

# Spectral predictions for diagnostics

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**Abstract:** The radiative transfer module in PLASIMO has been used to predict spectra for two different conditions. Using local thermodynamic equilibrium the spectrum of a metal-halide lamp and the spectrum of the sun are calculated. Additionally, the absorption of radiation in the atmosphere of the earth, a non-equilibrium environment, is calculated. These calculations demonstrate that PLASIMO can be used for interpreting measured spectra.

**Keywords:** Modelling, Radiation, Spectral predictions, Absorption, Spectra, Spectral lines

## 1. Introduction

One of the most common diagnostic methods applied on plasmas is optical emission spectroscopy. This method can provide a significant amount of information related to the species densities and temperatures. In order to obtain a qualitative link between the spectrum and the plasma properties and to interpret the spectrum accurately, a comparison between a measured spectrum and a model simulation is necessary. For this purpose a line of sight is considered that runs through a plasma. The plasma properties can either be coupled self-consistently to the radiation field or be specified in advance.

The self-consistent calculations are performed using the modelling platform PLASIMO [1]. The spectral calculations are performed using the raytracing module [2,3]. Previous calculations using this module focussed on atomic lines and a continuum interpretation of the rovibrational spectrum [4,5]. In this work the molecular spectra obtained from the continuum approximation are compared to the fully resolved rovibrational spectra. For demonstration purposes of the raytracing module, the method is applied to a metal-halide lamp and to the solar radiation that passes through the atmosphere of the earth.

A short introduction to radiation theory is given in section 2. Preliminary results for calculated spectra are shown in section 3. Since these calculations will rely heavily on input data and this data is not always available, the possibility of obtaining transition dipole moments from ab initio software is also demonstrated. The software packages that are used are DALTON and DIRAC. Examples of these calculations are shown in section 4.

## 2. Radiation theory

The radiative transfer equation is given by [3]

$$\frac{dI_{\nu}}{ds} = j_{\nu} - \kappa_{\nu}I_{\nu}, \quad (1)$$

where  $I_{\nu}$  represents the spectral radiance,  $j_{\nu}$  the emission coefficient,  $\kappa_{\nu}$  the absorption coefficient and  $\vec{s}$  the direction vector indicating the direction of the radiation. A subscript  $\nu$  indicates that the quantity should be evaluated for every frequency. Note that in this equation, scattering is neglected. The emission and absorption coefficients are given by [3]

$$j_{\nu} = \frac{h\nu}{4\pi} A_{ul} n_u \phi_{\nu}, \quad (2)$$

and

$$\kappa_{\nu} = \sigma_{abs} n_l - \sigma_{stim} n_u, \quad (3)$$

where  $A_{ul}$  is the transition probability from a given upper state  $u$  to a given lower state  $l$ ,  $\phi_{\nu}$  is the line profile and  $n$  represents the density. The cross sections for stimulated emission and absorption are given by

$$\sigma_{abs} = \frac{c^2}{8\pi\nu^2} A_{ul} \frac{g_u}{g_l} e^{\frac{h(\nu-\nu_0)}{k_B T}} \phi_{\nu}, \quad (4)$$

$$\sigma_{stim} = \frac{c^2}{8\pi\nu^2} A_{ul} \phi_{\nu}, \quad (5)$$

where  $g$  indicates the degeneracy of the considered state.

Calculations of the line profile are available both in the impact and the quasi-static approximation. In the impact approximation the resulting line profile is a Lorentzian profile. The type of interaction (resonance, Stark or van der Waals broadening) controls the width of the profile. In the quasi-static approximation the resulting line profile is often approximated with a Lévy distribution. When multiple broadening mechanisms are important the convolution between multiple profiles should be considered. The convolution between a Lévy and a Lorentz profile was obtained analytically by Stormberg [8,9]. Another analytical example is a Voigt profile which is the convolution of a Doppler profile (Gaussian) and a Lorentzian profile.

For larger pressures the standard Stormberg profile will provide inaccurate results and the actual potential energy difference between the upper and the lower state as a function of interatomic separation should be taken into account. This improved method assumes that the rovibrational structure can be approximated with a continuum. The continuum approach has for example been successfully applied by Hedges et al [10] to bound-free and free-free radiation in excimer systems. This approach calculates the frequency based on

$$\nu(r) = \frac{V_u(r) - V_l(r)}{h}. \quad (6)$$

The line profile is then calculated based on

$$\phi_{\nu} d\nu \propto 4\pi r^2 n_p f(r) \left| \frac{dr}{d\nu} \right| d\nu, \quad (7)$$

which states that the line profile depends on the distribution function  $f(r)$  of the perturbing species  $n_p$ . The perturbers are assumed to be distributed according to a Boltzmann distribution

$$f_u(r) \propto \exp\left(-\frac{V_u(r) - V_u(\infty)}{k_B T}\right). \quad (8)$$

Similarly, the distribution function of perturbers in the lower state is proportional to  $V_l(r)$ .

The actual rovibrational structure can also be calculated using (2) and (3). The frequency of the transition is calculated based on

$$\nu = \Delta E/h, \quad (9)$$

where the energy difference is given by

$$\Delta E = \Delta T_e + \Delta G + \Delta F. \quad (10)$$

The three contributions are the electronic, vibrational and rotational energy differences. The vibrational energy for a specific vibrational level  $\nu$  for a diatomic molecule is given by [11]

$$\frac{G(\nu)}{h} = \nu_e \left( \nu + \frac{1}{2} \right) - \nu_e x_e \left( \nu + \frac{1}{2} \right)^2 + \nu_e y_e \left( \nu + \frac{1}{2} \right)^3 + \dots, \quad (11)$$

and its rotational energy is given by

$$\frac{F(\nu, J)}{h} = B(\nu)J(J+1) - D(\nu)J^2(J+1)^2 + \dots \quad (12)$$

Note that for polyatomic molecules the expressions for the rovibrational energies are more complex.

The calculation of the absorption requires a degeneracy. The total degeneracy is the product of the electronic, vibrational and rotational degeneracies. For a diatomic molecule the vibrational degeneracy is equal to one. The rotational degeneracy can be calculated using  $g_J = 2(J+1)$ .

The transition probability can be calculated based on the transition dipole moment,  $D = \langle \Psi_l | \boldsymbol{\mu} | \Psi_u \rangle$ , with  $\boldsymbol{\mu}$  the dipole moment and  $\Psi$  the wave function. For diatomic molecules there are two contributions to  $D$ . The electronic contribution is given by  $\langle \Psi_{l,e} | \boldsymbol{\mu}_e | \Psi_{u,e} \rangle$ . The vibrational contribution can be written as  $\langle \Psi_{l,v} | \Psi_{u,v} \rangle$ . The square of the vibrational contribution is also called the Franck-Condon factor. Once the transition dipole moment is known, the transition probability is calculated using

$$A_{ul} = \frac{16}{3} \frac{g_l}{g_u} \frac{\pi^3 D^2 \nu^3}{h \epsilon_0 c^3}. \quad (13)$$

### 3. Calculated spectra

Two spectra are considered in this work. The first spectrum is calculated based on a self-consistent 1D cylindrical model of a metal-halide lamp containing Xe and InI. The contributions in the energy balance include thermal conduction, ohmic heating and radiation losses. The composition is calculated using local thermal equilibrium (LTE). Self-consistent diffusion is included based on a solution of the Stefan-Maxwell equations. The final spectrum for this case is shown in figure 1. The indicated spectrum correctly shows the absorption of radiation in the ultraviolet areas where the plasma is optically thick. In the visible and the infrared wavelengths the spectrum becomes optically thin and therefore the continuum generated by recombination of In and I is observed.

The second spectrum that is considered originates from the sun. Both the absorption through the solar and earth atmospheres are taken into account. This calculation will not be fully self-consistent, since the temperature as a function of altitude is fixed. A chemical model is then used to calculate the local composition. For the radiation

transport two strategies are adopted. The first strategy uses the continuum approach. The requirements for this method are the interaction potentials and the transition dipole moments. The second strategy resolves the rovibrational lines initially. In order to reduce the number of spectral points that is to be considered, the emission and absorption coefficients are summed to a single spectral mesh. The spectra calculated by both methods will be compared.

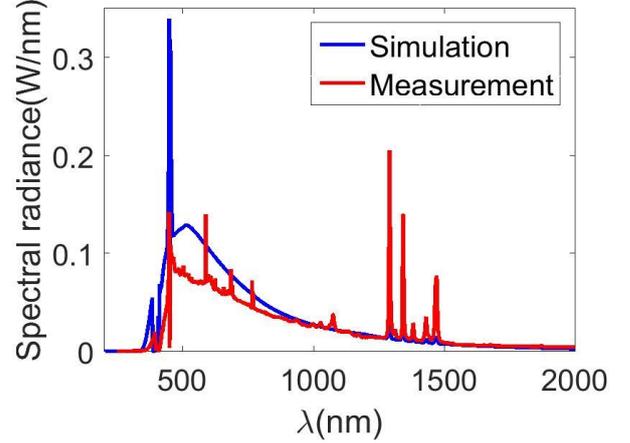


Fig. 1. A comparison is made between a measurement and a simulation for a metal-halide lamp containing InI and Xe.

### 4. Input data from ab initio calculations

An essential component for the calculation of spectra is the transition dipole moment (TDM). Both the continuum approach and the fully resolved rovibrational approach require this quantity. In addition the continuum approach also requires the interaction potentials. These quantities are not always available. For InI accurate potential curves and TDMs have been calculated using DIRAC. These results are displayed in figures 2 and 3. The interaction potentials show that with a large variety of wavelengths are possible due to the fact that most excited states remain unaltered at larger interatomic separations while the ground state energy changes rapidly. Figure 3 shows that the lowest excited state cannot radiate at large interatomic separations. For intermediate separations at about 6 Angstrom the transition TDM reaches a maximum. These positions correspond to infrared radiation. At lower separations the TDM decreases for wavelengths in the visible spectrum. For other excited states the TDM reaches a maximum for wavelengths in the ultraviolet. These transitions are responsible for the absorption in the UV.

### 5. Conclusions and Outlook

The radiative transfer module in PLASIMO has been used to predict spectra for two different conditions: LTE and non-equilibrium conditions. Calculating spectra is the first step to use spectral predictions for the interpretation of measurements. Currently, the densities and temperatures are used to predict the spectrum. A future step is to use the

measured spectrum to obtain the density and temperature profiles.

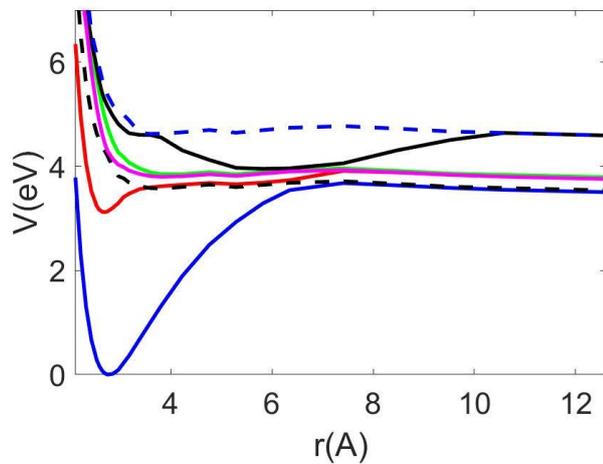


Fig. 2. The calculated interaction potentials for InI using DIRAC.

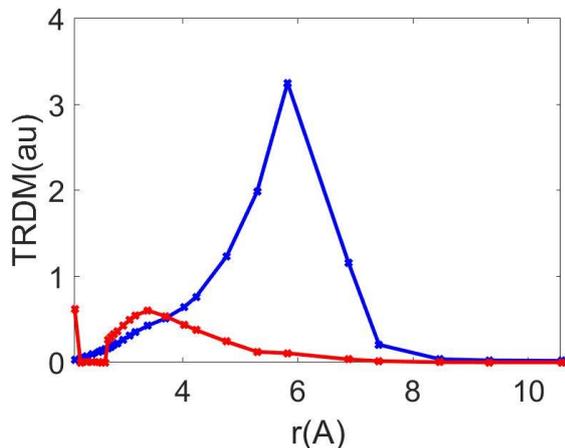


Fig. 3. Calculated transition dipole moments for the InI system using DIRAC. The blue and red curve correspond to the transition from the lowest two excited states to the ground state, respectively.

## 6. References

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