

Identifying a U-doublet at 631.7 GHz

T. Amano

*Department of Chemistry and Department of Physics and Astronomy,
The University of Waterloo, Waterloo, ON Canada N2L 3G1*

In search for the lowest *para* rotational transition of H_2O^+ , several notable unidentified lines have been detected in the range of 630-640 GHz in an extended negative glow discharge in trace of water with helium buffer gas. They are notable because all exhibit sizable Zeeman effect.

High-resolution spectroscopic investigation into H_2O^+ has been quite extensive, from the electronic transitions, the vibration-rotation lines to Far-infrared Laser Magnetic Resonance (LMR) experiments[1, 2]. Pure rotational lines, however, so far defy identifications despite extensive efforts by several groups. The water cation, H_2O^+ , is a so-called intermediate ion in a hydrogen abstraction reaction chain of O^+ , so it was thought to be much less abundant compared with H_3O^+ which is a terminal ion. However, recent observations with *Herschel Space Observatory* revealed surprisingly high number density in various molecular clouds[3, 4]. The detections have been made so far by monitoring its $1_{11} - 0_{00}$ $J = 3/2 - 1/2$ line at 1115.2 GHz which is the lowest rotational transition of the *ortho* modification.

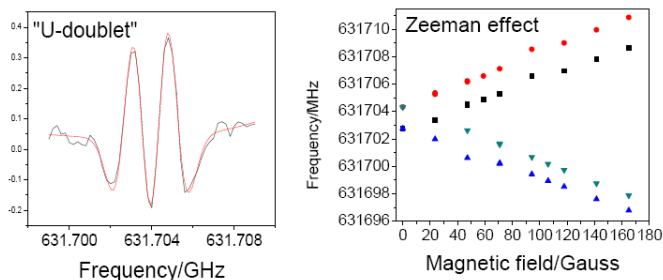


FIG. 1: An example of unidentified doublet observed with trace of H_2O with helium buffer of about 60 mTorr at liquid nitrogen temperature; (a) An example recorded with no magnetic field, (b) Zeeman shifts of this doublet. The selection rule is $\Delta M = \pm 1$.

This investigation originally aimed at determination of the laboratory transition frequency for the $1_{10} - 1_{01}$ transition, the lowest *para* transition. Recent global analysis of H_2O^+ with all the available spectroscopic data from

TABLE I: Observed transition frequencies for two distinct species (in MHz).

Species I		Species II
630938.437	630941.055	631930.786
631364.745		632067.360
631702.758	631704.330	633003.896

electronic to LMR made by Yu et al provides reasonably accurate frequencies for the fine structure splitting of the $1_{10} - 1_{01}$ transition. Guided by those values, the search was initiated by using a submillimeter-wave system at Waterloo. Liquid nitrogen cooled discharge in a gas mixture of H_2 and O_2 with helium as a buffer gas was used in initial search. The mixing ratio was adjusted by reducing hydrogen content from the optimum mixing ratio for production of H_3O^+ . A characteristic doublet was detected at 631.704 GHz, as shown in Fig. 1 (a). In the process of optimizing the chemistry, it was found that the best gas mixture for this doublet was found to be no hydrogen and no oxygen. The He buffer was replaced with either Ar or Ne. The signal was equally observable. The stainless steel electrodes were replaced with Cu electrodes, resulting in no effect for producing this doublet. Eventually it was found that trace of water which was deposited on the inner surface of the discharge tube cooled to liquid nitrogen temperature seemed to play an important role.

It was found that this doublet exhibited sizable Zeeman effect. The measured Zeeman shifts are shown in Fig. 1 (b). These lines appear to be hyperfine components. It was immediately clear that this doublet was not due to H_2O^+ , because the line searched for was a *para* transition that should not have hyperfine structure. The magnitude of the Zeeman shifts is smaller than that of a typical free radical in, for example, $^2\Pi_{3/2}$ states, but much larger than that for closed shell molecules.

During the course of searching for other lines, different class of lines have been detected. Those lines exhibit larger Zeeman effect than the one shown in Fig. 1 (b). Typical examples are shown in Fig. 2. This line at 633004 MHz is the strongest line observed so far in this experiment. In addition to this line, a pair of lines have been observed. Their chemical behaviour was similar to the 633004 MHz line. The intensity of these lines was enhanced by adding small amount of flow of water (because the cell was cooled down to liquid nitrogen temperature, we cannot really measure the pressure or amount of H_2O introduced into the cell). However, small amount of hydrogen or oxygen killed these lines. A small flow of CH_4 enhanced the signals. The pair of lines, 631931 MHz and 632068 MHz, showed resolved Zeeman pattern, as shown in Fig. 3. It suggests that the transitions are likely to be $J = 6 - 5$ (or $J = 6.5 - 5.5$).

The doublet at 631.704 GHz was found to be neutral to addition of hydrogen or oxygen, but it disappeared by adding the flow of water. However, apparently as water on the surface of the cell became deficient, the signal disappeared, so occasionally water should be replenished to see the doublet. In addition, two more lines of similar

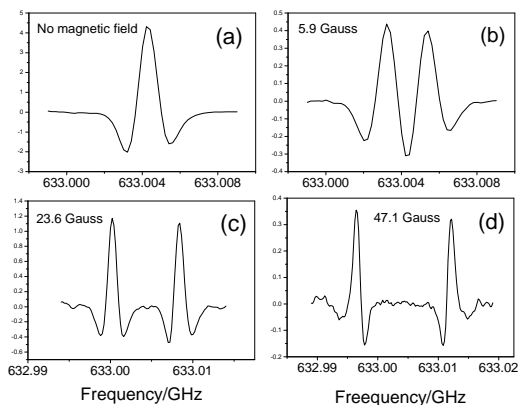


FIG. 2: The Zeeman effect of 633004 MHz line. The line shape shown in panel (d) suggests that the Zeeman components are not completely resolved due to similar g -factors for the upper and lower states.

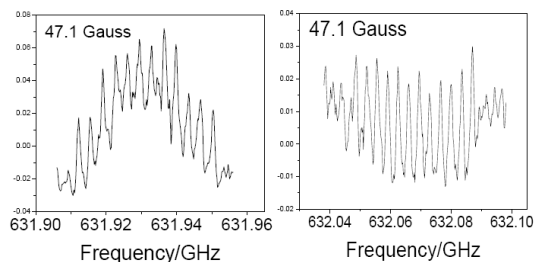


FIG. 3: The Zeeman splitting of 631931 MHz and 632068 MHz lines.

chemical behaviour and of similar Zeeman effect have appeared, as summarized in Table I. The 630940 MHz line is a doublet very similar to the 631704 doublet. Figure 4 shows a typical signal recorded with no magnetic field. However, the line at 631365 MHz appears to be a single line, but the Zeeman effect is very similar in size with the 631704 MHz doublet, as demonstrated in Fig. 5.

Considering the magnitude of the Zeeman effect, the species I may be a free radical in its ${}^2\Pi_{1/2}$ state. The doubling is likely to be hyperfine structure due to the proton. If so, OH in a high- v state is a candidate. It seems to be a wild assumption. Copeland et al[5] observed the emission spectra from high- v states, and determined the molecular constants up to $v = 13$. By extrapolating the relatively well-behaving rotational constants to higher v states, we estimated $J = 3/2 - 1/2$, ${}^2\Pi_{1/2}$ transition frequencies in the $v = 14$ state to be 632.0 GHz and 633.3 GHz. The

Λ -doubling splitting is highly uncertain, because the v -dependence of the Λ -doubling constants, p and q , might be very non-linear. A rough estimate indicates that levels of up to $v = 21$ can be accommodated in the ground electronic state. Are the 631704 and 630940 lines the Λ -doubling? Maybe, but the 630940 line is much weaker than the 631704 line. Then, what is the 631365 MHz line? If the 631704 doublet is the $J = 3/2 - 1/2$ in ${}^2\Pi_{1/2}$, there should be three hyperfine components; $F = 2 - 1, 1 - 0$ and $F = 1 - 1$. The weakest component might not be visible. However, the Zeeman splitting should be more complicated.

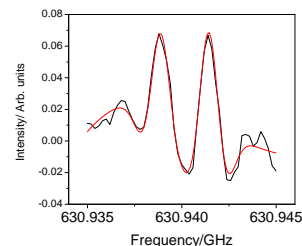


FIG. 4: A doublet appeared at 630940 MHz similar to the one at 631704 MHz (See Fig. 1).

What about the species II? The intensity was enhanced by adding small amount of CH_4 , which is indicative of a species containing carbon. The 633004 line may be $K = 0$, and the 631931 and 632068 pair can be the $K = 2$ doublet. If so, the widely split $K = 1$ lines should appear within a few GHz range. So far no such lines are detected. These lines show no sign of hyperfine structure. May the species contain only ${}^{12}\text{C}$ and ${}^{16}\text{O}$? Or *para* species of a molecule with two equivalent protons? If the lines of species II are really $J = 6 - 5$, the adjacent rotational transition frequencies are predictable. So far, the search has not been successful.

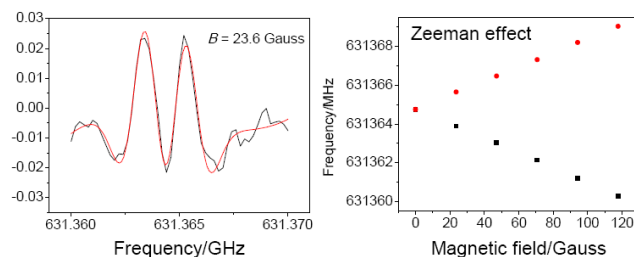


FIG. 5: The Zeeman splitting of 631365 MHz line.

[1] S. E. Strahan, R. P. Mueller, and R. J. Saykally. *J. Chem. Phys.*, **85**, 1252–1260 (1986).
 [2] P. Mürtz, L. R. Zink, K. M. Evenson, and J. M. Brown. *J. Chem. Phys.*, **109**, 9744–9752 (1998).

[3] V. Ossenkopf et al. *Astron. Astrophys.*, **518**, L111 (2010).
 [4] P. Schilke et al. *Astron. Astrophys.*, **521**, L11 (2010).
 [5] R. A. Copeland, B. R. Chalamala, and J. A. Coxon. *J. Mol. Spectrosc.*, **161**, 243–252 (1993).