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OPTICAL EMISSION OF MOLECULES IN COMBINED LASER AND ELECTROSTATIC FIELDS

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ABSTRACT

Optical properties of the emission from laser-induced electrostatic under combined pulse excitation were studied. An increase in line emission intensity by ≥ 4 times was obtained for combined laser pulse interaction under electrostatic field. Optimum nature was found correlated with an optimum expansion of combined state. The principal requirement is that the molecules must contain an isolated bond between a highly electronegative alone and a hydrogen (or light metal) that is sufficiently soft to allow torsional motion of the hydrogen atom.

Key words : Laser, Optical emission, Electrostatic field.

INTRODUCTION

Investigation of high-intensity laser-matter interaction is an active topic of research not only in laser spectroscopy but also in many fields of research and analysis. The capability of lasers to vaporize, dissociate, excite or ionize, specially from any kind of metallic interaction. The molecules in combined laser produced within an electrostatic field radiates various types of optical emission ranging from X-ray to visible wavelength regions. The study of atomic emission spectroscopy can provide significant information about the analytic behaviors of different ionized complexes. However, the applications of this technique is limited because of the electronegative nature of active elements. In the present work, the main objective has been considered for the dimensional orientation of such molecules in an electrostatic field[1,2]. Laser control scheme have been proved much more efficient. It was shown theoretically and experimentally that molecules can be two or three dimensional aligned in laser fields. However, the molecules may not be arranged in

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"a head versus tail" order. It was demonstrated that molecular orientation can be achieved by combining laser and electrostatic field[3,4]. Its basic principle is to select molecules that have the required instantaneous orientation rather than simultaneously force all molecules into the target state. As the orientation of the molecules making up the subensemble varies, they are dynamically substituted by other over a characteristics time depending on their rotational frequency. The proposed two-dimensional orientation control scheme makes use of the combined effects of electrostatic and laser fields[5,6]. The laser fields transfers proportion between vibronic states so that molecules aligned with a space fixed assign are selected.

This paper is organized as follows, in section 2, we present a qualitative analysis of the proposed combined control scheme. In section 3, we discuss conditions that must be satisfied by molecular parameters in order to implement efficient control and describe the corresponding class of molecules. In section 4, we fiscuss conditions that must be satisfied by molecular parameters in order to implement efficient control and describe the corresponding class of molecules. In section 4, we also discuss the results of numerical simultaneous of orientation dynamics. Sections 5, summarizes the result of present study and presents the main conclusions.

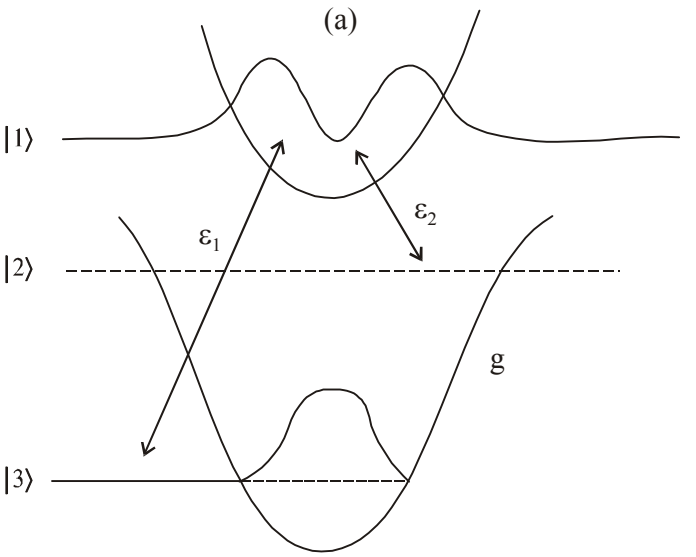

Fig. 1 : (a) Schematic diagram of the interaction between a three level system and laser fields

General scheme of laser-driven orientational selection of molecules

We consider the problem of selection of molecules with body-fixed axis m paralled to the unit basis vector e_z of a space fixed coordinate system form a randomly oriented ensemble.

Since the selected molecules must be characterized by a small angle α = m, $\hat{e}_z$ between the Z axis and m direction, population transfer from the ground vibranic state $|1\rangle$ to an excited vibrational state $|3\rangle$ must be induced, when m approaches e_z via thermal rotation and the reverse process $|3\rangle \rightarrow |1\rangle$ must occur as the required orientation is lost due to further rotation.

Population can be transferred between the stated $|1\rangle$ and $|3\rangle$ by coupling them to a high-lying intermediate vibranic state $|2\rangle$ with laser fields ξ_1 and ξ_2 whose frequencies ω_1 ω_2 are turned close to resonance with the $|1\rangle \leftrightarrow |2\rangle$ and $|3\rangle$ transitions, respectively. Since the field induced coupling depends on the angle between the field polarization vector and the molecular dipole moment, the field molecule interaction will be modulated by molecular rotation. Under this condition, appropriately polarized laser fields can be used to implement orientation dependent population transfer between $|1\rangle$ and $|3\rangle$ as a sequential stimulated Raman adiabatic passage[7-8] that does not involve significant population of the excited state $|2\rangle$.

To simply analyse, we consider one dimensional rotation of prolate of the prolate top molecules, assuming that the molecules-fixed axis *n* is aligned with the principal axis corresponding to the lowest moment of the inertial I_{min} corresponding component-ν_n of the rotational angular velocity-ν will have the largest value while the n axis will rotate with substantially lower angular velocities. The desired selection is achieved when the vectors $\langle 1|\hat{d}|2\rangle$ and $\langle 3|\hat{d}|2\rangle$ (d is the dipole moment operator) are aligned with m and the Stark shifts SE_q (q = 2, 3) induced by the static field ξ_0 relative to ground-state energy vary with molecular orientation as $\cos\alpha = \sin\beta\cos\phi$

$$SE_q(\xi_0, \beta, \phi) = \delta\, E_q^0(\xi_0|\sin\beta\cos\phi) \quad \ldots(1)$$

where, $\beta = (\hat{e}_z, n)$ denotes the angles between the n and Z axes. In the next section, we show that the latter condition is satisfied, if ξ_0 is parallel to e_z.

The laser field

$$\xi_1 = A_1 e_z \cos(\omega_1 t + \phi_1)$$

must be linearly polarized along e_z, and the field

$$\xi_2 = A_2 [e_x \cos(\omega_2 t + \phi_2) + e_y \sin(\omega_2 t + \phi_2)$$

must be circularly polarized perpendicular to e_z.

Neglecting, the effects due to off resonant transitions, we write the Hamiltonion for the coupled molecule field system as[9-10] –

$$\hat{H} = \hat{H}_0 + \hat{H}_0^I + \hat{H}_1^I + \hat{H}_2^I \quad \ldots(2)$$

Where, $\hat{H} = E_1 |1\rangle \langle 1| + E_2 |2\rangle \langle 2| - E_3 |3\rangle \langle 3|$ is the field force Hamiltonian with – E_p denoting the unperturbed energies of states $|P\rangle$ (P = 1, 2, 3). The terms $\hat{H}_0^I$, $\hat{H}_1^I$, and $\hat{H}_2^I$ represent the interaction between the molecules and the electrostatic field ξ_0 and the laser fields ξ_1 and ξ_2.

$$\hat{H}_0^I(\xi_0, \beta, \phi) = SE_2 |2\rangle \langle 2| + SE_3 |3\rangle \langle 3|$$

$$\hat{H}_1^I(\xi_1, \beta, \phi) = \hat{H}_{1,2}^I |1\rangle \langle 2| + hc$$

$$\hat{H}_2^I(\xi_2, \beta, \phi) = \hat{H}_{1,2}^I |3\rangle \langle 2| + hc \quad \ldots(3)$$

Where the matrix elements

$$\hat{H}_{P,r}^I = \hat{H}_{P,r}^I(\xi_i, \beta, \phi) = \langle P|\hat{d}|r\rangle \xi_i$$

characterize the field induced coupling. Using the Frank-condon approximation to describe rovibrational transitions, we rewrite –

$$\hat{H}_{P,r}^I \text{ as } \hat{H}_{1,2}^I = h\Omega_1 m e_z \cos(\omega_1 t + \phi_1)$$

$$\hat{H}_{3,2}^2 = h\Omega_2 m [e_x \cos(\omega_2 t + \phi_2) + e_y \cos(\omega_2 t + \phi_2)]$$

$$\Omega_1 = \frac{1}{\hbar} \sqrt{F_{1,2}} |A_1(t) \langle g|d|e\rangle_e|$$

$$\Omega_2 = \frac{1}{\hbar} \sqrt{F_{3,2}} |A_2(t) \langle g|d|e\rangle_e|$$

Here $F_{P,r}$ denote Frank-Condon factor $\langle g|\hat{d}|e\rangle_e$ is the reduced dipole transition

matrix element between the ground and excited states. Averaged over the electronic subsystem in the equilibrium nuclear configuration[9,10],

Introducing the determings

$$\Delta_1 = \frac{1}{\hbar}(E_2 - E_1) - \hbar\omega_1$$

$$\Delta_2 = \frac{1}{\hbar}(E_3 - E_1) - (\omega_1 - \omega_2)$$

and using the rotating wave approximation we change from Hamiltonian (2),within in the bare state bases $\{1\rangle,|2,|3\rangle\rangle\}$ to the effective Hamiltonian

$$\hat{H}_{eff} = \begin{pmatrix} 0 & g_1 & 0 \\ g_1^* & -\hbar\Delta_1 + SE_2 & g_2 \\ 0 & g_2^* & -\hbar\Delta_2 + SE_3 \end{pmatrix}$$

where,

$$g_1 = \frac{1}{2}\hbar\Omega_1 e^{-i S_1 \sin\beta\cos\phi}$$

$$g_2 = \frac{1}{2}\hbar\Omega_2 r^{-i S_2(n)}(\sin\phi + i\cos\beta\cos\phi)$$

are the complex Rabi frequencies and S_1 and S_2 phase shifts.

Laser driven population transfer between $|1\rangle$ and $|3\rangle$ via a weakly postulated intermediate $|2\rangle$ can be interpreted as a series of sequential processes of stimulated Raman adiabatic passage, Indeed for a given molecular orientation, the coupling induced by each laser field components is characterized by the absolute value of the Rabi frequency. $|g_1(t)|$ or $|g_2(t)|$. The curves of $|g_1(t)|$ and $|g_2(t)|$ versus ϕ in Fig. 1(a) demonstrate that the respective coupling strength between the molecule and the field components oscillate with period π, vanishing at $\phi = \pm\pi/2$ and $\phi = 0, \pi$ for ξ_1 and ξ_2, respectively. According the effect of ξ_1 and ξ_2 on a molecule rotating about the n axis (Fig. 1b) is similar to that of the train of over lapping pulses with a duration of ½ ν_n, whose shape is determined by $|g_1(t)|$ and $|g_2(t)|$. Since population transfer $|1\rangle \rightarrow |3\rangle$ is induced as $\phi = 0$ or π is approached. The components ξ_1 and ξ_2 act as pump and dump (strokes).

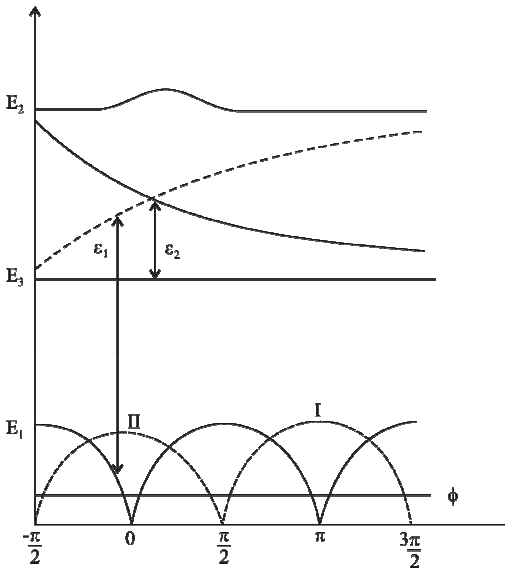

Fig. 1 (b) : Energy levels and laser-induced transitions in the three state system vs molecular rotation angle for B = π/2.

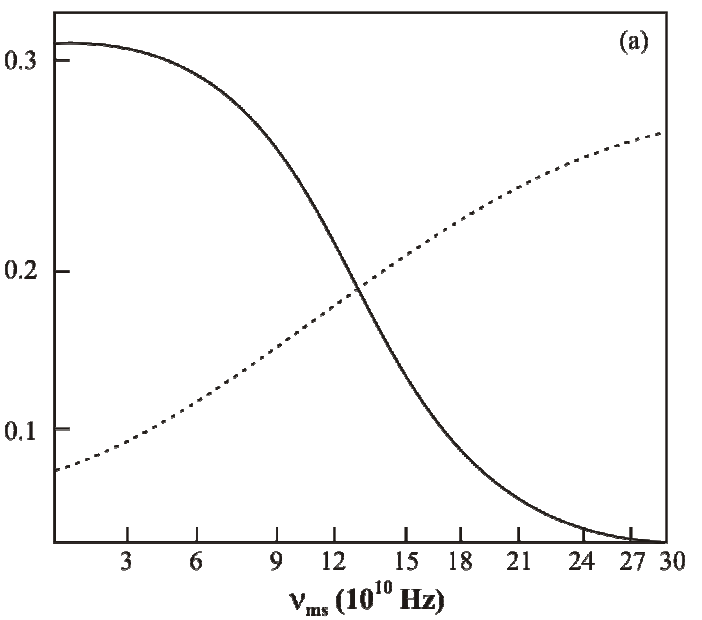

Fig. 2(a)

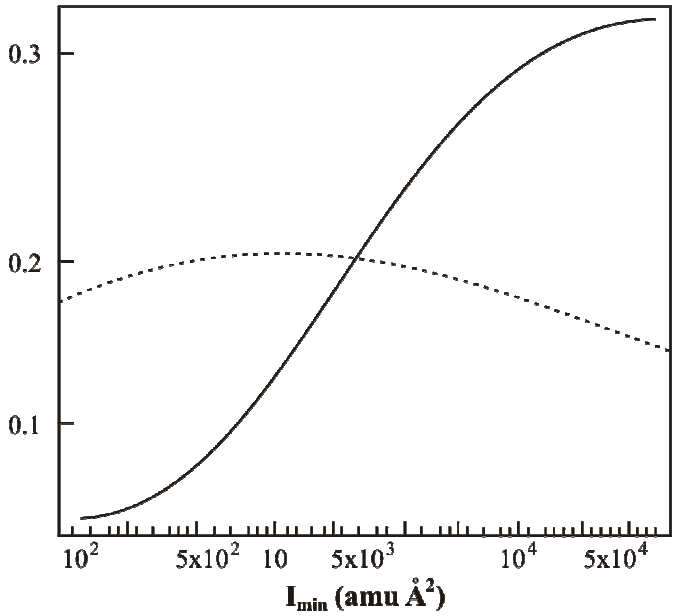

Fig. 2 (b)

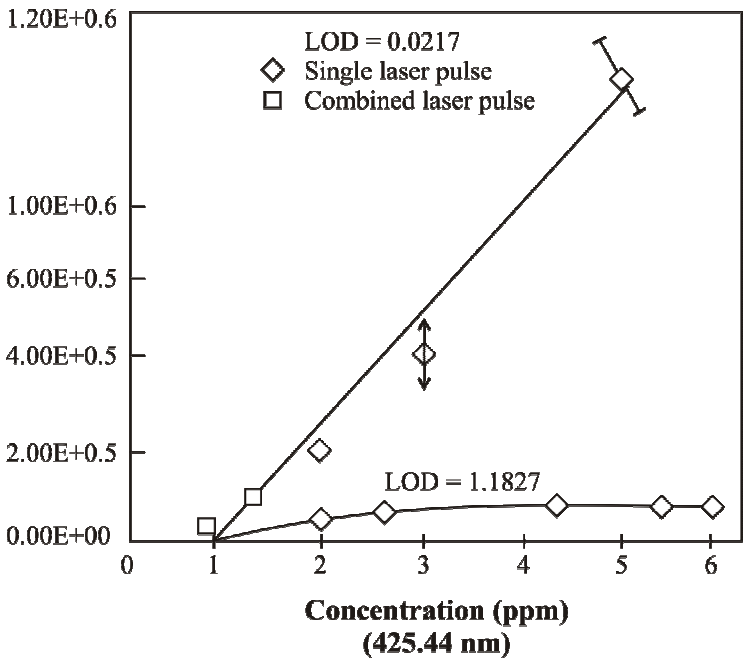

Fig. 3 : Variation in emission under single and combined excitation states at different time intervals

Requirements for molecular parameters corresponding to efficient combined laser and electrostatic fields

The combined-dependence $|SE_3|$ in Stark shift between $|3\rangle$ and $|1\rangle$ must vary as cos α and its maximum value $|SE_3^0|$ measured in units of $\hbar$ must be at least comparable to V and $\frac{1}{2}$. Similarly, the transition dipole moments $\langle 1|\hat{d}|2\rangle$ and $\langle 3|\hat{d}|2\rangle$ must be collinear with m and their magnitude must be such that –

$$|\langle 1|d|2\rangle|_{max} \approx |SE_3^0,$$

$$|\langle 3|d|2\rangle|_{max} \approx |SE_3^0$$

For fields, whose amplitude are so weak that both coupling to other levels and ionization are negligible. The energy of the states $|1\rangle$, $|2\rangle$ and $|3\rangle$ are separated from neighbouring vibronic energy levels by amounts substanitially larger than the rotational energy quantum $\hbar$v.

A specific class of molecules satisfying the conditions stated above is characterized as follows –

Each molecules contains a hydrogen (or a light metal) atom covalently linked to the rest of the molecule by a highly polar bond. Each molecule contains a hydrogen (or a light metal) atom covalently linked to the rest of the molecules by a highly polar bond with highly electronegative atoms.

We use a molecule fix frame with *m* axis pointing in an equilibrium direction of $\overrightarrow{X}H_\sigma$ in the ground state torsional state and define θ as the instantaneous angle m, $\overrightarrow{X}H_\sigma$, where $\overrightarrow{X}H_\sigma$ is the ground torsional state and define θ as the instantaneous angle $\overrightarrow{X}H$ onto the plane σ perpendicular to the torsional axis n.

The eigenstates $|v_1\rangle$ corresponding to low torsional quantum number v are localized in the neighborhood of θ = 0, where as the eigenstates $|v_n\rangle$ with energies near the torsional barrier are localized in the neighourhood of θ = π.

$$\langle v_1|\cos\hat{\theta}|v_1\rangle \approx \langle v_h|\cos\hat{\theta}|v_h\rangle \approx 1$$

These estimation justify the analysis of laser driven combined dynamics under normal conditions based on the classical treatment of rotations and the assumption of

constant rotational frequency. However, for the model of one dimensional rotation developed in the section 2 to be applicable.

Simulation of combined laser and electrostatic field

We analyze the efficiency of the proosed scheme as applied molecule of the class describe in the proceeding section. One can use the following typical expressions for the vibrational potential energies U_g and U_e of the such molecule in the ground and excited electronic states[11,12]

$$U_e(\theta, \beta, \phi) = hc\left[\frac{3}{2} D_g - [D_e - (\beta, \phi)]\right]\cos\theta + \frac{1}{2} D_e \cos(2\theta)$$

$$U_e(\theta, \beta, \phi) = hc\,[D_g - [D_g + \Delta D_g(\beta, \phi)]\cos\theta]$$

$D_e = 1000\ cm^{-1}$. $D_g = 500\ cm^{-1}$ and $\Delta D_e(\beta, \phi) = \Delta D_g(\beta, \phi) = 2 \sin\beta \cos\phi$ are the combined dependent corrections induced by electrostatic field. The laser field amplitudes are set from the following considerations. The adiabatically requirement implies that effective pump and dump pulse areas must be much larger that π, whereas the population transfer path to $|g, 10\rangle$ can be effectively blocked near $\phi = \pi$ only if $|\Omega_i| << |\delta E^0_3|$ $(i = 1, 2)$. Since the Stark shifts δE^0 are comparable to $h\nu_n$, both requirements cannot be met simultaneously. These settings correspond to moderate laser intensities on the order of $10^9\ w/cm^2$. The laser frequencies ω_1 and ω_2 are set to optimize the detunings Δ_1 and Δ_2. The efficiency of combined selection cannot be reliably evaluated for the class of molecules considered hereby approximately treating laser induced dynamics under normal conditions as adiabatic passage in a three state system, because non-adiabatic coupling effects cannot be completely eliminated and off resonant interactions must be taken into account at high laser interactions.

The complete dependence of $\langle\cos\alpha\rangle_g$ 10 and $|g, 10\rangle$ population on T and β is used to calculate $\langle\cos\alpha\rangle_g$ 10 and $|g, 10\rangle$ population averaged over on ensemble of randomly oriented molecules in rotational thermal equilibrium. The distribution molecules over $|v_n|$ can be written as,

$$\rho_r(|v_n|) = \frac{2}{\sqrt{2\pi v^2_{ms}}} \exp\left(\frac{-v^2}{2v^2_{ms}}\right)$$

with rms frequency v_{ms} of rotation about the n axis calculated as

$$v_{ms} = \frac{1}{2\pi}\sqrt{\frac{kT_{rot}}{I_{min}}}$$

where I_{rot} is the rotational temperature and k is Boltzmann constant.

Plot of $\langle \cos \alpha \rangle_g$ 10 (solid curves) and normalized |g, 10| (dashed curve) averaged over ensemble of randomly oriented molecules is rotational thermal equilibrium vs rms rotationa frequency v_{ms} (a) and momet of inertia I_{min} at T_{rot} = 300 K (b) computating were performed by assuming that the moment of inertia other that I_{min} are higher than 10^3 amu $Å^2$.

RESULTS AND DISCUSSION

Optical emission from combined laser and electrostatic fields under strong population were studied. The band width of emission line in the UV-VIS region of the spectrum, because their higher excitation cross-sections are similar. A very small increase in the emission intensity was noted for delayed single pulse excitation.

However, emission intensity was enhanced nearly 4 times (peak to peak), when the delay was increased to 3μs and the spectra are recorded after some delay. It was found that emission intensity increases with an increasing intensity of the first or second laser up to a certain level after which saturation was observed. The occurrence of saturation with an increasing in laser intensity is possible either due to self-absorption of emission in the cold high density or due loss in absorption of laser light.

Absorption of laser light in electrostatic fields

It is better to understand the absorption laser light in the preformed pulses. The possible absorption mechanism in such case is inverse Bremsstrahlung absorption, which takes place as a result of electron-ion collision in suitable temperature region. It is obvious that when the molecules are subjected to momentum changing collisions as they oscillate back and forth in the laser electric field. The laser light wave feels an effective damping. In this case, absorption coefficient (Kib) of optical emission can be written as –

$$\text{Kib } \alpha \ \frac{Zn_e^2}{T_e^{3/2}\left(1-\frac{n_e}{n_c}\right)^{1/2}}$$

Application of enhancement in emission

The variation in the line emission intensity with combined laser pulse was recorded in the single as well as double laser pulses excitations in order to compare the calibration curve. The curve shows the calibration curve for laser single pulse line emission at λ = 425.44 nm in single and combined laser pulses excitation mode. The slope of the linear variation was found more in combined laser excitation due to a large enhancement in the emission in the concentration range. Finally combined laser pulse excitation was found useful enhancing the emission form laser induced electrostatic field.

CONCLUSION

Optical properties of the emission from laser-induced electrostatic under combined pulse excitation were studied. An increase in line emission intensity by ≥ 4 times was obtained for combined laser pulse interaction under electrostatic field. Optimum nature was found correlated with an optimum expansion of combined state. The principal requirement is that the molecules must contain an isolated bond between a highly electronegative alone and a hydrogen (or light metal) that is sufficiently soft to allow torsional motion of the hydrogen atom. It would be interesting to explore the possibility of using the present scheme by means of a multimode laser field. We expect that this setting will avoid the use of electrostatic field as applied to every asymmetric molecule at higher rotational temperatures. However, further experimental as well as theoretical investigation are needed to better under stand the other effects of optical emission under combined laser pulse excitation in electrostatic field.

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