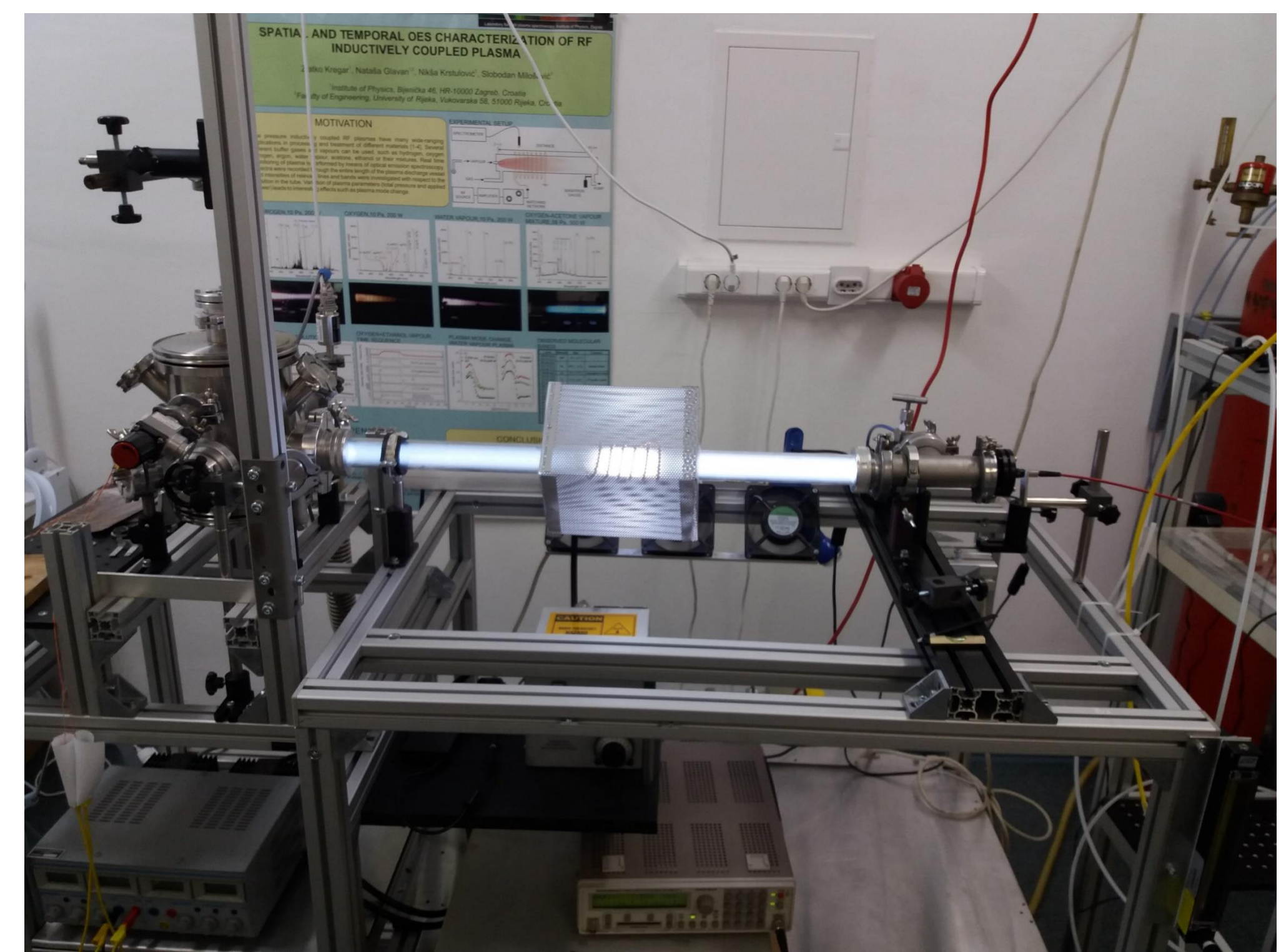# Optical spectra of carbon-monoxide molecule: fast quantum mechanical simulation

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The absorption cross section from a rovibrational state $(v'',J'',\Lambda'')$ of the lower electronic state to the rovibrational state of the upper electronic state $(v',J',\Lambda')$ (Lam et al. 1977, Chung et al. 1999) is

$$\sigma_{v'' J'' \Lambda''}^{v' J' \Lambda'}(\nu) = \frac{8\pi^3 \nu}{3hc} w_{\Lambda'} \frac{S_{J'' \Lambda''}^{J' \Lambda'}}{2J''+1} \left| \left\langle \phi_{v'' J'' \Lambda''} | D(R) | \phi_{v' J' \Lambda'} \right\rangle \right|^2 g(\nu - \nu_{tr})$$

and the spontaneous emission rate from the state $(v',J',\Lambda')$ to $(v'',J'',\Lambda'')$ is

$$A_{v' J' \Lambda'}^{v'' J'' \Lambda''}(\nu) = \frac{64\pi^4 \nu^3}{3hc^3} w_{\Lambda'} \frac{S_{J'' \Lambda''}^{J' \Lambda'}}{2J'+1} \left| \left\langle \phi_{v'' J'' \Lambda''} | D(R) | \phi_{v' J' \Lambda'} \right\rangle \right|^2 g(\nu - \nu_{tr})$$

$D(R)$ is the electronic transition dipole moment, $\mu$ is the molecular reduced mass, $g(v-v_{tr})$ the line-shape function, $s_{J''\Lambda''}^{J'\Lambda'}$ is the Hoenl-London factor, transition energy is $h\upsilon_{tr} = E_{v',J,\Lambda'} - E_{v'',J,\Lambda'}$, $w_\Lambda$ is the statistical factor dependent on the symmetry of electronic states

Energies and radial wave function can be obtained from the Schroedinger equation:

$$\left( E - V_\Lambda(R) - \frac{\hbar^2}{2\mu} \frac{J(J+1)-\Lambda^2}{R^2} + \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right) \phi(R) = 0$$

$V_\Lambda(R)$ is the potential of electronic state $\Lambda$

In the Fourier grid Hamiltonian method, rovibrational wave functions are represented on a finite number of grid points $R_i$ (i=1,…N), uniformly spaced by $\Delta R$. The Hamiltonian is represented by an NxN matrix

$$H_{i,j} = \frac{\hbar^2}{2\mu\Delta R^2} \left\{ \begin{array}{ll} \frac{\pi^2}{3} - \frac{1}{2i^2} & i=j \\ (-1)^{i-j} \frac{8ij}{(i^2-j^2)^2} & i \neq j \end{array} \right\} + \left[ V_\Lambda(R_i) + \frac{\hbar^2}{2\mu} \frac{J(J+1)-\Lambda^2}{R_i^2} \right] \delta_{i,j}$$

The *infinite* set of rovibrational states is represented on the grid by a *finite* set of states whose energies $E_{v,\Lambda}$ and wave functions $\Phi_{v,\Lambda}$ are the eigenvalues and eigenvectors of the Hamiltonian matrix. The *continuum* of free states is represented by a *discrete* set of unity-normalized wave functions having a node at the outer grid boundary $R_N = N \Delta R$.

The **absorption coefficient K(v)** is obtained by averaging over initial rovibrational levels with weighting factors $\rho(v'',J'',\Lambda'')$ and summing over all transitions, multiplied by the molecular number density $N_{AB}$.

$$K(\nu) = N_{AB} \frac{1}{Z_{\Lambda'}} \sum_{v'' v' J'' J'} \rho(v'',J'',\Lambda'') \sigma_{v'' J'' \Lambda''}^{v' J' \Lambda'}(\nu)$$

Where $Z_\Lambda$ is the partition function of molecular state $\Lambda$,

$$Z_\Lambda = \sum_{v,J} \rho(v,J,\Lambda)$$

Assuming **thermodynamic equilibrium**, the weighting factor is:

$$\rho(v,J,\Lambda) = \omega_J (2J+1) \exp\left( -\frac{E_{v,J}}{k_B T} \right)$$

where $\omega_J$ is a statistical factor dependent on nuclear spin $I$ with the values $I/(2I+1)$ for even $J$ and $(I+1)/(2I+1)$ for odd $J$

The **emission coefficient ε(v)** is obtained by averaging over upper rovibrational levels with weighting factors and summing over all transitions.

$$\varepsilon(\nu) = N_{AB} \frac{1}{Z_{\Lambda'}} \sum_{v'' v' J'' J'} \rho(v',J',\Lambda') A_{v' J' \Lambda'}^{v'' J'' \Lambda''}(\nu)$$

In order to simulate the plasma emission spectra in non-LTE condition, the rovibrational levels weighting factor can be aproximated by the relation

$$\rho(v,J,\Lambda,T_{vib},T_{rot}) = \omega_J (2J+1) \exp\left( -\frac{E_{v\Lambda vib}}{k_B T_{vib}} - \frac{E_{v\Lambda rot}}{k_B T_{rot}} \right)$$

where $E_{vJ\Lambda vib}$ and $E_{vJ\Lambda rot}$ are vibrational and rotational energies of the rovibrational state and $T_{vib}$ and $T_{rot}$ are the vibrational and rotational temperatures.

The emission intensity for the vibrational transition

$$I(\nu,T_{vib},T_{rot}) \propto \frac{\nu^4}{Z_{\Lambda'}(T_{vib},T_{rot})} \sum_{v'' v'} \sum_{J'' J'} \rho(v',J',\Lambda',T_{vib},T_{rot}) S_{J'' \Lambda''}^{J' \Lambda'} \left| \left\langle \phi_{v'' J'' \Lambda''} | D(R) | \phi_{v' J' \Lambda'} \right\rangle \right|^2 g(\nu - \nu_{tr})$$