



Nonresonant interaction of femtosecond laser pulse with centrosymmetric molecules

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ABSTRACT

We have derived a system of equations that describes the evolution of the density matrix of a centrosymmetric molecule interacting with a single nonresonant femtosecond laser pulse. The dynamics of the ground electronic state is expressed in terms of the effective Hamiltonian and the coherences between the ground and excited electronic states are functionals of the ground state density matrix. Using the time-dependent perturbation theory, we have calculated the energy deposited in the molecule as a result of rotational stimulated Raman scattering. The effective absorption coefficient is found to be proportional to the fourth power of the pulse amplitude and has a resonance-like dependence with respect to the pulse duration.

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1. Introduction

For centrosymmetric molecules, the first-order electric dipole transitions in a fixed electronic state are prohibited by the selection rules. In thermodynamic equilibrium at normal atmospheric temperature and pressure, practically all molecules reside in their ground electronic states. If such molecules interact with a laser pulse whose carrying frequency is well off resonance with the electronic transitions, so that multi-photon absorption into the excited electronic states is negligible, then the main coupling mechanism between the light and molecules will be the second-order scattering processes. As a result of this interaction, the electromagnetic field creates coherences between the ground and excited electronic states which serve as a source for the macroscopic polarization. The coherences created between different sublevels of the ground electronic state determine molecular vibrational dynamics as well as spatial orientation and alignment. Additionally, the Raman scattering, being an inelastic process, changes populations of the ground state sublevels. Depending on the initial state, this can be viewed as either absorption or emission of energy by the

molecule and quantitatively described in terms of an effective absorption coefficient [1].

The absorption coefficient due to spontaneous Raman scattering under normal conditions is negligibly small. For molecular nitrogen it is of the order of 10^{-12} cm⁻¹ [1]. On the contrary, the absorption caused by stimulated Raman scattering depends on the intensity of the laser light and can be readily detected, for example, using modern photoacoustic techniques [2].

To the best of our awareness, the first observation of the energy deposited in atmospheric gases as a result of interaction with a femtosecond pulse was reported in [3,4]. The authors used photoacoustic measurements and attributed the observed phenomenon to a new absorption mechanism. In the present paper, we develop a general approach for nonresonant interaction of centrosymmetric molecules with a femtosecond laser pulse and show that there is no need to resort to any new mechanism. The results of the referred experiment can well be explained by the conventional mechanism of stimulated Raman scattering.

2. Theory

2.1. Molecule in nonresonant pulse field

Consider a centrosymmetric molecule interacting with a femtosecond pulse described by the electric field strength

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$$\mathbf{E}(\mathbf{r}, t) = \frac{E_0(\mathbf{r}, t)}{2} \{ \mathbf{e} e^{i(\mathbf{kr} - \Omega t)} + \mathbf{e}^* e^{-i(\mathbf{kr} - \Omega t)} \}, \quad (1)$$

where the real amplitude $E_0(\mathbf{r}, t)$ determines the temporal shape of the pulse envelope and its spatial distribution traverse to the propagation direction; the complex polarization vector \mathbf{e} is normalized to unity

$$\mathbf{e} \cdot \mathbf{e}^* = 1. \quad (2)$$

We assume that the amplitude $E_0(\mathbf{r}, t)$ is a slow-varying function of time in the sense that the following relation is true

$$|\omega_{mn} \pm \Omega| \tau \gg 1, \quad (3)$$

where ω_{mn} is the electronic transition frequency and τ is the pulse duration.

In the long wave-length approximation ($\mathbf{kr} \ll 1$), the molecular Hamiltonian has a well-known form

$$H = H_0 + V(t), \quad (4)$$

where H_0 is the Hamiltonian of a free molecule and the interaction Hamiltonian is given by

$$V(t) = -\mathbf{dE}(\mathbf{r}, t), \quad (5)$$

where dependence of $\mathbf{E}(\mathbf{r}, t)$ on \mathbf{kr} in (1) should be omitted.

The electric dipole transitions in the ground state are prohibited by the parity conservation law, i.e.,

$$\langle \mu | V | \mu' \rangle = 0. \quad (6)$$

Here and henceforth, we use Greek letters to enumerate sublevels of the ground electronic state and Latin letters to denote the electronic terms.

As far as the initial conditions are concerned, we assume that at $t = -\infty$ the molecule was in the state of thermodynamic equilibrium described by the density matrix

$$\rho^0 = \frac{1}{Z} \exp(-\beta H_0), \quad \beta = 1/k_B T, \quad (7)$$

where the thermostat temperature T is such that the excited electronic levels are not effectively populated, i.e.,

$$\beta E_e \gg 1. \quad (8)$$

Under normal conditions, the duration of a femtosecond pulse allows one to neglect all relaxation processes including spontaneous decay and intermolecular collisions as being too slow.

2.2. Equations of motion

The equation of motion for the molecular density matrix $\rho(t)$ in the interaction picture reads

$$i\hbar \dot{\rho}(t) = [\tilde{V}(t), \tilde{\rho}(t)], \quad (9)$$

where

$$\tilde{\rho}(t) = \exp\left(\frac{i}{\hbar} H_0 t\right) \rho(t) \exp\left(-\frac{i}{\hbar} H_0 t\right). \quad (10)$$

An off-resonant interaction of light with a quantum system where the first-order processes are prohibited can be described in terms of the effective ground state dynamics [5,6]. To this end, we introduce the projection operators onto the ground and excited electronic manifolds

$$P_g = \sum_{\mu} |\mu\rangle \langle \mu|, \quad P_e = \sum_n |n\rangle \langle n|, \quad (11a)$$

$$P_g + P_e = 1. \quad (11b)$$

For any operator A , the following identity is true

$$A = A_{gg} + A_{ge} + A_{eg} + A_{ee}, \quad (12a)$$

$$A_{ij} = P_i A P_j, \quad i, j = e, g \quad (12b)$$

Using identity (12a) for the density matrix, we can rewrite Eq. (9) as the following system of equations

$$i\hbar \dot{\rho}_{gg} = \tilde{V}_{ge} \tilde{\rho}_{eg} - \tilde{\rho}_{ge} \tilde{V}_{eg}, \quad (13a)$$

$$i\hbar \dot{\rho}_{eg} = \tilde{V}_{ee} \tilde{\rho}_{eg} + \tilde{V}_{eg} \tilde{\rho}_{gg} - \tilde{\rho}_{ee} \tilde{V}_{eg}, \quad (13b)$$

$$i\hbar \dot{\rho}_{ee} = \tilde{V}_{ee} \tilde{\rho}_{ee} + \tilde{V}_{eg} \tilde{\rho}_{ge} - \tilde{\rho}_{ee} \tilde{V}_{ee} - \tilde{\rho}_{eg} \tilde{V}_{ge}. \quad (13c)$$

In the absence of multi-photon resonances and at the temperatures satisfying (8), we can altogether neglect the populations and coherences of the excited electronic states and consider only the ground state density matrix ρ_{gg} and the coherences ρ_{ge} ,

$$i\hbar \dot{\rho}_{gg} = \tilde{V}_{ge} \tilde{\rho}_{eg} - \tilde{\rho}_{ge} \tilde{V}_{eg}, \quad (14a)$$

$$i\hbar \dot{\rho}_{eg} = \tilde{V}_{ee} \tilde{\rho}_{eg} + \tilde{V}_{eg} \tilde{\rho}_{gg}. \quad (14b)$$

From (14b) it follows that the evolution of coherences is completely determined by the ground state matrix and can be expressed in the form of the functional

$$\tilde{\rho}_{eg}(t) = -\frac{i}{\hbar} \int_{-\infty}^t K_{ee}(t, t') \tilde{V}_{eg}(t') \tilde{\rho}_{gg}(t') dt', \quad (15)$$

where

$$K_{ee}(t, t') = \exp\left[-\frac{i}{\hbar} \int_{-\infty}^t \tilde{V}_{ee}(t_1) dt_1\right] \exp\left[\frac{i}{\hbar} \int_{-\infty}^{t'} \tilde{V}_{ee}(t_2) dt_2\right]. \quad (16)$$

Substituting Eq. (15) into (14a), we obtain in the markovian approximation a closed-form equation for the ground state density matrix

$$i\hbar \dot{\rho}_{gg}(t) = \delta \tilde{H}_{gg}(t) \tilde{\rho}_{gg}(t) - \tilde{\rho}_{gg}(t) \delta \tilde{H}_{gg}^\dagger(t), \quad (17)$$

where the effective Hamiltonian is given by the following expression

$$\delta \tilde{H}_{gg}(t) = -\frac{i}{\hbar} \int_{-\infty}^t \tilde{V}_{ge}(t) K_{ee}(t, t') \tilde{V}_{eg}(t') dt'. \quad (18)$$

The effective Hamiltonian (18) is not a Hermitian operator. As a consequence, the evolution described by Eq. (17) is not unitary and the trace of the ground state density matrix is not conserved.

Introducing the Hermitian and anti-Hermitian parts of δH , one can express the effective Hamiltonian through the shift and absorption operators, δE and $\delta \Gamma$ [7,8],

$$\delta H = \delta E - \frac{i\hbar}{2} \delta \Gamma, \quad (19a)$$

$$\delta E = \frac{1}{2}(\delta H + \delta H^\dagger), \quad \delta \Gamma = \frac{i}{\hbar}(\delta H - \delta H^\dagger), \quad (19b)$$

and rewrite Eq. (17) as follows

$$i\hbar \dot{\rho}_{gg}(t) = [\delta \tilde{E}_{gg}(t), \tilde{\rho}_{gg}(t)] - \frac{i\hbar}{2} \{\delta \tilde{\Gamma}_{gg}(t), \tilde{\rho}_{gg}(t)\}. \quad (20)$$

The first term in (20) describes the unitary evolution governed by the self-adjoint Hamiltonian δE , and the second term corresponds to the decay of the ground state due to absorption (emission) into excited electronic levels. Note that instead of using the state of equilibrium (7) and (8) for initial conditions, we could use any density matrix for which $\rho_{ee}(-\infty) = 0$ and $\rho_{eg}(-\infty) = 0$.

2.3. Effective Hamiltonian

The effective Hamiltonian (18) has a general form and differs from the known effective Hamiltonian of Ref. [5] by the presence of the kernel $K_{ee}(t, t')$. In the lowest order of the perturbation,

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