WHAT CAN MOLECULAR SPECTROSCOPY
TELL US ABOUT HOT BANDS?

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RESUMEN. Después de definir bandas calientes, estudiamos el caso del CO y demostramos que el modelo de orden cero es claramente inadecuado, tanto para las frecuencias como para las intensidades. El caso de las moléculas poliatómicas es más complejo principalmente a causa de las resonancias. Se seleccionan los ejemplos del dióxido de carbono y del agua para mostrar la importancia de las bandas calientes a alta temperatura.

ABSTRACT. After a definition of hot bands, we study the case of CO and show that, both for frequencies and for intensities, the zeroth order model is clearly inadequate. The case of polyatomic molecules is more complex mainly due to resonances. The examples of carbon dioxide and water are taken to show the importance of hot bands at high temperature.

Key words: LABORATORY SPECTRA – MOLECULAR PROCESSES

I. INTRODUCTION

First I would like to thank the organizers of this workshop for their kind invitation to this colloquium, which was, I must confess, somewhat unexpected, since, in a way I am here a **displaced person**, in the sense that I am not in my usual working conditions. I am a laboratory infrared spectroscopist, used to high spectral resolution, typically 0.001 - 0.005 cm^{-1}, which implies low pressures (less than 1 Torr) and what we call long pathlengths (up to 100 m). Most of the spectra I use are recorded at room temperature or sometimes at 250K. Since several of my recent works are related to problems found in the giant planets, in Titan or in the terrestrial stratosphere, the temperature of which are in the 70-250K range, these working conditions are quite adequate.

I usually study polyatomic molecules, with 3-7 atoms, mostly linear and symmetric top molecules, the most recent being $CH_3-C\equiv CH$, GeH_3Br and $HC\equiv C-C\equiv N$. The wavenumber scale of the spectra is very accurate, at best 2×10^{-5} cm^{-1} in precision and 2×10^{-4} cm^{-1} in accuracy for Fourier transform spectra. Therefore, when the situation is favorable, and we have a good model to fit the data, as it was the case in a recent work on propyne (Graner and Wagner 1990), we can fit more than 1700 experimental wavenumbers, with 17 free parameters, to a standard deviation of the residuals as low as 2.1×10^{-4} cm^{-1}.

As you see, all this is rather far from the situation in stellar atmospheres. Nevertheless the organizers of this workshop thought that I can bring you some interesting information concerning hot bands.

II. WHAT IS A HOT BAND ?

The idea has been known for a long time, if not the word. In Herzberg's book (Herzberg 1945) which is our bible, I find the following passage, on page 287:

'A somewhat different type of difference band is *that for which one and the same low-frequency vibration is excited in the upper and lower state* in addition to some vibrations in the upper state. In the simplest case..... we obtain a band that may be written $v_k + v_i - v_i$ ....(Dennison [ref. 280] calls such bands "upper stage" bands.) '

Fig.1
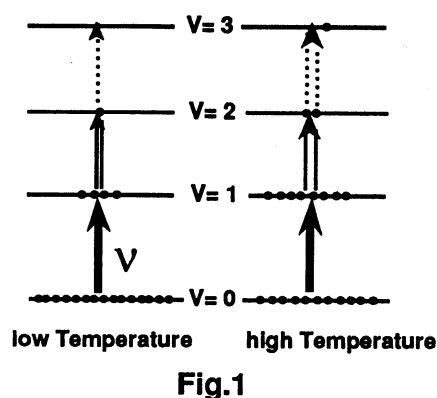
For those who are not familiar with hot bands, let us consider the case of a diatomic molecule, shown in Figure 1.

At low temperature, if the thermal equilibrium is reached, most molecules are in the ground state v=0, a few of them in the v=1 level and even fewer in the v=2, 3... levels. The ratio of the populations in the levels 0 and 1 is given by the following formula

$$N_1 / N_0 = \exp(-h v / K T)$$

where v is the transition frequency between levels 0 and 1 and K is the Boltzmann constant. If v is expressed in cm^{-1}, $h v$ is replaced by $h v c$ in the formula.

Therefore the intensity of the transition $2 \Leftarrow 1$, drawn in double lines, relative to the intensity of the transition $1 \Leftarrow 0$, drawn in solid line, is given by the same Boltzmann factor. When T increases, as shown on the right part of the figure, the Boltzmann factor increases, so do the relative populations of levels 1 and 0, and therefore the intensity of the $2 \Leftarrow 1$ transition increases too. This is the reason why it is called a hot band. The transition $3 \Leftarrow 2$, drawn in dotted line, is also a hot band and its intensity increases in the same way.

This drawing is made for *absorption* and implies that there is a *Boltzmann equilibrium* at a certain temperature. In *emission*, the population which counts is the population of the originating level of the transition, i.e. the upper level. Here we would have to consider N_2/N_1 instead of N_1/N_0.

For polyatomic molecules, the formula is slightly more complicated. The intensity of a hot band relative to the intensity of the cold band is given by

$$S_{hot} = d_i . S_{cold}.\exp(-h v / K T)$$

where d_i is the degree of degeneracy of the level involved, i.e. the lower level in absorption or the upper level in emission. For instance, in symmetric tops, if the level involved is of E type symmetry, $d_i = 2$.

TABLE I
BOLTZMANN FACTOR

	At 300 K	At 1000K	At 2500 K
$v = 400 \ cm^{-1}$	0.147	0.562	0.794
$v = 1000 \ cm^{-1}$	0.008	0.237	0.562
$v = 3000 \ cm^{-1}$	6×10^{-7}	0.013	0.178

Table I shows very clearly two effects:-First, for a given value of the frequency v, the population of excited levels increases very quickly with the temperature.
- Secondly, at a given temperature, the population of excited levels is very high if the molecules have low lying levels, which may happen either because the molecule is heavy or because it is flexible.

This effect is strongly exaggerated in polyatomic molecules with a high degree of symmetry such as SF_6 or UF_6. For SF_6, at 298K, only 31 % of the total number of molecules are in the vibrational

ground state and 17 % in the $v_6=1$ state at 346 cm^{-1}. For UF$_6$, at 308K, only 0.36 % of the total number of molecules are in the vibrational ground state, 0.55 % in the $v_6=1$ state at 144 cm^{-1} and so on...

H−C ≡ C−C ≡ N

v_6
P(17)

v_6
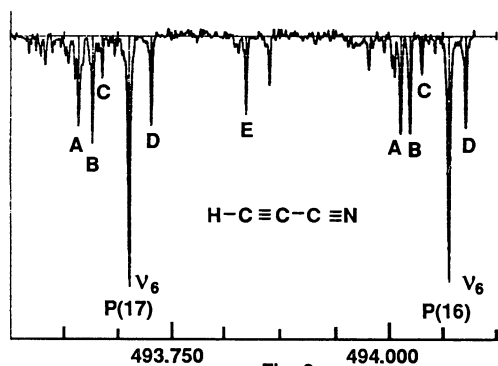P(16)

493.750   494.000

Fig. 2

Figure 2 shows a part of a spectrum we have recently studied: cyanoacetylene or propyne-nitrile (Arié *et al.* 1990). It is a linear molecule but with a long skeleton. You see that at room temperature, the strongest lines belong to the fundamental band v_6 but one can see very clearly *at least* 5 series belonging to hot bands, and probably more. The lowest level of this molecule is v_7 at 222 cm^{-1}.

My presence in this workshop would be useless if I could only speak about spectra at room temperature. Fortunately, I can also tell you about other techniques used in our laboratory to produce molecules in very excited vibrational levels.

I shall begin by a diatomic molecule, which is CO. I shall try not to overlap too much on the previous lecture by Dr Grevesse since I am referring partly to the same experimental material.
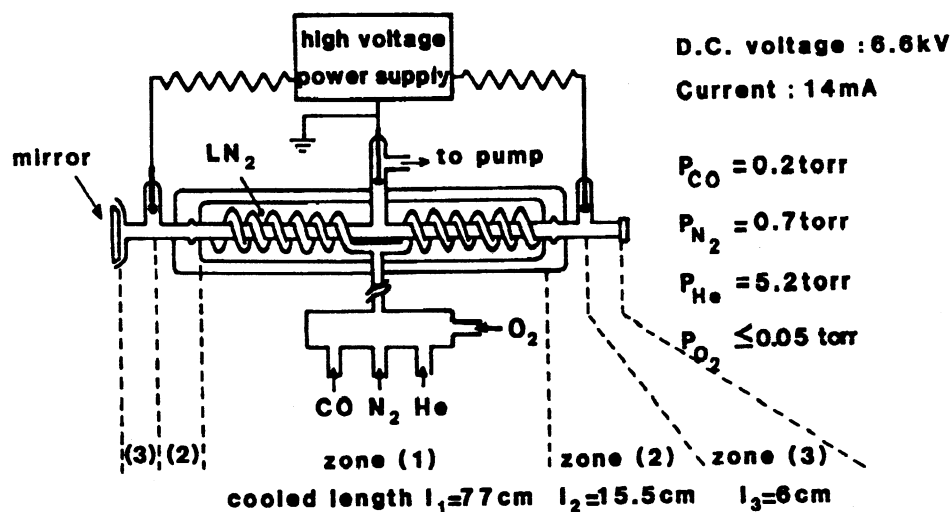

Fig.3. Discharge tube . Experimental parameters.

Figure 3 shows the discharge technique used by Robert Farrenq and his co-workers in our laboratory at Orsay (Farrenq *et al.* 1985). It is in fact a CO laser tube, cooled at liquid nitrogen temperature, but without the second mirror, so that the emission spectrum can be recorded on a Fourier transform spectrometer.
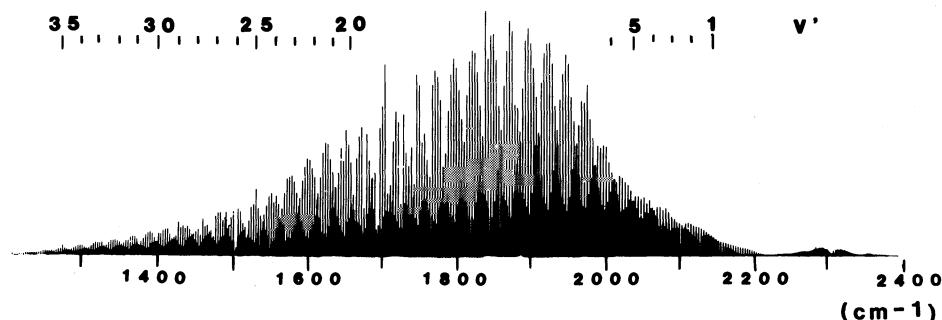
Fig.4

Figure 4 shows the spectrum observed in the region of the fundamental band of CO. Each of the bunches corresponds to the P branch of a hot band (the R branches are weaker here but there is no thermal equilibrium). You see that the band center of the fundamental band is at 2143 cm^{-1} i.e. 4.7 μm whereas the band center of the transition $20 \Rightarrow 19$ is at 1653 cm^{-1} i.e. 6 μm and the band center of the highest transition observed $40 \Rightarrow 39$ is at 1164 cm^{-1} i.e. 8.6 μm.

This should illustrate an important point: the **harmonic oscillator is a very bad model** for the energy levels of the CO molecule and of most diatomic molecules. It is even worst for the $\Delta v=2$ and $\Delta v=3$ sequences as shown in Table II. You see that the end of the $\Delta v=2$ sequence is close to the beginning of the $\Delta v=1$ sequence and that the $\Delta v=3$ sequence frankly overlaps the $\Delta v=2$ sequence.

TABLE II
BAND CENTERS OF OBSERVED CO BANDS

$\Delta v=1$ sequence		$\Delta v=2$ sequence		$\Delta v=3$ sequence	
$1 \Rightarrow 0$	2143 cm^{-1}	$2 \Rightarrow 0$	4260 cm^{-1}	$3 \Rightarrow 0$	6350 cm^{-1}
$2 \Rightarrow 1$	2117 cm^{-1}	$3 \Rightarrow 1$	4207 cm^{-1}	$4 \Rightarrow 1$	6271 cm^{-1}
....	....	....			
$20 \Rightarrow 19$	1653 cm^{-1}	$20 \Rightarrow 18$	3331 cm^{-1}	$20 \Rightarrow 17$	5034 cm^{-1}
....	....	....			
$40 \Rightarrow 39$	1164 cm^{-1}	$41 \Rightarrow 39$	2306 cm^{-1}	$40 \Rightarrow 37$	3567 cm^{-1}

Figure 5 shows a blow-up of the spectrum in the $\Delta v=2$ region. It is in fact an emission spectrum recorded in different conditions by Dr Jean Vergès, who provided this figure. You notice that in this case the R branch is quite stronger than the P branch and that there is a band head near J=72.

The best way to express the rovibrational energy levels of CO is to use the Dunham expansion, which is described in Table III.
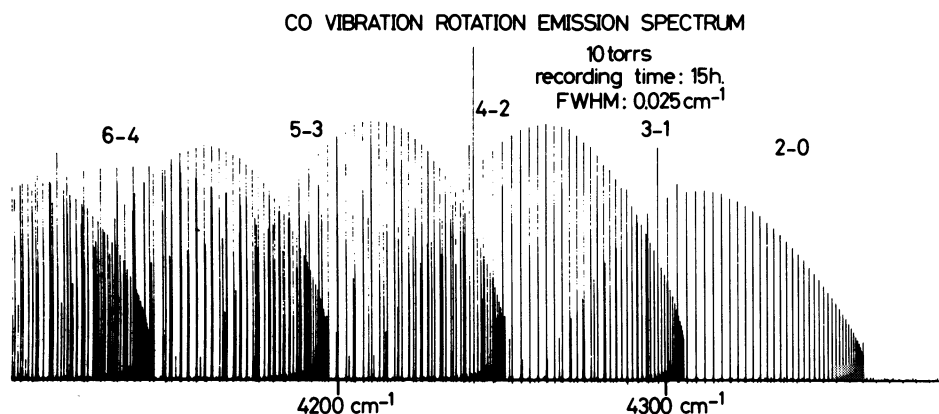
CO VIBRATION ROTATION EMISSION SPECTRUM

Fig.5

TABLE III
THE DUNHAM EXPANSION OF THE ENERGY LEVELS

For a diatomic molecule, the energy levels can be represented by

$$E(v,J) = \sum_{k,\ell} Y_{k,\ell} \left[v + \frac{1}{2} \right]^k \left[J(J+1) \right]^\ell$$

with

$$Y_{01} \cong B_e \qquad Y_{02} \cong -D_e \quad \cdots$$
$$Y_{10} \cong \omega_e \qquad Y_{20} \cong -\omega_e x_e \quad \cdots$$

For the electronic ground state of CO, the following Y_{kl} have been determined:

Y_{10}	$Y_{20} \cdots \cdots Y_{90}$	Y_{01}	Y_{71}
Y_{02}	Y_{42}	Y_{03}	Y_{23}
Y_{04}	Y_{24}	Y_{05}	Y_{15}
Y_{06}	(31 parameters altogether)		

The latest fit of all available data on the ground state of this molecule was recently done by R. Farrenq, N. Grévesse and collaborators (Farrenq *et al.* 1991). They found 31 significant parameters detailed in Table III. We are really far from the first order model using an harmonic oscillator plus a rigid rotor !

Now let us turn to the **INTENSITY** problems. The intensity of a rovibrational transition depends upon 2 factors: the transition moment and the populations of the levels. We have already considered the populations, which are given by the Boltzmann factor. Apart from this factor, in a diatomic molecule, the intensity of a rovibrational transition between two levels **v** and **v+n** is proportional to

$$\left| R_0^n \right|^2 \cdot \frac{(v+n)!}{v!\,n!} \cdot H_n(v) \cdot |m| \cdot F_{v,n}(m)$$

The product of the three first factors constitutes the vibrational part, the last two the rotational part. As usual, m = - J for the P branch and m = J+1 for the R branch.

The vibrational part is made of a term corresponding to the harmonic oscillator multiplied by an anharmonicity factor H. In the same way, the rotational part contains a factor called Herman-Wallis factor or F factor. Both of them would be equal to 1 in the zeroth order approximation. The H factor expresses the so-called electrical anharmonicity and the F factor expresses the rotation-vibration interaction. How good is this zeroth order approximation ?
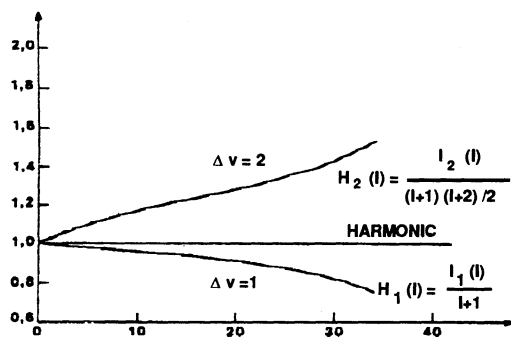
Figure 6 shows that, at least for CO, the anharmonicity factor can be quite different from 1, either larger or smaller. If we limit ourselves to v=20, H is about 0.9 for the $\Delta v=1$ sequence and 1.3 for the $\Delta v=2$ sequence.

As for the H-W factor, in the case of CO, it is not very large in the 1-0 transition, so that for m=50, the R and the P line have about the same size. But you can see on Table IV that for the harmonic bands, the coefficients C and D are much larger. The effect of this F-factor is that the R branch is much stronger than the P branch **if there is a thermal equilibrium.** The ratio is given in the last line of Table IV.

Fig.6 The anharmonicity factor H_n (v) for CO

I have also given the corresponding values for HCℓ, because they are more representative of a "typical" diatomic molecule.

Now, there is a last point I would like to mention. Most intensity calculations assume populations in Boltzmann equilibrium. I do not know how good this hypothesis is for your domain but I should tell you that it is not valid in our discharge experiments .

In the CO experiment I described earlier, it is possible to define a **rotational temperature** T ≅ 150 K but there is no Boltzmann equilibrium for vibrations.

TABLE IV
HERMAN-WALLIS FACTOR

$$F(m) = 1 + Cm + Dm^2 + ...$$

CO : exceptionally small F factor

	1-0	2-0	3-0	4-0
C	1.9×10^{-4}	5.1×10^{-3}	1.2×10^{-2}	3.4×10^{-2}
D	$7. \times 10^{-6}$	3.4×10^{-5}	$1. \times 10^{-4}$	3.7×10^{-4}
$\dfrac{F(50)}{F(-50)}$	1.017	1.61	2.85	16.11

More usual F factors:
H-Cℓ (1-0)   C= -2.56×10^{-2} D= 3.2×10^{-4}
F(-20)/F(20) = 2.66   F(-50)/F(50) = 5.92

You can define a vibrational temperature only for a pair of vibrational levels. The vibrational temperature defined in this way varies from 1900 to 30,000 K.

To summarize, even for diatomic molecules, the simplified model using a harmonic oscillator and a rigid rotor is extremely unsatisfactory for the frequencies of hot bands, due to the MECHANICAL anharmonicity and not valid for the intensities, due to both the anharmonicity factor and to the Herman-Wallis factor.

III. POLYATOMIC MOLECULES

The problem of hot bands in polyatomic molecules is much more difficult for several reasons, the first reason is the occurrence of **RESONANCES.**

As you know, polyatomic molecules have many normal modes. If a molecule contains N atoms, there are 3N-5 degrees of freedom for vibrations if it is linear and 3N-6 if it is not. Because of degeneracies, the number of normal modes is often smaller.
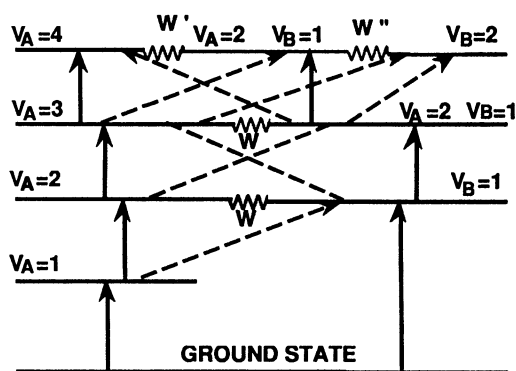
Figure 7 is an oversimplified model of a real situation. Let us suppose a molecule with only 2 modes A and B such that v_B is about twice v_A and that there is in the Hamiltonian an interaction term W which links the two levels $v_B=1$ and $v_A=2$, which are now mixed. Both their energies and their wavefunctions are changed by this interaction.

Then already if you consider the first hot band of v_A, i.e. $2v_A - v_A$, it is very different from the cold band v_A:
- rovibrational frequencies are considerably changed because of the changes in energy of $v_A=2$;

$V_A=4$ W' $V_A=2$ $V_B=1$ W" $V_B=2$
$V_A=3$ $V_A=2$ $V_B=1$
$V_A=2$ $V_B=1$
$V_A=1$

GROUND STATE

Fig. 7

- intensities are considerably changed because of the modifications in the wavefunctions and one can even see what we call **FORBIDDEN** transitions, which are in fact "perturbation allowed transitions", as shown by a slanted line on Fig. 7.

Now if you go one step further, you can be sure that the level $v_B=2$ is close to $v_A=4$. Maybe the distance between levels is smaller than before, maybe it is larger, all depends upon anharmonicity coefficients. Anyway, it is very likely that the interaction term W' will be larger, maybe twice as large or only $2^{1/2}$ as large as W. And therefore, the higher hot bands are likely to be even more perturbed and there will be more "forbidden transitions".

In fact, the situation is more complex than that, because you can also have COMBINATION levels, where both A and B modes are excited, such as $v_A=v_B=1$ on the "fourth floor" and $v_A=2$, $v_B=1$ on the "fifth floor". Therefore if you look in the region of the $3v_A - 2v_A$ hot band of v_A, both the upper and the lower state are perturbed, and because of the mixing between states, you can have, in principle, 4 different transitions, 2 of them permitted, 2 of them forbidden (the permitted ones are shown by vertical lines on the figure, the 'forbidden' ones by slanted lines).

At the next "floor", you have now a triad of levels $(v_A=4)$, $(v_A=2, v_B=1)$ and $(v_B=2)$, hence in principle 6 different hot bands, corresponding to $4v_A - 3v_A$ and so on.

This simplified scheme is more or less valid for ASYMMETRIC TOP molecules with the important difference that you can never find a molecule with only 2 modes. For LINEAR, SYMMETRIC TOP and SPHERICAL TOP molecules, there is a further complication due to the fact that some normal modes are **DEGENERATE**. For these modes, you have to introduce not only the classical vibrational quantum numbers v but also a secondary quantum number ℓ, related to the *vibrational angular momentum,* which can take the values v, v-2, v-4.........-(v-2), -v (altogether v+1 values). This still increases the complexity.

Moreover, there is another effect in linear molecules (and I should add in some subbands of symmetric top molecules) it is the so called ℓ-**type doubling**. The 2 levels with the same absolute value of ℓ should have the same energy but they are split into 2 components called + and - or **e** and **f** , with further selection rules on these symmetries:

$e \Leftrightarrow f$ for Q branches
$e \Leftrightarrow e$ and $f \Leftrightarrow f$ for P and R branches

Figure 2 illustrates the complexity introduced even in a linear molecule, as demonstrated by the spectrum of HC_3N.

The lowest band of this molecule is v_7 at 222 cm^{-1}. If we look at the region of 500 cm^{-1} (see Arié *et al.* 1990 for details),we have not only v_6 but also $v_6 + v_7 - v_7$, with 4 components and $2v_6 - v_7$ with 3 components. In some cases, the upper state energy levels can be represented by a simple polynomial in J(J+1) with only 3 parameters, but sometimes we have to use 4, 5 and even 6 parameters which proves that already at these low energies, there are perturbations due to Coriolis interactions.
You can therefore try to imagine the situation either at higher temperature in the same spectral region or, even at room temperature, in a higher frequency region.

IV. THE CASE OF CO_2

To help you to imagine the situation, I have taken another example which is CO_2. I know that it is a bad example for you because CO_2 is dissociated at stellar temperatures and therefore there is very little left. But it happens that CO_2 has been studied in great details and especially in our laboratory by D. Bailly and C. Rossetti. They make a DC discharge in a flow of CO_2+N_2 or CO_2+He or $CO_2+N_2 + He$ and the emission spectra is analyzed in a Fourier transform spectrometer.

Let us recall first a few facts about CO_2: it has three fundamental modes, v_1, v_2 and v_3, centered at 1337, 667 and 2349 cm^{-1} respectively, the second one being degenerate. The normal notation for levels is $v_1 (v_2)^\ell v_3$, but there is such a strong Fermi resonance between the levels 10^00 and 02^00 (in other words $v_1=1$ and $v_2=2$) which are very close that they are considered as members of a dyad and noted $(10^00,02^00)_I$ and $(10^00,02^00)_{II}$. Higher on the energy scale appear triads, tetrads...of heavily mixed levels, such as the one formed of 31^11 , 23^11 , 15^11 and 07^11 . The selection rule for this molecule is $\Delta\ell = 0$ for parallel bands and $\Delta\ell =\pm1$ for perpendicular bands.

Figure 8 shows under a very condensed form some parts of the spectra recorded by this method (Bailly *et al.* 1985). in the region of v_3, i.e. near 4 μm. The aspect of the spectra depends strongly upon the gas mixture put into the discharge. Here we show only the spectrum obtained with $CO_2 + N_2 + He$, other spectra with $CO_2 + N_2$ or $CO_2 + He$ can be found in Bailly *et al.* 1985. In all cases, there are many hot bands which are strongly shifted downwards from the v_3 fundamental band. The maximum observed shift is here 272 cm^{-1} between the band centers. Here again, anharmonicity plays a large role.
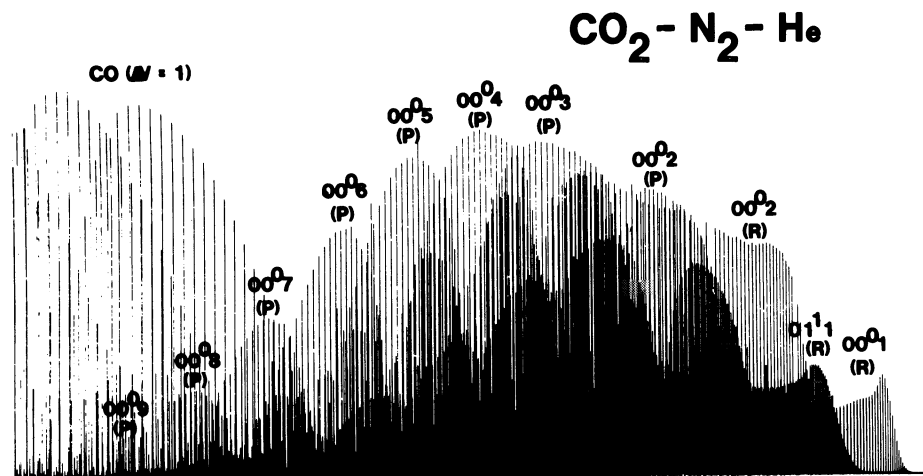
Fig.8

Recently, new spectra have been recorded by this technique both in the 4 µm region and in the region of v_2, i.e. near 15 µm. The present situation is the following:

Near 4 µm, 80 different vibrational transitions have been observed, all obeying the selection rules $\Delta v_1=\Delta v_2=\Delta\ell=0$ and $\Delta v_3=1$. The highest level from which a transition has been analyzed is $v_3=12$, at 26,550 cm^{-1}, or 60 % of the dissociation energy.

Near 15 µm, only 40 different vibrational transitions have been observed, all obeying the selection rules $2\Delta v_1+\Delta v_2= 0$, $\Delta\ell=\pm1$ and $\Delta v_3=0$. The highest level is near 8,000 cm^{-1}. As an example, transitions have been observed between two Fermi dyads $(11^10,03^10)$ and $(10^00,02^00)$. All four possible vibrational transitions have been analyzed in their detailed rovibrational structure.
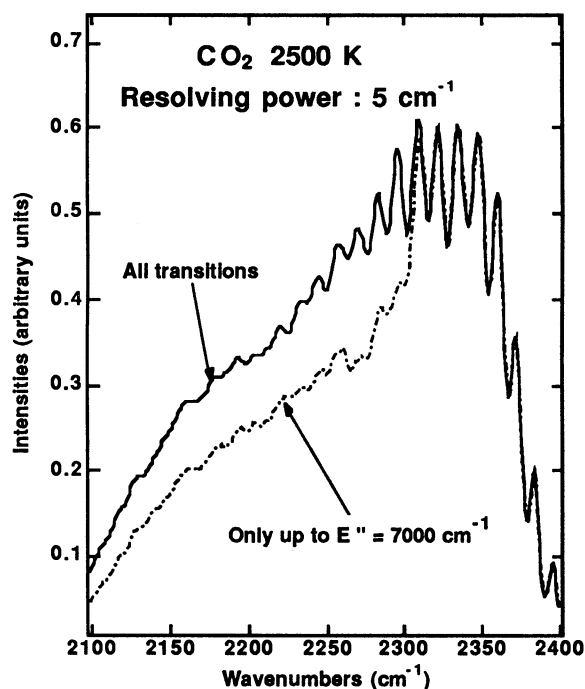
Since we have now a fairly good set of parameters for CO_2, I have asked my colleagues Bailly and Rossetti to compute **ABSORPTION** spectra of CO_2 in conditions somewhat similar to stellar atmospheres, i.e. at 2500K (Fig. 9). You see that if we ignore all vibrational transitions above 7000 cm^{-1}, we have almost no effect between 2300 and 2400 cm^{-1}, but a very important effect below 2300 cm^{-1}. This shows again that the effect of hot bands is not spread all over the spectrum but has more importance in some spectral region than in others.

Note that in Fig 9, we have assumed a Boltzmann equilibrium. This is not the case in the emission spectra recorded in the laboratory.

Fig.9

In these spectra, the rotational temperature T_R is about 385 K. On the other hand, it is possible to define a vibrational temperature T_{v3} for the mode v_3, by considering levels differing only by the quantum number v_3 (T_{v3} is between 1,700 and 3,800K, depending on the mixture) and a vibrational temperature T_{v2} for the mode v_2, by considering levels differing only by the quantum number v_2 (T_{v2} is between 430 and 680K).

The example of CO_2 would be also interesting to discuss in the context of INTENSITIES, HERMAN-WALLIS FACTORS and so on, but we have no space for this.
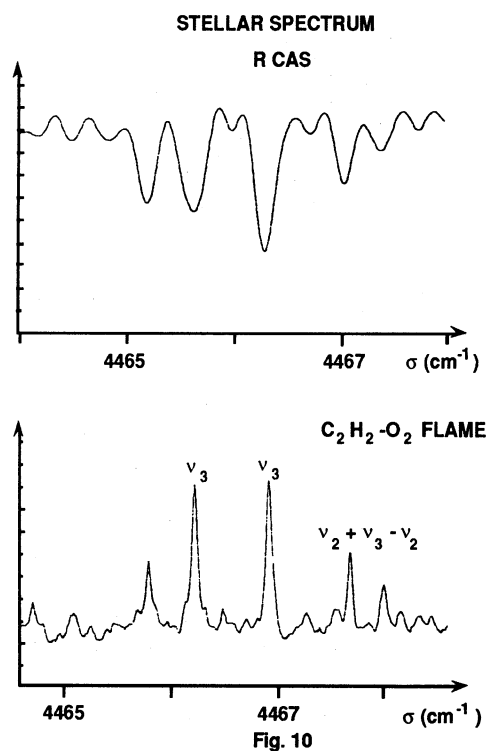
V. THE CASE OF WATER

STELLAR SPECTRUM

R CAS

C₂H₂-O₂ FLAME

Fig. 10

I would like to add a few words concerning H_2O. This is a difficult molecule for a spectroscopist because it is an asymmetric top and a light molecule. Extrapolations are therefore a very dangerous game. My colleagues Flaud and Camy-Peyret have spent many years studying high-resolution spectra of this molecule up to the visible. To reach these very high excited levels, they use 2 techniques: *absoption spectra* with Fourier transform spectrometers and very long pathlengths, up to 434 meters and *flame spectra* with H_2+O_2 or $C_2H_2+O_2$ flames at temperatures in the range 1,500-3,000 K. By the absorption technique, transitions up to 25,400 cm^{-1} or 394 nm have been observed, with lines belonging to $5 v_1 + 3 v_3$.

They have published in 1980 two papers with J.P. Maillard (Camy-Peyret *et al.* 1980; Flaud *et al.* 1980) which lead to the clear identification of H_2O in the spectrum of a cold star of the MIRA type, which is R-Cassiopea. Figure 10 is taken from one of these papers (Flaud *et al.* 1980). More recently, Camy-Peyret has been working again with flame spectra and I was told that he has assigned many lines belonging to new hot bands, such as transitions between the second hexad i.e. 7,600 - 9,000 cm^{-1} and the second triad (4,600 - 5,300 cm^{-1}).

VI. GENERAL CONCLUSION

I hope I have succeeded in convincing you that when you are dealing with high temperature situations, which is the case in your field, you cannot treat hot bands casually, as if they were just a copy at a smaller size of the fundamental bands. You have to take into account correctly their complexity, both concerning energy levels and intensities.

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