Dipole moment transitions in OH: theory

We study theoretically electric and magnetic dipole transitions in the OH radical from the electronic, vibrational, and rotational ground state ($X\,^2\Pi_{3/2}, J = 3/2, v = 0$) to the first electronically and vibrationally excited state ($A\,^2\Sigma^+, J = 1/2, v = 1$).

I. EXPERIMENTAL SITUATION

We consider Stark-decelerated molecules in the $X\,^2\Pi_{3/2}, J = 3/2, v = 0, f$ state, where $X\,^2\Pi_{3/2}$ designates the electronic ground state of OH for which $|\Omega| = 3/2$ is a nearly good quantum number. This is also called the F_1 spin-orbit manifold in the main text. Moreover, J is the eigenvalue of the angular momentum operator $\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}} + \hat{\boldsymbol{R}}$ with $\hat{\boldsymbol{L}}$ the electronic orbital angular momentum, $\hat{\boldsymbol{S}}$ the electronic spin, and $\hat{\boldsymbol{R}}$ the nuclear rotation, while v is the vibration quantum number and Ω is the projection quantum number of $\hat{\boldsymbol{J}}$ on the OH bond axis. Using microwave transitions also the $X\,^2\Pi_{3/2}, J = 3/2, v = 0, e$ state is populated, where the e and f labels denote the so-called spectroscopic parity. We are interested in magnetic and electric dipole transitions from the two rovibronic ground states of different parity to the first electronically excited $A\,^2\Sigma^+, J' = 1/2, v' = 1$ state. Since the latter state has $+$ parity upon inversion, electric dipole transitions are possible from the e ground state with $-$ parity and magnetic dipole transitions are possible from the f ground state with $+$ parity. Since the nuclear spin of OH is given by $I = 1/2$, we have a total angular momentum $F = 1$ or $F = 2$ prior to the dipole transitions, and $F = 0$ or $F = 1$ after the transitions.

As explained in the main text, great care was taken experimentally to control the polarization of the laser and the direction of the externally applied magnetic field. In the laboratory frame the x direction is parallel to the laboratory floor in the direction of the molecular beam. The z direction is the vertical direction in the laboratory, and in this direction the PMT is mounted. The right-handedness of the coordinate system then fixes the y axis. The magnetic field and the laser polarization are along the z-axis, while the propagation of the laser is in the y direction, see also Fig. 1 of the main text. After the Stark deceleration process, the molecules are initially all in the $X\,^2\Pi_{3/2}, J = 3/2, v = 0, f, F = 2$ state with the five M_F states equally populated. These states are thus populated with a fraction of 20%. Next, 2.5% of the molecules in the $M_F = 0$ state (i.e., 0.5% of the total amount of decelerated molecules) is pumped via a microwave transition to one of the three $X\,^2\Pi_{3/2}, J = 3/2, v = 0, e, F = 1, M_F$ states. All three possibilities, namely $M_F = 0, \pm 1$, are separately studied experimentally.

After the pumping, the electric and the magnetic dipole transitions are investigated. The magnetic dipole moment transitions take place from the $X\,^2\Pi_{3/2}, J = 3/2, v = 0, f, F = 2, M_F$ states, of which four levels ($M_F = \pm 1, \pm 2$) are occupied by 20% of the molecules and one level ($M_F = 0$) is occupied by 19.5%. The electric dipole moment transitions take place from a $X\,^2\Pi_{3/2}, J = 3/2, v = 0, e, F = 1, M_F$ state, for which we distinguish three different experimental cases. Case 1: 0.5% of the molecules are in the $M_F = 0$ state, case 2: 0.5% of the molecules are in the $M_F = 1$ state, case 3: 0.5% of the molecules are in the $M_F = -1$ state. In all three cases, the other M_F states of the ground state with spectroscopic e parity are unpopulated. Next, we show that, as a result, there are two independently measured intensity ratios. Namely, the ratio of the two different electric dipole transitions (case 2 and 3 have the same strength), and the ratio between the magnetic and the electric dipole transition strength. In the next sections, we calculate these ratios from first principles.

II. THEORY

The transition dipole moments were calculated with the MOLPRO [1] program package at the internally contracted multireference singles and doubles excitation configuration interaction (icMRSDCI) level. The orbitals were obtained with a state-averaged complete active space self-consistent-field (CASSCF) calculation employing the aug-cc-pVQZ one electron basis [2]. The active space contained the full valence space, the (1s) core orbital on the O atom and extra MOs of each symmetry. The C$_{2v}$ point group symmetry was used and the active space consisted of six a_1, three b_1, three b_2, and three a_2 orbitals. To determine the magnetic transition dipole moment, we calculated the matrix elements of the magnetic dipole moment operator $\hat{\boldsymbol{\mu}}_{\mathrm{mag}} = -\mu_{\mathrm{B}}\hat{\boldsymbol{L}}$ with the Bohr magneton $\mu_{\mathrm{B}} = 1/2$ in atomic units. The spin operator $\hat{\boldsymbol{S}}$ does not couple a Σ state to a Π state and hence does not contribute to the magnetic dipole transition moment. Since the transition dipole moments depend on the OH bond length r, we used a grid of 37 points ranging from $r = 1.2\ a_0$ to $r = 2.8\ a_0$, with extra points lying around the center of the grid. In order to determine the matrix elements for the transition dipole moments, we also needed the vibrational ground state of the $X\,^2\Pi$ potential, and the first vibrationally excited state of the $A\,^2\Sigma^+$ potential. We used the electronic potentials determined by Van

der Loo and Groenenboom [3], and calculated the vibrational states using the discrete variable representation (DVR) method based on sinc-functions [4]. Having performed all these calculations, we were able to determine the electric transition dipole moment in the body-fixed frame $\langle \mu_{\mathrm{el}}^{\mathrm{bf}} \rangle$ (the frame with its z axis along the OH bond vector), namely

$$\langle \mu_{\mathrm{el}}^{\mathrm{bf}} \rangle \equiv |\langle A\,^2\Sigma^+, v' = 1 | \hat{\boldsymbol{\mu}}_{\mathrm{el}} | X\,^2\Pi, v = 0 \rangle|. \tag{1}$$

The magnetic transition dipole moment $\langle \mu_{\mathrm{mag}}^{\mathrm{bf}} \rangle$ is defined in a similar way. We find that $|\langle \mu_{\mathrm{el}}^{\mathrm{bf}} \rangle| = 0.05249$ and $|\langle \mu_{\mathrm{mag}}^{\mathrm{bf}} \rangle| = 0.1417$ in atomic units. The body-fixed transition dipole moments only have components perpendicular to the OH bond axis for the $\Pi \to \Sigma$ transition. Introducing the projection of the electric transition dipole moment on the body-fixed z axis, $\mu_{\mathrm{el},k}^{\mathrm{bf}}$, we have that

$$\mu_{\mathrm{el},\pm 1}^{\mathrm{bf}} = i \frac{\langle \mu_{\mathrm{el}} \rangle}{\sqrt{2}} \qquad \text{and} \qquad \mu_{\mathrm{mag},\pm 1}^{\mathrm{bf}} = \mp \frac{\langle \mu_{\mathrm{mag}} \rangle}{\sqrt{2}}, \tag{2}$$

and in both cases $\mu_{\mathrm{el/mag},0}^{\mathrm{bf}} = 0$.

In the experiment, care is taken to polarize the laser in the space-fixed laboratory frame. As a result, in order to treat the interaction of the transition dipole moments with the laser field, we need to transform the transition dipole moments from the body-fixed to the space-fixed frame. The corresponding space-fixed transition dipole moments are given by

$$\mu_{\mathrm{el/mag},m}^{\mathrm{sf}} = \sum_k \mu_{\mathrm{el/mag},k}^{\mathrm{bf}} D_{mk}^{(1)*}(\phi, \theta, 0), \tag{3}$$

with ϕ and θ the polar angles of the OH bond axis in the space-fixed frame, and $D_{mk}^{(j)}(\alpha, \beta, \gamma) = e^{-im\alpha} d_{mk}^{(j)}(\beta) e^{-ik\gamma}$ with $d_{mk}^{(j)}(\beta)$ the Wigner d functions. To proceed, we first consider basis states for the OH radical that are not yet parity adapted and not mixed due to the presence of spin-orbit coupling. We consider the states $|\Lambda, S, \Omega, J, I, F, M_F\rangle$ with Λ the projection of the electronic angular momentum on the body-fixed axis, where J and I are coupled to F according to

$$|\Omega, J, I, F, M_F\rangle = \sum_{M_I, M_J} |J, \Omega, M_J\rangle |I, M_I\rangle \langle J, M_J, I, M_I | F, M_F \rangle, \tag{4}$$

where M_J, M_I, and M_F are the projections of the corresponding angular momenta on the space-fixed z axis. Moreover, $\langle J, M_J, I, M_I | F, M_F \rangle$ are the Clebsch-Gordan coefficients. The rotational wave functions are given by

$$|J, \Omega, M_J\rangle = \sqrt{\frac{2J+1}{4\pi}} D_{M_J, \Omega}^{(J)*}(\phi, \theta, 0). \tag{5}$$

For these states, we find

$$\langle J', \Omega', M_J' | D_{mk}^{(1)*} | J, \Omega, M_J \rangle = \sqrt{\frac{2J+1}{2J'+1}} C_{J,\Omega,1,k}^{J',\Omega'} C_{J,M_J,1,m}^{J',M_J'}, \tag{6}$$

with the shorthand notation $C_{J,M_J,I,M_I}^{F,M_F} = \langle J, M_J, I, M_I | F, M_F \rangle$. Using the following relation

$$\sum_{M_J, M_J', M_I} C_{J,M_J,1,m}^{J',M_J'} C_{J,M_J,I,M_I}^{F,M_F} C_{J',M_J',I,M_I}^{F',M_F'} = \sqrt{(2J'+1)(2F+1)}(-1)^{I+F+J'+1} C_{F,M_F,1,m}^{F',M_F'} \begin{Bmatrix} J & I & F \\ F' & 1 & J' \end{Bmatrix}, \tag{7}$$

with the curly brackets denoting the 6-j symbol, we obtain

$$\langle {}^2\Sigma^+, J', I', F', M_F' | \mu_{\mathrm{el/mag},m}^{\mathrm{sf}} | {}^2\Pi_\Omega, J, I, F, M_F \rangle = \delta_{I',I}(-1)^{I-J+J'+1-\Omega'-M_F'}$$
$$\times \sqrt{(2J+1)(2J'+1)(2F+1)(2F'+1)} \begin{Bmatrix} J & I & F \\ F' & 1 & J' \end{Bmatrix} \sum_k \mu_{\mathrm{el/mag},k}^{\mathrm{bf}} \begin{pmatrix} J & 1 & J' \\ \Omega & k & -\Omega' \end{pmatrix} \begin{pmatrix} F & 1 & F' \\ M_F & m & -M_F' \end{pmatrix}, \tag{8}$$

with the round brackets denoting the 3-j symbol. Equation (8) is valid for both the electric and the magnetic transition dipole moment.

For the parity adaptation, we consider first the Π state with $J = 3/2$ and $I = 1/2$, namely

$$|{}^2\Pi_{\pm\Omega}, F, M_F\rangle = |\Lambda = \pm 1, S = 1/2, \pm\Omega, J = 3/2, I = 1/2; F, M_F\rangle, \tag{9}$$

where $\Omega = 1/2$ or $3/2$. The parity adaptation is then performed as follows,

$$|{}^2\Pi_{|\Omega|}, F, M_F, \epsilon = \pm\rangle = (|{}^2\Pi_\Omega, F, M_F\rangle \pm |{}^2\Pi_{-\Omega}, F, M_F\rangle)/\sqrt{2}, \tag{10}$$

where the $\epsilon = +$ corresponds to spectroscopic e parity, while the $-$ corresponds to spectroscopic f parity. The relative sign in the wave function, ϵ, is related to the parity under inversion p by $p = \epsilon(-1)^{J-S}$. Due to the large and negative spin-orbit constant $A = -139.73$ cm^{-1}, Ω is almost a good quantum number, and the state with approximately $\Omega = 3/2$ is the ground state. We denote the latter by $F_1{}^2\Pi_{3/2}$, and it is given by

$$|F_1{}^2\Pi_{3/2}, F, M_F, \epsilon\rangle = c_{1/2}|{}^2\Pi_{1/2}, F, M_F, \epsilon\rangle + c_{3/2}|{}^2\Pi_{3/2}, F, M_F, \epsilon\rangle, \tag{11}$$

where $c_{1/2} = \sqrt{(X+Y-2)/2X}$ and $c_{3/2} = \sqrt{(X-Y+2)/2X}$ with $X = \sqrt{4(J+1/2)^2 + Y(Y-4)}$ and $Y = A/B$, see e.g. [5]. For the rotational constant, we used $B = 18.515$ cm^{-1}. The final state in the experiment is of $+$ parity. Moreover, for this state we have $J' = 1/2$ and $I' = 1/2$, so that $F' = 0$ or 1. The corresponding parity adapted wave function is given by

$$|{}^2\Sigma^+, F', M_F', +\rangle = (|{}^2\Sigma^+_{1/2}, F', M_F'\rangle + |{}^2\Sigma^+_{-1/2}, F', M_F'\rangle)/\sqrt{2}, \tag{12}$$

where on the right-hand side also $\Lambda' = 0$ and $S' = 1/2$ are implied.

By combining Eqs. (8), (11), and (12), we obtain for the transition dipole moment

$$\langle {}^2\Sigma^+, F', M_F', +|\mu^{\text{sf}}_{\text{el/mag},m}|F_1{}^2\Pi_{3/2}, F, M_F, \epsilon\rangle = \sqrt{(2J+1)(2J'+1)(2F+1)(2F'+1)}$$
$$\times (-1)^{I-J+1-M_F'} \begin{Bmatrix} J & I & F \\ F' & 1 & J' \end{Bmatrix} \begin{pmatrix} F & 1 & F' \\ M_F & m & -M_F' \end{pmatrix} \sum_{\Omega',\Omega,k} \frac{c_\Omega \epsilon^{\vartheta(\Omega)}}{2}(-1)^{J'-\Omega'}\mu^{\text{bf}}_{\text{el/mag},k} \begin{pmatrix} J & 1 & J' \\ \Omega & k & -\Omega' \end{pmatrix}, \tag{13}$$

where as before $J = 3/2$, $I = 1/2$, $J' = 1/2$, and $I' = 1/2$. Moreover, $\epsilon = \pm 1$, $\vartheta(x)$ is the step function, and we need to sum over $\Omega' \in \{\pm 1/2\}$ and $\Omega \in \{\pm 1/2, \pm 3/2\}$. The factor $\epsilon^{\vartheta(\Omega)}$ contains $\vartheta(-\Omega) = 0$ for $\Omega > 0$ and $\vartheta(-\Omega) = 1$ for $\Omega < 0$. It is present because for $\epsilon = +1$ (e symmetry) we have the positive combination in Eq. (10), while for $\epsilon = -1$ (f symmetry) we have a sign change for negative Ω. The expression in Eq. (13) is valid for both the magnetic and the electric transition. As follows from Eq. (2), the two transition dipole moments have a different k dependence, since the magnetic transition dipole moment changes sign when k changes sign, while the electric transition dipole moment does not. As a result, the sum on the right-hand side of Eq. (13) leads to the correct parity selection rules for the magnetic ($p = + \to +$) and electric dipole transitions ($p = - \to +$).

III. COMPARISON OF THEORY WITH EXPERIMENT

In section I, we distinguished between three different experimental cases for the electric dipole transition, characterized by the three different M_F states of the $X{}^2\Pi_{3/2}$, $J = 3/2$, $v = 0$, e, $F = 1$ state after the microwave transition. The electric dipole transition strength to the $A{}^2\Sigma^+$, $J' = 1/2$, $v' = 1$ state was determined experimentally for these three cases separately. By the symmetry of the experiment, case 2 with $M_F = 1$ and case 3 with $M_F = -1$ are equivalent. Moreover, since the experimental results are in arbitrary units, we can thus compare only a single ratio of the two inequivalent electric dipole intensities with theory. Since the electric field of the laser is in the space-fixed z direction, it couples to the z component of the space-fixed transition dipole moment, so that $m = 0$. Looking at Eq. (13), we find that the two inequivalent cases only differ in the value of the conserved M_F and the final angular momentum F', where only $F' = 0$ gives a nonzero contribution for case 1 and only $F' = 1$ for case 2 (and 3). We note that the part of Eq. (13) that depends on F', M_F, and M_F' is given by

$$\xi(\text{case}) = \sqrt{2F'+1}(-1)^{-M_F'} \begin{Bmatrix} J & I & F \\ F' & 1 & J' \end{Bmatrix} \begin{pmatrix} F & 1 & F' \\ M_F & m & -M_F' \end{pmatrix}, \tag{14}$$

where $J = 3/2$, $J' = 1/2$, $I = 1/2$, $F = 1$ and $m = 0$ for the electric dipole transition. For case 1, we have $F' = 0$ and $M_F = M_F' = 0$, while for case 2 we have $F' = 1$ and $M_F = M_F' = 1$. As a result, we find the ratio between the two electric dipole transition strengths analytically as the ratio of the squares of the two transition dipole moments, resulting in

$$\text{signal ratio} = \frac{\xi(\text{case }1)^2}{\xi(\text{case }2)^2} = 4. \tag{15}$$

This is because all other terms of Eq. (13) drop out of the ratio. Also other quantities as the laser intensity and the molecular density drop out of the ratio because they are assumed to be kept constant for the two experimental cases. The analytic result of Eq. (15) was confirmed experimentally (see main text).

Next, we wish to calculate the ratio between the electric and the magnetic dipole transition intensity. We note that the initial state for the magnetic dipole transitions is the same for the three experimental cases. Namely, it is given by a statistical mixture of $X\,^2\Pi_{3/2}, J = 3/2, v = 0, f, F = 2, M_F$ states, of which four levels ($M_F = \pm 1, \pm 2$) are occupied by 20% of the molecules and one level ($M_F = 0$) is occupied by 19.5%. For the electric transition, we define the following line strength S^{el} for case 1, namely

$$S^{\text{el}} = 0.005 |\langle ^2\Sigma^+, F' = 0, M'_F = 0, + | \mu^{\text{sf}}_{\text{el},0} | F_1\,^2\Pi_{3/2}, F = 1, M_F = 0, + \rangle|^2, \tag{16}$$

where the factor of 0.005 represents the 0.5 % population of the initial level and we have $\epsilon = +$ (e symmetry or $-$ parity) for the initial state. Since the magnetic field of the laser points in the x direction of the laboratory frame, we define the following line strength for the magnetic transition

$$S^{\text{mag}} = \frac{\alpha^2}{2} \sum_{M_F} P(M_F) \sum_{M'_F} |\langle ^2\Sigma^+, F' = 1, M'_F, + | (\mu^{\text{sf}}_{\text{mag},1} - \mu^{\text{sf}}_{\text{mag},-1}) | F_1\,^2\Pi_{3/2}, F = 2, M_F, - \rangle|^2, \tag{17}$$

where $P(M_F)$ accounts for the fraction of molecules in each initial state, so that $P(M_F) = 0.2$ for $M_F = \pm 1, \pm 2$ and $P(0) = 0.195$, and $\epsilon = -$ (f symmetry or $+$ parity) for the initial state. Here, $\alpha = 1/137.036$ is the fine-structure constant, which is included to account for the relative strength of the magnetic field of the laser compared to the electric field. Using Eqs. (16) and (17), we find for the ratio between the electric and the magnetic dipole moment for case 1 that

$$\text{signal ratio} = \frac{S^{\text{el}}}{S^{\text{mag}}} = 25.8. \tag{18}$$

This is to be compared with the experimental measured ratio of 18 ± 8.

Finally, we note that the above measured result depends on the fraction of molecules in each of the prepared quantum states. If the two ground states (e and f) have an equal number of molecules before the dipole transitions and if spatial orientation plays no role (for example in the case of an unpolarized laser, or with all M_F states equally populated), then the signal ratio would have been simply given by

$$\frac{1}{\alpha^2} \frac{|\langle \mu_{\text{el}} \rangle|^2}{|\langle \mu_{\text{mag}} \rangle|^2} = 2576, \tag{19}$$

which therefore represents most directly the relative importance of magnetic and electric dipole transitions from the $X\,^2\Pi_{3/2}, v = 0$ state to the $A\,^2\Sigma^+, v' = 1$ state.

IV. DISCUSSION

In the present theoretical treatment several approximations were made. First, we have separated the vibrational motion from the rotational motion. To partly compensate this approximation, we used a spectroscopic rotational constant, which effectively includes the effect of the vibrational motion, and we added a centrifugal term $J(J+1)/2\mu r^2$ to the electronic potentials when calculating the vibrational wave functions. Here, r is the OH bond length and μ is the reduced mass of OH. If we excluded the centrifugal term, then the calculated signal ratios changed only by about 0.5%, showing that these types of corrections are small. We also did not consider the r dependence of the spin-orbit coupling, which affects the mixing of the $\Omega = 1/2$ and the $\Omega = 3/2$ states in the $^2\Pi$ state. The spin-orbit coupling varies less than 1% in the range of interest to us. Moreover, we did not include a Λ-doublet Hamiltonian, which mixes in higher electronic states and causes the energy splitting between states of different parity in the $^2\Pi$ state. The resulting effect on the wave functions is very small, so that also the effect on the dipole transitions is expected to be small. Finally, we did not consider electric quadrupole transitions. An electric quadrupole transition can couple states with $\Delta F = \pm 2$. Since in our experiment the laser propagates in the y-direction and is polarized in the z-direction, only the (space-fixed) Q_{zy} component of the transition quadrupole moment is non-zero, see Eq. (4.13.9) in [6]. This leads to the selection rule $\Delta M_F = \pm 1$ for our experimental situation. These transitions were not seen in the experiment. Electric quadrupole transition with $\Delta F = 0, \pm 1$ should be in the same order of magnitude as transition with $\Delta F = \pm 2$ and can therefore be neglected. From calculations of the transition quadrupole moment with MOLPRO, we estimate that the quadrupole transitions are about 100 times weaker than the magnetic dipole transitions, which is consistent with our experimental findings.

Another theoretical issue is that the Franck-Condon overlap between the $v = 0$ and $v' = 1$ is small and sensitive to shifts in the electronic potentials. As an example of this, we note that the calculated ratio for the $v = 0 \to v' = 1$ transition differs by almost a factor of 30 from the $v = 1 \to v' = 0$ transition. To get additional insight in the sensitivity of our theoretical results to the method for calculating electronic potentials, we re-calculated the $^2\Pi$ and $^2\Sigma$ potentials using the explicitly correlated RCCSD(T)-F12 method with an aug-cc-pV5Z basis set [1].

In addition, we constructed RKR potentials using the program of Le Roy [7] and the spectroscopic data of Crosley et al. [8]. With the three independently calculated potentials we found a maximum deviation of only 3% for the electric transition dipole moment and 2% for the magnetic transition dipole moment. Moreover, we performed convergence checks of the electronic structure calculations for the dipole moment functions by changing the parameters in the configuration-interaction procedure that accounts for the effects of dynamic electron correlation. For the electric transition dipole moment this gave a maximum deviation of about 5%. The magnetic transition dipole moment seemed to be better converged, with deviations of less than 1%. Combining these errors we estimate an uncertainty of about 10% for the ratio of the squared transition dipole moments. This estimate is only crude, however. The convergence of configuration-interaction calculations is typically not very regular. Furthermore, systematic errors in the calculation of the potentials, such as the Born-Oppenheimer approximation, could influence the Franck-Condon factor.

[1] H.-J. Werner, P. J. Knowles, and *et al.*, MOLPRO: *a package of ab initio programs, version 2010.1*, URL `http://www.molpro.net`.
[2] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[3] M. P. J. van der Loo and G. C. Groenenboom, J. Chem. Phys. **126**, 114314 (2007).
[4] G. C. Groenenboom and D. T. Colbert, J. Chem. Phys. **99**, 9681 (1993).
[5] P. F. Bernath, *Spectra of Atoms and Molecules* (Oxford University Press, New York, 2005).
[6] D. P. Craig and T. Thirunamachandran, *Molecular quantum electrodynamics* (Academic, London, 1984)
[7] R. J. Le Roy, RKR1 2.0: A Computer Program Implementing the First-Order RKR Method for Determining Diatomic Molecule Potential Energy Curves, University of Waterloo Chemical Physics Research Report CP-657R (2004); URL `http://leroy.uwaterloo.ca/programs/`.
[8] J. Luque and D.R. Crosley, J. Chem. Phys. 109, 439 (1998).