the same levels as those in the anomalous splittings do not show any significant deviations from the values predicted by the effective Hamiltonian fit. (The levels involved in the outlier from Carter et al., however, are not sampled in any of the other data sets.) In the case of transition #10 from this work, a large deviation is being heavily blended.

Tables IV and V summarize the $A^2\Sigma^+, v' = 0$ parameters for OH and OD, respectively, calculated in this work and those from other works based on measurements of

### Table III. Parameters for the $X^2\Pi_{3/2}, v'' = 0$ ground state, in MHz, derived from the global fit by B. J. Drouin [17]

|          | $^1$OH | $^1$OD |
|----------|--------|--------|
| $B$      | 555661.4693 | 296158.6891 |
| $D$      | 57.229 288.3 | 16.143 28 |
| $H \times 10^3$ | 4.281 065 6 | 0.6400 |
| $L \times 10^9$ | -448.6944 | -35 |
| $M \times 10^{12}$ | 33.315 | 1.3 |
| $P \times 10^{18}$ | -838.20 | -6.0 |
| $Q \times 10^{21}$ | -796.21 | -9.4 |

### Table IV. Fitted parameters for the $A^2\Sigma^+, v' = 0$ state of $^1$OH, in MHz.

|          | This work | Stark et al. [8] | Coxon [7] |
|----------|-----------|------------------|-----------|
| $T$      | 971954529.3367(92) | 971954376(3) | 971954664(54) |
| $B$      | 508601.5755(48) | 508603.2686(66) | 508599(2) |
| $D$      | 61.87563(38) | 61.8903(36) | 61.853(15) |
| $H \times 10^3$ | 3.65 | 3.82(11) | 3.687(44) |
| $L \times 10^9$ | -0.41 | -0.60 | -0.412(57) |
| $M \times 10^{10}$ | -0.11 | -0.021 | -0.109(27) |
| $\gamma$ | 6777.8146(84) | 6775.74(18) | 6762(10) |
| $\gamma_D$ | -1.43445(67) | -1.379(11) | -1.430(54) |
| $\gamma_H \times 10^3$ | 0.2 | 0.069 | 0.228(60) |
| $b_F$    | 772.124(20) |               |           |
| $c$      | 161.927(52) |               |           |
| $c_I$    | -0.0458(59) |               |           |

### Table V. Fitted parameters for the $A^2\Sigma^+, v' = 0$ state of $^1$OD, in MHz.

|          | This work | Stark et al. [8] | Coxon [7] |
|----------|-----------|------------------|-----------|
| $T$      | 973940524.927(20) | 973940470(3) | 973940860(60) |
| $B$      | 271124.825(11) | 271123.980(48) | 271117.4(36) |
| $D$      | 17.3445(14) | 17.3428(13) | 17.2758(78) |
| $H \times 10^3$ | 0.54 | 0.561(36) | 0.4932(84) |
| $L \times 10^9$ | -3.4 | -39 | -18.04(2) |
| $M \times 10^{12}$ | -2.1 | -2.1 | -3.51(87) |
| $\gamma$ | 3614.160(20) | 3616.72(14) | 3600.6(6) |
| $\gamma_D$ | -0.4062(55) | -0.4011(66) | -0.3580(72) |
| $\gamma_H \times 10^6$ | 1 | 13 |           |
| $b_F$    | 118.454(21) |               |           |
| $c$      | 24.899(59) |               |           |
| $c_I$    | -3.7 |               |           |
| $c_{Qq_0}$ | 0.269(24) |               |           |

$^a$ Parameter held fixed at value from Coxon [7]

$^b$ Value from our OH fit, scaled by reduced mass ratio and proton-deuteron g-factor ratio (in total, approximately 0.08136)

$^c$ Represents difference between $M$ in excited and ground states.
electronic transitions. Because the previous articles use slightly different definitions of the effective Hamiltonian, their parameters have been adjusted to match our definition. For the A state, the other articles define the centrifugal distortion constants for $\gamma$ in terms of $J^2$ instead of $\hat{N}^2$. Accounting for this requires modifying the parameters as follows:

$$B = B_{\text{prev}} + \gamma_{D,\text{prev}}/2 + \gamma_{H,\text{prev}}/4$$  \hspace{1cm} (9)
$$D = D_{\text{prev}} - \gamma_{H,\text{prev}}$$  \hspace{1cm} (10)
$$\gamma = \gamma_{\text{prev}} - \gamma_{D,\text{prev}}/4 + \gamma_{H,\text{prev}}/16$$  \hspace{1cm} (11)
$$\gamma_D = \gamma_{D,\text{prev}} + \gamma_{H,\text{prev}}/2$$  \hspace{1cm} (12)

In order to compare the values given for the $A\,^2\Sigma^+$, $v' = 0$ band origin, the ground state effective Hamiltonian must be considered as well. Stark et al. [8] and the OD paper from Coxon [6] use a ground state Hamiltonian based on a Van Vleck transformation of a Hamiltonian containing a unique perturbing $^2\Sigma^+$ state (for which matrix elements are given in [23]), while the OH paper from Coxon [7] uses a Hamiltonian derived using spherical tensor methods, with an $\hat{R}^2$ rotational Hamiltonian [24]. With the Hamiltonians used by Stark et al. and in Coxon’s OH paper, the A-state band origin can be approximately converted to our notation using the formula

$$T' = T'_{\text{prev}} + B''_{\text{prev}} + D''_{\text{prev}}.$$  \hspace{1cm} (13)

The Hamiltonian used in Coxon’s OD paper includes an additional $A$-doubling $o$ parameter, so the band origin from this work has been converted [25] using the formula

$$T' = T'_{\text{prev}} + B''_{\text{prev}} + D''_{\text{prev}} - o''_{\text{prev}}/2.$$  \hspace{1cm} (14)

In equations [13] and [14] parameters with a single prime refer to $A$-state parameters, while those with a double prime refer to $X$-state parameters.

Based solely on the uncertainties quoted in the previous works, our fits have determined the $A$-state band origins with at least two orders of magnitude higher precision and the rotational constant $B$ with approximately one order of magnitude higher precision. It should be noted, however, that the band origins and rotational constants given by these previous works often differ from our values by much more than the stated uncertainties should allow. In the case of Stark et al. [8], the band origins for OH and OD differ from our values by 51$\sigma$ and 18$\sigma$, respectively, while the rotational constants $B$ differ by 25$\sigma$ and 18$\sigma$, respectively. While there is some ambiguity in the conversion of the $A$-state band origins, using another method for the conversion (based on the difference of the term values of the absolute ground state in the two models, ignoring hyperfine effects) only resulted in larger discrepancies. While it is difficult to say with certainty why the deviation is so large, we suspect some combination of a pressure shift due to the 2.2-Torr of helium in the discharge source used in the previous work, as well as errors in the absolute positions of the Fe I lines used for calibration [26].

The parameters determined in the previous hyperfine-resolved studies [18, 20, 21] generally show much better agreement with those presented here. The $b_F$, $c$ and $\gamma$ parameters in ter Meulen et al. [15] agree with our parameters for OH to within two standard deviations; while $\gamma_D$ differs by 3.7$\sigma$, this discrepancy could be due to the inclusion of a $\gamma_H$ parameter in this work, which was absent in the previous source. The $b_F$, $c$, and $\epsilon Q_{\theta}$ parameters for OD reported by Carter et al. [20] also agree to within two standard deviations, while those in Xin et al. [21] differ by less than 1$\sigma$. A high level of agreement should not be surprising, since the data from all of these works has been included in our parameter fits. For the same reason, the values reported here also have a slightly smaller uncertainty than those reported previously.

V. CONCLUSIONS

The results presented in this work represent some of the most precise Doppler-broadened measurements of molecular electronic transitions to date, comparable in relative precision to the recent measurements of the P7 P7 $B$-band transition in O$_2$ by Bielska and coworkers [27]. By measuring all experimentally-accessible transitions from the rovibronic ground state, we have also been able to determine the A-state spectroscopic constants, particularly the band origin and rotational constants, with far higher precision than in previous measurements. Fitting multiple measured transitions to an effective Hamiltonian model also serves as a cross-check of the measurement precision of the individual transition frequencies.

We expect that the experimental precision can be improved by an additional order of magnitude by canceling the residual magnetic fields and measuring the transition frequencies with Doppler-free saturation spectroscopy. Future work will also focus on measuring transitions to higher vibrational levels of the A state. With sufficient data, we can hopefully start to construct a global model of the $A\,^2\Sigma^+$ electronic state, similar to the one produced by Drouin for the $X\,^2\Pi$ ground state.

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