STATE-RESOLVED MODELING FOR THE ENERGY TRANSFER PROCESSES IN LASER-INDUCED FLUORESCENCE OF DIATOMIC MOLECULES

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This work presents a generic framework for modeling the energy transfer processes between rovibronic quantum states in diatomic molecules upon laser excitation. A comprehensive set of rate equations (denoted here as the master equation) was developed to describe the interactions between radiation processes (i.e. absorption, stimulated emission and fluorescence), collision processes (including rotational energy transfer, vibrational energy transfer, and electronic quenching), and losses such as inter-system crossing an chemical reactions (including predissociation and ionization). The rate coefficients were fully parameterized using physical quantities such as the transnational temperature of the exited molecule, the energy gap and the start/end quanta across the transfer process, and the numerical expressions of parameterization were guided by a critical review of the existing literature. A stiff ODE solver with adjustable step-size was implemented to accommodate the wide range of physical timescales involved in the master equation. To demonstration the utility of the current modeling approach, simulations were performed for OH and NO molecules excited by selected transitions in the A-X (0,0) and (1,0) bands, and the spectro-temporal features of the predicted fluorescence signals were analyzed and validated against previous experimental results. Additional simulations were also conducted at extreme conditions of ultra-short laser pulses and very high laser energies, which revealed non-monotonic trends resulting from complications of strong non-linearity and spectral-temporal correlation at these conditions, indicating the existence of an optimal pulse length or laser energy (not necessarily the shorter or higher the better) for typical LIF applications. This modeling framework will be released online soon and should prove useful in aiding the design and analysis of modern quantitative LIF measurements.

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