FAR-INFRARED SPECTROSCOPY ON OD^+

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The rotational transition $N = 2 \leftarrow 1$ of the OD^+ ion in the $X\,^3\Sigma^-$, $v = 0$ state has been observed with partially resolved hyperfine structure. Spectra were recorded using a tunable laser sideband spectrometer. Analysis yielded improved values of rotational constants.

1. Introduction

Spectroscopic information on the molecular ions OH^+ and OD^+ was, until recently, limited to ultraviolet emission spectra of the $A\,^3\Pi_i$–$X\,^3\Sigma^-$ system, thoroughly investigated by Merer et al. [1]. In 1985 we reported the observation and analysis of the lowest rotational transition ($N = 1 \leftarrow 0$) in the $X\,^3\Sigma^-$, $v = 0$ ground state of the OH^+ ion [2] and Oka and colleagues measured the fundamental vibration–rotation band of OH^+ [3]. Like the ions HCO^+, CO^+, N_2H^+ observed earlier [4], this ion is of interstellar interest. Detection of OH^+ in interstellar clouds, which has not been reported yet, may be facilitated by the accurate molecular constants we presented. As announced in the report on OH^+ [2], we now present the observation of the $N = 2 \leftarrow 1$ rotational transition of the isotopic OD^+ ion, together with more experimental details on the measurements.

2. Experimental details

Spectra of OD^+ were recorded with the same spectrometer (fig. 1) used for the detection of OH^+. Tunable far-infrared radiation is generated by mixing radiation of klystrons and a HCN laser in Schottky-barrier diodes. The HCN laser [5], operated at either 891 GHz or 964 GHz, has a maximum power output of ≈50 mW. The uncertainty in frequency of the free running laser during a measurement is estimated to be 1 MHz. Klystrons in the range 50–110 GHz are used. They are phase locked, via an intermediate K-band klystron, to a synthesized frequency generator (HP 8660B, frequencies up to 1 GHz). As an ultimate reference oscillator a Rb frequency standard is used. Sideband radiation is generated in a Schottky-barrier diode mounted in an open mixer [6] and re-radiated in the direction opposite to that of the fundamental laser beam. Spatial separation of fundamental and sideband radiation is established by means of a diplexer [6]. A monochromator is used for further wavelength selection. Thus, using fundamental and second-harmonic frequency of the klystrons, sideband radiation is obtained in the range 700–1200 GHz with a maximum power of ≈50 μW. An increase of power level by an order of magnitude has been achieved by changing the configuration of the open mixer.

Molecular ions are produced inside a hollow-cathode dc discharge cell which is temperature controlled with liquid nitrogen [4]. This cell, sealed off with polyethylene Brewster windows, was designed for single-pass operation. A coil wrapped around the tube enables application of magnetic fields for additional identification of spectral lines or, if desired, Zeeman modulation. A wide range of gas flows and pressures is made possible by a pumping line consisting of a diffusion pump, a Roots pump and a rotary pump. The pumping capacity is ≈20 mbar ℓ/s.

For phase-sensitive detection a square-wave modulation of the discharge current at ≈300 Hz is applied.

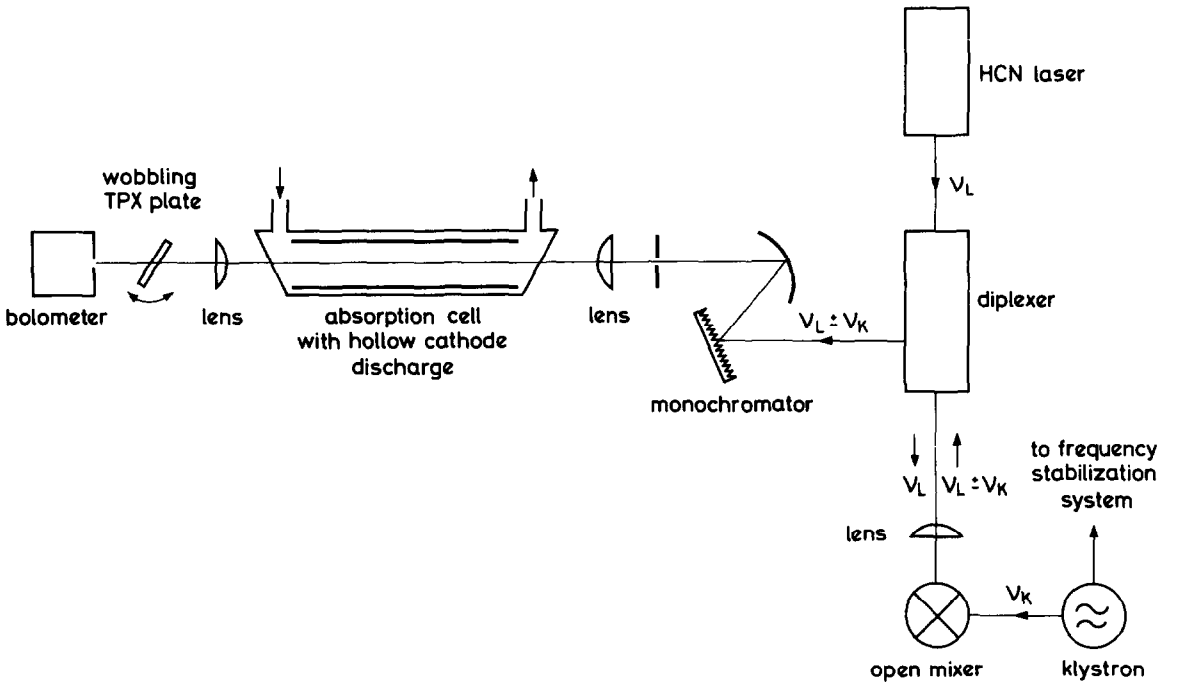

Fig. 1. A schematic view of the far-infrared spectrometer.

A disadvantage of this modulation scheme is the additional modulation of the refractive index of the plasma. In combination with a relatively high pressure in the discharge cell (up to 0.1 mbar) this causes a slight offset of the baseline with periodic variations superimposed, due to interfering reflections in the apparatus. The amplitude of these variations sometimes exceeds the noise level by a factor of 50 and the period is about ten times the linewidth, which greatly complicates searching for weak spectral lines. A better baseline behaviour was achieved by using a TPX plate (4 mm thickness) mounted on a galvo driver in the radiation beam. Wobbling this plate at a frequency of $\approx$60 Hz with an amplitude of $\approx 10^{\circ}$ causes a modulation of the optical path length and thus a smoothening of the baseline offset. In combination with a typical RC time of 1 s, the periodic variations were suppressed by a factor of five. When recording the spectra, an additional suppression of baseline variations was achieved by using signal averaging techniques; scans without D_2 admitted to the discharge medium were subtracted from scans with D_2. For detection a He-cooled bolometer is used.

The OD^+ ions were produced by discharging He with a 5–10% admixture of equal amounts of O_2 and D_2. An increase in gas flow to $\approx$10 mbar ℓ/s was essential for observation of the spectra, but a further increase by a factor of three did not improve the signal-to-noise ratio (at best 40 at $RC = 1$ s). The pressure in the pumping line just below the cell was $\approx 5 \times 10^{-2}$ mbar. The hollow cathode was cooled with liquid nitrogen. Optimum discharge current was $\approx$600 mA. Under these circumstances the plasma inside the hollow cathode had a dark blue-green colour with weak pink "flames". The colour of the positive column in a side tube of the cell varied from creamy blue at the anode side to creamy pink at the cathode side.

The observation absorption coefficients for OD^+ vary from $\approx 6 \times 10^{-5}$ to $\approx 10^{-6}$ cm^{-1}. Assuming a rotational temperature of 200 K and assuming that OD^+ has about the same transition dipole moment as OH^+ (2.32 D [7]) we estimate the concentration of OD^+ ions to be $\approx 5 \times 10^9$ cm^{-3}.

3. Results and discussion

We have observed three of the six components of the spin multiplet of the $N = 2 \leftarrow 1$ rotational transition of OD^+. Of the remaining three components, one has a very small intensity ($J = 1 \leftarrow 2$) and the other two ($J = 1 \leftarrow 0, J = 2 \leftarrow 2$) are predicted in a frequency region that can only be reached using the second harmonic frequency of a klystron. In such a region the maximum available power is ≈ 1 μW, yielding signals below the present detection limit.

For the searches we used frequencies calculated from the rotational constants determined by Merer et al. [1]. The components $J = 3 \leftarrow 2, J = 2 \leftarrow 1$ and $J = 1 \leftarrow 1$ have been observed with partially resolved hyperfine structure; the experimental frequencies are listed in table 1. The spectral lines have collision broadened widths of ≈ 5 MHz. Fig. 2 shows a recording of the $J = 1 \leftarrow 1$ transition and part of the $J = 3 \leftarrow 2$ transition

The observed frequencies have been fitted to a Hamiltonian describing the rotational and fine structure [8] and the magnetic hyperfine structure [9] of a $^3\Sigma$ state. The hyperfine parameters $b + c/3$ and c associated with the deuterium nucleus are related to those of the hydrogen nucleus via the ratio of their

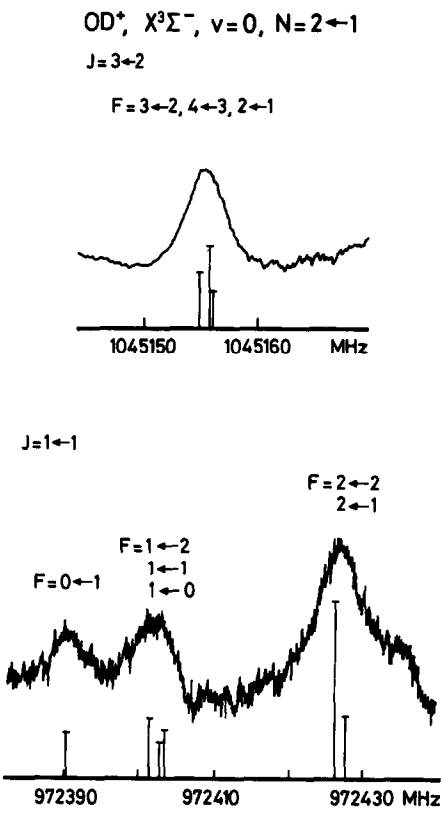

Fig. 2. Recordings of the $N = 2 \leftarrow 1$ rotational transition of OD^+. The upper trace was recorded in a single scan. The lower trace is the result of applying signal-averaging techniques. The bar spectrum shows the line positions calculated from the constants in table 2.

Table 1
Observed frequencies (in MHz) of the $N = 2 \leftarrow 1$ transition of OD^+

$J' \leftarrow J''$	$F' \leftarrow F''$	Observed	Obs. – calc.
3 2	3 2		0.5
3 2	4 3	1045155.3(1.0)	−0.4
3 2	2 1		−0.6
3 2	2 2	1045170.1(1.7)	0.3
3 2	3 3	1045177.1(1.7)	0.7
2 1	3 2		0.2
2 1	2 1		0.8
2 1	1 0	1050817.2(1.0)	−0.5
2 1	2 2		0.7
2 1	1 1		−0.1
2 1	1 2		1.4
1 1	0 1	972390.8(1.5)	0.3
1 1	1 2		0.7
1 1	1 1	972402.3(1.5)	−0.8
1 1	1 0		−1.2
1 1	2 2	972426.8(1.7)	0.7
1 1	2 1		−0.8

respective magnetic g factors [10] and have been calculated from the constants of OH^+ [2]. By using these constants and an estimated value of $eqQ = 150$ kHz for the contribution of the quadrupole interaction, the hyperfine spectrum of each spin component was calculated. The experimental frequencies, in some cases representing a composition of two or more (up to six) closely spaced unresolved transitions, confirmed this calculation and yielded the following hyperfine-free origins of the spin components:

$\nu_0(J = 3 \leftarrow 2) = 1045156.81(65)$ MHz,

$\nu_0(J = 2 \leftarrow 1) = 1050817.29(85)$ MHz,

$\nu_0(J = 1 \leftarrow 1) = 972414.55(73)$ MHz.

Table 2
Molecular constants (in MHz) for the $X^3\Sigma^-$, $v = 0$ ground state of OD^+

	This work	Ref. [1]
B	262834.91(83)	262845(21)
D	16.32(10) [a]	16.32(10)
λ	64192.4(2.2)	64177(260)
γ	−2407.25(98)	−2368(33)
$(b + c/3)_D$	−11.64(8) [b]	
c_D	19.28(15) [b]	

[a] Parameter constrained within its uncertainty to value from ref. [1].
[b] Parameter calculated from OH^+ values [2].

No significant value for the quadrupole interaction constant eqQ could be obtained.

With these origins the rotational constant B, the spin–spin interaction constant λ and the spin–rotation interaction constant γ were determined. The centrifugal distortion constant D could not be determined since only one rotational transition was observed. It was therefore constrained within its uncertainty to the value obtained from the optical spectrum [1]. Table 2 shows all molecular constants determined. The somewhat larger uncertainty in the rotational constant B, compared with the result for OH^+ [2], is due to the greater effect of the uncertainty in D in case of a $N = 2 \leftarrow 1$ transition. The larger uncertainty in λ and γ is caused by a weaker dependence of the observed frequencies on these constants.

We conclude that the improved values of the rotational and fine structure constants for the electronic and vibrational ground state determined from the present high-resolution spectra of the OD^+ ion are in reasonable agreement with values of Merer et al. [1], considering the extensive deperturbation they had to apply.

Recently we have been able to compare our experimental values for the hyperfine constants of OH^+ with values computed to third order in many-body perturbation theory by Veseth [11]. It turned out that the experimental and calculated values are in agreement within ≈5%.

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