Low-N lines of the $A^6\Sigma^+$–$X^6\Sigma^+$ (1,0) band of CrH

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The (1,0) band of the $A^6\Sigma^+$–$X^6\Sigma^+$ electronic transition of CrH has been observed by laser-induced fluorescence following the reaction of laser-ablated Cr atoms with methanol under supersonic free-jet cooled conditions. Rotational assignments of the levels with $N \leq 3$ have been made by combination differences and dispersed fluorescence experiments on selected lines. These assignments complement those made from previously-recorded Fourier transform emission spectra, in which higher-N lines were assigned. The low-N rotational levels are extensively perturbed, presumably by levels of the $a^4\Sigma^+$, $v = 1$ and $B^6\Pi$, $v = 0$ states.

1. Introduction

The $A^6\Sigma^+$–$X^6\Sigma^+$ electronic transition of diatomic chromium hydride, CrH, has recently become important in the field of astrophysics because of its surprising intensity in the spectra of a newly-recognised class of cool sub-stellar objects, the so-called brown dwarfs.[1,2] The spectra of these objects do not show the characteristic near infrared bands of TiO and VO that are used to classify the warmer M-type stars. Brown dwarfs are classified into two types: the L dwarfs that display bands of FeH and CrH, and the cooler T dwarfs ("methane dwarfs") that show overtone bands of hot methane and water. The bands of the near infrared electronic transitions of CrH and FeH are in fact the spectral signatures used to classify L dwarfs. CrH has also been tentatively identified in the spectra of sunspots[3] and various other cool stars.[4]

The most prominent bands of CrH in the L dwarf stellar spectra are the $A^6\Sigma^+$–$X^6\Sigma^+$, (0,0) and (0,1) bands, whose R heads lie at 861 and 997 nm, respectively. These bands were first seen by Kleman and Liljeqvist,[5] and later analysed rotationally by Kleman and Uhler.[6] The upper state was found to be perturbed, though the nature of the perturbing state was not clear until a higher resolution Fourier transform emission study by Ram, Jarman and Bernath[7] showed that it is a $^4\Sigma^+$ state. The (1,0) band, at 764 nm, is less prominent in the stellar spectra[2] because it overlaps the A band of O_2 ($b^1\Sigma_g^+$–$X^3\Sigma_g^-$, 0,0), which is always present in Earth-bound observations; nevertheless it is the next strongest band in the transition after the (0,0) band,[6] so that its properties are important for an understanding of the $A^6\Sigma^+$ state.

The $A^6\Sigma^+$–$X^6\Sigma^+$, (0,0) band has now been thoroughly analysed,[6,7] but the (1,0) band has not been completely assigned so far because of strong low-N perturbations in the $v' = 1$ level. The first rotational analysis, by O'Connor,[8] used a heavy-current discharge. This gave a very hot spectrum, showing rotational lines up to $N'' = 27$, but the line density near the band centre, together with the perturbations, hampered the assignment of the low-N lines. More recently, Bauschlicher et al.[9] used both a hollow cathode source and a microwave discharge in their Fourier transform emission studies of the band. These gave cooler spectra, allowing more of the low-N lines to be assigned, but the lowest rotational lines still defied analysis. In the present paper we show how the reaction of laser-ablated chromium with methanol under supersonic jet expansion conditions gives a strong cold spectrum which shows mostly those lines that could not be assigned previously, and allows nearly all the lowest-N levels of the upper state to be located.

Because of its astrophysical importance, quite a number of other studies of the spectrum of CrH have been carried out recently, both experimentally and theoretically. For example, Halfen and Ziurys[10] have recorded the $N = 1$–0 pure rotational transition and Ghigo et al.[11] have carried out a comprehensive ab initio calculation of the properties of the low-lying sextet electronic states. A recent bibliography has been given by Shin, Brugh and Morse[12] in their paper on the radiative lifetimes of the $A^6\Sigma^+$, $v' = 0$ and 1 levels.

2. Experimental details

In this work the CrH molecules were made by reaction of laser-ablated Cr atoms with methanol, and detected by laser-induced fluorescence. The procedures have been described in detail in previous papers.[13,14] Briefly, the third harmonic output (355 nm) of a pulsed Nd:YAG laser was focussed onto the surface of a Cr rod (Goodfellow Corp.), and the resulting metal plasma reacted with a mixture of 30 psi of helium containing methanol at its room temperature vapour pressure coming from a pulsed molecular beam valve (General Valve Series 9). The products then expanded into a large vacuum chamber through which the beam from a tuneable pulsed laser (Lumonics HD500) was passed. The fluorescence excited by the tuneable laser was detected by a Hamamatsu R943 photomultiplier after passing through a 0.75 m monochromator (Spex, Model 1702). The

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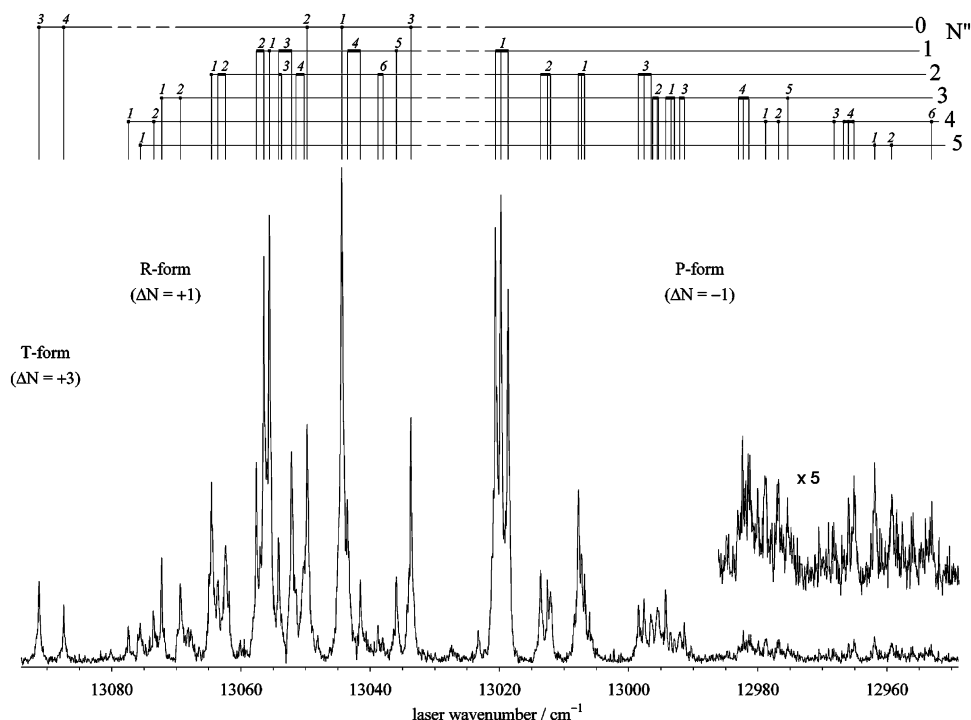
Fig. 1 Laser induced fluorescence spectrum of the $A^6\Sigma^+$–$X^6\Sigma^+$ (1,0) band of CrH recorded under supersonic jet-cooled conditions. The line assignments are indicated by tie-lines above the spectrum: the values of N'' are shown as large figures on the right, while the upper state spin component labels are indicated by smaller italic figures above the vertical tie-lines (*e.g.* 1 for F_1). The ground state spin splittings are indicated by the groupings of the vertical tie-lines, but the individual components are not labelled. This spectrum was recorded by monitoring fluorescence at -1595 cm^{-1} ($\Delta G''_{1/2}$), except in the region of the T-form lines where the fluorescence was monitored at -1632 cm^{-1}, corresponding to the R-form lines of the (1,1) band.

monochromator filters out strong scattered laser light, and was set to detect fluorescence to the $v = 1$ level of the ground state. Some calibration was provided by optogalvanic spectra from a uranium–argon hollow cathode lamp, but since the number of useful lines near 760 nm is small, and the line-width of our pulsed dye laser is about 0.07 cm^{-1}, it was preferable to use the frequencies of those CrH lines that also appear in previously-recorded Fourier transform spectra.[9]

The Fourier transform spectra[9] were taken with the 1 m spectrometer at the McMath-Pierce telescope of the National Solar Observatory at Kitt Peak. Two sources were used. One was a Cr hollow cathode lamp containing 2.8 Torr of Ne and 100 mTorr of H_2 operating at 460 V and 765 mA; the other was a microwave discharge through a mixture of 15% H_2 in He containing a small amount of CrO_2Cl_2. The hollow cathode spectrum was calibrated using measurements of the neon lines appearing in it,[15] and the microwave discharge spectrum was calibrated from it using common CrH lines. The microwave discharge gave a comparatively cool spectrum which showed many of the previously-unassigned low-N lines of CrH; the measurements used in this work come from that spectrum. The line positions are expected to be accurate to between 0.002 and 0.004 cm^{-1}.

3. Results

Fig. 1 shows the laser excitation spectrum of the $A^6\Sigma^+$–$X^6\Sigma^+$, (1,0) band of CrH, as observed by monitoring the (1,1) band,

under supersonic free jet expansion conditions. The strongest lines have $N'' = 0$ and 1, and the branches die out at about $N = 5$, consistent with a rotational temperature of about 40 K. Since the ground state has been well characterised by infrared laser magnetic resonance[16,17] and microwave spectroscopy,[10] it was reasonably straightforward to assign the strong lines using ground state combination differences. To assign the weaker lines, and those affected by perturbations, some rotationally-resolved emission spectra were taken. These spectra were recorded by tuning the excitation laser to the line of interest, narrowing the slits of the monochromator and scanning its frequency across the (1,1) band; in this way the strong scattered laser light is eliminated. A spectrum of this type contains up to four lines, whose separations follow the ground state rotational energy expression $BN(N + 1)$, and immediately identify their N''-values; the one closest to the pure $v'' = 1$–0 vibrational interval of 1595 cm^{-1} from the laser frequency has the same N''-value as the line excited. The value of $\Delta N = N' - N''$ was usually obvious from the relative intensities of the lines in the emission pattern, since the main branch lines ($\Delta N = \Delta J$) are normally stronger than the spin satellite lines ($\Delta N \neq \Delta J$). However this is not always so at the very low N values of our spectra, and care was sometimes needed.

The line assignments have been indicated in Fig. 1 by their N values (large figures at the right) and their upper state electron spin component (smaller italic figures over the tie-lines). As in the (0,0) band the upper state spin splittings are much larger than the ground state spin splittings. For space reasons we

Table 1 Assigned lines in the $A^6\Sigma^+ - X^6\Sigma^+$, (1,0) band of CrH from this work. Values in cm^{-1}

N''	Branch	E/cm^{-1}	N''	Branch	E/cm^{-1}	N''	Branch	E/cm^{-1}
0	$^TR_{31}$	13 099.262?	2	R_3	13 061.834	3	$^PR_{13}$	12 993.415*[a]
		91.270			54.202*[a]		$^PQ_{12}$	93.415*[a]
	$^TQ_{41}$	87.449		$^RQ_{32}$	53.712		$^PR_{35}$	92.908
	$^TP_{51}$	80.126?		R_4	51.493[a]		$^PQ_{34}$	92.051[a]
	$^RQ_{21}$	49.745		$^RQ_{43}$	50.345*		P_3	91.297[a]
	R_1	44.393[a]		$^RQ_{65}$	38.797		$^PR_{46}$	82.960[a]
	$^RP_{31}$	33.669[a]		$^RP_{64}$	38.119[a]		$^PQ_{45}$	82.265[a]
				$^PR_{24}$	13.596[a]		P_4	81.409[a]
1	$^RQ_{21}$	13 057.588[a]		$^PQ_{23}$	12.547		$^PQ_{56}$	75.378
	R_2	56.461[a]		P_2	12.139[a]			
	R_1	55.596[ab]		P_1	07.765	4	R_1	13 077.422[ab]
	R_3	54.202*		$^PR_{13}$	07.295		R_2	73.500[ab]
	$^RP_{31}$	52.167[a]		$^PQ_{12}$	06.803[a]		P_1	12 978.748[ab]
	$^RQ_{43}$	43.487[a]		$^PR_{35}$	12 998.460[a]		P_2	76.784[a]
	$^RP_{42}$	41.529		$^PQ_{34}$	97.599		P_3	68.230[a]
	$^RP_{53}$	35.956[a]		P_3	96.504		$^PR_{46}$	66.792
	$^PR_{13}$	20.627[a]					$^PQ_{45}$	65.922[a]
	P_1	19.784[a]	3	R_1	13 072.275[b]		P_4	65.072[a]
	$^PQ_{12}$	18.649[a]		R_2	69.404[b]		P_6	53.229[a]
2	R_1	13 064.603[ab]		$^PR_{24}$	12 996.504*			
	$^RQ_{21}$	63.576		$^PQ_{23}$	95.506*	5	R_2	13 075.593[ab]
	R_2	62.435		P_2	95.506*		P_1	12 961.913[ab]
				P_1	94.272[ab]		P_2	59.289[ab]

[a] Line that could also be identified in the microwave discharge Fourier transform emission spectra of ref. 9. The wavenumber given here is from new measurements of these spectra. [b] Line identified in the hollow cathode Fourier transform emission spectra of ref. 9. * Blended line.

have not labelled the ground state spin components in Fig. 1. The most obvious ground state splittings occur in the strong P(1) triplet at 13 020 cm^{-1}. Reading from left to right, these three lines are $^PR_{13}(1)$, $P_1(1)$ and $^PQ_{12}(1)$. They represent transitions from the three spin components of the $N = 1$ level of the ground state to the upper state $N = 0$ level. Some $\Delta N = 3$ (T-form) lines have been identified at the blue end of the band; these lines are actually weaker than Fig. 1 indicates, because to enhance their signal-to-noise ratio the monochromator was temporarily set to monitor the corresponding R-form lines rather than the much weaker T-form lines of the (1,1) band.

The lines assigned in the jet-cooled spectra are listed in Table 1. It turns out that many of them are present in the Fourier transform emission spectra of the microwave discharge used in ref. 9, but could not be assigned there because of perturbations. They have been remeasured for this work, and the wavenumbers listed in the Table come from those

measurements. Essentially this work has identified the perturbed low-N lines that were seen, but not assigned, before. A few lines which were assigned from hollow cathode spectra in ref. 9 are marked in the Table.

The upper state energy levels up to $N = 7$, as presently known, are listed in Table 2. They were obtained by adding the line frequencies to the ground state energy levels calculated from the constants of ref. 9, and averaging the results where appropriate. The levels with $N' \leq 3$ come from our new assignments, except for $F_1'(2)$ and $F_1'(3)$ which are from the data of ref. 9. The data for higher N also come from the data of ref. 9. Some of the assignments in ref. 9 are from lines in the hollow cathode spectra that are not confirmed by the microwave discharge spectra; for those levels involved the energies are given in parentheses.

It will be seen that two of the $N = 3$ levels in Table 2 are marked "?". These are derived from lines at the blue end of the band (marked "?" in Table 1) which are shown by wavelength-

Table 2 Assigned energy levels of the $A^6\Sigma^+$, $v = 1$ state of CrH, up to $N = 7$. Values in cm^{-1}

N	F_1	F_2	F_3	F_4	F_5	F_6
0	13 031.878					
1	13 044.393	13 049.704	13 033.661			
2	13 067.691	13 069.687	13 065.378	13 054.728	13 047.205	
3	13 101.213	13 099.992	13 098.971?	13 087.516	13 080.126?	13 074.024
			13 091.338			
4	13 145.615	13 143.685	(13 141.606)	—	—	—
5	13 199.886	13 196.736	(13 192.228)	—	—	—
6	13 264.572	13 259.990	13 252.109	13 236.125	(13 227.324)	—
7	13 339.391	13 333.445	13 322.499	13 310.545	13 295.455	13 288.701

[a] Assignments for $N \geq 4$, and $F_1(2)$, $F_1(3)$, are from ref. 9; the remainder are from this work. Values in parentheses are not confirmed by the microwave discharge Fourier transform spectra, but may still be correct. Values marked "?" are probable assignments from T-form lines. The $F_6(7)$ entry is based on lines assigned in ref. 8; these lines appear in the microwave discharge spectra.

Table 3 Rotational constants for the $A^6\Sigma^+$, $v = 1$ state of CrH, as determined from a least squares fit to the levels with $N \leq 6$ given in Table 2. Values in cm^{-1}. Error limits are 3σ. The levels in parentheses or marked with "?" in Table 2 were omitted from the data set, as were $F_2(1)$, $F_2(3)$, $F_3(3)$, $F_4(3)$, $F_3(6)$ and $F_4(6)^a$

T_0	13 034.015	±0.203
B	5.1131	0.0154
D	0.000 13	Fixed
λ	1.5496	0.0414
γ	1.2870	0.0315
γ_D	0.001 86	0.001 68

^{a} rms error = 0.1332.

resolved fluorescence to be T-form lines with $N'' = 0$. One of these lines, which is probably an extra $^TR_{31}(0)$ line, appears to be confirmed by combination difference with a weak R(2) line, but the $^TP_{51}(0)$ line has been assigned on the basis of the calculated level positions. These two assignments are probably right, but should not be considered secure. It is interesting that an extra $^TR_{31}(0)$ line can be assigned. The separation of the two $^TR_{31}(0)$ lines is about 8 cm^{-1}, which is consistent with the shifts of up to about 4 cm^{-1} noted in the line lists of ref. 9.

All the strong lines of Fig. 1 could be identified as belonging to the A–X, (1,0) band, though a few weaker lines clearly do not belong to it. An example is the line at 13 023.28 cm^{-1}, immediately to the blue side of the P(1) group. Wavelength-resolved fluorescence shows that it is an R(1) line. Since the authentic R(1) lines lie more than 15 cm^{-1} to the blue, this must presumably be an extra line resulting from another perturbation.
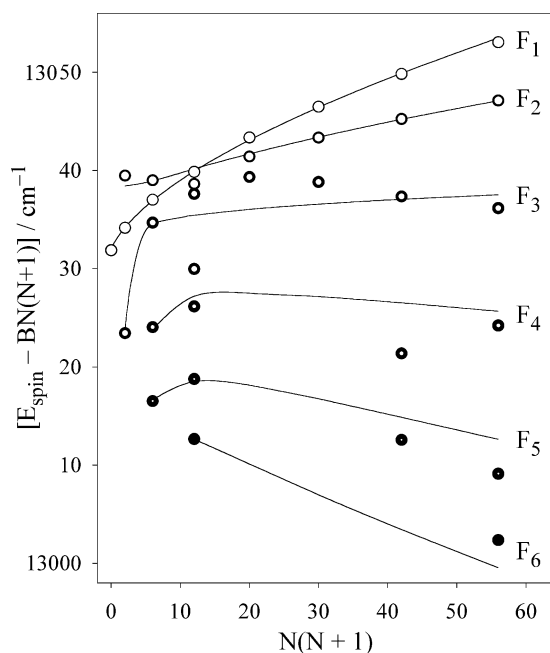

Fig. 2 Spin structure of the $A^6\Sigma^+$, $v = 1$ level of CrH. The observed energies of the six spin components (F_1–F_6) are plotted as progressively filled circles; the curves represent the energies calculated using the constants of Table 3. Several perturbations are evident; see text for details.

A least squares fit has been made to the upper state energy levels, up to $N = 6$. In view of the perturbations the results can only approximate the true spin and rotational constants, but for what they are worth they are given in Table 3. The spin structure of the $A^6\Sigma^+$, $v = 1$ level, up to $N = 7$, is shown plotted against $N(N + 1)$ in Fig. 2. To expand the scale, the rotational energy, 5.113 $N(N + 1)$ cm^{-1} has been subtracted from the observed energy levels. The curves in the figure represent the positions calculated from the constants in Table 3. It appears that the F_1 component of the upper state is the least perturbed, with only a small perturbation of about 0.25 cm^{-1}, between $N = 3$ and 4. Two perturbations occur in the F_2 component at low N, but after $N = 4$ the levels are well behaved. The strongest perturbations occur in the F_3 component, with the $N = 3$ level showing a doubling of about 8 cm^{-1}, as described above. The branches involving the F_4, F_5 and F_6 components are intrinsically weak at low N because of unfavourable line strength factors.[19] Also they are probably quite heavily perturbed, which means that they will be hard to locate, in both the jet-cooled and the discharge spectra. No levels with $N = 4$ and 5 have been identified for these spin components.

4. Discussion

In view of the astrophysical importance of CrH we have aimed in this work to establish the energies of the low-N rotational levels of the $A^6\Sigma^+$, $v = 1$ state, and to provide a line list for astrophysical applications. Spectra taken at medium resolution under supersonic free-jet conditions have allowed the assignment of a number of lines that could not be assigned in previously-taken high resolution Fourier transform emission spectra because of strong perturbations. The results now give the energies of all the levels up to $N = 3$.

Although the energies are known in most cases to an accuracy of about 0.002 cm^{-1}, the data are not sufficient to allow a detailed deperturbation of the observed structure. From the previous Fourier transform results[9] it is known that the $A^6\Sigma^+$, $v = 0$ state is perturbed by a $^4\Sigma^+$ state that lies 367 cm^{-1} below it. Data for CrD, where similar perturbations in the $A^6\Sigma^+$, $v = 0$ and 1 states have been found in high resolution Fourier transform spectra,[18] give the vibrational numbering of the $^4\Sigma^+$ state and show that it has a slightly higher vibrational frequency than the $A^6\Sigma^+$ state. This means that, in CrH, the $v = 1$ level of the $A^6\Sigma^+$ state will be perturbed by a $^4\Sigma^+$ state that lies rather closer than is the case for $v = 0$. Perturbations will therefore be expected at lower N than in the $v = 0$ state.

Another complication is the presence of the $B^6\Pi$ state at almost the same energy. This state was discovered very recently in further supersonic jet-cooled experiments,[20] and its $^6\Pi_{-3/2}$, $v = 0$ level found to lie near 12 850 cm^{-1}. Its spin–orbit coupling constant, A, is about 38 cm^{-1}, which means that its six spin–orbit sub-states will span the energy range up to about 13 040 cm^{-1}. Since the $A^6\Sigma^+$, $v = 1$ state described in this work lies at 13 034 cm^{-1}, there will be perturbations at the very lowest N values. It is likely that some of the extra lines identified in this work belong to the $B^6\Pi$–$X^6\Sigma^+$ transition. Preliminary spectra of the $A^6\Sigma^+$–$X^6\Sigma^+$, (2,0) and (3,0) bands

of CrH show that their rotational structures are even more disorganized, consistent with the fact that they lie in the centres of the B–X, (1,0) and (2,0) bands.

Acknowledgements

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