Kinetic Model for the Iodine Photodissociation Laser

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Citation: Journal of Applied Physics **40**, 4767 (1969); doi: 10.1063/1.1657286
View online: http://dx.doi.org/10.1063/1.1657286
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/40/12?ver=pdfcov
Published by the AIP Publishing

−200 atm (see Temperley,[10] Lehman, and Young,[11] and Hayward[12]). The discrepancy between theory and practice appears to be due to the fact that the experiments do not measure the attraction between water molecules but the attraction between water molecules and an adsorbing surface (wall of the container or solid particles). The properties of this surface become important and could explain the difference in values obtained by the various researchers, who were really measuring the strength of the forces of adsorption. This leads us to believe that the negative pressures developed as the water recedes from the adsorbent surface cannot be very high. In the case of the moving rod, the adsorbent, having made it possible to nucleate a cavity on its surface, moves away. When the water rushes in, the collision of water against water converging from opposite directions may create a pressure high enough both to dissolve the air that might be present in the bubble, and to bond water molecules. The high speed films show that the liquid tears again as the compression is followed by rarefaction. When this happens, the negative pressure could be high.

When cavitation is produced by impact, it appears that the bubble always grows at the wall and that, after its collapse, new bubbles appear at different locations but close to the original one. If these new bubbles are created in the bulk of the water, away from the wall, the same arguments used for the case of the moving rod could apply here. On the other hand, if they form at the wall, the case is again one of desorption and the negative pressures generated should not, according to the arguments presented, be very high. Temperley[10] has proposed "that a prior application of pressure···may make it (the liquid) adhere better." However, there are no well founded arguments to support this contention.

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ACKNOWLEDGMENTS

The authors are indebted to Dr. Guy G. Goyer for his advice and assistance; to Charles L. Frush for building the cooling system; to Roger Ewy and James L. Digby for the photography, and to Nancy Knight and Ronald Cox for reviewing the manuscript.

JOURNAL OF APPLIED PHYSICS VOLUME 40, NUMBER 12 NOVEMBER 1969

Kinetic Model for the Iodine Photodissociation Laser*

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A kinetic model for the four level iodine laser is presented which includes pumping, radiative, and collisional transfer between levels. Numerical results obtained are shown to be in good agreement with available experimental data. The model correctly predicts the influence of pressure level and flash lamp parameters on the laser output and the occurrence of spiked pulses.

Flash photolysis of CF_3I has resulted in laser action from the magnetic dipole transition in atomic iodine ($^2P_{1/2} \rightarrow {}^2P_{3/2}$ at 1.315 μ).[1] Extensions to other alkyl iodides[2] and further experimental evaluations of the CF_3I system have been reported.[3–6] A simple kinetic rate equation model, useful for predicting population inversions, gains and efficiencies, is presented in this article. The model includes pumping, radiative, and collisional effects and the dependence of the output on operating pressure and flash lamp parameters.

Pollack,[3] using a two level laser model, achieved a reasonable fit to experimental data based on matching the model to observed outputs at the optimum point. This matching procedure, as well as the model's use of an average decay rate (instead of integrating the equations numerically), ramp flash input, and only two levels, has its limitations. In the following model these restrictions are removed.

The CF_3I laser may be represented as the four level system shown in Fig. 1 with overall reaction mechanism:

$$CF_3I \xrightarrow{h\nu^*} CF_3\cdot + I(^2P_{1/2}),$$

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I(^2P_{3/2}),$$

$$2CF_3\cdot \longrightarrow C_2F_6,$$

$$I(^2P_{1/2}) \longrightarrow I(^2P_{3/2}) + h\nu_{23},$$

$$2I(^2P_{3/2}) + M \longrightarrow I_2 + M,$$

where $\nu^* > \nu$ and M represents an inert body.

* Work supported by Wisconsin Alumni Research Fund.
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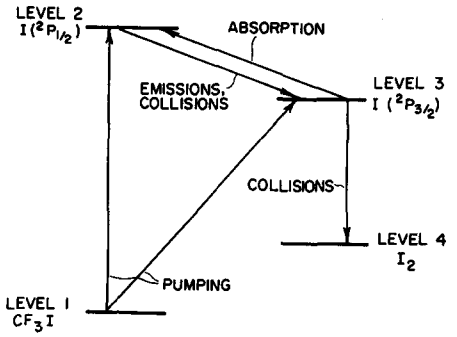

FIG. 1. The four level iodine laser.

The kinetic equations include the effects of photolytic pumping from level 1 to levels 2 and 3, stimulated and spontaneous emissions, level 2 to level 3, absorption, level 3 to level 2, and bimolecular and termolecular collisions between levels 2 and 3, levels 2 and 4, and levels 3 and 4.

The two body collisional reactions[5,7,8] are

$$I(^2P_{1/2})+M\rightarrow I(^2P_{3/2})+M, \quad (1)$$

$$I(^2P_{1/2})+CF_3I\rightarrow CF_3\cdot+I_2, \quad (2)$$

with the first reaction being predominant. Since I_2 is a much more effective quencher of $^2P_{1/2}$ iodine atoms than any other species in the system, its contribution alone is included in Eq. (1). In addition three body collisions are neglected. This assumption should be good for small pulsed times ($<50\,\mu$sec) due to the long $^2P_{3/2}$ iodine atom lifetime.[4]

The kinetic equations are

$$dN_1/dt=-[X(t)+Y(t)]-\eta_2N_1N_2, \quad (3)$$

$$dN_2/dt=X(t)-A_{23}N_2(1+\Gamma)+A_{23}(\Gamma/2)N_3 -\eta_2N_1N_2-\eta_1N_2N_4, \quad (4)$$

$$dN_3/dt=Y(t)+A_{23}N_2(1+\Gamma)-A_{23}(\Gamma/2)N_3+\eta_1N_2N_4, \quad (5)$$

$$dN_4/dt=2\eta_2N_1N_2, \quad (6)$$

where N_i ($i=1, 2, 3, 4$) represents the number of iodine atoms in each level and $\sum_i N_i$ is the initial number of CF_3I molecules present in the system.

The dimensionless cavity radiation density is

$$\Gamma(\nu_{23})=W(\nu_{23})/\Omega_{23},$$

where $W(\nu_{23})$ is the radiation density, $\Omega_{23}=8\pi h\nu_{23}^3/c^3$, and ν_{23} is the transition frequency. In Eqs. (3)–(5) the net pumping rates to the $^2P_{1/2}$ and $^2P_{3/2}$ states are given by

$$X(t)=\int\alpha(\nu)\gamma(\nu)E^*(\nu,t)\,d\nu,$$

$$Y(t)=\int\beta(\nu)\gamma(\nu)E(\nu,t)\,d\nu,$$

where α and β are absorption coefficients, γ is a coupling constant, and $E(\nu, t)$ represents the effective net energy pumping supplied by the flash lamp, dependent on pulse shape parameters, the photodissociation energy, and the recombination rate of CF_3 radicals and iodine atoms. A_{23} is the Einstein coefficient for spontaneous emission, η_1 and η_2 are reaction rate constants for Eqs. (1) and (2), and the factor of $\frac{1}{2}$ arises in Eqs. (4) and (5) from the ratio of the upper and lower state degeneracies.

The four kinetic equations must be combined with the evolution equation[9] for Γ:

$$d\Gamma/dt=(\Gamma A_{23}/\phi)[N_2-(N_3/2)]-\beta\Gamma,$$

where β is a loss coefficient, and ϕ is the dimensionless line width factor. Spontaneous contributions to the coherent radiation density are neglected.

Prior to a numerical solution of the kinetic equations the transition probability, coupling constant, absorption coefficients, energy pumping functions, initial radiation density, and loss coefficient must be specified.

The coupling constant and absorption coefficients, at a given pressure, are average values[4,5] over the portions of the lamp spectrum responsible for $^2P_{1/2}$ or $^2P_{3/2}$ iodine atom formation. The energy function is obtained by approximating the lamp pulse as a triangular wave and specifying the pumping factors of rise time, pulse width (FWHH), and total energy input.[10] Quenching effects, found to be important for high energy flashes[2] due to temperature rises, have been described in our model by having fast pulse falloff rates at high energy inputs. A range of low initial radiation densities[10] are assumed with the magnitude having little effect on the results. The loss coefficient, β, is assumed constant and may be varied from 0%–15%/pass.

The transition probability, A_{23}, is calculated from the

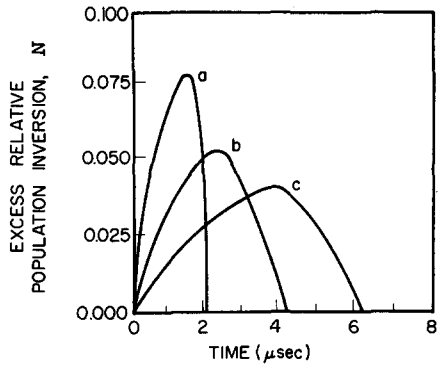

FIG. 2. Initial time dependence of the excess relative population inversion (10 Torr pressure). (a) 2000 J, 20 μsec rise time, 50 μsec FWHH. (b) 1000 J, 20 μsec rise time, 50 μsec FWHH. (c) 1000 J, 20 μsec rise time, 100 μsec FWHH.

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relation

$$A_{23}=(64\pi^4\nu_{23}^3/3hc^3)\,|\,\bar{R}_{23}\,|\,|\,\bar{R}_{32}\,|,$$

where R is the magnetic dipole transition moment for the forbidden $^2P_{1/2}\rightarrow{}^2P_{3/2}$ transition given by

$$\bar{R}_{23}=\int\Psi_2^*[(e/2Mc)\,(\bar{L}+2\bar{S})]\Psi_3 dV.$$

Here $\bar{L}$ and $\bar{S}$ are the orbital and spin angular momentum operators and Ψ_2 and Ψ_3 are the $^2P_{1/2}$ and $^2P_{3/2}$ wave functions for the iodine atom. The calculation is based on using appropriate linear combinations of the six degenerate ^2P wave functions of Slater[11] determinantal form

$$\Psi(^2P_{3/2})=[1/(5!)^{1/2}]\times\sum_i D_i\det{}_i[\lambda_{1i}(1),\lambda_{2i}(2)\cdots\lambda_{5i}(5)],$$

$$\Psi(^2P_{1/2})=[1/(5!)^{1/2}]\times\sum_i C_i\det{}_i[\lambda_{1i}(1),\lambda_{2i}(2)\cdots\lambda_{5i}(5)].$$

Orbital functions, λ_i, of the type proposed by Slater and compiled by Griffith[12] are employed. The evaluation of the transition moment then reduces to calculating the effect of the $\bar{L}$ and $\bar{S}$ operators[13] on the spherical harmonics and Pauli spin functions contained in the λ_i. The orthogonality properties of the spin functions and spherical harmonics considerably simplify the evaluation. By this method A_{23} is estimated to be 9.1 sec^{-1}. This value lies within the 20% confidence limits imposed by Garstang[14] on his estimate of 7.8 sec^{-1}.

With these approximations the equations have been solved by a Runge–Kutta–Gill integration technique using step sizes ranging from 0.1 to 1 μsec. For pure CF_3I fill pressures from 0.1 to 300 Torr and for a range of flash lamp parameters, the populations of each level have been calculated as functions of time. Instantaneous gains have been calculated from standard equations,[15] using either Lorentz or Doppler broadening, and then integrated numerically to give the overall efficiency and output.

In Fig. 2 a plot of the excess relative population inversion,

$$N=(N_2/N_3)-(N_2/N_3)_T,$$

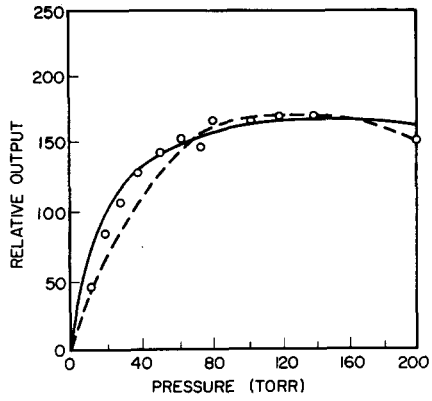

FIG. 3. Relative power output for CF_3I versus pressure. O, experimental results from Ref. 3. – – –, model results from Ref. 3. ——, kinetic model results, 800 J, 20 μsec rise time, 50 μsec FWHH.

where $(N_2/N_3)_T$ is the threshold value of 0.5, versus time, shows the behavior in the first few microseconds. Rapid pumping leads to an abrupt rise in the inversion. Once a reasonable inversion is achieved its immediate decline thereafter corresponds to a buildup in the photon density and the onset of a laser pulse. The results agree with Pollack's[3] findings that as pumping energy and pressure increase the laser pulses exhibit faster rise times. Successive buildups and declines in the inversion are observed throughout the initial twenty microsecond period indicating that laser spiking does occur. As pumping energy and cavity relaxation times are increased the spikes smooth out as expected.[9] Pollack's[3] experimental results and somewhat simpler model for relative laser output with pressure are compared to our model in Fig. 3. Agreement with experiment is good except in the higher pressure region where additional collision reactions become important.

Gains obtained vary from threshold to 150 dB/M compared to a reported value[1] of 106 dB/M. Overall efficiencies range up to 0.3% and threshold gains are achievable at 0.3 Torr.

The results seem to be reasonable enough to warrant the model's use as a first approximation for predicting system performance. To obtain better results a number of refinements should be included:

(i) temperature dependency of the rate constants
(ii) more accurate description of lamp pulses and absorption coefficients
(iii) effects of three body collisions

Further analysis on laser spiking and pulse shapes and comparison with experimental data taken in our laboratory will be attempted using an improved model based on these refinements.

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