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Communication: Magnetic dipole transitions in the OH $A^2\Sigma^+ \leftarrow X^2\Pi$ system

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We report on the observation of magnetic dipole allowed transitions in the well-characterized $A^2\Sigma^+ - X^2\Pi$ band system of the OH radical. A Stark decelerator in combination with microwave Rabi spectroscopy is used to control the populations in selected hyperfine levels of both Λ -doublet components of the $X^2\Pi_{3/2}$, $v = 0$, $J = 3/2$ ground state. Theoretical calculations presented in this Communication predict that the magnetic dipole transitions in the $A^2\Sigma^+$, $v = 1 \leftarrow X^2\Pi$, $v = 0$ band are weaker than the electric dipole transitions by a factor of 2.58×10^3 only, i.e., much less than commonly believed. Our experimental data confirm this prediction. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4751475>]

The hydroxyl radical (OH) plays a central role in many areas of chemistry and physics, and is one of the most extensively studied molecular species to date. In 1950, Meinel discovered that emission from vibrationally excited OH radicals in the earth's atmosphere is responsible for the infrared nighttime air glow.¹ Detection of the 18 cm absorption lines in the radio spectrum of Cassiopeia A by Weinreb *et al.* in 1963 revealed the presence of OH in interstellar space.² Shortly after, the OH radical was identified as the first molecule to form astrophysical (mega)masers.^{3,4} Since then, a wealth of spectroscopic investigations has been carried out in the microwave, infrared, and ultraviolet part of the spectrum, unraveling the electronic, vibrational, rotational, and hyperfine structure of the OH radical.

The OH ($^2\Pi$) radical (together with the similar NO ($^2\Pi$) radical) has also been established as the paradigm for molecular collisions studies. Interest in these open-shell radical species stems from their importance in combustion and atmospheric environments, as well as from their complex rotational structure that exhibits spin-orbit and Λ -doublet splittings. Ingenious methods have been developed to select OH ($^2\Pi$) radicals in a single rotational (sub)level, to orient them in space,^{5,6} and to tune their velocity.⁷ These methods have allowed collision experiments of transient species at the fully state-resolved level, and have contributed enormously to our present understanding of how intermolecular potentials govern molecular collision dynamics.

Recently, the OH radical has emerged as a benchmark molecule in the rapidly developing field of cold molecules.⁸ The OH radical was one of the first molecular species to be slowed down⁹ and to be confined in traps.¹⁰ In the near future, comparison of high-resolution spectroscopic data on cold OH radicals in the laboratory with interstellar megamaser observations may reveal a possible time variation of fundamental constants.¹¹

In the vast majority of experiments, ground state OH radicals are detected via laser induced fluorescence (LIF) after optical excitation on electric dipole allowed (EDA) transitions of the $A^2\Sigma^+ \leftarrow X^2\Pi$ band using a pulsed dye laser. An important property of the $A - X$ band is that it allows one to probe selectively the population of individual Λ -doublet components of opposite parity within a rotational state. Although the Λ -doublet splittings are typically much smaller than the bandwidth of pulsed dye lasers, the measurement of populations in selected Λ -doublet components is facilitated by the parity selection rules of EDA transitions and the large energy splitting between levels of opposite parity in the $A^2\Sigma^+$ state (see inset to Figure 1). Similar schemes are used to probe Λ -doublet component resolved populations in other $^2\Pi$ molecules such as NO, CH, and SH.

Extreme care, however, must be taken when using this approach. In recent experiments in our laboratory, molecular beams of OH with an almost perfect quantum state purity were produced via the Stark deceleration technique. In these experiments, $\geq 99.999\%$ of OH radicals in the $^2\Pi_{3/2}$, $J = 3/2$ rotational ground state reside in the upper Λ -doublet component of f symmetry; the lower Λ -doublet component of e symmetry is effectively depopulated in the Stark-deceleration process. When the populations in the e and f components were probed using LIF via the $A \leftarrow X$ transition, however, the apparent population in the e state appeared at least one order of magnitude too large. A spectroscopic re-investigation using a laser with a much narrower bandwidth revealed that magnetic dipole allowed (MDA) transitions were responsible for this effect.¹²

Magnetic dipole allowed transitions have rarely been observed in laser excitation spectra of heteronuclear molecules.¹³ Their existence is generally neglected in quantitative measurements of state populations, potentially leading to a significant misinterpretation of detector signals. In

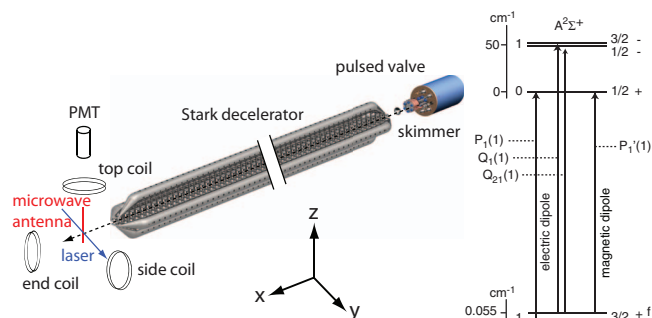


FIG. 1. Scheme of the experimental setup. The inset shows the electric dipole allowed and magnetic dipole allowed transition used for the detection of the two Λ -doublet components in the OH ground state.

homonuclear molecules, MDA transitions between electronic states are well known to result in “forbidden” band systems that violate the rigorous selection rules for electric dipole transitions. The most famous example is the atmospheric oxygen band, which appears in the red part of the solar spectrum. In contrast, MDA transitions in heteronuclear molecules mostly exist as weak satellite lines parallel to strong EDA transitions. The general rule of thumb is that MDA transitions are about a factor 10^5 weaker than the corresponding EDA transitions.¹⁴ Already in the 1920s, weak satellite lines in the $A - X$ emission band of OH were observed that appeared to correspond to transitions to the “wrong” Λ -doublet component.^{15–18} These lines were tentatively attributed to the MDA transitions by van Vleck in 1934,¹⁹ but received little attention ever since.

Here, we present a detailed analysis of MDA transitions in the $A^2\Sigma^+ \leftarrow X^2\Pi$ band of OH. We show that the satellite MDA transitions are surprisingly strong, and only three orders of magnitude weaker than the main EDA transitions. In our experiment we use a Stark-decelerator to produce packets of OH radicals that reside exclusively in the upper Λ -doublet component of f symmetry. A controlled fraction of the population is transferred to the lower component of e symmetry by using a microwave field. The MDA and EDA $A^2\Sigma^+, v = 1 \leftarrow X^2\Pi, v = 0$ transitions originating from the f and e level, respectively, are spectroscopically resolved using a narrowband pulsed dye laser. The observed ratio of the signal intensities agrees well with theoretical calculations for the EDA and MDA transition strengths.

The relevant energy levels and electronic transitions are shown in the inset to Figure 1. The electronic ground state of OH has a $X^2\Pi$ configuration. Each rotational level, labeled by J , splits into two Λ -doublet components which are separated by 0.055 cm^{-1} for the $J = 3/2$ rotational ground state. The upper and lower components have $+$ and $-$ parity, and are indicated by the spectroscopic labels f and e , respectively. Each of the Λ -doublet components of the $J = 3/2$ state is split into $F = 1$ and $F = 2$ hyperfine levels. The four resulting levels are referred to hereafter as $|X, f, +, F = 2\rangle$, $|X, f, +, F = 1\rangle$, $|X, e, -, F = 2\rangle$ and $|X, e, -, F = 1\rangle$.

The first electronically excited state of OH has a $A^2\Sigma^+$ configuration. In our experiments, only the $N = 0, J = 1/2$ rotational ground state of $+$ parity is of relevance. This state is split into two hyperfine states $F = 0$ and $F = 1$ that are

separated by 0.026 cm^{-1} , and are referred to hereafter as $|A, +, F = 0\rangle$ and $|A, +, F = 1\rangle$. The EDA ($P_1(1)$) and MDA ($P'_1(1)$) $A - X$ transitions couple the $|X, e, -\rangle$ and $|X, f, +\rangle$ states to the $|A, +\rangle$ states following the parity changing and parity conserving selection rules for EDA and MDA transitions, respectively.

Our experimental setup is schematically shown in Figure 1. A packet of OH ($X^2\Pi_{3/2}, v = 0, J = 3/2, f$) radicals with a velocity of 448 m/s is produced by passing a molecular beam of OH through a 2.6 m long Stark decelerator.²⁰ The Stark decelerator efficiently deflects molecules in the $|X, e, -\rangle$ states. A phase angle $\phi_0 = 50^\circ$ is used to ensure that the OH radicals that exit the decelerator reside exclusively in the $|X, f, +, F = 2\rangle$ state. The end of the Stark decelerator is electrically shielded to prevent any electric stray fields to penetrate into the interaction area.

A controlled fraction of the OH radicals is transferred into the $|X, e, -, F = 1\rangle$ state by inducing the $|X, f, +, F = 2\rangle \rightarrow |X, e, -, F = 1\rangle$ transition at 1.72 GHz with a microwave pulse. For this purpose a 90 mm long microwave antenna is installed 38 mm downstream from the decelerator and perpendicular to the molecular beam axis. No frequency-matched microwave resonator was used. The microwaves are reflected by the vacuum chamber walls filling the whole vacuum chamber, and we assume the microwaves to be unpolarized. The microwave duration and power can be controlled via a microwave switch and attenuator, respectively. The magnetic field in the interaction region is controlled by three copper coils with a diameter of 31 cm each, that are mounted 30 cm from the interaction area. One coil is positioned above the interaction area, one at the side and one at the end.

Two lasers are used to detect the OH radicals via LIF using the $1-0$ band of the OH $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ transition around 282 nm . The first laser, a pulsed dye laser (PDL) with a bandwidth of 1.8 GHz , is used to probe the population in the $|X, e, -\rangle$ state via the EDA $P_1(1)$ transition. The second laser, a pulsed dye amplifier (PDA) seeded by a single mode ring dye laser, has a bandwidth of 120 MHz and is used to separate the $P_1(1)$ and $P'_1(1)$ transitions. The power of the PDL and PDA lasers is adjusted to ensure that the transitions are induced under saturated and unsaturated conditions, respectively, and both lasers are linearly polarized in the z direction (see Figure 1 for the definition of the coordinate system). The off-resonant fluorescence is imaged into a photomultiplier tube (PMT).

In the presence of a magnetic field, the $F = 1$ and $F = 2$ hyperfine states split into 3 and 5 M_F Zeeman sublevels, respectively, that are readily resolved in the microwave spectrum. This is illustrated in Figure 2(a) that shows the $|X, f, +, F = 2\rangle \rightarrow |X, e, -, F = 1\rangle$ spectrum around 1.72 GHz , recorded with the broadband PDL system. In the black spectrum no currents are applied to the coils, and nine transitions can be identified corresponding to the nine allowed $|X, f, +, F = 2, M_F\rangle \rightarrow |X, e, -, F = 1, M_F\rangle$ transitions that are split by the earth's magnetic field.

For an unambiguous interpretation of the EDA and MDA $A - X$ transitions, and to measure their relative strengths, it is convenient to choose the laser polarization direction parallel to the space quantization axis. The earth's magnetic field,

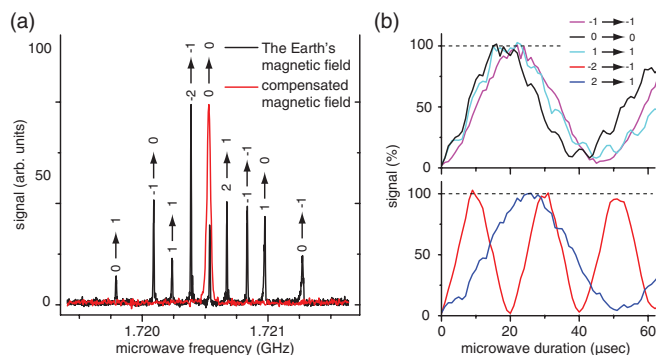


FIG. 2. (a) Frequency scan over the $|X, f, +, F=2\rangle \rightarrow |X, e, -, F=1\rangle$ transition in the presence of the earth's magnetic field (black) and the compensated magnetic field (red). Spectra are scaled to each other to facilitate a better comparison. The nine $|X, f, +, F=2, M_F\rangle \rightarrow |X, e, -, F=1, M_F\rangle$ transitions are indicated. (b) Rabi oscillations of selected $|X, f, +, F=2, M_F\rangle \rightarrow |X, e, -, F=1, M_F\rangle$ transitions.

however, is not suitable for this, as the direction of the magnetic field vector is in general not parallel to the laser polarization axis. We therefore follow the approach to first compensate the earth's magnetic field by applying currents to the three coils, and then to apply a controlled magnetic field that is parallel to the z axis, i.e., the laser polarization axis. The red curve in Fig. 2(a), shows the microwave spectrum that is recorded when currents of 2.10 A, 1.60 A, and 0.35 A are passed through the top, side, and end coils, respectively. It is seen that in this configuration the earth's magnetic field is compensated and the nine lines merge into one. An additional magnetic field in the z direction can be added by changing the current in the top coil, while keeping the current in the other coils constant. We have chosen to reverse the current in the top coil to generate a magnetic field with a magnitude that is twice as large as the z -component of the earth's magnetic field.

A controlled fraction of the population in each of the $|X, f, +, F=2, M_F\rangle$ levels can be transferred to an individual M_F component of the $|X, e, -, F=1\rangle$ level by applying a microwave pulse with a controlled pulse duration and power. In Figure 2(b), the fluorescence intensity is shown that is measured for five different microwave transitions as a function of the microwave pulse duration. Clear Rabi oscillations are observed, with different Rabi frequencies for each transition due to the differences in transition strength and the unpolarized microwave radiation. These Rabi oscillations were measured for all nine transitions shown in Figure 2(a), and for each transition it was observed that the maxima of the oscillations yield equal signal intensity. We thus conclude that the OH radicals that exit the Stark decelerator are equally distributed over the five M_F levels of the $|X, f, +, F=2\rangle$ state before the microwave field is applied.

Three different microwave transitions are induced that transfer population from the $|X, f, +, F=2, M_F=0\rangle$ into the $M_F=1$, $M_F=0$ and $M_F=-1$ levels of the $|X, e, -, F=1\rangle$ state, respectively. These transitions are indicated by the red, black, and blue arrows in the inset in Figure 3. For each transition, the microwave pulse duration and power was carefully chosen to transfer $(2.5 \pm 1)\%$ of all molecules from the

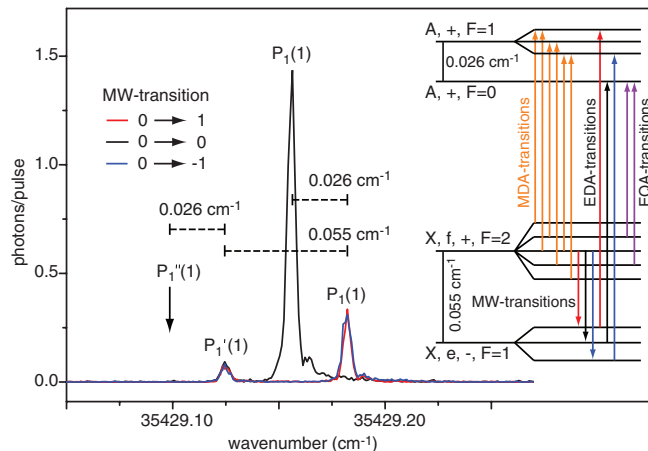


FIG. 3. The EDA and MDA OH(A-X) transitions for three different microwave transitions (marked red, black, and blue). The corresponding microwave transitions to prepare a population in selected M_F components of the $|X, e, -, F=1\rangle$ state are shown in the inset and the EDA $P_1(1)$, MDA $P_1'(1)$, and EQA $P_1''(1)$ transitions are indicated. The $|X, f, +, F=1\rangle$ and $|X, e, -, F=2\rangle$ levels are not shown in the inset, because the experiment does not populate these levels. The arrow indicates the position of possible EQA transitions $P_1''(1)$.

$|X, f, +, F=2, M_F=0\rangle$ level. Since this $M_F=0$ level contains one-fifth of all $F=2$ molecules, $99.5\% \pm 0.2\%$ of the OH radicals remain in the $|X, f, +, F=2\rangle$ state, in all three cases. The error (2σ) is given by the statistical spread of the Rabi oscillations.

The EDA $P_1(1)$ and MDA $P_1'(1)$ A – X transitions are then investigated in these three cases by probing the populations in the $|X, e, -\rangle$ and $|X, f, +\rangle$ states with the narrowband PDA system. This laser can spectroscopically resolve the Λ -doublet splitting in the $|X\rangle$ state and the hyperfine splitting in the $|A\rangle$ state, but not the hyperfine splittings in both $|X\rangle$ states or any Zeeman splittings. For parallel laser polarization and magnetic field direction, both the EDA and the MDA transitions obey the hyperfine selection rule $\Delta F=0, \pm 1$. The EDA transition has the additional selection rule $\Delta M_F=0$ (with $\Delta F \neq 0$ for $M_F=0$), while MDA transitions can only couple states with $\Delta M_F=\pm 1$. As indicated in Figure 3, there are thus six MDA transitions and only one EDA transition for each case.

In Figure 3 the MDA $P_1'(1)$ and the EDA $P_1(1)$ transitions are shown that are recorded in the three cases. The MDA $P_1'(1)$ transitions appear at the same position and with equal intensity in all spectra. Depending on the M_F level that is populated in the $|X, e, -, F=1\rangle$ state, the EDA $P_1(1)$ transition either couples to the $|A, +, F=0\rangle$ (for $M_F=0$) or the $|A, +, F=1\rangle$ state (for $M_F=\pm 1$). These transitions are clearly resolved in the spectra. The former transition appears four times more intense than the latter two transitions that are of equal intensity, as is expected theoretically.²¹ The Λ -doublet splitting is also recognized.

Having observed the MDA transition one might wonder about the presence of electric quadrupole allowed (EQA) transitions. For parallel laser polarization and magnetic field direction, an EQA transition can couple states with $\Delta F=\pm 2$, $\Delta M_F=\pm 1$. In the experiment no EQA $|A, +, F=0\rangle \leftarrow |X, f, +, F=2\rangle$ transition was observed, indicating that EQA

transitions in the OH ($A-X$) band are at least two orders of magnitude weaker than MDA transitions. This finding is supported by the theoretical estimate of the EQA transition strength.²¹

The relative strength of the $A-X$ MDA and the EDA transitions can be deduced from the measured spectra, and compared to theory. The strengths of the transitions are calculated from the magnitude of the two transition dipole moments, given by $\mu_{\text{el/mag}} = |\langle A^2\Sigma^+, v=1 | \hat{\mu}_{\text{el/mag}} | X^2\Pi, v=0 \rangle|$.²¹ We find $\mu_{\text{el}} = 0.0525$ a.u. and $\mu_{\text{mag}} = 0.142$ a.u. for the electric and magnetic transition dipole moments, respectively, so that $\frac{1}{\alpha^2} \cdot \mu_{\text{el}}^2 / \mu_{\text{mag}}^2 = 2.58 \times 10^3$. Here, α is the fine-structure constant accounting for the relative strength of the magnetic field compared to the electric field of the laser. Magnetic dipole transitions in the OH ($A-X$) band are thus only three orders of magnitude weaker than electric dipole transitions.

Taking into account the experimental initial distribution of molecules over the quantum states, as well as the direction of the laser polarization and the magnetic field, we find a theoretical ratio of 25.8 for the fluorescence intensities of the EDA $|A, +, F=0\rangle \leftarrow |X, e, -, F=1, M_F=0\rangle$ transition and the combined six MDA $|A, +, F=1\rangle \leftarrow |X, f, +, F=2\rangle$ transitions.²¹ The uncertainty in this ratio is estimated to be about 10%.²¹ This value agrees well with the experimental value of (18 ± 8) , obtained by comparing the strong central with the left peak in Figure 3. The experimental error is mainly given by the statistical error of the population transfer in the microwave field from the $|X, f, +, F=2, M_F=0\rangle$ to the $|X, e, -, F=1, M_F\rangle$ levels.

In this work we reported on the direct measurement of magnetic dipole transitions in laser excitation spectra of the OH $A^2\Sigma^+, v=1 \leftarrow X^2\Pi_{3/2}, v=0$ band. These satellite transitions appear only three orders of magnitude weaker than the corresponding main electric dipole transitions, and can potentially lead to a misinterpretation of detector signals when the Λ -doublet-resolved state populations in OH ($X^2\Pi$) are measured. This finding may seem of limited significance in some experiments; in experiments in which large differences in Λ -doublet populations are expected it may be essential. In particular in state-of-the-art molecular beam

experiments with unprecedented state purity and precision, magnetic dipole transitions should be carefully considered.

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²¹See supplementary material at <http://dx.doi.org/10.1063/1.4751475> for a detailed description of the theoretical calculation.