Fluorescence Model Text

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I. MODEL DESCRIPTION

We developed a simple fluorescence model based on a collisionless environment driven by three processes: (1) spontaneous emission, (2) stimulated emission, and (3) absorption. 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. For brevity, we restrict the following discussion to a two-level system, with extension to many-levels achieved by simply increasing the size of the relevant matrices to include all relevant energy levels. 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), $A_{j\rightarrow i}$, is known, the coefficients for (2) and (3) follow as

$$B_{j\rightarrow i} = \frac{c^3 \pi A_{j\rightarrow i}}{\hbar \omega^3} \tag{1}$$

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

where $\omega = 2\pi f_{ji}$, $g_j = 2J_j + 1$, and $g_i = 2J_i + 1$ [1]. For a given pair of levels j and i, the change in population of the upper state j is written

$$\frac{dn_j}{dt} = -A_{j\rightarrow i} n_j - B_{j\rightarrow i} n_j \int_{\lambda_{ji}-\Delta\lambda}^{\lambda_{ji}+\Delta\lambda} \rho(\lambda) d\lambda + B_{i\rightarrow j} n_i \int_{\lambda_{ji}-\Delta\lambda}^{\lambda_{ji}+\Delta\lambda} \rho(\lambda) d\lambda \tag{3}$$

with B_{ji} and B_{ij} from Eqn's. 1 and 2, and $\rho(\lambda)$ is the flux per wavelength interval incident on the population n_j at the energy of the transition from level j to level i. Here we have assumed the line shape, $\phi(\lambda)$, is constant over $\lambda \pm \Delta\lambda$. Selection of the integration limits is discussed later. The population of the lower state, n_i, may be written similarly as

$$\frac{dn_i}{dt} = A_{j\rightarrow i} n_j + B_{j\rightarrow i} n_j \int_{\lambda_{ji}-\Delta\lambda}^{\lambda_{ji}+\Delta\lambda} \rho(\lambda) d\lambda - B_{i\rightarrow j} n_i \int_{\lambda_{ji}-\Delta\lambda}^{\lambda_{ji}+\Delta\lambda} \rho(\lambda) d\lambda \tag{4}$$

Abbreviating $\int_{\lambda_{ji}-\Delta\lambda}^{\lambda_{ji}+\Delta\lambda} \rho(\lambda) d\lambda = \sigma_{ji}$, the above system of equations for levels i and j may be written in matrix form as

$$\begin{bmatrix} -B_{i\rightarrow j}\sigma_{ji} & A_{j\rightarrow i} + B_{j\rightarrow i}\sigma_{ji} \\ B_{i\rightarrow j}\sigma_{ji} & -A_{j\rightarrow i} - B_{j\rightarrow i}\sigma_{ji} \end{bmatrix} \begin{bmatrix} n_i \\ n_j \end{bmatrix} = \begin{bmatrix} dn_i/dt \\ dn_j/dt \end{bmatrix} \tag{5}$$

In equilibrium, the populations are constant in time and thus the right hand side of Eq. 5 is equal to 0. The system of equations coupling the energy levels together thus takes the form

$$\mathbf{A}\vec{x} = 0 \tag{6}$$

where the rates for processes (1) - (3), are stored in matrix $\mathbf{A}$ with populations contained within column vector $\vec{x}$. Each *depopulating* rate (e.g. the contribution of $A_{j\rightarrow i}$ to dn_j/dt in Eq. 3) 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 matrix population, we seek the non-trivial solution of Eq. 6, $\vec{x} \neq 0$. This is achieved by solving for the eigenvectors and eigenvalues of matrix $\mathbf{A}^T\mathbf{A}$, whose eigenvector belonging to the smallest eigenvalue is taken as the equilibrium solution. Alternatively, the matrix solution could be derived using Singular Value Decomposition (SVD), from which the solution follows as the eigenvector belonging to the smallest singular value of $\mathbf{A}$. The transition intensity from level j to level i then

Rating	Percentage (%)
AAA	≤ 0.3
AA	≤ 1
A+	≤ 2
A	≤ 3
B+	≤ 7
B	≤ 10
C+	≤ 18
C	≤ 25
D+	≤ 40
D	≤ 50
E	> 50

TABLE I. A value accuracy scale in the NIST Atomic Spectra Database [2].

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follows from the level population n_j as

$$I_{j\to i} = n_j A_{j\to i} \hbar\omega \tag{7}$$

where given the directionality of the stimulated emission along the sun-comet vector, the contribution of stimulated emission to the observed line intensities is neglibible.

The above procedure was coded in Python and made available with documentation at LINK. SI units are utilized throughout, with conversions indicated where possible. First, Einstein A coefficients, Ritz wavelengths, and level information (energies, J values) were retrieved from the NIST Atomic Spectra Database (ASD) [2]. For a given transition, stimulated emission and absorption coefficients follow from Eqn's 1 and 2, yielding 6 contributions to the rate matrix for each transition. We use the high-resolution Kurucz solar spectrum[3] from Kurucz (see e.g. Ref. [4]). From the solar irradiance, $F(\lambda)$, the flux per wavelength interval at distance $r_{\rm comet}$, $\rho(\lambda)$, follows as

$$\rho(\lambda) = \pi \times 10^{-3} \big(\frac{R_{\rm Sun}}{r_{\rm comet}}\big)^2 F(\lambda) \tag{8}$$

where the factor $\pi \times 10^{-3}$ converts from ergs cm^{-2} s^{-1} ster^{-1} nm^{-1} to W m^{-2} nm^{-1} and $R_{\rm Sun} = 6.957 \times 10^8$ m. The stimulated emission and absorption rates, $W_{j\to i}$ and $W_{i\to j}$, follow from numerical integration as $W = B \int_{\lambda-\Delta\lambda}^{\lambda+\Delta\lambda} \rho(\lambda) d\lambda$. $\Delta\lambda$ is chosen as 4 wavelength bins centered around λ_{ji}, approximately ± 0.002 nm, equivalent to a linewidth of $\sim$2 km s^{-1} at 300 nm. When calculating the rates, W, the doppler shift of the solar spectrum resulting from the comet's motion is included, where we assumed a heliocentric velocity of -36.7 km s^{-1} during the observation [5]. Where necessary, a blackbody is used to estimate the radiation field at wavelengths outside the scope of the Kurucz spectrum, e.g. wavelengths in the ultraviolet beneath $\sim$300 nm.

After matrix population, the equilibrium level populations, $\vec{x}$, are found by solving for the eigenvalues and eigenvectors of the matrix $\mathbf{A}^T\mathbf{A}$ using the Numpy **np.linalg.eig** package. The solution belonging to the smallest eigenvalue is taken as the equilibrium solution. Solutions from the more-complicated Numpy and SciPy SVD packages show agreement with the simpler approach adopted here. Line intensities are then calculated from Eq. 7, which we renormalize such that the strongest line intensity is set to 1. Given the low geocentric velocity of Hyakutake during the observation of the archived data, we consider no doppler shift for the observed (air) wavelengths.

Though some A values may have large uncertainties in excess of 50%, line intensities from the model cannot simply be attributed an uncertainty equal to that of the A value. For each A value, the 6 resulting contributions to the rate matrix modify the population dynamics. Therefore, we adopted the following procedure for approximating the uncertainty of the model intensities from the A value uncertainties. The primary atomic data, the Einstein A values, were sourced from the NIST ASD [2], in which each A value is assigned an accuracy rating. The NIST A value accuracy scale is shown in Table I, and spans from $\leq$ 3% to >50 %. Error bars on the model intensities are derived using a Monte-Carlo-like procedure. For each iteration, A values are adjusted randomly within the range specified by the NIST uncertainty rating. For the lowest accuracy rating (E, >50%), we allow variations up to $\pm$100%. We then derive an error bar for each intensity, $\Delta I_{j\to i}$, as the standard deviation of the line intensity following 10^6 iterations.

In total for Fe I, we included all 2542 transitions with known A values, leading to a total of 434 (out of 846) levels involved in the model. Though more than 50% of the transitions are outside our spectral window, they may affect the level populations and were thus included. For Ni I, 522 transitions were incorporated, involving 133 of the 288 known levels of Ni I.

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