Hyperfine structure of the hydroxyl free radical (OH) in electric and magnetic fields

Kenji Maeda¹, Michael L Wall² and Lincoln D Carr¹

¹ Department of Physics, Colorado School of Mines, Golden, Colorado 80401, USA
² JILA, NIST and Department of Physics, University of Colorado, Boulder, Colorado 80309, USA
E-mail: kenji.bosefermi@gmail.com

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Abstract

We investigate single-particle energy spectra of the hydroxyl free radical (OH) in the lowest electronic and rovibrational level under combined static electric and magnetic fields, as an example of heteronuclear polar diatomic molecules. In addition to the fine-structure interactions, the hyperfine interactions and centrifugal distortion effects are taken into account to yield the zero-field spectrum of the lowest $^2\Pi_{3/2}$ manifold to an accuracy of less than 2 kHz. We also examine level crossings and repulsions in the hyperfine structure induced by applied electric and magnetic fields. Compared to previous work, we found more than 10% reduction of the magnetic fields at level repulsions in the Zeeman spectrum subjected to a perpendicular electric field. In addition, we find new level repulsions, which we call Stark-induced hyperfine level repulsions, that require both an electric field and hyperfine structure. It is important to take into account hyperfine structure when we investigate physics of OH molecules at micro-Kelvin temperatures and below.

1. Introduction

The hydroxyl free radical (OH molecule) is a simple but fascinating molecule in various fields of science; chemistry, astronomy, and physics. In chemistry, the OH molecule was the first short-lived molecule to be investigated by microwave spectroscopy and by gas-phase electron paramagnetic resonance [1, 2], and was also the first free radical to be detected in a molecular beam [3]. In astronomy, it was found that the OH molecule was the first interstellar molecule detected at radio frequencies [4, 5]. The OH/IR stars, which exhibit OH line emission bright at near infrared wavelength, yielded so much intensity as OH sources that they led to an interpretation based on maser amplification, inspiring the concept of astrophysical masers [6]. Also, the OH molecule is important in atmospheric and climate science, including calculations of the lifetime of atmospheric methane and aerosol-based pollutants; recently a large OH hole in the atmosphere has been identified over Europe, reminiscent of ozone holes identified in other regions of the world in past decades [7]. In the field of cold and ultracold physics, the hydroxyl free radical has received a renewed attention as a constituent of quantum dipolar systems. A gas of OH molecules has been recently trapped and evaporatively cooled to milli-Kelvin temperatures at JILA [8].

Although there are many studies of the single-particle spectrum of the OH molecule in the context of chemistry and radio-astronomy as mentioned above, in the presence of electric and magnetic fields the energy spectra of OH have been calculated previously only to energy scales of milliKelvin temperatures (or frequencies of megaHertz) [8–17], far from the sub-microKelvin temperatures at which OH molecules will become quantum degenerate. Therefore, as a necessary step towards a correct description of a quantum degenerate molecular gas of OH molecules at sub-microKelvin temperatures, we investigate its hyperfine structure in the lowest electronic and rovibrational states under combined electric and magnetic fields. In addition to the fine-structure interactions, we fully consider the hyperfine interactions and centrifugal distortion effects to obtain the zero-field spectrum of the lowest $^2\Pi_{3/2}$ manifold to an accuracy of less than 2 kHz ~ 100 nK. As OH nears the quantum degenerate regime, producing a sample in a single quantum state will require manipulation.
of the hyperfine degrees of freedom, as was the case for ultracold KRb molecules [18]. Our results are essential for achieving this high degree of control over hyperfine states with the required spectroscopic precision. We also examine level crossings and repulsions in hyperfine structure in the presence of applied electric and magnetic fields to explore how these level crossings and repulsions change when we change the relative angle between the electric and magnetic fields. It has never been performed before us to couple the 16 states in the lowest $^2\Pi_{3/2}$ manifold with the 80 excited states in the presence of strong fields and obtain such accuracies comparable with ultracold temperatures.

Ahead of ultracold molecules, ultracold gases of atoms with magnetic dipole moments, or atomic dipolar gases, have been intensely investigated. Gases of chromium [19], dysprosium [20], and erbium [21] have been trapped and cooled down to quantum degeneracy in experiments. Due to their anisotropic long-range dipole–dipole interactions, atomic dipolar gases are expected to exhibit novel quantum phenomena: spin textures [22–24], dipolar relaxation [25], Einstein–de Haas effects [26, 27] in their bosonic species, and ferronematic [28, 29] and antiferroamatic–C phases [30] in their fermionic species. However, dipole–dipole interactions between atoms are fixed in strength by their permanent magnetic dipole moments. In contrast, polar molecules offer an electric dipole moment that is directly tunable via an applied electric field and can be made orders of magnitude larger than dipole moments in atoms. Cold and ultracold gases of molecules with electric dipole moments—molecular dipolar gases—are at or rapidly approaching quantum degeneracy in experiments, e.g., KRb [31], RbCs [32], RbSr [33], OH [8], and SrF [34]. Recently, it has been shown that the single-particle spectrum and the dipole–dipole interactions of magnetic dipoles in a magnetic field can be simulated by symmetric top molecules subject to an electric field [35], and we stress that the hydroxyl radical (OH molecule), the subject of this article, also has the symmetric top structure in its electric dipole moment. Thus, our study of OH spectra will become the foundations for quantum many-body physics with OH molecules, which has tunable dipole moments in experiments, that is, more flexible than when atomic dipolar gases used for the above novel quantum phenomena.

This paper is organized as follows. Section 2 provides a brief preliminary overview of the OH molecule for readers who may be less familiar with the molecular physics of this free radical. In section 3, the hyperfine structure of OH is explored in the absence of external fields. We first introduce the effective Hamiltonian for the OH molecule and numerically diagonalize it to obtain the energy spectrum of OH in the lowest energy manifold. Section 4 deals with the effects of applied electric and magnetic fields, that is, the Stark and Zeeman effects in OH. We calculate the Stark and Zeeman spectra independently, and then examine the energy spectra in the presence of both electric and magnetic fields at relative angles of $0^\circ$, $45^\circ$, and $90^\circ$. In the presence of combined electric and magnetic fields, we find a new type of level repulsion, which we call Stark–induced hyperfine level repulsion appearing only in the presence of hyperfine interactions and an electric field. For previously identified level repulsions, we compare our results to previous work and show that the coupling with the excited states gives non-negligible contributions to the values of magnetic fields where these level repulsions occur. Section 5 is devoted to the summary and concluding remarks.

## 2. Overview of the hydroxyl radical

The OH molecule can be obtained by dissociation of a hydrogen atom from a water molecule $\text{H}_2\text{O}$, as shown in figure 1(a). Thus, the OH molecule has a chemically reactive, or radical, electron in its open shell. Other free radicals, like the NH and CH radicals shown in figures 1(b) and (c), are also easily obtained from stable molecules, $\text{NH}_3$ (ammonia) and $\text{CH}_4$ (methane), respectively.

In principle, a full solution of the OH molecular structure accounts for the motion of an oxygen nucleus, a hydrogen nucleus, and nine electrons. However, due to the large mass difference between electrons $m_e$ and nuclei $m$, one can perform a singular perturbation expansion in the mass–ratio parameter $(m_e/m)^{1/4}$, and find a separation of energy scales $\Delta E_{\text{vib}}/\Delta E_{\text{el}} \approx \Delta E_{\text{rot}}/\Delta E_{\text{vib}} \approx (m_e/m)^{1/2}$, where $\Delta E_{\text{el}}, \Delta E_{\text{vib}}$, and $\Delta E_{\text{rot}}$ are the

![Figure 1](image.png)

**Figure 1.** Free radicals: (a) OH, (b) NH, and (c) CH. The dotted lines represent dissociation of one or more hydrogen atoms to make free radicals from chemically stable, non-reactive, molecules.
energetic separations between the ground state and the first excited state in electronic, vibrational, and rotational energy levels, respectively. The lowest-order approximation in \((m_e/m)^{1/2}\), known as the Born–Oppenheimer approximation [36, 37], considers that the electrons move in an adiabatic potential set by the slow motion of the nuclei, and hence a separable electronic-nuclear wavefunction. For most molecules, the Born–Oppenheimer approximation is excellent by virtue of the separation of energy scales above. However, in OH a particular breakdown of the Born–Oppenheimer approximation occurs in the form of a splitting of otherwise degenerate molecular levels through non-adiabatic effects, which is caused by the peculiar electronic state structure of OH.

In particular, taking as an approximation that the electronic orbitals of OH can be described by their free-space counterparts, i.e., atomic orbitals of the oxygen and hydrogen atoms, the OH molecule has the molecular orbitals and their energy levels for electrons shown in figure 2(a). Among the 2p atomic orbitals of the oxygen atom, the 2p_z orbital has overlap with the 1s atomic orbital of the hydrogen atom, while the 2p_x and 2p_y orbitals do not have overlap in spatial average and they are renamed as 2pσ molecular orbitals. Then, the 2p_z orbital of the oxygen atom and 1s orbital of the hydrogen atom interact in–phase to form a bonding molecular orbital 2pσ, or out-of-phase to form an antibonding molecular orbital 2pσ*. Thus, the lowest energy electron configuration of the OH molecule, called the \(X^2Π\) state, is given by

\[
X^2Π : (1s)^2 (2σ)^2 (2pσ)^2 (2pσ^*)^3,
\]

as shown in figure 2(b), and the first excited electronic state, called the \(A^2Σ\) state, becomes

\[
A^2Σ: (1s)^2 (2σ)^2 (2pσ)^2 (2pσ^*)^4,
\]

as shown in figure 2(c). Here the superscripts of the braces represent the numbers of electrons occupying taken into account electronic spin degrees of freedom.

Defining \(A\) as the projection of electronic orbital angular momentum along the symmetry axis of the molecule, we have \(A = ± 1\) in the \(X^2Π\) electronic state, while \(A = 0\) in the \(A^2Σ\) electronic state. The two-fold degeneracies in states with \(|A| \neq 0\) are called \(A\)-doubling, which comes from the fact that the Hamiltonian of a diatomic molecule is invariant under a reflection with respect to a plane containing the symmetry axis of the molecule while \(A\) changes its sign under such reflection. A splitting between these levels (\(A\)-doubling splitting), which is an effect outside of the Born–Oppenheimer approximation, results by admixture of the rotational levels in the \(X^2Π\) state with the corresponding levels of the \(A^2Σ\) state via electronic spin–orbit interaction and the nuclear rotational–electronic orbit interaction [38]. This is because each rotational level of the \(A^2Σ\) state has a definite parity with respect to spatial inversion, either positive or negative, and thus interacts with only one of the two parity states in the \(X^2Π\) state. The electronic ground \(X^2Π\) state and the first excited \(A^2Σ\) state are far separated from each other by \(4 \text{ eV} \sim 10^3 \text{ THz} \sim 5 \times 10^4 \text{ K}\), which is the largest energy scale in the hierarchy of energy levels. Fuller details on electronic structures of molecules can be found in [39].

In addition to the electrostatic Coulombic potentials, molecular Hamiltonians have a lot of microscopic terms which explain relativistic effects, fine and hyperfine structure, e.g., there are 27 terms derived for general diatomic molecules in [40] including electronic spin–spin, spin–orbit couplings and electronic spin–nuclear...
spin coupling. Such microscopic interactions give energy scales comparable to thermal energies in cold and ultracold temperatures (10 mK – 10 nK), while the above electronic and vibrational motions corresponds to much higher temperatures, $10^4$ and $10^5$ K, respectively. Thus for the purpose of cold and ultracold physics, it is convenient to derive an effective Hamiltonian which operates only within nuclear rotational, electronic spin, and nuclear spin degrees of freedom in the vibrational and electronic (vibrionic) ground state. Such an effective Hamiltonian is obtained by including the effects of off-diagonal matrix elements in the original Hamiltonian which couple the vibrionic ground state to other excited states. The effective Hamiltonian of our interest should act only on a subspace spanned by the vibronic ground states of the non-relativistic kinetic, vibrational, and electrostatic Coulomb Hamiltonian, while reproducing the eigenenergies of the full Hamiltonian, which includes nuclear rotation, electronic spin–spin, spin–orbit couplings and electronic spin–nuclear spin coupling, and so on. We remark that the centrifugal distortion corrections are obtained by the admixture of the vibrational ground and excited states.

Throughout this paper, we will employ the effective Hamiltonian for the OH molecule acting on rotational, fine and hyperfine levels in its vibronic ground state and investigate its energy levels in the presence of electric and magnetic fields. A detailed derivation and fuller expression for the effective Hamiltonian can be found in [40].

### 3. Hyperfine structure of OH molecule without external fields

In a study of molecular spectroscopy, especially at low temperatures where vibrational degrees of freedom for nuclei are frozen out, we often use a quantum rotor model, replacing a molecule by a quantum-mechanically rotating rigid body with several angular momenta [40, 41]. The quantum rotor model takes into account not only the rotation but also interactions between angular momenta, depending on the species of molecule. Since the OH molecule in its electronic ground state is a diatomic molecule with a nuclear spin of $I = 1/2$ and has an electron in the open 2p-shell, there are four main kinds of angular momenta: the rotational angular momentum of the nuclei $\mathbf{R}$, the electronic orbital angular momentum $\mathbf{L}$, the electronic spin angular momentum $\mathbf{S}$, and the nuclear spin angular momentum $\mathbf{I}$, see figure 3. Furthermore, the total angular momentum without the nuclear spin is conventionally defined as $\mathbf{J} = \mathbf{R} + \mathbf{L} + \mathbf{S}$, and the geometric part of angular momenta as $\mathbf{N} = \mathbf{R} + \mathbf{L}$. Here we remark that for the OH molecule in its $^2\Pi$ states the magnitudes of the angular momenta $\mathbf{L}$, $\mathbf{S}$, and $\mathbf{I}$ are fixed to be $L = 1$, $S = 1/2$, and $I = 1/2$, respectively, while the rotational quantum number $R$ takes non-negative integer values. In this section, we review the quantum rotor model of the OH molecule in the absence of external fields, and then numerically calculate its energy spectrum including hyperfine structure, leading to the lowest 16 states and therefore reproducing experimental data to an accuracy of 2 kHz. For definitions of spherical tensor operators and their formulae, readers can refer to standard textbooks, e.g., [40].

#### 3.1. The zero-field effective Hamiltonian for OH

We first summarize the zero-field effective Hamiltonian for the OH molecule in the $v = 0$ level of the $X^2\Pi$ state. Throughout this paper, we use notations in molecular spectroscopy to represent the vibrational and electronic ground state of molecules by $v = 0$ and $X$, respectively, and to classify the molecular states with $^2\Pi_{\Lambda+\Sigma}$, where
\[ \Lambda \text{ and } \Sigma \text{ are the projections of the electronic orbital and spin angular momenta along the molecule-fixed } z\text{-axis, respectively, and } \Pi \text{ stands for } |\Lambda| = 1 [40, 41]. \text{ Further, throughout this paper, we shall choose units such that } \hbar = 1 \text{ unless quoting an energy in frequency units.}

The effective Hamiltonian is given by [9, 10, 40, 42]

\[ \hat{H}_0 = \hat{H}_{SO} + \hat{H}_{MR} + \hat{H}_{SMR} + \hat{H}_{LD} + \hat{H}_{HF} + \hat{H}_{CD}, \]

(3)

where \( \hat{H}_{SO} \) represents the spin–orbit coupling,

\[ \hat{H}_{SO} = A_{SO} T_{q=0}^1 (\textbf{I}) T_{q=0}^1 (\hat{\mathbf{s}}), \]

(4)

\( \hat{H}_{MR} \) represents the rotational energy of the molecule,

\[ \hat{H}_{MR} = B_N \mathbf{N}^2, \]

(5)

\( \hat{H}_{SMR} \) is the spin–molecular rotation coupling,

\[ \hat{H}_{SMR} = \gamma T^1 (\mathbf{j} - \hat{\mathbf{s}}) \cdot T^1 (\hat{\mathbf{s}}), \]

(6)

\( \hat{H}_{LD} \) denotes the \( \Lambda \)-doubling terms,

\[ \hat{H}_{LD} = \sum_{q = \pm 1} e^{-2i\phi} \left[ -Q T_{2q}^1 (\mathbf{j}) + (P + 2Q) T_{2q}^2 (\mathbf{j}, \hat{\mathbf{s}}) \right], \]

(7)

and \( \hat{H}_{HF} \) represents the hyperfine interactions,

\[ \hat{H}_{HF} = a T_{q=0}^1 (\mathbf{i}) T_{q=0}^1 (\textbf{i}) + b T^1 (\mathbf{i}) \cdot T^1 (\hat{\mathbf{s}}) + \frac{7\gamma}{3} c T_{q=0}^2 (\mathbf{i}, \hat{\mathbf{s}}) + d \sum_{q = \pm 1} e^{-2i\phi} T_{2q}^2 (\mathbf{i}, \hat{\mathbf{s}}) + c_i T^1 (\mathbf{i}) \cdot T^1 (\mathbf{j} - \hat{\mathbf{s}}) + c_i \sum_{q = \pm 1} e^{-2i\phi} \frac{1}{2} \left[ T_{2q}^2 (\mathbf{i}, \hat{\mathbf{s}}) + T_{2q}^2 (\mathbf{j} - \hat{\mathbf{s}}, \mathbf{i}) \right]. \]

(8)

Finally, the centrifugal distortion corrections to the above terms are given by

\[ \hat{H}_{CD} = -D \left( \mathbf{N}^2 \right)^3 + H \left( \mathbf{N}^2 \right)^3 + \gamma_D \left[ T^1 (\mathbf{j} - \hat{\mathbf{s}}) \cdot T^1 (\hat{\mathbf{s}}) \right] \mathbf{N}^2 + \sum_{q = \pm 1} e^{-2i\phi} \left\{ \frac{-Q_D}{2} \left[ T_{2q}^2 (\mathbf{j}, \hat{\mathbf{s}}) \mathbf{N}^2 + \mathbf{N}^2 T_{2q}^2 (\mathbf{j}, \hat{\mathbf{s}}) \right] \right\} + \frac{P_D + 2Q_D}{2} \left[ T_{2q}^2 (\mathbf{j}, \hat{\mathbf{s}}) \mathbf{N}^2 + \mathbf{N}^2 T_{2q}^2 (\mathbf{j}, \hat{\mathbf{s}}) \right] + \frac{Q_H}{2} \left[ T_{2q}^2 (\hat{\mathbf{s}}, \mathbf{j}) \left( \mathbf{N}^2 \right)^2 + \left( \mathbf{N}^2 \right)^2 T_{2q}^2 (\hat{\mathbf{s}}, \mathbf{j}) \right] + \frac{P_H + 2Q_H}{2} \left[ T_{2q}^2 (\hat{\mathbf{s}}, \mathbf{j}) \left( \mathbf{N}^2 \right)^2 + \left( \mathbf{N}^2 \right)^2 T_{2q}^2 (\hat{\mathbf{s}}, \mathbf{j}) \right] + d_D \sum_{q = \pm 1} e^{-2i\phi} \frac{1}{2} \left[ T_{2q}^2 (\mathbf{i}, \hat{\mathbf{s}}) \mathbf{N}^2 + \mathbf{N}^2 T_{2q}^2 (\mathbf{i}, \hat{\mathbf{s}}) \right]. \]

(9)

Note that these operators are written for calculation of their matrix elements with use of a Hund’s case (a) basis in the molecule-fixed frame [40, 41], and that \( q \) denotes the component of the spherical tensor operator and \( \phi \) is the azimuthal coordinate of the electronic orbit in the molecule-fixed frame. For the OH molecule, the Hund’s case (a) basis consists of the simultaneous eigenstates of angular momenta, \( \mathbf{I}^2, \hat{\mathbf{s}}^2, J^2 \) and \( \mathbf{I}^2 \), projections on the molecule-fixed \( z \)-axis, \( \mathbf{L}_z, \hat{\mathbf{S}}_z, \) and \( \mathbf{J}_z \), and projections on the space-fixed \( z \)-axis, \( \mathbf{I}_z \) and \( \hat{\mathbf{J}}_z \), specified by \( |L\Lambda, \Sigma, J, \Omega J, M_J, M_J \rangle \) with \( L = 1, A = \pm 1, S = 1/2, \Sigma = \pm 1/2, J \geq 1/2, \Omega = A + \Sigma, -J \leq M_J \leq J, I = 1/2, \) and \( M_I = \pm 1/2 \). Table 1 lists the values of molecular parameters of equations (4)–(9), extracted from [10], and figure 4 shows the energy scales of the effective Hamiltonian for OH. It is clear that one must take into account the centrifugal distortion corrections and the hyperfine interactions in order to obtain access to and investigate the physics of OH molecules at microKelvin temperatures and below.

\[ 4 \text{ We can get an insight into centrifugal distortion corrections, especially the first term of equation (9), based on classical mechanics [40]. Suppose that in the rotating molecule with its angular velocity } \omega \text{ and equilibrium distance } r_0 \text{ of the nuclei, we determine the intermolecular distance } r_{\text{cl}} \text{ by requiring that the centrifugal force } m\omega^2r_{\text{cl}} \text{ is balanced by the restoring force } k (r_{\text{cl}} - r_0) \text{ with the curvature } k \text{ of the intermolecular potential at } r_0. \text{ The rotational energies are modified to } E = R_{cl}^2/(2m_0k) + k (r_{\text{cl}} - r_0)^2/2 \text{ where } R_{cl} = m\omega^2r_{\text{cl}} \omega \text{ is the classical angular momentum. Assuming the stiffness of the molecule } (k \gg m\omega^2), \text{ we obtain } E \approx R_{cl}^2/(2m_0k) - R_{cl}^2/(2m_0k) \text{ to the lowest order in } m\omega^2/k, \text{ and the term proportional to } R_{cl}^2 \text{ is a centrifugal distortion correction.} \]
3.2. The zero-field energy spectrum

We will investigate the energy spectrum of the Hamiltonian equation (3), focusing on the hyperfine structure of the lowest 16 states in the $\Pi^2_32$ manifold. Before going into details of the spectrum, let us overview the hierarchy of energy scales in the OH molecule. First of all, for the OH molecule the spin–orbit coupling gives the largest energy scale $\sim A_{so}^{4}$THz. Noting that the matrix elements of the spin–orbit coupling in equation (4) are diagonal in the Hund’s case (a) basis and proportional to $\Lambda \Sigma$, the $\Pi^2_32$ states can be classified in two cases: one with $\Lambda \Sigma = 1/2$, and the other with $\Lambda \Sigma = -1/2$. The former case has the lower energy and it is also labeled by $|\Lambda + \Sigma| = 3/2$, called the $^2\Pi_{3/2}$ manifold, while the latter is labeled by $|\Lambda + \Sigma| = 1/2$, corresponding to the $^2\Pi_{1/2}$ manifold. The next largest energy scale is given by the rotational energy of molecule in equation (5) with $B_N \sim 0.5$THz. Since in the $^2\Pi_{1/2}$ manifold the molecular–axis projections $\Lambda$ and $\Sigma$ point in the same direction, the total angular momentum starts from $J = 3/2$ and increases by positive integers as the nuclei rotate faster. On the other hand, in the $^2\Pi_{3/2}$ manifold $\Lambda$ and $\Sigma$ point in opposite directions, and thus the total angular

Table 1. Molecular parameters for OH in the $v = 0$ level of the $X^2\Pi$ ground state (in MHz) [10].

| Parameter | Value |
|-----------|-------|
| $A_{so}$ | $-4168639.13(78)$ |
| $B_N$    | $555660.97(11)$ |
| $\gamma$ | $-3574.88(49)$ |
| $Q$      | $-1159.991650$ |
| $P$      | $7053.09846$ |
| $a$      | $86.1116$ |
| $b_F$    | $-73.2537$ |
| $c$      | $130.641$ |
| $d$      | $56.6838$ |
| $e_i$    | $-0.09971$ |
| $e_i'$   | $0.643 \times 10^{-1}$ |
| $D$      | $57.1785(86)$ |
| $H$      | $0.4236 \times 10^{-2}$ |
| $\theta_0$ | $0.7315$ |
| $Q_{D0}$ | $0.4420320$ |
| $P_0$    | $-1.550962$ |
| $Q_{H4}$ | $-0.8237 \times 10^{-4}$ |
| $P_4$    | $0.1647 \times 10^{-3}$ |
| $d_{D1}$ | $-0.02276$ |

Figure 4. Energy scales of the effective Hamiltonian for OH in the $v = 0$ level of the $X^2\Pi$ ground state. Each energy scale is estimated by the size of matrix elements in the subspace of the lowest 96 states on a logarithmic scale. We consider frequency $\nu$, wavenumber $\lambda$, and temperature $T$ as units of energy by multiplying them through by the fundamental constants $\nu h$, $hc/\lambda$, and $k_B T$, respectively. These units of energy relate to each other: $1$ MHz $\simeq 50$ $\mu$K $\simeq 3.3 \times 10^{-3}$ cm$^{-1}$. 

molecular rotation
spin–orbit coupling
spin–molecular rotation coupling
$\Lambda$-doubling terms
centrifugal distortion corrections
hyperfine interactions

frequency
$1$ THz $1$ GHz $1$ MHz $1$ kHz
wave number
$10$ cm$^{-1}$ $10^{-2}$ cm$^{-1}$ $10^{-5}$ cm$^{-1}$ $10^{-8}$ cm$^{-1}$
temperature
$10$ K $10$ mK $10$ $\mu$K $10$ nK
momentum can take the minimum, \( J = 1/2 \). Third, the spin–molecular rotation coupling in equation (6), where \( \gamma \sim -3 \) GHz, becomes diagonal in our basis if we only consider the lowest 24 states consisting of \( J = 3/2 \) states in the \( ^2\Pi_{1/2} \) manifold and \( J = 1/2 \) states in the \( ^2\Pi_{3/2} \) manifold. However, there appear off-diagonal matrix elements that contribute when we take into account higher rotational states, and have to be folded in as corrections. Fourth, the \( \Lambda \)-doubling terms equation (7) with \( Q \sim -1 \) GHz and \( P \sim 7 \) GHz yield the \( \Lambda \)-doubling splittings in the spectrum, especially assigning 1 GHz splitting in the lowest \( J = 3/2 \) states of the \( ^2\Pi_{3/2} \) manifold. We remark that to obtain the \( \Lambda \)-doubling splittings in the \( J = 3/2 \) states of \( ^2\Pi_{3/2} \) we must include at least the \( J = 3/2 \) states of \( ^2\Pi_{1/2} \) in our model. Note also that the \( \Lambda \)-doubling terms hybridize fixed-\( \Omega \) states, yielding the parity-conserved states in \( ^2\Pi_{3/2} \) as an appropriate basis in the absence of external fields,

\[
\begin{align*}
[ & L, S, J, |\Omega\rangle, M_J; I, M_I; \epsilon \rangle = \{ [L, |A\rangle]S, \{\{L, J, |\Omega\rangle, M_J\}I, M_I]\}
+ \epsilon (-1)^{J-S}[L, -|A\rangle]S, \{-\{L, J, |\Omega\rangle, M_J\}I, M_I]\} / \sqrt{2},
\end{align*}
\]

Here \( \epsilon \) takes values of 1 and –1 corresponding to the positive and negative parity states, respectively. Finally, hyperfine interactions equation (8) and centrifugal distortion effects equation (9) give further microscopic structure in energy of tens of megaHertz. As we will see later, the hyperfine interactions play a significant role in the emergence of level repulsions when we apply electric and magnetic fields.

We proceed to determine the energy spectrum of the Hamiltonian equation (3) numerically. Since we are interested in the spectrum of the lowest 16 states in the \( ^2\Pi_{3/2} \) manifold, we employed cutoffs for the unbounded quantum number \( J \) to consider a finite-dimensional subspace of states. More precisely, we restricted ourselves to states with \( J = 1/2 \) (8 states) and \( J = 3/2 \) (16 states) in the \( ^2\Pi_{1/2} \) manifold, and \( J = 3/2 \) (16 states), \( J = 5/2 \) (24 states), and \( J = 7/2 \) (32 states) in the \( ^2\Pi_{3/2} \) manifold, that is, the lowest 96 states as shown in figure 5. Note that each rotational level labeled by \( J \) has further internal degrees of freedom, i.e., signs of \( \Lambda (\Lambda = \pm |A\rangle) \), projections of \( J (M_J = 0, \pm 1, \ldots, \pm J) \), and projections of the nuclear spin \( (M_I = \pm 1/2) \), thus it contains \( 4(2J + 1) \) states.

Figure 5 also shows a closeup of the hyperfine structure in \( J = 3/2 \) states of \( ^2\Pi_{3/2} \) where we described the \( \Lambda \)-doubling splittings by \( 'e' \)-states for the negative parity states and \( 'P' \)-states for the positive parity states, and hyperfine splittings with transition frequencies \( f_1, f_2, f_3, \) and \( f_4 \).

![Figure 5](image-url)
the Hund’s case (a) basis consisted of the lowest 96 states, and calculated the energy spectrum of the lowest 16 states in the \( ^3\Pi_{3/2} \) manifold. Table 2 summarizes our numerical results along with experimental data [3, 43, 44]. The largest deviation from the experimental data is in our calculation of important aspects. First, our study is the combined effects of magnetic and electric distortion, down to few kiloHertz accuracy, which leads to observable spectral differences, as we shall show. Stark-induced hyper

4. Hyperfine structure of OH molecule in combined electric and magnetic fields

In this section, we will add the Stark and Zeeman Hamiltonians to the zero-field Hamiltonian equation (3) in order to study the energy spectra under combined electric and magnetic fields. We first examine the Stark and Zeeman effects for the spectrum of \( J = 3/2 \) states in the \( ^3\Pi_{3/2} \) manifold separately, and then investigate the energy spectra in the presence of combined electric and magnetic fields. While the spectroscopy of OH in combined fields has been studied by several authors [8, 12, 17, 45], our results are distinguished in two important aspects. First, our study is the first to include all effects, including hyperfine structure and centrifugal distortion, down to few kiloHertz accuracy, which leads to observable spectral differences, as we shall show. Second, we find a new class of level repulsions not discovered in any of the papers mentioned, which requires the combined effects of magnetic and electric fields with hyperfine structure. We call these new avoided crossings Stark-induced hyperfine level repulsions.

Before discussing spectra, a remark about symmetries is in order. In order to classify which of the level crossings we see are true level crossings and which are only very narrow avoided crossings, we would need to classify the effective Hamiltonian according to its symmetries in each field configuration. For the case in which the electric and magnetic fields are collinear, which includes the field-free situation as a special case, we have the conservation of the total angular momentum along the field direction \( M_F \). Away from this case, there are no apparent symmetries associated with the constituent angular momenta. However, we can still gain insight into which crossings are likely to be avoided by considering selection rules on off-diagonal matrix elements which are a consequence of the rotational symmetry of the basis functions we use to expand the Hamiltonian. This is similar in spirit to the Hund’s cases, where quantum numbers, e.g. \( J \), are not rigorously conserved but approximately conserved, and so can be used to label quantum states (see also [15]). Table 3 collects such selection rules based on the quantum numbers \( J \) and \( M_F \) of our basis states for the field cases of interest. In what follows, we will focus on the spectral features of OH in combined fields at the level of \( \sim 1 \) kHz accuracy.

Finally, it has been shown in a recent paper [17] that an effective Hamiltonian restricted to the lowest rotational level of OH without hyperfine structure has the property that its spectrum is reflection symmetric about zero energy, and this property enables the spectrum to be determined analytically due to the characteristic polynomial being of degree four. This property has further been shown to be linked to a ‘chiral symmetry’ generated by a rotation operator which anticommutes with the Hamiltonian. We note that such a property can only be present at the effective Hamiltonian level, as any Hamiltonian involving multiple rotational levels will manifestly not display the requisite reflection symmetry about zero energy. Further, if such a symmetry did exist for the effective Hamiltonian of the lowest rotational level with hyperfine structure, it would still not render that effective Hamiltonian analytically solvable, due to the characteristic polynomial still being of too high degree. Hence, while discussion of such symmetries is interesting, it does not assist in determining the spectrum of the OH molecule with hyperfine structure to our desired precision, and we will not investigate such symmetries here.
4.1. The effective Hamiltonian of OH molecule in combined electric and magnetic fields

Let us consider the quantum rotor model for the OH molecule in the presence of combined electric and magnetic fields. Figure 6 shows a field configuration of electric and magnetic fields in which the magnetic field \( B \) is chosen parallel to the space-fixed Z-axis, and the electric dc field \( E_{dc} \) is in the space-fixed XZ-plane making an angle of \( \theta_{BE} \) with the magnetic field. The electric dipole moment operator \( \hat{d} \) is parallel to the symmetry axis of molecule and \( \theta_{de} \) is the angle between \( \hat{d} \) and \( E_{dc} \). The Euler angles are labeled by \( \omega = (\phi, \theta, \chi) \), though the angle \( \chi \) is not shown here for simplicity.

![Figure 6. Field configuration and Euler angles defining a general orientation of the molecule-fixed axes. The magnetic field \( B \) is chosen parallel to the space-fixed Z-axis, and the electric dc field \( E_{dc} \) is in the space-fixed XZ-plane making an angle of \( \theta_{BE} \) with the magnetic field. The electric dipole moment operator \( \hat{d} \) is parallel to the symmetry axis of molecule and \( \theta_{de} \) is the angle between \( \hat{d} \) and \( E_{dc} \). The Euler angles are labeled by \( \omega = (\phi, \theta, \chi) \), though the angle \( \chi \) is not shown here for simplicity.](image)

Table 4. \( g \)-factors for OH in the \( X^2\Pi \) state [9].

| \( g' \) | \( g'_{L} \) | \( g'_{S} \) | \( g'_{r} \) | \( g'_{e} \) |
|-------|-------|-------|-------|-------|
| 1.00107(15) | 2.00152(36) | -0.633(19) \times 10^{-3} | 4.00(56) \times 10^{-3} | 6.386(30) \times 10^{-3} | 2.0446(23) \times 10^{-3} |

**4.1. The effective Hamiltonian of OH molecule in combined electric and magnetic fields**

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\[
\hat{H} = \hat{H}_0 + \hat{H}_S + \hat{H}_Z. 
\]  

Here the zero-field Hamiltonian \( \hat{H}_0 \) is given in equation (3). The Stark Hamiltonian \( \hat{H}_S \) is given by

\[
\hat{H}_S = -\hat{d} \cdot E_{dc},
\]  

where \( \hat{d} \) is the electric dipole moment operator of OH, having a non-zero component along the molecule-fixed z-direction,

\[
T_4^J(\hat{d}) = \mu_{\alpha}^{(c)} \delta_{J, 0}\n\]  

with its permanent electric dipole moment \( \mu_{\alpha}^{(c)} = 1.65520(10) \) Debye [46]. Noting that the angle between \( \hat{d} \) and \( E_{dc} \), \( \theta_{de} \), satisfies \( \cos \theta_{de} = \cos \theta_{BE} \cos \theta + \sin \theta_{BE} \sin \theta \cos \phi \), we can rewrite the Stark Hamiltonian equation (12) as

\[
\hat{H}_S = -\mu_{\alpha}^{(c)} E_{dc} \sum_{p=0, \pm 1} d_{p0}^{(1)}(\theta_{BE}) \mathcal{D}_{p0}^{(1)*}(\alpha),
\]  

with the matrix elements of the Wigner D-matrix \( \mathcal{D}_{pq}^{(l)} \) and those of the reduced rotation matrix \( d_{pq}^{(1)} \) [40, 41]. In (11), the Zeeman Hamiltonian of the OH molecule is defined as
which contains, in order, the electronic orbital Zeeman effect, the electronic spin isotropic Zeeman effect, the rotational Zeeman effect, the nuclear spin Zeeman effect, and the electronic spin anisotropic Zeeman effect. Finally, the last two terms in equation (15) are parity-dependent and non-cylindrical Zeeman effects. The g-factors for OH in the ΠX2 state are listed in table 4.

4.2. The stark effect

We first examine how the Stark effect modifies the zero electric-field energy spectrum of OH in the absence of the magnetic field; $B_Z = 0$ and $\theta_{BE} = 0^\circ$. As in the calculation of the zero-field energy spectrum, we restricted ourselves to the lowest 96 states of OH, and diagonalize the Hamiltonian $\hat{H}_0 + \hat{H}_S$, given in equations (3) and (14), to obtain the Stark effect of the $v=0$, ΠX23/2 ground state. Since in the electronic and vibrational ground states electric dipole moments of molecules depend only on their rotational structures, their matrix elements can be specified by quantum numbers $J, \Omega$, and $M_J$ in the Hund’s case (a) basis, with the electric field along the space-fixed Z-direction.

Thus, the diagonal matrix elements of the Stark Hamiltonian $\hat{H}_S$ with the electric field along the space-fixed Z-direction become

\begin{equation}
\left\{ L \Lambda, \Sigma \Omega, J \Omega M_J, I M_I \right\} \hat{H}_S \left\{ L \Lambda, \Sigma \Omega, J \Omega M_J, I M_I \right\} = -\mu^{(e)} \frac{\Omega M_J}{J(J+1)}.
\end{equation}

yielding a linear Stark effect, that is, a first order energy shift in the applied electric field. However, due to the A-doubling terms, the Hund’s case (a) basis states are not the eigenstates of the zero-field Hamiltonian of OH. Instead, we can take the parity-conserved states equation (10) as an appropriate basis for zero or small applied fields. In this basis, the matrix elements become
\[
\langle L, S, J | \Omega | M_f, IM_f; \epsilon \rangle = -\mu_{dc}^{(\epsilon)} E_{dc} \frac{|\Omega|}{J(J+1)} \left( 1 - \epsilon \epsilon' \right)
\]

(18)

showing that the diagonal matrix elements (\(\epsilon = \epsilon'\)) vanish and that the Stark shift is quadratic, i.e., second order in the applied electric field. This comes from the fact that the electric field is a vector field, a vector-valued function which is odd under spatial inversion, and thus the electric field mixes parity states [12, 47]. The structure of the matrix elements equations (17) and (18) implies that states with different parities repel each other as the electric field is increased, and eventually form straight lines with opposite signs in their slopes.

Figure 7 shows the Stark spectrum of OH in the \(v = 0, X^2\Pi_{3/2}, J = 3/2\) ground state. Balancing one half of the A-doubling splitting \(\Delta_{11}\) with the linear Stark effect equation (17) averaged over \(\Omega M_f = 3/4\) and 9/4, we can estimate the critical value of the electric field \(E_c = 2499.84\ \text{V cm}^{-1} \sim 2.5\ \text{kV cm}^{-1}\), which determines whether the Stark effect becomes linear or quadratic at a given electric field. For weak electric fields \(E_{dc} < E_c\), the zero-field Hamiltonian \(\hat{H}_0\) dominates over the Stark term \(\hat{H}_S\), and its perturbative effect based on the parity-conserved states gives quadratic curves as shown in figure 7(a). On the other hand, for strong electric fields \(E_{dc} > E_c\), the Stark term becomes dominant, and the energy spectrum is well approximated by the linear Stark effect equation (17). Figures 7(b) and (c) show the hyperfine structure in the presence of the electric field for states adiabatically connecting to odd and even parity states in zero field, respectively. Note that since the projection of the total angular momentum, \(M_f\), is a good quantum number even in the presence of the electric field [47] (more generally, in collinear, but not crossed, electric and magnetic fields), there are always two-fold degeneracies with \(M_F = \pm |M_F|\) except for \(M_F = 0\).

4.3. The Zeeman effect

We proceed to consider the effect of non-zero static magnetic fields in the absence of the electric field; \(E_{dc} = 0\). As before, we treat only the lowest 96 states of OH and diagonalize the Hamiltonian \(\hat{H}_0 + \hat{H}_Z\), given in equations (3) and (15), to study the Zeeman effect of the \(v = 0, X^2\Pi_{3/2}, J = 3/2\) ground state. The Zeeman Hamiltonian of OH is dominated by contributions from the electronic orbital and spin isotropic Zeeman effects, as is seen from table 4. In the Hund’s case (a) basis, the diagonal matrix elements of these two operators can be written as

\[
\langle L, \Sigma, \Omega | \Omega | M_J, IM_J; \epsilon \rangle = \mu_B \frac{|\Omega|}{J(J+1)} \left( g^x + g^y \right)
\]

(19)

which become in the parity-conserved basis of the \(2 \Pi_{3/2}\) states

\[
\langle L, S, J | \Omega | M_J, IM_J; \epsilon \rangle = \mu_B \frac{|\Omega|}{J(J+1)} \left( g^x + g^y \right)
\]

(20)

Note here that the magnetic field is a pseudovector field, a vector-valued function which is even under spatial inversion, and therefore the magnetic field does not mix parity states while the electric field does [12, 47]. This can be seen in the matrix elements equation (20) which are diagonal in the parity-conserved basis. We illustrate this behavior in our Zeeman spectrum figure 8(a) with closeups shown in figures 8(b) and (c). The Zeeman spectrum of OH in the \(v = 0, X^2\Pi_{3/2}, J = 3/2\) ground state is composed of two spectra with parity states opposite to each other. The A-doubling splitting separates these two spectra by \(\Delta_{11}\), but except for such splitting they almost coincide with each other since the dominant part of the Zeeman effect equation (20) is the same for both the e- and f-states. To quantify the crossover from hyperfine-dominated spectra to Zeeman-dominated spectra, we set the hyperfine splittings \(\Delta_{11}^{(e)}\) and \(\Delta_{11}^{(f)}\) equal to the linear Zeeman effect equation (20) averaged over \(M_J = 1/2\) and 3/2, and then obtain the critical values of the magnetic field; \(B_{c}^{(e)} = 63.2576\ \text{G}\) for the e-states and \(B_{c}^{(f)} = 65.5859\ \text{G}\) for the f-states. For strong magnetic fields \(B_Z > B_{c}^{(e)}, B_{c}^{(f)}\), the Zeeman effect becomes dominant over the hyperfine structure in the zero-field, and the energy spectrum is well approximated by the linear Zeeman effect equation (20) in which every energy level can be specified by the quantum number \(M_f\) with hyperfine structure labeled by \(M_J\), as shown in figures 8(d)–(g). In contrast to the Stark spectrum figure 7(a), the A-doubling splitting remains relevant over the whole range of the magnetic field.

---

5 If we define the critical value of the electric field just by \(k_{c}E_{c} = \Delta_{11}/2\), we obtain \(E_{c} = 999.935\ \text{V cm}^{-1} \sim 1\ \text{kV cm}^{-1}\) [12]. This definition is simpler than ours but seems inconsistent because it takes into account algebraic factors for the A-doubling splitting while not for the Stark effect.
4.4. Energy spectra in combined electric and magnetic fields

In the presence of both electric and magnetic fields, the energy spectrum of the OH molecule becomes more complicated since the Stark effect mixes parity states while the Zeeman effect does not. In addition, the hyperfine interactions equation (8) give rise to a new kind of level repulsion, which we call Stark-induced hyperfine level repulsion.

Figure 8. (a) The Zeeman effect for OH in the $v = 0, X^2\Pi_{1,2}, J = 3/2$ ground state. The closeups of hyperfine structure (b) for odd parity states (f-states) in zero field and (c) for even parity states (e-states) almost coincide with each other, except for the $\Lambda$-doubling splitting, since the dominant part of the Zeeman effect equation (20) is the same. (d)–(g) show the level crossings between opposite parity states $|\pm \rangle_M$, approaching to the asymptotic states (d) $|\pm \rangle_M = |3/2, J\rangle$ and (e) $|\pm \rangle_M = |1/2, J\rangle$, respectively.

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Figure 9. (a) The Zeeman effect for OH in the \( v = 0, X^2 \Pi_{2,3}, I = 3/2 \) ground state, subject to a bias electric field with its strength \( E_{dc} = 500 \text{ V cm}^{-1} \) and relative angle to the magnetic field \( \theta_{BE} = 0^\circ \). (b) The closeups of hyperfine structure for odd parity states (f-states) in zero field and (c) for even parity states (e-states). (d)–(g) show the level crossings between opposite parity states \( \left| M_I = \pm 1/2 \right\rangle \) and \( \left| M_I = \pm 1/2 \right\rangle \), similar to figures 8(d)–(g); however, here level repulsions also appear in (f) and (g) due to the Stark effect and hyperfine interactions.
(a) The Zeeman effect for OH in the $v=0$, $X^2\Pi_2^2$, $J = 3/2$ ground state, subject to a bias electric field with its strength $E_{bc} = 500 \text{ V cm}^{-1}$ and relative angle to the magnetic field $\theta_{bc} = 45^\circ$. (b) The closeups of hyperfine structure for odd parity states (f-states) in zero field and (c) for even parity states (e-states). (d) and (e) show the level repulsions between opposite parity states $|\ell; M_e; J = 3/2\rangle$ and $|\ell; M_f; J = 1/2\rangle$ approaching the asymptotic states (d) $|\ell; M_e; J = 3/2\rangle$ and (e) $|\ell; M_f; J = 3/2\rangle$, and (e) $|\ell; M_e; J = 3/2\rangle$ and (e) $|\ell; M_f; J = 1/2\rangle$, respectively. In contrast to figures 8(d) and (e), all the crossings become avoided crossings, or level repulsions, in (d) and (e) as can be seen from (f)–(i) due to the field configuration allowing for transitions with $\Delta M_f = 0, \pm 1$. 

We first fix the strength of the electric field $E_{dc}$ and its angle $\theta_{BE}$ relative to the magnetic field, as shown in figure 6. Then, we numerically diagonalize the effective Hamiltonian with external fields equation (11) and plot the energy spectrum of the lowest 16 states as a function of the applied magnetic field. Figure 9(a) shows the spectrum with the electric field parallel to the magnetic field, $\theta_{BE} = 0^\circ$ and strength $E_{dc} = 500$ V cm$^{-1}$. We observed that figure 9(a) is quite similar to the pure Zeeman spectrum figure 8(a). In this case, from the conservation of angular momentum, the matrix elements of the Stark term equation (12) becomes non-zero only between states with $\Delta J = 0$, $\pm 1$, and $\Delta M_J = 0$ (selection rule for $\theta_{BE} = 0^\circ$). On the other hand, states with different parities but same $M_J$ are separated by the $\Lambda$-doubling splitting $\Delta_{LD}$, and the magnetic field keeps them apart since the Zeeman effect equation (20) does not mix parity states. Therefore, one might consider that applying parallel electric and magnetic fields does not qualitatively change the pure Zeeman spectrum. However, looking at hyperfine structure, figures 8(b)–(g) and 9(b)–(g), we found that there are qualitative differences. In particular, the electric field causes level repulsions where both the Stark effects and hyperfine interactions play a significant role. First of all, the closeups figures 9(b) and (c) differ from figures 8(b) and (c), respectively, since the Stark effects break the hyperfine degeneracies in zero fields into the degeneracies with $M_F = \pm |M_J|$, as can be seen in figures 7(b) and (c). Secondly, and even more intriguing, there are level repulsions in figures 9(f) and (g), which do not appear in the pure Zeeman spectrum figures 8(f) and (g). This is because under the electric field the energy eigenstates change from fixed-parity states into fixed-$\Omega$ states and such fixed-$\Omega$ fractions trigger level repulsions via hyperfine interactions. We remark that, due to the conservation of angular momentum, the hyperfine interactions have non-zero matrix elements between the same parity states with $\Delta M_J = -\Delta M_J$; this explains why only one of the four level crossings becomes level repulsion in figures 9(f) and (g). These level repulsions in the Zeeman spectrum can be observed only when we take into account both Stark effect and hyperfine interactions, thus our appellation Stark-induced hyperfine level repulsions. There is no qualitative difference between figures 8(d), (e) and 9(d), (e) since the condition for the hyperfine interaction, $\Delta M_J = -\Delta M_J$, is not satisfied.

In the case of non-parallel electric and magnetic fields, $\theta_{BE} = 45^\circ$, the selection rule of the Stark term equation (12) for $\theta_{BE} = 45^\circ$ becomes $\Delta J = 0$, $\pm 1$ and $\Delta M_J = 0$, $\pm 1$, yielding level repulsions between different parity states with $\Delta M_J = \pm 1$ around $B \sim 1300$ G as figure 10(a), where the strength of the electric field is set to be $E_{dc} = 500$ V cm$^{-1}$. These level repulsions, directly caused by the Stark effect, have energy gaps of 200–300 MHz and dominate over Stark-induced hyperfine level repulsions whose energy gaps are on the order of 10 MHz for $E_{dc} = 500$ V cm$^{-1}$. There are level repulsions also in figures 10(b) and (c) satisfying the selection rule $\Delta M_J = \pm 1$, that do not appear in figures 9(b) and (c) for $\theta_{BE} = 0^\circ$. The left- and right-most level repulsions in figure 10(d) come from the Stark effect with $\Delta M_J = \pm 1$, while the left- and right-most level repulsions in figure 10(e) from the Stark effect with $\Delta M_J = \pm 1$ and $\Delta M_J = 0$. We found another kind of level repulsion in figures 10(d) and (e), see also figures 10(f)–(i). The upper- and lower-most level repulsions in figure 10(d) require not only the Stark effects with $\Delta M_J = \pm 1$ and $\Delta M_J = 0$ but also the hyperfine interactions; and the upper- and lower-most level repulsions in figure 10(e) require the Stark effect with $\Delta M_J = \pm 1$ and the hyperfine interactions. As we will see next, some of these level repulsions become level crossings for $\theta_{BE} = 90^\circ$ since the Stark effect with $\Delta M_J = 0$ vanishes in that case.

When we apply an electric field perpendicular to the magnetic field, the selection rule of the Stark term equation (12) is $\Delta J = 0$, $\pm 1$ and $\Delta M_J = \pm 1$. Then, the Zeeman spectrum shown in figure 11(a), where $\theta_{BE} = 90^\circ$ and $E_{dc} = 500$ V cm$^{-1}$, has level repulsions between different parity states with $\Delta M_J = \pm 1$ around $B \sim 1300$ G as also seen in figure 10(a). Also, figures 11(b) and (c) are qualitatively the same as figures 10(b) and (c), respectively, and their quantitative differences mainly result from differences in the transverse components of the electric field. The absence of a Stark effect with $\Delta M_J = 0$ changes some of the level repulsions into level crossings; the upper- and lower-most level repulsions in figure 10(d) and the left- and right-most level repulsions in figure 10(e) become level crossings, as seen in figures 11(d) and (e).

4.5. Comparison with previous work

Finally, we shall compare our results with previous work on OH molecules. Recent works on the single-particle spectrum of OH in the presence of electric and/or magnetic fields dealt with phenomenological models which explicitly include the Lambda-doubling splitting $\Delta_{LD}$ and restrict themselves only to the lowest 16 states in the $^2\Pi_{1/2}$ manifold [8, 12, 13], or even to the lowest eight states neglecting hyperfine structure [14–17]. There exists one study which takes into account the effects of the higher rotational states and states in the $^2\Pi_{3/2}$ manifold [45], but still it neglects the hyperfine structure, centrifugal distortion effects, rotational Zeeman effect, electronic spin anisotropic Zeeman effect, and parity-dependent and non-cylindrical Zeeman effects. These effects are not negligible when we investigate cold and ultracold physics of OH molecules, as shown in figure 4. As an illustration, we make a comparison of the OH spectrum between the result of [8] and ours. Figure 12 shows the Zeeman spectrum of OH in the presence of an electric field with strength $E_{dc} = 500$ V cm$^{-1}$ and
relative angle to the magnetic field $\theta_{BE} = 90^\circ$, where figure 12(a) is taken from [8] and figure 12(b) is our result. In figure 12(a), $X_i$ labels the crossings of the $|e; 3/2\rangle$ state with the $|f; M_f = i\rangle$ states ($i = -3/2, -1/2, 1/2$). We can see that the crossing $X_{-3/2}$ occurs around $B = 500$ G in figure 12(a), while it occurs around $B = 430$ G in figure 12(b). Also, the crossings $X_{-1/2}$ and $X_{1/2}$ occur around $B = 750$ G and $B = 1500$ G, respectively in figure 12(a), while they occur around $B = 660$ G and $B = 1300$ G, respectively in figure 12(b). The crossing
points of $X_i$ are reduced by more than 10% in our results since the states with $J = 3/2$ in the $\Pi_{3/2}^2$ manifold, which are not considered in the reduced model of [8], give non-negligible contributions via the electronic spin isotropic Zeeman coupling to the states with $J = 3/2$ in the $\Pi_{3/2}^1$ manifold.

5. Conclusions

We studied the single-particle energy spectra of the hydroxyl free radical OH in its lowest electronic and rovibrational level both in zero field and in combined electric and magnetic fields. The hyperfine interactions and centrifugal distortion effects are fully taken into account to yield the zero-field spectrum of the lowest $\Pi_{3/2}^2$ manifold to an accuracy of less than 2 kHz; in comparison, previous results obtained an accuracy of a few MHz. Our more precise calculations are necessary to enable accurate investigation of both the single-molecule and many-body physics of OH molecules at microKelvin temperatures and below, which we expect will be achieved in the near future. We also examined level crossings and repulsions in hyperfine structure caused by applied electric and magnetic fields. The level repulsions play a significant role in experiments allowing for transitions between low-field seeking and high-field seeking states. We found that in order to estimate the values of magnetic fields at the level repulsions in the ground states of the $J = 3/2$, $\Pi_{3/2}^2$ manifold it is necessary to include the coupling with the excited states of the $J = 3/2$, $\Pi_{3/2}^1$ manifold. In this paper, we dealt only with static electric and magnetic fields, leaving the microwave dressing of OH for future work. The microwave dressing via AC electric fields makes it possible to realize multi-component systems with both degeneracy and dipole–dipole interactions between different components, and thus explore a rapidly growing field, that is, quantum simulation of multi-component dipolar systems with ultracold molecules.

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