Chemical kinetics on extrasolar planets

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Chemical kinetics plays an important role in controlling the atmospheric composition of all planetary atmospheres, including those of extrasolar planets. For the hottest exoplanets, the composition can closely follow thermochemical-equilibrium predictions, at least in the visible and infrared photosphere at dayside (eclipse) conditions. However, for atmospheric temperatures \( \lesssim 2000 \) K, and in the uppermost atmosphere at any temperature, chemical kinetics matters. The two key mechanisms by which kinetic processes drive an exoplanet atmosphere out of equilibrium are photochemistry and transport-induced quenching. I review these disequilibrium processes in detail, discuss observational consequences and examine some of the current evidence for kinetic processes on extrasolar planets.

1. Introduction

In two short decades, the study of extrasolar planets has evolved from a relatively esoteric, theory-driven, scientific diversion to a fully fledged, observation-driven, vibrant profession \[1,2\]. With 859 exoplanets discovered as of January 2013 \[3\] and with thousands more Kepler planetary candidates waiting to be confirmed \[4,5\], our Sun has lost its status as a unique planetary host. However, each planetary system discovered to date displays its own unique properties, and the sheer diversity of those properties is staggering. Most of the known exoplanets are expected to possess atmospheres of some sort, but those atmospheres will be equally diverse and often have no Solar System analogues. Can we use basic physical and chemical principles to predict the characteristics and behaviour of exoplanet atmospheres? How good are our predictions, and what do we learn from comparisons of observations and theory?

Current observational techniques used to analyse exoplanet atmospheres include direct imaging \[6–8\]
and transit and eclipse measurements [9–12]. Because exoplanets are so much fainter than their host stars, atmospheric characterization by direct imaging has so far only been viable for young, bright, hot planets that orbit relatively far from their host stars, and concrete information on atmospheric composition has only recently been reported from this technique [13–21]. Transit and eclipse observations, where light from the system is observed to dim as the planet passes in front of and behind the host star as seen from the observer, have been more fruitful in determining atmospheric composition, but observational biases still limit the types of planets that can be studied in this manner. Transits have a higher probability of being observed for planets orbiting very close to their host stars, and the signal is stronger for larger planets. Therefore, close-in giant planets—the so-called ‘hot Jupiters’ and ‘hot Neptunes’—currently dominate exoplanet atmospheric observations, and my review of exoplanet chemistry will focus on such planets. Transit and eclipse observations have enabled the first-ever detections of neutral and ionized atoms such as Na, H, O, C⁺, Si²⁺, Mg⁺ and K [9,22–26] and molecules such as H₂O, CH₄, CO₂ and CO [27–41] in exoplanet atmospheres.

The first-order properties of exoplanet atmospheres can be predicted theoretically based on the planet’s mass, internal heat flux (and/or age), assumed bulk elemental composition and incident stellar flux [42]. Given these basic parameters, models of thermochemical equilibrium, cloud condensation, and radiative and convective energy transport can be used to predict the composition and thermal structure within the planet’s atmosphere, as well as the observable spectral behaviour [43–51]. Chemical equilibrium is a convenient starting point for these types of calculations, as the abundances of individual species can be calculated in a straightforward manner for any given temperature, pressure and elemental composition through minimization of the Gibbs free energy of the system [44,47]. The actual pathways (e.g. chemical reactions) required to achieve that equilibrium do not matter, and nor does the history of the system, thus greatly simplifying the calculations. At high temperatures, such as those within the deep atmospheres of hot Jupiters, chemical reactions can overcome energy barriers to proceed equally well in both the forward and reverse directions, and the chemical-equilibrium assumption is justified. However, for cooler regions of the atmosphere, or when incident ultraviolet (UV) photons or high-energy ionizing/dissociating particles are present, chemical equilibrium becomes more difficult to achieve, and chemical kinetics or other disequilibrium mechanisms can control the composition.

The two main kinetics-related disequilibrium processes expected to modify abundances within exoplanet atmospheres are photochemistry and transport-induced quenching. Photochemistry refers to the chemical kinetics that results from the absorption of short-wavelength stellar photons or high-energy corpuscular radiation like cosmic rays. Transport-induced quenching refers to the mechanism by which the atmospheric composition is driven away from chemical equilibrium as a result of the dominance of transport processes like convection or large-scale ‘eddy’ diffusion (e.g. from gravity-wave breaking or wave-driven circulation) over chemical reactions [52–54]. While often considered second-order effects, both of these disequilibrium processes can significantly alter the composition and hence the radiative properties, thermal structure and even dynamics of the atmosphere, making them important processes to consider in theoretical models. As an example, the photolysis of methane on Jupiter and the other giant planets within our own Solar System leads to the generation of complex hydrocarbons, introducing numerous trace photochemical products into the Jovian stratosphere (e.g. [55]). Some of these products, such as C₂H₂ and C₂H₆, become key infrared (IR) coolants [56], while some of the more refractory products can condense in the stratosphere to form hazes that absorb sunlight and provide localized heating [57]. The photochemical products strongly influence the spectral behaviour, radiative energy transport and thermal profile, which feed back to affect the stratospheric circulation (e.g. [58]). Owing to the intense UV flux incident onto the atmospheres of close-in transiting exoplanets, photochemistry is expected to play a significant role on hot Jupiters [59–71], although the observable consequences may be restricted to high altitudes in some cases, particularly for the hotter atmospheres. Transport-induced quenching can potentially affect the composition throughout the visible
and IR photosphere of exoplanets [47,67,68,71–77], thereby affecting the thermal structure and spectral behaviour.

Here, I review current knowledge of these two disequilibrium processes and discuss how atmospheric properties, such as the thermal structure, bulk elemental abundance and transport properties, can affect the predicted composition. I also briefly discuss the observational evidence for disequilibrium compositions.

2. Transport-induced quenching

Transport-induced quenching within giant-planet atmospheres was first described by Prinn & Barshay [52] to explain the observed 1 part per billion (ppb) abundance of CO in Jupiter’s upper troposphere, despite the negligible amount expected at local temperature–pressure conditions from chemical-equilibrium arguments. As a parcel of gas is transported through the atmosphere, the mole fraction of a constituent can become ‘quenched’ when the transport time scales drop below the chemical kinetics time scales required to maintain that constituent in equilibrium with other species. The mole fraction of that species then remains fixed at that quenched abundance. Quenching typically occurs when the temperature of the system drops low enough that reactions no longer occur equally well in both the forward and reverse directions; however, pressure changes can also play a role. The best-studied quenching process is that of CO–CH4 interconversion shutting down as a result of vertical mixing because of the importance of that process for Solar System giant planets [52,78–82], brown dwarfs [75,76,83–89] and extrasolar giant planets [17,65,67,68,72,74,90,91]. In fact, CO–CH4 quenching has particularly important observational consequences for hot Jupiters and brown dwarfs because their atmospheric temperature profiles often cross the boundary between regions in which CH4 or CO is the dominant carbon constituent, with transport-induced quenching then leading to CO and/or CH4 mole fractions that are orders of magnitude different from chemical-equilibrium predictions. The resulting spectral implications can be major (see above references). Although time-constant arguments have historically been used to predict the quenched abundances of CO and CH4, Bézard et al. [81], Moses et al. [67] and Visscher & Moses [76] discuss some of the pitfalls of such techniques that can arise if the underlying assumptions are not sound. Many investigators instead now solve the full continuity equations for a large number of species to track transport-induced quenching [66–68,70,71,76,77,82], a technique that has the added benefit of more accurately predicting the profiles of other potentially spectrally active species (e.g. CO2, C2H2, HCN) once some critical ‘parent’ molecules are quenched.

However, these more sophisticated models are also only as good as their inputs and assumptions, and, although the kinetics of the C–H–O system has been well studied owing to combustion-chemistry and terrestrial atmospheric-chemistry applications [92–94], the exact mechanism involved with CH4–CO quenching in reducing environments has not been strictly established. As originally hypothesized [52], individual reactions that convert oxidized carbon (e.g. CO, CO2, HCO, H2CO, CH2OH, CH3O, CH3OH) to reduced carbon (e.g. CH4, CH3, C2H2, C2H4, C2H6) and vice versa are of critical importance to the problem, as reactions within the oxidized or reduced families tend to be faster. The reaction H2 + H2CO ⇌ OH + CH3 was originally proposed as the rate-limiting step for CO–CH4 conversion [52,54,80], but this reaction is probably too slow under typical brown-dwarf or giant-planet conditions to be a key player in the dominant interconversion mechanism [67,76,79,81,82,85]. Yung et al. [79] suggest that the reaction H + H2CO + M → CH3O + M is the rate-limiting step as a potential bottleneck to the necessary conversion of the strong CO bond to a weaker single-bonded C–O species. However, more recent studies point to alternative reactions being the rate-limiting steps; the most thorough and updated discussions of the problem are presented in [67,76].

Figure 1 demonstrates that the quenched abundances of species such as CH4 and NH3 are very sensitive to the individual reactions and rate coefficients in the adopted reaction mechanism for these kinetics–transport models. Moreover, once molecules like CH4 and NH3 quench, the abundances of other species such as C2H2 and HCN can be affected, and the profiles of minor
species can become complicated. Because the full reaction mechanisms for the Moses et al. [67] and Venot et al. [71] studies have been published online, intercomparisons between these models is relatively straightforward. Therefore, I focus my discussion on these two models and apply the mechanisms to the day-side atmosphere of HD 189733b. Venot et al. [71] do not provide a detailed discussion of their dominant CH$_4$ → CO quench mechanism, but it is clear that interconversion between these two species is more efficient in their model than in Moses et al. [67], as the CH$_4$ mole fraction in the Venot et al. model continues to follow the equilibrium predictions to higher altitudes (lower pressures/temperatures) than in Moses et al. The resulting quenched CH$_4$ abundance is therefore lower in the Venot et al. [71] model than in the Moses et al. [67] model.

A detailed examination of the two mechanisms reveals that the main difference with respect to the CH$_4$ quench behaviour derives from the adopted rate coefficients for the reaction H + CH$_3$OH → CH$_3$ + H$_2$O. The Venot et al. [71] mechanism originates from combustion-chemistry studies that use the Hidaka et al. [96] rate-coefficient estimate for this reaction; some previous giant-planet quenching studies also initially adopted this rate coefficient [82]. However, as is discussed by Visscher et al. [82] and Moses et al. [67], the H + CH$_3$OH → CH$_3$ + H$_2$O reaction probably proceeds with a very large energy barrier and is therefore much slower than was estimated by Hidaka et al. [96]. When a more realistic rate coefficient for this reaction, as calculated
from \textit{ab initio} transition-state theory \cite{67}, is incorporated into the Venot \textit{et al}. \cite{71} mechanism, the resulting quenched CH$_4$ mole fraction is more in line with that of Moses \textit{et al}. \cite{67}, with remaining differences being largely due to the adoption of a larger rate coefficient for H$_2$O + CH$_2$ $\rightarrow$ CH$_3$OH in the Venot \textit{et al}. model (which again seems to be based on an estimate (e.g. \cite{97})) than in the Moses \textit{et al}. model (where the rate-coefficient calculations of \cite{98} have been adopted).

Although I think that CH$_4$−CO quenching is unlikely to proceed exactly as described in the Venot \textit{et al}. mechanism, owing to some problems with individual rate coefficients as discussed above, it is possible that other reactions and/or rate coefficients not considered by either Moses \textit{et al}. \cite{67} or Venot \textit{et al}. \cite{71} (or any other investigations) could be dominating on hot Jupiters. As an example, Hidaka \textit{et al}. \cite{96} favoured a fast rate for H + CH$_3$OH $\rightarrow$ CH$_3$ + H$_2$O precisely because they were looking for an effective way to reproduce the observed yield of CH$_4$ in their methanol decomposition experiments. If that reaction is not responsible, as I indeed suggest it is not, then other reactions must be taking up the slack, and it remains to be demonstrated whether any of the updated reaction rate coefficients in the Moses \textit{et al}. \cite{67} and Venot \textit{et al}. \cite{71} mechanisms, or those of other investigations \cite{64,66,70}, can reproduce all available experimental data. The quenched abundance of CH$_4$ should therefore be considered accurate only to within a factor of 2 owing to kinetics uncertainties, with other factors such as atmospheric transport properties and thermal structure contributing additional uncertainty. It is obvious from figure 1, however, that CO−CH$_4$ quenching matters on HD 189733b and probably on other close-in hot Jupiters, with potential observable consequences, just as on brown dwarfs and directly imaged extrasolar giant planets \cite{13,17,75,84,86}. The colder the exoplanet atmosphere, the deeper the quench point and the larger the quenched CH$_4$ mole fraction that could be present in the visible−IR photosphere \cite{67}.

Similarly, interconversion between the main nitrogen species N$_2$ and NH$_3$ can be kinetically inhibited in planetary and brown-dwarf atmospheres \cite{54,99–102}, leading to quenching of both species. The N$_2$−NH$_3$ quench point probably occurs deeper in the atmosphere than the CO−CH$_4$ quench point, but the kinetics of nitrogen species under high-temperature, high-pressure, reducing conditions is even more uncertain than those of carbon and oxygen. The key to the kinetics of interconversion of N$_2$ and NH$_3$ is likely to be the reduction of the strongly triple-bonded N$_2$ into progressively weaker N−N bonded N$_2$H$_x$ species, followed by thermal decomposition or disproportionation reactions converting the N$_2$H$_x$ molecule into two NH$_x$ species. Initial suggestions for the rate-limiting steps in the process \cite{80,99,100}, for example N$_2$ + H$_2$ $\rightarrow$ 2NH, have given way to other suggestions because the above reaction will probably be too slow to play any significant role in the N$_2$−NH$_3$ conversion \cite{102}. Alternative suggestions for the rate-limiting step in NH$_3$ quenching include (i) N$_2$H$_3$ + M $\rightarrow$ H + N$_2$H$_2$ + M \cite{102}, where M is any additional atmospheric species in this three-body reaction, (ii) 2NH$_2$ $\rightleftharpoons$ N$_2$H$_2$ + H$_2$ \cite{66} and (iii) NH + NH$_2$ $\rightarrow$ N$_2$H$_2$ + H \cite{67}. These are all viable possibilities, and published rate coefficients for these reactions or their reverses are available from theoretical calculations \cite{103–106} or experiments \cite{107}, but large uncertainties and discrepancies for these and other potentially important reaction rate coefficients exist in the literature. The predicted quenched abundance of NH$_3$ on HD 189733b differs by about an order of magnitude when using the Venot \textit{et al}. \cite{71} mechanism as opposed to that of Moses \textit{et al}. \cite{67}. Ammonia diverges from the equilibrium profile much deeper with the Moses \textit{et al}. \cite{67} mechanism, and, although the NH$_3$ does not truly quench until higher altitudes because transport time scales are only slightly smaller than kinetic conversion time scales in the nearly isothermal region between a few bars and roughly 0.1 kbar in the HD 189733b model \cite{67}, the resulting quenched NH$_3$ abundance is significantly greater in the Moses \textit{et al}. \cite{67} model than in the Venot \textit{et al}. \cite{71} model. The main
differences appear to be related to reactions of NH2 with NH2 and/or NH3. Venot et al. [71] have adopted very large rate coefficients for some reactions that convert NH2 to N2Hx species based on the work of Konnov & De Ruyck [108,109]. For example, the Venot et al. rate coefficient for NH2 + NH3 → N2H3 + H2 (based on [108]) is more than three orders of magnitude larger at 1600 K than the expression used in Moses et al. [67] (based on [110]), and this reaction plays a major role in the efficient interconversion of NH3 = N2 in the Venot et al. [71] mechanism. However, the rate-coefficient expression advocated by Konnov & De Ruyck [108] is simply an ad hoc eightfold reduction of a previous estimate [111], which Konnov & De Ruyck altered to keep that reaction from having any adverse effects on their experimental simulations [108]. As such, the Konnov & De Ruyck expression is more of an upper limit than a true recommendation. In fact, the NH2 + NH3 → N2H3 + H2 reaction probably has a significantly higher barrier than the Konnov & De Ruyck expression indicates, and the reaction is not expected to be important under conditions relevant to hydrazine combustion or ammonia pyrolysis [110]. It is also unlikely to be important for NH3−N2 quenching in giant-planet atmospheres if the rate coefficient has an energy barrier similar to that suggested by Dean et al. [110] (see also [67]). However, further rate-coefficient information on this reaction is needed before it can truly be ruled out as a participant in the NH3 = N2 interconversion process. The adoption of a fast rate coefficient for this reaction strongly influences the low derived NH3 abundance in the Venot et al. model.

The NH2 + NH2 → N2H2 + H2 reaction represents a more interesting case, as the product pathways and rate coefficients are not well known for the NH2 + NH2 reaction. Venot et al. [71] adopt a relatively large rate coefficient for this reaction based on Konnov & De Ruyck [109], which in turn was influenced by the experimental study of Stothard et al. [107] that indicates that N2H2 (as an unidentified isomer) is an important product in the NH2 + NH2 reaction at room temperature. Theoretical models [103,104,106], by contrast, suggest that the standard pathways producing H2 + N2H2 (various isomers) are relatively unimportant at room temperature. In the Klippenstein et al. [103] calculations, for instance, two NH2 radicals interact on a singlet potential energy surface via barrierless addition (i.e. to form N2H4), with the stabilization of the adduct dominating especially at low temperatures and high pressures, or potential elimination of H and H2 occurring at higher temperatures (e.g. to form H + N2H3 or H2 + various isomers of N2H2). On the triplet surface, the NH2 + NH2 reaction can occur via hydrogen abstraction to form NH + NH3 [103], which is especially important at high temperatures. The barriers leading to H2 + N2H2 are sufficiently high on the singlet surface in the Klippenstein et al. [103] models that the product channels forming various isomers of N2H2 are unimportant even at the moderately high temperatures relevant to NH3 quenching on the giant planets (1500–2100 K). Moses et al. [67] have adopted the rate-coefficient recommendations of Dean & Bozzelli [104] for the H2 elimination pathways, which are more in line with the Klippenstein et al. [103] recommendations than with the Konnov & De Ruyck [109] recommendations, and the resulting NH2 + NH2 → N2H2 + H2 or → H2NN + H2 pathways are not very important in NH3 → N2 conversion in their HD 189733b and HD 209458b models. On the other hand, Asatryan et al. [106] suggest that there could be a potential low-energy pathway to NH2 + NH2 → cis-N2H2 + H2 that could occur through a ‘activated’ N2H4 intermediate even at moderately low temperatures. Stereoselective attack of cis-N2H2 by H2 then leads to N2 + 2H2 with a comparatively low barrier. As mentioned by Altinay & Macdonald [112], this suggested pathway needs further theoretical verification, but, if plausible, it might lead to a more efficient means of NH3 → N2 conversion in exoplanet atmospheres than has been implemented in the Moses et al. [67] model.

In all, the Moses et al. [67] and Venot et al. [71] mechanisms can be considered to bracket the low and high ends of possible NH3 ≈ N2 conversion efficiencies, and the expected quenched NH3 abundance on transiting exoplanets is uncertain by about an order of magnitude (see also Venot et al. [71]). To improve that situation, we need reliable rate coefficients for several reactions involving NH3 and N2Hx species at temperatures of roughly 1500–2200 K and pressures of 1–1000 bar. Of particular interest are rate coefficients for the various possible pathways involved with the reactions of NH2 + NH2, NH2 + NH3, NH + NH2, NH + NH3, H2 + N2H2 (various isomers), H2 + N2H3 and H + N2Hx, and the thermal decomposition of N2H4, N2H3...
and various N$_2$H$_2$ isomers. As the chemistry of ammonia and hydrazine is also important on Jupiter and Saturn, extension to temperatures of approximately 100 K would also be valuable for the investigation of tropospheric photochemistry on those planets.

Carbon monoxide and molecular nitrogen also technically quench when CO−CH$_4$ and N$_2$−NH$_3$ interconversion reactions cease to be able to compete with vertical transport processes. However, because these molecules are the dominant carbon and nitrogen constituents at the quench points in the HD 189733b and HD 209458b models [67,71], the quenching behaviour for these species is less obvious, as their equilibrium mole fractions are expected to remain constant to higher altitudes anyway. If the quench points on exoplanets were to occur in a region where both CH$_4$ and CO (or N$_2$ and NH$_3$) have similar abundances, then the quenching of both species would be more obvious.

Once major molecules such as NH$_3$ and CH$_4$ are quenched, the abundance of other species can be strongly affected. For example, figure 1 illustrates that the HCN and C$_2$H$_2$ abundances depart from equilibrium when NH$_3$ and CH$_4$ quench on HD 189733b, and these molecules continue to react with the quenched ‘parent’ molecules up to higher altitudes, causing their column abundances to greatly exceed equilibrium predictions. Acetylene maintains a pseudo-equilibrium with H$_2$ and quenched CH$_4$ up to approximately 0.1 bar in this model (see [67] for more information about the important reaction schemes). The large bulge in the C$_2$H$_2$ abundance at higher altitudes is due to photochemical and disequilibrium thermochemical kinetics processes. Similarly, HCN maintains a pseudo-equilibrium with quenched NH$_3$ and CH$_4$ (with a net reaction NH$_3$ + CH$_4$ = HCN + 3H$_2$; see Moses et al. [67] for detailed reaction schemes) to approximately 0.1 mbar, above which the downward transport of photochemically produced HCN dominates the profile. Transport-induced quenching can therefore affect species abundances even before their own quench points are reached, and full kinetics models are needed to describe this behaviour.

Quenching does not occur solely in the vertical direction. Possible horizontal quenching was first discussed by Cooper & Showman [72]. Time-constant arguments [67,72] indicate that horizontal winds have the potential to transport gas species to cooler atmospheric regions before the species have time to equilibrate, which could particularly affect transit observations of the cooler terminator regions. Similarly, quenching (vertical or horizontal) can affect the atmospheric composition of close-in eccentric exoplanets [113] such that the large swings in temperature over the orbit may not necessarily be accompanied by large changes in atmospheric composition if orbital time scales are shorter than chemical reaction time scales. Agúndez et al. [77] have followed up these ideas with a more sophisticated kinetics model to investigate horizontal quenching on HD 209458b under the simplifying assumptions of constant zonal winds as a function of altitude, latitude and longitude, with no photochemistry or vertical transport included. They find that horizontal quenching is indeed very important, especially at pressures less than roughly 0.1 bar (depending on the species). The horizontal quenching suppresses longitudinal abundance gradients, greatly reducing dayside versus terminator abundance differences, resulting in major observational consequences. Essentially, Agúndez et al. [77] find that abundances above the 0.1 bar level are quenched horizontally to dayside equilibrium values, whereas quenching due to vertical mixing controls the abundances at deeper levels down to the quench point. The resulting terminator and nightside abundance profiles differ from models based on either thermochemical equilibrium or kinetics considering vertical transport only, and the main prediction is a reduction in the mid- to high-altitude abundance of species such as CH$_4$ and NH$_3$ that are relatively unstable at the high dayside temperatures of HD 209458b but that would nominally be stable at cooler terminator and nightside temperatures.

Clearly, the chemical profiles in the three-dimensional situation will be complicated, and kinetics and transport-induced quenching in both the vertical and horizontal directions must be considered to accurately reflect the situation in the real atmosphere. The inclusion of vertical mixing in such longitudinally variable models is an important next step, as it would more realistically capture the dayside abundances of vertically quenched species like NH$_3$ and CH$_4$, and thus more accurately predict the horizontally quenched terminator and nightside
abundances. The addition of photochemistry to the problem will complicate things further, as photochemical time constants tend to be very short in the upper atmospheres of these planets. Ultimately, it will be valuable to move towards the inclusion of more sophisticated kinetics directly within the three-dimensional general circulation models, as the disequilibrium constituents can affect the radiative properties of the atmosphere, and the resulting feedback on the temperatures and even dynamics could be important.

3. Photochemistry

The consequences of photochemistry on the atmospheric composition of exoplanets have been explored by numerous groups [59–71,114]. I briefly review how photochemistry affects the carbon, nitrogen and oxygen species in the 0.1–1000 mbar region of hot Jupiters and hot Neptunes, i.e. the pressure region at which the IR transit and eclipse observations have their highest sensitivity. Higher-altitude thermospheric photochemistry is discussed in [61–63], and sulfur photochemistry is discussed in [64]. Little work has yet been done on the photochemistry of other elements such as phosphorus, alkalis or metals owing to a lack of relevant kinetic information.

Although stellar UV photons are the ultimate instigators of photochemistry, the resulting abundances of the observable photochemical products on hot Jupiters depend less on the magnitude of the incident UV flux than on the overall atmospheric thermal structure (and hence the stellar flux in the visible and near-IR) because of the high sensitivity of the ‘parent’ molecule abundances to temperature. Near-solar-composition atmospheres that are hotter than about 1600 K in the 0.1–1000 mbar region will contain CO, H2O and N2 as their dominant heavy molecular constituents. These molecules are relatively stable against photochemical destruction and/or tend to recycle efficiently (e.g. [67]) so that photochemistry does not remove them from the 0.1–1000 mbar region (unless temperatures are so high that these molecules, too, become unstable). Cooler atmospheres will contain more CH4 and NH3, which are more interesting from a photochemical standpoint.

Examples of the influence of atmospheric temperatures on the photochemical composition are shown in figures 2 and 3. First, I present the thermal profiles of three hypothetical ‘hot’, ‘warm’ and ‘cool’ exoplanets in figure 2, along with some important chemical-equilibrium boundaries. Although these temperatures are based on published profiles for specific exoplanets [68,116,117], I use them generically here for the photochemical models shown in figure 3, which all assume a
Figure 3. Mole fraction (volume mixing ratio) profiles for the generic cool (i), warm (ii) and hot (iii) exoplanets, assuming thermochemical equilibrium (a) or thermochemical and photochemical kinetics and transport (b). All models assume a solar elemental composition, and the transport models assume a uniform eddy diffusion coefficient of $10^9 \text{ cm}^2 \text{ s}^{-1}$. Note the decrease in the importance of CH$_4$ and NH$_3$ going from the ‘cool’ to the ‘hot’ exoplanet. (Online version in colour.)

solar composition of elements and an arbitrary constant-with-altitude eddy diffusion coefficient of $10^9 \text{ cm}^2 \text{ s}^{-1}$. The assumed incident stellar flux in the models, however, remains consistent with the adopted thermal structure, so that the hot planet is receiving a larger overall incident flux. Note from figure 2 that the thermal profile of the ‘cool’ exoplanet lies in a regime in which CH$_4$ is the dominant carbon species throughout much of the atmosphere except at very low pressures, whereas the profile transitions from the NH$_3$ regime to the N$_2$ regime deeper in the atmosphere. The thermal profile of the ‘warm’ exoplanet lies in the N$_2$-dominated regime, but crosses the equal-abundance boundary between CO and CH$_4$ near 10 bar. The thermal profile for the ‘hot’ planet lies solidly within the N$_2$ and CO stability regimes. The location of the thermal profile within these chemical stability boundaries controls what ‘parent’ molecules are available to initiate photochemistry. Figure 3 then shows the expected composition from the consideration of either thermochemical equilibrium (left-hand side of plot) or disequilibrium chemistry due to thermochemical and photochemical kinetics and vertical transport (right-hand side of plot), using the models described in Moses et al. [67,68].
One obvious consequence of photochemistry on all of these close-in exoplanets, regardless of the thermal structure, is the huge production rate of H at high altitudes (due to H₂ photolysis, H₂ thermal decomposition in the planet’s expected hot thermosphere, and H₂O photolysis and subsequent catalytic destruction of H₂). The atomic H then diffuses downwards to affect the chemistry of other molecules. The catalytic H₂O photolysis source of H was first described by Liang et al. [59]. Similar catalytic destruction mechanisms involving CH₄ and NH₃ [67] operate in the cool and warm exoplanet atmospheres, where these molecules are more abundant. Atomic H is expected to become the dominant atmospheric constituent at relatively high (microbar) pressures, with the exact transition from H₂ to H depending on the soft X-ray and extreme ultraviolet (EUV) flux from the host star, thermospheric temperatures and hydrodynamic winds [62]. Hydrodynamic descriptions and ion chemistry are needed to accurately model the chemical behaviour at altitudes above approximately 1 µbar on highly irradiated planets [61,62], so the high-altitude results presented here are phenomenological only. Neutral O, C and N from the photodestruction of CO, N₂ and H₂O are undoubtedly going to be important at high altitudes on highly irradiated planets, but hydrodynamic winds probably drag these atomic constituents to higher altitudes than are shown in this hydrostatic model.

On very hot exoplanets, like the ‘hot’ generic giant planet shown in figure 3, photochemistry is relatively unimportant (see also [67,68,70]). Photolysis of CO and N₂ leads to the high-altitude production of atomic species such as C and N that are not predicted to be important under equilibrium conditions. Such atomic species (as well as O) and their ions could be observable in UV transit observations (e.g. [23]). At high altitudes, hydroxyl radicals (OH) are also produced from H₂O photolysis or reaction with atomic H, and HCN is produced from CO and N₂ photolysis through schemes such as those described at the beginning of section 3.5 in Moses et al. [67], but neither of these species remains stable in regions where atomic H dominates. Some production of NO (peaking at ppm abundances) and even O₂ (peaking at 10 ppb abundances) occurs, but these species are confined to a narrow altitude region where CO and N₂ photolysis is effective (i.e. before CO and N₂ self-shield) and will not be abundant enough to be observable for solar-composition atmospheres. In fact, virtually all of the interesting photochemistry is confined to this narrow altitude region where the CO and N₂ photolysis rates peak. Although H₂O photolysis continues to much deeper levels, the photolysis products tend to recycle rapidly back to H₂O in the H₂-dominated atmosphere. Temperatures are high enough throughout the bulk of the IR photosphere at approximately 0.0001–1 bar such that kinetic reactions can maintain equilibrium, despite the perturbing influence of photolysis of H₂O and other less-abundant species. For the hottest planets, the reaction rates are fast enough that vertical transport-induced quenching is not important either, for reasonable assumptions about vertical eddy diffusion coefficients. If quenching occurs at all, it occurs at high altitudes (low pressures), where the photochemically active molecules such as NH₃ and CH₄ have very low equilibrium abundances, so are not major players in the subsequent chemistry. Thermochemical equilibrium is therefore a reasonable assumption for the atmospheric composition of the hottest of the hot Jupiters, although horizontal quenching may still occur if longitudinal thermal gradients are expected to be large (i.e. the terminator abundances may not necessarily be in equilibrium). There is no specific critical temperature at which disequilibrium processes cease to be important, as the disequilibrium species gradually phase out with increasing temperature, and the results depend on transport processes as well, but both photochemistry and transport-induced quenching become less and less important with increasing effective temperature of the planet and can safely be ignored for photospheric temperatures \( \gtrsim 2000 \text{ K} \).

For the ‘warm’ generic exoplanet shown in figure 3, both photochemistry and transport-induced quenching are more important than for the hotter exoplanets. Although the relatively stable molecules like CO, H₂O and N₂ remain the dominant carriers of O, C and N, the quench points for CH₄–CO and N₂–NH₃ interconversions are deeper in the atmosphere (assuming ‘reasonable’ transport parameters) where the NH₃ and CH₄ mole fractions are relatively large. Once quenched, these species are mixed upwards into regions where they can be photochemically destroyed. Neither NH₃ nor CH₄ is stable in the large background bath of
H atoms diffusing down from higher altitudes. Moreover, NH₃ is photolysed at longer wavelengths than are the more abundant CO, H₂O and N₂ such that NH₃ is not shielded against photolysis, and the longer-wavelength UV photons penetrate to deeper atmospheric levels where ammonia photodissociation is important. Ammonia photolysis and subsequent catalytic destruction of H₂ [67] adds an additional source of H atoms down to approximately 10 mbar in the atmosphere of the warm exoplanet, which leads to the photosensitized destruction of CH₄, and the subsequent coupled photochemistry of NH₃ and CH₄. Some of the nitrogen from the photodestruction of NH₃ ends up in N₂ (with intermediates like N and even NO) through schemes such as the following:

\[
\begin{align*}
2(\text{NH}_3 + h\nu &\rightarrow \text{NH}_2 + H) \\
\text{H}_2\text{O} + h\nu &\rightarrow \text{OH} + H \\
2(\text{NH}_2 + H &\rightarrow \text{NH} + \text{H}_2) \\
2(\text{NH} + H &\rightarrow \text{N} + \text{H}_2) \\
\text{N} + \text{OH} &\rightarrow \text{NO} + H \\
\text{N} + \text{NO} &\rightarrow \text{N}_2 + \text{O} \\
\text{O} + \text{H}_2 &\rightarrow \text{OH} + H \\
\text{OH} + \text{H}_2 &\rightarrow \text{H}_2\text{O} + H \\
2\text{H} + \text{M} &\rightarrow \text{H}_2 + \text{M}
\end{align*}
\]

Net: \(2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2\)

Some of the nitrogen ends up in HCN through schemes such as this:

\[
\begin{align*}
\text{NH}_3 + h\nu &\rightarrow \text{NH}_2 + H \\
\text{NH}_2 + H &\rightarrow \text{NH} + \text{H}_2 \\
\text{NH} + H &\rightarrow \text{N} + \text{H}_2 \\
\text{H} + \text{CH}_4 &\rightarrow \text{CH}_3 + \text{H}_2 \\
\text{N} + \text{CH}_3 &\rightarrow \text{H}_2\text{CN} + H \\
\text{H}_2\text{CN} &\rightarrow \text{HCN} + H
\end{align*}
\]

Net: \(\text{NH}_3 + \text{CH}_4 \rightarrow \text{HCN} + 3\text{H}_2\)

In fact, HCN is the ultimate product of the coupled NH₃–CH₄ photochemistry, and it becomes an important atmospheric constituent in the IR photosphere for all but the hottest of the hot Jupiters. As discussed in the previous section, HCN is also an important thermochemical product that can form in ‘warm’ exoplanets from the kinetics of quenched CH₄ and NH₃ [67] via a pseudo-equilibrium that continues between these species despite the cessation of reactions involved with the N₂–NH₃ and CO–CH₄ quenching.

Hydrogen cyanide is therefore an important disequilibrium product that has been largely ignored to date by exoplanet spectral modellers (with the exception of [67–69,118,119]), despite the fact that HCN will be a major constituent whenever atmospheric temperatures are cool enough that CH₄ and NH₃ quench at significant abundances. For atmospheres with near-solar elemental compositions, HCN is likely to be even more abundant than molecules like CO₂ that are typically considered in spectral models (figure 3).

Acetylene (C₂H₂) is another potentially important disequilibrium product on extrasolar giant planets [60,65–71]. It is not formed efficiently in the ‘warm’ exoplanet model presented here, owing to the relatively high stratospheric temperatures adopted for this planet, but it can form in abundance on cooler planets both through CO photolysis at high altitudes, and through schemes
initiated by the reaction of photochemically produced H with CH$_4$ [67]. Acetylene tends to be more prevalent at high altitudes on these planets because, at higher pressures, it is converted efficiently back to methane (and/or to the more hydrogen-saturated ethane on cooler giant planets).

The photochemistry of oxygen compounds on the generic ‘warm’ exoplanet is comparatively less interesting than that of carbon and nitrogen. Photolysis of carbon monoxide occurs only at very high altitudes, and CO, with its strong carbon–oxygen bond, is kinetically stable at lower altitudes once the EUV photons responsible for photodissociation have all been absorbed higher up. Water photolysis continues to lower altitudes, but the photolysis products are efficiently converted back to H$_2$O as long as sufficient H$_2$ is present. Thus, both CO and H$_2$O follow their equilibrium profiles throughout the 0.0001–1 bar photospheric region. Carbon monoxide maintains a kinetic equilibrium with CO and H$_2$O via the reaction CO + H ⇌ CO + OH throughout most of the photosphere. Some minor excess CO$_2$ is produced photochemically at high altitudes as a result of CO and water photolysis, but the large background H abundance allows efficient recycling back to CO. At lower altitudes, CO$_2$ can be photolysed by longer-wavelength UV photons to form primarily CO + O(1D) or CO + O, but the O(1D) and O react with H$_2$ to form OH, and the OH reacts with the CO to re-form the CO$_2$, so CO$_2$ is photochemically stable, again as long as sufficient H$_2$ is present. Carbon dioxide therefore maintains its equilibrium abundance throughout the 0.0001–1 bar photospheric region in warm giant-planet atmospheres.

The photochemistry within the atmosphere of the ‘cool’ exoplanet shown in figure 3 is fundamentally different from that of warmer planets whose photospheres reside within the CO stability field (e.g. [66,69]). Methane is now the stable parent molecule for the subsequent carbon photochemistry, and the resulting net production rates for complex hydrocarbons are larger than those for the hotter planets. As discussed by Line et al. [66], C$_2$H$_x$ species become important photolysis products at high altitudes, although they tend to be converted back to methane at lower altitudes. Coupled NH$_3$−CH$_4$ photochemistry as described above and in Moses et al. [67] and Line et al. [66] is effective, and HCN becomes a major photochemical product both locally at various altitudes and from a column-integrated standpoint. Consistent with Line et al. [66], I expect the CH$_4$ to remain stable throughout the 0.0001–1 bar IR photosphere on cooler giant planets. Coupled H$_2$O−CH$_4$ photochemistry converts the methane to CO at higher altitudes, but these processes are less effective at lower altitudes owing to a lack of production of reactive radicals once H$_2$O (and CH$_4$) photolysis shuts down due to H$_2$O self-shielding at approximately 10$^{-4}$ bar and once H has been scavenged back into stable hydrogen-saturated molecules. There are numerous effective pathways for this coupled H$_2$O−CH$_4$ photochemistry: (i) atomic O produced from H$_2$O photolysis can react with CH$_3$, C$_2$H$_2$, C$_3$H$_2$ and C$_3$H$_3$ to form carbon–oxygen bonded species that eventually form CO; (ii) CH can react with water to form H$_2$CO and ultimately CO; and (iii) C reacts with NO produced from coupled N$_2$−H$_2$O photochemistry to form N + CO. The carbon-bearing radicals and molecules involved with the above schemes derive ultimately from the reaction of methane with H released from water photolysis. Some CO$_2$ is produced from this coupled CH$_4$−H$_2$O photochemistry, but CO$_2$ itself is photolysed to produce CO, and the reaction CO + OH → CO$_2$ + H cannot recycle CO$_2$ fast enough at these temperatures to maintain the CO−H$_2$O−CO$_2$ equilibrium. Carbon dioxide is therefore not a major photochemical product in this cool exoplanet model.

Transport-induced quenching does enhance the abundance of CO in the IR photosphere of the ‘cool’ exoplanet, and photochemical production of CO occurs at high altitudes, but the column abundance of CO never rivals that of methane in the IR photosphere. I therefore agree with the conclusions of Line et al. [66] that disequilibrium processes cannot remove methane in favour of CO and/or CO$_2$ on cooler, solar-composition, giant planets like GJ 436b.

Owing to the prevalence of both NH$_3$ and CH$_4$ in cooler giant exoplanets, photochemical production of complex hydrocarbons and nitriles is favoured in the atmospheres of these cool planets compared to hotter planets. Benzene (C$_6$H$_6$) and cyanoacetylene (HC$_3$N), for example (not shown in figure 3 for reasons of clarity), both achieve peak mole fractions of approximately 2 × 10$^{-7}$ in the generic cool exoplanet. While these species will not condense at the atmospheric
conditions relevant to this planet, continued production of refractory species not considered in this model is likely, and the formation of high-altitude photochemical hazes is therefore more probable on these cooler exoplanets (cf. [60,67,120]).

4. Sensitivity of disequilibrium chemistry to transport parameters and bulk elemental ratios

I discussed the sensitivity of disequilibrium chemistry and composition on hot Jupiters to atmospheric temperatures in the previous section; the sensitivity to vertical transport parameters like eddy diffusion coefficients \( K_{zz} \) is discussed in detail in earlier studies [67,69,120]. The composition is mainly sensitive to the \( K_{zz} \) profile through its influence on the quench pressure in transport-induced quenching, and hence through its effect on the abundance of quenched species. If the quenched species are photochemically active at higher altitudes, there can be important consequences with respect to the resulting abundance of photochemical products like HCN, \( \text{C}_3\text{H}_3 \) and complex hydrocarbons and nitriles. The greater the strength of atmospheric mixing at the quench pressures (i.e. the larger the \( K_{zz} \) values), the deeper the quench points will be, and the greater the resulting abundance of quenched disequilibrium species such as \( \text{CH}_4 \) and \( \text{NH}_3 \) on warm Jupiters. That also leads to greater lower-atmospheric abundances of kinetically dependent species like HCN and \( \text{C}_2\text{H}_2 \). Similarly, on cooler exoplanets where \( \text{CH}_4 \) is the dominant carbon species, a greater \( K_{zz} \) at the \( \text{CO} \rightarrow \text{CH}_4 \) quench point leads to a greater quenched abundance of \( \text{CO} \). Quenching of \( \text{NH}_3 \) and/or \( \text{N}_2 \) is also very sensitive to \( K_{zz} \) values on cooler exoplanets, where smaller \( K_{zz} \) values could push the quench point into the \( \text{N}_2 \)-dominated regime, allowing \( \text{N}_2 \) rather than \( \text{NH}_3 \) to be the dominant nitrogen component in the upper atmosphere, with a corresponding reduction in the column abundances of all disequilibrium nitrogen species.

The strength of vertical mixing in the upper atmosphere also affects the abundance of photochemically produced constituents. The greater the \( K_{zz} \) values in the upper atmosphere, the higher the altitude to which the parent molecules can be carried, with a corresponding increase in the column abundance of species that are produced photochemically at high altitudes. The gradient of the \( K_{zz} \) profile can affect how rapidly photochemically produced species are transported downwards to their thermochemical destruction regions, and thus the overall column abundance below the high-altitude production region [55,121].

Bulk elemental abundances within the exoplanet atmosphere also affect the predicted equilibrium and disequilibrium compositions. The metallicity of the atmosphere, for example, can strongly influence the expected chemical-equilibrium abundances of heavy molecules [47,65–67,69,120,122,123]. All molecules that contain heavy elements tend to exhibit an increase in abundance when the metallicity is increased. However, the increase in metallicity (all other parameters being equal) leads to a greater increase in \( \text{CO} \) in comparison with \( \text{CH}_4 \) and a greater increase in \( \text{N}_2 \) in comparison with \( \text{NH}_3 \), and molecules with three or more heavy nuclei, like \( \text{CO}_2 \), are even more sensitive to metallicity. The above references all emphasize the potential importance of \( \text{CO}_2 \) as a probe of the atmospheric metallicity on exoplanets, because an increase in metallicity by a factor of \( x \) tends to increase the abundance of \( \text{CO}_2 \) by a factor of \( x^2 \). Photochemical products such as NO, \( \text{C}_2\text{H}_x \) or HCN that depend on the abundance of the augmented heavy species tend also to become more abundant as the metallicity increases, although the response of disequilibrium species can sometimes be subtler. For example, Moses et al. [67] find that the quenched \( \text{CH}_4 \) mole fraction in the IR photosphere of their HD 189733b model actually decreases when the metallicity is increased by a factor of 10 because the \( \text{CH}_4 \rightarrow \text{CO} \) conversion schemes become more effective when the \( \text{H}_2\text{O} \) and \( \text{CO} \) abundances increase, such that \( \text{CH}_4 \) quenches at higher altitudes where the mole fraction is smaller.

The bulk atmospheric elemental ratios can also strongly affect the composition, from both equilibrium- and disequilibrium-chemistry standpoints. The effect of the C/O ratio on the equilibrium composition has been discussed in [68,70,117,119,124–126]; the disequilibrium chemistry consequences have been discussed in [68,70]. The C/O ratio strongly influences the
abundance of spectrally active molecules such as CO$_2$, H$_2$O, CH$_4$, HCN and C$_2$H$_2$, particularly on hot Jupiters that are warm enough that CO is expected to be the dominant form of carbon. For C/O ratios less than 1 in thermochemical equilibrium at photospheric pressures, methane rapidly decreases in importance with increasing temperature as more and more of the carbon is sequestered in CO, and species such as C$_2$H$_2$ and HCN are unimportant at all temperatures. At C/O ratios greater than 1, methane is less temperature-sensitive, and species like HCN and C$_2$H$_2$ rapidly gain in importance with increasing temperature such that they eventually become the dominant carriers of carbon behind CO. The resulting effects on the atmospheric spectrum can be major [68,117,119,124]. Other elemental ratios, such as N/O and C/N, will have similar interesting effects that have been less well studied.

5. Observational consequences of disequilibrium chemistry

Both transport-induced quenching and photochemistry will affect the spectral properties of exoplanet atmospheres through their influence on the composition. Some of these spectral consequences for extrasolar giant planets have been discussed [17,67–69,72,74,77,91,118,119,123, 127–129]. On the whole, the effects can be minor (figure 4) because the disequilibrium processes tend not to affect the dominant heavy constituents within the 0.0001–1 bar region (e.g. where CO and H$_2$O dominate on warmer hot Jupiters, and where H$_2$O and CH$_4$ dominate on cooler hot Jupiters), and these dominant species—water in particular—control the spectral properties throughout most of the IR. The disequilibrium effects are then expected to be mostly apparent within IR windows where water does not strongly absorb, such as the 1.4–1.8, 2.0–2.5, 3–5 and 8–16 $\mu$m regions.

One effect that can be less subtle is the consequence of CO−CH$_4$ quenching on hotter giant planets with strong longitudinal thermal gradients, such that CO is expected to be the dominant thermochemical-equilibrium carbon phase on the dayside, but CH$_4$ is expected to be the dominant carbon phase at the terminators and/or nightside. As was emphasized by Cooper & Showman [72], CO−CH$_4$ quenching (both vertical and horizontal) can prevent CH$_4$ from forming in significant quantities in the cooler regions, where equilibrium arguments would expect it to be significant, and the consequences for transit spectra and for predicted spectral variations as a function of orbital phase can be major [72,74,77,123,130]. If CO−CH$_4$ quenching in high-temperature regions prevents CH$_4$ from being present in significant quantities in cooler atmospheric regions, the resulting planetary spectrum can exhibit excess opacity in the 2.3–2.4 and 4.5–4.9 $\mu$m wavelength regions, where CO has strong vibrational bands, and reduced opacity in the 2.15–2.45, 3.15–3.45 and 7.2–8.2 $\mu$m wavelength regions, where CH$_4$ has strong vibrational bands. Transit and nightside spectra will be particularly sensitive to such CO quenching effects.

On the other hand, vertical quenching of CH$_4$ can potentially supply methane to both the dayside and terminator photospheres on ‘warm’ Jupiters in excess of what would be expected in equilibrium, particularly if the CO−CH$_4$ quench point is at or below the base of the ‘photosphere’. If horizontal thermal gradients still exist at the CO−CH$_4$ quench point, the final photospheric CH$_4$ abundance on planets such as HD 189733b and HD 209458b will be a complicated function of both vertical and horizontal quenching. However, in essence, vertical quenching will supply methane to the photosphere, and strong horizontal winds and horizontal quenching will help to homogenize that methane as a function of longitude. Starting from realistic thermal profiles from general circulation models [95], Moses et al. [67] find that, even in the absence of horizontal quenching, vertical transport-induced quenching supplies a quenched CH$_4$ mole fraction to the photosphere that differs by a factor of only a few between the terminator and dayside models, compared with the large difference of those disequilibrium predictions in comparison with equilibrium expectations (figure 1). Therefore, transport-induced quenching is expected to provide excess photospheric methane in comparison with equilibrium predictions for both HD 189733b and HD 209458b, with some notable spectral consequences, particularly for the cooler HD 189733b (see [67] and figure 4). The main consequence is an increase in
absorption at approximately 2.15–2.45, 3–4 and 7–9 µm from what would be expected based on equilibrium compositions.

Quenching of NH₃ on hot Jupiters over a wide range of temperatures can influence the spectrum by providing additional opacity in the 1.5, 2.0, 2.2–2.3, 3.0, 5.5–7.0 and 8–12 µm regions, where NH₃ has strong bands. Ammonia and methane quenching provide a thermochemical-kinetics source of HCN, which photochemistry can also enhance in the upper atmosphere. Disequilibrium HCN then provides excess absorption in the 1.53, 1.85, 2.8–3.1, 6.5–7.5 and 13–16 µm wavelength regions, with particularly strong contributions at approximately 3 and 14 µm. As can be seen from figure 4, these disequilibrium nitrogen species can have a notable influence on the exoplanetary spectra within the water absorption windows, and I encourage the inclusion of HCN and NH₃ in exoplanet spectral models—and encourage the acquisition of high-temperature line parameters for NH₃ and HCN so that spectral modellers can reliably include these species in their calculations.

Acetylene is another photochemical product that can have a potentially important influence on the spectra of cooler planets. Given its predicted abundance on HD 189733b [65,67,71], C₂H₂ will not have much of an influence on spectra from that planet (see [67] and figure 4), being overshadowed by the more abundant HCN and CH₄ in the approximately 3 and 7–8 µm regions where C₂H₂ has bands, but acetylene also has several distinct bands in the 1–3 µm and 12.5–15 µm regions (with a strong ν₅ Q branch at approximately 13.7 µm) that might provide a unique spectral signature for cooler planets where C₂H₂ is expected to be more abundant. Acetylene will also be a more important constituent for atmospheres with higher C/O ratios [68,70,119], and, if there are reasons to expect a high C/O ratio for any given planet (e.g. [68,117,119]), both HCN and C₂H₂ should be considered in spectral calculations.

6. Current evidence for disequilibrium chemistry on exoplanets

In §5, I discussed some of the expected observational consequences of disequilibrium chemistry on the spectral properties of exoplanets, but it remains to be demonstrated whether actual observations provide any evidence for these effects. Here, I look at some of the existing claims for disequilibrium compositions in the IR photospheres of extrasolar giant planets, and discuss whether photochemistry and transport-induced quenching can account for the observed behaviour or whether other processes or atmospheric characteristics must be responsible for that behaviour.

![Figure 4](http://rsta.royalsocietypublishing.org/)
Disequilibrium chemistry in the troposphere/stratosphere has been suggested to bring about the following observed hot Jupiter or hot Neptune characteristics:

— **Weak CH$_4$ absorption on young, directly imaged giant planets.** Near-IR spectra and narrow-band photometry suggest that CH$_4$–CO quenching occurs on several of the better studied directly imaged exoplanets, such as those in the HR 8799 system [13–15,17,20,21] and 2M1207b [18]. Quenching of CO at much greater than equilibrium abundances is expected to have important spectral consequences on such planets [131], and indeed is very likely from theoretical grounds, leading to greatly enhanced CO abundances and possible CO/CH$_4$ ratios greater than unity [17]. Although clouds and potential non-solar metallicities can complicate the interpretation [16,17,19,20], the lack of evidence for strong methane absorption does seem to indicate the occurrence of disequilibrium transport-induced quenching of CO and CH$_4$ on these planets. This conclusion is further reinforced by recent high-spectral-resolution observations of HR 8799c [21], which show features due to water and CO but not to methane.

— **Near-IR detections of CH$_4$ on HD 189733b and HD 209458b.** Swain et al. [31] report the detection of CH$_4$ on HD 189733b from transit spectroscopy obtained from the NICMOS instrument on the *Hubble Space Telescope* (HST). The relatively large amount of methane inferred from these observations [31,34] is in excellent agreement with predictions that include disequilibrium transport-induced quenching of CH$_4$ [65,67,76]. However, the lack of detection of methane (and the corresponding low upper limit) on the dayside of the planet with the same instrument [33] is in conflict with disequilibrium chemistry predictions that include vertical transport [65,67,71,76], making the case for methane via disequilibrium processes inconclusive on HD 189733b. Although photochemical and thermochemical kinetics processes are expected to remove CH$_4$ from the upper portions of the dayside atmosphere on HD 189733b, the overall column abundance should not be affected much, and transport-induced quenching (both vertical and horizontal) should ensure dayside and terminator methane abundances that differ by a factor of only a few. By the same token, the large dayside abundance of methane inferred from *HST/NICMOS* eclipse observations of HD 209458b [32] seems too large to be explained by transport-induced quenching [67]. If the spectral signatures are robust, I suggest that alternative (yet to be identified) molecules should be considered as possible candidates for the absorption, or that the atmosphere has a C/O ratio greater than solar. With regard to the latter point, I note that, although the *Spitzer* IR photometric data from eclipse cannot provide meaningful constraints on the CH$_4$ abundance of HD 209458b [34], the relatively low water abundance inferred from both the *HST/NICMOS* spectra and *Spitzer* photometric data [32,34] is also consistent with an inferred high C/O ratio on HD 209458b, but the relatively high derived CO$_2$ abundance from *HST/NICMOS* data [32] is not. I conclude that the methane detections on both HD 189733b and HD 209458b do not provide any unambiguous evidence for disequilibrium CH$_4$ quenching on these planets. Further near-IR observations, especially from space-based platforms, such as the *James Webb Space Telescope* (JWST) [132,133], *Finesse* [134] or *EChO* [135], could help to resolve this issue.

— **Orbital phase curves for HD 189733b at 3.6 and 4.5 µm.** Knutson et al. [129] report phase-variation observations for HD 189733b over a full orbit that may have implications with respect to CO–CH$_4$ transport-induced quenching. They find that three-dimensional circulation models that assume chemical equilibrium have spectral signatures that compare well with *Spitzer* photometric channel fluxes for conditions in the dayside atmosphere at or near the secondary eclipse, but that the models considerably overpredict the flux in the 4.5 µm channel on the nightside. Knutson et al. [129] suggest that this nightside behaviour at 4.5 µm, plus generally insufficient model absorption at 4.5 µm in transit simulations, could be a signature of CO quenching, such that more CO exists in the terminator and nightside atmosphere than is predicted from equilibrium models.
This trend is indeed the expected one for CO–CH$_4$ quenching, but it is not clear from the information provided in [129] how much of the carbon is tied up in CH$_4$ in their nightside equilibrium model atmosphere and/or whether the magnitude of the quenching effect would be sufficient to produce the observed behaviour. (Note that the disequilibrium models of Line et al. [65], Moses et al. [67,68] and Venot et al. [71] have a lower CH$_4$/CO ratio in general than that considered in the Knutson et al. [129] quench discussion.) Nor is it clear whether other bulk atmospheric model parameters, such as a non-solar metallicity or C/O ratio, could produce the described behaviour. Therefore, although the observations are certainly suggestive of disequilibrium quenching effects, additional models that explore a more complete range of parameter space, as well as higher-spectral-resolution observations in the 1–5 $\mu$m region that could help to separate contributions from CO and CH$_4$, would help to place the claim of disequilibrium effects on a firmer foundation. The observed phase-curve behaviour for HD 189733b at 3.6 $\mu$m is also interesting in that the minimum-to-maximum brightness temperature range over the orbit is greater at 3.6 $\mu$m than at 4.5 $\mu$m [129], despite equilibrium expectations that the 3.6 $\mu$m band should have weaker average opacity than the 4.5 $\mu$m band and thus probe deeper atmospheric levels where the thermal structure is not as variable. Additional disequilibrium opacity sources, such as HCN or quenched methane, could be causing the 3.6 $\mu$m channel to probe higher altitudes. However, the fact that the eclipse depth at 3.6 $\mu$m corresponds to a larger brightness temperature than at 4.5 $\mu$m [129] suggests that the 3.6 $\mu$m channel does indeed probe deeper levels on the dayside, as expected, and the larger phase variations at 3.6 $\mu$m then might involve opacity changes at deep levels, which are not predicted from disequilibrium models. Again, further explorations of parameter space are required before the interesting observed behaviour can be better understood.

Large inferred CO$_2$ abundance on HD 189733b. The HST/NICMOS secondary-eclipse observations of Swain et al. [33] seem to require an unexpectedly large abundance of CO$_2$ in the dayside atmosphere of HD 189733b [34,136,137], leading to the suggestion that CO$_2$ is supplied by photochemical processes [34]. However, thermo/photochemical kinetics and transport models [65,67,71] predict only small high-altitude increases due to photochemistry in the otherwise low expected CO$_2$ equilibrium abundance. In fact, retrievals that are based on the Swain et al. [33] data [34,136,137] suggest that the inferred CO$_2$ abundance is greater than that of water on HD 189733b—a situation that is very unlikely in a hydrogen-dominated atmosphere even under disequilibrium conditions. Therefore, as is emphasized by Moses et al. [68], the HST/NICMOS secondary-eclipse data, if robust, suggest that either (i) some other molecule is responsible for the absorption attributed to CO$_2$, (ii) the atmospheric metallicity of HD 189733b is extremely high (e.g. several thousand times solar to allow CO$_2$/H$_2$O ratios greater than 1, which seems inconsistent with the high H and He content indicated by the planet’s mass–radius relationship [42]) or (iii) all the current photochemical models are missing a major mechanism that irreversibly converts H$_2$O and CO into CO$_2$ (which seems unlikely in a hydrogen-dominated atmosphere). The Swain et al. [33] HST/NICMOS data therefore do not provide convincing evidence for disequilibrium processes on HD 189733b, and some other factor must be at play here.

Spitzer/IRS absorption at approximately 14 $\mu$m on HD 189733b. Spitzer/IRS secondary-eclipse spectra of HD 189733b [29] exhibit broad features consistent with water absorption in the 5–10 $\mu$m region on HD 189733b. Although not discussed by Grillmair et al. [29], the IRS spectra also exhibit a notable downturn at longer wavelengths that is suggestive of a 13.5–14.5 $\mu$m absorption band, whereas Spitzer/IRS and MIPS broadband photometric observations at 16 and 24 $\mu$m [138] jump back to higher brightness-temperature values. If the downturn in the flux at the longer wavelengths in the IRS spectrum is a real property of the atmosphere and not an observational artefact, it can be seen from figure 5 that this behaviour is reminiscent of a strong predicted absorption feature at 14 $\mu$m due to HCN
produced from thermochemical and photochemical kinetics in the disequilibrium models of Moses et al. [68] (see also [119]). This identification is certainly not definitive, and a more thorough investigation of model parameter space may suggest other alternatives, but I note that the HCN produced from disequilibrium processes on HD 189733b is expected to survive throughout the atmosphere on both the dayside and nightside. Searches for additional evidence for HCN on HD 189733b at other relevant wavelengths in transit and eclipse data might be worthwhile.

—— Relative 3.6–4.5 \( \mu \text{m} \) flux ratio on GJ 436b. Broadband Spitzer secondary-eclipse observations of the hot Neptune GJ 436b [127], and in particular the high observed flux at 3.6 \( \mu \text{m} \) in combination with the low flux (i.e. non-detection) at 4.5 \( \mu \text{m} \), suggest that CO and not CH\(_4\) is the dominant carbon constituent on the dayside of this cooler exoplanet, in serious conflict with chemical-equilibrium predictions [91,127]. Stevenson et al. [127] and Madhusudhan & Seager [91] suggest that disequilibrium processes are responsible for this observed behaviour, with transport-induced quenching in combination with a high metallicity (10\( \times \) solar) producing the large required atmospheric CO and CO\(_2\) abundances in the photosphere, and photochemistry removing the large expected CH\(_4\) abundance [91]. However, Line et al. [66] convincingly demonstrate that photochemistry cannot remove CH\(_4\) from the bulk of the photosphere, and the thermal profiles derived from the general circulation models of Lewis et al. [116] for metallicities up to 50\( \times \) solar do not predict a high enough CO abundance at depth or anywhere else in the atmosphere for transport-induced quenching to supply the necessary CO mole fraction to the IR photosphere [140]. Therefore, if the observations are robust, some process or atmospheric property other than transport-induced quenching and photochemistry must

Figure 5. Synthetic eclipse spectra for HD 189733b from a Moses et al. [68] disequilibrium chemistry model that assumes a C/O ratio of 0.7 and a metallicity of 4\( \times \) solar (solid black line), compared with Spitzer broadband photometric points at 3.6 and 4.5 \( \mu \text{m} \) [129] and 5.6, 8, 16 and 24 \( \mu \text{m} \) [130,138,139] (large circles with error bars; red online), with Spitzer/IRS spectra [29] (medium circles with error bars; green online), and with HST/NICMOS spectra [33] (small circles with error bars; blue online). The light grey circles without error bars represent the model results convolved over the Spitzer broadband channels. The insert in the upper left shows the thermal profile adopted in the modelling (figure is adapted from [68], with spectral calculations from N. Madhusudhan). (Online version in colour.)
be responsible for the behaviour, such as an extremely high metallicity [140] and/or high-altitude clouds, unless existing photochemical models are missing key mechanisms that efficiently convert water and methane to CO at relevant GJ 436b conditions.

The above discussions emphasize that many of the observational oddities that appear inconsistent with equilibrium chemistry in a near-solar-composition atmosphere also remain inconsistent with disequilibrium chemistry in such atmospheres. Photochemistry and transport-induced quenching are undoubtedly occurring on extrasolar giant planets, but the observational evidence gathered to date is not yet compelling, with the exception of CO quenching on young, directly imaged exoplanets. Certain atmospheric characteristics of hot Jupiters as described above, however, suggest that kinetic effects matter. Future observations are needed to help to firm up these tantalizing hints of disequilibrium behaviour; in the process, we will gain a better understanding of the underlying processes that control the planet’s current atmospheric composition and its possible past and future evolution.

7. Conclusion

The ability to detect and characterize the atmospheres of extrasolar planets represents a phenomenal success story in modern astronomy. We are, however, still in a learning phase, both in terms of the cutting-edge observational and analysis techniques needed to retrieve molecular abundances on hot Jupiters and in terms of the theoretical models needed to interpret the observations. Disequilibrium chemistry models play an important role in the process. Photochemistry and transport-induced quenching will drive the exoplanet atmospheric compositions away from chemical equilibrium, and these effects will have observational consequences.

The main lessons learned to date from disequilibrium chemistry models are that transport-induced quenching is expected to affect the relative abundances of the carbon-bearing molecules CO and CH4 and the nitrogen-bearing molecules N2 and NH3, which can have a notable impact on the transit, eclipse and orbital-phase-variation observations in the spectral regions where these molecules have absorption bands. If the atmospheric thermal profile crosses the stability regimes where CO−CH4 or N2−NH3 are stable in chemical equilibrium, the effects can be relatively major. If the thermal profile resides solidly within one regime or another, the effects can be subtle. Very hot planets will tend to kinetically maintain equilibrium, and disequilibrium effects will be confined to very high altitudes, except perhaps where the hotter parcels of gas are rapidly transported to cooler terminator or nightside regions. On warm to moderately hot Jupiters, H2O and CO will remain at near-equilibrium abundances throughout the IR photosphere, but transport-induced quenching will increase the abundance of CH4 and NH3 above equilibrium expectations. Further thermochemical and photochemical processing of the quenched CH4 and NH3 can lead to significant production of HCN (and in some cases C2H2), which can add opacity sources that fill in windows between water absorption bands. Carbon dioxide is relatively unaffected by disequilibrium chemistry but remains a very minor atmospheric constituent on hot Jupiters unless the atmospheric metallicity is significantly higher than solar. On cool exoplanets, where methane is expected to be stable, transport-induced quenching can increase the expected abundance of CO, but photochemistry is not expected to remove methane from the troposphere and stratosphere. Methane and ammonia photochemistry on such planets will result in the production of complex hydrocarbons and nitriles that might produce high-altitude photochemical hazes. On exoplanets of a wide variety of temperatures, HCN and NH3 will be important disequilibrium constituents that should not be ignored in observational analyses.

Higher-resolution IR spectra from existing and future ground-based and space-based telescopes promise to provide the ‘smoking guns’ needed to identify disequilibrium chemical constituents and their underlying kinetic controlling mechanisms.

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References


