

MOLECULAR DATA FROM SOLAR SPECTROSCOPY

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RESUMEN. La meta esencial de la espectroscopía solar es derivar las condiciones y los procesos físicos que prevalecen en las capas externas del sol. Cuando los datos atómicos y moleculares que se requieren para interpretar el espectro solar son de precisión incierta, o a menudo inexistentes, se puede recurrir a la espectroscopía solar para determinar estos datos básicos. El sol se considera entonces una "fuente de laboratorio" de la cual podemos derivar mejores datos moleculares. Se demuestra, a través de algunos ejemplos, cómo el análisis de las transiciones moleculares que se encuentran en los espectros solares en el visible e infrarrojo se puede utilizar para refinar nuestro conocimiento de las constantes moleculares, y para comprobar la precisión de los datos moleculares disponibles, tales como las probabilidades de transición y las energías de disociación de algunas moléculas diatómicas.

ABSTRACT. We show through a few examples how the analysis of molecular transitions present in the solar visible and infrared spectrum can be used to refine our knowledge of the molecular constants and to test the accuracy of available molecular data like transition probabilities and dissociation energies for a few diatomic molecules.

Key words: ATOMIC PROCESSES - MOLECULAR PROCESSES - SUN: ATMOSPHERE - SUN: SPECTRA

I. INTRODUCTION

In spite of the efforts made by molecular spectroscopists, theoreticians as well as experimentors, there is still a lack of accurate data (structure, dissociation energies, transition probabilities) for many molecular species which are of interest for molecular opacity computations.

The mean structure of the solar photosphere and its physical processes are now well known and, in many cases, the sun itself has proven to be a very good "laboratory source" for atomic as well as molecular spectroscopy.

We recall that the line absorption coefficient of a molecule AB essentially depends on two physical parameters, the line oscillator strength, $f_{\nu J}$, and the dissociation energy, D_0^0 , as well as on the number densities of the relevant atoms, N_A and N_B , in the photospheric layers:

$$\kappa_{\nu J}(AB) \propto N_A N_B f_{\nu J} 10^{D(AB) \cdot \theta} \quad (1)$$

where θ is the reciprocal temperature, $\theta = 5040/T$, very near to unity under solar photospheric conditions. From a comparison of observed and synthetic solar spectra it is possible to derive the "solar" value of a missing physical parameter if the other is known; we can also derive a relation between the two parameters if they are both uncertain.

Diatomic molecules are well represented in the solar visible and infrared spectrum through electronic transitions of CN, C₂, CH, NH, OH; vibration-rotation transitions of CO, CH, NH and OH; and pure rotation transitions of OH and NH. We shall essentially limit ourselves here to transitions which can be measured and interpreted with high accuracy, i.e. in the visible and infrared spectra. But many other molecular transitions are present in the solar spectrum. They are either very weak, like the transitions of MgH, FeH, CH⁺, SiH, SiH⁺,..., or fall in the UV, like the electronic transitions of H₂ and CO. Solar studies of those transitions have already been used to derive molecular data like in the case of CH⁺ (Grevesse and Sauval 1971a, Sinha and Tripathi 1990), SiH and SiH⁺ (Grevesse and Sauval 1971b), MgH (Lambert et al. 1971; Grevesse and Sauval 1973),...

We show hereafter through a few examples how the study of molecular transitions present in the solar visible and infrared spectrum can be used to refine our knowledge of the *molecular constants* and/or to test the accuracy of available molecular data like *dissociation energies and transition probabilities*.

II. C₂ AND CH TRANSITIONS

Grevesse et al. (1991) very recently redetermined the solar carbon abundance as derived from a large number of lines produced by different independent indicators of this abundance like the vibration-rotation lines of CH, lines of the electronic A - X transition of CH, lines of the C₂ Swan and Phillips systems and permitted and forbidden lines of C I. After careful measurement of a large number of lines belonging to all these species and a careful discussion of the atomic and molecular data needed to derive the solar abundance of carbon, we found a remarkable agreement among the results derived from the different indicators. All the results converge to $A_C = 8.60$ (where A_C is the solar abundance of carbon relative to hydrogen in the usual scale where $A_C = \log N_C/N_H + 12$) with very small dispersions, ± 0.05 dex. In the course of this study many interesting molecular results have been obtained.

a) CH vibration-rotation

The most recent laboratory analyses of the infrared vibration-rotation lines of the X ²Π state by Lubic and Amano (1984) and Bernath (1987) are limited to the 1-0, 2-1 and 3-2 bands and to rather low rotational quantum numbers, $N'' = 9$. From many other unsuccessful trials by various groups, it is clear that it is very difficult, if not impossible, to excite CH to higher energies in laboratory sources.

New high-resolution, low-noise solar spectra, free from any telluric lines, have been obtained by the ATMOS (Atmospheric Trace MOleculE Spectroscopy; Farmer and Norton 1989) Fourier transform spectrometer experiment onboard the Space Shuttle (Spacelab 3 flight, April 29 - May 6, 1985). Based on Bernath's (1987) line positions, we easily detected the low N'' lines of CH on these new solar photospheric spectra which cover the range from 650 to 4800 cm⁻¹ (2.3 to 16 μm). The extension of the solar identifications to higher N'' -values, for which no wavenumber was available, has been cautiously made step by step. We have thus been able to follow the R branches up to $N'' = 34$ for the 1-0 and 2-1 bands and

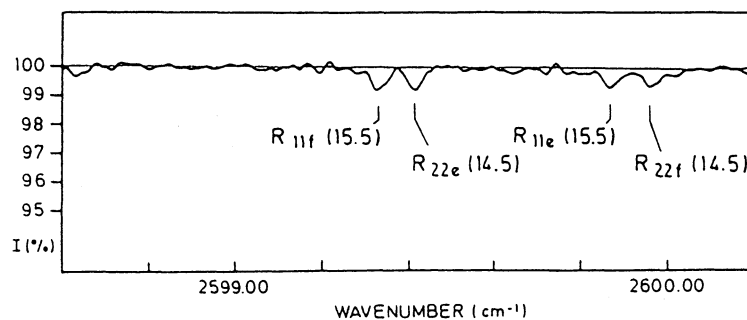


Figure 1: The solar spectrum from ATMOS in the region of the 4-3 band of CH. The four solar lines at $N''=15$ have not yet been observed in the laboratory, not even in the recent investigation of Bernath et al. (1991).

up to $N'' = 31$ for the 3-2 band. For the P branches, about three times weaker than the R branches, it was only possible to add a few lines to the laboratory observations. We also predicted the positions of lines of the 4-3 band and many R lines up to $N'' = 24$ have been identified for the first time (see Fig. 1).

All these new solar CH lines have been used, together with the few lines observed in the laboratory, to derive new molecular constants of the CH ground state (Ménét et al. 1989). Very recently Bernath et al. (1991) have redetermined the spectroscopic constants of the $X^2\Pi$ state on the basis of our solar observations and of their first laboratory measurements of the 4-3 band (but limited to low N'' lines) as well as more accurate positions of electronic transitions.

b) CH A - X transition

We also show, in the same study, that the transition probabilities derived from the experimental lifetime of the $v' = 0$ state by Bauer et al. (1989) and from the theoretical results of Larsson and Siegbahn (1983, 1986) for the $v' = 0$ and $v' = 1$ states are very accurate.

c) C_2 Swan

In their paper, Grevesse et al. (1991) also reanalyzed the C_2 d $^3\Pi_g - a^3\Pi_u$ Swan system. They discuss the transition probability of the 0-0 band and conclude that all the recent experimental and theoretical results converge to $\tau_0 = 98 \pm 5$ ns or $f_{00} = 3.03 \cdot 10^{-2}$, in disagreement with earlier results around $\tau_0 = 120$ ns.

The principal uncertainty in the analysis is the dissociation energy of C_2 where values ranging from 6.10 to 6.25 eV have been found by different authors. In order for the solar carbon abundance derived from the C_2 Swan band to agree with the values derived from the other carbon abundance indicators mentioned above, we had to adopt $D_0^0 = 6.21$ eV, the value recommended by Huber and Herzberg (1979).

d) C_2 Phillips

We also reanalyzed the C_2 Phillips system, A $^1\Pi_u - X^1\Sigma_g^+$, based on our previous investigation (Brault et al. 1982). Although these lines are faint and much more difficult to measure than other molecular lines of C_2 and CH, we could test this band rather accurately, the dispersion of the results being no larger (± 0.05 dex) than the one found when using other carbon indicators.

Apart from the dissociation energy discussed above, the main uncertainty comes from the transition probabilities which have been the subject of considerable discussion in recent years. To summarize (see Grevesse et al. 1991 for a detailed discussion), theoretical transition probabilities are considerably larger, by factors 1.5 to 2, than the most recent experimental results. Our solar analysis showed that, in order for the carbon abundance as derived from the C_2 Phillips band to agree with the results from other indicators, we had to use the most recent and most accurate theoretical transition probabilities of Langhoff et al. (1990), excluding the lower experimental values.

III. CO TRANSITIONS

In the high resolution and low noise ATMOS solar spectra (Farmer and Norton 1989), more than 7000 vibration-rotation lines of the fundamental $^1\Sigma^+$ state of four isotopic species of carbon monoxide ($^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ which is about 500 times less abundant than $^{12}C^{16}O$; and eventually, for the first time in the solar photospheric spectrum, $^{12}C^{17}O$ which is about 2500 times less abundant than $^{12}C^{16}O$) are detected in the spectral range 1350 - 2328 cm^{-1} (fundamental bands, from 1-0 to 20-19) and 3410 - 4360 cm^{-1} (first overtone bands, from 2-0 to 14-12). In some spectral regions, as illustrated in Figures 2 and 3, the solar spectrum looks really like a pure CO absorption spectrum. On ground-based spectra, the $\Delta v = 2$ sequence is strongly polluted by a large number of telluric lines and the $\Delta v = 1$ sequence is heavily masked by strong and large telluric absorptions.

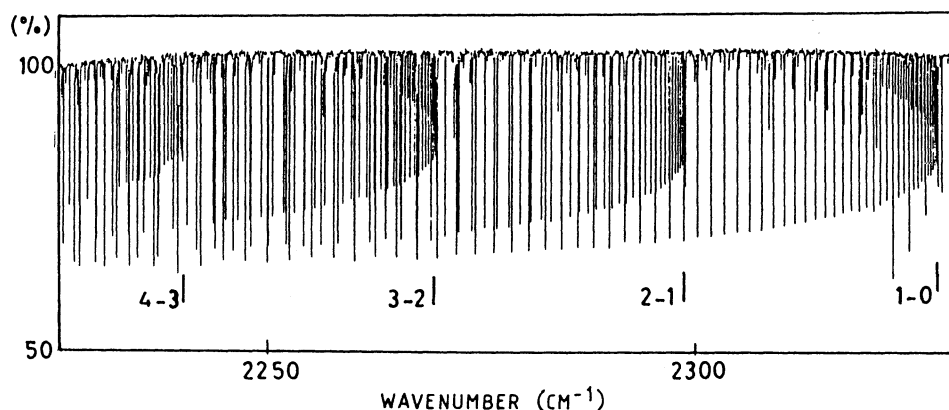


Figure 2: Part of the infrared solar spectrum as seen from ATMOS showing many lines of the fundamental bands of carbon monoxide. The bandheads of the 1-0, 2-1, 3-2 and 4-3 bands are clearly visible.

When analyzing these solar data, we soon realized that the available molecular constants for the $^{12}\text{C}^{16}\text{O}$ ground state (Guelachvili et al. 1983) could not reproduce the observed solar wavenumbers for the high J -value lines seen, for the first time, in the solar photospheric spectrum. The deviation between observed and predicted line positions increases with increasing rotational excitation, starting at J around 80 - 90. This was to be expected because laboratory data on CO vibration-rotation transitions are limited to rotational quantum numbers lower than $J=94$ whereas the solar data allow to see the CO transitions to much higher rotational excitation ($J = 133$).

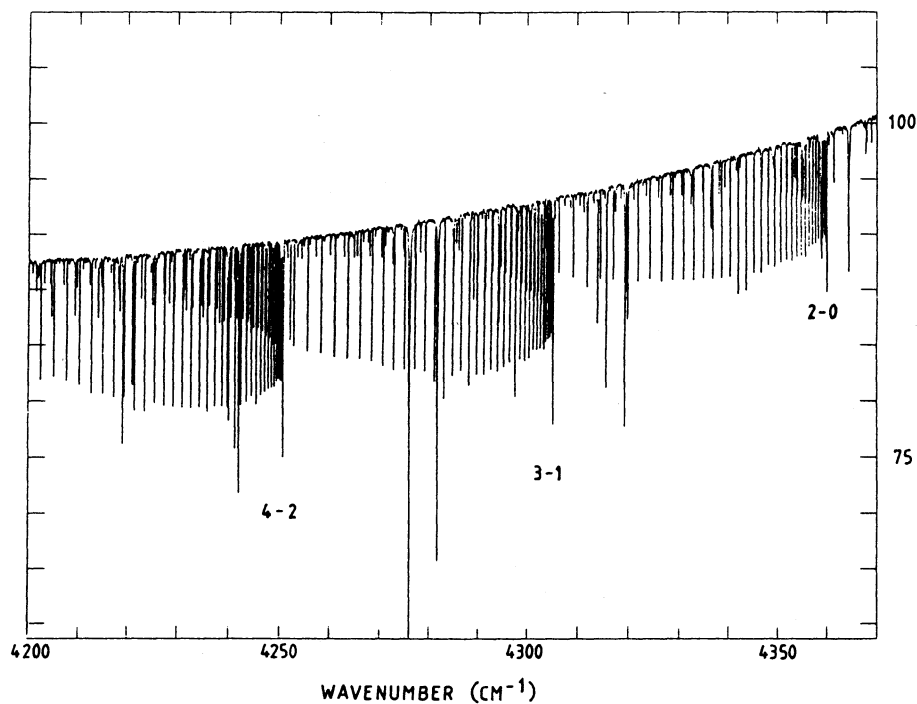


Figure 3: Part of the infrared solar spectrum as seen from ATMOS showing the first overtone bands of carbon monoxide. The bandheads of the 2-0, 3-1 and 4-2 bands are clearly visible.

We have therefore decided to add these new accurately measured solar line positions (about 3700) to the data bank of line frequencies, which includes all the previous accurate laboratory positions available (about 14 000). With this data bank of line frequencies, Farrenq et al. (1991) very recently redetermined a new set of 31 Dunham coefficients - a record number of molecular parameters in fact - which reproduce both all accurate laboratory wavenumbers and our new solar line positions of high rotational excitation with a standard deviation of about 0.01 mK (10^5 cm^{-1}).

We note here that it is not the first time the solar spectrum is used as a laboratory source as far as CO is concerned. Goldberg and Müller (1953) already used the CO lines detected in the solar infrared spectrum (91 lines of the $\Delta v = 2$ sequence) in order to derive an improved set of molecular constants. From the measured intensities of solar CO lines of the first overtone bands, Tsuji (1977) concluded that the experimental Herman-Wallis factors obtained by Roux et al. (1972, 1974) should be regarded as highly doubtful.

IV. OH TRANSITIONS

The solar infrared spectrum also shows vibration-rotation lines and pure rotation lines of the ground state, $X^2\Pi$, of OH. Even if many OH lines are perturbed by telluric absorptions, Sauval et al. (1984) analyzed about 100 pure rotation lines of OH on ground-based solar spectra ($760 - 960 \text{ cm}^{-1}$, $v = 0, 1, 2, 3$ and N'' from 22 to 37). Grevesse et al. (1984) analyzed vibration-rotation P lines of OH belonging to the 1-0, 2-1 and 3-2 bands ($2400 - 3300 \text{ cm}^{-1}$). These two works clearly show how sensitive the strengths of those lines are to the electric dipole moment function (EDMF). We succeeded in selecting, among different EDMF's available, the one that definitely explained the observed strength of the solar OH lines, excluding all the other ones.

The solar ATMOS spectra from space nicely show all these lines without any telluric absorption. On these new spectra we can follow the pure rotation lines within the $v = 0, 1, 2$ and 3 vibrational levels to lower and much higher rotational excitations, even much higher than what is known from laboratory studies, at least for the pure rotation transitions. If no new line is observed among the vibration-rotation transitions, the true solar spectrum, as seen from space, from 600 to 1100 cm^{-1} , is almost uniquely made of pure rotation lines of OH (see Fig. 4) which extend to N'' -values as high as 44 ($v'' = 0$) and $N'' = 38$ ($v'' = 3$).

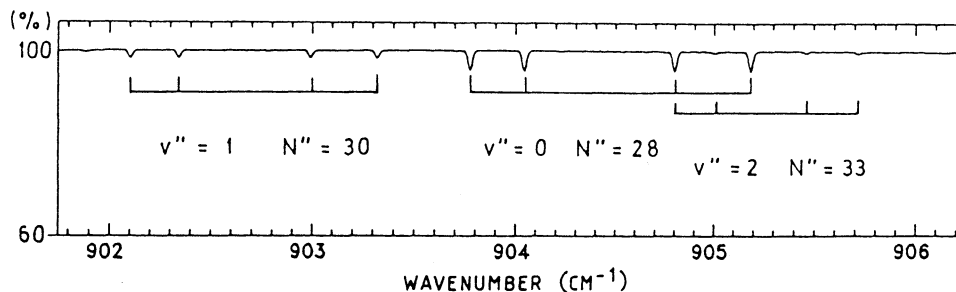


Figure 4: The solar spectrum from ATMOS in the region of the pure rotation lines of OH (for $v''=0, 1$ and 2)

V. CN TRANSITIONS

The red system of CN ($A^2\Pi - X^2\Sigma^+$) is a very strong source of opacity in cool stars. Molecular opacity due to this transition has recently been reconsidered in detail by Jørgensen and Larsson (1990). Two important problems are met with this system. There are still uncertainties about the transition probabilities of the different bands. For the 0-0 band, for example, recent theoretical results by Lavendy et al. (1984), Knowles et al. (1988) and Bauschlicher et al. (1988) cluster around $f_{00} = 2.36 \cdot 10^{-3}$ whereas the most recent laboratory measurement leads to $f_{00} = 1.9 \cdot 10^{-3}$ (Davis et al. 1986). For a more detailed discussion see Jørgensen and Larsson (1990) and Bauschlicher et al. (1988). On the other hand, stellar

application of these opacities requires an accurate knowledge of the dissociation energy of CN. And here also the D_0^0 -value is not well known. Recent values range from the theoretical value, $D_0^0 = 7.65$ eV, obtained by Bauschlicher et al. (1988), to the higher experimental results: $D_0^0 = 7.77$ eV, measured by Costes et al. (1990), and $D_0^0 = 7.74$ eV, measured by Huang et al. (1992).

The solar spectrum offers a unique opportunity to test these data. This was already done by Sneden and Lambert (1982). We have remeasured the equivalent widths of CN lines belonging to 28 bands which are present in the solar spectrum, using the solar atlases of Delbouille et al. (1973, 1981). In doing these measurements we took great care of possible blends among those CN lines through careful examination of the profiles of the lines (FWHM).

We present hereafter preliminary results obtained for the 0-0 band. Using the same model of the photosphere as the one used in our analyses of carbon and nitrogen discussed in this paper, the observed equivalent widths of about 70 CN lines of the 0-0 band are better reproduced with $f_{00} = 2.36 \cdot 10^{-3}$, corresponding to the mean of the most recent theoretical studies mentioned above, and a dissociation energy $D_0^0 = 7.77$ eV. This value of D_0^0 agrees with the most recent laboratory measurement mentioned above and seems to rule out the lower theoretical value (7.65 eV). We recall here that, under solar photospheric conditions, there is a straightforward relationship between f_{00} and D_0^0 (see Eq. 1),

$$\Delta \log f_{00} = - \Delta D_0^0 \text{ (eV)}.$$

VI. NH TRANSITIONS

On the ATMOS solar spectra, Grevesse et al. (1990) have identified for the first time vibration-rotation lines of NH ($X^3\Sigma$ state) near $3 \mu\text{m}$. This solar analysis allowed a test of the accuracy of available electric dipole moment functions.

The solar spectrum also shows pure rotation lines of NH, never observed previously in the laboratory (Geller et al. 1991). Unfortunately, these lines are very faint and appear as "unresolved triplets" ($v'' = 0, N'' = 20$ to 35 ; $v'' = 1, N'' = 21 - 29$) and no new information concerning the NH ground state can be obtained from the newly discovered solar pure rotation lines.

VII. CONCLUSIONS

We all agree that the ultimate goal of solar spectroscopy is to derive the physical conditions and processes that prevail in the solar outer layers. But in many cases the atomic and molecular data needed to interpret the solar spectrum are either of uncertain accuracy or eventually missing. In such cases, solar spectroscopy can be used to determine these basic data. The sun is then considered as a very good "laboratory" source. It has revealed to be very successful in atomic spectroscopy (Johansson and Learner 1990; Johansson 1991). We have shown here it is also a successful source for the spectroscopy of diatomic molecules allowing to test the accuracy of available molecular data like transition probabilities (C_2 , CN, CH), transition moments (OH, NH) and dissociation energies (CN, C_2), and to refine our knowledge of molecular constants (CH, CO).

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