High Precision Spectroscopy of Molecular Ions

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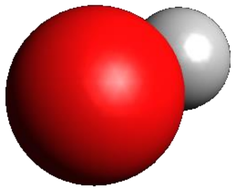
Why Study Molecular Ions?

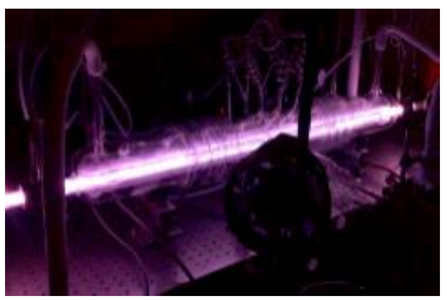
Astrochemistry



Galaxy Arp 220, a location where OH^+ has been used to determine the flux of cosmic ray ionization. hubblesite.org

To date, there have been over 180 molecular species identified in the interstellar medium (ISM). The chemistry of the ISM is dominated by molecular ions. One such example, OH^+, is vital to the formation of water in molecular clouds and can be used to measure the cosmic ray ionization of hydrogen[2]. To aid astronomers in its detection, we are able to indirectly measure a precise THz rotational spectrum in the laboratory.

Fundamental Physics



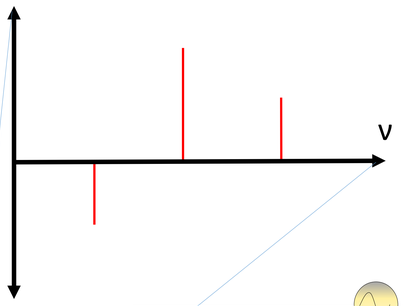
As a three-proton two-electron system, H_3^+ is the simplest polyatomic molecule. Due to its fundamental nature, it serves as an important benchmark for state-of-the-art *ab initio* calculations of molecular potential energy surfaces and spectra that go beyond the Born-Oppenheimer approximation[5].

Spectroscopic Technique

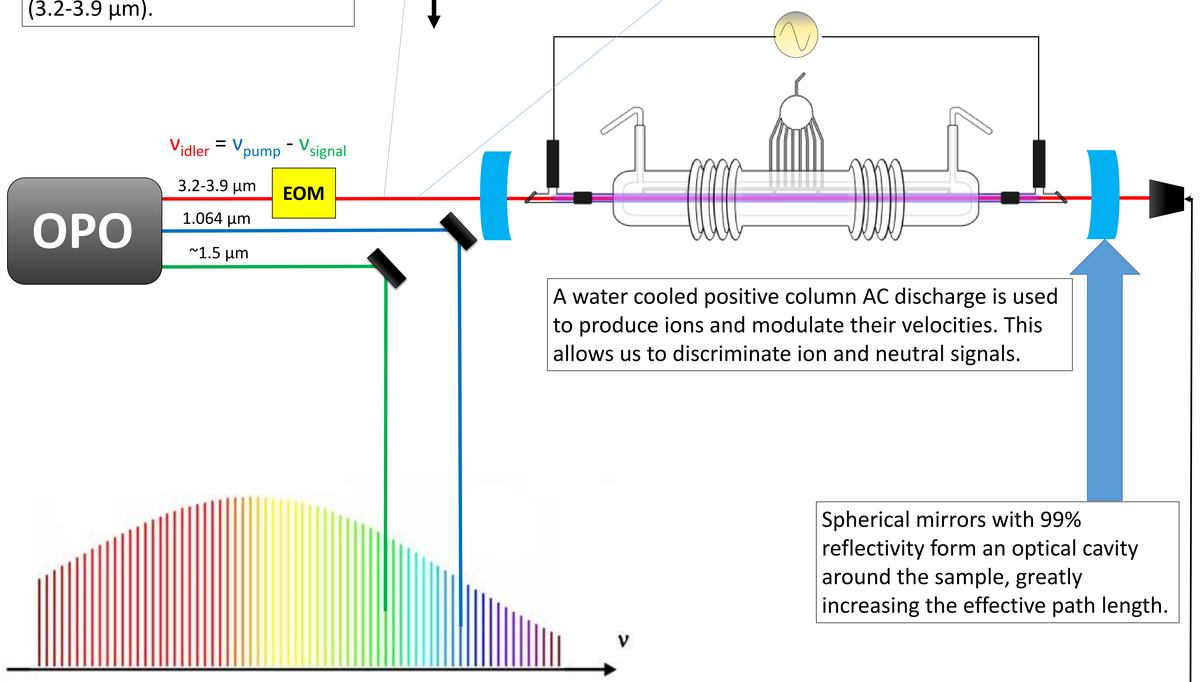
Noise **I**mmune **C**avity **E**nhanced-**O**ptical **H**eterodyne **V**elocity **M**odulated **S**pectroscopy [3]

NICE-OHVMS

An optical parametric oscillator (OPO) takes a pump photon (1064 nm) and splits it into two photons of lower energy, the signal (~1.5 μm) and the idler (3.2-3.9 μm).



An electro-optic modulator (EOM) phase modulates the light to generate RF side bands at ~80 MHz. This technique is used to lower technical (1/f) noise.



A water cooled positive column AC discharge is used to produce ions and modulate their velocities. This allows us to discriminate ion and neutral signals.

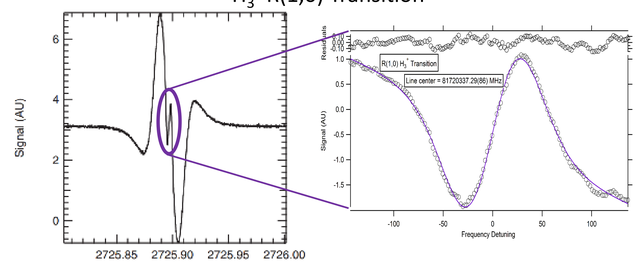
Spherical mirrors with 99% reflectivity form an optical cavity around the sample, greatly increasing the effective path length.

An optical frequency comb produces light at highly precise intervals. Making it a very stable and accurate frequency standard, this allows for accurate calibration of the measured spectra.

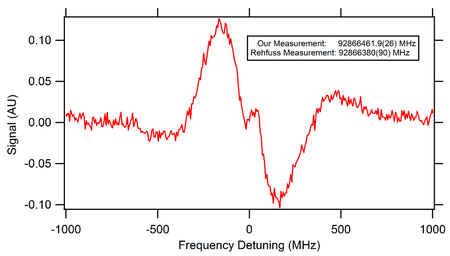
A photodiode diode detector is used to measure the absorbance of the sample.

Results

H_3^+ R(1,0) Transition

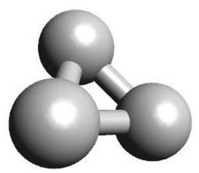


OH^+ R(4) $F_1 \leftarrow F_1$ Transition



Previous measurements of mid-infrared transitions of molecular ions have uncertainties that are on the order of hundreds MHz (~0.003 cm^{-1}). NICE-OHVMS is able to measure transitions with MHz precision by fitting the sub-Doppler features[1]. This technique has been used to measure 20 transitions of H_3^+ and 30 transitions of OH^+, improving the precision by orders of magnitude. This technique has also been used to study other ions including HCO^+, HeH^+, and CH_5^+.

Future Work



In the near future, the survey of highly precise H_3^+ transitions will be expanded, covering the P and Q-Branches as well as hot band and overtone transitions. A complementary survey of its deuterated isotopologues; H_2D^+ and D_2H^+ will also be pursued. These species govern the deuterium fractionation in the interstellar clouds and to date there have been very few high precision measurements made[4].

References

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[2] N. Indriolo, D.A. Neufeld, *et al.*, *Astrophys. J.* (2015), **800**, 40.
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