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Permanent Electronic Excitation of a Molecular Layer on a Surface through Phase Conjugation

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The dynamics of an atom (or molecule) located near the surface of a four-wave mixing phase conjugator is studied. This device consists of a slab of nonlinear material, which is illuminated by two strong counterpropagating laser beams. The atomic dipole field induces a polarization in the nonlinear material, and as a result, a phase-conjugated replica is emitted toward the atom. This effectively leads to a four-wave mixing process at the site of the atom, during which two pump photons are annihilated in favor of an electronic excitation of the atom. The mismatch in energy is emitted as a single fluorescent photon. In the steady state the atom acquires a finite population of the excited level, although there is no direct optical pumping of the atomic transition. It is shown that this population is determined entirely by the Fresnel reflection coefficients of the medium. In case of magnetic degeneracy of the levels, the distribution over the sublevels is furthermore determined by geometrical Clebsch−Gordan coefficients. Three cases of low angular momentum are worked out in detail, as examples.

1. Introduction

Attempts to manipulate the properties of molecules or atoms in order to enhance chemical reaction rates or scattering cross sections have a long history. Thermal excitation through collisions in a vapor or flame has been the traditional method to alter the state of an atom, and this has also been a diagnostic tool for the study of chemical reactions. Information on species in a flame can be obtained from a measurement of emitted fluorescence, if any, or from photoabsorption measurements.[1] After the invention of the laser, radiative excitation of atoms has become the method of choice. Laser intensity, frequency, and polarization can be adjusted in order to populate a particular atomic state, making this method far more selective. When a magnetic field is applied, the atomic levels split, and with a narrow-band tunable laser a specific magnetic substate can be populated by optical pumping. Alternatively, with a proper choice of polarization a specific sublevel can be excited, thereby effectively creating a two-state system without degeneracies in the levels.[2]

More recent attempts to alter atomic or molecular properties or behavior is through a change of environment, without direct laser irradiation or collisions. The first experimental observation of the modification of molecular properties through the environment was made by Drexhage.[3] Molecules were deposited on a metallic surface with an optically neutral buffer layer of adjustable thickness in between. It was observed that the lifetime for spontaneous decay of an excited molecular state depends on the thickness of the buffer, e.g., the distance between the molecule and the metal. This phenomenon can be explained in a variety of ways. On one hand, it can be considered to be a result of the fact that when fluorescence is emitted during spontaneous decay, part of this radiation will reflect at the surface and return to the site of the atom. This changes the local electric field, which in turn affects the damping rate of the emission process.[4] The mechanism can therefore be considered an interference effect between directly emitted and reflected radiation. On the other hand, from a quantum mechanical point of view, the presence of the metal changes the mode structure of the electromagnetic vacuum, and this in turn modifies the process of spontaneous decay.[5]

In this paper we propose a new method for the manipulation of properties of molecules that are confined to the surface of a dielectric substrate (as in the quoted experiment). We take the medium to be a nonlinear crystal, which acts as a phase conjugator (see next section). In such a configuration, molecules can be excited spontaneously without any direct laser pumping, thereby avoiding the buildup of coherences in the system. An atom or molecule acquires a finite population of the excited level, even in the steady state (equilibrium). This scheme would provide a novel technique for creating a layer of molecules in a permanently excited electronic state. It turns out that the process, described below, is also moderately selective for magnetic degeneracies, which opens the possibility for preparing molecular layers with a predetermined molecular polarization.

2. Optical Phase Conjugation

The setup for optical phase conjugation through four-wave mixing is shown schematically in Figure 1. The substrate consists of a nonlinear transparent crystal, which is pumped by two strong counterpropagating laser beams. When a monochromatic light wave (inc) is incident upon the surface of this phase conjugator (PC), then, apart from a specular wave (r), a phase conjugated image (pc) is created by four-wave mixing in the crystal. This reflected wave counterpropagates the incident wave and can be regarded as the time-reversed image of the incident beam.[6,7] For a transparent crystal the specular wave is very weak (it is generated by the nonlinear interaction) as compared to the pc wave and can therefore be neglected.

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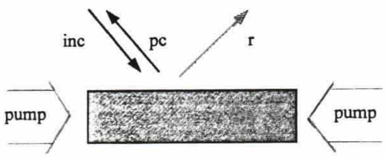

Figure 1. Schematic setup of a four-wave mixing PC. The nonlinear medium is pumped by two counterpropagating lasers. An incident plane wave has a counterpropagating plane wave as its phase-conjugate image. The usual reflection (r) is in the specular direction, but this will be neglected here through the assumption that the medium is transparent.

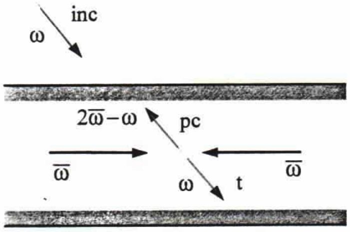

Figure 2. An incident wave with frequency ω couples to the pump beams with frequency $\bar{\omega}$. Four-wave mixing then results in the creation of a phase-conjugate image (pc) with frequency $2\bar{\omega} - \omega$ and in an amplification of the incident field, which leaves the crystal as the transmitted (t) wave.

Reflection coefficients for the pc wave can have values on the order of unity and can even exceed unity. In the latter case, the incident wave is effectively amplified, as has been demonstrated experimentally to be possible.[8]

When a molecule in an excited electronic state is situated on the surface of a PC, it can emit a fluorescent photon in the direction of the surface. Then the reflected pc field is a wave that travels back to the location of the molecule, thereby modifying the local field. At first thought it seems that the molecule can subsequently absorb the reflected photon, leaving the molecule again in the excited state. Such a mechanism would effectively enhance the lifetime of the excited state, in a process analogous to the alteration of lifetimes of molecular levels near an ordinary dielectric (mirror). It turns out, however, that the quantum nature of fluorescence prohibits this mechanism. To understand this, let's consider the mechanism of phase conjugation in more detail. An incident light beam is represented by an electric field with a positive frequency part proportional to the annihilation operator a for a photon in the given mode. Suppose this incident field has the form

$$\vec{E}^{(+)}_{\mathrm{inc}}(\vec{r},t) = E_o a \vec{\epsilon} e^{i(\vec{k}\cdot\vec{r}-\omega t)} \tag{1}$$

with $\vec{k}$ the wave vector and $\vec{\epsilon}$ the polarization vector of the photon mode. Due to boundary conditions at the surface, this wave will couple to a wave inside the crystal with the same frequency and wave vector. The third-order susceptibility then couples this field to the counterpropagating pump beams with frequency $\bar{\omega}$. For a photon exchange process to occur, energy conservation requires that there should be a coupling to a fourth field with frequency $2\bar{\omega} - \omega$. Then two pump photons can be annihilated and converted into two photons with frequencies ω and $2\bar{\omega} - \omega$. Conservation of momentum then requires that the two created photons counterpropagate. The photon with frequency ω adds to the incident field, thereby amplifying it, and the photon with frequency $2\bar{\omega} - \omega$ leaves the crystal as the pc wave. This situation is illustrated in Figure 2. The positive frequency part of the reflected pc field then becomes

$$\vec{E}^{(+)}_{\mathrm{pc}}(\vec{r},t) = E_o P^* a^{\dagger} \vec{\epsilon} e^{-2i\bar{\omega}t} e^{-1(\vec{k}\cdot\vec{r}-\omega t)} \tag{2}$$

with P the Fresnel reflection coefficient. The factor $\exp(-2i\bar{\omega}t)$ accounts for the annihilation of the two pump photons. The field that is transmitted through the layer has the form

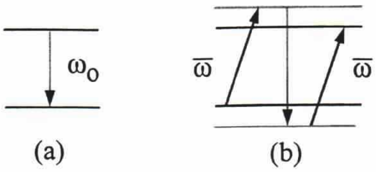

Figure 3. Illustration of the mechanisms involved in spontaneous excitation. Diagram a shows ordinary spontaneous decay from the excited state, accompanied by the emission of a photon with frequency ω_o. Diagram b shows that an atom in the ground state can absorb two pump photons, and in order for energy to be conserved, a fluorescent photon (dashed arrow) with frequency $2\bar{\omega} - \omega$ will be emitted. The net result for the atom is that it makes a transition from the ground state to the excited state.

$$\vec{E}^{(+)}_{t}(\vec{r},t) = E_o T a \vec{\epsilon} e^{i(\vec{k}\cdot\vec{r}-\omega t)} \tag{3}$$

with T the Fresnel coefficient for this wave. By solving Maxwell's equations for this configuration explicitly, the coefficients P and T can be evaluated,[9] and it turns out that they obey the relation

$$|T^2| - |P^2| = 1 \tag{4}$$

showing that $|T| \geq 1$ indeed, but there is no restriction on the range of values for $|P|$.

The situation for fluorescence radiation is slightly more complicated due to the different nature of such radiation. Suppose that initially the atom is in an excited state, as in diagram a of Figure 3, and let the resonance frequency be ω_o. During spontaneous decay to the ground state, a photon with frequency ω_o is emitted. When the atom is in its ground state, it is still surrounded by its dipole field, although the field does not contain any photons. This dipole field then serves as the incident field on the PC, polarizing the medium. This, in turn, leads to the emission of phase-conjugated radiation, which travels to the site of the atom. Direct excitation of the atom through absorption of this pc radiation would violate conservation of energy, and therefore this does not occur. The process shown in diagram b of Figure 3, however, does conserve energy. First a photon with frequency $\bar{\omega}$ is absorbed, slightly off resonance, and then a fluorescent photon is emitted. Subsequently a second photon with frequency $\bar{\omega}$ is absorbed, leaving the atom in the excited state. From energy conservation it then follows that the intermediate fluorescent photon must have a frequency of $2\bar{\omega} - \omega_o$, and this photon serves as the phase-conjugate replica of the incident photon. Such a picture is supported by the fact that the emission spectrum for an atom in this situation has two lines, one at ω_o and one at $2\bar{\omega} - \omega_o$.[10] It is interesting to note that for the case of fluorescence the four-wave mixing actually occurs at the site of the atom, and not directly in the medium, as was the case in Figure 2. It can be shown[11] from retardation times for propagation to the far field that both fluorescent photons emanate from the location of the atom, and not directly from inside the medium, thereby again supporting the interpretation of Figure 3.

3. Electric Field Correlation

When atoms or molecules are located near the surface of a PC, then the three-photon process depicted in Figure 3b is responsible for a finite population of the excited levels. To determine these populations, we adopt relaxation theory that couples the atomic dipole moment (the system) to the modified vacuum near the PC (the reservoir). Without the medium (vacuum), the positive frequency part of the electric field is given by the superposition of plane waves

$$\vec{E}^{(+)}_{\rm inc}(\vec{r},t) = \sum_{\vec{k}\sigma}\sqrt{\frac{\hbar\omega}{2\epsilon_{\rm o}V}}a_{\vec{k}\sigma}\vec{\epsilon}_{\vec{k}\sigma}{\rm e}^{{\rm i}(\vec{k}\cdot\vec{r}-\omega t)} \tag{5}$$

and this field will be regarded as the incident field for the medium. Here, V is the quantization volume, $\vec{k}\sigma$ represents a transverse mode, and $\omega = c|\vec{k}|$ is the dispersion relation. Each plane wave gives rise to a pc wave and a t wave, as in Figure 2, with amplitudes given by the appropriate Fresnel coefficients. Since the Fresnel coefficients for the t waves are related to the Fresnel coefficients for pc waves as in eq 4, only the coefficients $P_{\vec{k}\sigma}$ determine the reflected field surrounding the PC. For the polarization of the waves we take $\sigma = {\rm s}$ and $\sigma = {\rm p}$ for surface- and plane-polarized waves, respectively, in the usual way.

The function that determines atomic spontaneous decay is the Fourier transform of the autocorrelation function of the electric field at the position of the atom, e.g.,

$$f(\omega)_{mn} = \hbar^{-2}\int_0^\infty {\rm d}\tau\,{\rm e}^{{\rm i}\omega\tau}\langle E(\vec{r},\tau)_m\, E(\vec{r},0)_n\rangle \tag{6}$$

with $m, n = x, y, z$. We shall take the surface of the PC to be the xy-plane and the atom to be located on the z-axis, above the surface. Due to the cylinder symmetry of the system and to symmetry for reflection in a plane through the z-axis, there are only two independent functions $f(\omega)_{mn}$ rather than nine. We shall write

$$f(\omega)_\perp = f(\omega)_{zz},\quad f(\omega)_{||} = f(\omega)_{xx} = f(\omega)_{yy} \tag{7}$$

and the other six functions vanish. A lengthy but straightforward calculation then yields[12]

$$f(\omega)_q = \frac{\omega_{\rm o}^{\;3}}{6\pi\epsilon_{\rm o}\hbar c^3}\begin{cases}1 + y_q & \text{for}\quad \omega = \omega_{\rm o}\\ y_q & \text{for}\quad \omega = -\omega_{\rm o}\end{cases} \tag{8}$$

with $q = \perp$ or $||$. The effect of the presence of the PC is incorporated in the parameter functions y_q, which are found to be

$$y_\perp = {}^3/_4\int_0^1 {\rm d}u(1 - u^2)|P_{\rm p}|^2 \tag{9}$$

$$y_{||} = {}^3/_8\int_0^1 {\rm d}u(|P_{\rm s}|^2 + u^2|P_{\rm p}|^2) \tag{10}$$

In eq 8 a small imaginary part, the Lamb shift, has been suppressed, and we have assumed that the frequency dependence of the Fresnel coefficients is symmetric around $\bar{\omega}$, e.g., $P_\sigma(2\bar{\omega} - \omega_{\rm o}) = P_\sigma(\omega_{\rm o})$. The integration variable is $u = \cos\theta_{\rm inc}$, with $\theta_{\rm inc}$ the angle of incidence of the plane wave of the corresponding Fresnel coefficient. Without a PC present we would have $y_\perp = y_{||} = 0$. For an ideal PC the Fresnel coefficients would not depend on the angle of incidence, and this would give $y_\perp = y_{||} = |P|^2/2$.

4. Spontaneous Decay of a Two-State System

A molecule near the surface of a PC can effectively be modeled by a two-state system provided that only one molecular transition frequency $\omega_{\rm o}$ is close to the pump frequency $\bar{\omega}$. Let the excited state be $|{\rm e}\rangle$ and the ground state $|{\rm g}\rangle$, separated by an energy of $\hbar\omega_{\rm o}$. The electronic state of the molecule is represented by a density operator ρ, obeying the Liouville equation

$${\rm i}\frac{{\rm d}\rho}{{\rm d}t} = (L_{\rm a} - {\rm i}\Gamma)\rho \tag{11}$$

with $L_{\rm a}$ accounting for the free evolution,

$$L_{\rm a}\rho = \omega_{\rm o}[P_{\rm e},\rho] \tag{12}$$

in terms of the projector $P_{\rm e} = |{\rm e}\rangle\langle{\rm e}|$ onto the excited state. The molecular dipole moment $\vec{\mu}$ couples to the electric field through the interaction Hamiltonian $H_{\rm I} = -\vec{\mu}\cdot\vec{E}$, and from this an explicit expression for the relaxation operator Γ in eq 11 can be derived. The result is

$$\Gamma\rho = {}^1/_2A_{\rm e}(P_{\rm e}\rho + \rho P_{\rm e} - 2P_{\rm g}\langle{\rm e}|\rho|{\rm e}\rangle) + {}^1/_2A_{\rm g}(P_{\rm g}\rho + \rho P_{\rm g} - 2P_{\rm e}\langle{\rm g}|\rho|{\rm g}\rangle) \tag{13}$$

with $P_{\rm g} = |{\rm g}\rangle\langle{\rm g}|$. The Einstein coefficient $A_{\rm e}$ is given by[13]

$$A_{\rm e} = 2f(\omega_{\rm o})_\perp\langle{\rm e}|\vec{\mu}_\perp\cdot\vec{\mu}_\perp|{\rm e}\rangle + 2f(\omega_{\rm o})_{||}\langle{\rm e}|\vec{\mu}_{||}\cdot\vec{\mu}_{||}|{\rm e}\rangle \tag{14}$$

and for $A_{\rm g}$ we replace $f(\omega_{\rm o})_q$ by $f(-\omega_{\rm o})_q$. It is interesting to note that the relaxation constants do not depend on the distance between the molecule and the surface, which has been known for a long time.[14] The coefficients $A_{\rm e}$ and $A_{\rm g}$ are the inverse lifetimes for the excited and ground states, respectively, and because y_q from eq 8 is positive, the lifetime of the excited state is always smaller than for an atom in free space. And, of course, in free space we always have $A_{\rm g} = 0$.

When we indicate the populations of the levels $|{\rm e}\rangle$ and $|{\rm g}\rangle$ by $n_{\rm e}$ and $n_{\rm g}$, respectively, then it follows from eqs 11–13 that they obey the set of equations

$$\frac{{\rm d}n_{\rm e}}{{\rm d}t} = -A_{\rm e}n_{\rm e} + A_{\rm g}n_{\rm g} \tag{15}$$

$$\frac{{\rm d}n_{\rm g}}{{\rm d}t} = -A_{\rm g}n_{\rm g} + A_{\rm e}n_{\rm e} \tag{16}$$

and they are subject to the constraint $n_{\rm e} + n_{\rm g} = 1$. The solution for $n_{\rm e}(t)$ is

$$n_{\rm e}(t) = \frac{1}{A_{\rm e} + A_{\rm g}}\{A_{\rm g} + {\rm e}^{-(A_{\rm e}+A_{\rm g})t}([A_{\rm e} + A_{\rm g}]n_{\rm e}(0) - A_{\rm g})\} \tag{17}$$

given the initial value $n_{\rm e}(0)$. Then $n_{\rm g}(t) = 1 - n_{\rm e}(t)$. The steady-state populations are found to be

$$n_{\rm e}(\infty) = \frac{A_{\rm g}}{A_{\rm e} + A_{\rm g}},\quad n_{\rm g}(\infty) = \frac{A_{\rm e}}{A_{\rm e} + A_{\rm g}} \tag{18}$$

showing that the excited state $|{\rm e}\rangle$ acquires a finite population. Such a steady-state population can never be obtained for a molecule near a linear medium, since spontanous decay will eventually leave any molecule in the ground state.[15] Here, effective four-wave mixing at the site of the molecule leads to spontaneous excitation, with the necessary energy provided by the pump beams propagating through the crystal.

Equation 11 can also be solved for the coherence between the levels, with the result

$$\langle{\rm e}|\rho(t)|{\rm g}\rangle = \langle{\rm e}|\rho(0)|{\rm g}\rangle{\rm e}^{-{\rm i}\omega_{\rm o}t-(1/2)(A_{\rm e}+A_{\rm g})t} \tag{19}$$

For $t \rightarrow \infty$ this coherence vanishes, and the population of the levels has the form of a thermal distribution. With direct optical pumping of the molecule, as a means of creating a steady-state population in the upper level, there would be a finite steady-state coherence remaining between the levels. This would affect possible molecular reactions, since the two levels do not evolve independently due to this coherence. In excitation by means of a PC, there is no coupling between the time evolution of the populations and the coherence, so that at all times the molecule is effectively in a thermal-equilibrium type of state.

5. Two-Level Atom

The perpendicular and parallel components of the dipole operator $\vec{\mu}$ contribute differently to the Einstein coefficients A_e and A_g, because $f(\omega_o)_\perp$ is not equal to $f(\omega_o)_\parallel$, in general. However, their contributions are additive, as in eq 14, resembling a situation of spherical symmetry. The difference between $f(\omega_o)_\perp$ and $f(\omega_o)_\parallel$ can be revealed by considering an atom, rather than a molecule, near the surface of the PC. Let the excited state and ground state have angular momenta j_e and j_g, respectively, and let the transition be dipole allowed. Then the excited state and ground state are $(2j_e + 1)$- and $(2j_g + 1)$-fold degenerate, respectively, and the sublevels are labeled by their magnetic quantum numbers m_e and m_g, respectively. The generalization of eq 13 for the relaxation operator Γ can be expressed in terms of the dipole-allowed atomic raising operator

$$d_q = \sum_{m_e, m_g} (j_g m_g 1 q | j_e m_e) |j_e m_e\rangle\langle j_g m_g|, \quad q = 0, \pm 1 \tag{20}$$

with $(j_g m_g 1 q | j_e m_e)$ a Clebsch–Gordan coefficient. We find

$$\Gamma\rho = \sum_q G_q^e \{d_q d_q^+ \rho + \rho d_q d_q^+ - 2 d_q^+ \rho d_q\} + \sum_q G_q^g \{d_q^+ d_q \rho + \rho d_q^+ d_q - 2 d_q \rho d_q^+\} \tag{21}$$

in terms of the parameters

$$G_q^e = |\langle j_e \| \mu \| j_g \rangle|^2 f(\omega_o)_q, \quad G_q^g = |\langle j_e \| \mu \| j_g \rangle|^2 f(\omega_o)_q \tag{22}$$

and with $f(\omega)_o = f(\omega)_\perp$ and $f(\omega)_{\pm 1} = f(\omega)_\parallel$.

From eqs 21 and 11 we can now derive the rate equations for the populations of the magnetic sublevels. When we write $\langle m_e \rangle \equiv \langle j_e m_e | \rho | j_e m_e \rangle$ for the population of level $|j_e m_e\rangle$ and similarly $\langle m_g \rangle$ for the populations of the ground levels, we obtain

$$\frac{d\langle m_e \rangle}{dt} = -A_{m_e} \langle m_e \rangle + 2 \sum_{m_g, q} G_q^g (j_g m_g 1 q | j_e m_e)^2 \langle m_g \rangle \tag{23}$$

$$\frac{d\langle m_g \rangle}{dt} = -A_{m_g} \langle m_g \rangle + 2 \sum_{m_e, q} G_q^e (j_g m_g 1 q | j_e m_e)^2 \langle m_e \rangle \tag{24}$$

The Einstein coefficients for the magnetic sublevels are defined by

$$A_{m_e} = 2 \sum_{m_g, q} G_q^e (j_g m_g 1 q | j_e m_e)^2 \tag{25}$$

$$A_{m_g} = 2 \sum_{m_e, q} G_q^g (j_g m_g 1 q | j_e m_e)^2 \tag{26}$$

These parameters are the inverse lifetimes of the sublevels, and obviously they depend on the magnetic quantum number. This implies, for instance, that in the steady state the populations of the various sublevels might be different, a situation that cannot occur with spherical symmetry (unless $f(-\omega_o)_q \equiv 0$, meaning that there is no excitation). In the case of spherical symmetry, like for an atom in free space and only black-body excitation, the Einstein coefficients simplify to

$$A_{m_e} = 2 |\langle j_e \| \mu \| j_g \rangle|^2 f(\omega_o) \tag{27}$$

$$A_{m_g} = 2 \frac{2j_e + 1}{2j_g + 1} |\langle j_e \| \mu \| j_g \rangle|^2 f(-\omega_o) \tag{28}$$

where now $f(\omega)$ is independent of q. This shows that then A_{m_e} and A_{m_g} are independent of the magnetic quantum numbers. The slight asymmetry between the two expressions is due to the fact that both Einstein coefficients are expressed in terms of the same reduced matrix element $\langle j_e \| \mu \| j_g \rangle$. With the relation[16]

$$\frac{2j_e + 1}{2j_g + 1} |\langle j_e \| \mu \| j_g \rangle|^2 = |\langle j_g \| \mu \| j_e \rangle|^2 \tag{29}$$

the expression for A_{m_g} becomes

$$A_{m_g} = 2 |\langle j_g \| \mu \| j_e \rangle|^2 f(-\omega_o) \tag{30}$$

in the case of spherical symmetry. The Einstein coefficients for the magnetic sublevels have the property

$$A_{m_e} = A_{-m_e}, \quad A_{m_g} = A_{-m_g} \tag{31}$$

The Einstein coefficient A_{m_e} from eq 25 is a sum over at most three terms due to the fact that the Clebsch–Gordan coefficients can only be nonzero for $m_g + q = m_e$, with $q = -1, 0, 1$. From eq 24 it follows that the term $2G_q^e (j_g m_g 1 q | j_e m_e)^2$ is the rate constant for the transition $|j_e m_e\rangle \rightarrow |j_g m_g\rangle$. This factor is called the branching ratio for level $|j_e m_e\rangle$, and the sum over all ground levels is A_{m_e}. Therefore, A_{m_e} is the rate constant for spontaneous decay of level $|j_e m_e\rangle$ irrespective of the final state. Similarly, $2G_q^g (j_g m_g 1 q | j_e m_e)^2$ is the rate constant for spontaneous excitation in the transition $|j_g m_g\rangle \rightarrow |j_e m_e\rangle$ and the sum is A_{m_g}.

The coherences can be evaluated explicitly, and in analogy to eq 19 we now find

$$\langle j_e m_e | \rho(t) | j_g m_g \rangle = \langle j_e m_e | \rho(0) | j_g m_g \rangle e^{-i\omega_o t - (1/2)(A_{m_e} + A_{m_g})t} \tag{32}$$

showing that the coherence between any pair of upper and lower levels evolves independently and vanishes in the steady state.

6. No Excitation

Without spontaneous excitation, like near a linear medium, we have $G_q^g = 0$, and the solution of eq 23 is immediately found to be

$$\langle m_e(t) \rangle = \langle m_e(0) \rangle e^{-A_{m_e} t} \tag{33}$$

When we substitute this into eq 24, this equation can also be integrated, with the result

$$\langle m_g(t) \rangle = \langle m_g(0) \rangle + 2 \sum_{m_e, q} \langle m_e(0) \rangle G_q^e (j_g m_g 1 q | j_e m_e)^2 \frac{1 - e^{-A_{m_e} t}}{A_{m_e}} \tag{34}$$

The steady-state solution becomes

$$\langle m_e \rangle = 0 \tag{35}$$

$$\langle m_g \rangle = \langle m_g(0) \rangle + 2 \sum_{m_e, q} G_q^e (j_g m_g 1 q | j_e m_e)^2 \frac{\langle m_e(0) \rangle}{A_{m_e}} \tag{36}$$

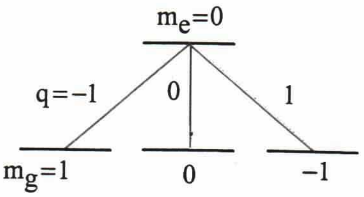

Figure 4. Schematic diagram of an atom with angular momentum quantum numbers $j_e = 0$ and $j_g = 1$. The dipole selection rules permit transitions with $m_g + q = m_e$, and these are indicated by dashed lines. Here, all transitions are allowed.

It appears that this long-time solution depends on the initial state and is therefore not unique.

7. Steady-State Solutions for the Two-Level System

If the steady-state limit exists for the density matrix, then it must hold that

$$\frac{d\langle m_e\rangle}{dt} = \frac{d\langle m_g\rangle}{dt} = 0 \tag{37}$$

which simplifies eqs 23 and 24 to

$$A_{m_e}\langle m_e\rangle = 2\sum_{m_g,q} G^g_q (j_g m_g 1 q|j_e m_e)^2 \langle m_g\rangle \tag{38}$$

$$A_{m_g}\langle m_g\rangle = 2\sum_{m_e,q} G^e_q (j_g m_g 1 q|j_e m_e)^2 \langle m_e\rangle \tag{39}$$

a homogeneous set of $2(j_e + j_g + 1)$ equations. With eq 31 and the symmetry properties of Clebsch−Gordan coefficients, we can then show that

$$\langle m_e\rangle = \langle -m_e\rangle, \quad \langle m_g\rangle = \langle -m_g\rangle \tag{40}$$

which reduces the number of equations to $j_e + j_g + 1$. The dependency of the set is lifted by the normalization

$$\sum_{m_e}\langle m_e\rangle + \sum_{m_g}\langle m_g\rangle = 1 \tag{41}$$

When we sum eqs 38 and 39 over m_e and m_g, respectively, they both yield the relation

$$\sum_{m_e} A_{m_e}\langle m_e\rangle = \sum_{m_g} A_{m_g}\langle m_g\rangle \tag{42}$$

expressing that the total decay rate equals the total excitation rate.

a. $j_e = 0, j_g = 1$. For $j_e = 0$ we have $m_e = 0$, and the excited state is the nondegenerate state $|00\rangle$. We indicate its population by $\langle e\rangle$. Suppose it is coupled to a ground state with $j_g = 1$, which has three substates, as illustrated in Figure 4. The Clebsch−Gordan coefficients for the three transitions are $\pm 1/\sqrt{3}$, which gives for the Einstein coefficients of the ground state $A_{m_g} = {}^2/_3 G^g_q$, with $q = -m_g$, according to eq 26. Since $m_g + q = 0$ for every transition, the right-hand side of eq 39 has only one term, and the equation reduces to

$$G^g_q\langle m_g\rangle = G^e_q\langle e\rangle \tag{43}$$

with $q = -m_g$. Then we introduce the two parameters

$$r_q = \frac{G^g_q}{G^e_q} \tag{44}$$

with $q = \perp = 0$ and $q = \parallel = \pm 1$. Equation 43 together with the normalization 41 then determine the solution, which is found to be

$$\langle e\rangle = \frac{r_\parallel r_\perp}{r_\parallel r_\perp + 2r_\perp + r_\parallel} \tag{45}$$

$$\langle \pm 1\rangle = \frac{r_\perp}{r_\parallel r_\perp + 2r_\perp + r_\parallel} \tag{46}$$

$$\langle 0\rangle = \frac{r_\parallel}{r_\parallel r_\perp + 2r_\perp + r_\parallel} \tag{47}$$

The solution for the populations depends only on the ratio parameters r_q, which can be written as

$$r_q = \frac{f(-\omega_o)_q}{f(\omega_o)_q} \tag{48}$$

because of eq 22. This shows that the steady-state level populations are independent of the reduced dipole matrix element $\langle j_e\|\mu\|j_g\rangle$ and only depend on the field correlation functions $f(\omega)_q$. Moreover, with eq 8, r_q can be expressed as

$$r_q = \frac{y_q}{1 + y_q} \tag{49}$$

showing that the populations are determined entirely by the two parameters y_q, as given by eqs 9 and 10. These parameters, in turn, only depend on the Fresnel reflection coefficients for the phase-conjugating medium. The Einstein coefficient for the excited level is

$$A_{m_e} = {}^2/_3(2G^e_\parallel + G^e_\perp) \tag{50}$$

and it can be verified that this leads to an identity for eq 38.

b. $j_e = 1, j_g = 0$. For $j_e = 1$, $j_g = 0$ we have three excited states and one ground state. We shall indicate their steady-state populations by $\langle 1\rangle$, $\langle 0\rangle$, $\langle -1\rangle$, and $\langle g\rangle$, in obvious notation. The Einstein coefficients for the excited levels are $A_{m_e} = 2G^e_q$, with $q = m_e$, and for the ground state we find

$$A_{m_g} = 2(2G^g_\parallel + G^g_\perp) \tag{51}$$

For the populations of the levels we now obtain

$$\langle g\rangle = \frac{1}{2r_\parallel + r_\perp + 1} \tag{52}$$

$$\langle \pm 1\rangle = \frac{r_\parallel}{2r_\parallel + r_\perp + 1} \tag{53}$$

$$\langle 0\rangle = \frac{r_\perp}{2r_\parallel + r_\perp + 1} \tag{54}$$

expressed again in terms of the parameters r_q. The populations of the excited levels are different and determined uniquely by the parameters y_q.

c. $j_e = j_g = 1/2$. For the case of $j_e = j_g = 1/2$, both the ground state and the excited level are 2-fold degenerate. There are now four possible transitions, as illustrated in Figure 5. The relevant Clebsch−Gordan coefficients are $\mp\sqrt{2/3}$ for $q = \pm 1$ and $\pm 1/\sqrt{3}$ for $q = 0$, which gives for the Einstein coefficients

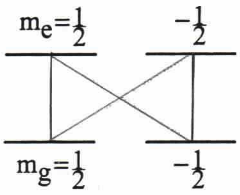

Figure 5. Diagram of an atom with $j_e = j_g = 1/2$ and its allowed transitions.

$$A_{m_\alpha} = {}^2/_3(2G_\parallel^\alpha + G_\perp^\alpha), \quad \alpha = \mathrm{e, g} \tag{55}$$

When we indicate the population of each excited level by ⟨e⟩, and similarly by ⟨g⟩ for the ground state, then eq 42 gives $A_{m_e}\langle \mathrm{e}\rangle = A_{m_g}\langle \mathrm{g}\rangle$, and the normalization becomes $2\langle \mathrm{e}\rangle + 2\langle \mathrm{g}\rangle = 1$. We then immediately find

$$\langle \mathrm{e}\rangle = \frac{1}{2}\frac{2G_\parallel^e + G_\perp^e}{2G_\parallel^e + G_\perp^e + 2G_\parallel^g + G_\perp^g} \tag{56}$$

and for ⟨g⟩ we exchange e and g in this expression. From eq 22 it follows that the dependence on the reduced matrix element $\langle j_e\|\mu\|j_g\rangle$ cancels out, so that the populations are again determined by the field correlation function only and thereby by the parameters y_q only.

8. Conclusions

It was shown that an atom or molecule near the surface of a PC can excite spontaneously, leading to a permanent population of the excited electronic state. It is essential that the PC is of the four-wave mixing type, rather than a photorefractive device, since it is the four-wave mixing process that converts the pump photons into phase-conjugated fluorescence. During this three-photon process, as shown in Figure 3, the atom makes effectively a transition from the ground state to the excited state. After this process, the atom decays back to the ground state under emission of an ordinary fluorescent photon. This cycle repeats continuously, leading to a finite population of the excited level. On the other hand, it turns out that the lifetime of the excited level decreases, as compared to its value in empty space, but this only affects the transient behavior.

In the steady-state equations (38) and (39) every term is proportional to $|\langle j_e\|\mu\|j_g\rangle|^2$, and therefore this factor cancels. This implies that the steady-state populations are independent of the atomic dipole moment and are entirely determined by the properties of the PC, through the Fresnel reflection coefficients. These coefficients can be controlled experimentally, because they depend (in a complicated way) on the pump intensity, frequency, and polarization. The distribution of population over the magnetic sublevels, in the case of degeneracy, is therefore determined by the Fresnel coefficients. In addition, this distribution has a geometric dependence on Clebsch−Gordan coefficients, which determine the branching ratios for magnetic sublevels. The evolution toward this steady state has a time scale on the order of $1/A_{m_{\mathrm{e,g}}}$, so that the relaxation time is inversely proportional to $|\langle j_e\|\mu\|j_g\rangle|^2$.

In contrast to spontaneous excitation near a PC, population of an excited electronic level through strong coherent optical pumping creates permanent coherences in an atom (in the steady state). Furthermore, in the weak-field limit, excited-state populations are proportional to $|\langle j_e\|\mu\|j_g\rangle|^2$ and the pump intensity. This indicates that the mechanism of spontaneous excitation is essentially different from direct optical excitation. It leaves the atom in a state resembling a thermal equilibrium state, whereas in the case of optical pumping the atom is essentially in a coupled laser-atom state, a so-called dressed state. On the other hand, incoherent optical pumping (with a broad-band laser) would also avoid the creation of coherences, so that the stationary atomic state in that case resembles the steady state near a PC. However, the excitation mechanism is rather different, and the steady-state populations depend in a different way on the controllable parameters. In this view, spontaneous excitation near a PC can be considered an alternative to common incoherent optical pumping. Even though the steady states in both methods are formally equivalent, other properties of the atom are not. For instance, near a PC an atom will continuously emit a two-line fluorescence spectrum, reflecting the occurrence of the three-photon cycle from Figure 3.

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(13) It is assumed that the molecule only has a transition dipole moment. A permanent dipole moment would not contribute to the relaxation constants. This means that $\langle \mathrm{e}|\vec{\mu}_\perp\cdot\vec{\mu}_\perp|\mathrm{e}\rangle = |\langle \mathrm{e}|\mu_z|\mathrm{g}\rangle|^2$, and a similar expression holds for the second term in eq 14.

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(15) It should be noted that the presence of black-body radiation would have the same effect, but in the visible region of the spectrum and at room temperature this effect is negligible compared to spontaneous excitation.

(16) We use the Wigner−Eckart theorem in the form $\langle j_e m_e|\mu_q|j_g m_g\rangle = (j_g m_g 1 q|j_e m_e)\langle j_e\|\mu\|j_g\rangle$.

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