The chemistry of interstellar H_nO^+: Beyond the Galaxy

Floris van der Tak

SRON Netherlands Institute for Space Research, Landleven 12, 9747 AD Groningen, The Netherlands

Abstract. The astrochemistry of the H_nO^+ (n=1..3) ions is important as the main gas-phase formation route for water, and as tracer of the interstellar ionization rate by cosmic rays and other processes. While interstellar H_3O^+ has been known since the early 1990's, interstellar OH^+ and H_2O^+ have only recently been detected using the Herschel space observatory and also from the ground. This paper reviews detections of H_nO^+ toward external galaxies and compares with ground-based work. The similarities and differences of the H_nO^+ chemistry within the Galaxy and beyond are discussed.

Keywords: ISM: molecules – radio lines: galaxies – galaxies: active – galaxies: AGN – galaxies: starburst – galaxies: evolution
PACS: 98

INTRODUCTION

The field of astrochemistry is a rich and rapidly growing field: as of Summer 2010, over 150 molecular species are known to occur in interstellar and circumstellar environments. Most of these species are simple di- and triatomic radicals and ions, but in regions shielded from stellar ultraviolet radiation, polyatomic molecules are able to survive as well. Molecular complexity in space reaches its peak in the so-called hot cores, where the products of surface chemistry on small solid particles (dust grains) evaporate into the gas phase, leading to organic species such as simple sugars and alcohols. While the astronomers' definition of a complex molecule (more than 4 atoms) is quite far from the chemists' one, the observations show that considerable molecular richness is built up in space despite the rather unfavourable conditions. See Herbst and van Dishoeck [1] for a review of the subject.

Oxygen is the third most abundant element in the Universe, after hydrogen and helium, and the two most abundant oxygen-bearing molecules are CO and H_2O. The formation and destruction of CO are well understood: in dense molecular clouds, all gas-phase carbon is locked up in CO, while at low (column) densities, photodissociation limits the CO abundance. The main chemical activity of CO in dense clouds is its freeze-out onto grain surfaces at low temperatures and high densities, and its subsequent evaporation into the gas phase when the grains are warmed up. In contrast, the formation and destruction of H_2O is an interplay between gas-phase and grain surface reactions and photodissociation. This dependence makes H_2O an excellent tracer of astrophysical conditions, in particular instances when energy is injected into interstellar gas clouds.

The gas-phase formation of H_2O proceeds via two channels. In the neutral-neutral route, O and OH react with H_2 to form OH + H and H_2O + H, respectively, but both reactions have activation barriers so that this mechanism is only effective at gas temperatures above $\approx$250 K. At lower temperatures, the ion-molecule route dominates, starting with the reaction of O with H_3^+ or by charge exchange between O and H^+. Reactions of O^+, OH^+ and H_2O^+ with H_2 produce H_3O^+, which recombines with an electron to form H_2O + H, as well as OH + H_2. While observational evidence for this route existed from ground-based observations of H_3O^+ [2], direct evidence for the intermediate products OH^+ and H_2O^+ was lacking until the launch of ESA's *Herschel* space observatory.

EXTRAGALACTIC H_nO^+ WITH HERSCHEL

The nucleus of the galaxy M82 is well known for its high rate of star formation. To measure the abundance of H_2O in M82, Weiss et al. [3] have obtained spectra of the H_2O $1_{10}-1_{01}$, $1_{11}-0_{00}$ and $2_{02}-1_{11}$ transitions with the high-resolution HIFI spectrometer onboard Herschel. Unexpectedly, the spectrum near 1113 GHz shows absorption in the H_2O^+ $1_{11}-0_{00}$ line at 1115 GHz, which is stronger than the neighbouring H_2O line. The authors infer column densities of $4\times10^{14}\,\mathrm{cm}^{-2}$ for H_2O and $3\times10^{14}\,\mathrm{cm}^{-2}$ for H_2O^+. This high relative abundance of H_2O^+ is surprising as H_2O^+ reacts quickly with H_2 to form H_3O^+. The observations thus indicate that a significant fraction of hydrogen is in atomic form, unless another process is reducing the H_2O abundance.

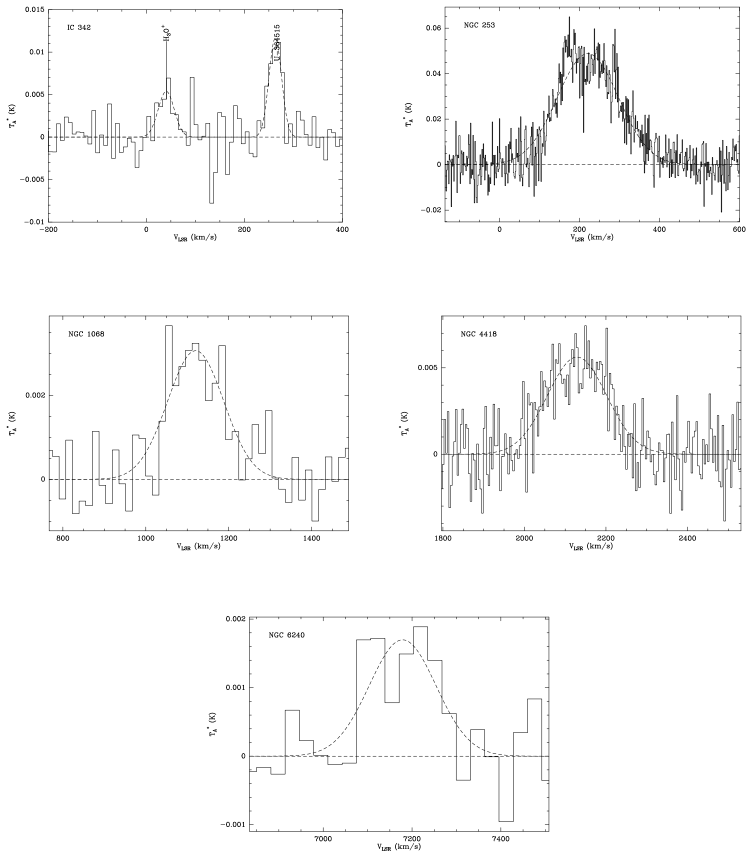

FIGURE 1. Recent detections of H_3O^+ with the JCMT [7].

Even more extreme conditions are found in the galaxy Mrk 231, where a supermassive black hole is probably responsible for the high infrared luminosity. An FTS spectrum of the Mrk 231 nucleus, taken with SPIRE on Herschel, shows emission in high-*J* lines of CO and H_2O, in the H_2O^+ 1115 GHz line, and in the OH^+ $1_0 - 0_1$, $1_2 - 0_1$ and $1_1 - 0_1$ lines near 909, 972, and 1033 GHz [4]. While the ISO-LWS spectra of Mrk 231 and Arp 220 show hints of OH^+ lines [5], the H_2O^+ detection is the first outside the Solar System, where Herzberg identified H_2O^+ in cometary spectra [6]. The high brightness of the CO lines in Mrk 231 arising from levels up to 460 K above ground, and the significant lower limits of $\sim 2 \times 10^{-10}$ for the OH^+ and H_2O^+ abundances indicates that X-ray emission from the black hole vicinity is driving the heating and the chemistry in the nucleus of Mrk 231.

EXTRAGALACTIC H_nO^+ FROM THE GROUND

Whereas H_2O^+ cannot be observed from the ground, detection of OH^+ has been achieved with the APEX telescope [8], although not yet toward extragalactic objects. In contrast, the first detection of extragalactic H_3O^+ by van der Tak et al. [9] is now being followed up in several ways (Figure 1). While Aalto et al. [7] concentrate on the 364 GHz line in a larger source sample, the line survey by Requena-Torres et al. [10] covers two lines of H_3O^+ to constrain the excitation of H_3O^+, which reduces the uncertainty of the column density estimates. The blend of the 307 GHz line with a CH_3OH line can be resolved since their broad-band spectra include >10 other CH_3OH lines.

The estimate of $N(H_2O)$ toward the nucleus of the starburst galaxy M82 from Weiss et al. [3] exceeds the estimate of $N(H_3O^+)$ from van der Tak et al. [9] by a factor of only ≈3.3, which is incompatible with models of pure gas-phase chemistry, even under strong irradiation by ultraviolet photons or X-rays. Models of X-ray irradiated gas such as expected in the vicinity of a supermassive black hole predict H_2O/H_3O^+ ratios of $\sim$100, while models of UV-irradiated gas around young massive stars predict even higher ratios: $H_2O/H_3O^+ \sim 1000$ for a young starburst, dropping to $\sim$300 after $\sim$10 Myr, when supernova explosions start enhancing the local ionization rate by energetic particles ('cosmic rays').

Additional ionizing radiation to increase the production rate of H_2O^+ seems unavailable, and increasing the atomic fraction of the gas is problematic since OH^+ and H_2O^+ require H_2 for their formation too. Therefore the solution to the low observed H_2O/H_3O^+ ratio in M82 may be an enhanced destruction rate of H_2O. The photodissociation rate of H_2O is $\approx 70\times$ higher than that of OH^+ [11, 12], while the rate for H_2O^+ is negligible [13]. The rate for H_3O^+ may be high like H_2O and NH_3, to which it is iso-electronic, or low like that of OH^+ and H_2O^+. In the latter case, a scenario is possible where H_2O molecules from icy grain mantles are ejected into the gas phase by shocks and subsequently photodissociated into O and OH. The dissociation products then participate in 'standard' ion-molecule chemistry (§ 1) which produces H_3O^+. Weiss et al. [3] use similar arguments to explain the observed H_2O^+/H_2O ratio in M82. This production mechanism of H_2O^+ is similar to that in comets, where H_2O^+ is made by photoionization as well as electron impact ionization of evaporating H_2O [14]. In the case of M82, shocks are more likely to cause the grain mantle evaporation than stellar radiation which only heats small volumes of gas. Shock waves pervade the nucleus of M82 as a result of cloud-cloud collisions due to the shape of the stellar bar potential [15]. However, the H_2O/H_2O^+ ratio in Comet Halley is $\sim 10^5$ [14] and it is not clear if the different radiation field can explain the difference with M82. Testing the photoevaporation-ionization hypothesis for H_3O^+ requires measurement or calculation of its photodissociation cross-section.

COMPARISON WITH THE GALACTIC CASE

The OH^+ and H_2O^+ ions have been detected on a number of Galactic lines of sight: the 971 GHz line of OH^+ and the 607 and 1115 GHz lines of H_2O^+ with the *Herschel* telescope [16, 17] and the 909 GHz line of OH^+ from the ground with the APEX telescope [8]. In all Galactic cases, the lines appear in absorption toward a background source of dust continuum emission, even if the neighbouring H_2O 1113 GHz line appears in emission [18].

The nucleus of M82 follows the behaviour of many Galactic lines of sight in that the H_2O and H_2O^+ lines at 1113 and 1115 GHz both appear in absorption, implying a low excitation of the molecules. This condition can be quantified as $T_{\rm ex} < T_{\rm bg}$, where the excitation temperature $T_{\rm ex}$ is defined through the Boltzmann equation and the radiation temperature of the background $T_{\rm bg}$ is defined through the Rayleigh-Jeans law. A low excitation temperature is expected for the OH^+ and H_2O^+ lines, because of the high line frequency ($\nu \sim 1$ THz) and the significant molecular dipole moments (μ=2.3 and 2.4 D, respectively). The spontaneous decay rate A_{ul} scales as $\mu^2\nu^3$, so that any excitation mechanism would have to be very fast ($\sim 10^{-2}$ s^{-1}) to be able to compete with radiative decay. The situation is different for the extragalactic H_3O^+ detections in emission: the lower line frequency ($\approx$400 GHz) reduces both the radiative decay rate and the intensity of the dust continuum background, which scales as ν^α with α between 2 (optically thick case) and 4 (optically thin case). In addition, the excitation of H_3O^+ may be enhanced by absorption of far-infrared photons, an effect known as 'pumping'.

Perhaps the most surprising aspect of the Mrk 231 observations is that the OH^+ and H_2O^+ lines appear in emission, which implies a very high excitation rate as discussed above. The same result holds for the HF J=1$\rightarrow$0 line, which appears in emission toward Mrk 231, unlike all Galactic lines of sight [19]. These molecules all trace interstellar gas where a significant fraction of the hydrogen is in atomic rather than molecular form, so that three excitation mechanisms are possible: collisions with H, collisions with H_2, and pumping by infrared photons.

Estimating the relative importance of collisional and radiative excitation requires collisional rate coefficients, which do not presently exist for OH^+ and H_2O^+. For HF such data do exist [20] and a calculation of its excitation may be useful as a guide. Unlike HF, the excitation of OH^+ and H_2O^+ needs a non-equilibrium treatment, as their timescales for formation, excitation and destruction are similar. In summary, understanding the chemistry of extragalactic H_nO^+ requires several sets of basic molecular data: photodissociation rates for H_3O^+, and inelastic de-excitation rate coefficients for OH^+ and H_2O^+ with H, H_2 and e as collision partners. Searches for OH^+ and H_2O^+ emission within the Galaxy will also be useful: the existing pointed observations are biased toward strong continuum sources but future larger-scale mapping observations may reveal Galactic sources of OH^+ and H_2O^+ emission.

ACKNOWLEDGMENTS

The author thanks Ewine van Dishoeck and Rowin Meijerink (Leiden), Susanne Aalto and John Black (Onsala), Friedrich Wyrowski (Bonn) and Geoff Duxbury (Glasgow) for useful discussions.

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