Probing the Extent of Vertical Mixing in Brown Dwarf Atmospheres with Disequilibrium Chemistry

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Abstract

Evidence of disequilibrium chemistry due to vertical mixing in the atmospheres of many T- and Y-dwarfs has been inferred due to enhanced mixing ratios of CO and reduced NH3. Atmospheric models of planets and brown dwarfs typically parameterize this vertical mixing phenomenon with the vertical eddy diffusion coefficient, Kzz. While Kzz can perhaps be approximated in the convective regions in the atmosphere with mixing length theory, in radiative regions, the strength of vertical mixing is uncertain by many orders of magnitude. With a new grid of self-consistent 1D model atmospheres from Teff of 400–1000 K, we assess how molecular abundances of CO and NH3, as well as other gases, change with gravity. We compare our models with available near-infrared and spectroscopic data of several T- and Y-dwarfs and assess their atmospheric vertical mixing profiles. These models provide a new constraint on the vertical mixing in substellar atmospheres, with significant implications for chemistry and climate modeling.

Unified Astronomy Thesaurus concepts: Brown dwarfs (185); T dwarfs (1679); Y dwarfs (1827); Atmospheric composition (2120)

1. Introduction

1.1. Molecular Abundances and Nonequilibrium Chemistry

The astronomical community is now ready to observe the atmospheres of a diverse range of exoplanets and brown dwarfs in unprecedented detail with the James Webb Space Telescope (JWST; Gardner et al. 2006; Pontoppidan et al. 2022). These atmospheres are complex systems with a range of physical processes like radiative/convective energy transport, chemical reaction networks, clouds/haze formation, and dynamical processes like vertical mixing. With high signal-to-noise ratio (S/N) spectra from JWST for these substellar atmospheres, we can probe the unique opportunity to observe these physical and chemical processes and compare to state-of-the-art theoretical models. Therefore, it is crucial to develop and update these models by including necessary complex processes and assessing how uncertainties in physical and chemical parameters affect the structure, abundances, and spectra of these atmospheres.

One such complex process in substellar atmospheres is atmospheric dynamics. Dynamics is a 3D process. In the case of solar system planets, atmospheric dynamics can be directly studied with spatially and time-resolved imaging or spectroscopy. Although we cannot spatially resolve brown dwarfs and exoplanets, dynamical processes can still be studied by their impact on molecular abundances and condensate clouds, which affect their spectra and lightcurves. Surface inhomogeneities can be probed via rotationally modulated lightcurves (Karalidi et al. 2015; Metchev et al. 2015; Cushing et al. 2016; Vos et al. 2022), often in two dimensions when observed at a single wavelength. Spectra, which probe a range of atmospheric pressures, provide a potential view of dynamics in the additional dimension of atmospheric depth. Processes like convection, the breaking of gravitational waves, and convective overshoots can impact both the chemical and cloud structure of these atmospheres by causing non-vertical transport of atmospheric gases and particles across many atmospheric scale heights (Freytag et al. 2010; Parmentier et al. 2013; Bordwell et al. 2018; Tan 2022).

Dynamical processes can also alter the abundances of atmospheric gases in the visible atmosphere by transporting gas molecules through several scale heights, on a timescale faster than chemical reactions are able to locally equilibrate to their new surroundings. This leads to departures from the chemical equilibrium, often assumed as a starting point in exoplanet and brown dwarf atmospheric models (e.g., Marley et al. 2021). The dynamics-induced transport of gases and particles along the radial dimension of these atmospheres is called “vertical mixing.” Vertical mixing can lead to disequilibrium chemical abundances in substellar atmospheres for gases like CO, CH4, H2O, NH3, CO2, PH3, and HCN (Moses et al. 2011; Tsai et al. 2017; Fortney et al. 2020; Tsai et al. 2021).
Because most of these gases are major sources of opacities in substellar atmospheres (H₂O, CH₄, CO, etc.), their spectra can be altered significantly.

Vertical mixing also directly affects cloud formation through its effect on molecules like H₂O in Y-dwarfs and colder exoplanets (Ackerman & Marley 2001; Morley et al. 2014; Gao et al. 2020). Vertical mixing transports condensable vapor from the deeper atmosphere to lower pressures and temperatures, where they condense. Moreover, mixing counteracts gravitational settling, and therefore helps to dictate the size of cloud particles that can remain aloft. As a result, the atmospheric vertical mixing significantly impacts the cloud opacity by controlling the cloud vertical extent and particle size distribution. As both the chemical and cloud structure of these atmospheres impact radiative and convective energy transport, vertical mixing also affects the temperature structure of substellar atmospheres.

There is already decades-deep literature on observations and modeling of disequilibrium chemistry in Jupiter and Saturn (Beer 1975; Larson et al. 1977; Prinn & Barshay 1977; Larson et al. 1978; Fogley & Prinn 1985; Visscher et al. 2010b), and in T-dwarfs and early Y-dwarfs (Fogley & Lodders 1996; Noll et al. 1997; Oppenheimer et al. 1998; Saumon et al. 2003; Golimowski et al. 2004; Hubeny & Burrows 2007; Geballe et al. 2009; Visscher et al. 2010a; Visscher & Moses 2011; Leggett et al. 2012; Sorahana & Yamamura 2012; Zahnle & Marley 2014; Miles et al. 2020). We briefly summarize the key developments in the field in Section 1.2. But, more recently, Miles et al. (2020) obtained M-band spectra of four late T- and early Y-dwarfs and used archival M-band spectra of two T-dwarfs and a Y-dwarf to infer the strength of vertical mixing in their atmospheres as a function of

\[ \text{function of } T_{\text{eff}}. \]

They determined the CO abundance in each of these objects by fitting models to spectra. One-dimensional brown dwarf atmospheric models with equilibrium chemistry were post-processed to include the effect of disequilibrium chemistry due to vertical mixing to interpret the observed CO abundances and infer the vigor of vertical mixing in these atmospheres. This demonstrated that measurements of chemical abundances of various gases along with 1D forward models can be used to constrain vertical mixing in substellar atmospheres. However, disequilibrium chemistry can lead to significant changes in the atmospheric state of these objects compared to equilibrium chemistry calculations due to the feedback of the modified chemical abundances of gases on the atmospheric temperature structure (Hubeny & Burrows 2007; Phillips et al. 2020; Karalidi et al. 2021).

The Miles et al. (2020) paper and new modeling work points to the possibility of using upcoming high-S/N JWST spectra of brown dwarfs to probe their atmospheric structure and atmospheric chemistry in a much more detailed way. The rationale of our study here is to specifically examine how differences in the strength of vertical mixing, and how it is typically parameterized in convective and radiative atmospheric regions, give rise to distinct differences in model spectra. Comparison with measured spectra now and in the future can then be used to assess the mixing speed in convective and radiative regions, yielding novel constraints on atmospheric physics.

1.2. Modeling Approaches

Mixing in substellar atmospheres is a 3D process. Both 2D and 3D models have been used to study vertical mixing in hotter brown dwarfs and hot Jupiters (Freytag et al. 2010; Parmentier et al. 2013; Bordwell et al. 2018; Tan & Showman 2021; Tan 2022). However, a full exploration of the relevant parameter space of brown dwarf mixing properties is currently not feasible with 3D models. Moreover, these 3D models often include simplified or gray radiative transfer, so in detail, the calculated temperature structures yield model spectra that are not yet an adequate match to measured spectra (Mukherjee et al. 2021; Tan & Showman 2021). Chemical equilibrium is also often assumed in General Circulation Models (GCMs; e.g., Showman et al. 2009; Lee et al. 2021), but some models also treat chemical species within a passive transport framework (e.g., Parmentier et al. 2013; Komacek et al. 2019; Tan 2022) to explore the effects of atmospheric mixing on chemical structure of substellar atmospheres.

One-dimensional self-consistent models, which iterate to a radiative-convective equilibrium (RCE) solution, given specified atmospheric physics and chemistry, include many of the complex physical processes of real atmospheres and can be used to produce high-S/N model observables. Given the relatively fast computational times, they are important in exploring wide ranges of parameter space (e.g., Marley et al. 1996; Burrows et al. 1997; Marley & McKay 1999; Burrows et al. 2003; Fortney et al. 2008; Morley et al. 2014; Gandhi & Madhusudhan 2017; Malik et al. 2017; Marley et al. 2021). Although such models only include one dimension, the effects of dynamics can still be included. This is typically done by approximating vertical mixing as a diffusive process, and parameterizing this diffusive “speed” with a single vertical eddy diffusion coefficient, \( K_{zz} \) (Allen et al. 1981), which has dimensions of [L^2/T], where [L] and [T] represent length and time, respectively. However, theoretical and observational constraints of \( K_{zz} \), and its dependence on temperature and pressure, are uncertain by several orders of magnitude today (Fortney et al. 2020; Miles et al. 2020; Phillips et al. 2020).

The vigor of vertical mixing could very well have a complex behavior, even within the atmosphere of a single object. Brown dwarf atmospheres have convective and radiative zones. In the convective zones, mixing is expected to be comparatively efficient with higher values of \( K_{zz} \), compared to the radiative zones, which are stable to convection. Theoretically, \( K_{zz} \) has been approximated with mixing length theory in the convective zones of these atmospheres (e.g., Gierasch & Conrath 1985; Smith 1998; Ackerman & Marley 2001). However, this approximation is still uncertain due to uncertainties in key parameters in the mixing length theory like the mixing length itself. Theoretical understanding of \( K_{zz} \) is even more primitive in the case of radiative zones. Typically, \( K_{zz} \) is varied by a factor of a million or more, with its effects on the temperature structure and atmospheric abundances inadequately explored. This poor knowledge of \( K_{zz} \) leaves large gaps in our understanding of vertical mixing on chemistry, clouds, and temperature structure.

Previously, several authors computed RCE models that treated nonequilibrium chemical abundances self-consistently with the atmospheric temperature structure (e.g., Hubeny & Burrows 2007; Phillips et al. 2020; Karalidi et al. 2021). However, these models were all computed either within the framework of a constant \( K_{zz} \) value in the atmosphere, with an exploration of \( K_{zz} \) varied across many orders of magnitude (e.g., Phillips et al. 2020; Karalidi et al. 2021), or with \( K_{zz} \) computed using mixing length theory in the convective zones...
and constant $K_{zz}$ in the radiative zones (e.g., Hubeny & Burrows 2007). We build on these works, but aim for a more precise assessment of how a changing $K_{zz}$ within a given atmosphere, due to convective- and radiative zone mixing, alters atmospheric abundances and spectra. The output from 3D GCMs shows that $K_{zz}$ can vary by several orders of magnitude with pressure in a substellar atmosphere (Freytag et al. 2010; Parmentier et al. 2013; Tan 2022), but this has not yet been implemented within a self-consistent RCE model.

Observations from Miles et al. (2020) showed that T-dwarfs with $T_{eff}$ between 400 and 800 K have much smaller $K_{zz}$ than expected from convective mixing. They also found a factor of 100 increase in the inferred $K_{zz}$ in these brown dwarfs when $T_{eff}$ decreased below $\sim$400 K. Miles et al. (2020) suggested an explanation for this behavior if, in the warm objects with $K_{zz}$ between $\sim$400 K, gases are “quenched” within a radiative part of the atmosphere (lower $K_{zz}$), but in a convective part of the atmosphere in objects with $T_{eff} < 400$ K. Therefore, already available observations demand models with higher complexity than a constant $K_{zz}$ approach. This is especially needed to prepare these models adequately to interpret the much higher-quality data expected from JWST.

In this work, we enhance the models presented in Karalidi et al. (2021) by inclusion of temperature- and pressure-dependent $K_{zz}$ profiles within the 1D RCE framework. We use this model to explore the complex interconnections between $K_{zz}$, the temperature structure, molecular abundances, and spectra in late T- and early Y-dwarfs. We use this model and already available ground-based spectroscopic data of six brown dwarfs to address the following questions:

1. How does a self-consistent treatment of vertical mixing affect the $T(P)$ profile?
2. Does a self-consistent treatment of $K_{zz}$ cause changes in the radiative and convective zone locations and depths in brown dwarfs compared to equilibrium chemistry models?
3. In what objects can we expect quenching of gases like CO, CH$_4$, and NH$_3$ to occur in radiative zones instead of convective zones?
4. Are photometry and spectroscopy of brown dwarfs between 1 and 14 $\mu$m sensitive to the $K_{zz}$ in the radiative and convective zones?
5. How much can we learn about the atmospheric properties of late T-dwarfs by applying self-consistent disequilibrium chemistry models on already available infrared spectral data?
6. Can JWST be used to accurately infer the vertical mixing strength in radiative zones and convective zones of brown dwarfs?

We briefly discuss our new Python-based atmospheric model in Section 2. We present our results in Section 3 followed by discussion of our results in Section 4, and conclude in Section 5.

2. Modeling Substellar Atmospheres

We have adapted the Fortran-based EGP substellar atmospheric model to Python. This new Python version of the EGP code is open-source and available as a part of the widely used Python exoplanet atmospheric modeling tool PICASO (Batalha et al. 2019), as a part of the PICA3.0 (Mukherjee et al. 2022) release. The numerical and functional details of the code along with a series of benchmarks with previously available models are presented in Mukherjee et al. (2022). The EGP model has been used by our group for substellar atmospheres for over two decades (Marley et al. 1996; Fortney et al. 2005, 2007, 2008; Marley et al. 2012; Morley et al. 2014; Karalidi et al. 2021; Marley et al. 2021). Recently, Karalidi et al. (2021) updated the Fortran-based EGP code with the capability to include constant $K_{zz}$ and its impact on chemistry self-consistently. We have converted this version of the code in Python and have modified it by including the capability to treat the pressure-dependent variable $K_{zz}$ in substellar atmospheres. Here we briefly describe the model methodology used in this work, and we refer the reader to Mukherjee et al. (2022) for a more detailed discussion of the numerical methodology of our models.

2.1. Python-based Implementation of EGP with Disequilibrium Chemistry

We divide the 1D model atmosphere into 90 pressure layers (91 layer boundaries or levels) with logarithmically spaced pressure values. From an initial guess temperature–pressure ($T(P)$) profile, the model iterates on the $T(P)$ profile, atmospheric chemistry, and radiative/convective energy transport using a Newton-Rhapson method, yielding temperature corrections at each pressure level. These iterations continue until it finds the converged atmospheric state in which RCE is satisfied throughout the atmosphere. Self-consistent modeling of effects like disequilibrium chemistry due to vertical mixing requires simultaneous calculation of gas abundances and opacities with the iteration on the $T(P)$ profile instead of interpolation on a precomputed grid.

Each chemical reaction in the atmosphere proceeds with a characteristic timescale $t_{\text{chem}}$, which is a strong function of temperature, pressure, and the chemical composition of the atmosphere. Zahle & Marley (2014) used 1D chemical kinetics models to parameterize the $t_{\text{chem}}$ expression for the major O-, C-, H-, and N-bearing reactions in substellar atmospheres. These reactions often are a part of a large network of chemical reactions with many chemical species but still can be represented by simpler net reactions between a few species of interest. The net chemical reactions between O-, C-, H- and N-bearing gases we consider here are

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &\rightleftharpoons \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} &\rightleftharpoons \text{CO}_2 + \text{H}_2 \\
2\text{NH}_3 &\rightleftharpoons \text{N}_2 + 3\text{H}_2 \\
\text{CH}_4 + \text{NH}_3 &\rightleftharpoons \text{HCN} + 3\text{H}_2 \\
2\text{CO} + \text{N}_2 + 3\text{H}_2 &\rightleftharpoons 2\text{HCN} + 2\text{H}_2\text{O} \\
\text{CO} + \text{NH}_3 &\rightleftharpoons \text{HCN} + \text{H}_2\text{O}
\end{align*}
\]

Vertical mixing in the atmosphere also proceeds on a typical timescale, which is associated with the eddy diffusion coefficient $K_{zz}$,

\[
t_{\text{mix}} = \frac{H^2}{K_{zz}}
\]

where $H$ is the local scale height of that atmospheric layer. $t_{\text{chem}}$ is generally much shorter than $t_{\text{mix}}$ in high-pressure, high-temperature regions of the atmosphere where gas abundances are expected to follow chemical equilibrium. But as the atmosphere gets colder at lower pressures, $t_{\text{chem}}$ rises exponentially and becomes much longer than $t_{\text{mix}}$. The pressure at which the
intersection between the two timescales occurs is called the “quench pressure” or “quench level.” At all pressure levels lower than the quench pressure (higher up in the atmosphere), atmospheric abundances for the relevant chemical compounds take on the abundances at the relevant quench pressure, rather than those of equilibrium chemistry at the local $P$ and $T$. In the brown dwarf context, this behavior was first predicted by Fedgy & Lodders (1996) and observed by Noll et al. (1997).

Within our model, the $T(P)$ profile is used to calculate $K_{zz}$ as a function of each model layer’s pressure. $K_{zz}$ in the convective zone is calculated with mixing length theory (Gierasch & Conrath 1985),

$$K_{zz} = \frac{H}{3} \left( \frac{L}{H} \right)^{1/3} \left( \frac{RF}{\mu \rho_a c_p} \right)^{1/3}$$

where $H$ is the local scale height of the atmosphere, $L$ is the turbulent mixing length, $R$ is the universal gas constant, $\mu$ is the mean molecular weight of the atmosphere, $\rho_a$ is the atmospheric density, $c_p$ is the atmospheric specific heat at constant pressure, and $F$ is the convective heat flux. The convective heat flux is given by the difference between $\sigma T_\text{eff}^4$ and the radiative flux at each layer within the convective zones of the atmosphere. The maximum convective heat flux would then be $\sigma T_\text{eff}^4$. Here the convective heat flux is calculated self-consistently in each layer. The turbulent mixing length $L$ is set to be equal to the scale height ($H$) in our models. But in order to explore scenarios where convective mixing is less effective, we also simulate cases where the mixing length is smaller than the atmospheric scale height $H$ by a factor of 10. Note that this turbulent mixing length ($L$) was only changed in Equation (2) and not in Equation (1). The mixing length in Equation (1) remained the same as the local atmospheric scale height throughout this study. For further background, we refer the reader to previous works (e.g., Smith 1998; Bézard et al. 2002; Visscher et al. 2010b; Visscher & Moses 2011; Bordwell et al. 2018) exploring the relationship between mixing length and the scale height in Equation (1).

Over the past several years, various parameterizations of $K_{zz}$ in the radiative zones of substellar atmospheres have been discussed in the literature (e.g., Parmentier et al. 2013; Wang et al. 2015; Zhang & Showman 2018). As a starting point, we use the parameterization from Moses et al. (2022),

$$K_{zz} = \frac{5 \times 10^8}{\sqrt{P_{\text{bar}}}} \left( \frac{H_{1\text{bar}}}{620 \text{ km}} \right) \left( \frac{T_{\text{eff}}}{1450 \text{ K}} \right)^4$$

where $P_{\text{bar}}$ is the pressure in bars and $H_{1\text{bar}}$ is the atmospheric scale height at $10^{-3}$ bars. The $5 \times 10^8/\sqrt{P_{\text{bar}}}$ dependence was estimated by Parmentier et al. (2013) using tracer transport in 3D GCM for hot Jupiter HD209458b. This dependence was found to be valid for this object between $10^{-6}$—1 bars. The $P^{-0.5}$ dependence captures the increase of $K_{zz}$ with lowering pressure in the radiative zone, as mixing can be efficient in low-pressure ($P \sim 10^{-4}$ bars) parts of the radiative atmosphere due to mechanisms like gravitational wave breaking (Freytag et al. 2010). The factor $H_{1\text{bar}}T_{\text{eff}}^4$ was also included in the parameterization, as this factor shows good correlation with the measured $K_{zz}$ (via photochemical models) of solar system planets (including Jupiter, Saturn, Uranus, Neptune, Earth, and Venus) and exoplanets (Moses et al. 2005; Zhang & Showman 2018; Moses et al. 2022). But, as the $T(P)$ structure of brown dwarfs can be quite different from that of irradiated planets, we also explore deviations from this parameterization where this relation is increased or decreased by factors of 100 to explore the relevant parameter space. As the $T(P)$ profile iterates toward the converged solution, the $K_{zz}$ in convective zones, given by Equation (2) and the $K_{zz}$ in radiative zones, given by Equation (3), evolve as well. The mixing timescale in each atmospheric layer is then calculated in every iteration from this $K_{zz}$ using Equation (1). The quench pressures of each of these chemical species are found by comparing $I_{\text{max}}$ with $t_{\text{chem}}$ expressions from Zahnle & Marley (2014). The abundances of CO, CH₄, NH₃, CO₂, H₂O, and HCN are allowed to follow equilibrium chemistry at pressures higher than their relevant “quench pressure,” and their abundances are quenched above the quench pressure level. But as the $T(P)$ profile iterates to the converged solution, the quench pressure of various gases also changes at each step as both the $t_{\text{chem}}$ and $I_{\text{max}}$ are dependent on the $T(P)$ profile of the atmosphere. This requires the RCE model to include “on-the-fly” calculations of both chemistry and opacities in order to include disequilibrium chemistry self-consistently in the calculations.

As in Karalidi et al. (2021), we use the “on-the-fly mixing” method of opacities following the methodology of Amundsen et al. (2017). In this work we focus on the quenching of CO, CH₄, H₂O, NH₃, N₂, HCN, and PH₃. Of these, only CO, CH₄, H₂O, and NH₃ are major opacity sources. Therefore, we mix the correlated-k opacities of all of the other sets of gases that follow equilibrium chemistry as the volume mixing ratio of these gases evolves due to quenching with the $T(P)$ profile of the atmosphere. As in Karalidi et al. (2021), given inaccuracies inherent in the flexible Amundsen et al. (2017) resort-rebin approach necessitate the use of a denser grid of 661 wavelength bins, compared to the 196 used for our equilibrium chemistry models (Marley et al. 2021).

We benchmark the code in two ways: (1) by setting $K_{zz} = 0$ and finding that the on-the-fly mixing method still converges to the equilibrium chemistry solutions from Marley et al. (2021), and (2) by testing the resulting models against results obtained by Phillips et al. (2020) with nonzero but constant $K_{zz}$ values. The benchmarking results are presented in Mukherjee et al. (2022). The code results match well with both models. In future work, the code will be further enhanced via coupling with a 1D chemical kinetics model VULCAN (Tsai et al. 2017, 2021) so that it can self-consistently treat both vertical mixing and photochemistry. This Python-based code will be open-sourced as a part of the PICASO 3.0 package. Next, we discuss results obtained by applying this code to model disequilibrium chemistry and characterize mixing strengths in late T- and early Y-dwarf atmospheres.

3. Results

We performed a detailed 4D parameter space exploration of how varied vigor of vertical mixing in brown dwarf atmospheres affects the atmospheric state and spectra. We produced a grid of models by varying four physical parameters: $T_{\text{eff}}$, gravity, radiative zone $K_{zz}$, and convective zone mixing length $L$. The gravity has been varied across five values 316, 562,
Disequilibrium chemistry leads to enhanced CO and depleted CH₄, NH₃, and H₂O abundances in T- and Y-dwarfs. This leads to major changes in the wavelength-dependent optical depths in the atmosphere. The top four panels of Figure 1 show the $\tau = 1$ pressure levels, for specific gases, for a T-dwarf with $T_{\text{eff}} = 700$ K and log($g$) = 5.0 in the presence and absence of quenching due to vertical mixing. These $\tau = 1$ pressure levels are strongly wavelength dependent. Here $K_z$ has been assumed to follow Equation (2) in the convective zones and Equation (3) in radiative zones. The disequilibrium chemistry pressure levels are shown as the solid lines, and the corresponding equilibrium chemistry levels are shown as the dotted lines. The pressure-dependent volume mixing ratios of these gases under chemical equilibrium and disequilibrium are also shown in the top $x$-axis in each of the top four panels by the dashed and solid black lines, respectively.

The bottom panels in Figure 1 depicts the log of the ratio in the $\tau = 1$ pressure level between these two models. Values greater than zero represent shallower depth probed, due to an increase in an absorber of interest, for instance CO in yellow. Overall, since major opacity sources of H₂O, NH₃, and CH₄ are depleted, and they absorb across a broad wavelength range, one sees deeper, to a higher pressure, in a disequilibrium chemistry model.

A manifestation of these effects is shown in Figure 2, which shows the temperature structure (top left), CO mixing ratios (top right), and spectra (bottom) three models at $T_{\text{eff}} = 500$, 700, and 1000 K and log($g$) = 5. The solid lines include induced quenching, and the dashed lines represent equilibrium chemistry. The $K_z$ for these models evolved self-consistently following mixing length theory in the convective zones and following Equation (3) in the radiative zones.

Disequilibrium abundances mainly lead to colder $T(P)$ profiles compared to equilibrium chemistry models, as can be seen in Figure 2. In the overall optically thinner disequilibrium chemistry atmosphere (see Figure 1), one must see down to a higher pressure to obtain a given $T$. This effect was also seen in Karalidi et al. (2021) for constant $K_z$ models.

Volume mixing ratio profiles of CO for each of these models are shown in the top-right panel of Figure 2. As described earlier, disequilibrium chemistry greatly enhances the CO

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**Figure 1.** The top panels show the $\tau = 1$ pressure levels for specific gaseous absorbers in a model T-dwarf with $T_{\text{eff}} = 700$ K and log($g$) = 5.0 in the presence and absence of quenching due to vertical mixing. $\tau = 1$ pressure levels for H₂O, CH₄, CO, and NH₃ are shown in the first, second, third, and fourth columns, respectively. The equilibrium chemistry pressure levels are shown by the dashed lines, whereas the disequilibrium chemistry pressure levels are shown by the solid lines. The volume mixing ratio as a function of the pressure of each gas in the presence (solid lines) and absence (dashed lines) of vertical-mixing-induced quenching are also shown by the black lines in the top $x$-axis of each of the top four panels. The bottom panel shows the logarithm of the pressure ratio of these $\tau = 1$ levels with equilibrium chemistry and disequilibrium chemistry for the gaseous absorbers. The zero mark represents no change in these pressure levels. Positive values represents an increase in absorption in the disequilibrium chemistry models compared to equilibrium chemistry models. The main point here is that disequilibrium chemistry leads to large opacity changes in the atmosphere.

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1000, 1780, and 3160 ms⁻² (log($g$) from 4.5–5.5 with an interval of 0.25 dex). The $T_{\text{eff}}$ range is 400–1000 K with an interval of 25 K.

To explore the role of the radiative zone $K_z$ in our grids, we multiply Equation (3) by multiplicative factors of $\times 100$, $\times 1$, and $\times 0.01$. We refer to these parameter values as “Moses × 100,” “Moses,” and “Moses/100,” respectively, after Moses et al. (2022). The mixing length parameter in the convective zones ($L$ in Equation (2)) has been varied between the scale height $H$ and 0.1 $\times H$ to explore scenarios where mixing in the convective zone is less efficient than the typically assumed mixing length theory in 1D models. Furthermore, for reasons discussed in Section 4, we ran two sets of models—one where PH₃ is quenched given its appropriate $t_{\text{chem}}$ and another where PH₃ follows equilibrium chemistry while other molecules are quenched. This parameter space has a total of $5 \times 25 \times 3 \times 2 = 1500$ self-consistent RCE models. All of these models are cloud-free and assume solar metallicity and C/O ratio, following Marley et al. (2021). We have not included clouds in our models, as at the temperature range of our grid (400–1000 K), clouds are not expected to be a significant opacity source in the upper atmosphere. The model grid is publicly available via Zenodo.⁶ We present our key findings from this grid of models below beginning with the feedback of disequilibrium chemistry on $T(P)$ profiles of brown dwarfs.

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3.1. Effect of Disequilibrium Chemistry on the $T(P)$ Profile of Brown Dwarfs

Disequilibrium chemistry leads to enhanced CO and depleted CH₄, NH₃, and H₂O abundances in T- and Y-dwarfs. This leads to major changes in the wavelength-dependent optical depths in the atmosphere. The top four panels of Figure 1 show the $\tau = 1$ pressure levels, for specific gases, for a T-dwarf with $T_{\text{eff}} = 700$ K and log($g$) = 5.0 in the presence and absence of quenching due to vertical mixing. These $\tau = 1$ pressure levels are strongly wavelength dependent. Here $K_z$ has been assumed to follow Equation (2) in the convective zones and Equation (3) in radiative zones. The disequilibrium chemistry pressure levels are shown as the solid lines, and the corresponding equilibrium chemistry levels are shown as the dotted lines. The pressure-dependent volume mixing ratios of these gases under chemical equilibrium and disequilibrium are also shown in the top $x$-axis in each of the top four panels by the dashed and solid black lines, respectively.

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⁶ 10.5281/zenodo.7076995
abundances above quench level. However, even deep down, below the quench level, there are important CO abundance differences due to differences in the converged \( T(P) \) profile. As equilibrium chemistry models have hotter \( T(P) \) profiles, at given pressures, than disequilibrium chemistry models, they also have higher CO abundances. This drives home the point that a self-consistent treatment of disequilibrium chemistry (as in Section 2.1) is needed rather than post-processing self-consistent equilibrium chemistry models with quenched abundances. Even if one obtains the correct quench pressures

**Figure 2.** The top-left panel shows the \( T(P) \) profile of brown dwarf models with \( \log(g) = 5 \) and \( T_{\text{eff}} \) of 500, 700, and 1000 K. The solid \( T(P) \) profiles assume disequilibrium chemistry self-consistently whereas the dotted profiles show equilibrium chemistry calculations. The convective zones are shown with thicker lines for each \( T(P) \) profile. To differentiate the convective zones of the equilibrium chemistry models from the disequilibrium chemistry models, they are shown with much thicker lines compared to the convective zones of disequilibrium chemistry models. The top-right panel shows the plotted CO volume mixing ratio profiles for these brown dwarf models. The solid lines show the mixing ratio with disequilibrium chemistry whereas the dotted lines show calculations from equilibrium chemistry. The bottom panel shows the normalized thermal emission spectra of these brown dwarfs. The solid lines show the disequilibrium chemistry results, while the dotted spectra represent the equilibrium chemistry calculations. The \( J, H, K', L' \), and \( M' \) bands are also shown as shaded regions of different colors. The main point here is that self-consistent treatment of disequilibrium chemistry leads to large changes in the \( T(P) \) profile, abundances, and thermal emission spectra.
during post-processing equilibrium chemistry models, one would calculate a physically inconsistent and higher abundance of CO at the upper atmospheres than self-consistent disequilibrium chemistry models.

The thermal emission spectra of these models are shown in Figure 2 (bottom panel). The fluxes from these objects were normalized by their maximum flux and are plotted from the hottest model \((T_{\text{eff}} = 1000 \text{ K})\) at the top to the coldest model \((T_{\text{eff}} = 500 \text{ K})\) at the bottom. Large differences in outgoing thermal flux can be seen in the \(H\), \(K\), \(L\), and \(M\) bands between the equilibrium chemistry and disequilibrium chemistry model spectra. Comparing these differences with the differences in the \(\tau = 1\) pressure levels in Figure 1 makes it clear that the differences in the \(H\), \(K\), and \(L\) bands arise due to changes in the \(\text{CH}_4\) abundance profiles. Another major difference is in the \(M\) band. CO enhancement and modest \(\text{H}_2\text{O}\) depletion leads to a major suppression of thermal flux between 4.5 and 5 \(\mu\text{m}\) in the disequilibrium models.

Although \(\text{NH}_3\) abundances show large changes between equilibrium chemistry and the disequilibrium chemistry models, it still is not the major opacity source at the shorter IR wavelengths. It becomes a major opacity source at 11 \(\mu\text{m}\) and causes a distinct feature in the spectra. The bottom panels of Figure 2 show a significant change in this \(\text{NH}_3\) feature due to disequilibrium chemistry. Quenching of \(\text{NH}_3\) causes this feature to become slightly less prominent compared to chemical equilibrium models.

Other carbon- and nitrogen-bearing molecules like HCN, \(\text{N}_2\), and \(\text{CO}_2\) are also quenched due to \(K_{\text{zz}}\). But these molecules do not have readily apparent absorption features in the infrared at these spectral resolutions in a solar metallicity mixture. \(\text{N}_2\) is essentially transparent in solar metallicity mixtures, and detecting \(\text{CO}_2\) is very difficult from the ground. However, JWST, like AKARI (Sorahana & Yamamura 2012), can detect disequilibrium abundances of \(\text{CO}_2\) in brown dwarfs with higher metallicity. As our models have solar metallicity, we do not specifically discuss these signatures here.

Of particular interest to our work here are the changes in \(T(P)\) structure, and the locations of the radiative and convective zones shown in Figure 2. We examine the causes for these differences in more detail in Figure 3 for a brown dwarf with \(T_{\text{eff}} = 700 \text{ K}\) and \(\log(g)\) of 4.5. The left panel of Figure 3 shows the \(T(P)\) profile of this brown dwarf under equilibrium chemistry by the dashed line, and the \(T(P)\) profile of the brown dwarf with chemical disequilibrium is shown by the solid line. The radiative zones are shown with narrower lines whereas the convective zones are shown with thicker lines.

There are significant changes in the location and number of radiative and convective zones in the two profiles, with the disequilibrium model having one convective zone at depth and a radiative zone at lower pressure. However, the equilibrium models find two convective zones and two radiative zones. To examine why, the right panel in Figure 3 shows the wavelength-dependent absorptivity in several layers of these atmospheres with the dashed (equilibrium chemistry) and solid (disequilibrium chemistry) lines. The absorptivity is given by \(A = (1 - e^{-\tau})\). A high absorptivity (close to 1) corresponds to an opaque wavelength whereas a low absorptivity corresponds to a transparent wavelength window. The normalized local blackbody Planck function \(B_\lambda\) is also plotted for each layer for the equilibrium (dashed black line) and disequilibrium chemistry (solid black line) models for comparison with the absorptivity. We follow Marley & Robinson (2015) for the explanation of this phenomenon below.

As the atmosphere becomes colder with lower pressure in both models, the peak of the local \(B_\lambda\) shifts to longer wavelengths. In the deep atmosphere \(\sim 100\) bar, gaseous optical depths are very high, which causes the absorptivity to be very close to 1 across all wavelength ranges for both cases. The atmosphere is opaque to radiative energy transport in these pressure layers for both cases, and convection ensues at these pressure levels. This is the case at pressures higher than \(\sim 40\) bars for both models. At about 20 bars, some transparent windows start to appear. Since the equilibrium chemistry model is hotter than the disequilibrium chemistry model, the peak of its local blackbody emission coincides more closely in wavelength with the transparent opacity windows between 0.8 and 1 \(\mu\text{m}\) in the atmosphere at these pressures. This causes the equilibrium chemistry model to be radiative in these pressure ranges whereas the disequilibrium chemistry model is still convective as its local blackbody emission still peaks at longer wavelengths where the atmosphere is opaque at \(\sim 20\) bars pressure. As the atmosphere gets colder with lower pressure, large transparent windows develop between 0.5 and 2 \(\mu\text{m}\), but as these layers are much colder, their blackbody peaks are at wavelengths greater than 2 \(\mu\text{m}\).

At \(\sim 2\) bars, the blackbody peak of the chemical equilibrium model hits another opaque range between 2 and 3 \(\mu\text{m}\). This causes it to develop another, detached convective zone at these pressures. At pressures lower than this range, a large transparent opacity window develops between 3.5 and 5 \(\mu\text{m}\) in both the models. The disequilibrium model is more transparent than the equilibrium model between 3.5 and 4.5 \(\mu\text{m}\) (due to less \(\text{CH}_4\) and \(\text{H}_2\text{O}\)) but is more opaque than the equilibrium model between 4.5 and 5 \(\mu\text{m}\) (due to more \(\text{CO}\)). As the local blackbody function of both models also peaks between 3.5 and 5 \(\mu\text{m}\) in these pressure layers, these differences in transparency between the two atmospheres cause a large change (\(\sim 150\) K) between their \(T\) and \(P\) profiles in these pressures. As the cooler local blackbody peak of the disequilibrium model more closely overlaps with the opaque window in the disequilibrium model between 4.5 and 5 \(\mu\text{m}\), its atmosphere is still convective in these pressures, while the equilibrium model is radiative. At pressures lower than \(\sim 0.8\) bars, both atmospheres are radiative as more transparent windows start appearing in longer wavelengths with decreasing pressure. With these differences in the \(T(P)\) profile and convective/radiative zones between models with chemical equilibrium and disequilibrium, the next important question to be investigated is whether gases like \(\text{CO}, \text{NH}_3\), and \(\text{H}_2\text{O}\) are quenched in the radiative or convective zones of models with chemical disequilibrium. Results from our model grid on this question are presented next.

3.2. Quenching in the Radiative Zone or the Convective Zone?

Quenching of gases can occur in convective zones or radiative zones. Vertical mixing in convective zones is expected to be very efficient, yielding a high \(K_{\text{zz}}\) and correspondingly low \(t_{\text{max}}\). The top three panels of Figure 4 show the \(T(P)\) profile of a brown dwarf with \(T_{\text{eff}} = 700\) K and \(\log(g)\) of 4.5 (left panel), the mixing and chemical timescales \(t_{\text{mix}}\) and \(t_{\text{chem}}\) for the same brown dwarf (middle panel), and the volume mixing ratios of various molecules (right panel) in the brown dwarf atmosphere. This brown dwarf has a single convective and radiative zone. The mixing timescale \(t_{\text{mix}}\) is shown by the dashed black line whereas the \(t_{\text{chem}}\) for \(\text{CO}\) and
other chemical reactions are shown with differently colored dashed lines. The $t_{\text{mix}}$ profile has been calculated using mixing length theory in the convective zone and with Equation (3) in the radiative zone. The mixing timescales in radiative zones are expected to be longer at depth, due to the lack of efficient dynamical mixing processes. However, as briefly described in Section 2, the mixing timescale is expected to be short in the much-lower-pressure regions ($P \sim 10^{-4}$ bars) due to the presence of gravitational wave breaking mechanisms (Moses et al. 2005; Freytag et al. 2010; Moses et al. 2011).

$t_{\text{mix}}$ is much longer than $t_{\text{chem}}$ at pressures $>100$ bars, and therefore, CO and CH$_4$ are expected to follow chemical
equilibrium in these high-pressure high-temperature parts of the atmosphere. But the $\text{CO} \rightarrow \text{CH}_4$ reaction is a very strong function of both temperature and pressure (Zahnle & Marley 2014). Therefore, it increases by 12 orders of magnitudes within one order of magnitude in pressure and a change of 500 K in temperature. As a result, the two timescales cross each other at about $\sim 30$ bars at the quench pressure ($P_Q$). The abundances of both of these molecules, and $\text{H}_2\text{O}$, are quenched to constant values above $P_Q$ as a result, as shown in the top-right panel of Figure 4. As different net chemical reactions proceed at different rates and have different $t_{\text{chem}}$, their $P_Q$ will also be different.

Self-consistent chemical equilibrium models of T-dwarfs with $T_{\text{eff}}$ within the range of 400–800 K have shown the presence of an upper detached convective zone in addition to the deeper convective zone (Burrows et al. 1997; Marley et al. 2021), with a radiative zone in between. The $T(P)$ profile in this scenario is shown in the bottom-left panel of Figure 4 for a brown dwarf with $T_{\text{eff}}$ of 700 K (as above) but with a log($g$) of 5.25. This detached zone appears when the $T(P)$ profile of the atmosphere is such that the radiative energy transport in the deeper atmosphere becomes efficient due to the opening of a molecular opacity window at near-infrared wavelengths (Marley & Robinson 2015), as shown in Figure 4. The resulting “sandwiched radiative zone” is very likely to have a much slower rate of vertical mixing (longer $t_{\text{mix}}$) compared to the convective zones. As these radiative zones appear at high pressures ($P \geq 10$ bars), it is possible that molecules like CO, CH$_4$, and NH$_3$ are quenched in the radiative zone instead of the convective zone. Note that the mixing timescale profile in the top-middle panel in Figure 4 shows a “kink”-like structure in $t_{\text{mix}}$ values between 10 and 30 bars. This kink is due to the decrease in the convective heat flux ($F$ in Equation (2)) in the convective zone around that region. This can happen in convective regions where a nonnegligible (but smaller than the convective heat transport) amount of energy transfer in a convective zone still occurs via radiation. This leads to a smaller convective heat flux in these regions.

The bottom-middle panel of Figure 4 shows this scenario. Within our modeling framework, the $t_{\text{mix}}$ is low (high $K_{zc}$) in the deep convective zone, and $t_{\text{mix}}$ is high (low $K_{zc}$) in the deep sandwiched radiative zone. The $P_Q$ for CO in this case is within the sandwiched radiative zone. Therefore, if one is trying to
probe the \( K_{zz} \) of this hypothetical object with constant \( K_{zz} \) models (e.g., Miles et al. 2020), one would infer a much lower \( K_{zz} \) than what is expected from Equation (2). However, the reason for this is not because of sluggish mixing in the convective zone, but rather quenching is occurring in a radiative zone where mixing is expected to be sluggish.

Such a scenario was suggested in fits to observations presented in Miles et al. (2020). They inferred the \( K_{zz} \) for several late T- and early Y-dwarfs and found that the \( K_{zz} \) for objects with \( T_{eff} \) between 400 and 800 K are much smaller than expectations from mixing length theory. Although equilibrium chemistry models find the sandwiched radiative zone between \( T_{eff} \) of 400 and 800 K (e.g., Allard et al. 2012; Marley et al. 2021), it is not clear if the self-consistent treatment of disequilibrium chemistry preserves these sandwiched radiative zones and also if molecules like CO or NH\(_3\) actually quench in these sandwiched radiative zones. Next, we investigate this scenario in more detail.

We can expand the modeling work shown in Figure 4 over a range in \( T_{eff} \) and \( \log (g) \) to assess under what conditions a sandwiched radiative zone occurs in self-consistent nonequilibrium models. Figure 5 shows the appearance of the sandwiched radiative zones across this phase space in the presence and absence of vertical mixing. The colors shown in Figure 5 represent \( \log_{10}(P_{bot}/P_{top}) \) where \( P_{bot} \) and \( P_{top} \) are the pressures at the bottom and top of the sandwiched radiative zone, respectively.

If the model does not find a sandwiched radiative zone, this number will be zero. The top panel in Figure 5 shows the sandwiched radiative zones in chemical equilibrium models. The other three panels show the appearance of the second radiative zone with three different magnitudes of mixing in the radiative zone, all assuming the mixing length \( L \) is \( H \) in the convective region. Under the assumption of equilibrium chemistry, it is clear that the sandwiched radiative zones appear between \( T_{eff} \) of 450 and 800 K for a \( \log(g) \) of 4.5. However, for objects with \( \log(g) \) of 4.75 and higher, the sandwiched radiative zones only appear between 450 and 600 K in chemical equilibrium models. For models with disequilibrium chemistry, the models that show the presence of this sandwiched radiative zone appear at a different set of \( T_{eff} \) and \( \log(g) \) values. As can be seen in Figure 5 (second, third, and fourth panels), high-gravity models with \( \log(g) \) of 5.0 and greater have this sandwiched radiative zone between \( T_{eff} \) of \( \sim 500 \) and 800 K. For models with \( \log(g) \) of 4.75, the sandwiched radiative zone appears between 500 and 750 K. However, for models with \( \log(g) \) of 4.5, the sandwiched radiative zone is nonexistent when quenching due to vertical mixing being taken into account. The thickness of these zones is typically smaller, too, as can be seen from the less-yellow shading.

Figure 6 shows the appearance of this sandwiched radiative zone if the convective mixing length \( L \) is smaller, only \( 0.1 \times H \). The second, third, and fourth panels in Figure 6 show that larger numbers of models now develop this sandwiched radiative zone compared to models with \( L = H \) shown in Figure 5. The sandwiched radiative zone does indeed appear at low gravity (\( \log(g) = 4.5 \)) when \( L = 0.1 \times H \). Additionally, the radiative zones tend to appear at higher \( T_{eff} \) than for \( L = H \) models. This shows that the strength of vertical mixing in both the radiative and convective zones can influence the presence and absence of multiple convective zones.

The effect of radiative and convective \( K_{zz} \) on the chemical abundances is more complex than it may appear. The presence of a sandwiched radiative zone does not guarantee that quenching occurs in the radiative zone. Furthermore, radiative zone quenching can also occur in atmospheres with a single radiative zone and single convective zones. We investigate the resulting photospheric CO abundances in \( T_{eff} \) versus \( \log(g) \) space in Figure 7. The top panel shows the CO abundance in
models in chemical equilibrium. The second, third, and fourth panels show models with disequilibrium chemistry. Each of these panels represents models with different values of $K_{zz}$ in Figure 6.

Appearance of the second radiative zone in the $T_{\text{eff}}$ vs. log($g$) parameter space in our grid is shown. The colors show the value of the quantity $\log_{10}(P_{\text{bot}}/P_{\text{top}})$ where $P_{\text{bot}}$ and $P_{\text{top}}$ are the pressures at the bottom and top of the sandwiched radiative zone, respectively. The top panel shows this for the case of equilibrium chemistry. The subsequent panels show the presence of the second radiative zone if different strengths of $K_{zz}$ are chosen, keeping the convective zone mixing length fixed at $0.1 \times H$. Dark blue indicates no second convective zone at depth.

Figure 6. Appearance of the second radiative zone in the $T_{\text{eff}}$ vs. log($g$) parameter space in our grid is shown. The colors show the value of the quantity $\log_{10}(P_{\text{bot}}/P_{\text{top}})$ where $P_{\text{bot}}$ and $P_{\text{top}}$ are the pressures at the bottom and top of the sandwiched radiative zone, respectively. The top panel shows this for the case of equilibrium chemistry. The subsequent panels show the presence of the second radiative zone if different strengths of $K_{zz}$ are chosen, keeping the convective zone mixing length fixed at $0.1 \times H$. Dark blue indicates no second convective zone at depth.

Figure 7. The top panel shows the equilibrium chemistry abundance of CO at pressures where $T = T_{\text{eff}}$ in our $T_{\text{eff}}$ vs. gravity grid of chemical equilibrium models. The second, third, and fourth panels depict the quenched CO abundance within the $T_{\text{eff}}$ vs. gravity parameter space in our disequilibrium chemistry models. The second, third, and fourth panels correspond to models with radiative zone $K_{zz}$ values of “Moses,” “Moses $\times 100$,” and “Moses/100,” respectively, while the convective zone mixing length $L$ was fixed at the scale height $H$. Models where CO was quenched at the radiative zone are marked with black hatches. CO was quenched at a convective zone in the rest of the models. Models with radiative zone CO quenching show much smaller CO abundance compared to models with convective zone quenching.

models in chemical equilibrium. The second, third, and fourth panels show models with disequilibrium chemistry. Each of these panels represents models with different values of $K_{zz}$ in
the radiative zone while the mixing length in the convective zone is fixed to $H$. Models where CO, CH$_4$, and H$_2$O are quenched in radiative zones are marked with black hatches.

The rest of the models still have CO quenching, but in the convective zones instead.

The CO abundances in these models with radiative zone CO quenching also show large differences from CO abundances in models with convective zone quenching. These differences appear as discontinuities in the CO abundance heat map shown in the second, third, and fourth panels of Figure 7. The reason behind these discontinuities is mainly the smaller $P_Q$ of CO in models with radiative zone quenching compared to models with convective zone quenching.

However, Figure 8 shows that CO abundances over $T_{\text{eff}}$ and log($g$) will change if the mixing length in the convective zone is smaller. Here, again, $L = 0.1 \times H$, leading to smaller $K_{zz}$ values, and longer $t_{\text{mix}}$ in the convective zone. This causes quenching to often occur in the top or sandwiched radiative zone in a significantly larger fraction of the $T_{\text{eff}}$ and log($g$) parameter space compared to the nominal $L = H$ scenario in Figure 7. For models with log($g$) = 4.75 and greater, all models with $T_{\text{eff}} \geq 550$ K show radiative zone quenching of CO and CH$_4$ in this case. Both Figures 7 and 8 makes it clear that the chemical properties of brown dwarfs that will have either radiative zone or convective zone quenching depend on the vigor of mixing in both of these types of zones.

Furthermore, since $t_{\text{chem}}$, and hence the $P_Q$, of different gaseous species are different, this means that models where CO quenches in radiative zones are not necessarily models where CO$_2$ or NH$_3$ also quenches in the radiative zone. This effect can be clearly seen in Figure 9, which shows the same set of models as in Figure 7, but now with the CO$_2$ abundances and its radiative/convective quench behavior. Because the $t_{\text{chem}}$ for the thermochemical equilibrium of CO$_2$ is orders of magnitude shorter than for CO and CH$_4$, the models where CO$_2$ quenches in the radiative zone are also different than those where CO/CH$_4$ quenches in the radiative zone. If the mixing length in the convective zone is $H$, CO$_2$ radiative zone quenching occurs mostly in models that are hotter than 700 K and have gravity higher than log($g$) of 5. The same effect for quenching of NH$_3$ has been shown in Figure 10 in models with $L = 0.1 \times H$. Comparing Figures 10 with 8 shows that the radiative zone quenching of NH$_3$ occurs in only a small subset of lower-temperature (500–800 K) models with radiative zone quenching of CO, when $L = 0.1 \times H$. The $t_{\text{chem}}$ for the reaction between N$_2$ ↔ NH$_3$ is the slowest among the other reactions described in Section 2.1. As a result, if $L = H$, NH$_3$ always gets quenched in the deep convective zone in the parameter space explored by our grid. Even if the convective mixing length is smaller ($L = 0.1 \times H$), NH$_3$ gets quenched in the convective zone of the majority of the models except in some where deeper “sandwiched” radiative zones develop. But in order to measure these quenched abundances observationally and infer the $K_{zz}$ profile of the atmosphere, we need to investigate the effect of $K_{zz}$ on observables, such as the emission spectra of these brown dwarfs, which we discuss next.

### 3.3. Effect of Radiative and Convective Zone $K_{zz}$ on Emission Spectra

We have established in Section 3.2 that gases like CO, CH$_4$, and CO$_2$ can be quenched in the sandwiched radiative zones or single radiative zones in a subset of late T- and early L-dwarfs. In Figures 11, 12, and 13, we show how thermal emission spectra are sensitive to the vigor of vertical mixing in the radiative zone of these objects. These spectra, with a spectral

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**Figure 8.** The same as Figure 7 except with the mixing length in convective zones fixed at 0.1 × $H$. In these models, CO is mostly quenched in a radiative zone.
resolution of 600, are calculated using the thermal emission calculation module of Picaso (Batalha et al. 2019), using the same opacities that were used for model convergences to RCE. Sources of these opacities can be found in Marley et al. (2021).

The thermal emission spectra between 4.2 and 5.0 μm, across a range of $T_{\text{eff}}$ between 400 and 1000 K with steps of 100 K, are shown for log$(g)$ values of 5 and 5.5 in the two top panels of Figure 11. The choice of the wavelength range

Figure 9. The same as Figure 7 but for quenching of CO$_2$. Given the different $k_{\text{chem}}$ for CO$_2$ compared to CO, the quench levels are entirely different.

Figure 10. The same as Figure 8 but for quenching of NH$_3$. Given the different $k_{\text{chem}}$ for NH$_3$, compared to CO, the quench levels are entirely different.
focuses on the role of CO, which has significant impacts on the spectrum in the $M$ band between 4.4 and 5 μm. H$_2$O is the primary absorber between 4.0 and 4.4 μm. These models assume $L = H$ in the convective zones. The bottom panels of Figure 11 show the spectrum from the same set of models except for $L = 0.1 \times H$. Spectra arising from different strengths of vertical mixing in the radiative zones are shown with different line styles in all of the panels.

Sensitivity of the $M$-band spectrum to radiative zone $K_{zz}$ values is more common for higher-gravity objects with log($g$) of 5.0 and 5.5. If the convective mixing length is $H$, then this sensitivity appears between models with $T_{\text{eff}}$ 550 and 700 K for.
log($g$) of 5. However, if the convective mixing length is $0.1 \times H$, then this sensitivity appears much more commonly between models with $T_{\text{eff}}$ of 500 and 1000 K for log($g$) = 5.0. At higher gravity, log($g$) of 5.5, the sensitivity of $M$-band spectra to radiative zone $K_{zz}$ appears at both convective mixing lengths of $H$ and $0.1 \times H$. In the top-right panel of Figure 11, this sensitivity appears between 500 and 1000 K, whereas in the bottom-right panel of Figure 11, this sensitivity appears between 500 and 1000 K.

While the $M$ band shows the greatest sensitivity to $K_{zz}$ in the radiative and convective zones, smaller differences in the spectra arise in other wavelengths as well. The top panels of

**Figure 12.** $H$-band thermal emission spectra of models from our grid are shown in the top-left and -right panels, whereas the bottom-left and -right panels show the $K$-band emission spectra. Models with log($g$) = 5 and different $T_{\text{eff}}$ between 400 and 1000 K are shown in each panel. From bottom to top, spectra for $T_{\text{eff}}$ values of 425, 700, 850, 900, and 1000 K are shown in all of the panels. The top-left panel shows the thermal emission spectra of models that have convective mixing length set at $H$ but have different $K_{zz}$ parameterizations like Moses, Moses/100, and Moses × 100, which are represented by different line types in the panels (solid, dashed, and dashed–dotted lines). The top-right panel shows the same but for models with convective mixing length set at $0.1 \times H$. The bottom-left and -right panels show the sensitivity of the $K$-band spectrum to radiative zone $K_{zz}$ when $L = H$ and $L = 0.1 \times H$, respectively. The shaded region shows the wavelength range where CH$_4$ is the most important absorber.
Figure 12 shows the sensitivity of the $H$-band spectra to the radiative zone $K_{zz}$ across various values of $T_{\text{eff}}$ for brown dwarf models with $\log(g) = 5.0$. The top-left panel shows models with $L = H$, whereas the top-right panel shows models with $L = 0.1 \times H$. The sensitivity mainly appears between 1.69 and 1.75 $\mu$m in models where CH$_4$ is quenched in the radiative zone, as it is the main opacity source at these wavelengths. CH$_4$ is also the main opacity source between 2–2.2, 3.2–3.5, and 3.5–4 $\mu$m. As a result, the spectra at these wavelength ranges also show some sensitivity to the radiative zone $K_{zz}$ of the deep

Figure 13. Thermal emission spectra of brown dwarfs between 3 and 3.5 $\mu$m are shown in the top-left and -right panels. Emission spectra of the same models in the $L$ band are shown in the bottom-left and -right panels. Models with $\log(g) = 5$ and different $T_{\text{eff}}$ between 400 and 1000 K are shown in each panel. From bottom to top, spectra for $T_{\text{eff}}$ values of 425, 700, 850, 900, and 1000 K are shown in all of the panels. The top-left panel shows the emission spectra of models that have convective mixing length set at $H$ but have different $K_{zz}$ parameterizations like Moses, Moses/100, and Moses \times 100, which are represented by different line types in the panels (solid, dashed, and dashed–dotted lines). The top-right panel shows the same but for models with convective mixing length set at 0.1 $H$. The bottom-left and -right panels show the sensitivity of the $L$-band spectrum to radiative zone $K_{zz}$ when $L = H$ and $L = 0.1 \times H$, respectively. The shaded region shows the wavelength range where CH$_4$ is the most important absorber.
atmosphere. This sensitivity between 2–2.2, 3.2–3.5, and 3.5–4 μm is shown in the bottom panels of Figure 12 as well as the top and bottoms panels of Figure 13, respectively. Examining different spectral regions for a given object (that are sensitive to both CH₄ and CO) will help in constraining the radiative zone $K_{zz}$, as both gas species abundances can be used as probes. Apart from the emission spectra itself, other observables like broadband IR colors and magnitudes of brown dwarfs are also known to be sensitive to $K_{zz}$ (e.g., Saumon et al. 2003; Karalidi et al. 2021), which we explore next.

### 3.4. Color–Magnitude Diagrams

Coupling our atmospheric model grid with brown dwarf evolutionary models from Marley et al. (2021) enables us to generate color–magnitude diagrams (CMDs) of these brown dwarfs. These evolutionary models track the $T_{\text{eff}}$, log(g), and bolometric luminosity as a function of age for each brown dwarf mass. The procedure is the same as in Marley et al. (2021), although our models here are slightly not self-consistent, as the upper boundary condition for the Marley et al. (2021) cooling tracks assumes equilibrium chemical abundances.

Figure 14 shows the observed CMD of brown dwarfs in various standard infrared filter combinations. We show $J$ versus $J-H$, MKO $L'$ versus $L'-M'$, and WISE W1 versus W1-W2 in the first, second, and third rows, respectively. The mid-infrared wavelengths are most sensitive to disequilibrium chemistry effects. Model tracks for three different log(g) (4.5, 5.0, and 5.5) values are shown in the three columns for each combination of filters. The database maintained by Trent Dupuy (Dupuy & Liu 2012; Dupuy & Kraus 2013; Liu et al. 2016) has been used for the observational data. The red model tracks in all of the panels represent models with convective mixing length set at $H$, whereas the blue tracks represent models with convective mixing length set at 0.1 × $H$. Each line type (solid, dotted, and dashed–dotted) in both of these colors represents models with the different radiative zone $K_{zz}$ values “Moses × 100,” “Moses,” and “Moses/100,” respectively. The black dashed lines represent CMD tracks from the equilibrium chemistry models.

In the $J$ versus $J-H$ filter combination CMD, it appears that models treating disequilibrium chemistry self-consistently provide a slightly better fit to the observed photometry than the equilibrium chemistry, for models at log(g) of 5.0–5.5, representative of the field sample. The disequilibrium chemistry models with different convective mixing lengths shown by the blue and red tracks almost fall on top of each other as the $J$- and $H$-band fluxes are not particularly sensitive to CO abundance but have some sensitivity to CH₄ abundance.

The chemical equilibrium model CMD tracks follow a much redder sequence in the MKO $L'$ versus $L'-M'$ CMDs compared to the observed photometry. The disequilibrium chemistry models are comparatively much bluer. As discussed in the previous sections, enhanced CO abundance in the disequilibrium chemistry model causes the $M'$-band and the W2-band fluxes to be fainter than the equilibrium chemistry models. On the other hand, depleted CH₄ abundance in disequilibrium chemistry models causes higher fluxes in the $L'$ and W1 bands. Both of these effects causes the disequilibrium model tracks (shown by the red and blue lines) to be significantly bluer than the equilibrium chemistry model tracks (shown with the black line) in the $L'$ versus $L'-M'$ and W1 versus W1-W2 CMDs.

It is interesting to note the nonmonotonic behavior. At higher gravity (log(g) = 5.0 and 5.5), some disequilibrium chemistry models show radiative zone quenching instead of convective zone quenching. As a result, these atmospheres have lower photospheric CO compared to disequilibrium chemistry with convective quenching, but a much higher CO abundance compared to the equilibrium chemistry models. Therefore, the models with radiative zone quenching are redder than disequilibrium chemistry models with convective zone quenching but bluer than equilibrium chemistry models, “jutting out” to the red for some models.

The second and third rows in Figure 14 also show that disequilibrium models with $L = H$ with convective zone quenching of CO are much bluer than the observed sequence. However, disequilibrium models with $L = 0.1 \times H$ provide a generally better fit to the mid-IR photometry. This suggests that longer $r_{\text{max}}$ values in the deeper atmosphere provide a better fit to the photometry from the T- and Y-dwarf population than the $r_{\text{max}}$ calculated from assumptions like free convection. However, this result is empirical in nature and needs further validation from 3D tracer transport models like those in Bordwell et al. (2018). Coupling our models with 1D chemical kinetics models will also help us in interpreting these trends better, which is something we will address in future studies. It seems clear that even lower $K_{zz}$ values for the faintest models may be necessary, as the data are generally more consistent with equilibrium chemistry models at log(g) of 5.0–5.5. We also note that we have not included clouds within our models, and they might have some impact on the model magnitudes presented here especially for the faintest end of these tracks, as H₂O clouds are expected to form in the colder objects ($T_{\text{eff}} \lesssim 450$ K; Morley et al. 2014).

### 3.5. Comparing to Spectroscopic Observations

We compare our grid of atmospheric models with ground-based spectral observations of six late T- and early Y-dwarfs. We aim to determine the atmospheric properties of brown dwarfs—Gliese 570D (Burgasser et al. 2000), 2MASS J0415-0935 (Burgasser et al. 2002), WISE 0313 (Kirkpatrick et al. 2011), UGPS 0722 (Cushing et al. 2011), WISE 2056 (Schneider et al. 2015), and WISE 1541 (Schneider et al. 2015)—with our models. Although Miles et al. (2020) had the Y-dwarf WISE 0855 in their sample, we exclude this object from our analysis, as it is expected to have optically thick water clouds in its atmosphere due to its cold $T_{\text{eff}}$ ($\sim 250$ K), and our model grid only extends to a $T_{\text{eff}}$ of 400 K. As noted in Section 3, this choice for the lower bound on $T_{\text{eff}}$ in our model grid was made because our models lack a self-consistent treatment of clouds with disequilibrium chemistry, currently.

For comparing our models with observational data, which includes both near-infrared and $M$-band spectra, we use the goodness-of-fit parameter, $G_k$, defined as (Cushing et al. 2008),

$$G_k = \frac{1}{n - m} \sum_{i=1}^{n} \left( \frac{f_i - C_i F_{\text{obs}}^i}{\sigma_i} \right)^2$$

where $n$ is the number of observational data points, $m$ is the number of free parameters being fit, $w_i$ are the weights of fitting $i$th data point, $f_i$ is the $i$th observed flux, $F_{\text{obs}}^i$ is the $i$th model flux point of the $k$th model, and $\sigma_i$ is the error in the $i$th observed

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http://www.as.utexas.edu/~tdupuy/plx
Figure 14. Color–magnitude diagrams (CMDs) of observed brown dwarfs in different filters are shown with overplotted equilibrium and disequilibrium chemistry model tracks with different strengths of convective and radiative zone vertical mixing. The top row shows the $J$ vs. $J-H$ where the models with a convective zone mixing length of $H$ and different radiative zone $K_{zz}$ are shown with various red line types. Models with a convective zone mixing length of $0.1 \times H$ and different radiative zone $K_{zz}$ are shown with various blue line types, and the equilibrium chemistry models are shown by the dashed black lines. Each column shows the same data, but the model tracks with different values of log($g$). The second row shows the $L'$ vs. $L'-M'$ whereas the third row shows the W1 vs. W1-W2.
flux. The factor $C_k$ is a renormalization factor for the model fluxes. If the observed fluxes are flux calibrated, then $C_k$ represents the factor $R^2/D^2$, but if the observed fluxes are not flux calibrated, then $C_k$ represents the factor $\alpha R^2/D^2$, where $\alpha$ represents the unknown flux normalization of the observed flux. The $C_k$ factor is given by (Cushing et al., 2008),

$$C_k = \frac{\sum_{i=1}^n w_i F_i^k}{\sum_{i=1}^n w_i (F_i)_{obs}^2}.$$  

(5)

Since there is no reported bias in any of the data sets we use, $w_i$ is always fixed at 1 for our analysis.

3.5.1. Gliese 570D and 2MASS J0415-0935

Gliese 570D is a T7.5 dwarf (Burgasser et al., 2006) that has a measured spectrum in the $M$ band with two different instruments—AKARI (Sorahana & Yamamura, 2012) and GEMINI/NIRI (Geballe et al., 2009). We used the $M$-band spectra of Gliese 570D reported in Geballe et al. (2009) because it has a higher S/N ratio. We also use the NIRC 1–2.5 $\mu$m spectra of Gliese 570D (GI 570D) reported in Burgasser et al. (2002) and Spitzer Infrared Spectrograph (IRS) 5–14 $\mu$m spectra of Gliese 570D reported in Suárez & Metchev (2012). We adopt the methodology described in Sorahana & Yamamura (2012) for fitting the spectrum of GI 570D with our grid of models. First, we use our grid of models to calculate $C_k$ using only the $M$-band GEMINI/NIRI data for GI 570D. Using this set of calculated $C_k$, we calculate the $G_k$ parameter using our models and the $M$-band GEMINI/NIRI data for GI 570D. Then we select all of the models with values of the $G_k$ parameter between $min(G_k)$ and $min(G_k) + 1$. This step gave us 131 models that best fit the $M$-band GEMINI/NIRI data for GI 570D. The $G_k$ parameters for these 131 models are distributed between 0.9899 and 1.9550.

The top-left panel of Figure 15 shows the observed $M$-band spectrum of GI 570D (Geballe et al., 2009) with red points, the observed NIRC spectrum of GI 570D (Burgasser et al., 2002) with black points, and the Spitzer IRS spectrum (Suárez & Metchev, 2022) with brown points. The range of fluxes covered by the 131 best-fitting models, to the $M$-band spectra, are reused for this, following the methodology of Sorahana & Yamamura (2012). The model among these 131 models that fits this shorter- and longer-wavelength data as well (has the least $G_k$) is taken to be the overall best-fit model from the grid. This model spectrum is shown in the top-right panel of Figure 15, and it has a $G_k$ value of 0.9899. This large difference between the $G_k$ values from the $M$-band data and the NIRC+IRS data is mainly because of the
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Figure 16. The top-left panel shows the observed \(M\)-band spectra of 2M 0415 with red points, the \(1–2.5 \mu m\) observations of 2M 0415 with black points, and the Spitzer IRS measurements with brown points. The flux values sampled by the top 101 models with the smallest \(G_t\) parameter after fitting the \(M\)-band spectra only are shown by the shaded blue region. The top-right panel shows the best-fit model obtained by fitting the \(M\)-band spectra, the \(1–2.5 \mu m\) data, and the Spitzer 5–14 \(\mu m\) data for 2M 0415. The bottom-left panel shows a comparison of the best-fit model with the \(M\)-band spectra only. The three bottom-right panels show, respectively, the \(T(P)\) profile of the best-fit model, the \(t_{\text{mix}}\) and \(t_{\text{chem}}\) of different quenched species as a function of pressure, and the rightmost panel shows the volume mixing ratios of CO, CH\(_4\), NH\(_3\), H\(_2\)O, CO\(_2\), and PH\(_3\).

large difference in the uncertainties in the fluxes from these two sets of observations.

The best-fit model has a \(T_{\text{eff}}\) of 725 K and a \(\log(g)\) of 5.0. The \(K_{cz}\) in the convective zone for this model is Moses, and the convective mixing length is \(0.1 \times H\). The \(M\)-band spectra of this model compared to the \(M\)-band data for Gl 570D are also shown in the bottom-left panel. The \(T(P)\) profile, mixing timescale and chemical timescales, as well as the mixing ratio profiles of various gases in this model are shown in the three bottom-right panels. The \(T(P)\) profile and the \(t_{\text{mix}}\) profile both show that this model has two convective zones. The \(t_{\text{chem}}\) and \(t_{\text{mix}}\) shown in the middle panel of the three bottom-right panels of Figure 15 also show that CO, CH\(_4\), H\(_2\)O, HCN, and NH\(_3\) are quenched in the sandwiched radiative zone for this best-fit model, whereas CO\(_2\) is quenched in the upper detached convective zone. The \(C_k\) value of this best-fit model is \(1.72 \times 10^{-19}\). The measured parallax of Gl 570D is 171.22 mas (Dupuy & Liu 2012). This corresponds to a distance (D) of 5.84 pc. We get a radius of 1.04 \(R_J\) for Gl 570D combining these values together. The radius of a brown dwarf with \(T_{\text{eff}} = 725 \text{ K and } \log(g) = 5.0\) can also be interpolated from evolutionary grids like the SONORA BOBCAT models (Marley et al. 2021). We find this interpolated radius to be 0.89 \(R_J\), which is somewhat smaller than our calculated radius. But as we also note in Section 3.4, these evolutionary tracks were computed assuming chemical equilibrium.

We use the same technique for fitting the AKARI \(M\)-band spectrum (Sorahana & Yamamura 2012) and the NIRC + Spitzer IRS spectrum (Burgasser et al. 2002; Suárez & Metchev 2022) of 2MASS J0415-0935 (2M 0415). The top-left panel of Figure 16 shows the \(M\)-band spectra of 2M 0415 with red points, the NICR measurements are shown with black points, and the Spitzer IRS measurements are shown with brown points. The \(\min(G_k)\) obtained by fitting the \(M\)-band spectra only is 0.8755, and the flux range covered by all of the models with \(G_k\) between 0.8755 and 1.8583 is shown with the blue shaded region in the top-left panel. These models were then used to obtain the best-fitting model with the shorter- and longer-wavelength data. The best-fit model has a \(G_k\) of 514.28. This model has a \(T_{\text{eff}}\) of 675 K and a \(\log(g)\) of 4.75. The \(K_{cz}\) in the radiative zone for this model is Moses, and the convective mixing length is \(0.1 \times H\). The measured parallax of 2M 0415 is 175.2 mas (Dupuy & Liu 2012), which corresponds to a distance of 5.707 pc. Combining this with the best-fit model \(C_k\) value (1.84 \(\times 10^{-19}\)) provides a radius of 1.05 \(R_J\) for 2M 0415. The interpolated radius from the SONORA BOBCAT grid for this object is 0.98 \(R_J\). This shows much better agreement with the calculated radius of the object compared to Gl 570D. The \(M\)-band spectrum of this best-fit model compared to the \(M\)-band data for 2M 0415 is also shown in the bottom-left panel. Atmospheric properties of the best-fit model are shown in the three bottom-right panels. This best-fit model has a second sandwiched radiative zone, and CO, CH\(_4\), H\(_2\)O, and HCN are quenched in this sandwiched radiative zone, whereas CO\(_2\) is quenched in the upper detached convective zone.
Miles et al. (2020) obtained $M$-band observations of the late T- and early Y-dwarfs WISE 0313, UGPS 0722, WISE 2056, and WISE 1541. However, these $M$-band spectra are not flux calibrated. Using photometry collected from various studies and the \texttt{SONORA} evolutionary tracks, Miles et al. (2020) found ranges of $T_{\text{eff}}$ and log($g$) values for these objects. We use our models along with these photometry data sets (see Table 2 in Miles et al. 2020 for photometry obtained from Gehalle et al. 2001; Golimowski et al. 2004; Knapp et al. 2004; Patten et al. 2006; Skrutskie et al. 2006; Lucas et al. 2010; Kirkpatrick et al. 2011, 2012; Leggett et al. 2013; Wright et al. 2014; Leggett et al. 2015; Schneider et al. 2015; Esplin et al. 2016; Luhman & Esplin 2016; Schneider et al. 2016; Leggett et al. 2017; Cutri et al. 2021) to find a similar range of $T_{\text{eff}}$ values for each of these sources. Figure 17 shows the map of $\chi^2$ values in a $T_{\text{eff}}$ versus log($g$) parameter space obtained by comparing our models with observed photometry of WISE 0313. It is clear that the $\chi^2$ values are sensitive to the $T_{\text{eff}}$ of models, but there is not much sensitivity to the log($g$) of the models. This method helps us in identifying a range ($\delta T = 100$ K) of $T_{\text{eff}}$ values for each object. Then using models within this $T_{\text{eff}}$ range, we try to determine the best-fit atmospheric model by comparing our model spectral shapes with the shape of the $M$-band spectra of these four objects. We use the same metrics $G_k$ and $C_k$ defined in Equations (4) and (5) for finding the best-fit models. However, as the observed spectra lack flux calibration, the $C_k$ now includes the $\alpha$ parameter as well, where $1/\alpha$ represents the unknown flux calibration of the observed spectrum. For each object, we use the models within the determined $T_{\text{eff}}$ ranges and allow all of the other parameters such as log($g$), radiative zone $K_{\text{zz}}$, and mixing length $L$ to vary while calculating the $G_k$ and $C_k$ values of the models using the $M$-band spectrum. Then, the model with the smallest $G_k$ value is chosen as the best-fit model for the object.

Figure 18 shows the results of this fitting exercise for all four objects. The four rows in Figure 18 show the results for WISE 0313, UGPS 0722, WISE 2056, and WISE 1541, respectively. The left columns show the best-fit spectra compared with the observational data for each object. The second column from the left shows the best-fit $T(P)$ profile for each object. The third column shows the best-fit mixing timescale and chemical timescale for CO as a function of pressure for these objects, and the fourth column depicts the best-fit volume mixing ratio for each object.

We find that the best-fit model describing the WISE 0313 and UGPS 0722 data has radiative zone quenching of CO/CH$_4$, whereas the best-fit model describing the WISE 2056 and WISE 1541 data has CO quenching in the convective zone. Table 1 shows the values of all of the parameters relevant to fitting the spectral data for all of these objects. We note that the best-fit log($g$) values obtained in this work are not from fitting any spectral shape/feature directly. As can be seen in Figure 5, log($g$) controls the presence/absence of a sandwiched radiative zone, which in turn dictates whether gases can be quenched in regions with low or high $K_{\text{zz}}$. These effects of log ($g$) on atmospheric chemistry lead to preference of certain log ($g$) values over others while fitting the data.

We choose our best-fit model to be the model with the smallest $G_k$ value, but we also find that there are quite a few models with $G_k$ values that differ from the minimum by only a small amount. This shows the presence of degeneracy in our models with the current precision of available data for these objects. This degeneracy will be broken with much higher-precision flux-calibrated $M$-band and shorter-wavelength spectra expected from JWST, which we discuss in Section 3.6.

### 3.5.3. Trends in Quench Timescales

We present the trend of the best-fit $K_{\text{zz}}$ at $P_G$ for CO in these sources in Figure 19. As we mainly fit the $M$-band spectra of these objects in our analysis, we are only sensitive to CO and H$_2$O abundances, and therefore, we can only fit the quench $K_{\text{zz}}$ of CO. Our best-fit quench $K_{\text{zz}}$ for CO as a function of the best-fit $T_{\text{eff}}$ for each object are shown with the red crosses in Figure 19. The best-fit quench $K_{\text{zz}}$ determined by Miles et al. (2020) are shown with the faded red crosses as a function of the best-fit $T_{\text{eff}}$ obtained by Miles et al. (2020) for each object. Although the overall trend of much lower $K_{\text{zz}}$ at the CO quench pressure than the theoretical maximum in objects with $T_{\text{eff}}$ between 600 and 800 K (found by Miles et al. 2020) still stands in this analysis, there are some differences in the best-fit $K_{\text{zz}}$ and $T_{\text{eff}}$ values between the two studies. These differences are due to multiple factors, which we discuss briefly here.

Our work uses RCE models that include disequilibrium chemistry self-consistently to fit the data, while equilibrium chemistry RCE models were post-processed by Miles et al. (2020).
to include quenching of gases to fit the data. The top-left panel of Figure 2 shows that including disequilibrium chemistry self-consistently can lead to large changes in the $T(P)$ profile of brown dwarfs compared to equilibrium chemistry models. This can be the reason behind the $\sim$50 K differences in the $T_{\text{eff}}$ values for these objects between the two studies. For five of the six analyzed objects in this work, our assessment of CO quenched $K_{\text{zz}}$ is somewhat smaller than previously found. As some of our best-fit
models have higher $T_{\text{eff}}$ than the best-fit models of Miles et al. (2020), CO is more abundant in the deeper atmosphere of our best-fit models than those of Miles et al. (2020). Figure 2 shows that CO abundance falls very rapidly with decreasing pressure in the deep atmosphere (which is under chemical equilibrium) in these colder brown dwarfs. Therefore, colder best-fit models in Miles et al. (2020) need to quench CO deeper in the atmosphere than our hotter best-fit models. So, the best-fit models presented in Miles et al. (2020) need higher CO quenched $K_{zz}$ compared to our best-fit models to produce the same CO abundance in the upper well-mixed atmosphere of these brown dwarfs. Additionally, the best-fit $K_{zz}$ presented in Miles et al. (2020) has been shown to be dependent on the gravity of the model used for fitting the data. In this work, we allowed gravity to be a free parameter while fitting the data, and compared our best-fit $K_{zz}$ in Figure 19 with the median $K_{zz}$ obtained by Miles et al. (2020) by trying out various values of log(g).

We can use our best-fit models with CO quenching to infer the quenched $K_{zz}$ of other quenched gases like CO$_2$, NH$_3$, or HCN in these best-fit models. The inferred quenched $K_{zz}$ values for the other gases in these objects are also shown in Figure 19. As each gas has a different $t_{\text{chem}}$, they are also quenched at different depths of the brown dwarf atmosphere, as shown in Figures 7 and 9 for CO and CO$_2$. This means that measuring the abundance of each gas can help us in measuring the height-dependent $K_{zz}$ profile in these brown dwarf atmospheres. For example, in Figure 19, the inferred quenched $K_{zz}$ for CO$_2$ are very different than the inferred quenched $K_{zz}$ of CO (or NH$_3$), as CO$_2$ is quenched at different pressures (having different mixing strengths) compared to CO. But inferring the height-dependent $K_{zz}$ profile of a single brown dwarf by using different gases as probes of $K_{zz}$ at different pressures is only possible with self-consistent disequilibrium chemistry models with height-dependent $K_{zz}$ profiles, such as the model grid presented in this work.

The theoretical maximum limit on the convective zone $K_{zz}$ for each best-fit model is also shown by the black points in Figure 19. This maximum limit on convective $K_{zz}$ was calculated using Equation (2) with the convective heat flux fixed at $\alpha T_{\text{eff}}$ and the mixing length $L$ fixed at the scale height of the atmosphere. It is clear from Figure 19 that all of the gases in all of these objects quench at lower $K_{zz}$ than this theoretical limit. But even though all of the objects analyzed in this work have much smaller CO quenched $K_{zz}$ than the maximum convective limit (shown with the black line), this does not mean that all of these “quenchings” occurred in the radiative zones in our models. For Gl 570D, 2M 0415, W0313, and UGPS 0722, CO is quenched in the radiative zones in our best-fit models, but W 2056 and W 1541 CO, along with all of the other molecules, are quenched in the convective zone with a much smaller mixing length than the scale height of the atmosphere, as was also suggested by the CMD analysis detailed in Section 3.4.

Finally, we note that our best-fit models, especially for objects that lack flux-calibrated spectra, are often degenerate with the present data, and better data from observatories like JWST will be instrumental in giving us better constraints on the $K_{zz}$ of these objects, which we discuss next.

### 3.6. Constraining Radiative Zone $K_{zz}$ with JWST

An important takeaway from Miles et al. (2020) and our work is that detailed analysis of atmospheric abundances can constrain $K_{zz}$ in brown dwarf atmospheres. There is strong evidence for mixing orders of magnitudes weaker than expectations from free convection with $L = H$. The launch of JWST begs the question of whether JWST data will be able to give us better constraints on the vigor of vertical mixing in these atmospheres. We can provide a test by simulating the JWST spectra using the JWST Exposure Time Calculator (Pontoppidan et al. 2016) with some of the emission spectra from our model grid. As an illustrative example, we use the spectrum of a 700 K object. In the left panels of Figure 20 we examine three models at log(g) = 3.6, with the radiative zone $K_{zz}$ is “Moses × 100,” “Moses,” and “Moses/100” and $L = H$. We assume that the source has a radius of 1R$_J$ and is at a distance of 5 pc. The temperature and distance chosen for this exercise are somewhat representative of objects like Gl 570D and 2M 0415.

The NIRSpec panels (which are three of the four figures) assume fixed slit mode with the G395M grating and the F290LP filter for these simulations. The results are impressive, with only a total of 10.39 minutes exposure time, simulated with 10 groups per integration, two integrations per exposure, and five exposures. It is clear from the top-left panel that the radiative zone $K_{zz}$ can be constrained to high precision with a total of ~10 minutes exposure time per object in this JWST observing mode. This time includes all five exposures used for this simulation. In order to emphasize the difference arising in the synthetic counts from the three models in the 4.5–5 μm range, the bottom-left panel shows a zoomed-in view of the 4.5–5 μm wavelength range, focusing on CO absorption, where the main sensitivity of the data to radiative zone $K_{zz}$ lies. The top-right panel shows a lower-gravity model (log (g) = 4.5), where a lower-pressure photosphere favors CO at the expense of CH$_4$. Here the blue model is simulated from a model where

### Table 1

| Source     | $T_{\text{eff}}$ Range(K) | Best-fit $T_{\text{eff}}$(K) | Best-fit log(g) | Radiative $K_{zz}$ | Convective L | $M$-band $G_k$ | J−H−K+SpitzerRS $G_k$ | $C_k$ |
|------------|---------------------------|-------------------------------|-----------------|---------------------|--------------|----------------|------------------------|------|
| Gl 570D   | 700–800                   | 725                           | 5.0             | Moses               | 0.1 $\times$ H | 1.414          | 669.06                 | 1.72 $\times$ 10$^{-19}$ |
| 2M 0415   | 600–700                   | 675                           | 4.75            | Moses               | 0.1 $\times$ H | 0.925          | 514.28                 | 1.84 $\times$ 10$^{-19}$ |
| WISE 0313 | 575–675                   | 675                           | 4.75            | Moses/100          | 0.1 $\times$ H | 3.849          | ...                    | 6.477 |
| UGPS 0722 | 500–600                   | 575                           | 4.75            | Moses $\times$ 100 | 0.1 $\times$ H | 23.884        | ...                    | 11.636 |
| WISE 2056 | 450–550                   | 525                           | 4.75            | ...                | 0.1 $\times$ H | 6.651          | ...                    | 14.575 |
| WISE 1541 | 400–450                   | 450                           | 4.75            | ...                | 0.1 $\times$ H | 5.243          | ...                    | 20.275 |

Note. The radiative zone $K_{zz}$ for models that do not quench at radiative zones are marked with a “−” as they could not be constrained.
the convective mixing length $L = H$, whereas the salmon-colored data is simulated from a model where the convective mixing length is $L = 0.1 \times H$. The radiative zone $K_{zz}$ of both the cases in this panel is "Moses $\times 100." Both of these models have the quenching of all relevant gases occurring in the convective zone. The large differences in the synthetic counts between the two models in the 3.5–4.25 $\mu$m range show that JWST data can also be used to probe differences in the convective zone $K_{zz}$ with exposure times of $\sim 10$ minutes.

Radiative and convective zone $K_{zz}$ can be probed with other wavelengths as well. The bottom-right panel in Figure 20 shows the simulated spectrum of the two cases shown in the top-right panel but when observed by the MIRI instrument. The MIRI LRS mode was used for this data simulation along with a 60 minute exposure time. Differences between the two model spectra arise between 5 and 9 $\mu$m. A comparison with Figure 1 shows that these differences mainly arise from different CH$_4$, H$_2$O, and NH$_3$ abundances due to differences in the convective zone $K_{zz}$.

4. Discussion

4.1. PH$_3$ Quenching

Under chemical equilibrium conditions, the major phosphorus-bearing molecule PH$_3$ is expected to be removed by oxidation at low temperatures in the visible atmospheres of giant planets and colder brown dwarfs. A number of oxidation products have been considered (see Visscher 2020), including P$_2$O$_6$ (e.g., Fegley & Lodders 1994; Visscher et al. 2006), P$_3$O$_6$ (Borunov et al. 1995), H$_3$PO$_4$ (Wang et al. 2016), or condensation of NH$_3$H$_2$PO$_4$ (Fegley & Lodders 1994; Visscher et al. 2006; Morley et al. 2018). Following the work of Visscher & Fegley (2005), Visscher et al. (2006), and Miles et al. (2020), as a representative example of PH$_3$ oxidation, we may consider the conversion of PH$_3$ into P$_2$O$_6$ via the net thermochemical reaction,

$$P_2O_6 + 12H_2 \rightarrow 4PH_3 + 6H_2O.$$  

However, the $t_{chem}$ of PH$_3$→P$_2$O$_6$ is such that it can be quenched in the deeper atmosphere, leading to a large enhancement of PH$_3$ in the photosphere. This effect makes PH$_3$ the major phosphorus-bearing gas in atmospheres of Jupiter and Saturn (Lodders 2004; Visscher & Fegley 2005). PH$_3$ is expected to be found in colder brown dwarfs as well (Visscher et al. 2006; Morley et al. 2018).

Due to the expected small affect of P-bearing molecules on brown dwarf temperature structures, we did not include PH$_3$ as a molecule to be mixed on-the-fly for converging to a final atmospheric state. However, in order to test the effect of PH$_3$ on the emergent thermal emission spectra, we post-process our converged disequilibrium chemistry model with quenched PH$_3$ abundance. The $t_{chem}$ for PH$_3$→P$_2$O$_6$ is given by Visscher & Fegley (2005),

$$t_{chem} = \frac{1.9 \times 10^{12}}{[OH]} \exp\left(\frac{6013.6}{T}\right)s$$  

where [OH] represents the number density of OH molecules in units of cm$^{-3}$. With our converged disequilibrium chemistry modules, we calculate the mixing ratio of OH molecules using (Visscher & Fegley 2005),

$$X_{OH} = \frac{KX_{H_2O}\sqrt{X_{H_2}}}{\sqrt{P}}$$  

where $X_{OH}$, $X_{H_2O}$, and $X_{H_2}$ represent the volume mixing ratios of each of these components, and $P$ represents the pressure in bars. The constant $K$ is temperature dependent and based on fits to thermodynamic data, and is given by,

$$K = 3.672 - \frac{14791}{T}$$
where $T$ is the temperature in kelvin. Using Equations (7), (8), and (9), we determine the $t_{chem}$ of PH$_3$ for all of our converged models. Then using our converged $t_{mix}$ profiles, we determine $P_Q$ for PH$_3$ and quench it, creating another set of our models that has quenched PH$_3$ abundances. Using these modified chemical compositions, we create another set of thermal emission spectra models with quenched PH$_3$ abundances.

Figure 21 compares the differences in spectra caused by the quenching of PH$_3$ with disequilibrium models where PH$_3$ is not quenched. This quenching of PH$_3$ increases the PH$_3$ volume mixing ratios dramatically, from $<10^{-30}$ under chemical equilibrium, to $\sim10^{-6}$–$10^{-7}$ due to quenching. The main impact of this increase appears between 4 and 4.5 $\mu$m in the thermal emission spectrum, as shown in Figure 21. This also

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**Figure 20.** Simulated data from JWST instruments are shown for one of our model brown dwarfs with $T_{eff}$ of 700 K. The three colors in the simulated data correspond to models with different radiative zone $K_{zz}$. The top-left panel shows the simulated NIRSpec spectra of a log (g) = 5.5 object with an exposure time of 10 minutes, while the bottom-left panel shows a zoomed version of the top-left panel to emphasize how JWST NIRSpec M-band observations can clearly distinguish between different $K_{zz}$ in the radiative zones for these T-dwarfs. The top-right panel shows the NIRSpec simulated data for a brown dwarf with $T_{eff}$ of 700 K and log(g) of 4.5. The two colors represent different $K_{zz}$ in the convective zone but the same $K_{zz}$ in the radiative zone. The bottom-right panel shows MIRI LRS simulated data for the same models shown in the top-right panels. To compare the differences between the simulated data from different models to the typical JWST noise, the ratio of the flux differences ($\delta F$) between various models and the simulated JWST noise ($N$) is shown below each of these panels. This shows that both convective and radiative zone $K_{zz}$ can be constrained with JWST.
suggests that PH₃ may become an important enough atmospheric opacity source to have a small effect on their T(P) profiles as well, which we will aim to explore in future work.

Figure 22 shows the parameter space of models where PH₃ quenches at the radiative and convective zones for different levels of radiative zone \( K_{zz} \) when the convective mixing length is \( H \). This also shows that depending on the properties of the object in question, PH₃ can also be used as a probe for determining radiative or convective zone \( K_{zz} \). The region around 4.0–4.4 \( \mu m \) is difficult to probe from the ground (Miles et al. 2020), but it is clear from Figure 21 that these PH₃ should be readily detectable with JWST. Interestingly, Morley et al. (2018) did not detect PH₃ between 4.0 and 4.4 \( \mu m \) in WISE 0855, even though it is theoretically expected to be present in its atmosphere. Determining the strength of these features, or their absence, will have important implications in understanding \( K_{zz} \) and phosphorus chemistry.

4.2. Clouds

The models presented in this work are cloud-free. However, H₂O condensation in the upper atmospheres of objects can begin at \( T_{eff} \lesssim 450 \) K (Morley et al. 2014), and these clouds can start becoming an important opacity source colder than \( \sim 400 \) K (Morley et al. 2014). Once water clouds become optically thick, they can change the overall energy balance of
the atmosphere impacting the $T(P)$ profile. The presence of disequilibrium chemistry causes a cooling down of the upper atmosphere, compared to equilibrium chemistry, but the opacity of clouds has the opposite effect of heating up the $T(P)$ profile.

Importantly, the cloud particle size and vertical extent are also quite sensitive to the mixing parameter $K_{zz}$, as mixing helps to keep cloud particles aloft against their gravitational settling (Ackerman & Marley 2001). Cloud particle sizes are an extremely important parameter in dictating their scattering properties (Ackerman & Marley 2001; Mukherjee et al. 2021), and hence, $K_{zz}$ has a large effect on the cloud opacities in these atmospheres. Therefore, it is clear that information about $K_{zz}$ gleaned from disequilibrium chemistry studies will be important in improving cloud models. Future studies should aim for a self-consistent treatment of disequilibrium chemistry and cloud formation with a self-consistent treatment of $K_{zz}$ within a given model atmosphere. Recently, Mang et al. (2022) showed that water clouds have a large impact on the $M$-band spectra of colder Y-dwarfs, with $T_{\text{eff}} \leq 400$ K, just below the lower $T$ edge of our study. Somewhat differently than in this work, Mang et al. (2022) calculated the radiative zone $K_{zz}$ needed for cloud modeling, by setting the mixing length to one-tenth of the scale height in the radiative zones. This approach also leads to smaller $K_{zz}$ in the radiative zones compared to the convective zones. When we extend our disequilibrium chemistry model to colder objects, inclusion of clouds in this framework is an important milestone.

5. Summary and Conclusion

In this work, we have used a newly developed Python-based 1D RCE model with the capability to self-consistently capture disequilibrium chemistry in brown dwarf and exoplanetary atmospheres. Using this model, we have created a self-consistent grid of brown dwarf models between $T_{\text{eff}}$ of 400 and 1000 K with an increment of 25 K and $\log(g)$ of 4.5–5.5 with an increment of 0.25. Instead of using a constant $K_{zz}$ prescription throughout the entire atmosphere, as was done in earlier work (e.g., Phillips et al. 2020; Karalidi et al. 2021), or self-consistent $K_{zz}$ in the convective zones and constant $K_{zz}$ in the radiative zones (e.g., Hubeny & Burrows 2007), we use a self-consistent $T(P)$ structure-dependent $K_{zz}$ profile for the entire atmosphere for our grid. In the convective zone, we use mixing length theory with two different mixing lengths, whereas in the radiative zones, we use various multiples of a $T$- and $P$-dependent $K_{zz}$ prescription. The idea behind these models was to assess whether disequilibrium chemical abundance can be used as a probe for temperature structure and mixing processes below the visible atmosphere in brown dwarfs. With this grid in hand, we conclude with the following points.

1. As found by others, a self-consistent treatment of disequilibrium chemistry causes cooling of $T(P)$ profiles, especially in the upper atmospheres of late T- and early Y-dwarfs.

2. Post-processing equilibrium chemistry models by quenching various molecules instead of using self-consistent models with disequilibrium chemistry should be avoided because this can lead to significant errors in the calculated abundances of molecules like CO, CH$_4$, and NH$_3$. This can also lead to incorrect $T(P)$ profiles.

Both of these results are especially relevant in the JWST era with significantly higher S/N mid-infrared data.

3. Self-consistent models including disequilibrium chemistry also show a large change in the location, depths, and number of radiative and convective zones in brown dwarfs compared to self-consistent models with equilibrium chemistry.

4. Depending on the strengths of radiative zone $K_{zz}$ and convective mixing length, gases like CO, CH$_4$, NH$_3$, CO$_2$, and PH$_3$ can be quenched in the radiative zones of brown dwarfs in a large fraction of the $T_{\text{eff}}$ and $\log(g)$ parameter space.

5. Different molecules have different $t_{\text{chem}}$ values, which leads them to quench at different pressure levels. This means that some molecules may quench in radiative zones, while others may quench in convective zones, in the same atmosphere, such that different molecules may be quenched by very different $K_{zz}$ values.

6. The $M$-band thermal spectra of objects where radiative zone quenching occurs are very sensitive to the $K_{zz}$ in the radiative zones. This can lead to nonmonotonic behavior in the CO abundance and spectra as a function of $T_{\text{eff}}$. This is especially exciting because it provides an avenue to observationally constrain the highly uncertain radiative zone $K_{zz}$ in these objects.

7. The mid-infrared photometric bands—MKO $L'$ and MKO $M$, and WISE 1 and 2—are quite sensitive to the $K_{zz}$ in the radiative zone. We also find that our models provide a better fit to the infrared photometry of these objects than chemical equilibrium models.

8. We use our models to fit the $M$-band spectra of six brown dwarfs: Gliese 570D, 2MASS J0415-0935, WISE 0313, UGPS 0722, WISE 2056, and WISE 1541. We determine the best-fit atmospheric state for these objects including the quench level $K_{zz}$ of quenched gases in these objects. Similar to Miles et al. (2020), we also find that these objects have $K_{zz}$ much smaller than the theoretical convective mixing limit. We also see that the best-fit quench $K_{zz}$ in these objects are very low between $T_{\text{eff}}$ of 675 and 800 K, while they show an increase with lowering $T_{\text{eff}}$ for objects with $T_{\text{eff}}$ below 575 K.

9. By performing some S/N calculations for JWST, we conclude that short exposure time observations can provide us with excellent measurements of the radiative and convective zone $K_{zz}$ in brown dwarfs.

10. We also expect JWST to find clearly detectable disequilibrium PH$_3$ abundances in the atmospheres of these objects.

The nonmonotonic behavior of atmospheric chemistry, as a function of $T_{\text{eff}}$ and $\log(g)$, found in this work indicates the need to explore these effects with even finer grid spacing than this work in parameters like $T_{\text{eff}}$ (25 K in this work), $\log(g)$ (0.25 dex in this work), and $K_{zz}$ (factor of 100 in this work). This remains the focus of a future model grid release. The model presented in this work will be updated to include self-consistent clouds in the near future. Additional future work will couple the code to the chemical kinetics model VULCAN (Tsai et al. 2017, 2021), which will enable a more rigorous self-consistent treatment of disequilibrium chemistry in our models. This will also allow us to include effects like the feedback of the disequilibrium abundances of gases like CH$_4$ on the entire chemical network of the atmosphere within our models, self-
consistently. This will also allow us to explore the empirical trends we find in this work, like probable slower convective mixing than typically calculated assuming free convection, more robustly. Moreover, such a coupling opens up the possibility to explore both photochemistry and vertical mixing together self-consistently, which is more relevant for irradiated exoplanets. This updated model will then be used to explore effects of vertical mixing and photochemistry for warm transiting giant planets and find additional observables to constrain $K_{zz}$ in such planets, an important comparison sample to the nonirradiated objects explored here.

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Software: PICASO 3.0 (Mukherjee et al. 2022), PICASO (Batalha et al. 2019), pandas (McKinney 2010), NumPy (Walt et al. 2011), IPython (Pérez & Granger 2007), Jupyter (Kluyver et al. 2016), matplotlib (Hunter 2007). The model grid presented in this work is publicly available via Zenodo with the DOI:10.5281/zenodo.7076995.

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