Fluorescence Model Text

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I. MODEL DESCRIPTION

We developed a fluorescence model assuming a collisionless and optically thin environment for the emitted photons, driven by three processes: spontaneous emission (1), stimulated emission (2), and absorption (3). While the rate for (1) is a fundamental property, the rates for (2) and (3) derive from the rate of (1) and the local radiation field at the comet. In the following we outline our fluorescence model; the presentation of the matrices and differential equations is limited to 2 levels for readability.

Consider two levels of a many-level system with a transition from upper level j to lower level i. If the Einstein A coefficient for (1), $A_{j\to i}$, is known, the coefficients for (2) and (3) may be expressed as

$$B_{j\to i} = \frac{\lambda_{ji}^5}{8\pi hc^2} A_{j\to i} \tag{1}$$

$$B_{i\to j} = \frac{g_j}{g_i} B_{j\to i} \tag{2}$$

where λ_{ji} is the (vacuum) wavelength of the transition, $g_j = 2J_j + 1$, and $g_i = 2J_i + 1$. For each B, the units [m^3 W^{-1} s^{-1}] ensure compatibility with the choice of solar spectrum described later. For a given pair of levels j and i, the change in population of the upper state j is written

$$\begin{aligned} \frac{dn_j}{dt} = -A_{j\to i}n_j - B_{j\to i}\rho(\lambda_{ij})n_j \\ +B_{i\to j}\rho(\lambda_{ij})n_i \end{aligned} \tag{3}$$

with B_{ji} and B_{ij} from Eqn's. 1 and 2, and $\rho(\lambda)$ is the flux per wavelength interval (W m^{-3}) incident on the population n_j at the energy of the transition from level j to level i. The population of the lower state, n_i, may be written similarly as

$$\begin{aligned} \frac{dn_i}{dt} = A_{j\to i}n_j + B_{j\to i}\rho(\lambda_{ij})n_j \\ -B_{i\to j}\rho(\lambda_{ij})n_i \end{aligned} \tag{4}$$

The above system of equations for levels i and j may be written in matrix form as

$$\begin{bmatrix} -\rho_{ij}B_{i\to j} & A_{j\to i} + \rho_{ij}B_{j\to i} \\ \rho_{ij}B_{i\to j} & -A_{j\to i} - \rho_{ij}B_{j\to i} \end{bmatrix} \begin{bmatrix} n_i \\ n_j \end{bmatrix} = \begin{bmatrix} dn_i/dt \\ dn_j/dt \end{bmatrix} \tag{5}$$

In equilibrium, the populations are constant in time and thus the right hand side of Eq. 5 is equal to 0. However, the matrix A is underdetermined, i.e. N equations and $N-1$ unknowns. We add an additional constraint by enforcing a normalization condition, $\sum_i n_i = 1$, by replacing all elements in row 0 of both the left and right matrices by 1. Our matrix equation thus takes the form

$$\mathbf{A}\vec{x} = \mathbf{B} \tag{6}$$

where the rates for processes (1) - (3) are stored in matrix $\mathbf{A}$ with populations contained within column vector $\vec{x}$. Each transition rate contributes to two matrix elements: a positive contribution to the off-diagonal element (i,j), and a negative contribution to the diagonal element (j,j). Similarly, stimulated emission contributes positively to element (i,j) and negatively to element (j,j). Absorption provides a negative contribution to the diagonal term of level i at (i,i), and an off-diagonal, positive contribution to the population of n_j in element (j,i).

After populating matrices A and B, the equilibrium population fractions $\vec{x}$ follow as $\vec{x} = A^{-1} \times B$. The transition intensity, i.e. the fluorescence efficiency of the transition (J s^{-1} particle^{-1}) *at the emitting source* from level j to level i then follows from the level population n_j as

$$I_{j\to i} = \frac{hc}{\lambda_{ji}} n_j A_{j\to i} \tag{7}$$

where given the directionality of stimulated emission along the sun-comet vector the contribution of stimulated emission to the observed line intensities is assumed to be negligible.

A. Computational Implementation

We implemented the fluorescence model discussed above in Python3 and made it publicly available on GitHub. The code requires only standard Python packages, and performs all mathematical operations using NumPy. SI units are utilized throughout, with conversions indicated where necessary.

First, Einstein A coefficients, Ritz wavelengths, and level information (energies, J values) were retrieved from the NIST ASD. For each transition, stimulated emission and absorption coefficients follow from Eqns 1 and 2. To generate absorption and stimulated emission *rates*, we combined computed and measured solar data into a high-resolution solar flux atlas spanning 150 nm - 81 μm. Where possible we have deferred to the measured spectra; however, measurements in the ultraviolet beneath 300 nm and in the infrared beyond ~1000 nm are difficult due to substantial atmospheric absorption. Our flux atlas was therefore compiled as follows:

- Between 150 - 199.935 nm, we utilized the high-resolution *computed* flux moments from Kurucz (Available at http://kurucz.harvard.edu/stars/sun/), $F_{\mathrm{c}}(\lambda)$, from which the flux per wavelength interval in vacuum at 1 AU, $\rho(\lambda)$, follows as

$$\rho(\lambda) = 4\pi \times 10^{-3} \big(\frac{R_\odot}{1\ AU}\big)^2 F_{\mathrm{c}}(\lambda) \tag{8}$$

  where $4\pi \times 10^{-3}$ converts from ergs cm^{-2} s^{-1} ster^{-1} nm^{-1} to W m^{-2} nm^{-1} and the radius of the Sun $R_\odot$ = 0.00465047 AU. The model internally converts from W m^{-2} nm^{-1} to W m^{-3}.

- Between 199.935 nm and 299 nm, we use the computed flux moments above after conversion to standard air wavelengths using a standard conversion.

- Between 299 nm and 1001.27 nm, we utilize the high-resolution solar flux measurements in air (W m^{-2} nm^{-1}) taken with the Fourier Transform Spectrometer at Kitt Peak National Observatory by Kurucz et al (Updated in 2005 and available at http://kurucz.harvard.edu/sun/irradiance2005/irradthu.dat). The static choice of solar spectrum may introduce small errors due to variations in the solar cycle.

- For wavelengths between 1001.27 nm - 81 μm, we utilize the computed flux moments discussed above; wavelengths are treated in vacuum.

Our compiled computed-measured flux atlas is made available in 3 parts (UV, VIS, IR) with our model code and spans ~150 nm - 81 μm, is continuous at the boundaries (199.935 nm, 1001.27 nm), and integrates to 1371.64 W/m^2 at 1 AU. If desired, the user is free to import and utilize any radiation field(s). For wavelengths outside the bounds of the solar spectra, the code is capable of assuming a blackbody radiation field, defaulted to 5777 K. Lastly, the flux per wavelength interval $\rho(\lambda)$ is re-scaled to the comet's heliocentric distance by a factor of $1/r_{\mathrm{h}}^2$.

When calculating the absorption and stimulated emission rates, $W = \rho(\lambda_{ij})B$, the Doppler shift of the solar spectrum resulting from the comet's heliocentric velocity (-36.7 km/s during the archived observations of Hyakutake) is included. After the initial matrix population, the inverse of the rate matrix (A^{-1}) is calculated using the NumPy **linalg.inv** package, from which the populations follow as $\vec{x} = A^{-1} \times B$. For large singular or near-singular matrices caused by missing atomic data or small heliocentric distances (i.e. large absorption rates), the code attempts a solution using a Psuedo-Inverse (**linalg.pinv**) and Singular Value Decomposition (**linalg.svd**). From the equilibrium populations, line intensities are calculated using Eq. 7, and vacuum wavelengths are doppler-shifted by the geocentric comet velocity before conversion to standard air wavelengths using a standard conversion.

Lastly, our model code directly imports the line and level lists which are downloaded from the ASD, and can thus be used to analyze any neutral or ionized atomic species for which the requisite data is available.