

Observation of the Lamb-dip of H_3^+ Molecular Ion

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The triatomic hydrogen molecular ion, H_3^+ , is the simplest polyatomic molecule. It plays a key role in chemical evolution in interstellar space and also in planetary atmosphere.^{1,2} High resolution spectroscopy not only gives us fundamental insight into its nature but also provides highly accurate information for theoretical calculations like determining the molecular structure, refining the potential energy surface (PES) and comparing with the results from vibrational band calculations. However, until now the uncertainty given by previous experimental measurements³⁻⁶ has been about 0.005 cm^{-1} , and it is expected to be hard to achieve higher accuracy due to the limitation imposed by the Doppler-limited resolution

We have developed a mid-infrared laser system, which uses an optical parametric oscillator (OPO) with enough power for saturating molecular vibration-rotation transitions. The experiment described here is shown in Figure 1. The OPO delivers 200 mW for single frequency idler wave at $3.66 \mu\text{m}$. Despite relatively high laser power, still we need a good ion source at relatively low gas pressure. In order to achieve this goal, an extended negative glow discharge scheme was employed. The discharge tube sealed with two CaF_2 Brewster windows at both ends was fitted with a pair of cylindrical stainless steel electrodes. A solenoid coil wrapped around the cell provided up to 300 Gauss axial magnetic field for extending the negative glow region of the discharge plasma. For increasing population at lower states and enhancing the efficiency for production of ions, the discharge plasma was cooled by flowing chilled ethanol at $-70 \text{ }^\circ\text{C}$.

The experiment was performed by a pump-probe scheme where the idler wave was sent through the absorption cell and was retro-reflected by a thick glass. The saturation signal was detected by a liquid-

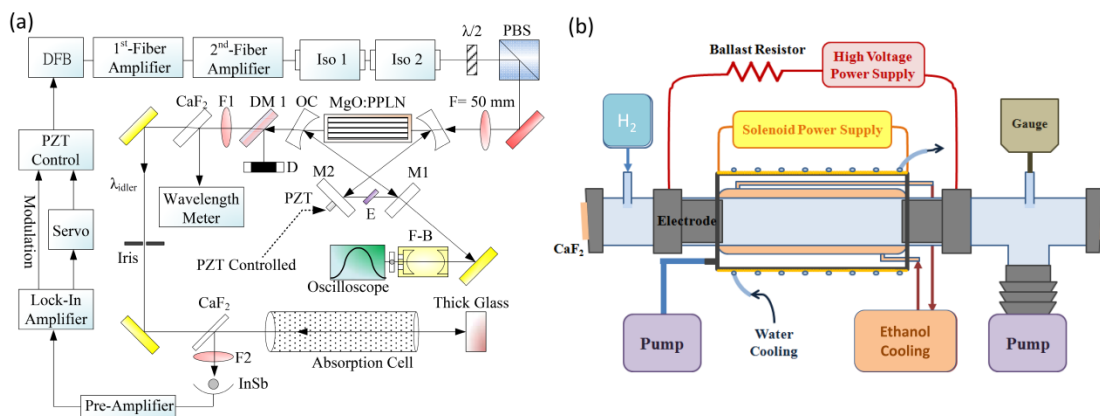


Figure 1.(a) The experimental setup;(b) The structure of the absorption cell. Iso: optical isolator, $\lambda/2$: half-wave plate, PBS: polarizing beam splitter, DM: dichroic mirror, E: etalon, OC: output coupler, F-B: scanning Fabry-Perot interferometer, F1: Collimating lens.

nitrogen cooled InSb detector and was demodulated by a lock-in amplifier.

The on-off modulation of the magnetic field in the discharge tube was achieved by applying a 95 Hz sinusoidal voltage to the coil for making changes of H_3^+ concentration. Figure 2(a) shows an example of Doppler broadened profile of the R(1,0) transition. The translational temperature can be estimated to be 305 K from the Doppler linewidth. When the pressure was reduced down to 33.2 mTorr, a saturation dip can be directly observed and was about 8 % burned into the Doppler line profile.

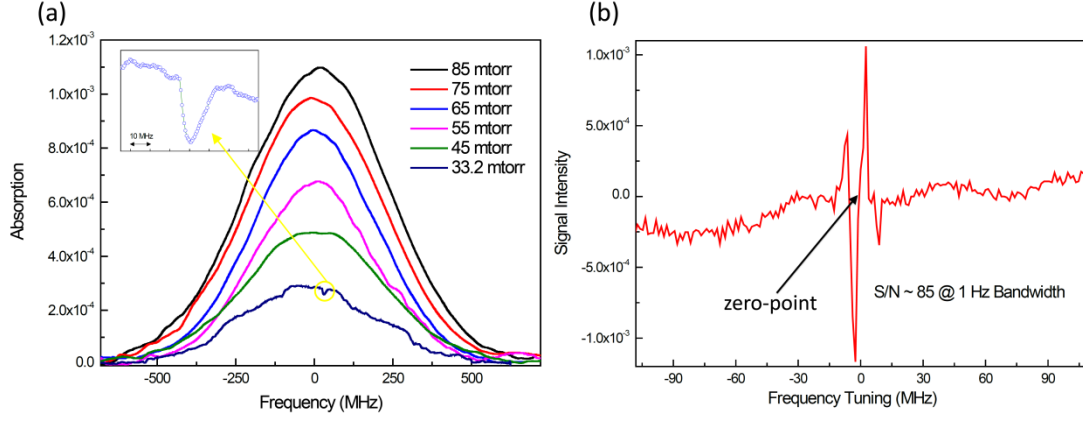


Figure 2.(a) The Doppler broadened profile;(b) The 3rd demodulated saturation signal.

For determining the absolute frequency, the heterodyne beat notes of pump wave and signal wave were measured with a fiber-based optical frequency comb simultaneously. The OPO pump wave was stabilized to the zero-point of the 3rd derivative signal (see Figure 2(b)) which was acquired by modulating the frequency of mid-infrared radiation. On the other hand, the heterodyne beat note of the OPO signal wave was frequency-locked to an RF synthesizer which was referenced to a GPS-disciplined Rubidium clock. The frequency of each tooth can be expressed as

$$f_{\text{comb}} = n \times f_{\text{rep}} \pm f_{\text{offset}}$$

The absolute frequency of the pump and signal waves can be written by

$$f_p = n_p \times f_{\text{rep}} \pm f_{\text{offset}} \pm f_{p,\text{beat}}$$

$$f_s = n_s \times f_{\text{rep}} \pm f_{\text{offset}} \pm f_{s,\text{beat}}$$

Therefore, the absolute frequency can be determined by subtracting f_p by f_s

$$f_i = f_p - f_s = (n_p - n_s) \times f_{\text{rep}} \pm f_{p,\text{beat}} \pm f_{s,\text{beat}} = n_i \times f_{\text{rep}} \pm f_{p,\text{beat}} \pm f_{s,\text{beat}}$$

Where the mode number n_i was roughly determined by the wavelength meter and the carrier-envelope offset frequency f_{offset} can be eliminated.

The transition frequency thus determined was 81720371550(109) kHz [2725.8981795(36) cm^{-1}]. The value agrees very well with that obtained from previous infrared spectroscopy⁵, 2725.898(5) cm^{-1} .

Systematic measurements of the homogeneous linewidth with different pressures and with different input powers yielded the pressure broadening coefficient, and the results will be discussed.

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