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Laser field induced charge transfer: Para-nitroaniline coupled to a quantum mechanical radiation field

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Summary. We present a preliminary model for describing a solvated intramolecular charge transfer reaction coupled to a quantum mechanical radiation field. Actual calculations of energies and couplings were performed with a recently developed self-consistent reaction field response method. The representation of dressed molecular states is used for calculating state populations for various laser fields. The state populations are sensitive to the properties of the laser field.

Key words: Charge transfer – Laser field – Quantum mechanical radiation field

1. Introduction

In this article, we consider interactions between molecules and quantized fields, in particular, strong fields. The effects of strong light fields on atoms has been studied both experimentally and theoretically [1–5], but few have attempted to describe fully the more complicated problem of molecules in strong fields, especially theoretically [6–17], and a systematic treatment is lacking. Most of the studies have been performed with radiation in the infrared region [8, 18, 15, 19–21, 11]. A greater number of degrees of freedom exist in the molecular problem (compared to the atomic one), and the dynamics resulting from the laser–molecule interaction can be quite complex. The observed results and the models for describing them depend on several parameters, namely, the intensity, whether the laser is pulsed or cw, and if pulsed, on the shape and duration of the pulse. However, in experiments at high intensities it can be difficult to characterize precisely the laser pulses [7].

The examination of such systems is relevant for understanding and controlling phenomena such as chemical reactions in solution by utilizing laser irradiation, giving insight into the relevant mechanisms in a problem as complex as this.

Within quantum optics, atomic systems interacting with a photon field have been studied in great detail and interesting effects have been postulated and demonstrated such as laser cooling of atoms below the single photon recoil limit, resonance fluorescence, and photon correlations in intense resonant or quasi-resonant laser beams [4, 22]. As an initial investigation of the effects of radiation fields on molecules we focus on a two-level molecular system and calculate from first principles the necessary quantities for investigating the evolution of the molecular system in the presence of radiation fields.

We will study a solvated molecular system undergoing an intramolecular charge transfer transition induced by interactions with a quantum mechanical radiation field. The monochromatic laser field is resonant or quasi-resonant with the charge transfer transition. The reason for utilizing a quantum mechanical radiation field is centered around the possibility of describing effects such as vacuum fluctuations, spontaneous emission, quantum beats and laser linewidths.

The molecular system interacts with the outer solvent and the laser field plus the reservoir of initially empty modes of the quantum mechanical radiation field. The molecular system is enclosed by a spherical cavity and immersed in a dielectric medium that is characterized by two polarization vectors, the inertial and the optical polarization vectors. The vector sum of the two polarization vectors yields the total polarization vector of the dielectric medium. The optical polarization vector is related to the electronic response of the dielectric medium to the presence of the molecular charge distribution within the solvent cavity, while the inertial polarization vector is related to the combined molecular motion and vibrational response of the dielectric medium to the presence of the molecular charge distribution within the solvent cavity. The optical response of the medium is given by the optical dielectric constant of the medium, and the total response by the static dielectric constant of the medium. The optical polarization vector is assumed to follow instantaneously the changes in the molecular charge distribution, whereas the inertial polarization has a characteristic relaxation time when responding to a sudden change in the molecular charge distribution of the solute.

The molecular system coupled to the outer solvent is first coupled to the radiation mode that initially is occupied with photons of a specific energy and polarization. This radiation mode is termed the laser mode. The solvated molecular system is also coupled to a radiation reservoir of initially empty photon modes. The electromagnetic radiation field is confined in an electromagnetic cavity having the volume V.

Our investigations are in the mesoscopic region which bridges the gap between a microscopic and a macroscopic system. A microscopic system could, for example, consist of a molecule interacting with a few photons in a microcavity. A macroscopic system would contain well over 100 photons. A mesoscopic system involves therefore tens of photons [3].

Schematically, we write the Hamiltonian for the total system as

$$H = H_{\text{mol}} + H_{\text{sol}} + W_{\text{mol-sol}} + H_{\text{laser}} + W_{\text{mol-laser}} + H_{\text{res}} + W_{\text{mol-res}}, \qquad (1)$$

where H_{mol}, H_{sol}, H_{laser} and H_{res} are the Hamiltonian for the molecular system, the solvent, the laser and the electromagnetic reservoir, and where $W_{\text{mol-sol}}$, $W_{\text{mol-laser}}$ and $W_{\text{mol-res}}$ are the coupling terms between the molecular compound and the solvent, the laser and the radiation reservoir, respectively. Within the quantum mechanical description of the electromagnetic radiation field, it is not possible to treat the radiation field as if it were composed of separate laser and reservoir radiation fields. However, we use it as a schematic representation of the system from which it is easy to reach the limit of a classical laser field. We have chosen to examine the molecule, para-nitroaniline (PNA), in solution and treat it as a two-level system (the energy difference between the two levels in solution with no laser field is 0.1805 a.u. or 1.188×10^{15} Hz), the two levels being the ground state and the first excited state, the charge transfer state. The validity of the assumption of the representation of the PNA molecule as a two-level system has been demonstrated in the case of hyperpolarizability of PNA [23, 24], both in the gas phase and in solution.

The PNA molecule is placed in a radiation field described by a quantum mechanical vector potential and associated electromagnetic fields. The field intensity is varied along with the frequency of the electromagnetic fields, and the effects of these variations on the evolution of the molecular system are considered. Different types of variations of the electromagnetic fields will be investigated, specifically pulse durations, time delay between pulses, detuning and field intensities.

Using a response method [25] we calculate the necessary energies and coupling elements needed for solving the evolution equations of the combined system consisting of solvated PNA and electromagnetic fields. The PNA molecule is solvated by including a dielectric medium, represented by two polarization vectors, the inertial and the optical polarization vector. In this way we simulate the effects of the outer solvent on the PNA molecule.

2. The model

The evolution of the total system, i.e., the molecular system, the radiation field and the outer solvent, is governed by Ehrenfest's equation

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle = \langle [A, H]\rangle, \tag{2}$$

where the expectation values of the operator $\langle A\rangle$ and the commutator between the operator and the Hamiltonian for the total system $\langle [A, H]\rangle$ are given by

$$\langle A\rangle = \mathrm{Tr}[A\rho] \tag{3}$$

$$\langle [A, H]\rangle = \mathrm{Tr}\{[A, H]\rho\} \tag{4}$$

and ρ is the density operator of the total system. The power of Ehrenfest's equation has been demonstrated in numerous investigations of how systems evolve in time [26–28]. The time evolution of the system is monitored through the change in the expectation values of suitable operators.

The following manifold of operators is of interest in our case:

$$\{a_r^\dagger a_s, a_s^\dagger a_r, b_k^\dagger, b_k, B_n^\dagger, B_n, d_{p\lambda}^\dagger, d_{p\lambda}\},$$

where r is not necessarily different from s. The operations $a_r^\dagger a_s$, $a_s^\dagger a_r$ operate on the electronic degrees of freedom and the operator $a_r^\dagger$ (a_r) creates (destroys) an electron in level r. The combined effect of two of these operators, for example, $a_r^\dagger a_s$, is to move the electron from level r to level s. The operators $b_k^\dagger$, b_k operate on the degrees of freedom of the outer medium, i.e., the condensed phase; the operator $b_k^\dagger$ (b_k) creates (destroys) a phonon in the kth mode in the condensed phase. These operators are grouped into two classes, one class corresponding to the modes in the dielectric medium responsible for the optical polarization vector (the high-frequency modes, denoted by the superscript *high*) and the other class corresponding to all other modes (the low-frequency modes, denoted by the superscript *low*, responsible for the inertial polarization). The operators $B_n^\dagger, B_n$ operate on the intramolecular degrees of freedom of the molecule; the operator $B_n^\dagger$ (B_n) creates (destroys) a vibration in the nth vibrational mode of the molecule. The last set of operators $d_{p\lambda}^\dagger$, $d_{p\lambda}$ operates on the photon degrees of freedom, i.e., the radiation field. The operator $d_{p\lambda}^{\dagger}$ ($d_{p\lambda}$) creates (destroys) a photon in the radiation field with momentum vector $\boldsymbol{p}$ and polarization λ.

The equations of motion for this manifold of operators are given by

$$\mathrm{i}\frac{\partial}{\partial t}\langle a_r^{\dagger} a_s \rangle = \langle [a_r^{\dagger} a_s, H] \rangle, \tag{5}$$

$$\mathrm{i}\frac{\partial}{\partial t}\langle b_k^{\text{high}} \rangle = \langle [b_k^{\text{high}}, H] \rangle, \tag{6}$$

$$\mathrm{i}\frac{\partial}{\partial t}\langle b_k^{\text{low}} \rangle = \langle [b_k^{\text{low}}, H] \rangle, \tag{7}$$

$$\mathrm{i}\frac{\partial}{\partial t}\langle B_n \rangle = \langle [B_n, H] \rangle, \tag{8}$$

$$\mathrm{i}\frac{\partial}{\partial t}\langle d_{p\lambda} \rangle = \langle [d_{p\lambda}, H] \rangle. \tag{9}$$

We consider the total system to consist of a molecule immersed in a condensed phase, a solution, and interacting with a radiation field. The molecular degrees of freedom are represented by the electronic and vibrational degrees of freedom of the molecule. A phonon bath represents the degrees of freedom of the condensed phase. The radiation field is given by the vacuum photon field and an applied laser field. The vacuum field gives rise to vacuum fluctuations and manifests itself through spontaneous emission of photons by excited molecular states.

The Hamiltonian for the total system is given as

$$H = H_{\mathrm{e}} + H_{\mathrm{v}} + W_{\mathrm{e-v}} + H_{\mathrm{s}} + W_{\mathrm{o-s}} + H_{\mathrm{r}} + W_{\mathrm{o-r}}. \tag{10}$$

The first term, H_{e}, is the many-electronic Hamiltonian for the electronic degrees of freedom for the molecular system. The second term, H_{v}, is the Hamiltonian for the intramolecular degrees of freedom contained in the molecular system. The third term, $W_{\mathrm{e-v}}$, is the vibronic coupling operator, and describes the coupling between the electronic and intramolecular degrees of freedom. The fourth term, H_{s}, is the Hamiltonian for the outer solvent. The fifth term, $W_{\mathrm{o-s}}$, is the interaction operator taking into account the electrostatic interactions between the molecular charge distribution and the outer solvent. The sixth term, H_{r}, is the Hamiltonian for the radiation field. The last term, $W_{\mathrm{o-r}}$, takes care of interactions between the radiation field and the molecular system. The radiation field is treated quantum mechanically and no separation of the laser mode and reservoir modes is made.

The many-electron Hamiltonian in second quantization is written as

$$H_{\mathrm{e}} = \sum_{r,s} h_{rs} a_r^{\dagger} a_s + \frac{1}{2} \sum_{r,s,t,u} (rs|tu) a_r^{\dagger} a_t^{\dagger} a_u a_s, \tag{11}$$

where we sum over molecular orbitals. The integrals h_{rs} and $(rs|tu)$ are the usual one- and two-electron integrals.

The intramolecular degrees of freedom are described by the harmonic approximation and the Hamiltonian for the intramolecular modes is given by

$$H_{\mathrm{v}} = \sum_{n} \Omega_n B_n^{\dagger} B_n, \tag{12}$$

where $\{\Omega_n\}$ and $\{B_n^\dagger, B_n\}$ are the frequencies and the boson operators for the modes, respectively. The boson operators obey the rules of ordinary boson algebra.

The vibronic coupling operator W_{e-v} is obtained by performing a first-order Taylor expansion of the many-electron Hamiltonian in terms of the intramolecular degrees of freedom around a given intramolecular configuration. This operator is written as

$$\begin{aligned} W_{e-v} &= \sum_n \left(\frac{\partial H_e(\{r_i\}, \{Q_n\}, \{k\})}{\partial Q_n} \right)_{Q_n = Q_n^0} (Q_n - Q_n^0) \\ &= \sum_n A_n H_n^{(1)} (B_n^\dagger + B_n), \end{aligned} \tag{13}$$

where $\{r_i\}$, $\{Q_n\}$ and $\{k\}$ represent the molecular system (involving the electronic degrees of freedom $\{r_i\}$ and nuclear degrees of freedom $\{Q_n\}$ of the molecular compounds) and the bulk solvent (containing both high- and low-frequency modes $\{k\}$), and where

$$H_n^{(1)} = \left(\frac{\partial H_e(\{r_i\}, \{Q_n\}, \{k\})}{\partial Q_n} \right)_{Q_n = Q_n^0} \tag{14}$$

$$\begin{aligned} (Q_n - Q_n^0) &= \frac{B_n^\dagger + B_n}{\sqrt{2M_n \Omega_n}} \\ &= \Delta Q_n (B_n^\dagger + B_n). \end{aligned} \tag{15}$$

M_n is the reduced mass of the mode n, ΔQ_n the zero point displacement along the mode n, and the coupling factor $A_n = \sqrt{2M_n \Omega_n}$.

The solution is represented by the following Hamiltonian:

$$H_s = \sum_k \omega_k b_k^\dagger b_k, \tag{16}$$

where $\{\omega_k\}$ and $\{b_k^\dagger, b_k\}$ are the frequencies and the boson operators for the modes, respectively, and the boson operators satisfy ordinary boson algebra.

The interaction operator representing the electrostatic interactions between the molecular charge distribution and the solution is given by

$$W_{o-s} = \sum_k \{\alpha_k M_k b_k^\dagger + \alpha_k^* M_k^\dagger b_k\}, \tag{17}$$

where α_k, α_k^* are parameters describing the dielectric interaction between the molecular charge distribution and the outer medium. The molecular charge distribution is expanded through a multipole expansion and is represented by the charge moment operators $\{M_k^\dagger, M_k\}$.

The radiation field, the combined laser field and vacuum radiation field, is represented by the following Hamiltonian:

$$H_r = \sum_{p\lambda} pc\, d_{p\lambda}^\dagger d_{p\lambda}, \tag{18}$$

where c is the speed of light and $p = |\boldsymbol{p}|$.

The interaction between the photons and the molecule is represented by [26]

$$W_{o-r} = -\frac{1}{c} \int \boldsymbol{A}(\boldsymbol{r}) \cdot \boldsymbol{J}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}, \tag{19}$$

where $A(\boldsymbol{r})$ is the vector potential of the radiation field in the Coulomb gauge and $J(\boldsymbol{r})$ is the current density operator of the molecular system.

The vector potential written in the Linderberg–Öhrn notation is given by [26]

$$A(\boldsymbol{r}) = \sum_{p\lambda} \sqrt{\frac{2\pi c}{pV}} [d_{p\lambda}^{\dagger} - (-1)^{\lambda} d_{p\lambda}] \boldsymbol{n}(\boldsymbol{p}) \mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} \tag{20}$$

and the molecular current density operator is given by

$$\begin{aligned} j_{\lambda}(\boldsymbol{p}) &= \boldsymbol{n}(\boldsymbol{p}) \cdot \int \mathrm{d}\boldsymbol{r} \boldsymbol{J}(\boldsymbol{r}) \mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} \\ &= \sum_{uv} (u|\, j_{\lambda}(\boldsymbol{p})|v) a_u^{\dagger} a_v \end{aligned} \tag{21}$$

where the summation is over all molecular orbitals, u, v. This allows us to rewrite the molecule–radiation field interaction operator as

$$W_{\mathrm{o-r}} = -\sum_{p\lambda} \sqrt{\frac{2\pi}{cpV}} [d_{p\lambda}^{\dagger} j_{\lambda}(\boldsymbol{p}) + d_{p\lambda} j_{\lambda}^{\dagger}(\boldsymbol{p})]. \tag{22}$$

The time-dependent statistical density operator is given by the direct product

$$\rho_{\mathrm{tot}}(t) = \rho_{\mathrm{m}}(t) \times \rho_{\mathrm{s}}(t) \times \rho_{\mathrm{r}}(t) \tag{23}$$

where the statistical operators $\rho_{\mathrm{m}}(t)$, $\rho_{\mathrm{s}}(t)$ and $\rho_{\mathrm{r}}(t)$ describe the molecular system, the outer solvent and the radiation field, respectively,

$$\rho_{\mathrm{s}}(t) = \mathrm{e}^{-\mathrm{i}S(t)} \rho_{\mathrm{s}}(0) \mathrm{e}^{\mathrm{i}S(t)} \tag{24}$$

where $\rho_{\mathrm{s}}(0)$ is the statistical density operator for the outer medium when uncoupled from the molecular charge distribution, and is assumed to be a Boltzmann distribution at temperature T:

$$\rho_{\mathrm{s}}(0) = \frac{\mathrm{e}^{-\beta \sum_k \omega_k b_k^{\dagger} b_k}}{\mathrm{Tr}\left[\mathrm{e}^{-\beta \sum_k \omega_k b_k^{\dagger} b_k}\right]}. \tag{25}$$

A unitary transformation takes account of the changes in the statistical density operator for the outer solvent due to interactions between the molecular charge distribution and the outer medium. The transformation operator S is given as

$$S(t) = \sum_k (X_k(t) b_k^{\dagger} + X_k^{*}(t) b_k). \tag{26}$$

The time-dependent parameters $X_k(t)$, $X_k^{*}(t)$ have values determined by the strength of the interactions between the molecular charge distribution and the outer solvent.

The radiation field is represented by the following density operator:

$$\rho_{\mathrm{r}}(t) = |r(t)\rangle\langle r(t)| \tag{27}$$

where

$$|r(t)\rangle = \mathrm{e}^{\mathrm{i}Z(t)} \prod_{p\lambda} \frac{(d_{p\lambda}^{\dagger})^{n_{p\lambda}}}{\sqrt{(n_{p\lambda})!}} |\mathrm{vac}\rangle, \tag{28}$$

in which the unitary transformation is given as

$$Z(t) = \sum_{p\lambda} (\xi_{p\lambda}(t) d_{p\lambda}^{\dagger} + \xi_{p\lambda}^{*}(t) d_{p\lambda}), \tag{29}$$

where $|\mathrm{vac}\rangle$ is the vacuum state for the electromagnetic field and $n_{p\lambda}$ is the occupation number for a state of the electromagnetic field with wave vector $\boldsymbol{p}$ and polarization λ. The unitary transformation takes care of the dynamical interaction between the molecular system and the electromagnetic field. For the situation where only electron–photon interactions are considered, we can write the total energy for a given electronic state, $|\Theta\rangle$, as a function of the parameters $\xi_{p\lambda}$ and $\xi'_{p\lambda}$ [29–31]

$$\begin{aligned} E(\xi_{p\lambda}) = {} & \langle \Theta | H_{\mathrm{e}} | \Theta \rangle - \sum_{p\lambda} pc\, \xi_{p\lambda}(t) \xi'_{p\lambda}(t) \\ & - \mathrm{i} \sum_{p\lambda} \sqrt{\frac{2\pi}{pcV}} \{\xi_{p\lambda}(t) \langle \Theta | j_{\lambda}^{\dagger}(\boldsymbol{p}) | \Theta \rangle \\ & - \xi'_{p\lambda}(t) < \Theta | j_{\lambda}(\boldsymbol{p}) | \Theta \rangle\}. \end{aligned} \tag{30}$$

By requiring the energy functional to be stationary with respect to variations in the parameters $\xi_{p\lambda}(t)$ and $\xi'_{p\lambda}(t)$ we obtain

$$\begin{aligned} E(\xi_{p\lambda}) = {} & \langle \Theta | H_{\mathrm{c}} | \Theta \rangle \\ & - \sum_{p\lambda} \left(\frac{2\pi}{p^2 c^2 V} \right) \langle \Theta | j_{\lambda}^{\dagger}(\boldsymbol{p}) | \Theta \rangle \langle \Theta | j_{\lambda}(\boldsymbol{p}) | \Theta \rangle, \end{aligned} \tag{31}$$

which shows the level shift due to the emission and absorption of virtual photons.

The statistical density operator for the molecular system is given by

$$\rho_{\mathrm{m}}(t) = |\Phi\rangle\langle\Phi| \times \rho_{\mathrm{v}}(t), \tag{32}$$

where $|\Phi\rangle$ is the electronic wave function for the molecular system and $\rho_{\mathrm{v}}(t)$ is the statistical density operator for the intramolecular degrees of freedom for the molecular compounds inside the solvent cavity. The latter is given as

$$\rho_{\mathrm{v}}(t) = \mathrm{e}^{-iV(t)} \rho_{\mathrm{v}}(0) \mathrm{e}^{iV(t)}, \tag{33}$$

where $\rho_{\mathrm{v}}(0)$ is the statistical density operator for a Boltzmann distribution at temperature T describing the uncoupled intramolecular vibrations

$$\rho_{\mathrm{v}}(0) = \frac{\mathrm{e}^{-\beta} \sum_n \omega_n B_n^{\dagger} B_n}{\mathrm{Tr}\left[\mathrm{e}^{-\beta} \sum_n \omega_n B_n^{\dagger} B_n \right]}, \tag{34}$$

and the unitary transformations represented by the operator $V(t)$ change the uncoupled statistical density operator, $\rho_{\mathrm{v}}(0)$, into the vibrational states where the coupling between the electronic and nuclear degrees of freedom for the molecular system are included:

$$V(t) = \sum_n (Y_n(t) B_n^{\dagger} + Y_n^{*}(t) B_n). \tag{35}$$

The changes in the statistical density operator for the molecular vibrational modes $\rho_{\mathrm{v}}(t)$ are given by the unitary transformation; the time-dependent coupling parameters $Y_n(t)$, $Y_n^*(t)$ determine how substantial the changes are.

The evolution of the electronic operators $\{a_r^\dagger a_s, a_s^\dagger a_r\}$ depends on the expectation values of the operators $\{b_k^\dagger, b_k\}$ and $\{B_n^\dagger, B_n\}$, since

$$\begin{aligned}
\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\langle a_r^\dagger a_s\rangle &= \langle[a_r^\dagger a_s, H_{\mathrm{e}} + H_{\mathrm{v}} + W_{\mathrm{e-v}} + H_{\mathrm{s}} + W_{\mathrm{o-s}} + H_{\mathrm{r}} + W_{\mathrm{o-r}}]\rangle \\
&= \langle[a_r^\dagger a_s, H_{\mathrm{e}}]\rangle_{\mathrm{e}} + \langle[a_r^\dagger a_s, W_{\mathrm{e-v}}]\rangle_{\mathrm{e,vib}} \\
&\quad + \langle[a_r^\dagger a_s, W_{\mathrm{o-s}}]\rangle_{\mathrm{o,s}} + \langle[a_r^\dagger a_s, W_{\mathrm{o-r}}]\rangle_{\mathrm{o,r}} \\
&= \langle[a_r^\dagger a_s, H_{\mathrm{e}}]\rangle_{\mathrm{e}} + \sum_n A_n\langle[a_r^\dagger a_s, H_n^{(1)}]\rangle_{\mathrm{e}}(\langle B_n^\dagger\rangle_{\mathrm{vib}} \\
&\quad + \langle B_n\rangle_{\mathrm{vib}}) + \sum_k \alpha_k\langle[a_r^\dagger a_s, M_k]\rangle_{\mathrm{e}}\langle b_k^\dagger\rangle_{\mathrm{s}} \\
&\quad + \sum_k \alpha_k^*\langle[a_r^\dagger a_s, M_k^\dagger]\rangle_{\mathrm{e}}\langle b_k\rangle_{\mathrm{s}} \\
&\quad + \sum_{p\lambda}\sqrt{\frac{2\pi}{pcV}}\{\langle[a_r^\dagger a_s, j_\lambda(p)]\rangle_{\mathrm{e}}\langle d_{p\lambda}^\dagger\rangle_{\mathrm{r}} \\
&\quad + \langle[a_r^\dagger a_s, j_\lambda^\dagger(p)]\rangle_{\mathrm{e}}\langle d_{p\lambda}\rangle_{\mathrm{r}}\}.
\end{aligned} \tag{36}$$

The evolution of the operators for the outer medium $\{b_k^\dagger, b_k\}$, the intramolecular degrees of freedom $\{B_n^\dagger, B_n\}$ and the field operators is given by

$$\begin{aligned}
\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\langle b_k\rangle_{\mathrm{s}} &= \langle[b_k, H_{\mathrm{s}}\rangle_{\mathrm{s}} + \langle[b_k, W_{\mathrm{o-s}}]\rangle_{\mathrm{c,s}} \\
&= \langle[b_k, H_{\mathrm{s}}\rangle_{\mathrm{s}} + \sum_{k'}\langle[b_k, b_{k'}^\dagger]\rangle_{\mathrm{s}}\langle\alpha_{k'}M_{k'}\rangle_{\mathrm{e}} \\
&\quad + \sum_{k'}\langle[b_k, b_{k'}]\rangle_{\mathrm{s}}\langle\alpha_{k'}^* M_{k'}^\dagger\rangle_{\mathrm{e}},
\end{aligned} \tag{37}$$

and

$$\begin{aligned}
\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\langle B_m\rangle_{\mathrm{vib}} &= \langle[B_m, H_{\mathrm{v}}]\rangle_{\mathrm{vib}} + \langle[B_m, W_{\mathrm{e-v}}]\rangle_{\mathrm{e-vib}} \\
&= \langle[B_m, H_{\mathrm{v}}]\rangle_{\mathrm{vib}} \\
&\quad + \sum_{m'}\langle[B_m, (B_{m'}^\dagger + B_{m'})]\rangle_{\mathrm{vib}}\langle A_{m'}H_{m'}^{(1)}\rangle_{\mathrm{c}},
\end{aligned} \tag{38}$$

and finally

$$\begin{aligned}
\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\langle d_{p\lambda}\rangle_{\mathrm{r}} &= \langle[d_{p\lambda}, H_{\mathrm{r}}]\rangle_{\mathrm{r}} + \langle[d_{p\lambda}, W_{\mathrm{o-r}}]\rangle_{\mathrm{c,r}} \\
&= \langle[d_{p\lambda}, H_{\mathrm{s}}]\rangle_{\mathrm{r}} + \sum_{p'\lambda'}\sqrt{\frac{2\pi}{p'cV}}(\langle[d_{p\lambda}, d_{p'\lambda'}^\dagger]\rangle_{\mathrm{r}}\langle j_{\lambda'}(p')\rangle_{\mathrm{e}} \\
&\quad + \langle[d_{p\lambda}, d_{p'\lambda'}]\rangle_{\mathrm{r}}\langle j_{\lambda'}^\dagger(p')\rangle_{\mathrm{e}})
\end{aligned} \tag{39}$$

3. Discussion of the model

In the limit of neglecting the reservoir modes, we obtain a picture of a molecular system dressed by laser photons. The coupling of the dressed molecular system to the reservoir of the initially empty photon modes introduces radiative cascading to the dressed molecular states, see Eq. (1). We grossly simplify the quantum description of the laser field by considering a laser cavity (with a volume V) possessing only one mode (of frequency ω_{L}) containing photons. For a molecular system represented as a two-level molecule coupled to a laser field, we can transform from the states $|GS, N+1\rangle$ and $|CT, N\rangle$ into dressed molecular states. The two states $|GS, N+1\rangle$ and $|CT, N\rangle$ correspond to the molecular ground state plus $N+1$ photons and the molecular CT state plus N photons. One photon is absorbed in the $GS \rightarrow CT$ transition.

The frequency of the laser mode (ω_{L}) is detuned an amount δ from the frequency of the molecular transition (ω)

$$\delta = \omega - \omega_{\mathrm{L}}. \tag{40}$$

For resonant or quasi-resonant laser fields, the two states $|GS, N+1\rangle$ and $|CT, N\rangle$ are nearly degenerate belonging to a sub-manifold $P_N = \{|GS, N+1\rangle, |CT, N\rangle\}$ where the complete manifold is given as $\{P_N\}$ for all N. Within a given sub-manifold we perform a diagonalization of the energy expression in terms of the two states in the sub-manifold.

The eigenvalues change with the detuning of the laser field and the coupling strength between the molecular states and the laser mode. In Fig. 1 we show how the eigenvalues change according to changes in detuning and the photon number, the latter reflecting the coupling strength. Coupling to the reservoir causes photons to appear in modes that initially were empty. These are the fluorescence photons the excited molecular state emits.

4. Calculations

The energies of and transition moments between the two molecular states in the presence of the outer solvent and the electromagnetic field are calculated using the recently developed and implemented solvent response methodology [32]. In Fig. 2 we present the excitation energies and transition moments between the two states as a function of the intensity of the vector potential. The intensity of the electromagnetic vector potential and the associated electric field is proportional to the number of photons and inversely proportional to the volume of the electromagnetic cavity. These calculations are self-consistent reaction field (SCRF) response calculations using the best basis set from Ref. [23], and the flexibility and accuracy of this basis set has been proven. In addition, it has been clearly demonstrated that in order to obtain absolute polarizabilities and hyperpolarizabilities, it is necessary to employ a correlated electronic structure method. The implemented solvent response methodology allows for multi-configuration self-consistent reaction field response calculations [23, 25]. Presently, we are not concerned with electron correlation; our primary interest lies in the development and implementation of a method for solving the time evolution equations of a solvated molecular compound interacting with a quantum mechanical radiation field. The geometry of PNA is from Refs. [23, 24].

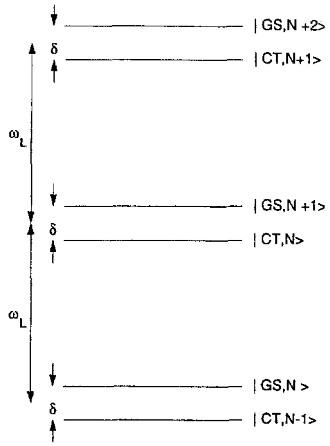

Fig. 1. The energy diagram of the dressed molecule

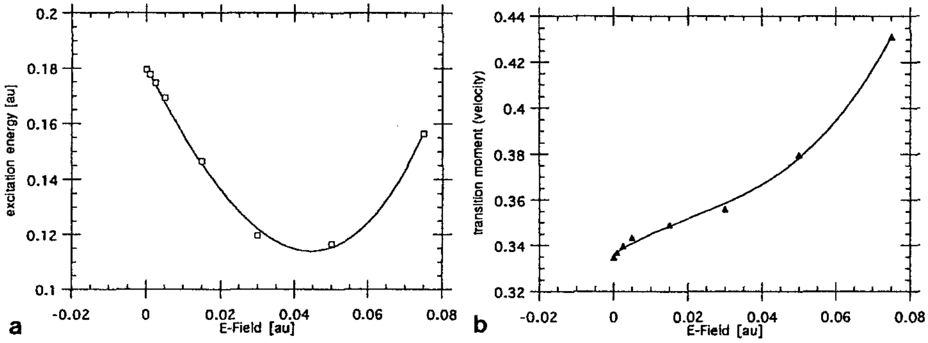

Fig. 2. a The calculated excitation energies and (**b**) transition moments between the ground state and charge transfer state of PNA in benzene as a function of the intensity of the vector potential

The SCRF response calculations give the excitation energies and transition moments for various intensities of the electromagnetic field at time equal to zero. The frequency of the laser mode lies in the region of the electronic transitions in the medium and well above the frequency of the vibrational modes in the solvent. Thus, since we assume that the frequency of the laser mode is well above the frequencies of intramolecular vibrations we neglect the possibility of the laser dissociating the molecule. We solve the time evolution equations by a sixth-order Runge–Kutta method employing the SCRF response calculated excitation energies, transition moments and couplings to the optical and inertial polarization vectors [28]. The inertial polarization vector is fixed at the value for $t = 0$ and corresponds to the inertial polarization vector of the ground state.

We neither consider the form of the cavity confining the electromagnetic field, nor do we take into account any possible shifts in the molecular levels due to the presence of this cavity. The quality factor, Q, of the radiation mode in the cavity is

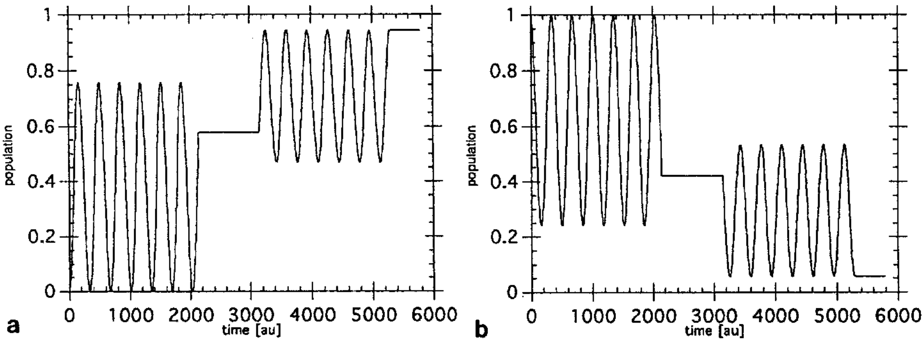

Fig. 3. The time evolution of the populations in (a) the $|CT, N\rangle$ state and (b) the $|GS, N+1\rangle$ state for the reference conditions: pulse length 2150 a.u. (52.01 fs); number of photons in the field 80; the detuning $\delta = 0.0018$ a.u.; and time between laser pulses 1000 a.u. (24.19 fs)

an expression of the lifetime of the mode in the cavity, the inverse of Q being proportional to the bandwidth of the cavity. As it is presently possible to achieve experimentally very high Q cavities in the optical region [3] (e.g., super high finesse optical resonators), we have ignored any decay of the laser mode in the optical cavity. The cavity volume is 5×10^6 a.u. and the cavity geometry is arbitrary.

5. Results

The length of the laser pulse, its intensity (i.e. the number of photons in the laser field), the detuning and the dead time (laser off) between one laser pulse and the next are varied. The reference values for the above parameters used in the calculations are the following: pulse length 2150 a.u. (52.01 fs); number of photons in the field 80; a detuning of $\delta = 0.0018$ a.u.; and a dead time between laser pulses of 1000 a.u. (24.19 fs).

The value for the line width of the PNA *CT* state used in all but one series of calculations is three orders of magnitude greater than the natural line width, in order to account for the broadening mechanisms in the solution. (In the remaining series of calculations, the line width was increased until a decay was observed, see Fig. 8.) This value of the lifetime of the CT state with broadening included is still long on the time scales under consideration (pulse lengths of approximately 2000 a.u., dead time between the pulses being about half as large, while the lifetime used of the order of 10^{-8} s or 4×10^8 a.u.) therefore essentially no decay from the charge transfer state to the ground state is observed.

If other modes were present in the model, we would observe a decay in the charge transfer population.

Figure 3 shows the time evolution of the $|CT, N\rangle$ state and the $|GS, N+1\rangle$ populations for the reference values of the parameters. There are two laser pulses, of equal pulse length, and a detuning $\delta = 0.0018$ a.u. Upon examining the figure, one notes that the population is conserved; as this is the case for all the calculations performed, for various values of the parameters listed above, we will present in the remaining figures the population of the charge transfer state only.

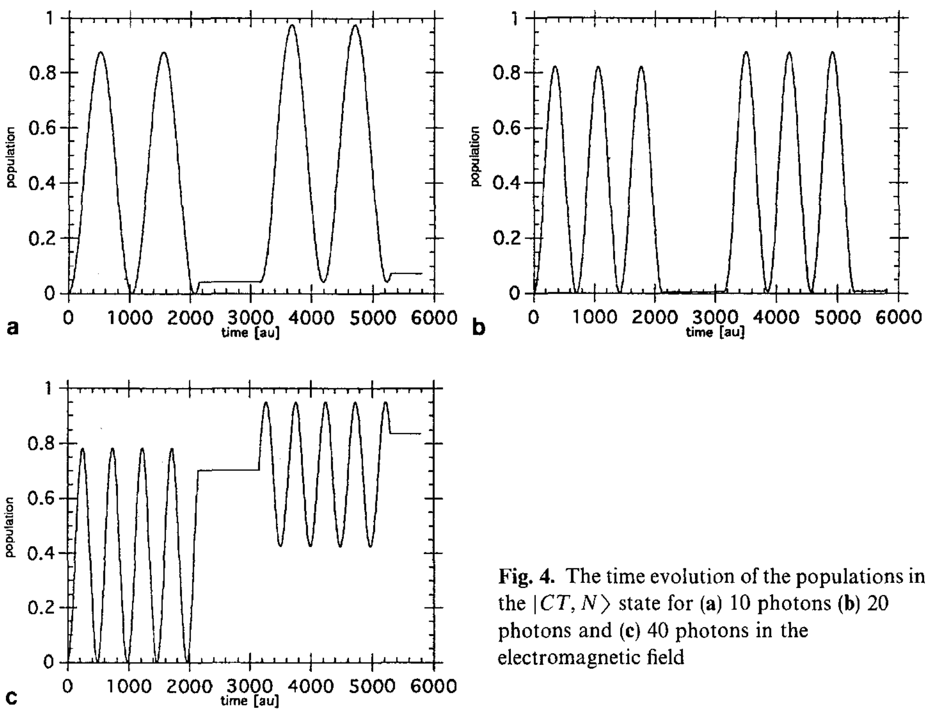

Fig. 4. The time evolution of the populations in the $|CT, N\rangle$ state for (**a**) 10 photons (**b**) 20 photons and (**c**) 40 photons in the electromagnetic field

In Fig. 4 we present how the population of the $|CT, N\rangle$ state varies in time for a field of 10, 20 and 40 photons, the values of the other parameters being those given above. The frequency of oscillation of the $|CT, N\rangle$ population increases with increasing photon number. This is not surprising since the increase in the photon number corresponds to an increase in the coupling between the two states, leading to a more rapid communication between the two states, $|GS, N + 1\rangle$ and $|CT, N\rangle$. One might also note that the final $|CT, N\rangle$ population depends strongly on where in the oscillation the population is when the pulse ends. In addition, one notes that the amplitude of the oscillation of the population is largest for the smallest number of photons in the field.

In Fig. 5, the changes in the $|CT, N\rangle$ state population with increasing laser pulse length are shown. One can see that by varying the pulse length, one can find a value which gives a large final population in the $|CT, N\rangle$ state after the second pulse. From this study we chose a pulse length of 2150 a.u.

Figure 6 shows how the final $|CT, N\rangle$ population depends on the dead time between pulses. Similar to Fig. 5, we can optimize the final $|CT, N\rangle$ population by adjusting the dead time accordingly.

Figure 7 shows how changing the detuning can affect the $|CT, N\rangle$ population. A positive δ ($\omega_L < \omega$) gives rise to the greatest amount of oscillation in the population and the possibility for achieving a large final population. For a positive detuning the dressed molecular state containing the largest component of the $|CT, N\rangle$ state is the lower one.

In Fig. 8 the populations of the $|CT, N\rangle$ state are presented for three successively larger values of the CT state line width. In this way, one observes how the

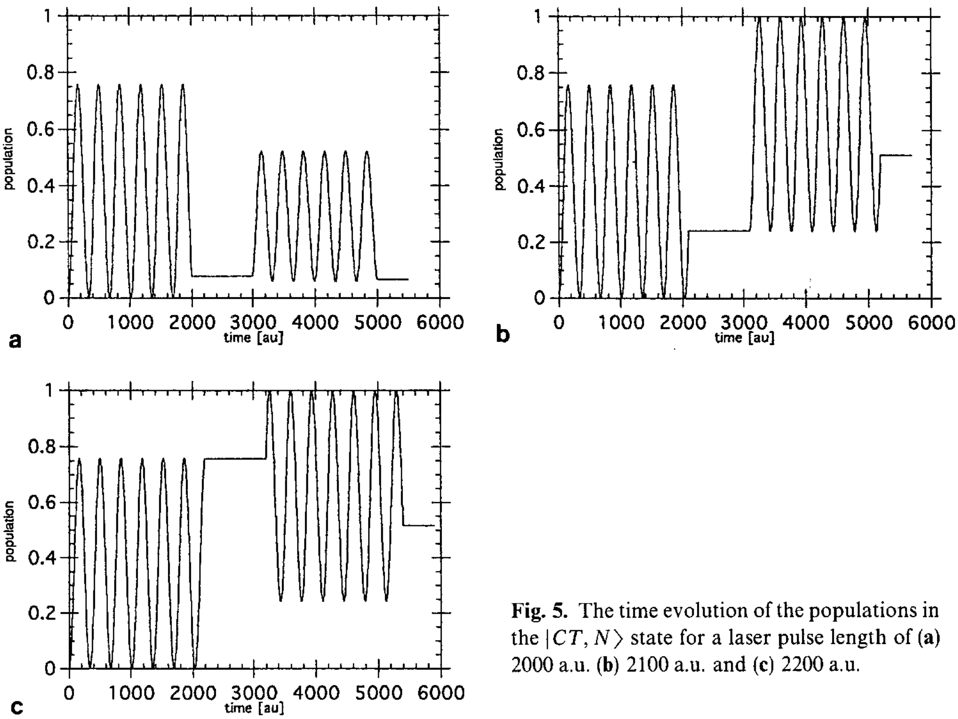

Fig. 5. The time evolution of the populations in the $|CT, N\rangle$ state for a laser pulse length of (**a**) 2000 a.u. (**b**) 2100 a.u. and (**c**) 2200 a.u.

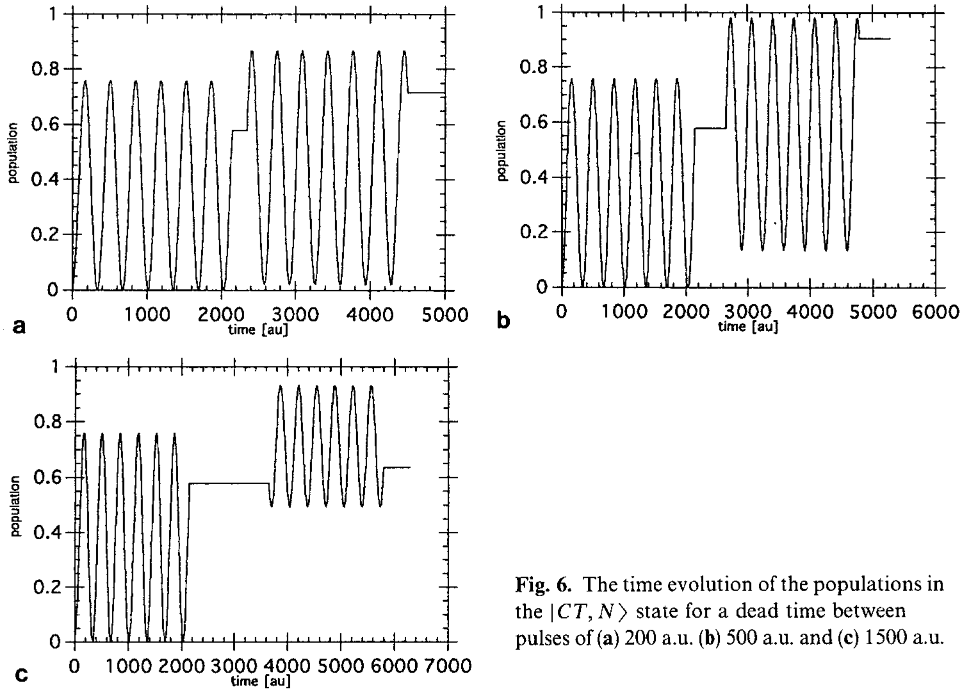

Fig. 6. The time evolution of the populations in the $|CT, N\rangle$ state for a dead time between pulses of (**a**) 200 a.u. (**b**) 500 a.u. and (**c**) 1500 a.u.

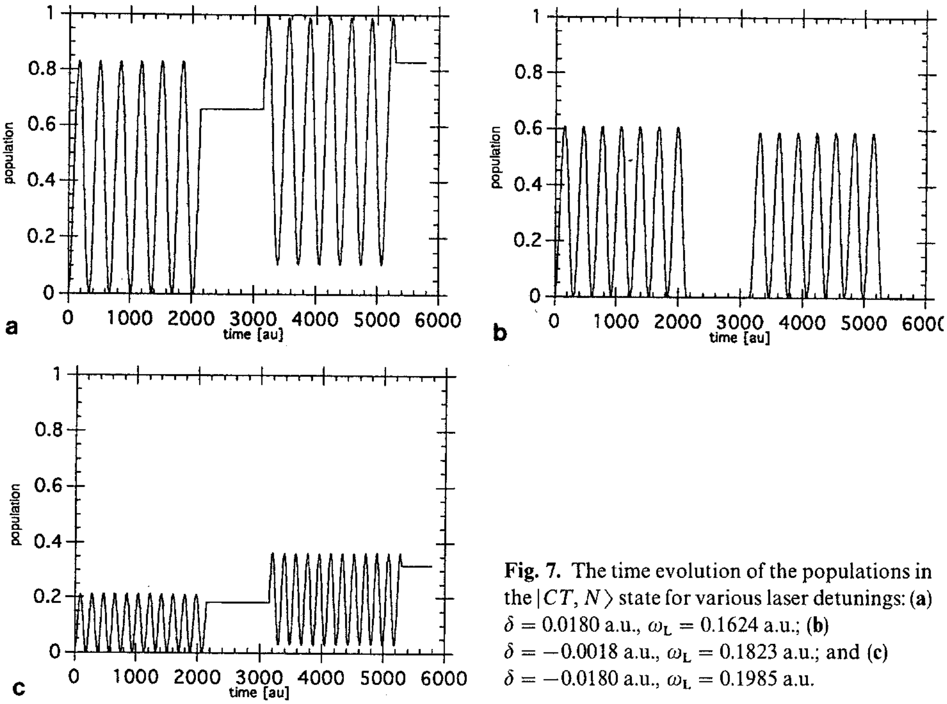

Fig. 7. The time evolution of the populations in the $|CT, N\rangle$ state for various laser detunings: (**a**) $\delta = 0.0180$ a.u., $\omega_L = 0.1624$ a.u.; (**b**) $\delta = -0.0018$ a.u., $\omega_L = 0.1823$ a.u.; and (**c**) $\delta = -0.0180$ a.u., $\omega_L = 0.1985$ a.u.

population changes when the damping is increased. A larger damping term in the equations of motion could be due to broadening mechanisms or losses.

The presented calculations do not allow for direct comparison with coupling between a fixed energy gap two-level system and a classical electromagnetic field, since in our calculations the energy gap and coupling to the electromagnetic field change with respect to the number of photons in the system.

6. Conclusion

Our concerns in the present article have been to establish a model and present preliminary studies involving a solvated intramolecular charge transfer compound coupled to a quantum mechanical radiation field, represented as an electromagnetic vector potential. We have shown that it indeed is possible to control the final population in the charge transfer state.

The present applications have been grossly simplified with respect to (i) the representation of the molecular vibrations; (ii) the outer solvent; (iii) the laser pulses; (iv) the electromagnetic microcavity; (v) the decay mechanisms for the excited state and (vi) the interactions between the solvent and the radiation field.

Point (i) could be improved in two ways: either by allowing the molecule to vibrate around its equilibrium nuclear configuration in both the molecular ground state and excited state, or by describing the nuclear motion utilizing wave packets.

Point (ii) relates to the fact that the inertial polarization vector is fixed to the value corresponding to the charge distribution of the initial state at time $t = 0$. This

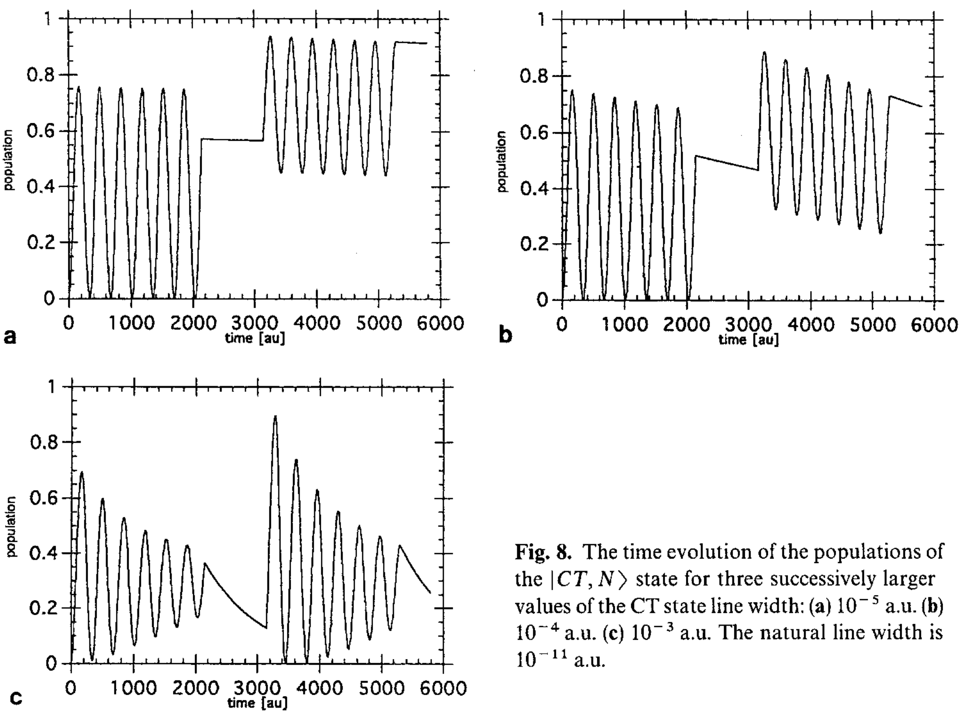

Fig. 8. The time evolution of the populations of the $|CT, N\rangle$ state for three successively larger values of the CT state line width: (**a**) 10^{-5} a.u. (**b**) 10^{-4} a.u. (**c**) 10^{-3} a.u. The natural line width is 10^{-11} a.u.

constraint could be relaxed by employing a Debye relaxation scheme for the inertial polarization vector, incorporating the characteristic relaxation time of the solvent to a sudden perturbation.

Improvements regarding point (iii) would be the most important point to consider in the future, and involve the utilization of more realistic laser pulses with appropriate line widths, envelopes and shapes.

With respect to point (iv), ultra-small microcavities like the one in the calculations presented here are not yet experimentally available, but trends are surely going in that direction [3]. The existence and availability of ultra-thin stretched fiber cables proves the point of accessibility of ultra-small microcavities. We have throughout our model assumed that we have a perfect electromagnetic cavity with a large *Q*-factor, reflecting no losses in the electromagnetic field.

The second to the last point, (v), addresses neglecting mechanisms of spontaneous emission other than that corresponding to the decay mechanism of the excited *CT* state into the *GS* state with the emission of a photon corresponding to the actual *GS*–*CT* transition. In this way we have not fully allowed all the reservoir modes to participate in the decay of the molecular *CT* state into the ground state. We have not addressed decay mechanisms related to collision mechanisms or energy transfer with the solvent.

The final point concerns modifications of the externally applied field to account for interactions between the solvent and the radiation field. These interactions give rise to the concept of a local electromagnetic field interacting with the solute.

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