CALCULATIONS OF THE FAR-WING LINE PROFILES OF SODIUM AND POTASSIUM IN THE ATMOSPHERES OF SUBSTELLAR-MASS OBJECTS

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ABSTRACT

At the low temperatures achieved in cool brown dwarf and hot giant planet atmospheres, the less refractory neutral alkali metals assume an uncharacteristically prominent role in spectrum formation. In particular, the wings of the Na-D (5890 Å) and K\(\text{i}\) (7700 Å) resonance lines come to define the continuum and dominate the spectrum of T dwarfs from 0.4 to 1.0 μm. Whereas in standard stellar atmospheres the strengths and shapes of the wings of atomic spectral lines are rarely needed beyond 25 Å from a line center, in brown dwarfs the far wings of the Na and K resonance lines out to thousands of angstroms detunings are important. Using standard quantum chemical codes and the unified Franck-Condon model for line profiles in the quasi-static limit, we calculate the interaction potentials and the wing line shapes for the dominant Na and K resonance lines in H\(_2\)- and helium-rich atmospheres. Our theory has natural absorption profile cutoffs, has no free parameters, and is readily adapted to spectral synthesis calculations for stars, brown dwarfs, and planets with effective temperatures below 2000 K.

Subject headings: atomic data — infrared: stars — stars: atmospheres — stars: fundamental parameters — stars: low-mass, brown dwarfs

1 INTRODUCTION

Absorption lines of the neutral alkali metals sodium (Na), potassium (K), cesium (Cs), rubidium (Rb), and lithium (Li) are prevalent in the spectra of L dwarfs, T dwarfs, and irradiated giant planets (Kirkpatrick et al. 1999, 2000; Burgasser et al. 1999, 2000, 2002; Burrows, Marley, & Sharp 2000, hereafter BMS00; Burrows et al. 2001, 2002; Liebert et al. 2000; Charbonneau et al. 2002; Martin et al. 1999). The atmospheres of such substellar-mass objects (SMOs) are cool enough that the neutral alkali atoms predominate. Furthermore, since aluminum, magnesium, iron, silicon, and calcium are sequestered in grains that have settled out, a cool atmosphere in the gravitational field of such a planet or star is depleted of these more refractory metals (Burrows & Sharp 1999; Lodders 1999; BMS00). As a consequence, the less refractory neutral alkali metals assume an importance in the optical and near-infrared spectra of SMOs and in their atmospheres from ~800 to ~2000 K that is unique among astronomical objects.

In standard stellar atmospheres, atomic lines are superposed on a background continuum and the concepts of equivalent width and curve of growth make conceptual and practical sense. An individual line is but a perturbation on the local spectrum. However, because of the rainout of metals in cool atmospheres and the consequent paucity of continuum and alternate opacity sources between 0.4 and 1.0 μm, the wings of the strong resonance doublets centered at ~7700 Å (K\(\text{i}\)) and 5890 Å (Na-D) assume the role of the continuum throughout most of this spectral range (BMS00; Tsuji, Ohnaka, & Aoki 1999). In particular, the red wing of the 4s\(^2\)S\(_{1/2}\)–4p\(^2\)P\(_{3/2}\) transitions of K\(\text{i}\) provides the pseudo-continuum in cool molecular atmospheres all the way from 0.77 to ~1.0 μm, and the Na-D doublet, centered as it is in the middle of the visible, determines the true color of brown dwarfs (magenta/purple; Burrows et al. 2001).

Hence, whereas in traditional stellar atmospheres the Lorentzian core and Gaussian wings of a line are not generally of relevance beyond ~20 Å detunings (Δλ from the line core), in cool substellar atmospheres the relevant reach of the Na\(\text{i}\) and K\(\text{i}\) resonance lines can be thousands of angstroms. Given this, to achieve accurate spectral fits for brown dwarf, L dwarf, T dwarf, and hot giant planet atmospheres, the shapes of the far wings of these alkali lines as a function of pressure and temperature must be ascertained.

In this paper, we perform ab initio calculations of the energy shifts of the ground and excited states of sodium and potassium immersed in H\(_2\)- and helium-rich atmospheres and obtain the resulting opacity profiles of the red and blue wings of the Na-D and K\(\text{i}\) resonance lines.

2 QUASI-STATIC THEORY OF ABSORPTION SPECTRA IN THE FAR WINGS OF ATOMIC SPECTRAL LINES

The energy levels of an atom of sodium or potassium immersed in a sea of molecular hydrogen will be perturbed by the potential field of the diatomic hydrogen.

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At a distance of \( R_i \), the molecular hydrogen will shift both the ground and the excited states of the alkali metal atom. The difference of these level shifts is the amount by which the corresponding absorption line will be shifted (Griem 1964; Breene 1957, 1981, p. 344):

\[
h\nu = h\nu_0 + V_m(R_i) - V_n(R_i) = h\nu_0 + \Delta V_{mn}(= \Delta V) ,
\]

where \( \nu \) is the photon frequency, \( \nu_0 \) is the unperturbed photon frequency, \( m \) and \( n \) indicate the excited and ground states, and for an \( H_2 \) perturber the potential shifts \( V \) are a function of the orientation (angle) of the molecule and the distance. Note that \( V_m(R_i) \) and \( V_n(R_i) \) are the potential shifts with respect to the asymptotic shifts at infinity; \( \Delta V \) is a total cross section.

Equation (2) indicates that the absorption cross section (3) can be multiple valued, at a given frequency there can be multiple Condon points. Expressions like equation (2) to obtain \( R_i(\nu) \) at a given absorption frequency yields an expression for the absorption cross section in the line wings at that frequency. Each solution for \( R_i(\nu) \) is called a Condon point, where the subscript \( i \) is now revealed to be the Condon point index. In principle, since \( \Delta V \) can be multiple valued, at a given frequency there can be multiple Condon points. Expressions like equation (3) must be summed for all such points to obtain the total cross section.

Expression (3) is not only missing the dipole transition moment (oscillator strength \( f_{mn} \)) but is not normalized by the dipole (Thomas-Reiche-Kuhn) sum rule to yield the correct cross section \( \sigma(\nu) \). Furthermore, it must be corrected at small detunings (large \( R_i \)). The correct expression for the absorption cross section in the wings of a spectral line in the quasi-static approximation is given by the unified Franck-Condon formula (Szudy & Baylis 1975, 1996)

\[
\sigma(\nu) = \sum_i \sigma_i(\nu) \sum_{i,j} \sigma_{ij}(\nu),
\]

where

\[
\sigma_i(\nu) = A \frac{R_i^2}{|\Delta V'(R_i)|} \left( \frac{\pi Z_i}{2} \right)^{1/2} \frac{L(z_i)}{z_i} \exp \left( -\frac{|V_0(R_i) - k_B T|}{h} \right),
\]

and

\[
\sigma_{ij}(\nu) = 2A \frac{R_i^2}{|\Delta V'(R_i)|} \left( \frac{\pi \sqrt{2}}{2} \right)^{1/2} \frac{M(Z_{ij})}{Z_{ij}} \exp \left( -\frac{|V_0(R_i) - k_B T|}{h} \right) .
\]

The A contains the transition oscillator strength and perturber number density and is given by

\[
A = 12\pi N_p \frac{\pi e^2}{m_e} f_{mn} .
\]

The argument \( z_i \) and \( Z_{ij} \) are given by the expressions

\[
z_i = \frac{1}{2} \left( \frac{\mu}{k_B T} \right)^{1/3} \left( \frac{\Delta V'(R_i)}{\hbar} \right)^2 \left( \frac{\Delta V''(R_i)}{\hbar} \right)^{-4/3}
\]

and

\[
Z_{ij} = \frac{1}{2} \left( \frac{\mu}{k_B T} \right)^{1/3} \left( \frac{\Delta V'(R_i) \Delta V'(R_j)}{\hbar} \right)^{1/2} \left( \frac{\Delta V''(R_i) \Delta V''(R_j)}{\hbar} \right)^{-2/3} ,
\]

where

\[
\Delta V'(R_i) = \frac{\partial \Delta V}{\partial R_i}
\]

and \( \mu \) is the reduced mass of the interacting pair. Here \( L(z_i) \) and \( M(z_i) \) are functions defined through the integrals

\[
L(z_i) = \int_0^\infty \frac{d\zeta}{\zeta^2} A^2 \exp \left( -z_i \zeta \right) e^{-\zeta^3} ,
\]

and

\[
M(z_i) = \int_0^\infty \frac{d\zeta}{\zeta^3} A^2 \exp \left( -z_i \zeta \right) e^{-\zeta^3} ,
\]

where \( Ai(x) \) is the Airy function and \( Ai'(x) \) is its derivative. The asymptotic behavior of \( L(z_i) \) and \( M(z_i) \) for positive \( z_i \) is

\[
L(z_i) = (36\pi z_i)^{-1/2}
\]

and

\[
M(z_i) = \left( \frac{z_i}{36\pi} \right)^{1/2} .
\]

Equation (5) is the expression that corresponds to equation (3), the sum is over the Condon points \( (i \) and \( j) \), and \( \sigma_{ij}(\nu) \) is the interference term between the Condon points.
The interference term is important only when \( R_i \sim R_j \), at which point \( \Delta V'(R_i) \) is formally zero. This singularity (seen in eqs. [3] and [5]) yields what is referred to as a “rainbow” or “satellite” feature (Beuc & Horvatic 1992) in the wings of an absorption spectrum. We expect such features in the Na I (5890 Å) and K I (7700 Å) absorption cross sections (eqs. 4 and 5). Note that at large \( z_i \), the expression \( \left( \pi z_i \right)^1/2 \left[ L(z_i) + M(z_i)/z_i \right] \) in equation (5) becomes a constant and equation (5) reduces to equation (3), modulo constants and the oscillator strength. Moreover, at large \( Z_{ij} \), the expression \( \left( \pi Z_{ij} \right)^1/2 \left[ L(Z_{ij}) - M(Z_{ij})/Z_{ij} \right] \) in equation (6) goes to zero.

The exponential terms in equations (5) and (6) provide natural cutoffs at positive (red) and negative (blue) detunings and depend only on the ground-state potential shifts and temperature. Such cutoffs have been shown to be necessary for reasonable spectral fits to T dwarf spectra longward of \( \sim 1.0 \mu \text{m} \) (Burrows et al. 2002) and are naturally provided by the quasi-static UFC theory.

The line cores (not the subject of this paper) are determined by distant encounters and are handled by assuming a van der Waals interaction potential with an adiabatic impact theory (Weisskopf 1933; Ch’en & Takeo 1957; Dimitrijevic’ & Peach 1990), as in BMS00 and Nefedov, Sinel’shchikov, & Usachev (1999). The result is a pressure broadened core of Lorentzian shape that applies out to only tens of wavenumber (cm\(^{-1}\)) detunings. The major contribution to the alkali line profile shape is determined by the statistical UFC theory, which applies beyond the core to thousands of wavenumber (and thousands of angstrom) detunings. The procedure for obtaining the wing absorption profiles is first to calculate the potential curves for the relevant levels of Na and K (§ 3 and § 4), then to calculate the Condon points, and finally to employ equation (4). We do this for Na + H\(_2\), Na + He, K + H\(_2\), and K + He interaction pairs and for the states that contribute to both the red and the blue wings of the 5890 and 7700 Å resonance features. For perturbations by H\(_2\), the potential interactions are functions of angle (orientation), introducing yet another degree of complexity.

3. TECHNIQUE FOR CALCULATING THE INTERACTION POTENTIALS AND LINE SHIFTS

The Na-D doublet of neutral sodium involves the \( 3s^2S_{1/2} - 3p^2P_{3/2,1/2} \) transitions, where the \( 2D \) transition (5890 Å) is from the 1/2 state to the 3/2 state with a multiplicity of 4 (=\( 2J + 1 \)) and the \( 1D \) transition (5896 Å) is from 1/2 to 1/2 with a multiplicity of 2. Hence, the ratio of the \( 2D \) and \( 1D \) line strengths is 2. The analogous transitions for potassium are \( 4s^2S_{1/2} - 4p^2P_{3/2,1/2} \) at 7665 and 7699 Å, respectively, with a similar strength ratio. Since the upper states of the \( 2D \) transitions are \( J = 3/2 \) states, they include \( p_x \) and \( p_y \) states that in molecular orbital theory can form bonding states with H\(_2\) (oriented perpendicularly). The \( p_z \) state associated with the \( 2P_{1/2} \) state is antibonding to H\(_2\). Figure 1 depicts the orientations of the interacting H\(_2\) and Na pair for C\(_{2v}\) symmetry (H \( \rightarrow \) H line perpendicular to the Na-H\(_2\) line). The potassium \( 4p \) states can be depicted in a perfectly analogous way. The \( ^2A_1 \) states depicted in Figure 1 are antibonding, and the interaction potential is purely repulsive at all distances \( R_i \). The \( ^2B_{1,2} \) states are attractive at large distances and repulsive at small distances.\(^3\) The ground states of both the Na + H\(_2\) and the K + H\(_2\) systems are repulsive for all distances \( R_i \). The upshot is that the energy difference between the \( ^2B \) state of the \( D_1 \) transition and the ground state decreases with decreasing \( R_i \) until \( R_i \) is quite small. Hence, the \( D_1 \) line, although it is blueward of the \( D_1 \) line for atoms in isolation, provides the red wing of the alkali line. Correspondingly, the \( D_1 \) line provides the blue wing.

A schematic of the excited-state minus ground-state energy shifts of the Na-D and K-I resonance lines is given in Figure 2. Figure 2 depicts the mapping between energy shift, line core, red wing, and blue wing. Note that \( \Delta V \) on the blue wing has a maximum (extremum), which results in a rainbow satellite feature. The absence of a corresponding extremum on the red wing means that there is no corresponding satellite feature redward of the line core.

To calculate the interaction potentials, we employ the multiconfigurational self-consistent field (MCSCF) variant of the quantum chemical code GAMESS (Schmidt et al. 1993). The Hartree-Fock (H-F) method is a self-consistent field approach that employs iteration to find a consistent solution to the multielectron, multicore wave function (its a Slater determinant) but assumes that the potential is a smoothed average and does not explicitly include electron-electron interactions. MCSCF is a post–H-F method that includes electron-electron interactions and exchange forces, the so-called configuration interaction (CI), but assumes that the CI term is small. It allows variation of not only the mixing coefficients of the various H-F configurations but also of the coefficients of the basis functions in the constituent molecular orbitals. In this way, the H-F orbitals from which the total wave function is constructed are optimized simultaneously. The MCSCF method requires care in the selection of the basis set but generally achieves a good solution for problems having low-lying excited states, as in the problem at hand. We use the complete active space self-consistent field (CASSCF) version of MCSCF and the 6-31G** split-valence basis set that incorporates Gaussian-type orbitals (Frisch et al. 1998). In practice, we first obtain a solution with the H-F method and then use this solution as a first guess in the full MCSCF/CASSCF calculation. This two-step approach has often proven necessary to achieve converged solutions.

We use the above methods and the GAMESS code to solve the many-electron Schrödinger equation for the wave functions and the energy levels of the various electronic states as a function of distance \( R_i \) for the composite system of alkali metal atom and either H\(_2\) or helium. For H\(_2\), this is done for a variety of orientations (from \( C_{2v} \) \( \theta = 90^\circ \) to \( C_{\infty v} \) \( \theta = 0^\circ \) ) [parallel] symmetries), and we keep the H-H bond length constant (Botschwina et al. 1981). We have included electron correlation effects successfully for He perturbations and for H\(_2\) perturbations germane to the red wings of both the Na and K lines. However, when calculating the blue wings for orientation angles other than \( 0^\circ \) or \( 90^\circ \), we had difficulty obtaining converged solutions with the electron correlation effects (CI) included. Hence, for the blue wings of the Na/K + H\(_2\) interaction pairs we have settled for the

\(^3\) Note that in order to connect to both communities, we use both the spectroscopist’s (\( A \) and \( B \)) and the physicist’s (\( P_{1/2,3/2} \)) nomenclature for the states.
pure H-F solutions. This approximation is good for large $R_1$ but begins to break down at small $R_1$ and large detunings.

For all the relevant $^2A$ and $^2B$ states we calculate the interaction potentials as a function of both distance and

\[ \frac{\Delta V}{\lambda} \]

(for H$_2$) angle of orientation. The calculations are done at hundreds of distances and (for H$_2$) for five angles ($\theta = 0^\circ, 20^\circ, 45^\circ, 70^\circ$, and $90^\circ$). Then we calculate the energy shifts ($\Delta V$) of the resonance transitions of Na and K. Although we reproduce the wavelengths of the isolated D$_2$ and D$_1$ lines of Na to within $\sim$14% (0.3 eV) and for K to within $\sim$21% (0.34 eV), we shift our calculated energy shifts by a constant amount that ensures that the line shift at very large $R_1$ is zero. This puts the line core exactly at the measured wavelength by construction. Furthermore, we do not calculate the dipole transition matrix elements as a function of $R_1$ but use the published oscillator strengths of the unperturbed Na and K resonance doublets in the calculation of the line profiles (eq. [7]). These incorporate the 2:1 strength ratio due to the spin degeneracy of the final states in the unperturbed D$_2$ and D$_1$ transitions.

4. POTENTIAL CURVES FOR THE Na + H$_2$, K + H$_2$, AND Na/K + He SYSTEMS

Figure 3 depicts the energy levels as a function of separation of the various states (relative to the ground state at infinite separation), for both Na and K perturbed by both helium and H$_2$. For H$_2$, the run of energy shift with $R_1$ for the four states is given for various orientation
angles. As Figure 3 shows, the ground-state interaction is always repulsive and is most repulsive for H$_2$ for colinear orientations ($C_\infty$ symmetry). This is the $V_0(R_i)$ term to be used in equations (5) and (6) in calculating the cutoff exponential. The $^2B$ states associated with the $p_x$ and $p_y$ atomic orbitals of sodium or potassium show a slight attraction for large angles (close to perpendicular) and large distances but then become universally repulsive as the hard core is approached (Botschwina et al. 1981). Figure 4 portrays the resulting transition energies for the D lines of both Na and K as a function of separation and angle. As is clear from the figure, the energy differences
for the transitions for which the excited states are $^2B$ states decrease with decreasing separation and, hence, are associated with the red wings of the spectral lines. Similarly, since the ground-state to $^2A_1$-state transitions have the opposite behavior, they are associated with the blue wings. Furthermore, the peaks seen at the bottom of Figure 4 at separations of $R_i \sim 2.4$–$2.5$ Å and $R_f \sim 3.1$–$3.2$ Å, respectively, for Na and K perturbed by H$_2$ imply that their blue wings have satellites at wavelengths of $\sim0.49$–$0.5$ and $\sim0.66$–$0.68$ µm. The K satellite might be near the Li feature at 6708 Å. Figure 2 schematically shows how the panels of Figure 4 merge to make the corresponding absorption profiles.

It is useful to compare these potential calculations with previous related work using different methods. Rossi & Pascale (1985, hereafter RP) have done $l$-dependent pseudo-potential calculations for the Na + H$_2$ and K + H$_2$ systems, and Botschwina et al. (1981) have done restricted Hartree Fock–self-consistent field (RHF-SCF) and pseudonatural orbital-coupled electron pair approximation (PNO-CEPA) calculations for the Na + H$_2$ system. The PNO-CEPA potential curves of Botschwina et al. are similar to those of RP. Neither did the calculations for the arbitrary H$_2$ orientations and small separations necessary to perform the line profile calculations that motivated this paper. Rather, they concentrated solely on separations greater than 2.0 Å and

![Figure 4](image_url)
on the $C_{\infty}$ and $C_{2v}$ symmetries. Nevertheless, their potential curves for these symmetries are similar to those found in Figure 3. For $C_{2v}$ symmetry and the Na + H$_2$ system, RP derive that the potential minimum for the $^2B_1$ state is at 2.4 Å and has a depth of 0.12 eV; we obtain 2.45 Å and 0.1 eV. For the $^2B_2$ state, RP derive corresponding numbers of 2.12 Å and 0.35 eV; we obtain 2.27 Å and 0.2 eV. For the K + H$_2$ system, RP derive for the $^2B_2$ state a minimum at 3.0 Å with a depth of 0.49 eV; we obtain 3.0 Å and 0.5 eV. RP estimate that the change in the potential of the $^2B_2$ state is 3.0 Å and 0.5 eV. RP estimate that the potential minimum for the $^2B_1$ state is 3.0 Å with a depth of 0.49 eV; we obtain 3.0 Å and 0.5 eV. RP estimate that the change in the potential of the $^2B_2$ state is 3.0 Å and 0.5 eV. RP estimate that the change in the potential of the $^2B_2$ state is 3.0 Å and 0.5 eV.

**5. THE ABSORPTION CROSS SECTIONS ON THE RED AND BLUE WINGS OF THE Na (5890 Å) AND K (7700 Å) RESONANCE LINES**

Using the UFC/quasi-static equations (5) and (6), we obtain the absorption spectra as a function of photon wavelength for the D$_2$ and D$_1$ lines of Na and K centered near 5890 Å (0.589 μm) and 7700 Å (0.77 μm), respectively. These are depicted in Figure 5 at a temperature of 1000 K and a total pressure of 1 atm. The contributions at various orientation angles of H$_2$, the angle-integrated spectra (solid lines), and the results for the Na + He and K + He systems are shown. The Lorentzian cores are not included on this plot. Since the ground-state potential shifts increase quickly at small separations (Fig. 3) and the associated exponential terms in equations (5) and (6) introduce a large cutoff, Condon points at such small separations make only a marginal contribution to the overall opacities. As a consequence, although there can be more than two Condon points (Fig. 4), we include at most the outer two in our theory. For the same reason, we ignore possible satellites on the very far red wings.

Figure 5 encapsulates the central results of our study. The cutoff on the red wing of the potassium feature due to the exponential term (eq. [5]) containing the ground-state interaction potential of the K + H$_2$ system is seen to be situated between 0.95 and 1.0 μm, close to the 0.98 μm used in Burrows et al. (2002). The cutoff of the red wing of the Na feature is near 0.8 μm but is a bit more gradual. The corresponding cutoffs for the alkali-He systems are more abrupt but of less importance because of the lower abundance of helium. It should be noted that for the temperatures in cool atmospheres the precise form and position of this cutoff is a sensitive function of the ground-state potential. Errors in the potential of $\lesssim$ 0.1 eV that may arise at small $R_i$ for the alkali-H$_2$ systems translate directly into shifts in the position of the turnover and in the magnitude of the cross section at the turnover. Such an effect is demonstrated by the difference between the cross sections with and without electron-correlation/configuration-interaction terms (depicted below in Fig. 7). Figure 5 also makes clear that the red and blue wings are asymmetrical, as one would expect from the discussion in § 4 and Figure 4.

The satellite features identified on the blue wings of both the Na and K features by the asterisks on Figure 5 have been alluded to before, but we note once again that our calculations are too imprecise to derive the detailed shape of the actual rainbow structures (which for the alkali-H$_2$ systems is a composite of the corresponding curves for the various angles). Nevertheless, the existence and approximate wavelengths of the satellites remain clear.

Figure 6 portrays the temperature and pressure dependences of the line profiles. Three curves (at 800, 1000, and 1500 K) show the temperature dependence at 1 atm pressure, and one curve at 1000 K and 10 atm shows, by comparison with the other 1000 K curve, the pressure dependence. Because of the $N_p$ dependence in equation (7), higher pressures lead to higher wing strengths. The Thomas-Reiche-Kuhn sum rule is still satisfied by a corresponding diminution in the strength in the Lorentzian core. Because of the exponential term, increasing the temperature raises the cross section in the far wings. However, because of the constraint of constant pressure, increasing the temperature slightly lowers the cross sections in the near wings.

It should be emphasized that, unlike the theory of BMS00 and the line profile formalism used in Burrows et al. (2002), there are no free parameters in our theory. The cutoffs and shapes arise naturally because the physics of the line-broadening process has been treated. Limitations on the accuracy of the current work are in the accuracy of the quantum chemistry calculations of the potential curves and in the use of the semiclassical formalism to treat the broadening. The earlier theory of BMS00 was constructed to fill the theoretical and experimental void concerning the far wing profiles of the alkali metal lines perturbed by molecular hydrogen. Burrows et al. (2002) followed with a simpler theory that used a Gaussian-truncated Lorentzian profile. Previously in astrophysics the character of the far wings of the K i and Na D resonance features perturbed by H$_2$ had not been needed.

Given our new calculations, it is useful to compare them with the stopgap theories of BMS00 and Burrows et al. (2002). Figure 7 is a comparison of the BMS00 (red) and Burrows et al. (2002; green) potassium cross sections with
the corresponding cross sections using the theory of this paper (blue). For the BMS00 prescription, we arbitrarily set the associated $q$-parameter equal to 0.5. A temperature of 1000 K and a pressure of 1 atm were assumed. The BMS00 and the Burrows et al. (2002) curves include the Lorentzian core, while the newly calculated quasi-static curve does not. Also shown are the new cross sections calculated without the CI (blue, dashed line). At the inner red wing, the theory of Burrows et al. (2002), in which the pressure-broadened Lorentzian was truncated with a Gaussian near 0.98 $\mu$m, is within a factor of 3 of the more detailed calculation but clearly deviates from it. However, on the red wing the simple theory of BMS00 is actually surprisingly close to the new result. On the far red wing, the cross sections of the new theory plummet more precipitously than either BMS00 or Burrows et al. (2002). This emphasizes even more strongly the existence of the steep cutoff inferred by Burrows et al. (2002) to be necessary in order to reproduce the Z ($\sim$1.0 $\mu$m) and J ($\sim$1.2 $\mu$m) band fluxes observed for the T dwarfs (Burgasser et al. 2002). Note, however, that the new cross sections on the far blue wing are as much as a factor of 4 higher than the corresponding cross sections of the old theories. The same result obtains for the blue wing of the Na-D line. In sum, although the BMS00 theory was good in the near red wings, in places the contrast between both the BMS00 and the Burrows et al. (2002) formulations and our
parameterless UFC calculations is large. As a result, we recommend that in the future the new theory be used for detailed T and L dwarf spectral calculations.

6. CONCLUSIONS

Using the quantum chemical code GAMESS, we have calculated as a function of distance the interaction potentials of the excited and ground states of sodium and potassium perturbed by H$_2$ and helium. For H$_2$, we also calculated the dependence of the interaction potentials on orientation angle. Using these potentials and the unified Franck-Condon formalism, we derived the absorption-line profiles in the wings of the Na-D doublet and the K $\text{$\iota$}$ resonance doublet at detunings of thousands of angstroms. These lines and their wings are of central importance in the atmospheres and spectra of brown dwarfs, T dwarfs, L dwarfs, and hot Jupiters. Our theory has no free parameters and naturally accounts for the cutoffs in the far red wings inferred to be present to explain the high $J$ and $Z$ band fluxes observed in T dwarfs (Burrows et al. 2002). However, the new cross sections differ from those used previously by having sharper cutoffs, stronger blue wings, and satellite features. Furthermore, the red/blue asymmetry is pronounced.

From our calculations using the full configuration interaction at the subset of useful H$_2$ orientation angles for which we were able to obtain convergence for the $^2A_1$ states (of relevance for the calculation of the blue wings) and from a comparison of the H-F and CI results for perturbations by helium, we have determined that the H-F and CI numbers

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{Representative temperature and pressure dependences of the absorption cross sections for the Na/K + H$_2$ systems. At 1 atm pressure, cross sections (in cm$^2$) at temperatures of 800 K (blue), 1000 K (red), and 1500 K (green) are depicted. Another curve at a pressure of 10 atm and a temperature of 1000 K is shown (purple). The left ends terminate at the central positions of the satellites. Note that the positions of these rainbow features are very weak functions of pressure and temperature and that the cutoff wavelength on the red wings (however defined) is an increasing function of temperature.}
\end{figure}
on the blue wings differ little, although the associated potential differences on the red wings can differ by ~0.1 eV. This gives us some confidence that, despite the fact that we use the H-F approach on the blue wings for perturbations by H2, our blue wing results are satisfactory. Fortunately, for all the red wing results, we were able to obtain full convergence using the MCSCF/CI formalism at all H2 angles.

The need for line wing strengths at such large detunings has few precedents in astrophysics. The next step is to incorporate the new alkali line opacities into a spectral synthesis code and to identify the differences between the fits using the old and the new algorithms. The line cores will be unchanged, but the blue wings and the spectra from 0.8 to 0.9 $\mu$m on the red wings of the K i line will be slightly altered, all else being equal. The major virtue of our new algorithm is that it is parameterless. As a result, we reduce by one (or even a few) the number of free parameters needed in fits to the increasing number of optical and near-IR spectra being measured for T dwarfs (in particular), thereby making the extraction of physical quantities such as effective temperature and gravity more robust and reliable.

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REFERENCES

Anders, E., & Grevesse, N. 1989, Geochim. Cosmochim. Acta, 53, 197
Beeg, R., & Horvatic, V. 1992, J. Phys. B, 25, 1497
Botschwina, P., Meyer, W., Hertel, I., & Reiland, W. 1981, J. Chem. Phys.,
75, 5438
Breene, R. G. Jr. 1957, Rev. Mod. Phys., 29, 94
———. 1981, Theories of Spectral Line Shape (New York: Wiley)
Burgasser, A. J., Kirkpatrick, J. D., Reid, I. N., Liebert, J., Gizis, J. E., &
Brown, M. E. 2000, AJ, 120, 473
Burgasser, A. J., et al. 1999, ApJ, 522, L65
———. 2002, ApJ, 564, 421
Burrows, A., Burgasser, A. J., Kirkpatrick, J. D., Liebert, J., Milsom, J. A.,
Sudarsky, D., & Hubeny, I. 2002, ApJ, 573, 394
Burrows, A., Hubbard, W. B., Lunine, J. I., & Liebert, J. 2001, Rev. Mod.
Phys., 73, 719
Burrows, A., Marley, M. S., & Sharp, C. M. 2000, ApJ, 531, 438 (BMS00)
Burrows, A., & Sharp, C. M. 1999, ApJ, 512, 843
Charbonneau, D., Brown, T. M., Noyes, R. W., & Gilliland, R. L. 2002,
ApJ, 568, 377
Ch’en, S. Y., & Takeo, M. 1957, Rev. Mod. Phys., 29, 20
Ch’en, S. Y., & Wilson, R. A. 1961, Physica, 27, 497
Dimitrijević, M. S., & Peach, G. 1990, A&A, 236, 261
Frisch, M. J., et al. 1998, Gaussian 98 (Pittsburgh: Gaussian, Inc.)
Griem, H. R. 1964, Plasma Spectroscopy (New York: McGraw Hill)
Holstein, T. 1950, Phys. Rev., 79, 744
Holtzmark, J. 1925, Z. Phys., 34, 722
Kirkpatrick, J. D., et al. 1999, ApJ, 519, 802
———. 2000, AJ, 120, 447
Kleinekathöfer, U., Tang, K. T., Toennies, J. P., & Yiu, C. L. 1996, Chem.
Phys. Lett., 249, 257
Liebert, J., Reid, I. N., Burrows, A., Burgasser, A. J., Kirkpatrick, J. D., &
Gizis, J. E. 2000, ApJ, 539, L155
Lodders, K. 1999, ApJ, 519, 793
Martin, E. L., Delfosse, X., Basri, G., Goldman, B., Forveille, T., &
Zapatero Osorio, M. R. 1999, AJ, 118, 2466
Nefedov, A. P., Sinel’shchikov, V. A., & Usachev, A. D. 1999, Phys. Scr.,
59, 432
Pontius, E. M., & Sando, K. M. 1983, Phys. Rev. A, 28, 3117
Rossi, F., & Pascale, J. 1985, Phys. Rev. A, 32, 2657 (RP)
Schmidt, M. W., et al. 1993, J. Comput. Chem., 14, 1347
Szudy, J., & Baylis, W. 1975, J. Quant. Spectrosc. Radiat. Transfer, 15, 641
———. 1996, Phys. Rep., 266, 127
Tsuji, T., Ohnaka, K., & Aoki, W. 1999, ApJ, 520, L119
Weisskopf, V. 1933, Z. Phys., 43, 1