

# Numerical practical work: OH spectrum in the upper atmosphere

Master 2 Compuphys  
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## 1 Introduction

A thin layer of OH radicals is present in the terrestrial atmosphere at an altitude of 87 km (with a thickness of about 6-10 km). These radicals result from a reaction of atomic hydrogen with ozone, the OH molecules being created with vibrational energy up to  $v = 9$ . When desexcitating these radicals create a near-infrared emission. This emission appears like waves in the sky, when observed in the near-infrared. The OH emission lines also appear as bright lines in the near-infrared spectra obtained with large telescopes.

The objective of this practical work is to create a code for computing these emission lines from laboratory data (energy levels and transition probabilities) and a Boltzmann distribution of the relative populations. Observational data have shown that it is possible to model with a good accuracy the emission spectrum with a rotational temperature close to the gas kinetic temperature (about 220 K at this altitude) and a vibrational temperature more important (because it is mainly due to the excess of energy available during the photodissociation process), of about 9000 K.

## 2 Rotation-vibration structure of OH bands

Figure 1 provides an overview of emission lines involved in the bands of interest. The ground electronic state is the  $X^2\Pi_i$  state. This state is constituted by two sub-states called  $X^2\Pi_{1/2}$  and  $X^2\Pi_{3/2}$ . This doublet structure is due to the interaction between the spin vector and the orbital electronic moment along the internuclear axis. Because this state is inverted the state  $X^2\Pi_{3/2}$  appears with a lower energy level compared to  $X^2\Pi_{1/2}$ .

The angular momentum can be used for numbering the rotational states. With this nomenclature in the  $X^2\Pi_{3/2}$  state the total angular momentum  $J$  (that takes into account the electronic spin) is equal to  $N + 1/2$  and, in the same way we have  $J = N - 1/2$  for the  $X^2\Pi_{1/2}$  state. Each lambda-doublet has a index “+” or “-” that depends of the parity of the electronic wavefunction with respect to a plane passing through the internuclear axis. Each lower doublet is labelled “e” and each upper doublet is labelled “f”.

The quotation used in figure 1 are the usual ones. The letters Q refer to the transitions with  $J'=J''$  (where ' refers to the upper state and '' to the lower state), P for the transitions with  $J'=J''-1$  and R for the transitions with  $J'=J''+1$ . Indices 1 and 2 refer to the substates involved ( $X^2\Pi_{3/2}$  or  $X^2\Pi_{1/2}$ ). The number in parenthesis indicates the  $J''$  value involved and “e” or “f” the type of doublet of the upper level involved in this transition.

Because the selection rules imply that symmetric levels interact only with asymmetric ones (i.e. the “+” with the “-”) and asymmetric levels with symmetric levels we can see that the “e” states interact only with the “e” states for the P and R lines, and “f” states for the Q lines, and that the “f” states interact with the “f” states for the P and R lines and the “e” states for the Q lines.

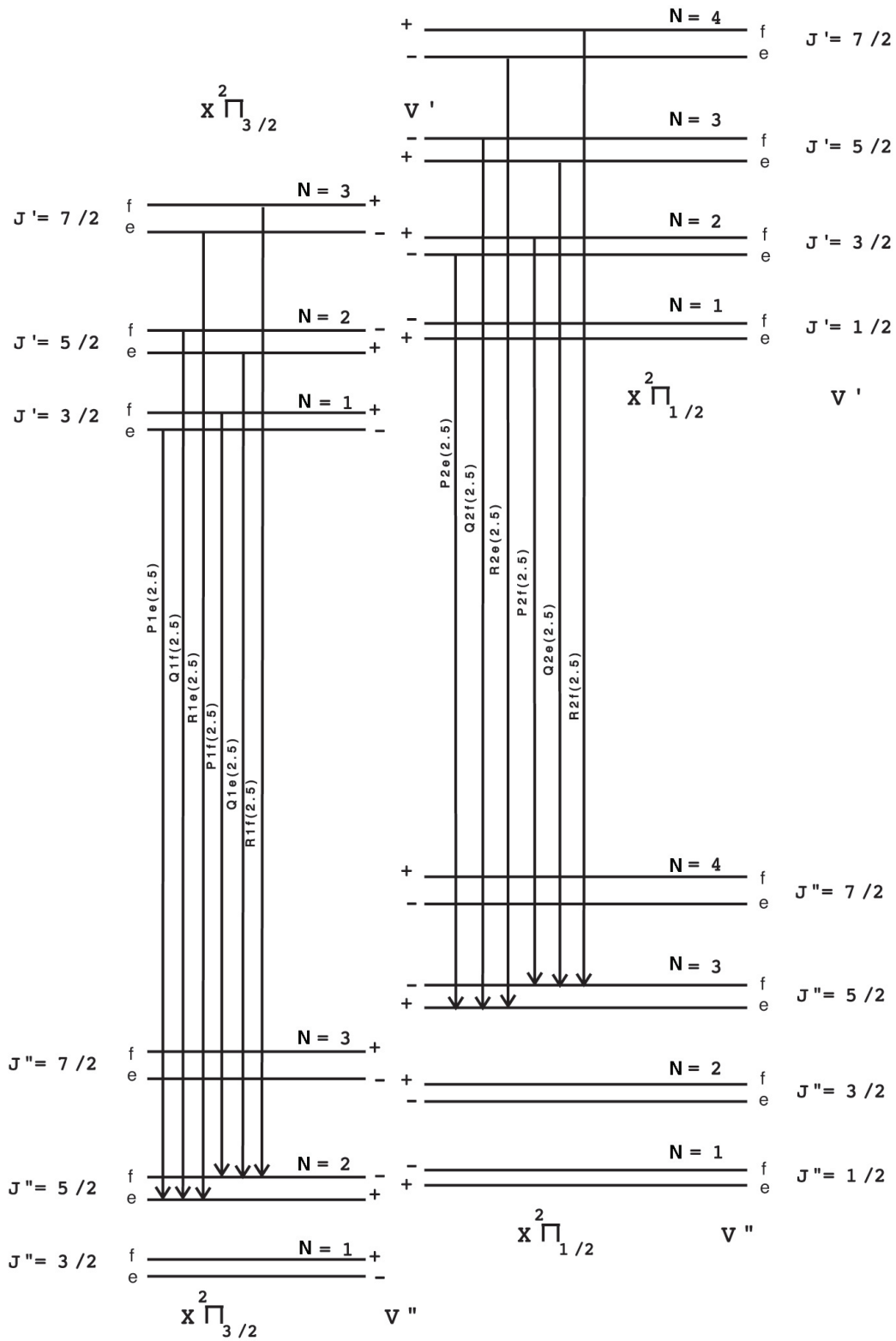


Figure 1: Energy levels involved in the infrared vibration-rotation bands of OH radical.

In figure 1 the satellite transitions, i.e. the transitions involving simultaneously the states  $X^2\Pi_{3/2}$  and  $X^2\Pi_{1/2}$  are not shown. Their transition probabilities are very weak, they do not generate bright emission lines and are not taken into account in this work.

### 3 Formulae

The necessary data for computing a synthetic spectrum are the energy levels and the transition probabilities. The energy levels permit to compute the lines wavelengths (as well as the relative population for a Boltzmann distribution) and the transition probabilities are necessary to compute intensities.

The energy levels have been computed with accuracy with laboratory experiments by Abrams et al. (1994). They provide these levels with a standard deviation of  $0.003 \text{ cm}^{-1}$  for all the levels with  $J=0.5$  to  $19.5$  and  $v=0$  to  $10$ . These data permit to compute all the wavelengths of infrared OH emission lines in the spectral region of interest ( $0.6$  to  $2.2 \text{ }\mu\text{m}$ ).

The transition probabilities were computed by Mies (1974). This article provides the transition probabilities, in  $\text{s}^{-1}$ , for the sequences  $\Delta v = v' - v'' = 1$  to  $5$  and  $J'=0.5$  to  $15.5$ . These data do not distinguish between the two  $\Lambda$  doublets, because it is the average between the two probabilities for each value (these values being, in a first approximation, equal). In this computation they will be considered as equal, consequently it will be the same transition probability that will be used for both  $\Lambda$  doublets ( $A_{line}$ ).

The intensity received from a line can be computed like this:

$$I(Rayleigh) = 10^{-6}(N_{v'}/Q_{v'})(2J' + 1)\exp\{-E(J')/(kT_{rot})\}A_{line}$$

The Rayleigh is a unit of brightness that corresponds to the emission of  $10^6$  photons per seconde and by  $\text{cm}^2$  in  $4\pi$  steradians.

The relative population of the different states can be valuably approximated in using a Boltzmann distribution with a rotational temperature  $T_{rot}$  equal to the gas kinetic temperature  $T_k$  (of the order of  $200 \text{ K}$  at this altitude).

In this formula:

$N_{v'}$  is the number of OH radicals located along the line of sight in the  $v'$  level (line of sight with an area of  $1 \text{ cm}^2$ ).

$Q_{v'}$  is a rotational partition function for the  $v'$  state.

$E(J')$  is the energy of the upper state.

$k$  is the Boltzmann constant.

$Q_{v'}$  must consider the two sublevels  $X^2\Pi_{3/2}$  et  $X^2\Pi_{1/2}$  (for both of them the e and f sublevels must be considered):

$$Q_{v'} = \left[ \sum_{J=3/2}^{15.5} (2J + 1)\exp\{-F_1(J)/(kT_{rot})\} \right] + \left[ \sum_{J=1/2}^{15.5} (2J + 1)\exp\{-F_2(J)/(kT_{rot})\} \right]$$

$F_1(J)$  and  $F_2(J)$  refer, respectively, to the rotational energy levels of the  $X^2\Pi_{3/2}$  and  $X^2\Pi_{1/2}$  states. If  $E(J')$  is expressed in  $\text{cm}^{-1}$ , the above formula can be written:

$$I(Rayleigh) = 10^{-6}(N_{v'}/Q_{v'})(2J' + 1)\exp\{-1.439E(J')/T_{rot}\}A_{line}$$

For computing the absolute intensities between two different bands it is necessary to know  $N_{v'}$  values. Unfortunately the vibrational temperatures cannot be approximated by the gas kinetic

temperature, as for the rotational temperature. A good approximation can be done, nevertheless, with a Boltzmann distribution based on a vibrational temperature  $T_{vib}$  between 8500 and 13 000 K.

If there are  $N$  OH radicals located along the line of sight, the different  $N_v$  values are given by the formula:

$$N_v = (N/Q) \exp\{-1.439G(v)/T_{vib}\}$$

where  $G(v)$  is the vibrational energy and  $Q$  is computed in a similar way to the ones of rotational levels:

$$Q = \sum_{v=0}^9 \exp\{-1.439G(v)/T_{vib}\}$$

## 4 Work to do

From the formulae given above and the data files providing the energy levels and transition probabilities (files `energies.dat` and `probas.dat`, see their structure below):

- Write a calculation code that give the intensity of all the emission lines for the sequences  $\Delta v=2$  to 5 in using  $T_{rot}=200$  K,  $T_{vib}=9000$  K and  $N=3 \times 10^{10}$  molecules.cm<sup>-2</sup>.
- Give the calculated intensities in an ascii file with the following columns: wavelength (nm), intensity (in Rayleigh),  $v'$ ,  $v''$ , considered substate (1 for  $X^2\Pi_{3/2}$  and 2 for  $X^2\Pi_{1/2}$ ),  $J'$ ,  $J''$
- Represent an overview of this spectrum with a spectrum containing all the emission lines (without convoluting by an instrument response function of the spectrograph).

## Appendix: structure of data files

The file **energies.dat** contains the energy levels, in cm<sup>-1</sup>, with the four columns providing, respectively, the  $F_{1e}$ ,  $F_{2e}$ ,  $F_{1f}$ ,  $F_{2f}$  energies (Abrams et al., 1994). The different lines correspond to the rotational levels  $J=0.5$  to 16.5, for the levels with  $v$  varying from 0 to 10.

The file **probas.dat** contains the transition probabilities (Einstein coefficients of spontaneous emission), in s<sup>-1</sup> with six columns corresponding to the  $P_1$ ,  $Q_1$ ,  $R_1$ ,  $P_2$ ,  $Q_2$ ,  $R_2$  lines (Mies, 1974). The two possible lines (i.e.  $P_{1e}$  and  $P_{1f}$ ) are not distinguished because their corresponding transition probabilities are supposed to be the same. The values corresponding to the transitions  $\Delta v = 2$  to  $\Delta v = 5$  ( $v'$  going from the minimum possible value up to 9 and corresponding to the upper level, with  $\Delta v = v' - v''$ ) are given.

## References

- Abrams M.C., Davis S.P., Rao M.L.P., R. Engleman Jr., J.W. Brault, 1994, "High-Resolution Fourier transform spectroscopy of the Meinel system of OH", Ap. J. Suppl. Series **93**, pp 351-395
- Mies F.H., 1974, "Calculated Vibrational Transition Probabilities of OH( $X^2\Pi$ )", J. of Mol. Spec. **53**, 150-188