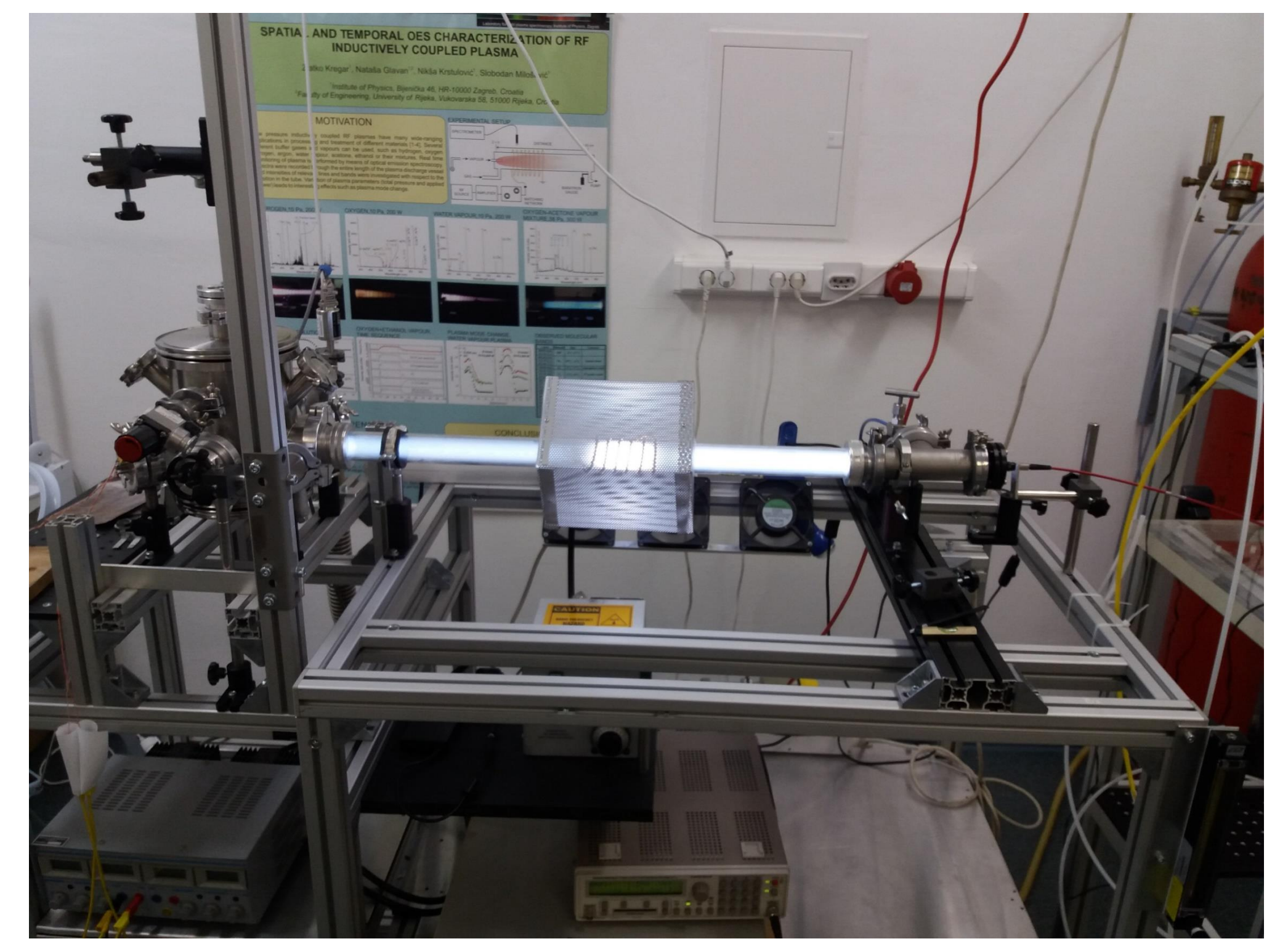


Optical spectra of carbon-monoxide molecule: fast quantum mechanical simulation

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

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

and the spontaneous emission rate from the state (v', J', Λ') to (v'', J'', Λ'') is

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

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

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

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

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

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

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

The *infinite* set of rovibrational states is represented on the grid by a *finite* set of states whose energies $E_{v,J,\Lambda}$ and wave functions $\Phi_{v,J,\Lambda}$ 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** $K(\nu)$ 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} .

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

Where Z_{Λ} is the partition function of molecular state Λ ,

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

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

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

where ω_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** $\epsilon(\nu)$ is obtained by averaging over upper rovibrational levels with weighting factors and summing over all transitions.

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

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

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

where $E_{v,J,\Lambda}$ and $E_{v,J,\Lambda}$ 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

$$I(\nu, T_{vib}, T_{rot}) \propto \frac{1}{Z_{\Lambda}(T_{vib}, T_{rot})} \sum_{v''J''\Lambda''} \sum_{v'J'\Lambda'} \rho(v', J', \Lambda', T_{vib}, T_{rot}) S_{J''\Lambda''}^{J'\Lambda'} \left| \langle \phi_{v''J''\Lambda''} | D(R) | \phi_{v'J'\Lambda'} \rangle \right|^2 g(\nu - \nu_{tr})$$

