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

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

with B_{ji} and B_{ij} from Eqn's. 1 and 2, $\phi(\lambda)$ is the line shape with $\phi(\lambda_{ji}) = 1$, 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. Selection of the functional form of the lineshape and the integration limits is discussed later. The population of the lower state, n_i, may be written similarly as

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

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

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

In equilibrium, the populations are constant in time and thus the right hand side of Eq. 5 is equal to 0. 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

follows from the level population n_j as

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

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 **here**. 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. To generate absorption and stimulated emission *rates*, we use both the computed and measured solar data of Kurucz (see e.g. Ref. [4]) to assemble a high-resolution solar spectrum spanning 150 nm - 81 μm. Between 300 nm and 1000 nm, we utilize the high-resolution solar flux measurements of Kurucz taken with the Fourier Transform Spectrometer at Kitt Peak National Observatory. As the data as presented at 1 AU, no initial re-scaling is required. For wavelengths between 150 nm - 300 nm and above ∼1000 nm, we utilize the high-resolution computed irradiance of Kurucz, from which the flux per wavelength interval, $\rho(\lambda)$, follows from the irradiance $F_{\rm c}(\lambda)$ as

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

where $\pi \times 10^{-3}$ converts from ergs cm^{-2} s^{-1} ster^{-1} nm^{-1} to W m^{-2} nm^{-1} and $R_{\rm Sun} = 0.00465047$ AU.

The combined computed-measured spectrum spans ∼150 nm - 81 μm, is continuous at the boundaries (299.007 nm, 1000.98 nm), and integrates to 1372 W/m^2 at 1 AU. The spectrum is made publicly available at the author's GitHub repository. For wavelengths outside the bounds of the solar spectra, the model (optionally) assumes a blackbody ($T_{\rm eff.} = 5777$ K) to derive an approximate integrated flux. Lastly, the flux per wavelength interval $\rho(\lambda)$ is re-scaled to the comet distance by a factor of $1/r^2_{\rm comet}$.

The stimulated emission and absorption rates, $W_{j\rightarrow i}$ and $W_{i\rightarrow j}$, follow from numerical integration as $W = B\int_{\lambda-\Delta\lambda}^{\lambda+\Delta\lambda}\rho(\lambda)\phi(\lambda)d\lambda$. $\Delta\lambda$ spans ±0.005 nm around each λ_{ji}. For the line profile, $\phi(\lambda)$, a two-component, normalized Voigt profile was initially tested as the convolution of (a) a Lorentzian component, resulting from the natural linewidth and (b) a Gaussian representing doppler broadening due to the thermal velocity of the particles in the coma. The two critical inputs are the half-width at half-maximum (HWHM) of the Lorentzian, γ, and the standard deviation of the Gaussian, σ, defined as

$$\gamma = \frac{\sum_{i'} A_{ji'}}{2\pi} \tag{9}$$

$$\sigma = \sqrt{\frac{k_{\rm b}T}{m}}\frac{f_{ji}}{c} \tag{10}$$

which yields the Voigt profile $V(\lambda) = \int_{-\infty}^{\infty} G(\lambda')L(\lambda')d\lambda'$. For levels dominated by E1 transitions e.g. $\sum_{i'}\frac{A_{ji'}}{2\pi} > 10^7$ s^{-1}, the Voigt profile is dominated by the doppler broadening component, even for temperatures at cometary conditions ($T \sim 50-100$ K). For the extreme case of the low-lying metastable levels with lifetimes of order ∼hundreds ms, the Voigt profile remains dominated by the doppler-broadened component. In all cases, the additional contributions of the Lorentzian component are negligible, and thus we consider only the Gaussian component with a temperature of 100 Kelvin. Tests at multiple temperatures up to 300 K show minimal deviations in line intensities. A 500-point grid defines each doppler-broadened line profile and was found to be sufficient for accurately reflecting the structure of the profile. Flux values for each of the points on the fine grid of the line profile are interpolated from the nearest neighbors of the Kurucz spectrum.

When calculating the rates, W, the doppler shift of the solar spectrum resulting from the comet's motion is included by shifting the rest wavelength and resulting line profile, where we have assumed a heliocentric velocity of -36.7 km s^{-1} during the observation [5]. 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 Numpy and SciPy SVD packages show agreement with the 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

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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each modify the totality of equilibrium level populations. Therefore, we adopted the following procedure for approximating the *uncorrelated* uncertainties 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 the following Monte-Carlo-like procedure. For each iteration, A values are adjusted randomly and uniformly within the range specified by the NIST uncertainty rating. For the lowest accuracy rating (E, >50%), we allow variations up to ±100%. We then derive an error bar for each intensity, $\Delta I_{j\rightarrow i}$, as the standard deviation of the line intensity following 10^6 iterations of this adjustment procedure. We note that this is likely an overestimate of the uncorrelated uncertainty, as a gaussian distribution (compared to the present uniformly distributed uncertainties) would favor lower variations for each A value adjustment.

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.

[1] C. J. Foot, *Atomic Physics* (Oxford University Press, Oxford, 1995), 1st ed.

[2] A. Kramida, Yu. Ralchenko, J. Reader, and and NIST ASD Team, NIST Atomic Spectra Database (ver. 5.6.1), [Online]. Available: `https://physics.nist.gov/asd` [2017, April 9]. National Institute of Standards and Technology, Gaithersburg, MD. (2018).

[3] Note1, downloaded from http://kurucz.harvard.edu/stars/sun/.

[4] R. L. Kurucz, ASP Conference Series **81** (1995).

[5] R. Meier, D. Wellnitz, S. J. Kim, and M. F. A'Hearn, Icarus **136**, 268 (1998).

[6] D. C. Morton, The Astrophysical Journal Supplement Series **130**, 403 (2000), URL `https://doi.org/10.1086%2F317349`.