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The electronic bands of CrD, CrH, MgD and MgH: application to the 'deuterium test'

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ABSTRACT

We compute opacities for the electronic molecular band systems $A^6\Sigma^+$–$X^6\Sigma^+$ of CrH and CrD, and $A^2\Pi$– $X^2\Sigma^+$ of MgH and MgD. The opacities are computed by making use of existing spectroscopic constants for MgH and CrH. These constants are adjusted for the different reduced masses of MgD and CrD. Frank–Condon factors are used to provide intensities for the individual vibronic bands. These results are used in the computation of synthetic spectra between $T_{\rm eff} = 1800$ and 1200 K with an emphasis on the realization of 'deuterium test', first proposed by Bejar et al. to distinguish brown dwarfs from planetary mass objects. We discuss the possible use of CrD and MgD electronic bands for the 'deuterium test'. We find CrD to be the more promising of the two deuterides, potentially, the most useful bands of CrH/CrD are the $\Delta v = +1$ and $\Delta v = -1$ at 0.795 and 0.968 μm.

Key words: stars: evolution – stars: fundamental parameters – stars: late-type – stars: low-mass, brown dwarfs.

1 INTRODUCTION

The 'deuterium test' was suggested as a method of identifying planetary mass objects among cool objects (Béjar, Zapatero & Rebolo 1999; Chabrier et al. 2000). In practice, it was proposed to search for absorption lines of molecules containing deuterium (HDO, CrD, FeD, etc.). Deuterium is burnt in stellar interiors via the fusion reaction ^{2}D(p,γ)^{3}He at temperatures ($T > 8 \times 10^5$ K). The interiors of substellar objects with $M < 13\ M_{\rm J}$, where $M_{\rm J}$ is a Jovian mass ($0.001\ {\rm M}_\odot$), do not reach temperatures high enough for deuterium to ignite (Saumon et al. 1996). As a result the deuterium abundance in the atmospheres of these objects is unchanged from the formation of these objects. This gives rise to the definition of a brown dwarf as an object which has insufficient mass to fuse ^{1}H to ^{4}He, but has sufficient mass to fuse^{2}H to ^{3}He. By comparison, a planetary mass object has insufficient mass to ignite fusion of any sort (Saumon et al. 1996).

In higher mass objects such as stars, deuterium burning is completed comparatively quickly (t = 1–3 Myr) during the evolution prior to the star's period on the main sequence (D'Antona & Mazzitelli 1998). The deuterium depletion rate depends on the mass of the star or brown dwarf and thus the 'deuterium test' can be used in a number of ways.

(i) Discern planets from brown dwarfs in a population of low-mass objects.

(ii) Determine the evolutionary status of young objects in open clusters with ages of several million years.

(iii) Study the evolution of the abundance of deuterium in the atmospheres of low-mass substellar objects, a phenomenon which is poorly understood. The rate of depletion of deuterium depends upon rotation, magnetic field strength, and other parameters which affect the efficiency of convection in low-mass objects.

Such investigations can usefully be combined with the 'lithium test' proposed by Rebolo, Martín & Magazzù (1992), Magazzù, Martín & Rebolo (1993). For stars ($M > 75\ M_{\rm J}$), the burning of lithium, Li (p,α)^{4}He, becomes efficient at evolutionary stages preceding the main sequence at interior temperatures of $T > 2.5 \times 10^6$ K (D'Antona & Mazzitelli 1998). The 'lithium test' has been successfully applied to identify brown dwarfs in a population of ultracool dwarf stars (Rebolo et al. 1996; Basri 2000). The lithium test is relatively easily applied to M dwarfs. The reason for this is that the resonance lines of neutral atomic lithium lie in the optical region of the spectrum, at 0.6708 μm. One blemish with the 'lithium test' is the severe blending of lithium lines with the background of TiO

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lines; none the less Li lines break through the molecular background. In the spectra of cooler M and L dwarfs Ti atoms are depleted on to dust particles (Tsuji et al. 1996; Jones & Tsuji 1997; Pavlenko 1998) so TiO absorption is weakened. In the L dwarf regime the appearance of lithium lines contends with dust opacity and the wings of K I and Na I resonance lines (see Pavlenko, Zapatero Osorio & Rebolo 2000b and references therein).

The realization of the 'deuterium test' is considerably more difficult. Conventionally, the deuterium abundance of hot objects is determined from analysis of multicomponent features on the background of the L_α 0.1215 μm H I line seen in emission. Unfortunately, this method cannot be used in the case of ultracool dwarfs which are covered by a thick envelope of neutral hydrogen. Observations also yield H I emission lines (H_α 0.6563 μm) formed in the outermost layers of hot chromospheres or accretion discs around young stars. However, such a plasma is variable and may be polluted by interstellar material.

Taking into account these circumstances, it is logical to analyse the spectral lines of deuterated molecules formed in the photospheric layers of ultracool dwarfs. The first investigation and analysis of the combined spectra of H_2O/HDO were carried out by Chabrier et al. (2000) and Pavlenko (2002). Due to the change in mass and the breakdown of molecular symmetry the vibration–rotation bands of HDO in the mid-infrared spectrum shift with respect to the H_2O bands. There are a few spectral regions which can be used for detection of HDO lines in the infrared spectra of ultracool dwarfs: 3.5–4, ∼5, 6–7 μm (Pavlenko 2002). The main problem is that despite the shift in wavelength such HDO lines will be on a background of far stronger H_2O lines.

A possible alternative to HDO are the diatomic hydrides. Strong molecular bands of diatomic metal hydrides such as MgH and CrH can be observed in the optical spectrum of ultracool dwarf stars. The MgH band system $A^2\Pi$–$X^2\Sigma^+$ can be observed at 0.47–0.6 μm, and the CrH band system $A^6\Sigma^+$–$X^6\Sigma^+$ show absorption features at 0.6–1.5 μm.

The molecules MgH and CrH have been known in astrophysics for a long time. MgH has been more extensively studied than CrH, because it can be observed in the spectra of G to M type stars. The dissociation energy of MgH is very low (1.285 eV) so lines of this molecule are very sensitive to the temperature and gravity variations in stellar atmospheres. MgH lines were used to determine temperatures in the atmospheres of cool giants (Wyller 1961) and the Sun (Sinha, Shukla & Tripathi 1979; Sinha & Joshi 1982), and for the determination of the surface gravity of stars (Bell & Gustafsson 1981; Bell, Edvardsson & Gustafsson 1985; Berdyugina & Savanov 1992; Bonnell & Bell 1993).

The pure rotational spectrum of MgH and MgD radicals ($X^2\Sigma^+$) in their ground state $v = 0$ and 1 vibrational modes has been studied by Ziurys, Barclay & Anderson (1993). The first MgH line list was computed by Kurucz (1993). Recently, more extensive studies of MgH transitions were performed by Weck et al. (2003a); Weck, Stancil & Kirby (2003b); Weck et al. (2003c) and Skory et al. (2003).

Although CrH has been known since Gaydon & Pearse (1937), its electronic spectrum remained relatively unstudied for many years. Engvold, Wohl & Brault (1980) identified lines of CrH in a spectrum of sunspots as formed by $X^6\Sigma^+$–$X^6\Sigma^+$ transitions. They used the results of studies of multiplicity of Σ terms of CrH by Kleman & Uhler (1959) and O'Connor (1967). Later Ram, Jarman & Bernath (1993) performed a rotational analysis of 0–0 band of the $A^6\Sigma^+$–$X^6\Sigma^+$ electronic transition and obtained improved rotational constants for the $v' = 0$ vibrational state. Combining these results with those of Bauschlicher et al. (2001) and Lipus, Bachem & Urban (1991) for the vibrationally excited transitions, Burrows et al. (2002) computed an extended line list for CrH.

Recently Shin, Bruch & Morse (2005) have measured radiative lifetimes of the $v = 0$, 1 levels of $A^6\Sigma^+$ state of CrH. These measured lifetimes are about 16–45 per cent longer that those obtained by Burrows et al. (2002). These results provide evidence that the oscillator strengths of Burrows et al. (2002) should be corrected by a factor of 0.8 for at least the transitions to the $v' = 0$.

The submillimeter spectra of CrH and CrD formed by pure rotational transitions in the ground electronic state, have been observed in the laboratory by Halfen & Ziurys (2004). Electronic bands of MgD and CrD are likely to be located in the same spectral regions as the corresponding bands of MgH and CrH. In this paper we model the bands of these molecules to analyse the possibility of their use for the determination of the D/H ratio in the atmospheres of ultracool dwarfs.

In Section 2 we present a description of the procedures used to compute the molecular bands of CrH, CrD, MgH and MgD. In Section 3 we present the vibrational–rotational constants of MgH, MgD, CrH and CrD. In Section 4 we present the results of the computation of molecular bands. In Section 5 we discuss the possibility of using the electronic bands of diatomic molecules for a realization of the 'deuterium test'.

2 PROCEDURE OF COMPUTATIONS

2.1 Profile of electron bands of diatomic molecule

In this paper we compute the profile of the electronic band averaged over its rotational structure (Naersisian, Shavrina & Yaremchuk 1989):

$$\int k_\omega \mathrm{d}\omega = \frac{A\, q_{v'v''}\, S_\mathrm{e} S_{j'j''}\, \omega_{j'j''}}{Q(T)} \times \exp\left[-\frac{hc(E''_\mathrm{e} + E''_v + E''_j)}{kT}\right] \times \left[1 - \exp\left(-\frac{h\omega_{j'j''}}{kT}\right)\right], \quad (1)$$

where as symbols $''$ label lower levels of transitions, $A = 8\pi^3(3hc)^{-1}$, k is Boltzmann's constant and T is the temperature, ω is a frequency and $q_{v'v''}$ are Franck–Condon factors for the corresponding transition, the strength of transition $S_\mathrm{e} = S_\mathrm{e}(0,0)\,\omega_{v'v''}/\omega_{0,0}$ (Schadee 1968), $Q(T)$ is the partition function of the molecule.

For a given frequency the sum of the contribution from the P, Q and R branches is

$$k_\omega = \frac{A\, S_\mathrm{e}\, F_\mathrm{e}}{n\lambda Q(T)} \sum q_{v'v''}\, C_{vj} \sum \left|\lambda_j^v\right|, \quad (2)$$

where

$$F_\mathrm{e} = \exp[-hcE''_\mathrm{e}/(kT)]/\delta E_\mathrm{e},$$
$$C_{vj} = (\delta E_\mathrm{e} + \delta E_v)(2j'' + 1)\exp[-hc(E''_j + E''_v)],$$
$$\lambda = 1/\delta\omega.$$

This method of the computation of the profiles of molecular bands was successfully applied to the modelling of the bands of TiO in the spectra of ultracool dwarfs (Pavlenko 1997b, c, 2000), and CN and C_2 bands in the spectra of evolved stars (Pavlenko & Yakovina 2000; Pavlenko, Yakovina & Duerbeck 2000a). It is worth noting that direct comparison of our Just Overlapping Line Approximation (JOLA) synthetic spectra with more sophisticated 'line-by-line' computations for line lists of a few molecules show good agreement

(Pavlenko 1997c) both in the profiles of bands and positions of the band heads.

The JOLA approach has been used for the modelling of the CrH bands $\Delta v = 0$ band system located at 0.8640 μm in the spectra of ultracool dwarfs (Pavlenko 1999, Pavlenko et al. 2000b). These bands are not considered for the deuterium test here, because the wavelengths of corresponding lines of CrH and CrD are nearly identical.

2.2 Computations of molecular constants of isotopic molecules

For a given electronic state, the energy levels of a diatomic molecule can, in general, be fitted by

$$\begin{aligned} E_{\mathrm{e},v,N} = {} & T_\mathrm{e} + \omega_\mathrm{e}(v+1/2) - \omega_\mathrm{e}x_\mathrm{e}(v+1/2)^2 \\ & + B_\mathrm{e}N(N+1) - \alpha_\mathrm{e}N(N+1)(v+1/2) \\ & - D_\mathrm{e}[N(N+1)]^2 \\ & + \beta_\mathrm{e}[N(N+1)]^2(v+1/2), \end{aligned} \tag{3}$$

where $T_\mathrm{e}, \omega_\mathrm{e}, \omega_\mathrm{e}\,x_\mathrm{e}, B_\mathrm{e}, \alpha_\mathrm{e}, D_\mathrm{e}$ and β_e are the various spectroscopic constants, v and N are vibrational excitation and rotational quantum numbers, respectively. To a good approximation the electronic structure of the various isotopic analogues of a given molecule are the same. However, as the nuclei have different masses, the reduced mass and moment of inertia of the molecule are different, resulting in different rotation–vibration frequencies. For the case of an anharmonic oscillator and non-rigid rotator model of the molecule, the rotational–vibrational constants depend upon the ratio of reduced mass $\mu_{ab} = m_a m_b/(m_a + m_b)$ of two isotopic molecules (see Craybeal 1988; Wang & Xia 1996).

Table 1. Reduced masses and ratios of reduced masses for molecules of interest.

Molecule	μ (u)	ρ
MgH	0.967 481	
		0.721 116
MgD	1.860 51	
CrH	0.988 438	
		0.713 873
CrD	1.939 58	

The ratios of spectroscopic constants of two isotopic species, labelled as 'o' and 'i', of reduced masses μ_o and μ_i, depend on the ratio $\rho = (\mu_\mathrm{o}/\mu_\mathrm{i})^{(1/2)}$. So the following approximations can be used:

$$\begin{aligned} (\omega_\mathrm{e})_\mathrm{i}/(\omega_\mathrm{e})_\mathrm{o} &= \rho, \\ (\omega_\mathrm{e}x_\mathrm{e})_\mathrm{i}/(\omega_\mathrm{e}x_\mathrm{e})_\mathrm{o} &= \rho^2, \\ (B_\mathrm{e})_\mathrm{i}/(B_\mathrm{e})_\mathrm{o} &= \rho^2, \\ (D_\mathrm{e})_\mathrm{i}/(D_\mathrm{e})_\mathrm{o} &= \rho^4, \\ (\alpha_\mathrm{e})_\mathrm{i}/(\alpha_\mathrm{e})_\mathrm{o} &= \rho^3, \\ (\beta_\mathrm{e})_\mathrm{i}/(\beta_\mathrm{e})_\mathrm{o} &= \rho^5. \end{aligned}$$

The reduced masses of the molecules of interest here are given in Table 1 using the dominant species ^{24}Mg and ^{52}Cr. The spectroscopic constants of MgH and CrH have been taken from Balfour & Cartwright (1976), Lemoine et al. (1988) and Bauschlicher et al. (2001). The computed spectroscopic constants for MgD and CrD are given in Table 2. We adopted oscillators strengths $f_\mathrm{e} = 0.059$ (Kuznezova et al. 1980) and 0.001 (Pavlenko 1999) for the MgH ($A^2\Pi$–$X^2\Sigma^+$) and the CrH ($A^6\Sigma^+$–$X^6\Sigma^+$) band system, respectively.

We calculated the Franck–Condon factors $q_{v'v''}$ for the MgH and CrH band profile computations. The RADEN program of Kuz'menko et al. (1984), and the FRANKQ program (Tsymbal 1977) were used, respectively. In the FRANKQ program a Morse potential is used to represent the true potential, and is solved for rotation–vibration motion. We compared the computed $q_{v'v''}$ values with the results of Nicholls (1981) and found only small differences. It is worth noting that the adopted system of $q_{v'v''}$ determines the relative strength of the (v'', v') bands, but not their location in the spectrum. In this work we are interested in the computation of the main bands of molecules of interest, therefore the choice of any $q_{v'v''}$ does not critically affect our main results.

2.3 Partition function and equilibrium constants

The internal partition function is given by a sum over all states:

$$Q_\mathrm{int} = \sum_{\mathrm{e},v,N} (2N+1)(2S+1)\exp\left[\frac{-(E_{\mathrm{e},v,N} - E_0)}{kT}\right], \tag{4}$$

where S is electronic spin, $E_{\mathrm{e},v,N}$ is the energy of the state with electronic excitation e, vibrational excitation v and with rotational

Table 2. Spectroscopic constants of MgH, MgD, CrH and CrD in cm^{-1}.

Molecule, data source		T_e	ω_e	$\omega_\mathrm{e}x_\mathrm{e}$	B_e	α_e	D_e	β_e
MgH,								
Balfour & Cartwright (1976)	$A^2\Pi$	19 216.8	1599.50	32.536	6.1913	0.1931	3.60×10^{-4}	6.1×10^{-6}
Lemoine et al. (1988)	$X^2\Sigma^+$	0.00	1495.25	31.637	5.6443	0.1845	3.53×10^{-4}	2.57×10^{-6}
MgD,								
this paper	$A^2\Pi$	19 216.8	1153.43	16.918	3.2195	0.072 41	9.73×10^{-5}	1.2×10^{-6}
Lemoine et al. (1988)	$X^2\Sigma^+$	0.0	1078.14	16.147	2.9668	0.068 294	9.61×10^{-5}	2.79×10^{-7}
CrH,								
Bauschlicher et al. (2001)	$A^6\Sigma^+$	11 552.7	1524.80	22.280	5.3427	0.141 349	3.01×10^{-4}	9.18×10^{-5}
	$X^6\Sigma^+$	0.0	1656.05	30.491	6.2222	0.180 978	3.52×10^{-4}	5.21×10^{-6}
CrD,								
this paper	$A^6\Sigma^+$	11 552.7	1088.32	11.35	2.7227	0.051 395	7.82×10^{-5}	1.70×10^{-5}
	$X^6\Sigma^+$	0.0	1182.00	15.533	3.1709	0.065 804	9.14×10^{-5}	9.66×10^{-7}
Ram & Bernath (1995)	$A^6\Sigma^+$	11 559.7	1066.42	–	2.7627	0.049 687	7.03×10^{-5}	–
	$X^6\Sigma^+$	11 559.7	1183.19	15.60	3.1754	0.065 908	9.09×10^{-5}	–

Table 3. A sample of internal partition functions, Q, as a function of temperature (powers of 10 are given in parenthesis). The full table is available in the online version of this article. Please see the Supplementary Material section for details.

T (K)	Q(MgH)	Q(MgD)	Q(CrH)	Q(CrD)
50	1.322(1)	2.440(1)	3.608(1)	6.855(1)
100	2.575(1)	4.815(1)	7.011(1)	1.351(2)
150	3.832(1)	7.194(1)	1.042(2)	2.018(2)
200	5.091(1)	9.582(1)	1.384(2)	2.687(2)
250	6.353(1)	1.199(2)	1.726(2)	3.359(2)

angular momentum N, E_0 is the zero-point energy. When rotational angular momentum is coupled to the electronic spin a splitting of the spin degeneracy occurs. For the case of the CrH X $^6\Sigma^+$ electronic states, $S = 5/2$, this results in six separate states with angular momentum $J = N \pm 5/2, N \pm 3/2, N \pm 1/2$. Similarly for MgH, X $^2\Sigma^+, J = N \pm 1/2$. The internal partition function is then expressed as

$$Q_{\rm int} = \sum_{{\rm e},v,J,N} (2J+1) \exp\left[\frac{-(E_{{\rm e},v,J,N} - E_0)}{kT}\right]. \quad (5)$$

Energy levels are computed using the rotation, vibration constants listed in Table 2. It is worth noting a good agreement of our data with the constants obtained by Ram & Bernath (1995) from the high-resolution spectroscopy of the $A^6\Sigma^+$–$X^6\Sigma^+$ system of CrD molecule. The partition functions of MgH, MgD, CrD are computed via direct summation of these levels, see equation (4). For CrH, we have obtained accurate energy levels from the line list of Burrows et al. (2002). This list of energy levels covers the $X^6\Sigma^+$ and $A^6\Sigma^+$ electronic states, extends from $J = 0.5$ to 39.5 and includes the vibrational states $v = 0$, 1, 2, 3 in the ground electronic state and $v = 0$, 1, 2 for the excited electronic state. The CrH partition function is calculated by the direct summation of the Burrows et al. (2002) energy levels. In addition, to cover the states omitted from the Burrows et al. (2002) line list, we supplement energy levels computed with the spectroscopic constants. The partition functions are listed in Table 3.

Figs 1 and 2 show the partition functions and the respective fits of Sauval & Tatum (1984). For CrH there is excellent agreement with the partition function of Sauval & Tatum (1984), but for MgH our partition function is slightly larger than that of Sauval & Tatum (1984) at low temperature and smaller at temperatures above 3200 K. Sauval & Tatum (1984) make use of a high-temperature approximation to the rotational partition function. This uses the rigid rotor approximation and is determined by rewriting the partition function sum as an integral from zero to infinity. In contrast our partition function sum is truncated at the dissociation energy D_0, which for MgH is only 1.285 eV. Thus at high temperature Sauval & Tatum (1984) predict a higher partition function than would be expected by direct summation of bound states.

We have calculated equilibrium constants for the reactions: MgH + D $\rightleftharpoons$ MgD + H and CrH + D $\rightleftharpoons$ CrD + H. The dimensionless equilibrium constants are given by

$$K = \frac{n(CrH)n(D)}{n(CrD)n(H)} = \frac{Q(CrH)Q(D)}{Q(CrD)Q(H)} \exp\left(-\frac{\Delta E}{kT}\right), \quad (6)$$

where n is the number density and ΔE is the energy difference between zero-point energies of CrH and CrD; Q is the total partition functions which can be factorized into internal and translational components, $Q = Q_{\rm int}\, Q_{\rm tran}$, where $Q_{\rm tran} = (2\pi M_i kT/h^2)^{3/2}$. g_j is the degeneracy of energy level j. By convention nuclear spin degeneracy is omitted but electronic spin degeneracy is included. Thus for a proton $Q_{\rm int} = 1$ and for an electron $Q_{\rm int} = 2$. The equilibrium constants are listed in Table 4. The equilibrium constants indicate that at low temperatures the formation of the deuterides are strongly favoured over the hydrides, but at high temperatures the hydrides become weakly favoured.

It is worth noting that in cool dwarfs hydrogen and deuterium are primarily found in their molecular forms, H_2, HD and D_2. In a full chemical equilibrium calculation the partition functions and dissociation energies of H_2, HD and D_2 will have an affect upon the abundances of the molecules of interest. So a more appropriate reaction may be MgH + HD $\rightleftharpoons$ MgD + H_2. However, to calculate

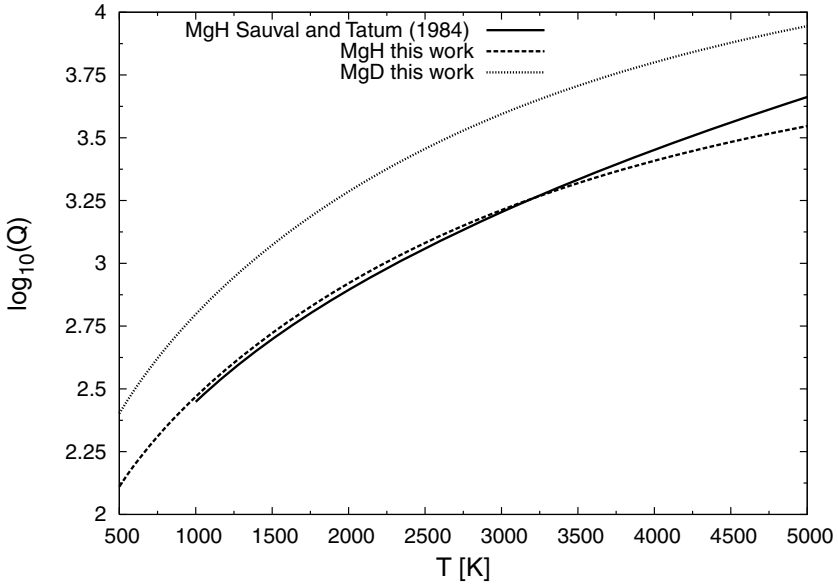

Figure 1. Partition functions of MgH and MgD computed in this work, and the fit of Sauval & Tatum (1984).

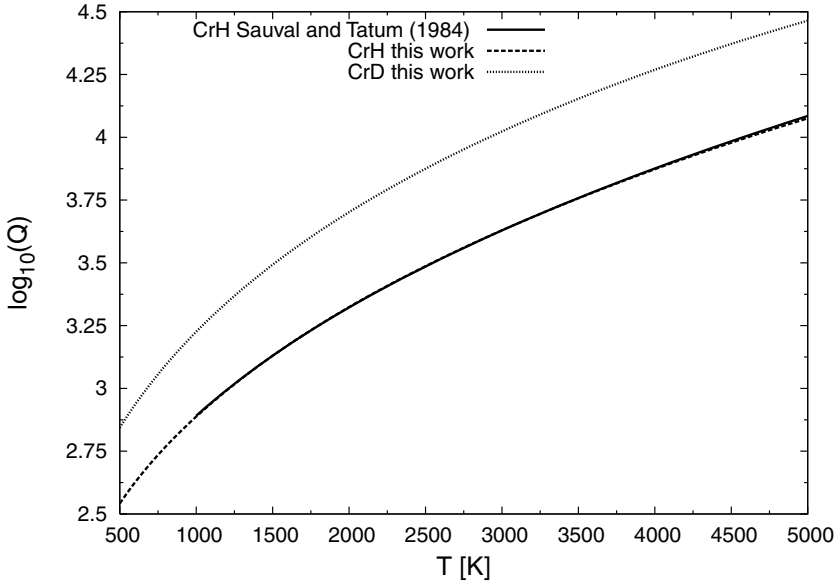

Figure 2. Partition functions of CrH and CrD computed in this work, and the fit of Sauval & Tatum (1984).

Table 4. A sample of equilibrium constants for deuterium exchange reactions (powers of 10 are given in parenthesis). The full table is available in the online version of this article. Please see the Supplementary Material section for details.

T (K)	K(MgH + D $\rightleftharpoons$ MgD + H)	K(CrH + D $\rightleftharpoons$ CrD + H)
50	3.998(3)	1.759(3)
100	7.504(2)	4.973(2)
150	1.994(1)	1.515(1)
200	3.250(1)	2.644(1)
250	4.350(1)	3.690(1)

equilibrium constant for this reaction would require the partition functions of Q(HD) and $Q(H_2)$ and their dissociation energies. Expressing the equilibrium constants relative to atomic D and H avoids any uncertainties arising from the partition functions and dissociation energies of H_2, HD and D_2. A calculation of the partition functions and dissociation energies of H_2, HD and D_2 is beyond the scope of this project.

In calculating the equilibrium constants we assumed that the electronic partition functions of H and D are identical. This is a good approximation as the main differences in the energy levels are proportional to the change in reduced mass and are thus small.

2.4 Ionization–dissociation equilibrium

The equations of ionization–dissociation equilibrium were solved for media consisting of atoms, ions and molecules. We took into account ∼100 components (Pavlenko 1998, 2000). The constants for equations of chemical balance were taken from Tsuji (1973) and Gurvitz, Weitz & Medvedev (1989). To find the densities of species we apply the technique applied by Kurucz (1975) in the ATLAS5–ATLAS12 programs. In the framework of the local thermodynamic equilibrium (LTE) approach, the densities of a molecule consisting of atoms labelled $1, 2, \ldots, n$ in the $k+$ ionization stage can be described by the Gouldberg–Waage equation

$$\frac{n^{p^+}_{1,2,\ldots,l}}{\prod_i^l n_i} = \frac{Q_{1,2,\ldots,n} Q_e^p}{\prod_i^n Q_i} \exp\left(-\frac{E_{1,2,\ldots,l}}{kT}\right), \quad (7)$$

where n_i is the number density of the i th component, Q_i are the total partition functions for species i and $E_{1,2,\ldots,l}$ is the dissociation energy (D_0) of molecule which consists of l atoms and has p^+ charge.

In the atlas program a computationally more convenient format is used:

$$\frac{\prod_i^l N_i}{N_{1,2,\ldots,l}} = \exp[-E_{1,2,\ldots,l}/kT + g(T)]. \quad (8)$$

Here the function $g(T)$ is given by

$$g(T) = b - T\{c + T[d - T(e + fT)]\} + \frac{3}{2}(l - p - 1) ln\, T. \quad (9)$$

Values of b, c, d, e (Table 5) are determined by the fitting to the data (see Table 4) using the least-squares minimization procedure for the temperature range 400–5000 K.

As was expected, at LTE the equilibrium constants of our hydrides and deuterides are very similar. Indeed, the equilibrium constants are $\sim Q_{\mathrm{int},i}/M_i, M_i$ is the mass of the i th species. Partition functions of the deuterated molecules are larger by approximately a factor of 2, which corresponds to the larger molecular weight of deuterium. Fitted chemical equilibrium constants computed for CrH, CrD, MgD and MgH are shown in Table 5.

2.5 Synthetic spectra

Synthetic spectra were computed using the program WITA6 (Pavlenko 2000) assuming LTE, hydrostatic equilibrium and a one-dimensional model atmosphere without sources and sinks of energy. Hereafter we use the term 'synthetic spectra' instead of 'spectral energy distributions' to simplify the text. Theoretical synthetic spectra were computed for the model atmospheres of dwarfs with effective temperatures $T_{\mathrm{eff}} = 1200$–1800 K from the COND grid of Allard et al. (2001) using solar metallicity (Anders & Grevesse 1989). Unless otherwise mentioned all models are for $\log g = 5.0$.

Table 5. Chemical equilibrium constants for MgH, MgD, CrH and CrD (powers of 10 in parenthesis).

Molecule	D_0 (eV)	b	c	d	e	f
CrH	2.863	3.690(1)	6.678(−3)	2.541(−6)	5.115(−10)	3.929(−14)
MgH	1.285[a]	3.605(1)	6.834(−3)	2.551(−6)	5.049(−10)	3.834(−14)
CrD	2.888	3.731(1)	6.919(−3)	2.607(−6)	5.192(−10)	3.967(−14)
MgD	1.311	3.648(1)	7.111(−3)	2.647(−6)	5.214(−10)	3.942(−14)

[a]From Shayesteh et al. (2007).

2.6 Atomic lines opacity

To compute the band profiles of the electronic bands in the spectra of late spectral class dwarfs one must account for absorption of the resonance lines of Na I (0.5891, 0.5897 μm) and K I (0.7667, 0.7701 μm), which are extremely strong. In fact, optical and near-infrared spectra of L and T dwarfs are governed by them (Pavlenko 1997a, 1998). Temperatures in the atmospheres of ultracool dwarfs are lower than 2000 K, therefore alkali atoms exist there mainly in the form of neutrals. Furthermore, due to the low opacity of the atmospheres of ultracool dwarfs their photospheres occur in high pressure layers. Strong resonance lines of the most abundant alkali metals, i.e. sodium and potassium, are formed in very dense and cool plasmas. Due to the high efficiency of pressure broadening, their formally computed equivalent widths may reach a few thousand angstroms (Pavlenko 2000). Burrows & Volobuyev (2003) show that we cannot use the conventional theory of collisional broadening. A more sophisticated theory involving quasi-stationary broadening should be used for them (see also Allard et al. 2003 and Zhu, Babb & Dalgarno 2006).

In this work we use the potentials of quasi-stationary chemical interactions of K and Na with the most numerous species, atomic He and molecular H_2 computed by GAMESS (Granovsky 2004). Our procedure is described in more detail in Pavlenko, Zhukovska & Volobuyev (2007). In calculations of K I profiles we used a combined profile: the cores of these lines were computed in the framework of the collisional approach and their wings ($\delta\lambda > 0.004$ μm) were treated by quasi-stationary theory.

3 RESULTS

3.1 MgH and MgD

Computed JOLA profiles of the electronic band system $A^2\Pi$–$X^2\Sigma^+$ of MgH and MgD are shown in Fig. 3. It is worth noting that a simulation based on a sound quantum mechanical model, including spin–orbit coupling in the $A^2\Pi$ state, agreed reasonably well with the JOLA calculation (see Hill 2007). First, the synthetic spectra were computed for the case of a solar abundance [N(H)/N(total) = 0.9]. Then all the hydrogen was replaced by deuterium [N(D)/N(Total) = 0.9]. As stated above, the aim of this paper is a comparative analyses of the possibilities of detection of the deuterated molecules MgD and CrD which are formed on the background of the electronic bands of the more abundant conventional hydrides MgH and CrH. The detection of MgD bands is very challenging for several reasons.

(i) The bands of MgD lie at relatively short wavelengths. High-precision observations of this spectral region are difficult in objects with low $T_{\rm eff}$.

(ii) The differences in the positions of the band heads of MgH and MgD are rather small. The MgD bands will be formed on a background of far stronger MgH bands.

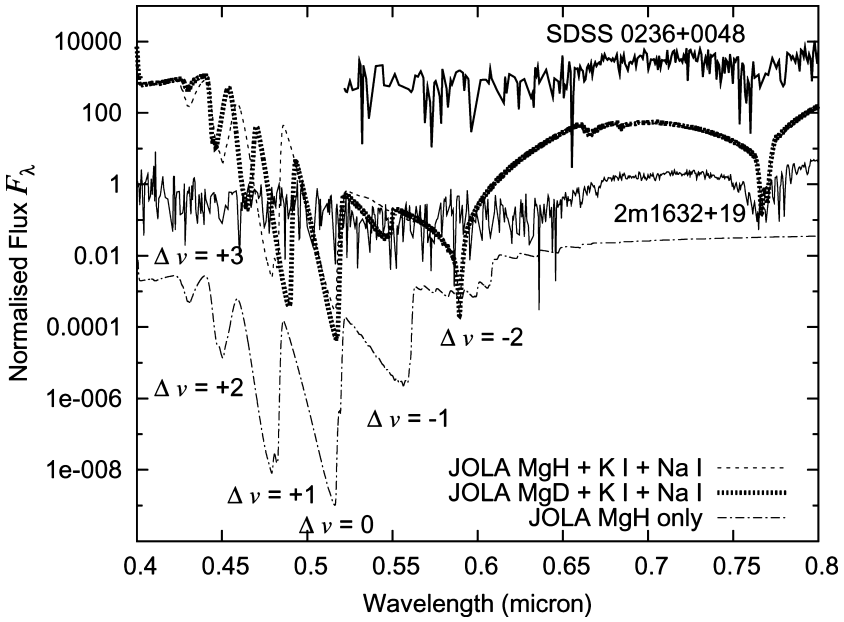

Figure 3. Molecular bands of the $A^2\Pi$–$X^2\Sigma^+$ system of MgH and MgD in the theoretical spectrum computed for a 1800/5.0/0 COND model atmosphere. Spectra are shown for D/H = 1. The lower line on the plot shows the pure spectrum of MgH computed in the framework of JOLA approximation. For comparison the observed spectra of two L dwarfs 2MASS1632+19 (Martín et al. 1999) and SDSS 0236+0048 (Leggett et al. 2001) are shown as solid lines.

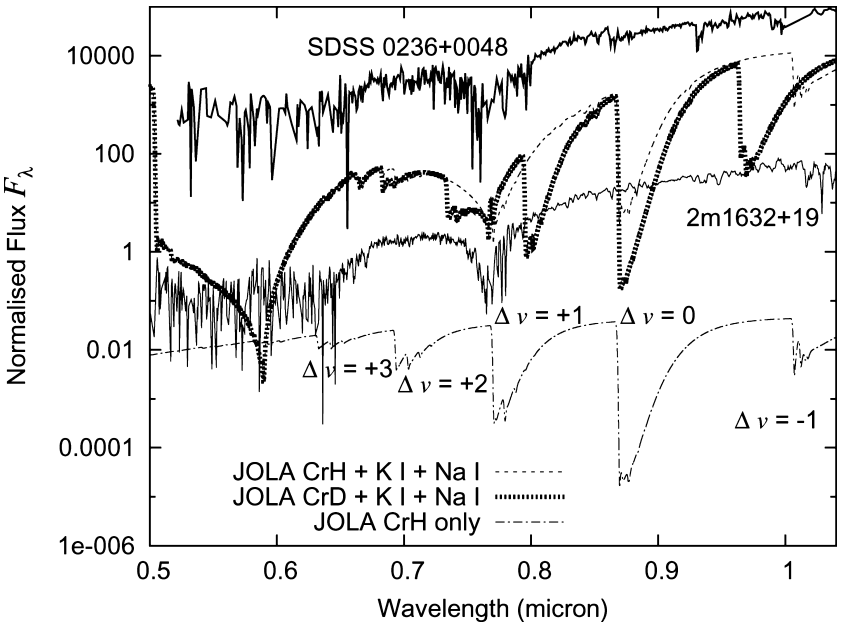

Figure 4. Molecular bands of the $A^6\Sigma^+$–$X^6\Sigma^+$ system of CrH and CrD and a theoretical spectrum computed for a 1800/5.0/0 COND model atmosphere. Spectra are shown for D/H = 1. The lower line on the plot shows the pure spectrum of CrH computed in the framework of JOLA approximation. For comparison the observed spectra of two L dwarfs 2MASS1632+19 (Martín et al. 1999) and SDSS 0236+0048 (Leggett et al. 2001) are shown as solid lines.

(iii) MgH and MgD bands in the spectra of cool dwarfs are close to a strong Na I resonance line and the lines of other molecules/atoms.

3.2 CrH and CrD

The relative behaviour of CrH and CrD bands is shown in Fig. 4. In general, the bands of the $A^6\Sigma^+$–$X^6\Sigma^+$ system occupy a larger wavelength range. Due to the larger reduced mass, distances between heads of CrD bands of different Δv are smaller than those for the CrH. As a result, bands of negative and positive Δv are shifted bluewards and redwards with respect to the corresponding CrH bands.

The transitions with $\Delta v = 1$ form a band head at 0.768 43 μm which coincides with the core of the strong K I resonance doublet. Thus in L dwarfs with strong CrH absorption the contribution of CrH has to be accounted in the modelling of 0.77 μm K I feature.

For the $\Delta v = 0$ case the bands of CrH and CrD are coincident. For the Δv positive case the CrD band heads are displaced to longer wavelengths of the CrH band head, thus the strongest CrD lines will be blended with the lines from the tail of the corresponding CrH band. Bands with $\Delta v = 2$ are blended with the K I resonance line. Bands with $\Delta v = 3$ are located in the spectral region of the so-called 'satellite rainbows' of the K I line (Burrows & Volobuyev 2003). For the Δv negative case the CrD band heads are displaced to shorter wavelengths of the CrH band head, these bands offer the best possibility of detection.

4 DISCUSSION

The detection of deuterated molecules in the spectra of ultracool dwarfs provides a challenge for both theoreticians and observers. Indeed, in the atmospheres of planetary mass objects ($M < 13M_J$) we cannot expect ratio D/H $>2 \times 10^{-5}$. This means the lines of deuterated molecules should be about 5000 times weaker than those of the hydrides. The ideal case would be a spectral region where the molecular bands are not blended. So a crucial requirement is a large difference in the wavelengths of the band heads of the hydrides and deuterides.

CrH appears to be more useful than MgH in the search for deuterated species. The band heads of CrD are displaced significantly from the band heads of CrH. Bands of CrH are observed in the spectra of the latest L dwarfs (Kirkpatrick et al. 1999). The CrD $\Delta v = -1$ bands are located in the 'near-infrared' spectra, where fluxes are much higher than in the 'optical' spectral regions.

In this paper we show that the most useful bands for the realization of the deuterium test are $\Delta v = +1$ and $\Delta v = -1$ ($\lambda = 0.795$ and 0.968 μm, respectively). The $\Delta v = -1$ band looks especially promising. It is located in the near-infrared region with an absence of strong background absorption features. However, portions of this CrD band will be swamped by the 0–0 FeH Wing–Ford band at 0.99 μm and possibly by water bands. Still, the case for CrD looks better than for HDO lines which are formed on a background of strong H2O lines (Pavlenko 2002). High quality line lists are required to test these possibilities fully.

It is worth noting that a potential problem lies in the possibility that Cr atoms are absorbed on to dust particles. The depletion of Cr will reduce the strength of both CrD and CrH bands. Fortunately as CrH bands are located in the same spectral region, we can 'scale' the CrD depletion processes by adjusting the strength of CrH bands.

For more precise studies, more accurate and detailed line lists of CrH and CrD are required. The calculation of such line lists would require new improved computations supported by new laboratory measurements. One problem that concerns us is that even when we have good agreement between the model and experimental data for the MgH or CrH molecule, there are still perturbations about which we know very little from experiments done so far. None the less, MgH is a non-starter for the deuterium test and as we note above, the model adopted in our paper is more likely to be reliable for CrH and CrD. It is worth noting that the use of the pure

rotational–vibrational bands located in the mid- and far-infrared spectral regions may offer an alternative. Indeed, the displacement between CrH and CrD rotation–vibration bands is even larger than for the case of electronic bands.

Nevertheless, we cannot be certain that we have identified the best candidate systems for the deuterium test. Future investigations of deuterated molecules in different spectral regions are important to determine which offers the best possibility for the realization of this test. The ideal solution would be to detect lines of deuterated molecule(s) in different spectral regions. This presents a serious observational challenge which can only be met in combination with careful laboratory measurement and the computation of high quality molecular spectra.

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SUPPLEMENTARY MATERIAL

The following supplementary material is available for this article.

Table 3. Internal partition functions, Q, as a function of temperature (powers of 10 are given in parenthesis).

Table 4. Equilibrium constants for deuterium exchange reactions (powers of 10 are given in parenthesis).

This material is available as part of the online paper from: http://www.blackwell-synergy.com/doi/abs/10.1111/j.1365-2966.2008.12522.x (this link will take you to the article abstract).

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