Methane as a dominant absorber in the habitable-zone sub-Neptune K2-18 b

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The transiting exoplanet K2-18 b, discovered in 2015 by the Kepler spacecraft1, orbits an M3 dwarf (effective temperature $T_e = 3,457 \pm 39$ K, radius $R_e = 0.411 \pm 0.038$ times the solar radius)2 at a distance of $0.143 \pm 0.006$ AU (ref. 3). These characteristics imply that K2-18 b receives essentially the same insolation as the Earth does from the Sun. With a mass $M_e = 8.63 \pm 1.35$ Earth masses4 and a radius $R_e = 2.61 \pm 0.087$ Earth radii5, K2-18 b is considered as a super-Earth or sub-Neptune. Following the transits of K2-18 b observed by Kepler/K2 in the visible domain, planetary transits were observed with the Spitzer Space Telescope at wavelengths of 4.5 μm (ref. 5) and 3.5 μm (ref. 6). An additional 9 transits were also observed with the Wide Field Camera 3 (WFC3) aboard the Hubble Space Telescope (HST)7 and analysed by Tsiaras et al.8. The data that cover the range 1.12–1.63 μm clearly show an increase in transit depth at 1.4 μm (Fig. 1 and Extended Data Fig. 1), coincident with a vibrational band of water vapour ($H_2O$). Using a model atmosphere and a retrieval algorithm, Tsiaras et al. concluded that water vapour was clearly detected, determined that other gases such as carbon monoxide (CO), carbon dioxide (CO$_2$), ammonia (NH$_3$) or methane (CH$_4$) were not present in measurable quantities, and concluded that a substantial fraction of the atmosphere is still made of hydrogen and helium. Another simultaneous study has corroborated this interpretation9. However, for such a mini-Neptune-type planet, one would expect substantial amounts of compounds beyond $H_2O$, such as CH$_4$ or NH$_3$. In this Matters Arising, we argue that the reported absorption is most likely due to methane.

We modelled the composition of K2-18 b using the Exo-REM radiative-equilibrium model7–9 adapted for irradiated giant exoplanets8 and calculated the expected transit spectra. Beyond $H_2/He$, Exo-REM incorporates 12 gaseous absorbers, including all potential ones in the HST transit data: that is, $H_2O$, CO, CO$_2$, CH$_4$, NH$_3$ and H$_2$S, but no cloud opacity. Mixing ratio profiles are calculated either from thermochemical equilibrium or allowing for some non-equilibrium chemistry between C-, O- and N-bearing compounds10. We investigated a range of metallicity of 1–1,000, some non-equilibrium chemistry between C-, O- and N-bearing compounds, an eddy-mixing coefficient ($K_m$), a parameter that controls the transport-induced quenching of chemical equilibria, we investigated a range of $10^6$–$10^{10}$ cm$^2$/s$^4$. Transmission spectra were calculated and compared with the HST transit depths along with the K2 and Spitzer transit depths1. The radius of the planet at a reference pressure level was set, for each model, to the value that minimizes the residuals with the data in a least square sense ($\chi^2$). The goodness of the fit was then estimated from this minimum value of $\chi^2$. With 19 degrees
of freedom (17 HST, 1 K2 and 2 Spitzer data points minus 1 free parameter (radius)), any value exceeding 21.4 would indicate that the model does not reproduce the data at the $1\sigma$ ($68\%$) confidence level. We obtained self-consistent models that agree with the data for metallicities of $70$–$800$ and any value of $K_m$. For these models, the temperature in the upper atmosphere probed by the HST data ($\sim 0.001$–$30$ mbar) is in the range $240$–$300$ K, the CH$_4$ mole fraction is $0.03$–$0.10$ and that of H$_2$O is $0.05$–$0.11$ (for example, Extended Data Fig. 2). The calculated transit absorption spectra exhibit a marked maximum around $1.4$ m, in agreement with the HST data (Fig. 1, Extended Data Fig. 3). However, this maximum is predominantly due to CH$_4$ absorption rather than to H$_2$O as previously concluded (Fig. 1, Extended Data Fig. 4). We would need to reduce the CH$_4$ mole fraction by an order of magnitude to reach similar absorption levels for H$_2$O and CH$_4$, even though the H$_2$O contribution ($\nu_1 + \nu_2$ and $2\nu_1$ bands) is intrinsically $\sim 20$ times stronger than that from the CH$_4$ band (isocad) and the abundances of the two species differ by at most $60\%$. The difference in absorptivity is due to the structure of the molecules. The infrared spectrum of CH$_4$ is much more congested than that of H$_2$O because of a larger number of vibrational degrees of freedom and couplings among overlapping bands. At the temperatures ($240$–$300$ K) and low pressures probed by the transit spectra, pressure broadening is weak, the strong lines are saturated and absorption occurs mostly through the much more numerous weak lines.

While our best-fitting model (metallicity of $180$, $K_m = 10^7$ cm$^2$ s$^{-1}$) including all absorbers agrees with the data at the $1\sigma$ confidence level ($\chi^2 = 17.3$) spectra in which only CH$_4$ absorption or only H$_2$O absorption is considered yield equally good fits ($\chi^2 = 18.4$ and $17.7$, respectively) (Fig. 1). Therefore, we agree with Tsiaras et al. that H$_2$O can provide the observed absorption at $1.4$ m but we disagree with the assertion that these HST data provide unambiguous evidence for its presence. In contrast, we find that CH$_4$ is by far the dominant absorber at this wavelength, assuming a Neptune-type composition with a moderately large metallicity, a case that was not considered in the three scenarios they investigated. The $1.4$-m band alone is thus more diagnostic of the presence of methane than of water vapour for relatively cold giant planets such as K2-18 b.

A Bayesian spectral analysis of the HST data corroborates this conclusion (Extended Data Fig. 5). Absorption from water vapour would dominate over methane only if more than $90\%$ of the carbon is sequestered in CO rather than in CH$_4$, contrary to expectations from chemical models, or if the planet’s C/O ratio is $8$–$26$ times lower than the protosolar value ($0.55$), a possibility that we regard as unlikely.

We have investigated up to what atmospheric temperature CH$_4$ absorption dominates over H$_2$O absorption at $1.4$ m in the transit spectra of sub-Neptunes. First, we kept the abundance profiles from our best-fitting atmospheric model (Extended Data Fig. 2) but assumed an isothermal atmosphere in the region probed by the transit spectra and varied its temperature ($T_{\text{atm}}$). As $T_{\text{atm}}$ increases, more and more energy levels are populated, and absorption occurs through an increasing number of transitions for both molecules. Methane then gradually loses its spectroscopic specificity at low temperatures and, for $T_{\text{atm}}>1,000$ K, absorption by the stronger water band prevails over that of methane (Fig. 2). In a second step, we considered self-consistent models in which we fixed the metallicity to $180$ and varied the planet’s effective temperature ($T_{\text{eff}}$) by modifying its distance to the star. In this case, H$_2$O absorption prevails over CH$_4$ for $T_{\text{atm}}>600$ K (Fig. 2). While this estimate relies on known chemical processes, a caveat is the depletion of methane observed in GJ 3470 b, a sub-Neptune with a low metallicity and $T_{\text{atm}}=600$ K, which suggests an inhibition of the CO to CH$_4$ conversion at deep, hot levels.

We have shown that the $1.4$-m region alone cannot be diagnostic of the presence of water vapour for the cool planet K2-18 b and even for mini-Neptunes having an effective temperature up to $600$ K, the absorption probably being mostly due to methane. A confusion arises from the similarity of the spectra of the two molecules from $1.10$ to $1.55$ m, as discussed in a previous study. Data from other spectral ranges, particularly in the interval $1.6$–$3.7$ m, would allow us to clearly discriminate between H$_2$O and CH$_4$ absorption and, in principle, determine the abundance ratio of the two species (Extended Data Fig. 1). Such a measurement would be very important to understand the internal structure of K2-18 b and the location of a possible liquid-water ocean.

**Methods**

**Self-consistent atmosphere models.** We modelled the atmosphere of K2-18 b with Exo-REM, a one-dimensional radiative-equilibrium model for giant planets recently adapted for irradiated planets. Exo-REM solves for the planet-average temperature and chemical composition profiles (Extended Data Fig. 2), based on the conservation of the total (radiative plus convective) flux and assuming either chemical equilibrium or allowing for quenching of the equilibria of CO–CH$_4$, CO–CO$_2$ and NH$_3$–N$_2$. In the latter case, the CH$_4$, CO$_2$ and N$_2$ abundances are held constant above their respective quench levels, which are defined by the equality of interconversion chemical time and atmospheric mixing time (parametrized by the eddy-mixing coefficient $K_z$). The chemical timescales are calculated from simple functional forms that span a range of warm extrasolar giant planets.

No photochemical processes are included. Exo-REM includes opacity from the collision-induced absorption of H$_2$–H$_2$, H$_2$–He and H$_2$O–H$_2$O pairs and from

**Fig. 2** | **Relative contributions of H$_2$O and CH$_4$ to the transit depth.** Shown is the ratio of the transit depth averaged over $1.335$–$1.415$ m, assuming only H$_2$O (blue) or CH$_4$ (red) absorption to the transit depth including all absorbers. The left panel shows calculations with the composition of our best-fitting model (having H$_2$O and CH$_4$ mole fractions of $0.109$ and $0.068$, respectively, in the upper atmosphere), and in which only the temperature of the upper atmosphere is varied. The right panel shows calculations with the composition and temperature profiles derived from our self-consistent Exo-REM model for a metallicity of $180$ and an eddy-mixing coefficient of $10^7$ cm$^2$ s$^{-1}$. In this case, H$_2$O absorption prevails over CH$_4$ absorption for $T_{\text{atm}}$ above $600$ K, a value lower than that in the left panel because the abundance of CH$_4$ decreases with increasing $T_{\text{atm}}$ as carbon is preferentially bound in CO. The horizontal dashed line corresponds to $1$, the maximum possible value of the plotted ratios.
molecular bands of H$_2$O, CH$_4$, CO, CO$_2$, NH$_3$, H$_2$S, PH$_3$, TiO, VO, FeH, Na and K. ExoREM makes use of the correlated k (c-k) method with absorption coefficients calculated on a pressure–temperature grid using the HITEMP (H$_2$O, CO, CO$_2$, H$_2$S, NH$_3$, PH$_3$, TiO, VO, K and FeH) library and theoretical results from NIST (National Institute of Standards and Technology) (Na and K) and ExoMol (all other species) spectroscopic databases (see ref. 10 for details and references).

We have checked that using the more complete POKAZATEL line list for H$_2$O does not noticeably produce more absorption in the calculated transit spectra. While self-consistent cloud models may now be included in ExoREM, here we chose to consider only cloud-free atmospheres. Simulations of the structure of K2-18 b with a general circulation model1 show that the H$_2$O cloud cover is strongly affected by atmospheric dynamics, being quite inhomogeneous in latitude and longitude and in some cases varying with time. We thus believe that it cannot be reliably treated in a one-dimensional radiative–convective equilibrium model. In addition, transit spectra calculated from the outputs of this general circulation model1 show that, for metallicities from 100 to 300, the effects of clouds in the HST/WFC3 range is relatively weak. We finally note that the presence of clouds/hazes was not conclusively detected in a recent study of the atmosphere of K2-18 b, in contrast to previous suggestions11.

We modeled the stellar flux using a spectrum of GJ 176, an M2.5 star with an effective temperature of 3,416 K (ref. 18) and similar to K2-18 in other stellar temperature-normal incidence. We added an internal heat source equivalent to an internal temperature of 0.25, to account for planet-averaged irradiation conditions compared with Jupiter to about 80–200 for Neptune (150–200 agree with the data at 8.63 Earth masses (refs. 1 and 2) and a 1 bar radius of 16,430 km. The spectral flux (stellar and planetary thermal emission) was modelled from 30 to 300,10 cm$^{-1}$ with c-k coefficients defined over 20 cm$^{-1}$ intervals. We ran ExoREM for metallicities (M) varying from 1 to 1,000, as compared with the present solar system elemental composition13. This range encompasses that found in the Solar System (from ~4 for Jupiter to about 80–200 for Neptune) and that expected for a 10 Earth-mass giant planet14 (20–400). The He/H ratio was fixed at 0.0839 (ref. 12). We investigated a range for the eddy-mixing coefficient ($K_m$) that parametrizes the strength of the vertical transport and thus the efficiency of the chemical quenching, from 10$^4$ to 10$^9$ cm$^{-3}$ s$^{-1}$. We also tested models at local thermochemical equilibrium. The atmospheric structure was simulated over a grid of 64 levels with pressures ranging from 200 bar to 10$^{-7}$ mb, sampled uniformly in log space.

Spectral calculations and comparison with data. We calculated transit spectra at 20 cm$^{-1}$ resolution by radially integrating the slant path transmittance over the Exo-REM atmospheric grid and using 64 lines of sight tangent to the pressure levels of the grid. We compared these synthetic spectra with the dataset consisting of the HST/WFC3 data around 1.4 μm, as reduced by Tsiaras et al., the K2 broadband visible measurement and the HST/WFC3 data (P. Chilinski/ExoREM, via P. Arriagada). We also tested models at local thermochemical equilibrium. The atmospheric structure was simulated over a grid of 64 levels with pressures ranging from 200 bar to 10$^{-7}$ mb, sampled uniformly in log space.

We conclude from this analysis that we would need to reduce the CH$_4$ mole fraction by a factor of 9–16 (for metallicities of 70–800) to reduce CH$_4$ absorption at the level of that of H$_2$O.

In models with M below 180, water vapour does not condense out and water clouds are therefore not expected. At higher metallicities, water condensation is predicted to occur between levels of 7 mbar and 250 K for M = 190 and 18 mbar and 264 K for M = 800. Because the condensation region does not extend above the 6 mbar region, cloud opacity is expected to have only a moderate effect on the transit spectrum.

Comparison with an atmospheric retrieval approach. To check our radiative transfer model, we simulated the transit spectrum of K2-18 b for the same atmospheric composition as shown in Extended Data Fig. 2, using the forward model of TauREX 3 (ref. 19 and used by Tsiaras et al.) accessible online (https://taurex3-public.readthedocs.io/en/latest/). As with ExoREM, we find that CH$_4$ absorption dominates at 1.4 μm despite the higher abundance of H$_2$O (Extended Data Fig. 5). A large fraction of the solutions has a CH$_4$ mixing ratio larger than a tenth of the H$_2$O one, corresponding to a CH$_4$-rich atmosphere whose absorption at 1.4 μm dominates by CH$_4$ in particular, the log[H$_2$O] and log(CH$_4$). Our best-fit Exo-REM model having a metallicity of 180 times solar (~0.96 and 1.2, respectively) are located in a dense region of the parameter space (Extended Data Fig. 5). A Neptune-like planet, with substantial amounts of methane, was not one of the three scenarios tested by Tsiaras et al., which probably explains why these authors found evidence for H$_2$O and excluded CH$_4$ as an important source of opacity at 1.4 μm.

Data availability

The observational data that support the findings of this study are included in the references. The model data that support the plots within this paper are available from the corresponding author upon request.

Code availability

The ExoREM source code and the input files used in this study are available from the corresponding author upon reasonable request. The current version of ExoREM is available through the Observatoire de Paris GitHub website: https://github.obspm.fr/Exoplanet-Atmospheres-LESLIA/exorem

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**Author contributions**

B.B. initiated the development of the Exo-REM model, performed the analysis and wrote the paper with the help of B.C. and D.B. B.C. contributed to the development of the Exo-REM model, compared Exo-REM and TauREx outputs and wrote the relevant section. D.B. calculated the tables of c-k absorption coefficients and adapted the Exo-REM model to irradiated planets, with contributions from B.B and B.C. All authors contributed to the interpretation of the results and commented on the manuscript at all stages.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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Extended Data Fig. 1 | Comparison of model transmission spectra with the observational data set. The transmission spectrum of K2-18b calculated from our best-fitting self-consistent model (red) is compared with the HST/WFC3 data, the Kepler/K2 data point and the Spitzer/IRAC measurements at 3.5 and 4.5 μm. A model including only H₂O absorption is shown in blue. For each model, the planet’s radius has been adjusted to minimize the χ² residuals. The location of the main absorption bands of H₂O (blue squares) and CH₄ (green squares) are indicated. While both models are similar in the spectral range covered by the HST data, they vastly differ at longer wavelengths where the CH₄ bands no longer coincide with the strong H₂O bands. The rightmost vertical axis represents the pressure levels for our best-fitting model having a metallicity of 180 (red).
Extended Data Fig. 2 | Best-fit atmospheric model. Temperature profile (thick black line) and abundance profiles of selected molecular absorbers (coloured lines) for our best-fit Exo-REM model. The metallicity is 180 and the eddy mixing coefficient is $10^8$ cm$^2$ s$^{-1}$. In this model, water vapour does not condense and water clouds are not expected to form. The mean molecular mass is 6.2 amu.
Extended Data Fig. 3 | Transmission spectra of K2-18 b calculated for different atmospheric compositions. Spectra calculated from our self-consistent model Exo-REM for a metallicity of 180 and an eddy mixing coefficient of $10^8$ cm$^2$ s$^{-1}$ are compared with HST data as reduced by Benneke et al. All absorbers are included in the spectral calculation shown in red. Spectra including absorption from H$_2$O only (blue) and from CH$_4$ only (green) are also shown. The planet’s radius has been adjusted in each case to minimize the residuals with the whole dataset.
Extended Data Fig. 4 | Contributions of different absorbers to the transit depth. Transmission spectra of K2-18 b calculated for the atmospheric composition shown in Extended Data Fig. 2 using the forward model of TauREx 3 (ref.23). The orange line corresponds to the spectrum with molecular absorption from H₂O, CH₄, CO, NH₃ and collision-induced absorption (CIA) from H₂-H₂ and H₂-He. Other coloured lines show the contribution of each molecule.
Extended Data Fig. 5 | Posterior distributions obtained from free retrievals. The retrieval tool TauREx 3 (https://taurex3-public.readthedocs.io/en/latest/) was applied to the HST data reduced by Tsiaras et al.\textsuperscript{6} with planetary radius (expressed in Jovian radius), temperature, log of H\textsubscript{2}O, CH\textsubscript{4} and N\textsubscript{2} volume mixing ratios, and cloud-top pressure (Pa) as free parameters. The posterior distributions of the log(H\textsubscript{2}O) and log(CH\textsubscript{4}) are very broad with a denser region for the ranges [-3.5:-1] and [-4:-0.3] respectively. A large fraction of the parameter space corresponds to a CH\textsubscript{4}-rich atmosphere whose absorption at 1.4 micron is dominated by CH\textsubscript{4}. The parameters of our best fit Exo-REM model having a metallicity of 180 (Extended Data Fig. 2), shown as an orange dot in the log(CH\textsubscript{4})-log(H\textsubscript{2}O) space, are globally consistent with the TauREx retrievals.