

# Observation of the rotational spectrum of OH<sup>-</sup>

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Recently Owrutsky, Rosenbaum, Tack, and Saykally<sup>1</sup> have reported the observation of the fundamental vibration-rotation spectrum of OH<sup>-</sup> in the 2.8  $\mu\text{m}$  region, based on the high resolution photodetachment spectroscopy of the same ion by Schultz, Mead, Jones, and Lineberger<sup>2</sup> and the theoretical predictions by Werner, Rosmus, and Reinsch<sup>3</sup> and Lee and Schaefer.<sup>4</sup> We had earlier looked for the rotational spectrum of OH<sup>-</sup> in the far infrared region using diode lasers and found a line at 366.863  $\text{cm}^{-1}$  which is shown in Fig. 1. The negative derivative shape with respect to the velocity modulation detection<sup>5</sup> with a reasonable  $1f/2f$  intensity ratio and the agreement of the observed frequency with the calculated ( $366.69 \pm 0.27 \text{cm}^{-1}$ ) from rotational constants by Schultz *et al.*<sup>2</sup> suggested strongly that the line was the  $J = 10 \leftarrow 9$  transition of OH<sup>-</sup>. Our attempt to confirm this finding by observing the  $J = 11 \leftarrow 10$  and  $J = 12 \leftarrow 11$  transitions, however, was hampered by the appearance of strong neutral lines and the limited tunability of diode lasers. After the report by Owrutsky *et al.*,<sup>1</sup> we measured the  $J = 11 \leftarrow 10$  line at 401.760  $\text{cm}^{-1}$ , and thus confirmed that the line at 366.863  $\text{cm}^{-1}$  is indeed that of OH<sup>-</sup>. We have heard that Sears<sup>6</sup> detected one line at 469.991  $\text{cm}^{-1}$  which is close to the calculated frequency of the  $J = 13 \leftarrow 12$  transition, but we have not been able to confirm it. During the four months following the observation of the first line, we investigated several chemical reactions in an attempt to increase the intensity of the OH<sup>-</sup> line. This note summarizes our observations.

We initiated the rotational spectroscopy of OH<sup>-</sup> inspired by our successful determination of the H<sub>3</sub>O<sup>+</sup> inversion splitting by measuring the  $1^- \leftarrow 1^+$  transition at 27  $\mu\text{m}$ .<sup>7</sup> During the study we found several transitions which are probably high  $J$  rotation-inversion transitions of H<sub>3</sub>O<sup>+</sup> (the  $0^- \leftarrow 0^+$  band); this showed us the possibility of observing high  $J$  rotational transitions of light molecular ions using diode lasers. While several other molecular ions have been studied,<sup>8</sup> our main target was the hydroxide ion OH<sup>-</sup>. The experimental setup was similar to that previously reported.<sup>9</sup> Briefly, the diode laser radiation from the LS-3 IR spectrometer was passed through an air-cooled ac discharge tube (12 mm i.d. and 80 cm long) and focused onto a Cu:Ge detector. The velocity modulation technique was used, since it is much more sensitive for charged species and produces opposite phase signals for positively and negatively charged ions. OH<sup>-</sup> was generated by 3 kHz ac glow discharges in different gas mixtures (NH<sub>3</sub>/O<sub>2</sub>, H<sub>2</sub>/O<sub>2</sub>, H<sub>2</sub>O/O<sub>2</sub>) at a total pressure of  $\sim 1.5$  Torr. The discharge current and voltage were  $\sim 150$  mA rms and 5 kV  $p$ - $p$ , respectively. Two Laser Analytics mesa-stripe geometry diodes were used to cover the 25–27  $\mu\text{m}$  region. The frequencies were measured with

respect to the FTIR spectra of CS<sub>2</sub><sup>10</sup> and <sup>13</sup>CS<sub>2</sub><sup>11</sup> by Jolma and Kauppinen.

The  $J = 10 \leftarrow 9$  transition was first observed in the discharge of NH<sub>3</sub> and O<sub>2</sub> which was used in the photodetachment studies of OH<sup>-</sup> by Hotop *et al.*<sup>12</sup> This line was later recorded using H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>O/O<sub>2</sub> discharges with less neutral interference (Fig. 1). The variation of the intensity of the OH<sup>-</sup> signal in the three gas mixtures has been carefully studied. Although the observed absolute intensities had a slight difference (NH<sub>3</sub>/O<sub>2</sub>  $\sim$  H<sub>2</sub>/O<sub>2</sub>  $\gtrsim$  H<sub>2</sub>O/O<sub>2</sub>), the variation of the intensities was similar for both NH<sub>3</sub>/O<sub>2</sub> and H<sub>2</sub>/O<sub>2</sub> mixtures having maxima close to a 1:1 mixing ratio. For the H<sub>2</sub>O/O<sub>2</sub> discharge, H<sub>2</sub>O with only a trace of O<sub>2</sub> produces the maximum intensity.

In sharp contrast to the case of H<sub>3</sub>O<sup>+</sup>, for which the optimum mixing ratio was H<sub>2</sub>/O<sub>2</sub>  $\sim 8$  (Ref. 9), the OH<sup>-</sup> concentration peaks at H<sub>2</sub>/O<sub>2</sub>  $\sim 1$ . A sharp drop of the OH<sup>-</sup> concentration was observed in the H<sub>2</sub>/O<sub>2</sub> discharge at a high H<sub>2</sub> concentration, where the discharge begins to be striated. The H<sub>3</sub>O<sup>+</sup> signal was insensitive to striations and peaks near this mixing ratio, whereas the OH<sup>-</sup> signal disappeared completely. The effect of adding inert gases Ar and He was also studied for the H<sub>2</sub>O/O<sub>2</sub> mixture. The signal increased slightly with the addition of Ar, whereas it decreased when He was added, probably because of the increased electron temperature in the He discharge plasma (the electron affinity of OH is 1.83 eV<sup>2</sup>).

During the experiment we noticed that the OH<sup>-</sup> signal decreased drastically when the discharge cell was cleaned. After checking various possibilities we suspected that a very thin, almost invisible, metal coating inside the discharge cell

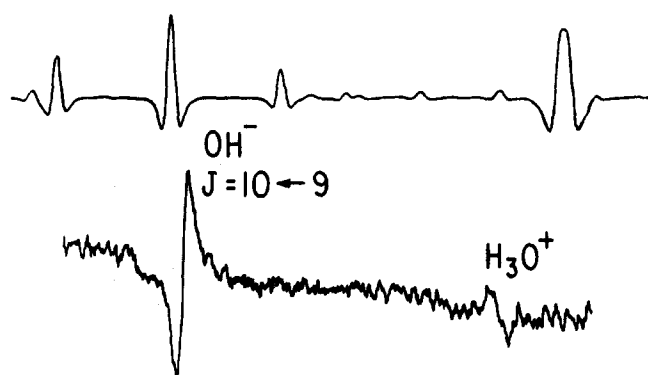


FIG. 1. The  $J = 10 \leftarrow 9$  transition of OH<sup>-</sup> at 366.863  $\text{cm}^{-1}$ . The small signal on the right is due to an unassigned transition of H<sub>3</sub>O<sup>+</sup>. Note that the two signals have opposite phase. The time constant of detection is 1 s. The upper trace is <sup>13</sup>CS<sub>2</sub> reference spectrum.

which was formed from the sputtering of electrodes was increasing the production of  $\text{OH}^-$ . In order to test this idea we coated the discharge cell with platinum and the  $\text{OH}^-$  signal increased by at least a factor of 10 relative to the clean cell. With the metal coating the discharge color was paler, probably indicating the lower electron temperature. The coating also prevented the formation of striations. These functions do not seem to depend on the metal used for coating. At the best condition in the platinum coated cell, the  $\text{OH}^-$  concentration was calculated to be  $\sim 10^{10}/\text{cm}^3$ , from the signal intensity using the predicted dipole moment of  $\text{OH}^-$  by Werner *et al.*<sup>3</sup> and the assumed rotational temperature of 600–800 K. This confirms the results of Owrutsky *et al.*<sup>1</sup> that negative ion can exist abundantly in a discharge.

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