

Detection of OH⁺ in its *a*¹Δ state by far infrared laser magnetic resonance

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The spectrum associated with the $J=3\leftarrow 2$ transition of OH⁺ in the *a*¹Δ($v=0$) state has been observed by far infrared laser magnetic resonance spectroscopy. A new microwave discharge source enabled the detection of this spectrum, which is the first observation of the rotational spectrum of an ion in a metastable state. Assignment and least-squares fitting of the observed transitions have determined the following molecular constants: $B_0=494.420\,388\,(22)$ GHz, the proton hyperfine parameter $a=74.84\,(32)$ MHz, $g'_L=1.000\,915\,(15)$, and $g_r=-0.001\,815\,(18)$, with the 1σ uncertainties of the last digits in parentheses. The relationship of these parameters to the geometric and electronic structure of OH⁺ is discussed.

I. INTRODUCTION

We report the observation and assignment of the far infrared (FIR) laser magnetic resonance (LMR) spectrum of the OH⁺ ion in its excited *a*¹Δ state, which to our knowledge is the first recorded rotational or vibrational spectrum of an ion in a metastable state. The OH⁺ ion has been the subject of previous experimental studies in both its triplet and singlet manifolds. The *A*³Π-*X*³Σ⁻ system in both OH⁺ and OD⁺ has been studied in detail by Merer *et al.*,¹ who also give references to earlier spectroscopic work on this electronic transition. They observed perturbations in the $v=1$ level of the *A*³Π state by the $v=0$ level of the *b*¹Σ⁺ state in both molecules, as well as a perturbation between the *A*³Π($v=1$) level and the *a*¹Δ($v=6$) level in OD⁺. Rotational transitions of OH⁺ and OD⁺ in the ground *X*³Σ⁻ state have been detected by absorption in the far infrared using tunable laser sideband,^{2,3} LMR,^{4,5} and tunable diode laser spectroscopy.⁶ Infrared vibration-rotation spectra of the fundamental^{5,7} and hot ($v''\leq 5$) (Ref. 8) bands of OH⁺ in its *X*³Σ⁻ state have also been reported.

Helm *et al.*⁹ recorded photofragment spectra of OH⁺ and assigned transitions to the *A*³Π-*X*³Σ⁻ system and tentatively to the *c*¹Π-*a*¹Δ system. In the singlet manifold, the (3,0) band of the *c*¹Π-*b*¹Σ⁺ system of OH⁺ has been studied by laser photofragment spectroscopy by Sarre and co-workers.¹⁰ They determined molecular parameters for the *c* and *b* states, of which the latter agreed with those derived from the perturbation analysis of Merer *et al.*¹ Katsumata and Lloyd¹¹ recorded photoelectron spectra of OH and OD, which showed ionizations to the *X*³Σ⁻ ($v=0, 1$) and *a*¹Δ($v=0$) states of the positive ions. They measured the term energy of the *a*¹Δ state with respect to the ground state as $T_0=2.19$ eV ($17\,700\text{ cm}^{-1}$). In addition to the experimental work, five *ab initio* calculations of OH⁺ have been reported.¹²⁻¹⁶

We have measured the lowest rotational transition ($J=3\leftarrow 2$) of OH⁺ in the *a*¹Δ state, near 100 cm^{-1} , by FIR LMR spectroscopy. Values of the rotational constant B , the orbital and rotational g factors, and the proton hyperfine constant a were obtained from a least-squares fit to the observed Zeeman transitions. We discuss the values of these parameters in relation to those of OH⁺ in the *X*³Σ⁻ state and of NH in the *a*¹Δ state.

II. EXPERIMENT

We have developed a microwave discharge source for the FIR LMR spectrometer at the National Institute of Standards and Technology for observing rotational spectra of ions and other transient species. Since this report on the OH⁺ *a*¹Δ state is one of the first experiments performed with this new source, a detailed experimental description is presented. The microwave discharge cavity shown in Fig. 1 was specifically designed to operate in the magnetic field close to the sample region of the LMR spectrometer. The basic design is that of cavity number 5,¹⁷ which is a one-quarter wavelength long coaxial cavity. In this cavity, the tuning screw, a quarter wavelength long center conductor, is moved off center to permit the addition of a 14 mm diameter gas flow tube along the center axis. A quartz disk is fused to one end of the flow tube and is sealed with high temperature (260 °C) silicone rubber sealant to the outside wall of the cell, a 35 mm diameter copper pipe, to form the bottom of the cavity. On the sample side of the quartz disk, which faces toward the FIR radiation field, a copper plate is soldered on one side to form the ground electrode, and the 2450 MHz discharge operates between the tuning screw and this plate. The cavity is positioned so that the ground plate and the bottom of the center conductor are lined up approximately parallel to the magnetic field, as shown in Fig. 1. Magnetic coupling to the cavity (and possibly directly to the plasma) is accomplished with a small loop on the end of a coaxial cable connecting the cavity to a microwave generator. Optimum coupling

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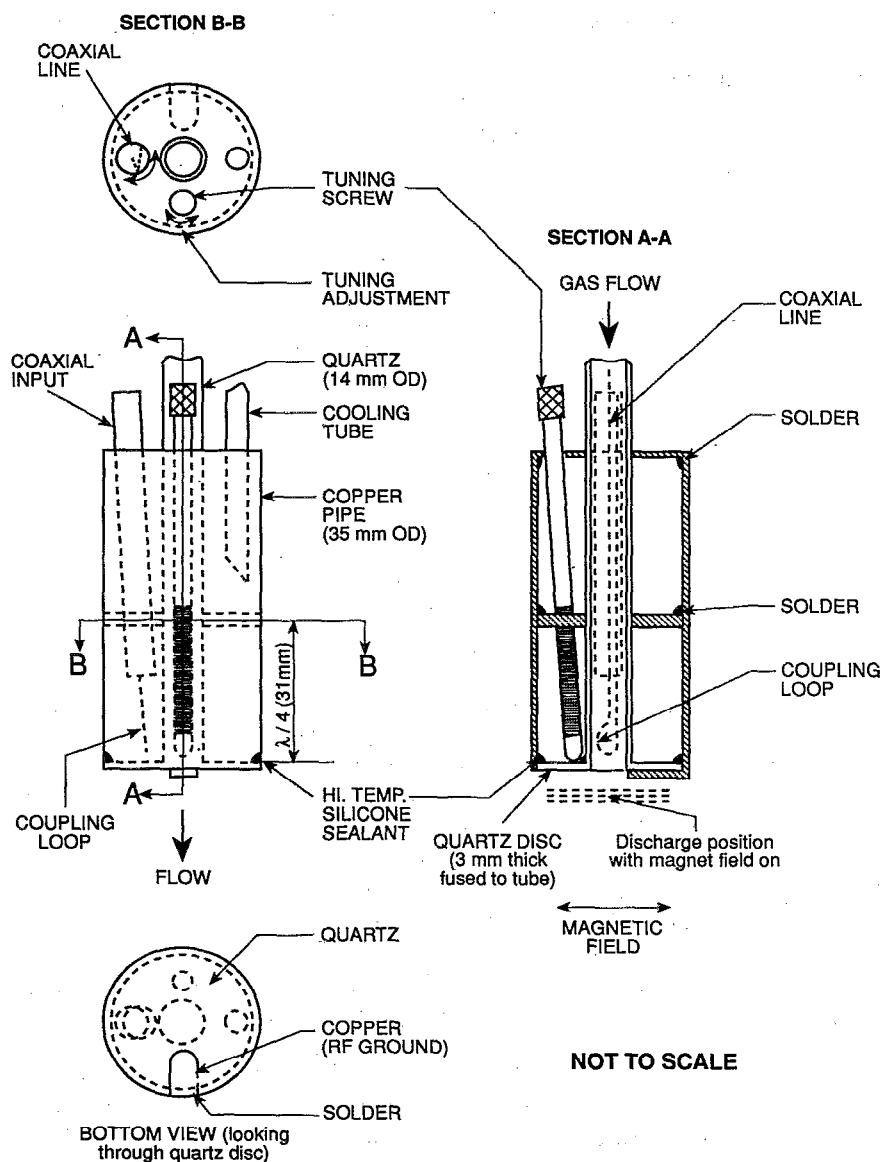


FIG. 1. A schematic diagram of the 2450 MHz ($\lambda=12.24$ cm) microwave discharge cavity. The aim of the design was to produce a discharge plasma at the mouth of the flow tube, as close as possible to the far infrared radiation field.

and tuning are achieved by rotating this loop (by twisting the coaxial line) to minimize the power reflected from the cavity.

The appearance of the discharge changes significantly when the magnetic field is present—the discharge extends parallel to the field from wall to wall. Considerable after-glow below the main discharge region is also observed. The discharge produces considerable noise on the FIR laser output and the microwave power is often reduced to improve the signal-to-noise ratio. In spite of this noise, we have observed the LMR spectra of OH^+ described in this paper as well as spectra of the N^+ , F^+ , and NH^+ ions in their ground and metastable states, all with signal-to-noise ratios in excess of 100:1 using 300 ms output time constants.¹⁸

In the present work, ultrahigh purity helium flowed

through the cell at a pressure of about 130 Pa (1 Torr), and the microwave discharge power was between 30 and 50 W. The manufacturer's analysis of the helium listed N_2 (1.4 ppm) and H_2O (0.2 ppm) as specific impurities, with total impurities of less than 3 ppm. The OH^+ signals did not increase by adding small amounts of water to the helium, or by freezing out any water in the helium line with a liquid nitrogen trap. These observations lead us to believe that the OH^+ ions are formed in the discharge by some reaction involving O_2 and H_2 (and not H_2O), which presumably are also present in the helium as impurities.

A detailed description of the optically pumped FIR LMR spectrometer used in this experiment can be found in Ref. 19. Two laser lines were used in this work—the 100.8 μm line of CH_3OH pumped by the 9R(14) CO_2 laser line and the 101.3 μm line of $^{13}\text{CH}_3\text{OH}$ pumped by 10R(12).

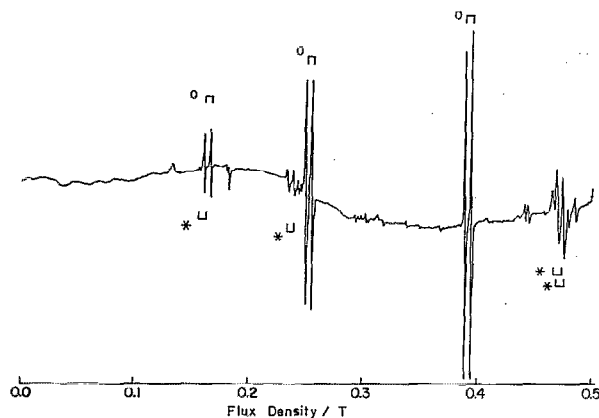


FIG. 2. A 0–0.5 T survey scan of the 101.3 μm laser magnetic resonance spectrum in σ polarization. The marked transitions occur within the $X^3\Sigma^-$ (O) and $a^1\Delta$ (*) states of OH⁺. The other, unassigned lines arise presumably from impurities.

The frequencies of these lines were measured specifically for this study.²⁰ There are no FIR laser lines close to the predicted frequencies of higher rotational transitions of OH⁺ in the $a^1\Delta$ state; thus, only the $J=3\leftarrow 2$ transition was observed. The frequency of the $J=3\leftarrow 2$ transition and the field strength pattern of its magnetic resonances were first estimated using the rotational and Zeeman parameters of the isoelectronic NH $a^1\Delta$ state.²¹ The observed transitions could be assigned securely to OH⁺ in the $a^1\Delta$ state both by their Zeeman patterns, which were similar to those of NH in the $a^1\Delta$ state,²¹ and by the characteristic doubling of each resonance, which results from the nuclear spin of the proton. Transitions occurring for OH⁺ in the $X^3\Sigma^-$ ground state were also observed on both laser lines; these were unambiguously assigned using the $X^3\Sigma^-$ molecular parameters of Gruebele *et al.*⁴

III. RESULTS AND ANALYSIS

Figure 2 displays a 0–0.5 T survey scan using the 101.3 μm laser line in σ polarization. We see transitions arising from OH⁺ in both the $X^3\Sigma^-$ and $a^1\Delta$ states, as well as transitions arising from unknown species. The spectrum in Fig. 3, which covers a small portion of the 100.8 μm spectrum shows the proton hyperfine structure of one of the resonances. In Table I, we list the magnetic field resonances for OH⁺ in the $a^1\Delta$ state observed for the two laser lines.

The data were subjected to a least-squares fit using the standard effective Hamiltonian for $a^1\Delta$ state²²

$$H = H_{\text{rot}} + H_{\text{hf}} + H_Z, \quad (1)$$

$$H_{\text{rot}} = B_0 N^2 - D_0 N^4, \quad (2)$$

$$H_{\text{hf}} = a L_z I_z, \quad (3)$$

$$H_Z = g'_L \mu_B \mathbf{B} \cdot \mathbf{L} - g_{\mu_B} \mathbf{B} \cdot (\mathbf{J} - \mathbf{L}), \quad (4)$$

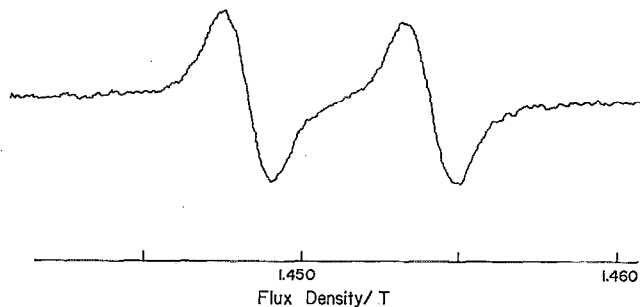


FIG. 3. The $M_J = -2 \leftarrow -2$ transition in the 100.8 μm π spectrum of OH⁺ ($a^1\Delta$) displaying the doublet hyperfine splitting arising from the proton. This spectrum was recorded with an output time constant of 300 ms.

where H_{rot} , H_{hf} , and H_Z are the rotational, proton hyperfine, and Zeeman Hamiltonians. The molecular Hamiltonian was set up in a nuclear spin decoupled basis set using the matrix elements given in Ref. 22.

Since only one rotational transition was observed, we fixed the centrifugal distortion constant D_0 to the value obtained by scaling D_0 for OH⁺ in the $X^3\Sigma^-$ state in the ratio of the corresponding parameters for the NH radical.^{21,22} Thus only four parameters were determined in the least-squares fit B_0 , a , g'_L , and g_r . The fitted values of these parameters and their estimated errors are given in Table II. The standard deviation of the fit is 0.43 MHz, which is comparable with the estimated precision of the data. The experimental uncertainty is limited by the uncertainty in the measurement of the magnetic flux density (estimated as one part in 10^4) and not by the repeatability of an individual measurement.

We also list in Table II the least-squares estimate of the zero-field frequency of the $J=3\leftarrow 2$ transition, which may be of interest in astronomy. This rotational transition has three hyperfine components whose assignments, calculated frequencies, and relative intensities are as follows: $F=5/2\leftarrow 5/2$ at 2960.287 GHz (2.9% relative intensity); $F=7/2\leftarrow 5/2$ at 2960.374 GHz (57.1% relative intensity); and $F=5/2\leftarrow 3/2$ at 2960.412 GHz (40.0% relative intensity). The absolute uncertainties in these transition frequencies are about 3 MHz and are dominated entirely by the uncertainties in the two laser frequencies (estimated as 3 MHz) and not by the statistical uncertainty in the value of $6B_0 - 108D_0$. However, the hyperfine splittings of this line can be estimated more precisely as 87.3(4) and 37.4(2) MHz.

IV. DISCUSSION

This work describes the first detection of the rotational spectrum of a molecular ion in a metastable state. The $a^1\Delta$ state of OH⁺ is very high lying—about 17 700 cm^{-1} above the $X^3\Sigma^-$ state—but is likely to be very metastable, since electric dipole transitions to the ground state are doubly forbidden. The development of a new microwave discharge source for observing LMR spectra of highly transient species was critical for this observation.

TABLE I. Observed LMR spectra of the a¹Δ(v=0), J=3←2 transition of ¹⁶OH⁺.^a

M _j '	M _j '	M _j '	M _j '	Flux density (Torr) ^b	Obs.—calc. (MHz)	Tuning rate (MHz/mT)
The 100.8 μm line of CH ₃ OH(2973.9411 ₅ GHz); σ polarization						
-1	1/2	-2	1/2	0.963 66	-0.656	14.046
-1	-1/2	-2	-1/2	0.968 86	0.865	14.045
0	1/2	-1	1/2	1.439 91	-0.210	9.444
0	-1/2	-1	-1/2	1.445 23	-0.137	9.444
The 100.8 μm line of CH ₃ OH (2973.9411 ₅ GHz); π polarization						
-2	1/2	-2	1/2	1.448 21	0.292	9.361
-2	-1/2	-2	-1/2	1.453 59	-0.152	9.361
The 101.3 μm line of ¹³ CH ₃ OH (2958.1988 ₀ GHz); σ polarization						
1	1/2	2	1/2	0.153 35	-0.556	-13.988
1	-1/2	2	-1/2	0.158 96	0.181	-14.007
0	1/2	1	1/2	0.231 56	0.177	-9.330
0	-1/2	1	-1/2	0.236 75 ^c	-1.681	-9.332
-1	1/2	0	1/2	0.465 86	-0.153	-4.653
-1	-1/2	0	-1/2	0.471 30 ^{d,e}	0.562	-4.653
3	1/2	2	1/2	0.469 58	0.316	-4.632
3	-1/2	2	-1/2	0.474 89	0.128	-4.631
The 101.3 μm line of ¹³ CH ₃ OH (2958.1988 ₀ GHz); π polarization						
2	1/2	2	1/2	0.231 94	-0.708	-9.312
2	-1/2	2	-1/2	0.236 90 ^e	-5.535	-9.317
1	1/2	1	1/2	0.468 26	0.191	-4.631
1	-1/2	1	-1/2	0.473 69	0.422	-4.631

^aExcept where noted, each datum was given one unit weight in the least-squares fit.

^bThe magnetic field measurements have an estimated uncertainty of one part in 10⁴.

^cOverlapped by an impurity line.

^dOverlapped by the 0.469 58 T line.

^eGiven zero weight in the least-squares fit.

The determination of the a¹Δ molecular parameters shown in Table II allows us to make comparisons with those for the X³Σ⁻ state and those for the a¹Δ and X³Σ⁻ states of the isoelectronic molecule NH. The fitted value of B₀ (494.4 GHz) is within 0.2% of the value (495.4 GHz) obtained by scaling B₀ for OH⁺ in the X³Σ⁻ state⁴ in the ratio of the corresponding parameters for NH.^{23,24} This result gives us confidence that our constrained value of D₀ obtained by a similar scaling, is appropriate. The derived value of the bond length of OH⁺ in its a¹Δ state, r₀ = 0.1043 nm, is very similar to that found in NH (a¹Δ), for which r₀ = 0.1045 nm.²¹

TABLE II. Molecular parameters for the a¹Δ states of OH⁺ and NH.^a

Constant	OH ⁺ a ¹ Δ(v=0) (This work)	NH a ¹ Δ(v=0) (Ref. 21)
B ₀	494 420.388(22)	493 043.182(95)
D ₀	56.81 ^b	50.45(11)
a	74.84(32)	70.9(14)
g _L	1.000 915(15)	1.001 03
g _r	-0.001 815(18)	-0.001 58(6)
v ₀ (J=3←2)	2 960 386.8(26) ^c	

^aValues are in megahertz except for the g factors, which are unitless. Calculated 1σ uncertainties in the last digits are given in parentheses.

^bThe parameter constrained to this value, as described in the text.

^cThe calculated frequencies of the three hyperfine components of this transition are given in the text.

The proton magnetic hyperfine parameter a reveals details of the chemical bonding in the OH⁺ molecule. This parameter can be written

$$a = \frac{1}{4\pi\epsilon_0\hbar c^2} 2\mu_B g_N \mu_N \sum_i \langle r_i^{-3} \rangle, \quad (5)$$

where the notation is standard; if SI units are used, a is given in hertz. *Ab initio* calculations^{12,13} show that the electronic configuration of the X³Σ⁻, a¹Δ, and b¹Σ⁺ states is

$$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2, \quad (6)$$

where the 1π orbital is predominantly O(2p) in character. For the a¹Δ state, with two π⁺ electrons, Eq. (5) reduces to²⁵

$$a = \frac{1}{4\pi\epsilon_0\hbar c^2} 2\mu_B g_N \mu_N \frac{2}{\Lambda} \langle r^{-3} \rangle_{2p} \\ = \frac{1}{4\pi\epsilon_0\hbar c^2} 2\mu_B g_N \mu_N \langle r^{-3} \rangle_{2p}. \quad (7)$$

Since the hyperfine interaction with the hydrogen nucleus arises from two pπ electrons centered on the oxygen atom, one predicts that the value of ⟨r⁻³⟩^{-1/3} determined from Eq. (7) should be similar to the bond length determined from the rotational constant. Using Eq. (7) and the fitted value of a, we find ⟨r⁻³⟩^{-1/3} = 0.1018 ± 0.0001 nm, which is 2.4% smaller than the bond length ⟨R⁻²⟩^{-1/2} = 0.1043 nm determined from B₀. Similar comparisons

can be made for the ¹Δ states of NH (Ref. 21) and PH,²⁶ where the values of $\langle r^{-3} \rangle^{-1/3}$ are only 0.6% and 0.8% smaller than the bond lengths. We carried out a more sophisticated numerical calculation²⁷ using an electron in a O⁺(2*pπ*) orbital at a distance of 0.1043 nm from a ¹H nucleus and obtained the value $\langle r^{-3} \rangle = 856 \text{ nm}^{-3}$, or $\langle r^{-3} \rangle^{-1/3} = 0.1053 \text{ nm}$. This result is not surprising—an electron in an oxygen-centered π orbital will, on average, be located at a distance somewhat larger than *r*₀ from the hydrogen nucleus. Thus the value of the hyperfine parameter *a* reveals a small but significant deviation of the electronic configuration of the OH⁺ *a*¹Δ state from that described by Eq. (6). The smaller than expected value of $\langle r^{-3} \rangle^{-1/3}$ may suggest a slight contamination of the *a*¹Δ state by the *A*³Π state lying 10 330 cm⁻¹ above it.^{1,11} These two states are mixed by the electron spin-orbit operator.

An analysis of the Zeeman parameters is also instructive for understanding the electronic structure of OH⁺. We can estimate the nuclear contribution (*g*_r^N) to the rotational *g* factor *g*_r using an expression given by Carrington *et al.*²⁸

$$g_r^N = \frac{m_e}{m_1 + m_2} \left(\frac{Z_1 m_2^2 + Z_2 m_1^2}{m_1 m_2} \right), \quad (8)$$

where *m*_{*i*} and *Z*_{*i*} are the masses and charges of the two nuclei and *m*_{*e*} is the mass of an electron. This expression gives *g*_r^N = 0.000 533 for ¹⁶O¹H⁺. Then, using the fitted value for *g*_r of -0.001 815(18), we find *g*_r^e = *g*_r^N - *g*_r = 0.002 348(18) for the electronic contribution. Furthermore, if we assume the pure precession hypothesis and that the *c*¹Π state is the only contributor to *g*_r^e, then we expect that²¹

$$g_r^e = \frac{4B_0(g_L + g_r^N)}{E_{\Pi} - E_{\Delta}}, \quad (9)$$

which yields *g*_r^e = 0.002 64. This agrees within 10% of the experimental value derived above. [In evaluating Eq. (9), we have used 24 980 cm⁻¹ for the energy separation *E*_Π - *E*_Δ, taken from the laser photofragment spectrum of the *c*¹Π - *b*¹Σ⁺ (3,0) band,¹⁰ combined with *ab initio* values of the *c*¹Π vibrational intervals¹³ and experimental values^{1,11} of the *b*¹Σ⁺ and *a*¹Δ term energies.] These calculations support the hypothesis that the electronic contribution to *g*_r observed in the *a*¹Δ state arises nearly entirely from mixing with the *c*¹Π state. The next higher ¹Π state is predicted to lie 83 000 cm⁻¹ above the *c*¹Π state.¹³

Finally, if the *a*¹Δ state is only perturbed by Π states, then the value of *g*_r^e is also given²¹ by *g*_r^e = 2Δ*g*_L = 2(*g*_L' - 0.9999). Using the fitted value *g*_L' = 1.000 915(15), this gives *g*_r^e = 0.0020. The close agreement with the preceding calculations of *g*_r^e gives further evidence for our interpretation.

In the future, we hope to be able to measure higher-*J* transitions within the *a*¹Δ state of OH⁺ by finding new FIR laser lines which are nearly coincident with these transitions; the observations of these transitions would enable a precise measurement of the centrifugal distortion constant

*D*₀. Similar LMR measurements of rotational transitions within the *a*¹Δ state of OD⁺ are desirable. Finally, the microwave discharge source described in this work undoubtedly forms OH⁺ in excited vibrational levels of its *a*¹Δ state, which would also be amenable to LMR detection and analysis.

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