EQUILIBRIUM CHEMISTRY IN A BROWN DWARF'S ATMOSPHERE: CESIUM IN GLIESE 229B

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ABSTRACT

The distribution of Cs in Gliese 229B's atmosphere reveals how equilibrium chemistry establishes the atmospheric composition. The rapid kinetics of cesium chemistry keeps the Cs abundance in thermochemical equilibrium and renders Cs a sensitive measure of chemical processes in brown dwarf atmospheres. Observations of Gliese 229B indicate a subsolar bulk abundance of Cs, the depletion of alkali metals in the upper atmosphere from condensation, and a partitioning of heavy elements different from that of the Sun.

Subject headings: infrared: stars — planets and satellites: general — stars: atmospheres — stars: individual (Gliese 229B) — stars: low-mass, brown dwarfs

1. INTRODUCTION

Substellar bodies range in character from the Jovian planets with radiative effective temperatures $T_{eff} = 50$–110 K to solitary brown dwarfs with $T_{eff} \sim 2000$ K. The temperatures of these objects determine the chemical composition of their atmospheres. Spectra of Jovian planets and cool brown dwarfs are dominated by absorption from reduced molecules (e.g., CH_4, H_2O, and NH_3). Low-mass stars and warmer brown dwarfs display features due to metals in atomic (e.g., Na, K) and molecular form, e.g., FeH, TiO, and VO (Kirkpatrick et al. 1999). Atomic cesium characterizes the bodies intermediate between planets and stars. Its features appear only in atmospheres having $T_{eff} \sim 800$–2000 K (Lodders 1999; Burrows & Sharp 1999; Kirkpatrick et al. 1999). In cooler objects cesium resides as CsCl; in hotter objects Cs^+ presides. This Letter analyzes Cs features in the optical spectrum of the coolest brown dwarf detected to date, Gliese 229B (Gl 229B). The rapid kinetics of cesium chemistry indicates that Cs-bearing species are in thermochemical equilibrium, which makes it an excellent probe of atmospheric chemistry.

2. OBSERVATIONS AND ANALYSIS

Oppenheimer et al. (1998) identified two Cs features (Table 1) in their Keck I spectra of Gl 229B (Fig. 1). The longer wavelength line is also seen in the *Hubble Space Telescope* spectra of Schultz et al. (1998).

We analyze Gl 229B's spectra with a radiative transfer calculation based on the discrete ordinates approach with eight angular streams (Stammes et al. 1988). We divide the atmosphere into 100 layers (extending from 0.063 to 200 bars), calculate the monochromatic flux at every 7.7×10^{-6} μm, and convolve the spectrum to a Gaussian function having an FWHM of 4×10^{-4} μm. The Cs absorption lines are visible in a continuum established by atmospheric dust, H_2O, K, and pressure-induced H_2-He absorption. We adopt the atmosphere composition and temperature pressure profile of Griffith, Yelle, & Marley (1998). We chose a gravity of 1000 m s^{-1} from the present allowed range (Marley et al. 1996; Allard et al. 1996). This assumption affects the values of absolute abundances of the constituents, less so the relative abundances of heavy elements. Absorption properties for the Cs lines are summarized in Table 1. Despite the high pressures probed, the ideal gas equation approximates the behavior of gases well; we estimate errors in density of less than 0.01%.

The pressure levels of the half-maximum values in the contribution functions calculated in the center of the Cs features occur at 4 and 15 bars. Thus, the atmospheric levels sampled lie largely between these pressures, where ambient temperatures range from 1100 to 1500 K. In this region, cesium undergoes a chemical transition from Cs (at $T > 1400$ K) to CsCl (at $T < 1400$ K).

We first analyzed the Cs features using distributions predicted from thermochemical equilibrium models by Lodders (1999) and independently by Burrows & Sharp (1999). The calculated spectral lines have depths exceeding those observed (Fig. 1). Uncertainties in the thermal profile slightly affect the depth of the calculated Cs features; a 20 K temperature increase above the nominal thermal profile at the line-forming region (7 bars) decreases the line strength by 5%. Because the Cs lines form at altitudes above most of the haze, their shapes are insensitive to uncertainties in the haze optical characteristics. Other potential opacity sources (e.g., the wings of potassium lines) do not significantly change the analysis of the cesium features. The uncertainties can not account for the mismatch between the calculations and the data; instead, a different Cs profile is indicated.

3. DISCUSSION

Before further addressing the equilibrium chemistry, we investigate disequilibrium processes. The two most likely nonequilibrium sources of Cs arise from photochemistry and vertical transport. We find these mechanisms ineffective at modifying the Cs distribution.

3.1. *Photochemical Production*

The pertubation in the Cs number density, [Cs], resulting from photochemistry can be estimated by assuming that Cs is supplied by the UV dissociation of CsCl, destroyed from reactions with Cl-bearing molecules, and exists in steady state, produced as quickly as it is destroyed. The production rate of Cs is

$$\frac{d[Cs]}{dt} = J[CsCl], \quad (1)$$

where J is the photolysis rate. We approximate the UV flux incident on Gl 229B as blackbody radiation from the $T_{eff} = 3500$ K primary, assumed (from the angular separation) to be

TABLE 1
CESIUM DATA

Property	D1	D2
Transition	$6s^2S_{1/2}$–$6p^2P_{1/2}$	$6s^2S_{1/2}$–$6p^2P_{3/2}$
Wavelength (nm)	894.35	852.11
Oscillator strength	0.35	0.71
Line strength ($cm^2\ cm^{-1}$)	3.10×10^{-13}	6.28×10^{-13}
HWHM ($cm^{-1}\ bar^{-1}$)[a]	$1.01\ (T/295)^{-0.75}$	$1.51\ (T/295)^{-0.75}$

[a] From Bernabeu & Alvarez 1980.

40 AU away from Gl 229B. An upper limit to the photolysis rate then follows by assuming that no other gas in Gl 229B's atmosphere besides CsCl absorbs 0.2–0.3 μm photons. Integration of the product of the cross section (Davidovits & Brodhead 1967) and the incident flux provides a value of $4.4 \times 10^{-5}\ s^{-1}$ for J. Atomic Cs is destroyed upon reacting with HCl,

$$Cs + HCl \rightarrow CsCl + H, \qquad (2)$$
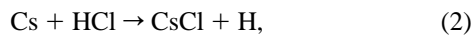
at a rate of

$$\frac{-d[Cs]}{dt} = k_2[Cs][HCl], \qquad (3)$$

where $k_2 = 5 \times 10^{-12}\ cm^3\ s^{-1}$ is the rate coefficient for the reaction (Clay & Husain 1990). Although NaCl and KCl are more abundant than HCl at certain levels (Figs. 3 and 4), we use the HCl rate as representative of any of the three reactions. Equating the production and destruction rates, the mole fraction of Cs is

$$q_{Cs} = \frac{f_{Cs}J}{J + k_2[HCl]}, \qquad (4)$$

where f_{Cs}, the elemental abundance of cesium in Gl 229B's atmosphere, is assumed to be solar (2.2×10^{-11}) and partitioned among Cs and CsCl. Estimating the density [HCl] to be near the solar Cl ($q_{HCl} = 3.1 \times 10^{-7}$) and unaffected by the minor presence of Cs, we calculate that photolysis enhances the abundance by $q_{Cs} \sim 10^{-16}$, far less than the values observed and the amount supplied by thermochemistry.

3.2. Vertical Transport

The effectiveness of transporting Cs to Gl 229B's upper atmosphere depends on the rate at which Cs reacts with ambient chlorine molecules: KCl, NaCl, or HCl (e.g., eq. [2]). We estimate the time constant for this reaction with $\tau_{chem} = (k_2[HCl])^{-1}$. Equating τ_{chem} to the time constant for vertical mixing at the 1280 K level (where the equilibrium value $q_{Cs} = 10^{-12}$), we derive an eddy-mixing coefficient of $K = 10^{12}\ cm^2\ s^{-1}$. This value is highly unlikely; it exceeds by many orders of magnitude that indicated by the CO features in Gl 229B's near-IR spectrum and that derived of free convection (Griffith & Yelle 1999). We therefore find that the reaction of Cs with HCl (and presumably NaCl and KCl) is fast enough that neither photochemical breakup of CsCl nor vertical transport of Cs affects the Cs distribution; it is most likely in thermochemical equilibrium.
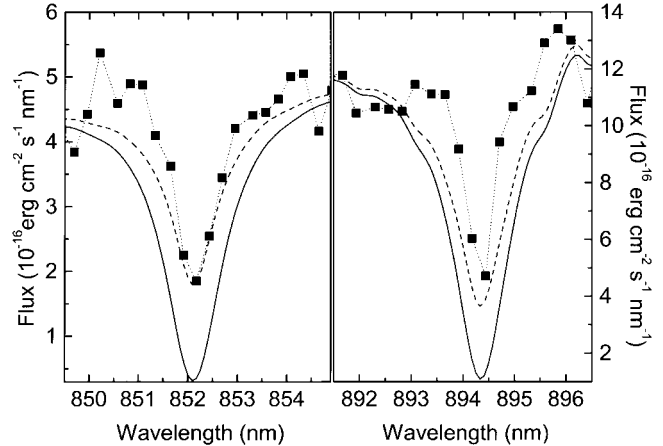

FIG. 1.—Keck I observations of Gl 229B (*squares*) from Oppenheimer et al. (1998). Synthetic spectra calculated from the Cs distributions of nonrainout (Burrows & Sharp 1999) and rainout models of solar composition (Lodders 1999) are shown by dashed and solid lines, respectively.

3.3. Thermochemical Equilibrium Models

Detailed studies by Lodders (1999) and Burrows & Sharp (1999) investigate the Cs chemistry in brown dwarfs. They explore the consequences of two separate assumptions: that condensation at depth eliminates elements from the higher observable levels of an atmosphere and that no rainout of elements occurs. While these differing premises both predict equal abundances for the two major Cs constituents (Cs and CsCl) at the 1400 K level, the Cs profiles disagree at lower pressures. The rainout model finds that the Cs abundance decreases more slowly than does the nonrainout model. Nonetheless, neither profile matches the observations (Fig. 1). This is not surprising because both studies assume a solar abundance of Cs, while there is good evidence that the metallicity is subsolar. An oxygen abundance $\sim\frac{1}{3}$ solar is indicated by Gl 229B's spectrum assuming the gravity and thermal profile taken here (Griffith et al. 1998). The metallicity of the primary, measured from FeH lines, is also consistent with subsolar abundances with values [Fe/H] = -0.2 ± 0.4 (Schiavon, Barbury, & Singh 1997) and [Fe/H] = -0.15 ± 0.15 (Mould 1978).

Our investigation of the Cs chemistry follows the general guidelines laid down by Lodders (1999) and Burrows & Sharp (1999), yet allows for heavy-element abundances below the solar values. The chemistry can be disentangled by considering the hierarchy in abundances of the participating condensibles and alkali, chlorine, and Cs molecules. Relevant condensation species are considered first because these reactions involve elements (e.g., S and Al) much more abundant than, and thus largely unaffected by, the chlorine and the alkali elements. The chlorine chemistry follows and establishes the most abundant chlorine-bearing molecules available to interact with Cs. We consider Na, NaCl, K, KCl, H, and HCl and assume that no other compounds contain chlorine, sodium, and potassium. Other members of the alkali chemistry, including cesium, are too scarce to consider in this step. Equilibrium among Cs and other alkali-bearing molecules establishes the Cs-to-CsCl ratio in the final step. We discuss our analysis in the reverse order from the calculation.

The equilibrium of Cs and CsCl with other chlorine mole-

cules can be described as

$$3Cs + HCl + NaCl + KCl \leftrightarrow 3CsCl + H + Na + K \quad (5)$$
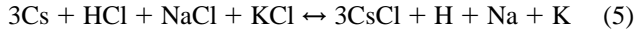
with an equilibrium constant

$$K_{Cs\text{-}CsCl} = \frac{P_{CsCl}^3 P_H P_{Na} P_K}{P_{Cs}^3 P_{HCl} P_{NaCl} P_{KCl}}, \quad (6)$$

where P_X denotes the partial pressure of species X. Equilibrium constants are calculated from the Gibbs free energies of formation obtained from the JANAF tables (Chase 1998). Equation (6) and the conservation of mass of elemental cesium provide a solution for the Cs mole fraction:

$$q_{Cs} = \frac{C f_{Cs}}{1 + C}, \quad (7)$$

where

$$C = \left(\frac{[Na][K][H]}{[NaCl][KCl][HCl] K_{Cs\text{-}CsCl}} \right)^{1/3}. \quad (8)$$

This expression can be evaluated after determining the abundances of Na, NaCl, K, KCl, H and HCl from three reactions of the form

$$X + YCl \leftrightarrow Y + XCl, \quad (9)$$
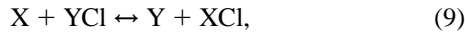
with the equilibrium constant $K_{X\text{-}Y}$. Here X and Y represent the pairs (K, Na), (H, K), and (Na, H). Two independent equations follow:

$$K_{K\text{-}Na} = \frac{P_{Na} P_{KCl}}{P_K P_{NaCl}}, \quad (10)$$

$$K_{H\text{-}K} = \frac{P_K P_{HCl}}{P_H P_{KCl}}. \quad (11)$$

Atomic hydrogen, regulated solely by equilibrium with H_2, has a mole fraction of $(K_{H_2-H} q_{H_2}/P)^{0.5}$. This, equations (10) and (11), and the three relations describing the mass conservation of Na, K, and Cl allow us to solve for the six unknowns: [HCl], [NaCl], [KCl], [H], [K], and [Na].

The condensation chemistry regulates the reservoir of Na and K and leads to the differing profiles of Cs in the rainout and nonrainout models (Lodders 1999; Burrows & Sharp 1999).

The nonrainout model (Burrows & Sharp 1999) finds that K and Na leave the atmosphere at the ~1400 and ~1300 K levels, respectively, through the condensation of high albite ($NaAlSi_3O_8$) and sanidine ($KAlSi_3O_8$). We calculate this effect by considering the equilibrium between the major Al, Si, Na, and K species as derived by Burrows & Sharp. There are two equations of the form

$$2X + H_2O + 13MgSiO_3(s) + MgAl_2O_4(s) \leftrightarrow$$
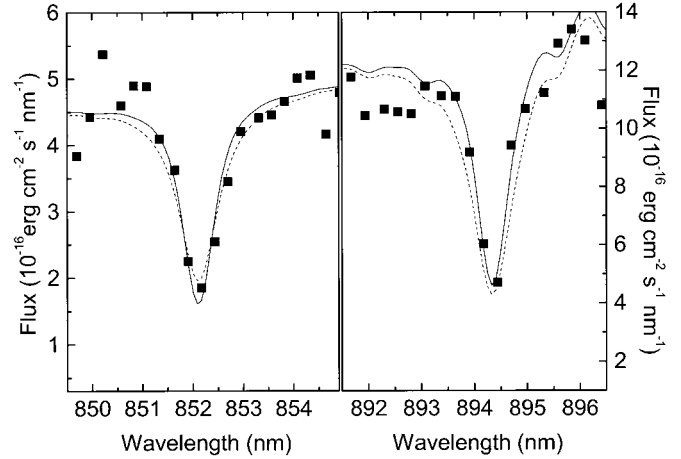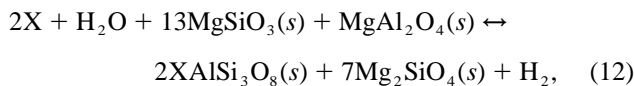$$2XAlSi_3O_8(s) + 7Mg_2SiO_4(s) + H_2, \quad (12)$$

FIG. 2.—Synthetic spectra calculated assuming no rainout, the condensation of sanidine and albite, and heavy element abundances $\frac{1}{3}$ the solar values (*dashed line*). Synthetic spectra calculated assuming rainout, the condensation of Na_2S, and heavy element abundances $\frac{1}{8}$ the solar values (*solid line*).

where X represents Na or K for albite or sanidine, respectively. The equilibrium constants are given by

$$K_{12} = \frac{P_{H_2}}{P_{H_2O} P_X^2}, \quad (13)$$

where all the activities are set to unity. Equation (13) is solved using the Gibbs free energy of formation values of Lodders & Fegley (1998) and assuming that all the Si, Al, and Na are distributed among the molecular forms participating in the equilibrium equations above. This simple treatment produces distributions for the alkali metals and Cs constituents close to those published by Burrows & Sharp for a solar abundance atmosphere.

Calculations by Lodders (1999) find that Al condenses below the observed levels and is unavailable to form albite and sanidine. Instead, Na is removed at ~1033 K by the condensation of Na_2S. We calculate the effects of the condensation of Na_2S on the Na chemistry by considering the equilibrium of

$$H_2S + Na \leftrightarrow Na_2S(s) + H_2 \quad (14)$$
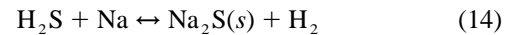
and the corresponding equilibrium constant

$$K_{14} = \frac{A_{Na_2S} P_{H_2}}{P_{Na} P_{H_2S}}, \quad (15)$$

where A_{Na_2S} is the activity of Na_2S, set to unity. For simplicity, we assume that S resides only in Na_2S and H_2S and sodium exists only as Na (since Cl is an order of magnitude less abundant than Na). Equation (15) can be solved for Na with the help of the elemental conservation relationships. This calculation produces a Cs profile in agreement with that of Lodders (1999) for a solar abundance atmosphere.

The best fit to the albite and sanidine condensation models has a cesium abundance f_{Cs} that equals $\frac{1}{2}-\frac{1}{3}$ of solar (Fig. 2), the same value found for the oxygen abundance by Griffith et al. (1998). However, the calculated spectral lines are wider than those observed. The Cs distribution for this model along with the alkali metal chemistry are shown in Figure 3. The Na_2S
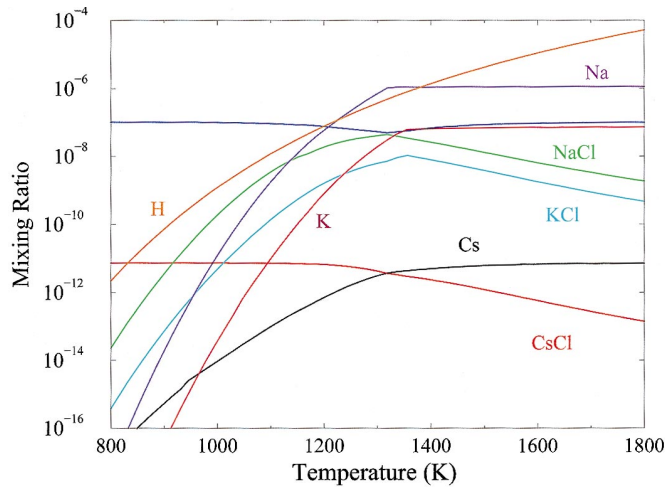
FIG. 3.—Alkali and Cs equilibrium abundances in Gl 229B's atmosphere, assuming $\frac{1}{3}$ the solar abundance of heavy elements and the nonrainout chemistry that leads to the condensation of albite and sanidine.
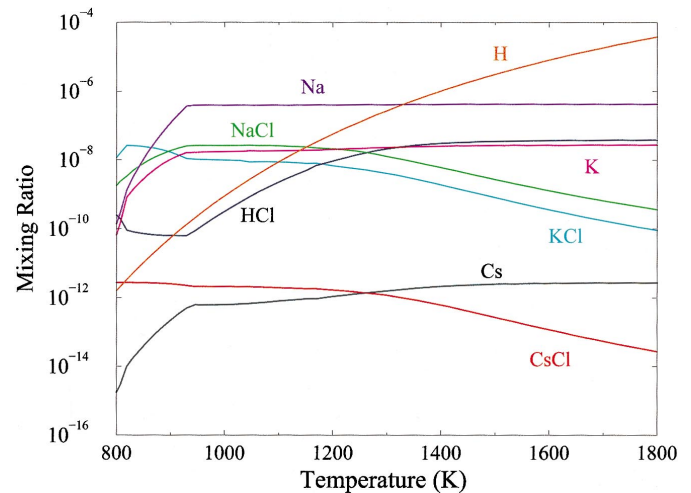

FIG. 4.—Alkali and Cs equilibrium abundances, assuming $\frac{1}{8}$ the solar abundance of heavy elements and the rainout chemistry leading to the condensation of Na_2S.

condensation models better interpret the lines since more Cs resides higher in the atmosphere and less Cs is needed at deeper levels to fit the depth of the features (Fig. 2). Yet, an elemental abundance of Cs 1/7 to 1/10 of solar is needed (Fig. 4). The widths of the Cs features imply that albite and sanidine do not form. Instead, Al may condense at depth and thus be absent in Gl 229B's observable atmosphere, as argued by Lodders (1999). We also point out that the formation of albite and sanidine might be hindered by kinetics because solid particulates are involved. In addition, a subsolar Cs/O ratio is indi-

cated, suggesting either a different bulk elemental abundance for the Gl 229 system or the sequestering of heavy elements in the interior of the brown dwarf.

In the atmospheres of brown dwarfs, the tenacity of Cs to remain in equilibrium makes it both (1) a sensitive measure of the elemental abundance of a heavy element and (2) a sensitive measure of the condensation chemistry of alkali metals in brown dwarfs.

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