LETTERS

Warm water vapour in the sooty outflow from a luminous carbon star

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The detection[1] of circumstellar water vapour around the ageing carbon star IRC +10216 challenged the current understanding of chemistry in old stars, because water was predicted[2] to be almost absent in carbon-rich stars. Several explanations for the water were postulated, including the vaporization of icy bodies (comets or dwarf planets) in orbit around the star[1], grain surface reactions[3], and photochemistry in the outer circumstellar envelope[4]. With a single water line detected so far from this one carbon-rich evolved star, it is difficult to discriminate between the different mechanisms proposed. Here we report the detection of dozens of water vapour lines in the far-infrared and sub-millimetre spectrum of IRC +10216 using the Herschel satellite[5]. This includes some high-excitation lines with energies corresponding to ~1,000 K, which can be explained only if water is present in the warm inner sooty region of the envelope. A plausible explanation for the warm water appears to be the penetration of ultraviolet photons deep into a clumpy circumstellar envelope. This mechanism also triggers the formation of other molecules, such as ammonia, whose observed abundances[6] are much higher than hitherto predicted[7].

For a star with a mass less than about nine solar masses, the last major nuclear burning phase is as an asymptotic giant branch (AGB) star[8]. A natural chemical division is created between C (carbon-rich AGB) stars, M-type AGB stars and S-type AGB stars. C-stars have a C/O ratio >1, and hence a surplus of carbon to drive an organic chemistry in the envelope; M-type AGB stars have a C/O ratio <1, yielding the formation of oxygen-bearing molecules; and S-type AGB stars have a C/O ratio of ~1.The detection of the ground-state transition of *ortho*-water (in which the proton spins are parallel), *ortho*-$H_2O(1_{1,0}–1_{0,1})$, in the envelope around the C-star IRC +10216 came as a surprise[1], as in thermodynamic equilibrium chemistry no oxygen-rich molecules (except CO) are expected in a carbon-rich environment. The vaporization of a collection of icy bodies (comets or dwarf planets) in orbit around the star was invoked to explain the presence of water vapour in this carbon-rich sooty environment. It was predicted[1] that water should be released in the intermediate envelope at radii larger than (1–5) $\times 10^{15}$cm. Later on, two other distinct mechanisms were considered as possible sources of the water vapour observed in IRC +10216, each one making a specific prediction for the spatial distribution of H_2O in the envelope: grain-surface reactions, such as Fischer-Tropsch catalysis on the surface of small grains[3], which would imply that water reaches its maximum abundance at a radius around 2×10^{15} cm; and formation in the outer envelope through the radiative association of atomic oxygen and molecular hydrogen[4]. It has also been suggested that water could be formed in the warm and dense inner envelope[9], although no specific formation mechanism has been proposed for such an origin.

On 12 and 19 November 2009, IRC +10216 was observed with the SPIRE[10] and PACS[11] spectrometers on board the Herschel Space Observatory[5]. Spectroscopic observations were obtained between 55 and 670 μm, at spectral resolving powers between 300 and 4,500 (ref. 12). Currently, many different molecules and their isotopologues have been identified: ^{12}CO, ^{13}CO, $C^{18}O$, $H^{12}CN$, $H^{13}CN$, NH_3, SiS, SiO, CS, $C^{34}S$, ^{13}CS, C_3, C_2H, HCl, $H^{37}Cl$, *ortho*-H_2O and *para*-H_2O. The detection of the low-excitation *ortho*-$H_2O(2_{1,2}–1_{0,1})$ transition at 179.5 μm was anticipated, as the energy difference between the $1_{1,0}$ and $2_{1,2}$ level is only 53 K, but the discovery of high-excitation *ortho*-H_2O lines with upper level energies around 1,000 K came as a surprise (Fig. 1 and Supplementary Figs 1–5). These high-excitation *ortho*-H_2O lines provide a strong diagnostic to help us understand the origin of water in carbon-rich sooty envelopes. Moreover, for the first time, *para*-H_2O lines have been detected from the envelope of a carbon-rich AGB star (Fig. 1 and Supplementary Figs 1–5).

The kinetic temperature in the envelope is typically around 2,000 K in the dense environment just above the stellar photosphere, and decreases to ~10 K in the tenuous outer envelope (Fig. 2). The presence of high-excitation *ortho*-H_2O lines can only be explained if water is present in the warm inner region of the envelope, at radial distances closer than ~15$R_\star$ (or 7.5×10^{14} cm for a stellar radius, $R_\star$, of 5.1×10^{13} cm). This immediately excludes the three mechanisms that only place water in the intermediate or outer regions of the envelope as the source of the water origin (Fig. 2). The mechanism involving the radiative association of O and H_2 in the outer envelope[4] can also be ruled out, in view of the low rate constant recently calculated for this reaction[13]. A possibility for the origin of water in the innermost

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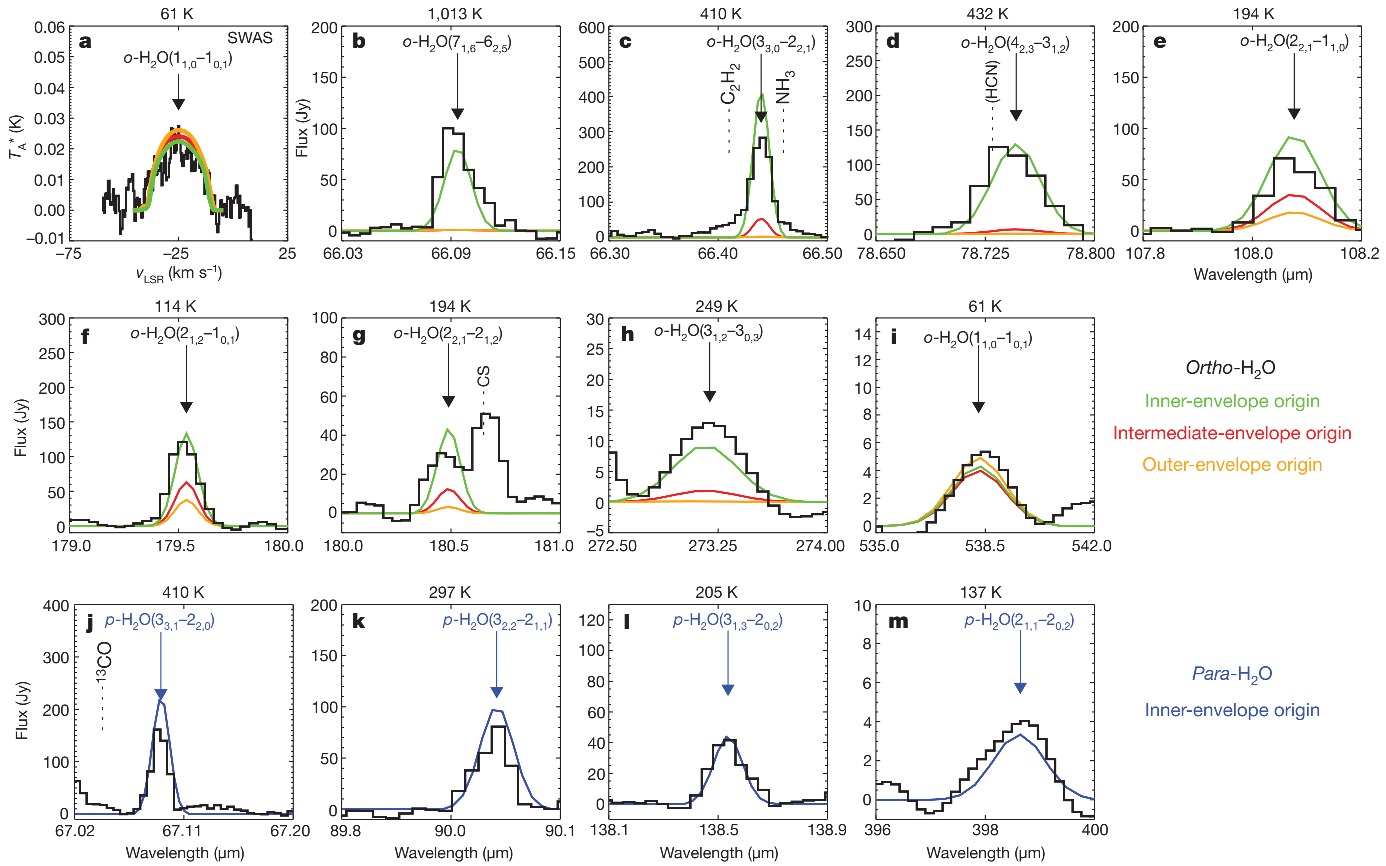

Figure 1 | Unblended *ortho*- and *para*-water lines detected with Herschel in IRC +10216. 39 *ortho*-H_2O and 22 *para*-H_2O lines are identified, including low- and high-excitation lines (see also Supplementary Figs 1–5). **a**, Ground-state *ortho*-H_2O line as observed with SWAS[1]. Units of intensity, T_A^*, are in K; v_{LSR}, velocity with respect to the local standard of rest ($-26\,km\,s^{-1}$ for IRC +10216). **b–i**, Continuum subtracted flux (in Jy) versus wavelength of observation for *ortho*-H_2O lines; **j–m**, *para*-H_2O lines. The HCN $\nu_2 = 4$ contribution to the *ortho*-$H_2O(4_{2,3}–3_{1,2})$ line in **d** is ~15 Jy. At the top of all panels, the upper energy level, E_{upper}, is given. The coloured lines show the non-local thermodynamic equilibrium predictions (Supplementary Information) for the different chemical mechanisms proposed as cause of water vapour in the envelope of IRC +10216. For the red and orange lines, the predictions of *ortho*-H_2O represent envelope models with a constant fractional abundance of *ortho*-H_2O (relative to H_2) out to 4×10^{17} cm, where it is photodissociated[9]. The abundance of *ortho*-H_2O was derived from the SWAS observations (**a**). The red model simulates *ortho*-H_2O originating in the intermediate envelope, with inner envelope radius, R_{int}, of 2.1×10^{15} cm and the derived abundance, [*ortho*-H_2O/H_2], of 2.5×10^{-7}. This model applies both for the hypothesis of the vaporization of icy bodies and the Fischer-Tropsch catalysis mechanism, predicting water around a few times 10^{15} cm. The orange model assumes *ortho*-H_2O to be generated in the outer envelope, with R_{int} of 4.3×10^{16} cm and [*ortho*-H_2O/H_2] equal to 6.7×10^{-7}. Finally, the green model shows the model predictions for *ortho*-H_2O present in the inner envelope, with a radial distribution of the fractional abundance as shown in Fig. 3. **j–m**, Four *para*-H_2O lines, where the blue line is based on the fractional abundance distribution as shown in Fig. 3, using an *ortho*-to-*para* H_2O ratio of 3:1.

regions[9] of the envelope is pulsationally induced shocks that result in a chemical stratification different from thermodynamic equilibrium chemistry. However, IRC +10216 has a C/O abundance ratio of 1.4 (ref. 14). Recent non-thermodynamic-equilibrium calculations[15] have shown that for a carbon-rich star with an even lower C/O ratio of 1.1, water should be almost completely absent in the inner wind, and might only exist between $1R_\star$ and $1.4R_\star$, with a H_2O/H_2 peak abundance around 5×10^{-5}. Simulating this situation, and assuming the (too high) water abundance of 5×10^{-5} over the full region between 1 and 1.4 $R_\star$, we predict water line intensities a factor of 3–10 lower than the PACS and SPIRE observations, ruling out the shock-induced non-thermodynamic-equilibrium chemistry as possible cause of water.

An alternative origin for the warm water vapour could be provided by photochemistry in the inner regions of the sooty circumstellar envelope (CSE) of IRC +10216. For a strictly isotropic and homogeneous mass loss process, the inner regions are well protected against the interstellar ultraviolet (UV) radiation by the circumstellar material located outwards (the visual extinction of interstellar light is more than 100 mag for the innermost regions in IRC +10216; ref. 4). Circumstellar envelopes are, however, not perfectly spherical but have inhomogeneities and a more or less clumpy structure. Observational evidence for the clumpy structure of the envelope around IRC +10216 has been found both at small and large scales through observations at near-infrared and visible wavelengths[16,17], as well as through millimetre-wave observations of different molecules[18–20] (Supplementary Information). The existence of a clumpy structure allows for a deeper penetration of a fraction of interstellar UV photons into the inner circumstellar layers, thus promoting dense and warm UV-illuminated inner regions. In such an environment, water could be formed from the photodissociation of the major oxygen-carrier molecules, mostly ^{13}CO and SiO (^{12}CO is hard to photodissociate due to self-shielding effects), and the subsequent liberation of atomic oxygen, which then converts into water through the chemical reactions (1) and (2):

$$O + H_2 \rightarrow OH + H \quad (1)$$

$$OH + H_2 \rightarrow H_2O + H \quad (2)$$

which are only rapid enough at temperatures above ~300 K. We stress that this mechanism does not necessarily extend to the whole inner CSE but only to those inner clumpy regions which are more exposed to the interstellar UV field. For the case where 10% of the total circumstellar mass is illuminated by interstellar UV photons through a cone where

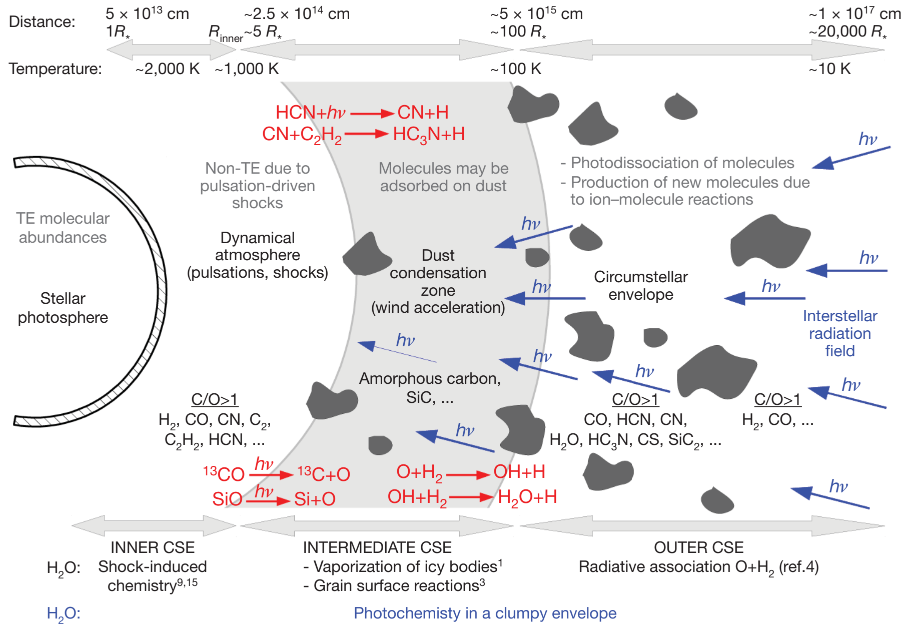

Figure 2 | Schematic overview of the envelope around a carbon-rich AGB star. Several chemical processes are indicated at the typical temperature and radial distance from the star in the envelope where they occur (not to scale). Thermodynamic equilibrium (TE) chemistry defines the abundances in the stellar atmosphere; shock-induced non-equilibrium chemistry takes place in the inner wind envelope[28]; dust–gas and ion–molecule reactions alter the abundances in the intermediate wind zone; molecules such as CO and HCN freeze out at intermediate radii[29]; and the penetration of cosmic rays and UV photons dissociates the molecules and initiates an active photochemistry that creates radicals in the outer wind region[30]. The different mechanisms hitherto proposed as origins of water in a carbon-rich environment are indicated at the bottom of the figure in grey at the typical distances where they occur. The penetration of the interstellar UV photons in a clumpy circumstellar environment is shown in blue. The resulting chemical processes important for the creation of H_2O and HC_3N are indicated in red.

matter only fills 70% of the solid angle of arrival of interstellar light, we predict that water would be formed in the inner envelope with a maximum abundance relative to H_2 in excess of 10^{-7} (Fig. 3 and the Supplementary Information). The predicted water line strengths for the case of a minor UV-illuminated component are shown in green in Fig. 1. The deduced amount of water is 0.003 Earth masses.

AGB stars also have a soft UV stellar radiation field[21,22]. Pulsationally induced shocks might generate a surplus of UV photons close to the stellar photosphere. However, even for a clumpy inner envelope, the densities just above the stellar photosphere are so high that the UV photons will be severely attenuated in the first few 10^{14} cm, in contrast to the outer envelope, where the material is much less dense.

The penetration of interstellar UV photons will result in the formation of hydrides, other than H_2O, in the inner envelope through successive hydrogenation reactions of heavy atoms (nitrogen, carbon or sulphur). Ammonia (NH_3, see Fig. 3) is an interesting example, as it has been observed in IRC +10216 and also in the CSEs of oxygen-rich AGB stars with abundances relative to H_2 in the range 10^{-7}–10^{-6} (refs 6, 23), much larger than the 1×10^{-12} predicted by thermochemical models[7,24]. Other molecules, such as HC_3N, which are typically formed by photochemistry in the outer layers, also have increased abundances in the inner regions, as seen in Fig. 3. The predicted higher abundance of HC_3N in the inner regions is confirmed by our recent observations of HC_3N (Fig. 4) with the IRAM 30-m telescope at Pico Veleta, for which the line profiles point towards the existence of a warm inner component. The discovery of high-excitation H_2O lines in the inner warm and dense envelope of an evolved carbon-rich star causes us to question our knowledge of the envelope chemistry, and outlines the importance of UV-induced photochemistry in the CSEs of evolved stars. In the case of oxygen-rich environments, the same mechanism predicts high abundances of carbon-rich species, such as HCN, CH_4 and CS (ref. 25), as has already been observed in several evolved stars[26,27].

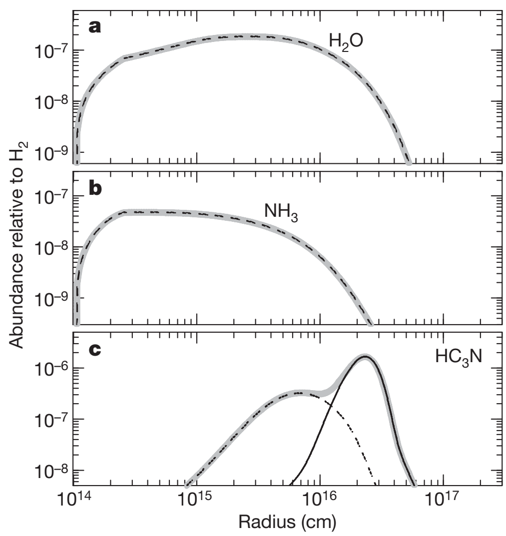

Figure 3 | Fractional abundances in the clumpy circumstellar environment of IRC +10216. The chemical model simulates a clumpy envelope structure, where a fraction of the interstellar UV photons is able to penetrate deep into the envelope (Supplementary Information). **a**–**c**, Predictions for the radial distribution of the fractional abundances relative to H_2 of H_2O (**a**), NH_3 (**b**) and HC_3N (**c**) for a model with a minor UV-illuminated component superposed on a major UV-shielded component. The minor component shown in this figure contains 10% of the total circumstellar mass ($f_M = 0.1$), which is illuminated by interstellar UV photons through a cone where matter fills 70% of the solid angle of arrival of interstellar light ($f_\Omega = 0.3$). Dashed black lines correspond to the minor UV-illuminated component, continuous black lines to the major UV-shielded component, and thick grey lines to the weighted average abundance over the two components. The weighted average abundance is computed as $\bar{X}_i(r) = (1 - f_M)X_i^{\rm major}(r) + (f_M)X_i^{\rm minor}(r)$, where $X_i^{\rm major}(r)$ and $X_i^{\rm minor}(r)$ are the abundance of the species i in the major UV-shielded and minor UV-illuminated component, respectively, as a function of radius r. Note that for H_2O and NH_3 the contribution from the major UV-shielded component is negligible, and the dashed and thick grey line coincide.

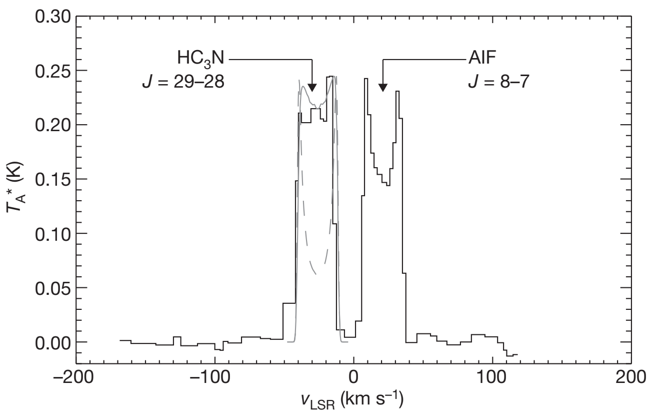

Figure 4 | HC_3N as observed in the envelope of IRC +10216. The HC_3N $J = 29-28$, $J = 33-32$ and $J = 37-36$ lines have been observed with the IRAM telescope. All three HC_3N lines show a clear flat-topped profile. Only the HC_3N $J = 29-28$ line is shown in this figure, and its line profile is compared to that of the AlF $J = 8-7$ line (black line). Both lines were observed with the same telescope, the same beam and the same pointing, and have been calibrated in the same way. Whereas the AlF line profile is 'U'-shaped, the HC_3N line is flat topped, clearly indicating that HC_3N arises from gas extending to inner radii. The grey lines show two model predictions: the dashed grey line corresponds to a model prediction only taking the major UV-shielded component into account, the full grey line shows the theoretical line profile for a model including both the major UV-shielded component and the minor UV-illuminated component. The spectrum is plotted in terms of intensity (T_A^* in K) versus v_{LSR} (in km s^{-1}).

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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