COMMUNICATIONS

Submillimeter spectroscopy on OH+: The rotational transition at 1 THz

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In this letter we report the first observation and complete analysis of the spin multiplet and hyperfine structure of the lowest rotational transition $(N = 1 \leftarrow 0)$ in the $X^3\Sigma^-$, $v = 0$ ground state of the hydroxyl cation OH+. Until now, spectroscopic information was limited to ultraviolet emission spectra of the $A^3\Pi_i$–$X^3\Sigma^-$ system of OH+ and OD+, whose structures and perturbations were thoroughly reinvestigated by Merer *et al.*[1] Recently, the first detection of the infrared spectrum of OH+ was reported by Oka's group.[2] Although identification of optical emission spectra revealed presence of the OH+ ion in comet tails,[3] its occurrence in interstellar space has not been established yet. The present study yields molecular constants for the ground state and provides accurate frequencies for the lowest transitions that may facilitate detection of OH+ in interstellar clouds.[4]

The absorption spectrometer used is an improved version of the one developed by van den Heuvel.[5] Tunable narrow-band radiation in the submillimeter region is generated in Schottky barrier diodes by frequency mixing of klystrons with lines from an HCN laser. Side bands cover the frequency range from 700 to 1200 GHz using fundamental (~ 50 μW FIR power) and second harmonic ($\sim 1\,\mu$W FIR) of the klystron frequencies. An increase of FIR power level by an order of magnitude has been achieved by improved coupling between radiation and diode. Ultimate sensitivity corresponds to a minimal absorption coefficient of $\sim 10^{-7}\,\text{cm}^{-1}$ for single pass of 1 m. Molecular ions are produced inside an absorption cell containing a hollow cathode discharge tube[6] with temperature controlled cooling. This type of discharge can sustain an ion-rich and field-free negative glow over the entire cathode volume. In general, modulation of the discharge current[7] has been applied. This modulation has clear advantages compared to frequency modulation: better baseline behavior, full square wave modulation independent of line width, better resolution (true line shapes) and discrimination of transient species. Additional identification of lines can be obtained from signal response to applied longitudinal magnetic fields of moderate strength (up to 10 mT); Zeeman splitting for paramagnetic states and strong decrease in case of ionic species.[8]

The OH+ ion was produced by discharging He with 10% admixture of equal amounts of O_2 and H_2. An increase of the gas flow by an order of magnitude (to ~ 10 mbar ℓ/s) proved essential to observation of OH+ spectra. Although further increase of flow may increase yield of OH+, signal to noise ratios (at best 40 at RC = 1 s) were sufficient to record the spectra. Pressure was about 6×10^{-2} mbar as measured in the pumping line. The hollow cathode tube was cooled by liquid nitrogen. Optimum discharge current was 600–700 mA. Observed absorption coefficients vary from 10^{-5} to $10^{-6}\,\text{cm}^{-1}$. From the calculated dipole moment[9] of 2.32 D and by assuming a rotational temperature of ~ 200 K, the concentration of OH+ ions is estimated to be a few 10^9 cm^{-3}.

Careful searches for the spectrum of the $N = 1 \leftarrow 0$ transition of OH+ were made. All three components of the spin multiplet have been observed $(J = 0 \leftarrow 1$, $J = 1 \leftarrow 1$, and $J = 2 \leftarrow 1)$ with resolved hyperfine structures; the frequencies are listed in Table I. The spectral lines have collision broadened widths of about 5 MHz.

The observed spectrum has been fitted to an appropriate Hamiltonian describing the rotational and fine structure[10] and the magnetic hyperfine structure[11] of a $^3\Sigma$ state. Hyperfine structure was treated separately and analyzed first. The parameters $b + c/3$ and c associated with the H nucleus have been determined as well as the hyperfine-free

TABLE I. Observed frequencies of the $N = 1 \leftarrow 0$ transition of OH+ (in MHz).

$J' \leftarrow J''$	$F' \leftarrow F''$	Observed	Obs − Calc
0 1	1/2 1/2	909 045.2(1.0)	0.1
0 1	1/2 3/2	909 158.8(1.0)	− 0.1
2 1	5/2 3/2	971 803.8(1.5)	0.5
2 1	3/2 1/2	971 805.3(1.5)	− 0.2
2 1	3/2 3/2	971 919.2(1.0)	− 0.0
1 1	$\nu(1/2 \leftarrow 1/2)$–$\nu(3/2 \leftarrow 1/2)$[a]	− 6.5(0.3)	0.1
1 1	3/2 1/2	1 033 004.4(1.0)	− 0.2
1 1	$\nu(1/2 \leftarrow 3/2)$–$\nu(3/2 \leftarrow 3/2)$	− 6.8(0.4)	− 0.2
1 1	3/2 3/2	1 033 118.6(1.0)	0.2

[a] Frequency interval between hyperfine transitions.

TABLE II. Molecular constants for the $X^3\Sigma^-$, $v = 0$ ground state of OH$^+$ (in MHz).

	This work	Ref. 1
B	492 345.84(27)	492 329.(23)
D^a	57.483(73)	57.483(73)
λ	64 245.01(54)	63 988.(344)
γ	− 4 532.71(36)	− 4 431.(41)
$(b + c/3)_H$	− 75.83(49)	
c_H	126.92(86)	

[a] Parameter constrained within its uncertainty to value from Ref. 1.

origins of the spin components of the rotational transition $N = 1 \leftarrow 0$; $J = 0 \rightarrow 1$: 909121.0(7) MHz, $J = 2 \leftarrow 1$: 971811.7(7) MHz, and $J = 1 \leftarrow 1$: 1033078.3(7) MHz. These origins were used to determine the rotational constant B, and spin–spin constant λ and the spin–rotation constant γ. The centrifugal distortion constant D was constrained within its uncertainty to the value obtained from the optical spectrum.[1] All molecular constants determined are given in Table II. Agreement with values from Merer et al.[1] is reasonable, considering the quite extensive deperturbation they had to follow. The hyperfine parameters show an expected resemblance with their values in the isoelectronic NH radical.[12]

We hope that the present study may facilitate astrophysical searches for the OH$^+$ ion. The frequencies of the magnetic dipole transitions $J = 1 \leftarrow 0$ and $J = 1 \leftarrow 2$ within the $N = 1$ triplet are now calculated about 400 MHz higher than before. Emission cross sections for these transitions have been calculated by Singh and de Almeida,[4] erroneously too large by a factor 10^4. Recently, we succeeded in recording spectra of the isotopic OD$^+$ ion. Results on OD$^+$ together with more details about the experiments will be published in a forthcoming paper.

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