Chroma+GAS: An Expedited Solution for the Chemical Equilibrium for Cool Stellar Atmospheres

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ABSTRACT

We describe a unique approach to economizing the solution to the general chemical equilibrium and equation-of-state problem for late-type stars, including diatomic and polyatomic molecules, that is fast, accurate, and suitable for responsive approximate data modelling applications, and to more intensive modelling approaches in which the calculation of the gas equilibrium must be expedited to allow other aspects to be treated more realistically. The method, based on a novel economization of the Newton's method of solution of the linearized Saha and conservation equations, has been implemented in Python and made available as a stand-alone package, GASPy, and has been integrated into the interactive Python atmosphere and spectrum modelling code ChromaStarPy. As a result, ChromaStarPy now computes the state of the gas, the number density of absorbers, and the surface flux spectrum, with consistent inclusion of 105 chemical species, including 34 diatomic, and 16 polyatomic, neutral molecules, as well as H^- and H_2^+, as well as many neutral and ionized atomic species. The economized method converges very rapidly and greatly improves the code's relevance to late-type stellar and brown dwarf spectrum modelling. We provide a brief overview of the GAS methodology, and present some illustrative results for the chemical equilibrium and spectrum for an M-type bright giant and dwarf, and a comparison to results of the PHOENIX/PPRESS package. All codes are available from the OpenStars www site: www.ap.smu.ca/OpenStars.

Subject headings: Stars: atmospheres, abundances, late-type Physical Data and Processes: astrochemistry, equation of state, opacity

1.   Introduction

A proper treatment of the coupled molecular chemical equilibrium, ionization equilibrium, and equation of state (EOS) that includes polyatomic as well as diatomic molecules is crucial for the computational modelling of late-type stellar atmospheres and spectra for two main reasons. 1) Molecule formation, especially that of H_2, CO, and N_2 in stars for which $N_C/N_O < 1$, can significantly deplete the supply of atomic species, thus affecting the ionization equilibrium and the free electron partial pressure, p_e, and the mean molecular weight, μ.

2) The electron pressure, needed to determine the ionization equilibrium depends, in cool stellar atmospheres, on a fairly large number of low-abundance, easily-ionized metal elements. These elements need to be included for an accurate solution of the ionization balance. 3) The strength of electronic and ro-vibrational molecular bands in the visible and near-IR emergent spectrum, F_λ, is sensitive to the equilibrium concentration of trace species, some of which give rise to spectral features that are MK classification diagnostics, such as TiO, VO, and CH. Therefore, for modelling the spectral line-forming regions of G, K, and M stars it is necessary to solve self-consistently the general coupled chemical equilibrium and EOS problem in the temperature range $\sim$1000 to $\sim$6000 K, and the total gas pressure range $\sim$10 to $\sim 10^5$ dyne cm^{-2}.

We describe a novel, fast, accurate general procedure, GAS, for quickly computing the self-consistent chemical equilibrium and ionization equilibrium of a gas of typical stellar composition, for the specified state variables of temperature and pressure. The elemental abundances and chemical species included in the solution are specified by an input file listing the species, the abundance of each element, and relevant atomic and molecular data for each species. The current implementation of the routine in GASPy solves the chemical

equilibrium problem for 105 species, including the first two or three ionization stages of 25 elements, H^-, 34 neutral diatomic molecules, H_2^+, and 16 neutral polyatomic molecules, and the corresponding EOS. GAS solves the completely linearized ionic and molecular Saha equations for the coupled ionization and molecular equilibrium by iterating these equations to convergence using the multi-dimensional Newton's method, and is a major module in the ATHENA stellar atmospheric modelling code. However, to date, GAS and ATHENA have only been described in university-archived theses (Bennett (1983), Bennett (1991)), although the Spectroscopy Made Easy (SME) package of Valenti & Piskunov (1996) was also based on the original GAS code of Bennett (1983).

There are other codes that solve the general chemical equilibrium and EOS problem, such as PPRESS (V15), the EOS module of version 15 of the PHOENIX stellar atmosphere and spectrum modelling code (Allard & Hauschildt (1995)), which is written in FORTRAN and uses the multi-dimensional Newton method to solve the linearized, coupled, ionic and molecular Saha equations for the partial pressures of 622 species, and FastChem (Stock *et al.* (2018)), written in C++, which employs a method based on decomposing the equations for the law of mass action and element conservation into a set of coupled non-linear equations that each have one variable. However, GAS has the advantage of being very fast because of its unique approach to economizing the solution, and is suitable for more interactive environments such as the Python integrated development environment (IDE), which allow a user to more quickly extract approximate results from fitting observed spectra. Moreover, 3D hydrodynamic atmospheric and radiative transfer codes such as that described in Freytag *et al.* (2012) must economize every other aspect of the gas equilibrium solution given the computational intensity of the problem, in which the abundance of absorbers must be calculated at $\sim 10^6$ 3D spatial grid points.

We have ported GAS from FORTRAN to Python and have integrated it into ChromaStarPy (CSPy, DOI: zenodo.1095687), an approximate general stellar atmospheric and spectrum modelling code written in Python and described by Short, Bayer & Burns (2018) and papers in that series. CSpy, now equipped with GAS, is comparable to the Spectroscopy Made Easy (SME) package described in Valenti & Piskunov (1996) and Piskunov & Valenti (2017). However, SME is a package for the Interactive Data Language (IDL) environment that was common on Unix workstations, and pre-dates the rise of Python as a common astronomical research environment. The Python version of CSPy is also available as a separate stand-alone application, GASPy. Both codes are available from the OpenStars www site: www.ap.smu.ca/OpenStars.

In Section 2, we provide an overview of the problem of determining the chemical equilibrium of a gas of stellar composition that handles regimes ranging from gas temperatures cool enough for molecules to form, to conditions warm enough that ionization occurs. We derive the equations that provide a general description of the state of this gas.

In Section 3 we describe the economized, linearization method for solving the chemical equilibrium problem, and provide an approach to obtain sufficiently accurate initial estimates to ensure convergence of the linearization method.

In Section 4 we describe related improvements to CSPy that are enabled by a more realistic chemical equilibrium treatment, in Section 5 we present sample equilibrium results and a comparison to the equilibrium computed with Phoenix and PPRESS, and in Section 6 we describe future work suggested by this development.

2. The GAS chemical equilibrium procedure

2.1. Introduction and Basic Equations

The GAS routine solves the chemical and ionization equilibrium problem for a gas of stellar composition in thermodynamic equilibrium at temperature T and pressure p. This requires solving the combined molecular and ionic Saha equations for the specified chemical species and ionization states. As an example, consider the chemical equilibrium responsible for the dissociation of the water vapor molecule H_2O into its constituent atoms:

$$H_2O \rightleftharpoons 2H + O \tag{1}$$

Then, the partial pressure of the constituents is related by a Saha equation of the form

$$K_{H_2O} = p_H^2 \, p_O / p_{H_2O} \tag{2}$$

and so

$$p_{H_2O} = p_H^2 \, p_O / K_{H_2O}. \tag{3}$$

The latter equation expresses the partial pressure of the molecular species H_2O in terms of the partial pressure of the constituent neutral atoms comprising that molecule.

Similarly, consider the ionization equilibrium of carbon,

$$C = C^+ + e^- \tag{4}$$

which implies that the partial pressure of a "parent" neutral species, such as C, can be related to the partial pressure of the singly-ionized form, C^+, and the electron pressure p_e, by a Saha equation of the form

$$I_{C^+} = p_{C^+} \, p_e / p_C \tag{5}$$

and

$$p_{C^+} = I_{C^+} \, p_C / p_e. \tag{6}$$

The equilibrium constants here, $K_{\mathrm{H_2O}}$ and $I_{\mathrm{C^+}}$, are functions of temperature only, assuming the equation of state can be represented by an ideal gas. Specifically, for a neutral atom X that ionizes to X^+, with the release of a free electron

$$X = X^+ + e^- \tag{7}$$

and the ionization equilibrium constant I_{X^+} has the standard Saha form given by

$$I_{X^+} = p_{X^+}\, p_e / p_X = \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} kT \left(\frac{2Q_{X^+}}{Q_X}\right) e^{-\chi_I/kT} \tag{8}$$

where k is the Boltzmann constant, h is the Planck constant, m_e is the electron mass, χ_I is the ionization energy of the neutral atomic species X, and Q_X, Q_X^+ are the internal partition functions of X and X^+. These partition function values are read from a user-supplied file ``gasdata''. This expression for the ionization equilibrium constant can be conveniently written in logarithmic form as

$$\log I_{X^+} = 2.5 \log T - 0.48 + \log(2Q_{X^+}/Q_X) - (5039.9/T)\chi_I \tag{9}$$

These examples demonstrate the molecular and ionic Saha equations which couple the partial pressures of the neutral atoms and the electron pressure to the molecular and ionic partial pressures. We now generalize these examples to include the arbitrary molecular dissociation and ionization equations that may occur between any constituent species of the gas in thermodynamic equilibrium. We also develop some nomenclature necessary for this task.

In what follows the index n refers to any arbitrary species in the gas other than free electrons, including atoms, ions, and molecules, and the index k refers to the neutral free atomic species of element k. Then the total gas pressure, p is just the electron pressure p_e and the sum of all the partial pressures p_n of all the constituent species present in the gas:

$$p = p_e + \sum_n p_n \tag{10}$$

Species n may carry a charge, i.e., be an ion, and so we define n' to be the index of the neutral "parent" species corresponding to ionic species n. For example, if species n is the H_2^+ ion, then n' refers to the H_2 molecule. If n is already neutral, then $n' = n$.

The equilibrium constant I_n involving species n, as defined by the ionic Saha equation, is then

$$I_n = p_n\, p_e^{q_n}/p_{n'} \tag{11}$$

so that for any species n,

$$p_n = I_n\, p_{n'}/p_e^{q_n} \tag{12}$$

where q_n is the charge (ionization state) of species n.

Now consider the dissociation of composite species AB into the component species A and B.

$$\mathrm{AB} \rightleftharpoons \mathrm{A} + \mathrm{B} \tag{13}$$

Here A and B may be single atoms, but may also be simpler molecules of the combined species AB, e.g., $H_2O \rightleftharpoons OH + H$.

The equilibrium constant K_{AB} for the dissociation of species A and B into the combined species AB can be written, following the general Saha equation, as

$$K_{\mathrm{AB}} = \frac{p_{\mathrm{A}} p_{\mathrm{B}}}{p_{\mathrm{AB}}} = f(T)\frac{Q_{\mathrm{A}} Q_{\mathrm{B}}}{Q_{\mathrm{AB}}} e^{-E_{\mathrm{AB}}/kT} \tag{14}$$

where the translational partition function, $f(T)$ is given by

$$f(T) = \left(\frac{2\pi m k T}{h^2}\right)^{3/2} kT \tag{15}$$

and $Q_{\mathrm{A}}, Q_{\mathrm{B}}, Q_{\mathrm{AB}}$ are the internal functions of the respective species, $p_{\mathrm{A}}, p_{\mathrm{B}}, p_{\mathrm{AB}}$ are the respective partial pressures, $m = m_{\mathrm{A}} m_{\mathrm{B}}/m_{\mathrm{AB}}$ is the reduced mass of the combined species AB, and E_{AB} is the dissociation energy into the ground states of A and B. The ionization equilibrium of equation 8 is just a special case of this with $\mathrm{A} = \mathrm{X}^+$ and $\mathrm{B} = e^-$.

Now for a particle, i.e., an atom, ion, or molecule of species n, we define N_n to be the total number of atoms present in that species. For example, if n referred to water, H_2O, then $N_n = 3$, whereas if n referred to neutral atomic hydrogen, H, then $N_n = 1$. We further define the quantity N_{nk} to be the number of atoms of element k present in a particle of species n in a molecule of species n. For example, again referring to species n of water, H_2O, and let element k refer to H, then $N_{nk} = 2$, since there are 2 atoms of H in a molecule of H_2O. We also let n_k be the index of the k-th element present in species n.

Since A and B can be any species, by repeated application of equation 14, the equilibrium constant K_n

$$K_n = \left(\prod_k p_{n_k}^{N_{nk}} \right) / p_n \qquad (16)$$

can be found for the complete dissociation of any neutral species n into its constituent neutral atoms in terms of the molecular partition functions and dissociation energies. To evaluate the equilibrium constants, Irwin (1981) fit low-order polynomials in $\ln T$ to the partition functions, Q, of molecules of astrophysical interest. The equilibrium constants, K, can then be evaluated analytically in terms of the parametrized Q values.

We adopt the simpler approach of Tsuji (1973) here and represent the values of the molecular equilibrium constants K_n by 4th-degree polynomial approximations in $\theta = 5039.9/T$. The necessary atomic and molecular data to determine the equilibrium constants I_n and K_n, including the coefficients of the Tsuji (1973) polynomials used to approximate K_n, are read from a file supplied with the GASPy code distribution.

Then, for any neutral atomic or molecular species, n, equation 16 can be solved to obtain the partial pressure p_n of species n

$$p_n = \left(\prod_k p_{n_k}^{N_{nk}} \right) / K_n \qquad (17)$$

Combining this result with the ionization equation 12, relating ionic partial pressures to

those of the neutral parent species, we obtain the partial pressure of any species n in terms of the elemental partial pressures p_k and electron pressure p_e.

$$p_n = \frac{I_n}{K_n p_\mathrm{e}^{q_n}} \prod_k p_{n_k}^{\mathrm{N}_{nk}} \tag{18}$$

Finally, we define the fictitious partial pressure of p_k^* to be the value of the partial pressure p_k if all molecules were fully dissociated and all atomic species were in the neutral state. We also define the fictitious total pressure p^* to be the total pressure if all molecules were fully dissociated and all atomic species were in the neutral state. Then,

$$p^* = \sum_k p_k^* \tag{19}$$

and for each neutral element k, the abundance α_k is

$$\alpha_k = p_k^*/p^* = \frac{\sum_n N_{nk} p_n}{\sum_n N_n p_n} \tag{20}$$

where p_k^* is the fictitious partial pressure of element k.

We are now in a position to state the equations needed to define the numerical problem of determining the equilibrium partial pressures of each species. Multiplying equation 20 by the right-hand side denominator,

$$\alpha_k \sum_n N_n p_n - \sum_n N_{nk} p_n = 0 \qquad \text{or} \tag{21}$$

$$\sum_n (\alpha_k N_n - N_{nk}) p_n = 0, \qquad k = 2, \cdots, K \tag{22}$$

where the last equation 22 expresses conservation of atoms of element k, for each of the total of K elements considered in the equilibrium solution. The equation for $k = 1$ (usually H) is omitted from the equation set because it is not linearly independent of the other $K - 1$ equations, since

$$\sum_n \alpha_k = 1 \tag{23}$$

Charge neutrality provides another equation: the sum of all partial pressures of charged species must be zero.

$$\sum_n p_n q_n - p_e = 0 \tag{24}$$

There is one final constraint: the total of all the partial pressures of the constituent species n must equal the total pressure p.

$$p_e + \sum_n p_n = p \tag{25}$$

From equation 24, this becomes

$$\sum_n p_n q_n + \sum_n p_n = p \tag{26}$$

$$\text{or} \quad \sum_n p_n(q_n + 1) = p \tag{27}$$

Equations 22, 24, and 27 define the problem, along with equation 18, which expresses the partial pressure of each species in terms of the partial pressures of the neutral atomic elements p_k, for $k = 2, \cdots, K$. This gives us a total of $K + 1$ equations. The unknowns are the K partial pressures p_k of the neutral atomic form of the elements included in the equilibrium, and the electron pressure p_e, for a total of $K + 1$ unknowns. The molecular equilibrium problem is therefore well-posed.

Summary of definitions in this section:

$n \equiv$ index denoting arbitrary chemical species in equilibrium gas

$k \equiv$ index of neutral free atomic species in elemental form

$n_k \equiv$ index of the k-th element present in species n

$n' \equiv$ index of the neutral "parent" species of ionized species n

$p_n \equiv$ partial pressure of species n

$p_k \equiv$ partial pressure of neutral, free atomic species k

$p_k^* \equiv$ fictitious partial pressure of element k

$p_e \equiv$ electron pressure

$p \equiv$ total gas pressure, including electron pressure

$p^* \equiv$ fictitious total pressure = pressure if all species (excluding p_e) dissociated

$q_n \equiv$ charge (ionization state) of species n = zero for neutral species

$N_{nk} \equiv$ number of atoms of element k in species n

$N_n \equiv$ total number of atoms in species n

$\alpha_k \equiv$ fractional abundance (by number) of element k in the gas

$I_n \equiv$ ionization equilibrium constant of ionized species n

$K_n \equiv$ molecular equilibrium constant of molecular species n

3.   The Method of Solution

The GAS procedure accepts values of the state variables temperature and pressure as input, and reads other necessary atomic and molecular data from an input file, including fractional elements abundances α_k, the composition of molecular species, ionization potentials, atomic partition functions, and coefficients of polynomial approximations of molecular equilibrium constants. The equilibrium solution depends on powers of the elemental partial pressures p_k and is inherently nonlinear. As such, the best approach to solve the set of molecular equilibrium equations is by linearization. This requires initial estimates be derived that are close to the exact solution, so that any differences from this exact solution are small. Then, the linearized form of the equilibrium equations, in which small departures from the exact solution are approximated by first-order terms, is solved. Because of the approximations inherent in linearization, these corrections are not exact, but if within the region of convergence, will yield an improved solution. In this way, this procedure can be iterated to convergence to the exact solution by carrying out successive solutions of the linearized equations.

Fundamentally, the equilibrium solution depends on the values of the total pressure p and electron pressure p_e, which for a given temperature T, determines the fictitious total pressure p^*. Given p^*, the fictitious partial pressures of the elements p_k^* are given by $p_k^* = \alpha_k p^*$. Then, the partial pressure of any species p_n can be found from equation 18. Since p and T are given as input, we need to invert this solution and determine $p^* = p^*(p, T)$ and $p_e = p_e(p, T)$. To determine reasonable initial estimates for the linearization, we first need to obtain reasonable estimates of p^* and p_e at temperature T.

The most abundant elements dominate the fictitious total pressure p^*, but abundant elements k that participate in molecule formation are inherently coupled in a nonlinear manner, so the main challenge is to devise a reasonably accurate initial estimate of their partial pressures p_k^0. This must be done on a case-by-case basis for the most abundant elements. We also need to determine an initial estimate of the electron pressure p_e^0, and this is nontrivial because at cool temperatures, the electron pressure is dominated by contributions from several metal elements of low abundance that are easily ionized. At high temperatures, p_e is dominated by ionization of abundant elements, mostly H. We address the approach to developing reasonable initial estimates in the next section. Note that we use a superscript "0" to indicate initial estimates of these quantities.

3.1.   Initial Estimates of Partial Pressures

The GAS routine obtains initial estimates of the electron and partial pressures by considering two groups of elements: Group 1 or "major" species, which contribute significantly to the gas pressure p, and Group 2 or electron donors ("metals"), which may be of low abundance but still contribute significantly to the electron pressure p_e, but do not form molecules. A few elements of low abundance that also associate into molecules are important opacity sources: these are classified as Group 3 or "minor" elements, and their

partial pressures can be found directly once p^* and p_e have been found from the Group 1 and 2 elements. An example of Group 3 species is TiO. The groups to which a particular species belongs are indicated in the file of atomic and molecular data read by GAS. The group type of a species is indicated by the priority code `ipr` in the input file of atomic and molecular data read by GAS.

GAS assumes there are six Group 1 elements: H, C, N, O, Si and S, and specific estimates of partial pressures of these elements are obtained for each on a case-by-case basis.

There are nine Group 2 elements included: He, Ne, Na, Mg, Al, K, Ca, Fe and Ni.

The Group 3 elements included are, somewhat arbitrarily: Cl, Sc, Ti, V, Vr, Mn, Co, Sr, Y and Zr.

To simplify the analysis, we assume that the composition of the gas is astrophysical, i.e., the gas is mostly made up of H and He, with minor contributions from heavier elements. We also assume:

- $p_n \ll p_H^*$ for all species n except for those containing H or He,

- $p_n \ll \{p_C^*, p_N^*, p_O^*, p_{Si}^*, p_S^*\}$ for a molecular species n containing a Group 1 element combined with *any* other elements, and

- Group 3 elements do not significantly contribute to either p^* or p_e.

Under these assumptions, the total pressure can be approximated by

$$p = p_H + p_{H_2} + p_{H^+} + p_{He} + p_e \tag{28}$$

and the total fictitious pressure by

$$p^* \approx p_H + 2p_{H_2} + p_{H^+} + p_{He} \tag{29}$$

so that $p^* = p + p_{\rm H_2} - p_{\rm e}$.

To get an approximate *first* initial estimate of $p_{\rm e}$, we consider two temperature regimes: (1) high-temperature gas, where the source of electron pressure is dominated by the ionization of H, and (2) low-temperature gas, where the electrons come mainly from the ionization of several metal elements of low abundance.

For the high T regime, for which $p_{\rm H_2}$ and $p_{\rm H^-} \ll p$, and for which $p_{\rm e} \approx p_{\rm H^+}$, $p_{\rm e}$ can be estimated from the approximation to the abundance equation for H. Thus, for the high temperature regime we assume

$$\alpha_{\rm H} = p_{\rm H}^*/p^* = (p_{\rm H} + 2p_{\rm H_2} + p_{\rm H^+} + p_{\rm H^-})/(p + p_{\rm H_2} - p_{\rm e}) \approx (p_{\rm H} + p_{\rm e})/(p - p_{\rm e}) \qquad (30)$$

or

$$\alpha_{\rm H}(p - p_{\rm e}) \approx p_{\rm H} + p_{\rm e} \approx p_{\rm e}(p_{\rm e}/I_{\rm H^+} + 1) \qquad (31)$$

which is a quadratic equation for $p_{\rm e} = p_{\rm e}^{\rm hi}$, the electron pressure estimate in the high-temperature regime

$$p_{\rm e}^{\rm hi} \approx \frac{1}{2}\left[-I_{\rm H^+}(1 + \alpha_{\rm H}) + \sqrt{I_{\rm H^+}^2(1 + \alpha_{\rm H})^2 + 4\alpha_{\rm H}I_{\rm H^+}p}\right] \qquad (32)$$

For the low T regime, we assume that $p_{\rm H^-}$, $p_{\rm H^+}$, and $p_{\rm e} \ll p$, and that $p_{\rm H_2}$ may be significant, and that $p_{\rm e}$ is determined by the ionization state of eight low-T electron donors that are relatively abundant "metals" with modest first ground state ionization potentials, $\chi_{\rm I}$: C, Na, Mg, Al, Si, K, Ca, and Fe, so that $p^* \approx p + p_{\rm H_2}$ and $p_{\rm Z^+} \approx p_{\rm e}$. For the derivation of this electron pressure estimate *only*, these eight electron donors are treated as a single fictitious element, Z, that does not form molecules, and can only ionize to the singly-ionized state. We assume a representative ionization potential of $\chi_{\rm I, Z} = 7.3$ eV, an abundance $\alpha_{\rm Z} = \sum_k \alpha_k$, and a corresponding fictitious equilibrium constant, $I_{\rm Z}^+$. The value of $I_{\rm Z}^+$ is calculated by assuming that $Q_n = 2Q_{n^+}$ so that the $\log(Q_{n^+}/Q_n)$ term in Eq. 9 is zero.

The electron pressure can then be estimated from the corresponding approximations to the abundance equations for Z and H. Thus, in the low temperature limit we assume for H

$$\alpha_H = \frac{p_H^*}{p^*} = \frac{(p_H + 2p_{H_2})}{(p + p_{H_2})} = \frac{\sqrt{K_{H_2}p_{H_2}} + 2p_{H_2}}{(p_H + p_{H_2})}, \tag{33}$$

which is a quadratic equation for p_{H_2}

$$p_{H_2} = \frac{2\alpha_H(2 - \alpha_H)p + K_{H_2}}{2(2 - \alpha_H)^2}\left\{1 - \sqrt{1 - [\frac{2\alpha_H(2 - \alpha_H)p}{2\alpha_H(2 - \alpha_H)p + K_{H_2}}]^2}\right\} \tag{34}$$

For the fictitious metallic electron donor, we assume

$$\alpha_Z = \frac{p_Z^*}{p^*} = \frac{(p_Z + p_{Z^+})}{p^*} \approx \frac{p_e}{(p + p_{H_2})}(1 + \frac{p_e}{I_{Z^+}}) \tag{35}$$

thus yielding a initial estimate for the electron pressure $p_e = p_e^{lo}$ in the low-temperature regime

$$pe^{lo} \approx -\frac{I_{Z^+} + \sqrt{I_H^2 + 4\alpha_Z I_Z^+(p + p_{H_2})}}{2} \tag{36}$$

where species Z^+ is the singly ionized stage of the fictitious metal Z, and p_{H_2} on the RHS is found from equation 34.

Then we take $p_e = \max(p_e^{lo}, p_e^{hi})$ as our initial estimate of the electron pressure.

Under these assumptions, key fictitious partial pressures can be approximated as follows:

$p_H^* = p_H + 2p_{H_2} + p_{H^+} + p_{H^-}$

$p_{He}^* = p_{He}$

$p_C^* = p_C + p_{CH} + p_{CO} + p_{C^+}$

$p_O^* = p_O + p_{OH} + p_{H_2O} + p_{CO} + p_{O^+}$

$p_N^* = p_N + p_{NH} + 2p_{N_2} + p_{N^+}$

$p_{Si}^* = p_{Si} + p_{SiO} + p_{SiS} + p_{SiH} + p_{Si^+}$

$p_S^* = p_S + p_{HS} + p_{H_2S} + p_{SiS} + p_{S^+}$

$p_{Cl}^* = p_{Cl} + p_{HCl} + p_{Cl^-}$

$$p^*_{\text{Ti}} = p_{\text{Ti}} + p_{\text{TiO}} + p_{\text{Ti+}}$$

$$p^*_{\text{V}} = p_{\text{V}} + p_{\text{VO}} + p_{\text{V+}}$$

$$p^*_{\text{Y}} = p_{\text{Y}} + p_{\text{YO}} + p_{\text{YO}_2} + p_{\text{Y+}}$$

$$p^*_{\text{Zr}} = p_{\text{Zr}} + p_{\text{ZrO}} + p_{\text{ZrO}_2} + p_{\text{Zr+}}$$

For all other elements, k, we calculate p^* assuming only the neutral, singly-ionized, and perhaps, doubly-ionized stages contribute: $p^*_k = \sum_{q_n=0}^{2} p_k^{(q_n)}$.

This first initial estimate of the electron pressure is refined by iterating the linearized charge conservation equation to obtain a significantly improved initial estimate. Experience has shown that the converged solution is independent of the value chosen for $\chi_{\text{I, Z}}$. For the linearization, we assume free electrons arise only from single ionizations of elements, k, so that

$p_{\text{e}} = \sum_k p_{k_+}$ and

$p^*_k = p_k + p_{k_+} = (1 + \frac{p_{\text{e}}}{I_{k+}})p_{k+}$

With $\alpha_k = p^*_k/p^*$ we have

$p_{k+} = (\frac{\alpha_k I_{k+}}{I_{k+} + p_{\text{e}}})p^*$

and the equation of charge neutrality can be rearranged to provide a non-linear expression for p_{e}

$p_{\text{e}} = \sum_k p_{k+} = p^* \sum_k \frac{\alpha_k I_{k+}}{I_{k+} + p_{\text{e}}}$

To clarify the dependence of p^* on p_{e} we define $\tilde{p} = p + p_{\text{H}_2}$ so that $p^* = p + p_{\text{H}_2} - p_{\text{e}} = \tilde{p} - p_{\text{e}}$ in the equation above and

$$p_{\text{e}} = (\tilde{p} - p_{\text{e}}) \sum_k \frac{\alpha_k I_{k+}}{I_{k+} + p_{\text{e}}} \tag{37}$$

If p^0_{e} is a current estimate of the actual electron pressure p_{e}, then $p_{\text{e}} = p^0_{\text{e}} + \delta p_{\text{e}}$, where we

assume the correction $\delta p_e \ll p_e$.

Then linearized charge neutrality equation, equation 37 becomes

$$\delta p_e = \frac{p^* \sum_k \frac{\alpha_k I_{k+}}{I_{k+} + p_e^0} - p_e^0}{1 + \sum_k \frac{\alpha_k I_k}{I_{k+} + p_e^0} + p^* \sum_k \frac{\alpha_k I_k}{(I_{k+} + p_e^0)^2}} \qquad (38)$$

This is the linearization that we iterate to refine our initial estimate of p_e^0 to obtain a value of p_e consistent to first order. With this revised estimate of p_e, GAS then computes initial estimates of the partial pressures for the neutral stage of the elements, p_k. The number conservation equations for each Group 1 element are based on the assumption that the molecules that these Group 1 elements participate in are limited to the two or three most important ones. We use initial estimates of the equilibrium constants defined by the ionic Saha equation (I_n) and the molecular Saha equation (K_n). Finally, we note that the molecular chemistry assumed here is based on a normal stellar composition gas with $N_C/N_O < 1$. Thus, for the initial estimate of p_H we assume

$$\alpha_H = \frac{p_H^*}{p^*} \approx \frac{p_H + 2p_{H_2} + p_{H^+} + p_{H^-}}{p + p_{H_2} - p_e} \qquad (39)$$

yielding

$$p_H = \frac{1}{2(2 - \alpha_H)/K_{H_2}} \left\{ -\left(1 + \frac{I_{H^+}}{p_e} + \frac{p_e}{I_{H^-}}\right) + \right.$$
$$\left. \sqrt{\left(1 + \frac{I_{H^+}}{p_e} + \frac{p_e}{I_{H^-}}\right)^2 + 4\alpha_H(2 - \alpha_H)\frac{(p - p_e)}{K_{H_2}}} \right\} \qquad (40)$$

along with improved estimates $p_{H_2} = p_H^2/K_{H_2}$ and $p^* = p + p_{H_2} + p_e$.

For the case of C we assume the abundance equation as follows

$$\alpha_C = \frac{p_C^*}{p^*} \approx \frac{p_C + p_{CH} + p_{CO} + p_{C^+}}{p^*} \qquad (41)$$

yielding an initial estimate

$$p_{\mathrm{C}} = \frac{\alpha_{\mathrm{C}} p^*}{1 + \frac{p_{\mathrm{H}}}{K_{\mathrm{CH}}} + \frac{p_{\mathrm{O}}}{K_{\mathrm{CO}}} + \frac{I_{\mathrm{C+}}}{p_{\mathrm{e}}}} \tag{42}$$

Then, similarly for O, we have the initial estimate

$$p_{\mathrm{O}} = \frac{\alpha_{\mathrm{O}} p^*}{1 + \frac{p_{\mathrm{H}}}{K_{\mathrm{OH}}} + \frac{p_{\mathrm{H}}^2}{K_{\mathrm{H_2O}}} + \frac{p_{\mathrm{C}}}{K_{\mathrm{CO}}} + \frac{I_{\mathrm{O+}}}{p_{\mathrm{e}}}} \tag{43}$$

We then substitute Eq. 42 into Eq. 43 to solve for the initial estimate of p_{O}, and then back-substitute into Eq. 42 to solve for the initial estimate of p_{C}.

A similar set of two abundance equations for two unknowns is set up for Si and S, with Eq. 43 substituted for p_{O} in the equation for Si. For N the abundance equations leads to

$$\frac{2 p_{\mathrm{N}}^2}{K_{\mathrm{N_2}}} + p_{\mathrm{N}}\left(1 + \frac{p_{\mathrm{H}}}{K_{\mathrm{NH}}} + \frac{I_{\mathrm{N+}}}{p_{\mathrm{e}}}\right) - \alpha_{\mathrm{N}} p^* = 0 \tag{44}$$

which is a quadratic equation for the initial estimate of p_{N}. Similar abundance equations can be solved for the initial estimates of the Group 3 elements that bond to H or O, including Ti, V, Y, and Zr, substituting the value of p_{O} from Eq. 43 into their equations, and for Cl, which depends on the value of p_{H}.

For any Group 2 elements for which an initial estimate is needed, for this purpose we assume the element is present in only the neutral or singly ionized form so that

$$p_n = \frac{\alpha_n p^*}{1 + I_{n+}/p_{\mathrm{e}}} \tag{45}$$

With this, we have obtained initial estimate of the gas and electron partial pressures that should be sufficiently accurate for the main linearization solution to converge.

3.2.   The Linearized Solution of the Economized Equations

The execution time required for the solution scales as n^2, where n is the number of species included in the chemical equilibrium. Therefore, GAS implements an "economized" solution based on a fictitious "metallic" element Z that represents those elements that only contribute electrons via ionization and are not significantly involved in molecular association: these are the Group 2 elements. GAS solves eight coupled linearized equations for the eight first order corrections: δp_H, δp_C, δp_N, δp_O, δp_{Si}, δp_S, δp_Z^*, δp_e.

The eight equations to be solved are the linearized versions of the five abundance equations for C, N, O, Si, S, and the fictitious metal Z, each of which expresses the constraint that the abundance of each element k is consistent with $\alpha_k = p_k^*/p^*$. One of the abundance equations is linearly dependent on the rest and should not be included. We have chosen to eliminate the abundance equation for H from the set. The remaining two equations are the total pressure equation: the sum of all the partial pressures must equal the total pressure, and the charge neutrality equation: the sum of all charge must be zero.

The abundance equation (equation 46) for each major (Group 1) element k is

$$\sum_n (\alpha_k N_n - N_{nk})p_n + \alpha_k p_Z^* = 0 \tag{46}$$

The initial estimate, p_n^0, obtained by the methods of the previous section should be close to the exact solution p_n. We can write the exact solution $p_n = p_n^0 + \delta p_n$, where the correction term δp_n is assumed small ($\delta p_n/p_n \ll 1$). Then, the equation can be written in terms of the small corrections, and only terms of first order in the correction terms kept. In this way, the equation is linearized, and the linear system solved for the corrections δp_n, which are then used to update the solution.

After i iterations, we obtain an estimate of the partial pressure δp_n^{i+1}, which can be added

to the previous solution to obtain an improved estimate

$$p_n^{i+1} = p_n^i + \delta p_n^{i+1} \tag{47}$$

This process is iterated repeatedly until the changes become small, and the system converges to the exact solution p_n.

The linearized version of equation 46 is

$$\sum_n (\alpha_k N_n - N_{nk})\delta p_n + \alpha_k \delta p_Z^* = \sum_n (N_{nk} - \alpha_k N_n)p_n + \alpha_k p_Z^* \tag{48}$$

where the superscript iteration number "i" has been dropped on the partial pressures estimates for clarity.

This provides equations for the corrections δp_n for *all species*, including molecules and ions, whereas our independent variables are the eight neutral Group 1 elements and p_e. To relate δp_n to δp_{n_k} and δ_e we linearize Eq. 18 as follows

$$p_n + \delta p_n = \frac{I_n}{K_n(p_e + \delta p_e)^{q_n}} \prod_k (p_{n_k} + \delta p_{n_k})^{N_{nk}} \tag{49}$$

which can be rearranged such that

$$\delta p_n = p_n\left(\sum_k \frac{N_{nk}}{p_{n_k}}\delta p_{n_k} - q_n\frac{\delta p_e}{p_e}\right) \tag{50}$$

assuming that $\delta p_{n_k}/p_{n_k} \ll 1$ and $\delta p_e/p_e \ll 1$. Substituting the above into Eq. 48 gives us the linearized mass balance equations for the eight Group 1 elements

$$\sum_n (\alpha_k N_k - N_{nk}) p_n \sum_k \frac{N_{nk}}{p_{n_k}} \delta p_{n_k}$$

$$- \frac{1}{p_e} \left[\sum_n (\alpha_k N_n - N_{nk}) p_n q_n \right] \delta p_e + \alpha_k \delta p_Z^*$$

$$= \sum_n (N_{nk} - \alpha_k N_n) p_n - \alpha_k p_Z^* \quad (51)$$

where k ranges over Group 1 elements only, and n refers only to species formed entirely from Group 1 elements.

Similarly, the linearized abundance equation for the fictitious metal Z is

$$\alpha_Z \sum_n N_n p_n \sum_k \frac{N_{nk}}{p_{n_k}} \delta p_{n_k}$$

$$- \frac{\alpha_Z}{p_e} (\sum_n N_n p_n q_n) \delta p_e - (1 - \alpha_Z) \delta p_Z^*$$

$$= -\alpha_Z \sum_n N_n p_n + (1 - \alpha_Z) p_Z^* \quad (52)$$

The total pressure equation (equation 54) is now

$$\sum_n p_n + p_Z + p_{Z^+} + p_e = p \quad (53)$$

With $p_n = p_n^0 + \delta p_n$, $p_e = p_e^0 + \delta p_e$, and $p_Z^* = p_Z^{*0} + \delta p_Z^*$ this linearizes to

$$\sum_n \delta p_n + \delta p_Z + \delta p_{Z^+} + \delta p_e = p - \sum_n p_n - p_Z - p_{Z^+} - p_e \quad (54)$$

where the superscript "0"s have been dropped on the initial partial pressure estimates for clarity. Substituting equation 50 for δp_n again, the linearized total pressure equation is

$$\sum_n p_n \sum_k \frac{N_{nk}}{p_{n_k}} \delta p_{n_k} + (1 - \frac{1}{p_e} \sum_n p_n q_n) \delta p_e + \delta p_Z^*$$

$$= p - \sum_n p_n - p_Z^* - p_e \quad (55)$$

The modified charge neutrality equation is

$$\sum_n p_n q_n + p_{Z^+} - p_e = 0 \quad (56)$$

With $p_n = p_n^0 + \delta p_n$, $p_e = p_e^0 + \delta p_e$, and $p_Z^* = p_Z^{*0} + \delta p_Z^*$ this linearizes to

$$\sum_n q_n \delta p_n + \delta p_{Z^+} - \delta p_e = p_e - \sum_n q_n p_n - \delta p_{Z^+} \quad (57)$$

where the superscript "0"s have been dropped on the initial partial pressures estimates for clarity. This result must be expressed in terms of the independent variable p_Z^*, which we do as follows

$$p_{Z^+} = \sum_m p_{m^+} = p^* \sum_m \frac{\alpha_m I_{m^+}}{I_{m^+} + p_e} = \frac{p_Z^*}{\alpha_Z} \sum_m \frac{\alpha_m I_{m^+}}{I_{m^+} + p_e} \quad (58)$$

so that the modified charge neutrality equation is now

$$\sum_n p_n q_n + \frac{p_Z^*}{\alpha_Z} \sum_m \frac{\alpha_m I_{m^+}}{I_{m^+} + p_e} = p_e \quad (59)$$

again, where the superscript "0"s have been dropped. Substituting Eq. 50 for δP_n again, the charge neutrality equation (Eq. 57) can be linearized to

$$\sum_n p_n q_n \sum_k \frac{N_{nk}}{p_{n_k}} \delta p_{n_k} - 1$$

$$+ \frac{1}{p_\mathrm{e}} \sum_n p_n q_n^2 + \frac{p_\mathrm{Z}^*}{\alpha_\mathrm{Z}} \sum_m \frac{\alpha_m I_m^+}{(I_{m^+} + p_\mathrm{e})^2} \delta p_\mathrm{e}$$

$$+ \frac{1}{\alpha_\mathrm{Z}} \left(\frac{\sum_m \alpha_m I_m^+}{(I_m^+ + p_\mathrm{e})} \right) \delta p_\mathrm{Z}^*$$

$$= - \sum_n p_n q_n - \frac{p_\mathrm{Z}^*}{\alpha_\mathrm{Z}} \sum_m \frac{\alpha_m I_m^+}{(I_m^+} + p_\mathrm{e}) + p_\mathrm{e} \quad (60)$$

where species m^+ are the singly ionized stages of the metals m contributing to the fictitious metal Z.

We have a set of eight equations for eight unknowns: Equation 51 for five of the Group 1 elements (we are over-constrained by one equation and omit the equation for δp_H), Eq. 52, Eq. 55, and Eq. 60, which we solve for the eight unknown corrections: δp_C, δp_N, δp_O, δp_Si, δp_S, δp_Z^*, and δp_e. The system is solved using the LINPACK procedure DGEFA to factorize the full matrix of coefficients, a, and to reduce it to upper triangular form by Gaussian elimination, and then the LINPACK procedure DGESL is used with a to solve for the corrections δX. If any of the diagonal elements of the upper triangular factor of a are zero, DGEFA will return the corresponding array subscript along with the other outputs, allowing us to detect cases where DGESL will divide by zero. Python implementations typically represent floating-point numbers as double-precision by default (64-bit). Currently, if the procedure does not achieve the convergence criterion within ten iterations, it will print a warning to the standard output.

Once the values of p_Z^* and p_e are converged, we recover the p values for the individual metals from their input abundances, α, as follows

$$p_m = \left(\frac{\alpha_m}{\alpha_{\rm Z}}\right)\frac{p_{\rm e}p_{\rm Z}^*}{(I_{m^+} + p_{\rm e})} \qquad (61)$$

3.3. Input

The GAS procedure (Bennett 1983) takes as input the equilibrium gas temperature T and the total gas pressure, p. Additionally, the code reads an arbitrary list of atomic, ionic, and molecular species, n, from a user-supplied file ("gasdata"), and the list should include the six elements that most strongly couple to the molecular equilibrium: H, C, N, O, Si, and S. The species-wise records specify the chemical symbol of the species (name[]), the "priority code" equal to 1, 2, or 3, indicating how that species is to be included in the treatment (ipr[]), the electronic charge in charge units (nch[]), the total number of different elements comprising that species (nel[]), and one or more pairs of values specifying the number of atoms of each element (nat[]) and the corresponding atomic number of that element (zat[]) that comprises that species. If the species is a neutral atom then the record includes the total abundance of that element (in all its forms), α_k as defined above, (comp[]), thus specifying the input chemical composition, and the atomic weight in amu (awt[]). If the species is an ion then the record includes the ground state ionization energy from the next lowest ionization stage in eV (ip[]), followed by the term $\log 2Q_{X^+}/Q_X$ appearing in the expression for the logarithm of the ionization constant ($\log I_{X^+}$) in equation 8. The values of that ratio of partition functions in the gasdata file are for $T = 5040$ K, from Allen (1973). If the species is a molecule, then the record includes the five coefficients of the quartic polynomial fit to the equilibrium constant, $K_n(T)$, defined by the molecular Saha equation for species n, as a function of temperature (Tsuji (1973)) (logk[]). There are currently 105 records covering all of the species included, and this arrangement allows new species to be added to the treatment *ad hoc* by adding records to the input file.

3.4. Output and performance

GAS produces consistently calculated values for ρ, p_e, μ, and the p_n values for all 105 species, n, currently being included. The convergence criterion is $(p_n^i - p_n^{i-1})/p_n^i < \epsilon$ for all six Group 1 species, the fictitious metal Z, and e^- particles. In ATHENA ϵ is set to 10^{-4} and the GAS procedure typically converges in 2 to 3 iterations for stars of $N_C/N_O < 1$, and for stars of any N_C/N_O value if $T_{kin}(\tau) > 3000$ K at all τ. Many more iterations may be required for stars of $N_C/N_O > 1$ and where $T_{kin}(\tau) < 3000$ K for some τ range because the starting approximation currently assumes that Group 1 elements are only depleted by molecules that dominate in an O-rich composition. Because CSPy is intended for rapid responsiveness that is just realistic enough for initial and demonstrative data modeling, we set ϵ to 10^{-2}. In practice we find that replacing the previous ionization equilibrium and EOS procedure in CSPy with GAS has a negligible effect on wall-clock time.

4. Implementation in CSPy

Previously, CPy arrived at values of $p_e(\tau_{Ros})$, $\rho(\tau_{Ros})$, $\mu(\tau_{Ros})$, and $p_n(\tau_{Ros})$ for atomic species by a straightforward iteration of the coupled ionic Saha equations starting from an initial guess at $p_e(\tau_{Ros})$ computed with the method described in Gray (2005). For stars of $T_{eff} < 5000$ K the value of $p_{TiO}(\tau_{Ros})$ was then computed *post facto* and all other molecules were neglected. This is still the procedure for stars of $T_{eff} > 6500$ K.

For stars of $T_{eff} < 6500$ K, CSPy now calls the GAS procedure to obtain the values of $p_e(\tau_{Ros})$, $\rho(\tau_{Ros})$, $\mu(\tau_{Ros})$, and $p_n(\tau_{Ros})$ for all neutral and singly ionized atomic species (and doubly ionized species for Mg and Ca), H^-, and all molecular species that are accounted for in GAS at all Rosseland optical depths τ_{Ros}. The call to GAS is part of an iterative procedure that includes calculation of the monochromatic ($\kappa_\lambda(\tau)$) and Rosseland

mean $(\kappa_{\mathrm{Ros}}(\tau))$ mass extinction coefficients, and integration of the hydrostatic equilibrium equation (HSE) on the τ_{Ros} scale to improve the estimates of $p(\tau_{\mathrm{Ros}})$ and $p(\tau_{\mathrm{Ros}})$. CSPy codes then evaluate the ionic Saha equation to obtain values for $p_n(\tau_{\mathrm{Ros}})$ for any atomic species not accounted for in GAS.

4.1. Improvements to molecular opacity

4.1.1. TiO opacity

Now that we can compute much more realistic values of p_{TiO}, we have increased the number of TiO bands that we include in the Just Overlapping Line Approximation (JOLA) (Zeidler-K.T. & Koester 1982) in the computation of the emergent synthetic spectrum. In addition to the original $C^3\Delta - X^3\Delta$ (α system, $\omega_{00} = 19341.7$ cm^{-1}), $c^1\Phi - a^1\Delta$ (β system, $\omega_{00} = 17840.6$ cm^{-1}) , and $A^3\Phi - X^3\Delta$ (γ system, $\omega_{00} = 14095.9$ cm^{-1}) systems that we were already including (Short, Bayer & Burns 2018), we now also include the $B^3\Pi - X^3\Delta$ ($\omega_{00} = 16148.5$ cm^{-1}), $E^3\Pi - X^3\Delta$ ($\omega_{00} = 11894.0$ cm^{-1}), $b^1\Pi - a^1\Delta$ ($\omega_{00} = 11272.8$ cm^{-1}), and $b^1\Pi - d^1\Sigma$ ($\omega_{00} = 9054.0$ cm^{-1}) systems. The molecular data for the four newly added systems is from Jorgensen (1994). Frustratingly, we continue to have to tune, *ad hoc*, the unknown "line strength" factor, S, in the calculation of the band oscillator strength (see Cox (2002)), and an honest description of the procedure should acknowledge that. The addition of these four bands allows the overall spectral energy distribution (SED) of M stars to be more realistic. Now that we have incorporated the GAS package, the way is open to adding many more JOLA bands to represent other important molecular absorption features, including the CH $\lambda 4300$ G band, which is another important molecular MK classification diagnostic.

4.1.2. Rayleigh scattering

GAS allows us to compute for the first time in CSPy the value of p_{H_2} and allows us to now compute the contribution of H_2 Rayleigh scattering to the total continuous extinction coefficient, $\kappa_\lambda^C(\tau)$. As described in Short (2017), we compute the contribution to Rayleigh scattering opacity for all sources with the routines ported from the Moog spectrum synthesis code (Sneden *et al.* 1973).

5. Results

In Figs. 1 and 2 we present partial pressure values with respect to that of H for a selection of the most important molecules, including TiO, throughout the atmosphere for, respectively, an evolved (low $\log g$) and an un-evolved (high $\log g$) M star of $T_{\rm eff} = 3600$ K and solar metallicity ($N_C/N_O < 1$). In Figs. 3 and 4 we show the surface flux spectrum, F_λ, in the region of the strongest absorption caused by the TiO α system electronic band, $C^3\Delta - X^3\Delta$ ($\omega_{00} = 19341.7$ cm^{-1}) for the same two models, and the comparison to relevant observed spectra taken from the MILES library (Sánchez-Blázquez *et al.* (2006), Falcón-Barroso *et al.* (2011)). Abundances are those of Grevesse & Sauval (1998).

We were only able to find two M dwarfs ($\log g > 4.5$) in the MILES library with a catalogue value of $T_{\rm eff} = 3600 \pm 500$ K, and one has [Fe/H] $= -1.50$ (BD+442051A, MILES catalogue number s0399). However, the TiO band in our synthetic spectrum is computed with the JOLA approximation, and an approximate *ad hoc* tuning of the line strength parameters, S, so we view the comparison as useful despite the discrepancy in [Fe/H] values. The other M dwarf (HD095735, MILES catalogue number s0398) is closer to solar metallicity with [Fe/H] $= -0.20$. We convolved our synthetic spectrum with a Gaussian kernel of FWHM equal to the nominal spectral resolution of the MILES spectrograph,

corresponding to $\Delta\lambda = 0.25$ nm. Given the moderate resolution and large λ range of our comparison, and the approximate nature of the JOLA treatment of molecular band opacity, we did not apply any other corrections to the synthetic spectrum, and its λ scale is that of rest wavelength in vacuum in the star's centre-of-mass frame.

5.1. Comparison to PHOENIX V15 and PPRESS

In Figs. 5 and 6 we present a comparison of p_n values for a smaller selection of important molecules as computed by CSPy with GAS and by PHOENIX V15 with PPRESS, for the same stellar parameters (3600/1.0/0.0) and (3600/5.0/0.0). For both calculations, the abundances were those of Grevesse & Sauval (1998). In Figs. 7 and 8 we show the values of other state variables, $T_{\rm kin}$, p, $p_{\rm e}$, and ρ, that affect the p_n values, as computed with both suites. The agreement in the p_n values between the two packages is closest in the upper atmosphere ($\tau_{1200} \leq 1$) where the atmospheric structure is in radiative equilibrium, and where $T_{\rm kin}(\tau)$ scales most closely with the value of $T_{\rm eff}$. This is to be expected because PHOENIX computes the radiative-convective equilibrium $T_{\rm kin}(\tau)$ structure properly throughout the entire atmosphere, whereas CSPy approximates the $T_{\rm kin}(\tau)$ structure by re-scaling it with $T_{\rm eff}$ from one or another of three template models computed with PHOENIX V15 that sample the three populated quadrants of the HR diagram. As a result, we expect the CSPy $T_{\rm kin}(\tau)$ structure and, thus, the p_n values, to be least realistic at depths of $\tau_{1200} > 1$ where the structure is convective.

6. Discussion and future work

The incorporation of GAS into CSPy allows investigators, including students, to study the behavior of molecular equilibrium as a function of $T_{\rm kin}$ and p throughout stellar atmospheres
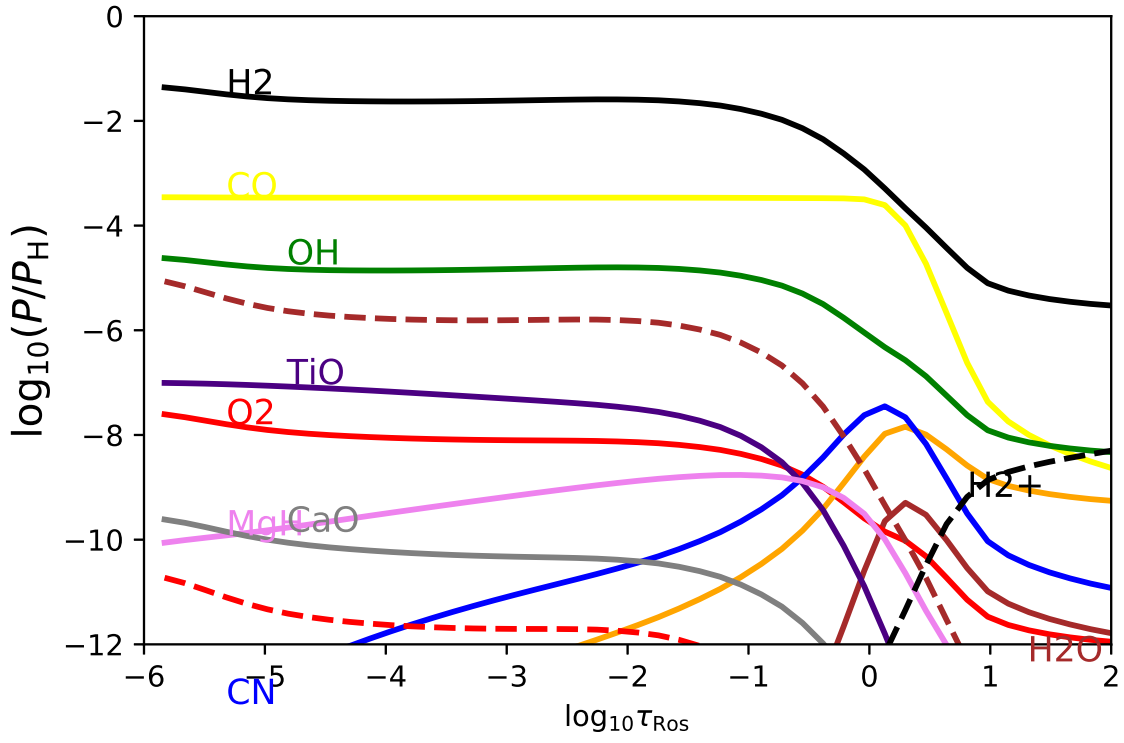
Fig. 1.— Partial pressures for select molecular species with respect to p_{H} as a function of Rosseland mean optical depth for a solar metallicity model of $T_{\mathrm{eff}} = 3600$ K and $\log g = 1.0$, representative of a bright M giant ($N_{\mathrm{C}}/N_{\mathrm{O}} < 1$) with strong TiO bands.
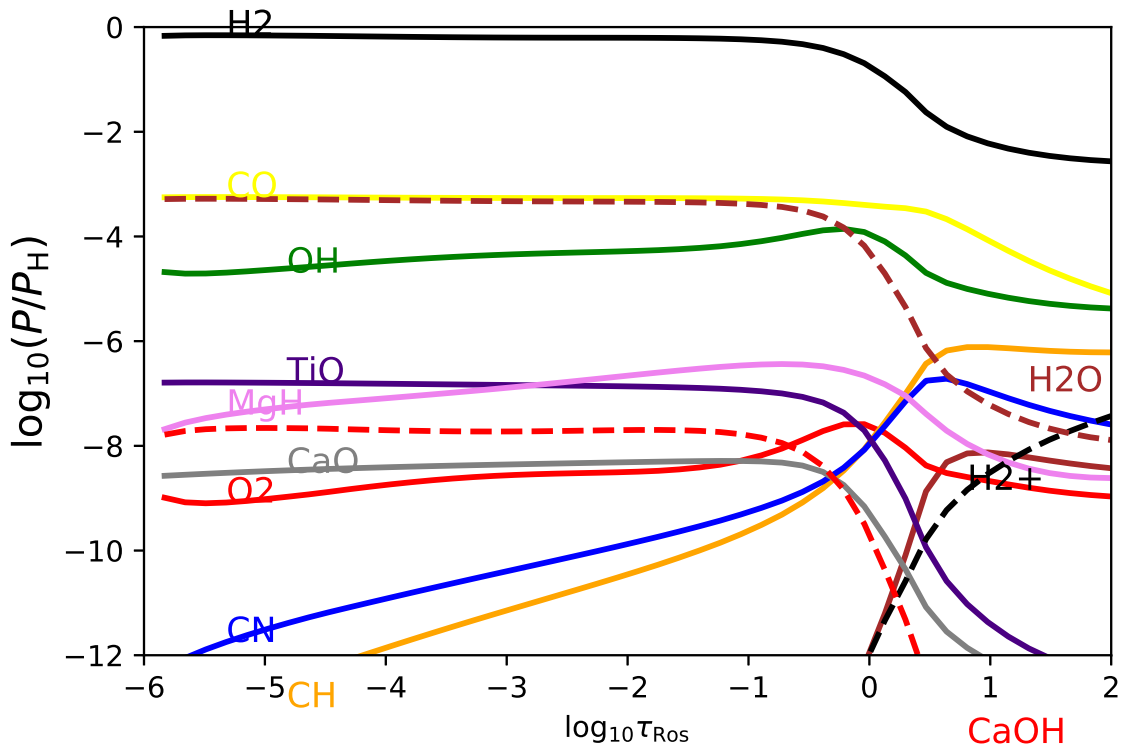
Fig. 2.— Same as Fig. 1, but for a model of $\log g = 5.0$, representative of a very late-type M dwarf.
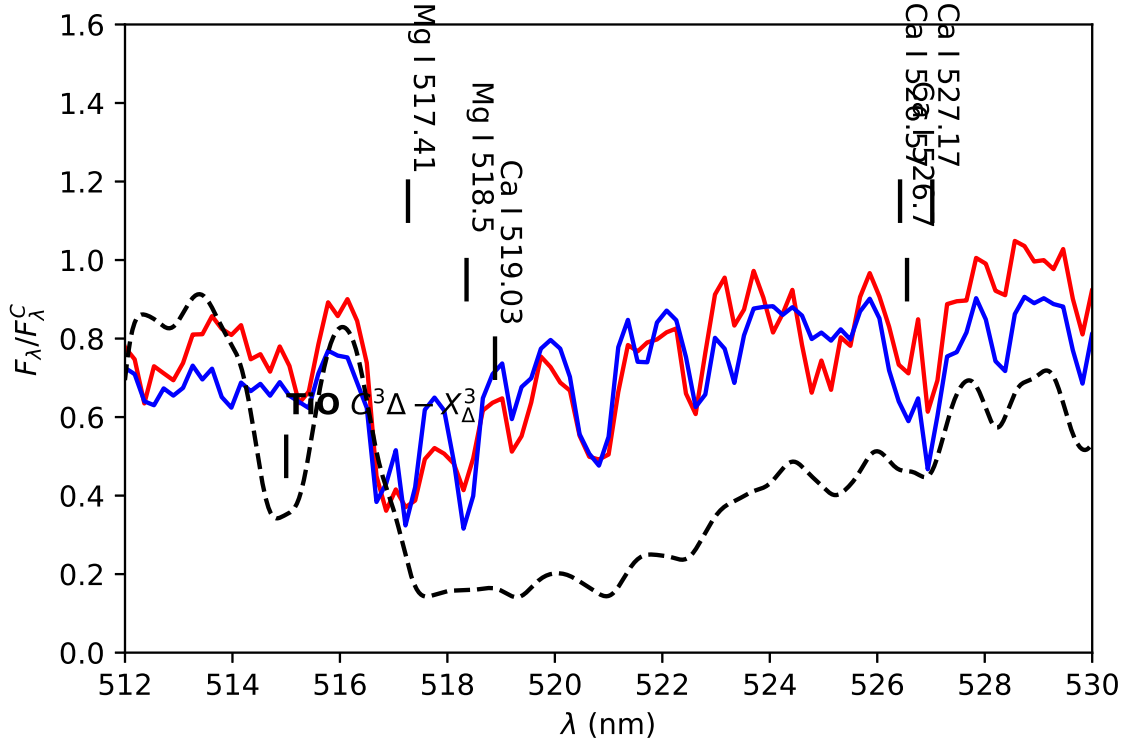
Fig. 3.— Region around the strongest absorption of the TiO α system electronic band, $C^3\Delta - X^3\Delta$ ($\omega_{00} = 19341.7$ cm^{-1}). Black line: Synthetic spectrum for a solar metallicity model of $T_{\mathrm{eff}} = 3600$ K and $\log g = 1.0$, representative of a bright M giant ($N_{\mathrm{C}}/N_{\mathrm{O}} < 1$), broadened to the nominal instrumental resolution of the MILES spectrograph ($\Delta\lambda = 0.25$ nm). Red line: Observed spectrum from the MILES library for a star with stated parameters in the MILES catalogue of $T_{\mathrm{eff}} = 3600$ K, $\log g = 1.10$, and [Fe/H] $= +0.02$ (HD007351, MILES catalogue spectral class M2 and designation s0053). Blue line: As for the red line, but for a star of stated $T_{\mathrm{eff}} = 3600$ K, $\log g = 0.80$, and [Fe/H] $= -0.19$ (HD147923, MILES spectral class M and designation s0593). A single-point renormalization factor of 0.8 was applied, *ad hoc*, to the MILES spectra.
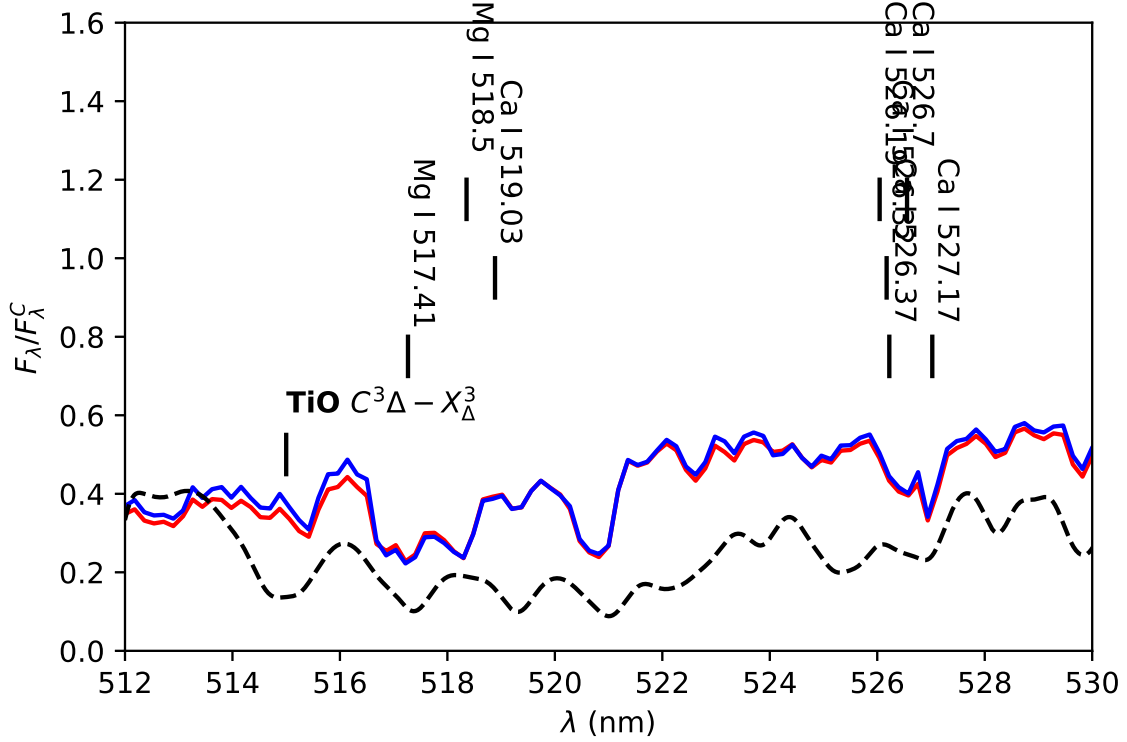
Fig. 4.— Same as Fig. 3, but for a model of $\log g = 5.0$, representative of a very late-type M dwarf, and observed MILES stars of stated $T_{\text{eff}} = 3620$ K, $\log g = 4.93$, and $[\text{Fe/H}] = -1.50$ (BD+442051A, MILES catalogue spectral type M2 V and designation s0399, red line), and $T_{\text{eff}} = 3551$ K, $\log g = 4.90$, and $[\text{Fe/H}] = -0.20$ (HD095735, MILES catalogue spectral type M2 V and designation s0398, blue line). A single-point renormalization factor of 0.5 was applied, *ad hoc*, to the MILES spectra.
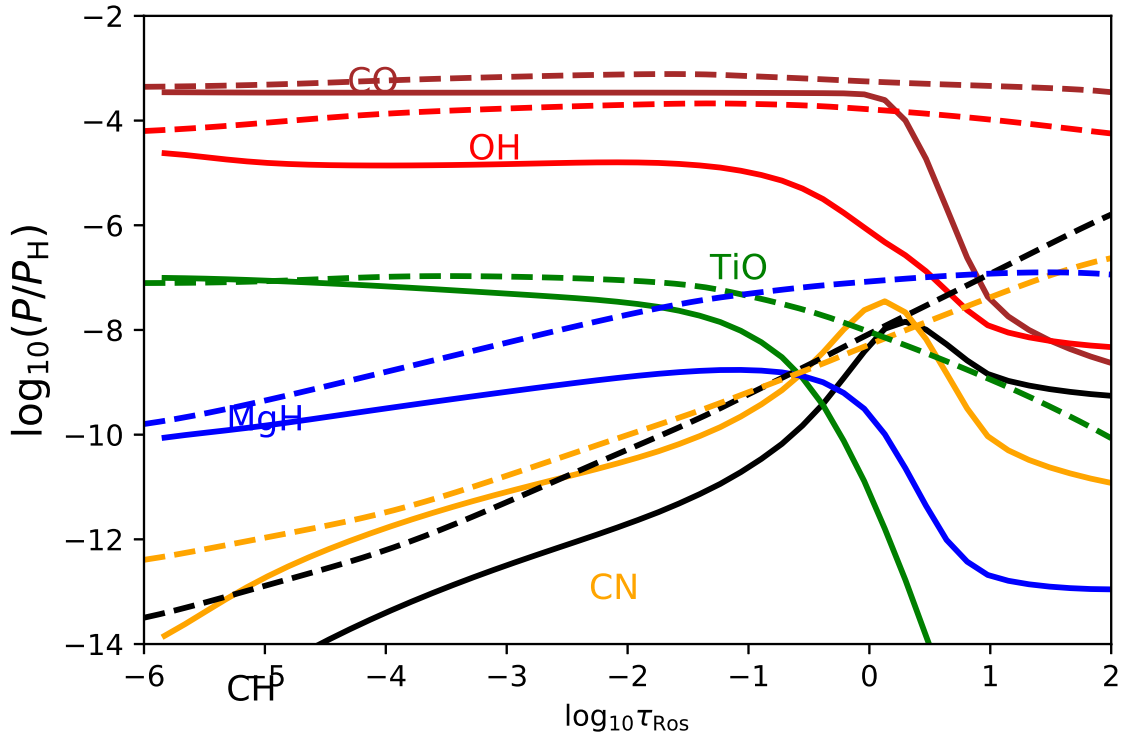
Fig. 5.— As for Fig. 1 for a smaller set of species, except that dashed lines are p_n values computed with PPRESS for a model structure converged with PHOENIX V15.
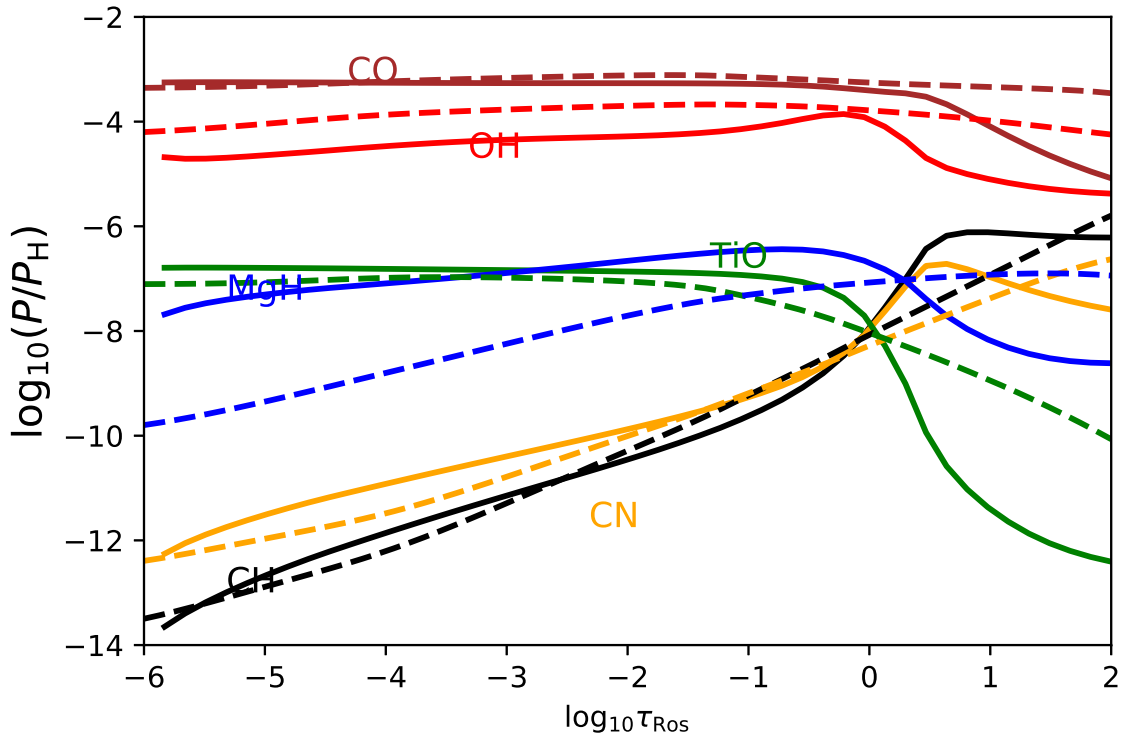
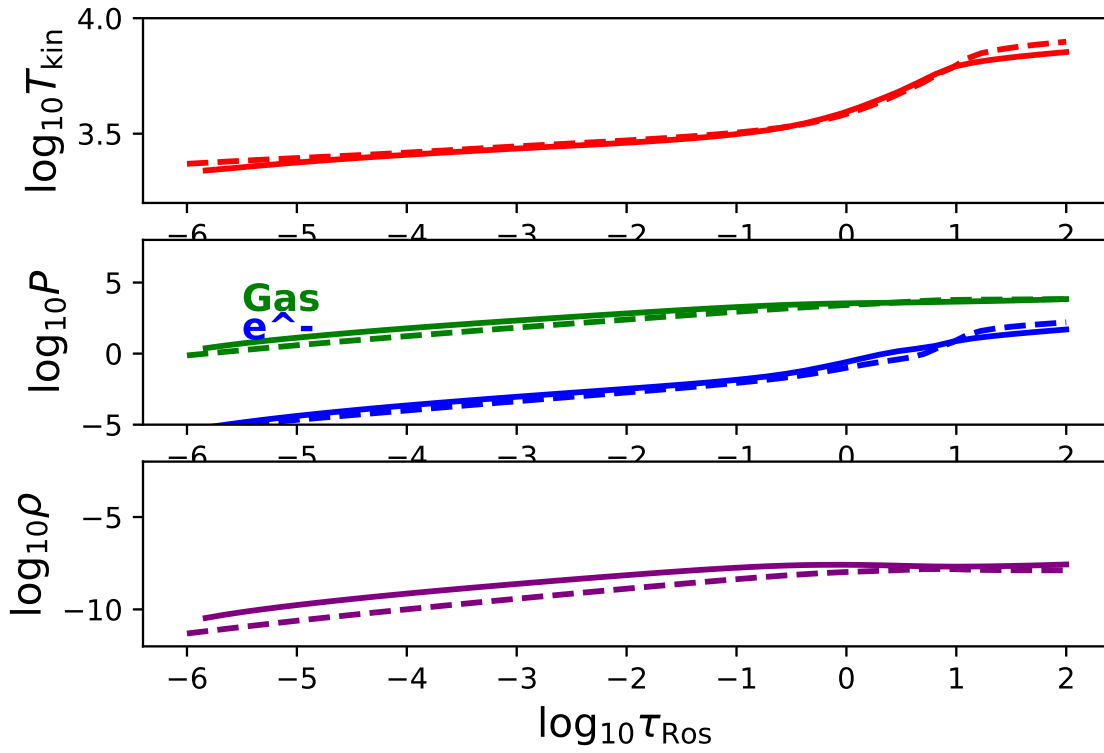Fig. 6.— As for Fig. 5 except for our model of $\log g = 5.0$.

Fig. 7.— Comparison of atmospheric structure quantities that affect the value of p_n for the model of $T_{\mathrm{eff}} = 3600$ K, $\log g = 1.0$ and $[\frac{\mathrm{Fe}}{\mathrm{H}}] = 0.0$. Values computed with CSPy and GAS (solid lines) and with PHOENIX V15 and PPRESS (dashed lines).
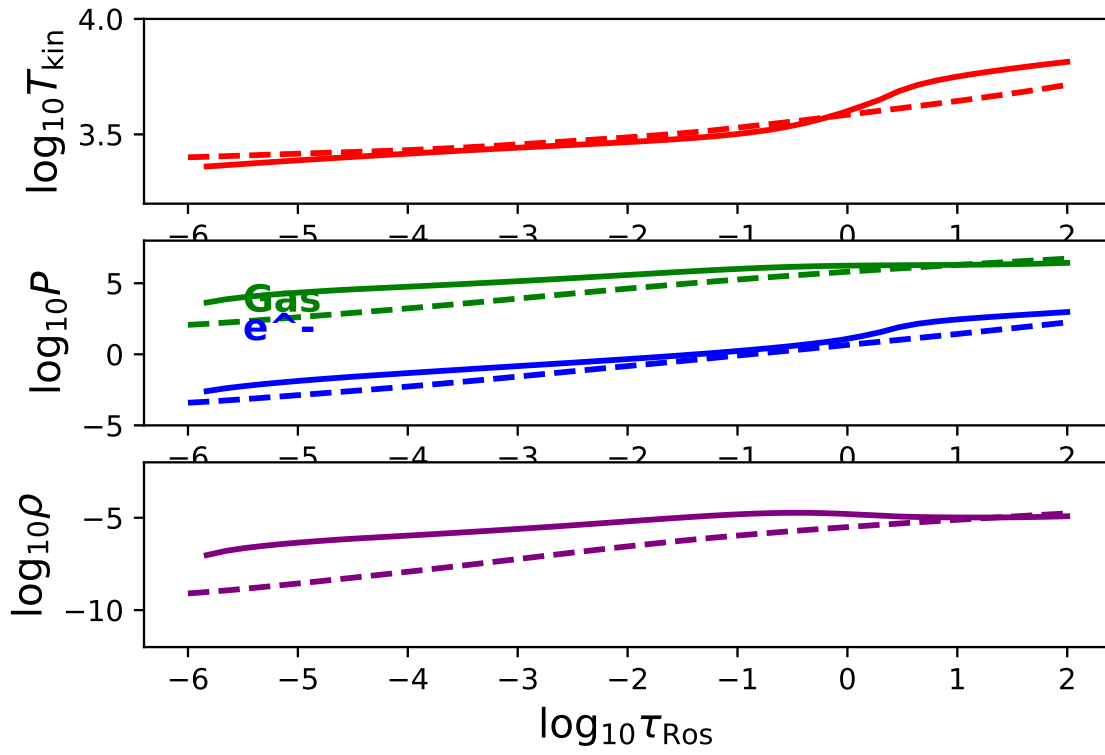
Fig. 8.— As for Fig. 7, except for a model of $\log g = 5.0$.

of arbitrary parameters, and to do so responsively in a Python integrated development environment (IDE). It also allows molecular band opacity to be treated more accurately, and adds impetus for including more molecular JOLA bands in the opacity calculation.

Because rapid responsiveness is valuable for the kinds of investigations CSPy is intended for, obtaining the T_{kin} structure properly by satisfying the thermal equilibrium condition is not currently feasible, and our T_{kin} structure is necessarily approximate. Molecule formation is sensitive to the T_{kin} value, so our values of p_n for molecular species are affected, as illustrated by the discrepancy between PHOENIX and CSPy seen in Fig. 6. A provisional measure suggested by these results is to add an additional PHOENIX template dwarf model with a T_{eff} value below 4000 K for producing scaled T_{kin} structures for very late-type dwarf stars.

Our p_n values for molecular species are directly dependent on the quartic parameterization of K_n of Tsuji (1973), and these in turn affect the values for all species through the coupled chemical equilibrium. We plan to undertake a critical review of the molecular data in the literature with the goal of updating our treatment of K_n, and any updates will be reported in a future paper on CSPy modelling of late-type stellar spectra. Similarly, our treatment of the partition function, Q_n, for the ionization equilibrium can be updated to reflect a more realistic T-dependence.

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