Theory of two-photon adiabatic passage: Absorption to and emission from N states

Moshe Shapiro
Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel
(Received 20 June 1995)

An analytic theory of resonantly enhanced two-photon excitation of N states with laser light of an arbitrary field is developed. Closed-form expressions for the time evolution of the system are derived. The formulation is used to explore adiabatic passage to a level embedded amongst N other levels. ''Counterintuitive'' pulse sequence is shown to lead to complete population transfer under adiabatic conditions. The reverse case of stimulated emission from N initial states is also studied. Complete population transfer to the ground state from an initial state satisfying the two-photon resonance condition is shown to be possible. [S1050-2947(96)02307-4]

PACS number(s): 42.50.Hz

I. INTRODUCTION

In recent years great progress has been made in our understanding of how to control dynamical processes with coherent light [1]. One obvious control target is that of the population of (bound or continuum) quantum states. A very attractive way of achieving such control is afforded by the using of ''adiabatic passage'' techniques, in which, under the action of an external field, a molecule or an atom locks onto an eigenstate of the combined field-matter Hamiltonian. By forcing the system to follow such eigenstates, the field, which is made to change slowly enough or is intense enough, guides the molecule from an initial state to the target state.

Adiabatic passage of three-level systems (Λ systems) was first discussed theoretically in the optics literature by Oreg *et al.* [2]. The use of a Λ configuration for population transfer was demonstrated experimentally [3–8] and especially by Bergmann and co-workers [3], who showed that adiabatic passage enables, under certain conditions, the *complete* transfer of population from one level to another. Contrary to ''π-pulses,'' which in principle achieve the same objective, the adiabatic passage effect is more ''robust'': it is much less sensitive to the exact attributes of the pulse.

In the three-level adiabatic passage experiments, as practiced by Bergmann *et al.*, one makes use of stimulated Raman scattering [hence the name STIRAP (stimulated Raman adiabatic passage)] to transfer the population from level 1 to level 3 via an intermediate level 2. The experiment is performed by first subjecting the molecule to laser frequency in near resonance with $\omega_{2,3}$—the transition frequency between level 3 and level 2—and then irradiating the system with a laser whose frequency is in near resonance with $\omega_{2,1}$–the transition frequency between level 1 and level 2. Bergmann and co-workers [3] showed that the above counterintuitive pulse sequence (''begin with the Stokes laser and end with the pump laser'') is necessary for the complete population transfer to take place. What are also required are strong enough lasers, such that the adiabatic conditions, $\Omega\Delta\tau \gg 1$, where Ω is the Rabi frequency and $\Delta\tau$ is the duration, of either pulse, apply.

Most molecular transitions, however, do not involve just three states. Usually the final level is embedded in a host of neighboring levels, which are also affected by the laser pulses. The hope is, however, that some of the salient features of the $2+1$ case would carry over to the $2+N$ case. In particular, it would be interesting to see whether complete population transfer with adiabatic passage techniques would survive the presence of neighboring states.

Various extensions of the three-level system were considered in the literature. In the context of two-photon absorption resonantly enhanced by N intermediate states, this was done by treating the effect of the intermediate states using second-order perturbation theory [9,10]. When the use of perturbation theory is justified (i.e., in the weak-field regime), the problem can be reduced to an effective two-level system thereby resurrecting the Feynman-Vernon-Hellwarth [11] vector model. Although such a model can be solved to all orders in the field, the procedure is not expected to be exact for strong fields because of the use of second-order perturbation theory in eliminating the N intermediate states.

Analytic solutions for a small number of intermediate states, which do not use second-order perturbation theory and are hence applicable to strong fields, were also developed [4,5]. It was concluded that under certain (more restrictive conditions) complete, or nearly complete, population transfer would still be possible. The case of a continuum of intermediate levels was also considered. Conflicting opinions exist as to whether complete population transfer is possible in this case [12,13]. We are of the opinion that in this case the conditions for complete population transfer are too restrictive to be realized by a realistic molecular [14], or even atomic [13] continua. The case when the final manifold is made up of a ''flat'' continuum was also studied [15]. In this case it was shown that under certain conditions complete population transfer is possible. However, that case is much simpler than the present N-level case because the ''flatness'' of the continuum guarantees that the continuum acts as an ideal sink, hence pulses with large enough area will be able to transfer all the initial population to that continuum.

In this paper we investigate the general case of N discrete final states and especially the effect of N neighboring levels on adiabatic passage to the level of interest. We proceed in analogy to the three-level problem by first solving the resonantly enhanced two-photon continuous wave (CW) excitation to the N-level problem. The solution is based on an essentially analytic expression for the eigenvalues and eigenvectors of the problem. In the second stage we replace the

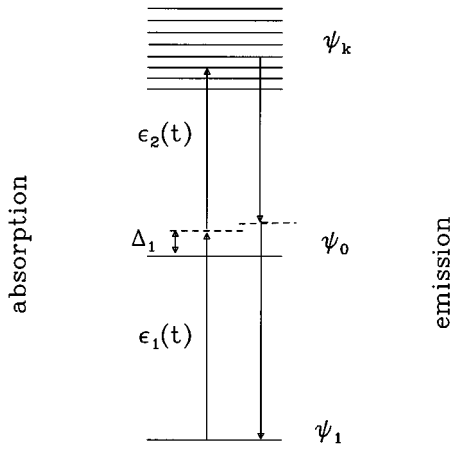

FIG. 1. Illustration of the level scheme and laser pulses for two-photon absorption and two-photon emission.

CW lasers with slowly varying (adiabatic) pulses. The CW solutions now become the adiabatic solutions, which, though approximate, are quite accurate for large area pulses. Finally, we prove analytically that it is possible, under the adiabatic conditions, to witness complete population transfer to one, and only one, of the N final levels. Conversely, we show that if we start with a manifold composed of N levels, we can transfer population from one of the manifold levels to a single level with 100% efficiency.

II. CW THEORY

In this section we present the CW solution of the resonantly enhanced two-photon excitation of N final states. The extension to the pulsed case is dealt with in the following sections.

Consider exciting a molecule in state ψ_1 by two CW laser fields of frequencies ω_1 and ω_2. We assume that ω_1 is in near resonance with the transition frequency of the ψ_1 state to an intermediate state ψ_0, and that ω_2 is close to a set of transition frequencies from the intermediate state ψ_0 to a manifold composed of N states ψ_k. The situation is depicted in Fig. 1.

The Hamiltonian of the system is written as

$$H=H_M-\mu_{0,1}\epsilon_1\cos(\omega_1 t)-\mu_{2,0}\epsilon_2\cos(\omega_2 t), \tag{1}$$

where H_M is the radiation-free Hamiltonian,

$$\mu_{0,1}\equiv\vec{\mu}_{0,1}\cdot\hat{\vec{\epsilon}}_1,\mu_{2,0}\equiv\vec{\mu}_{2,0}\cdot\hat{\vec{\epsilon}}_2, \tag{2}$$

and ϵ_1 and ϵ_2 are the amplitudes and $\hat{\vec{\epsilon}}_1$ and $\hat{\vec{\epsilon}}_2$ the polarization directions of the two fields. $\vec{\mu}_{0,1}$ and $\vec{\mu}_{2,0}$ are the transition-dipole operators coupling state 1 to state 0, and state 0 to the manifold of ψ_k states, respectively. Both the field amplitudes and the transition dipoles are assumed for simplicity to be real.

Denoting the eigenvalues and eigenfunctions of H_M as E_ν and ψ_ν, respectively, with ν serving as a combined index for the ground, intermediate, and N upper states, we can expand the full time-dependent wave function as

$$\Psi(t)=c_1\psi_1\exp(-iE_1t/\hbar)+c_0\psi_0\exp(-iE_0t/\hbar)+\sum_{k=2}^{N}c_k\psi_k\exp(-iE_kt/\hbar). \tag{3}$$

In what follows, the index k always signifies the $k=2,\ldots,N$ upper states of H_M.

Insertion of Eq. (3) into the time-dependent Schrödinger equation $i\hbar\partial\Psi/\partial t=H\Psi(t)$, use of the orthogonality of the ψ_ν eigenfunctions and the rotating-wave approximation (RWA) (which is perfectly justified because of the assumed near-resonance conditions), results in a set of first-order differential equations for the c_ν coefficients of the form

$$i\hbar\frac{d}{dt}c_1=-\mu_1\epsilon_1c_0\exp(-\Delta_1t),$$

$$i\hbar\frac{d}{dt}c_0=-\mu_1\epsilon_1c_1\exp(i\Delta_1t)-\epsilon_2\sum_{k=2}^{N}\mu_kc_k\exp(-i\Delta_kt),$$

$$i\hbar\frac{d}{dt}c_k=-\mu_k\epsilon_2c_0\exp(i\Delta_kt),\quad k=2,\ldots,N, \tag{4}$$

where

$$\mu_1\equiv\langle\psi_1|\vec{\mu}_{0,1}\cdot\hat{\vec{\epsilon}}_1|\psi_0\rangle,\quad \mu_k\equiv\langle\psi_k|\vec{\mu}_{2,0}\cdot\hat{\vec{\epsilon}}_2|\psi_0\rangle,$$

$$\Delta_1\equiv\frac{E_0-E_1}{\hbar}-\omega_1,\quad \Delta_k\equiv\frac{E_k-E_0}{\hbar}-\omega_2. \tag{5}$$

Defining the $\mathbf{c}$ coefficient column vector as, $\mathbf{c}\equiv(c_0,c_1,c_2,\ldots,c_k,\ldots)$, we can write Eqs. (4) in matrix notation as

$$\frac{d}{dt}\mathbf{c}=\frac{i}{\hbar}\mathbf{F}(t)\cdot\mathbf{c}, \tag{6}$$

where $\mathbf{F}$ is a matrix of the form,

$$\mathbf{F}=\begin{pmatrix} 0 & \mu_1\epsilon_1\exp(i\Delta_1t) & \cdots & \mu_k\epsilon_2\exp(-i\Delta_kt) & \cdots \\ \mu_1\epsilon_1\exp(-i\Delta_1t) & 0 & & 0 & \\ \vdots & & & & \\ \mu_k\epsilon_2\exp(i\Delta_kt) & 0 & & 0 & \\ \vdots & & & & \end{pmatrix}. \tag{7}$$

Defining the (diagonal) detuning matrix ,

$$\hat{\Delta}_{0,0}=0, \quad \hat{\Delta}_{1,1}=\Delta_1, \quad \hat{\Delta}_{k,k}=-\Delta_k, \tag{8}$$

we can write Eq. (6) as

$$\frac{d}{dt}\mathbf{c}=\frac{i}{\hbar}\exp(-i\hat{\Delta}t)\cdot\mathbf{f}\cdot\exp(i\hat{\Delta}t)\cdot\mathbf{c}, \tag{9}$$

where the **f** matrix is given as

$$\mathbf{f}=\begin{pmatrix} 0 & \mu_1\epsilon_1 & \cdots & \mu_k\epsilon_2 & \cdots \\ \mu_1\epsilon_1 & 0 & & 0 & \\ \vdots & & & & \\ \mu_k\epsilon_2 & 0 & & 0 & \\ \vdots & & & & \end{pmatrix}. \tag{10}$$

By multiplying Eq. (9) from the left by $\exp(i\hat{\Delta}t)$, and defining a **b** coefficient vector as

$$\mathbf{b}\equiv\exp(i\hat{\Delta}t)\cdot\mathbf{c}, \tag{11}$$

we eliminate the time dependence from the right-hand side (rhs) matrix to obtain

$$\frac{d}{dt}\mathbf{b}=\frac{i}{\hbar}\mathbf{g}\cdot\mathbf{b}, \tag{12}$$

where the **g** matrix is given as

$$\mathbf{g}=\begin{pmatrix} 0 & \mu_1\epsilon_1 & \cdots & \mu_k\epsilon_2 & \cdots \\ \mu_1\epsilon_1 & \hbar\Delta_1 & \cdots & 0 & \\ \vdots & \vdots & & & \\ \mu_k\epsilon_2 & 0 & \cdots & -\hbar\Delta_k & \cdots \\ \vdots & & & & \end{pmatrix}. \tag{13}$$

The structure of the above matrix equation is similar, though not identical, to that encountered for spontaneous emission [16]. The **g** matrix, which, contrary to the **F** matrix, is real, can be diagonalized by an orthogonal matrix **U**,

$$\mathbf{U}\cdot\mathbf{g}=\hat{\lambda}\cdot\mathbf{U}, \tag{14}$$

where $\hat{\lambda}$ is the (diagonal) eigenvalue matrix. Its eigenvalues are the roots of the following equation:

$$\lambda_\nu=\frac{\mu_1^2\epsilon_1^2}{\lambda_\nu-\hbar\Delta_1}+\sum_k\frac{\mu_k^2\epsilon_2^2}{\lambda_\nu+\hbar\Delta_k}. \tag{15}$$

Rewriting Eq. (15) as

$$(\lambda_{0,1}-\hbar\Delta_1)\lambda_{0,1}=(\mu_1\epsilon_1)^2+(\lambda_{0,1}-\hbar\Delta_1)\mathbf{Z}_{0,1} \tag{16}$$

and

$$(\lambda_k+\hbar\Delta_k)\lambda_k=(\mu_k\epsilon_2)^2+(\lambda_k+\hbar\Delta_k)\mathbf{Z}_k, \tag{17}$$

where

$$\mathbf{Z}_{0,1}\equiv\sum_k\frac{(\mu_k\epsilon_2)^2}{\lambda_{0,1}+\hbar\Delta_k} \tag{18}$$

and

$$\mathbf{Z}_k\equiv\sum_{k'\neq k}\frac{(\mu_{k'}\epsilon_2)^2}{\lambda_k+\hbar\Delta_{k'}}+\frac{(\mu_1\epsilon_1)^2}{\lambda_k-\hbar\Delta_1}, \tag{19}$$

we can write a simple iterative scheme for solving for λ_ν,

$$\lambda_{0,1}=\tfrac{1}{2}\{\hbar\Delta_1+\mathbf{Z}_{0,1}\mp[(\hbar\Delta_1-\mathbf{Z}_{0,1})^2+4(\mu_1\epsilon_1)^2]^{1/2}\} \tag{20}$$

and

$$\lambda_k=\tfrac{1}{2}\{-\hbar\Delta_k+\mathbf{Z}_k-s(k)[(\hbar\Delta_k+\mathbf{Z}_k)^2+4(\mu_k\epsilon_2)^2]^{1/2}\}, \tag{21}$$

where $s(k)=\mathrm{sgn}(\hbar\Delta_k+\mathbf{Z}_k)$.

Once the eigenvalues are calculated, the **U** matrix is obtained as

$$U_{\nu,0}=\left\{1+\left(\frac{\mu_1\epsilon_1}{\lambda_\nu-\hbar\Delta_1}\right)^2+\sum_k\left(\frac{\mu_k\epsilon_2}{\lambda_\nu+\hbar\Delta_k}\right)^2\right\}^{-1/2},$$

$$U_{\nu,1}=U_{\nu,0}\frac{\mu_1\epsilon_1}{\lambda_\nu-\hbar\Delta_1},$$

$$U_{\nu,k}=U_{\nu,0}\frac{\mu_k\epsilon_2}{\lambda_\nu+\hbar\Delta_k}. \tag{22}$$

Given **U** and $\hat{\lambda}$, we can solve Eq. (12) by multiplying it from the left by $\mathbf{U}^T$, to obtain that

$$\frac{d}{dt}\mathbf{a}=\frac{i}{\hbar}\hat{\lambda}\cdot\mathbf{a}, \tag{23}$$

where the **a** coefficient vector is defined as

$$\mathbf{a}\equiv\mathbf{U}^T\cdot\mathbf{b}=\mathbf{U}^T\cdot\exp(i\hat{\Delta}t)\cdot\mathbf{c}. \tag{24}$$

Equations (23) are easily integrated to yield

$$\mathbf{a}(t)=\exp\left(\frac{i}{\hbar}\hat{\lambda}t\right)\cdot\mathbf{a}(0). \tag{25}$$

Hence

$$\mathbf{c}(t)=\exp(-i\hat{\Delta}t)\cdot\mathbf{U}\exp\left(\frac{i}{\hbar}\hat{\lambda}t\right)\cdot\mathbf{a}(0), \tag{26}$$

or

$$\mathbf{c}(t)=\exp(i-\hat{\Delta}t)\cdot\mathbf{U}\cdot\exp\left(\frac{i}{\hbar}\hat{\lambda}t\right)\cdot\mathbf{U}^T\cdot\mathbf{c}(0). \tag{27}$$

Using the initial condition $\Psi(0)=\psi_1$, i.e., that

$$\mathbf{c}(0)=(0,1,\ldots,0,\ldots), \tag{28}$$

we obtain that

$$c_\nu(t)=\exp(-i\hat{\mathbf{\Delta}}_\nu t)\left\{U_{\nu,0}\exp\left(\frac{i}{\hbar}\lambda_0 t\right)U_{1,0}+U_{\nu,1}\exp\left(\frac{i}{\hbar}\lambda_1 t\right)U_{1,1}+\sum_k U_{\nu,k}\exp\left(\frac{i}{\hbar}\lambda_k t\right)U_{1,k}\right\}. \tag{29}$$

III. ADIABATIC PASSAGE IN TWO-PHOTON ABSORPTION

Equation (29) encapsulates the solution of the resonantly enhanced two-photon excitation problem of N levels with two arbitrarily strong CW fields. In order to investigate adiabatic passage, we let ϵ_1 and ϵ_2 vary (slowly) with time. This has the effect of introducing time dependence to the $\hat{\lambda}$ and $\mathbf{U}$ matrices. The time-dependent analog of Eq. (27), i.e., the adiabatic approximation, has the form

$$\mathbf{c}(t)=\exp(-i\hat{\mathbf{\Delta}}t)\cdot\mathbf{U}(t)\cdot\exp\left[\frac{i}{\hbar}\int_0^t dt'\hat{\lambda}(t')\right]\cdot\mathbf{U}(0)^T\cdot\mathbf{c}(0). \tag{30}$$

As in the CW case, we assume that the initial conditions are given by Eq. (28). Hence Eq. (30) for an individual c_ν coefficient assumes the form

$$c_\nu(t)=\left\{U_{\nu,0}(t)\exp\left[\frac{i}{\hbar}\int^t\lambda_0(t')dt'\right]U_{1,0}(0)+U_{\nu,1}(t)\exp\left[\frac{i}{\hbar}\int^t\lambda_1(t')dt'\right]U_{1,1}(0)+\sum_k U_{\nu,k}(t)\exp\left[\frac{i}{\hbar}\int^t\lambda_k(t')dt'\right]U_{1,k}(0)\right\}\times\exp(-i\hat{\Delta}_\nu t). \tag{31}$$

If we first switch on the ϵ_2 pulse and *then* the ϵ_1 pulse, we see immediately by Eq. (A2) that only the middle term in the above equation remains,

$$c_\nu(t)=\exp(-i\hat{\mathbf{\Delta}}_\nu t)U_{\nu,1}(t)\left[\frac{i}{\hbar}\int^t(t')dt'\right]. \tag{32}$$

The k states expansion coefficients, obtained by substituting Eq. (22) into Eq. (32), are,

$$c_k(t)=\frac{\mu_1\epsilon_1}{\lambda_k-\hbar\Delta_1}\left\{1+\left(\frac{\mu_1\epsilon_1}{\lambda_k-\hbar\Delta_1}\right)^2+\sum_{k'}\left(\frac{\mu_{k'}\epsilon_2}{\lambda_k+\hbar\Delta_{k'}}\right)^2\right\}^{-1/2}\times\exp\left[i\Delta_k t+\frac{i}{\hbar}\int^t\lambda_1(t')dt'\right]. \tag{33}$$

As we switch off $\epsilon_2(t)$ we obtain, according to Eq. (A5), that,

$$\lim_{\epsilon_2\to0}c_k(t)=-\mu_1\epsilon_1\left\{(\hbar\Delta_k+\hbar\Delta_1)^2\left[1-\left(\frac{\hbar\Delta_k+\mathbf{Z}_k}{\mu_k\epsilon_2}\right)^2\right]+(\mu_1\epsilon_1)^2\right\}^{-1/2}\exp\left[i\Delta_k t+\frac{i}{\hbar}\int^2\lambda_1(t')dt'\right]. \tag{34}$$

We see from Eq. (34) that if we keep ϵ_1 finite as we let $\epsilon_2(t)\to0$ all the $c_k(t)$ coefficients vanish except for the one, denoted as c_{k_1}, corresponding to a state satisfying the two-photon resonance condition,

$$\frac{E_{k_1}-E_1}{\hbar}-\omega_1-\omega_2=\Delta_{k_1}+\Delta_1=0. \tag{35}$$

It follows from Eq. (34) that in the $\epsilon_2(t)\to0$ limit with finite ϵ_1, the c_{k_1} coefficient goes over to

$$\lim_{\epsilon_2\to0}c_{k_1}(t)=-\exp\left[i\Delta_{k_1}t+\frac{i}{\hbar}\int^t\lambda_1(t')dt'\right]. \tag{36}$$

Hence, the probability of observing the k_1 state is

$$\lim_{\epsilon_2\to0}|c_{k_1}(t)|^2=1, \tag{37}$$

i.e., full population transfer. If we reverse the order of the pulses, we see from Eq. (33) that *all* the c_k coefficients vanish and the system returns adiabatically to the ground state.

The above conclusions are subject to the goodness of the adiabatic approximation. As shown previously [15], we can go beyond the adiabatic approximation by explicitly considering the time dependence of the $d\mathbf{U}(t)/dt$ matrix. The difference between the exact procedure and the adiabatic approximation is that instead of Eq. (23) we now have to solve the following equations:

$$\frac{d}{dt}\mathbf{a}=\left\{\frac{i}{\hbar}\hat{\lambda}(t)+\mathbf{A}(t)\right\}\cdot\mathbf{a}, \tag{38}$$

where

$$\mathbf{A}\equiv\frac{d\mathbf{U}(t)}{dt}\cdot\mathbf{U}^T, \tag{39}$$

is a nonadiabatic coupling matrix.

These equations cannot be integrated as easily as Eq. (23) because the $\mathbf{A}$ matrix is not diagonal. However, they suggest a simple iterative procedure in which one starts with the adiabatic solutions, Eq. (25), of the $\mathbf{a}(t)$ eigenvector,

$$\mathbf{a}^{(0)}(t)=\exp\left[\frac{i}{\hbar}\int_0^t\hat{\lambda}(t')dt'\right]\cdot\mathbf{a}^{(0)}(0), \tag{40}$$

and improves each component of the $\mathbf{a}(t)$ vector as

$$\frac{d}{dt}\mathbf{a}_\nu^{(1)}=\left\{\frac{i}{\hbar}\lambda_\nu(t)+\sum_{\nu'}A_{\nu,\nu'}\mathbf{a}_{\nu'}^{(0)}/\mathbf{a}_\nu^{(0)}\right\}\mathbf{a}_\nu^{(1)}. \tag{41}$$

The resulting solution is then reintroduced into Eq. (41), resulting in a general iterative step of the form

$$\mathbf{a}_\nu^{(n+1)}(t)=\mathbf{a}_\nu^{(0)}(t)\exp\left[\int_0^t dt'\,\frac{1}{\mathbf{a}_\nu^{(n)}(t')}\sum_{\nu'}A_{\nu\nu'}(t')\mathbf{a}_{\nu'}^{(n)}(t')\right]. \tag{42}$$

The iteration is continued until $|\mathbf{a}_\nu^{(n+1)}(t)-\mathbf{a}_\nu^{(n)}(t)|<\epsilon$, at which point it is easily verified that Eq. (38) is satisfied to an accuracy determined by the value of ϵ chosen.

The advantage of this iterative procedure is that the solution of Eq. (42) at each iteration scales as N^2. If the procedure converges within a few iterations (as it does for near adiabatic situations where the off-diagonal **A** matrix elements are small [17]), this method is much faster than the usual procedures for solving the time-dependent Schrödinger equation, which scale as N^3.

IV. ADIABATIC PASSAGE IN TWO-PHOTON EMISSION

We now consider the reverse case in which a system, initially in one of the excited ψ_k states, is stimulated by two pulses to emit to the end ψ_0 and the ψ_1 states. We wish to examine under what conditions population transfer to the ψ_1 state is complete. The situation is depicted in Fig. 1.

The $\Psi(0)=\psi_k$ initial condition is equivalent to imposing

$$c_{\nu\neq k}(0)=0,\quad c_k(0)=1 \tag{43}$$

in Eq. (30). We obtain that

$$\begin{aligned}c_\nu(t)=\Bigg\{&U_{\nu,0}(t)\exp\left[\frac{i}{\hbar}\int^t\lambda_0(t')dt'\right]U_{k,0}(0)\\&+U_{\nu,1}(t)\exp\left[\frac{i}{\hbar}\int^t\lambda_1(t')dt'\right]U_{k,1}(0)\\&+\sum_{k'}U_{\mu,k'}(t)\exp\left[\frac{i}{\hbar}\int^t\lambda_{k'}(t')dt'\right]U_{k,k'}(0)\Bigg\}\\&\times\exp(-i\hat{\Delta}_\nu t).\end{aligned} \tag{44}$$

If we switch on ϵ_1 before ϵ_2 it follows from Eq. (A6) that

$$c_\nu(t)=-U_{\nu,k}(t)\exp\left[\frac{i}{\hbar}\int^t\lambda_k(t')dt'\right]\exp(-i\hat{\Delta}_\nu t). \tag{45}$$

When the initial k state is not in two-photon resonance [Eq. (35)] with the ground state, we see from Eq. (A2) that

$$c_1(t\to\infty)=0. \tag{46}$$

On the other hand, if the initial ψ_k state does satisfy the two-photon resonance condition, it follows from Eq. (A4) that

$$c_1(t\to\infty)=-\exp\left[\frac{i}{\hbar}\int^\infty(\lambda_{k_1}(t')+\hbar\Delta_{k_1})dt'\right], \tag{47}$$

i.e., that

$$P_1 1(t\to\infty)=|c_1(t\to\infty)|^2=1. \tag{48}$$

By switching on ϵ_1 *before* ϵ_2 we can affect complete population transfer from the initial k level to the ground state, *provided* that we tune the carrier frequencies of ϵ_2 and ϵ_1 to be in two-photon resonance with the ground state and the adiabatic conditions are satisfied. This pulse sequence, though the reverse of the one used to affect complete population transfer in absorption, may still be classified as ''counterintuitive'' because we first switch on the pulse that acts between the unpopulated levels.

ACKNOWLEDGMENTS

This work was supported by the Israel Academy Fund for Basic Research and by the U.S.-Israel Binational Science Foundation.

APPENDIX A: THE LIMITING BEHAVIOR OF THE U MATRIX

In this appendix we examine the limiting behavior of the **U** eigenvector matrix when either $\epsilon_1\to 0$ for finite ϵ_2, or $\epsilon_2\to 0$ for finite ϵ_1.

1. $\epsilon_1\to 0$, at finite ϵ_2

In this case we obtain from Eq. (20) that

$$\lambda_1\to\hbar\Delta_1+\frac{\mu_1^2\epsilon_1^2}{\hbar\Delta_1-\mathbf{Z}_1}. \tag{A1}$$

When $k=k_1$, i.e., none of the k states satisfies the two-photon resonance condition [Eq. (35)] we obtain from Eq. (22) that

$$\begin{aligned}&U_{1,0}\to\frac{\mu_1\epsilon_1}{\hbar\Delta_1-\mathbf{Z}_1}\to 0,\quad U_{1,1}\to U_{1,0}\frac{\hbar\Delta_1-\mathbf{Z}_1}{\mu_1\epsilon_1}\to 1,\\&U_{1,k}\to 0\quad k\neq k_1.\end{aligned} \tag{A2}$$

When one of the k states satisfies the two-phonon resonance condition, the above formulas must be changed because the $\mu_{k_1}\epsilon_2/(\lambda_1+\hbar\Delta_{k_1})$ term in Eq. (22) diverges as $(1/\mu_1\epsilon_1)^2$. In that case,

$$U_{1,0}\to\frac{\lambda_1+\hbar\Delta_{k_1}}{\mu_{k_1}\epsilon_2}\underset{\epsilon_1\to 0}{\to}0, \tag{A3}$$

and it follows from Eq. (22) that

$$U_{1,k_1}=U_{1,0}\frac{\mu_{k_1}\epsilon_2}{\lambda_1+\hbar\Delta_{k_1}}\underset{\epsilon_1\to 0}{\to}1. \tag{A4}$$

2. $\epsilon_2\to 0$, at finite ϵ_1

In the $\epsilon_2\to 0$ limit, Eq. (2) can be solved directly for the k eigenvalues. By expanding the square root in Eq. (21) we obtain that

$$\lambda_k=-\hbar\Delta_k-\frac{(\mu_k\epsilon_2)^2}{\hbar\Delta_k+\mathbf{Z}_k}. \tag{A5}$$

Using Eqs. (22) and (A5) we obtain that

$$U_{k,0}\rightarrow\frac{\mu_k\epsilon_2}{\hbar\Delta_k+\mathbf{Z}_k}\underset{\epsilon_2\rightarrow 0}{\rightarrow}0,\quad U_{k,1}\underset{\epsilon_2\rightarrow 0}{\rightarrow}0,$$

$$U_{k\neq k'}\underset{\epsilon_2\rightarrow 0}{\rightarrow}0,\quad U_{k,k}\rightarrow -U_{k,0}\frac{\hbar\Delta_k+\mathbf{Z}_k}{\mu_k\epsilon_2}\underset{\epsilon_2\rightarrow 0}{\rightarrow}-1. \quad \text{(A6)}$$

3. The 0 row

It is of interest to compute the limiting behavior of the $U_{0,\nu}$ components in order to determine what factors affect the population of the intermediate state. It follows from Eq. (20) that unless by some coincidence $\hbar\Delta_1=\mathbf{Z}_0$, or there is one k_0 such that

$$\hbar\Delta_{k_0}=-\mathbf{Z}_0+\frac{(\mu_1\epsilon_1)^2}{\hbar\Delta_1-\mathbf{Z}_0}, \quad \text{(A7)}$$

λ_0 goes over in the $\epsilon_1\rightarrow 0$ limit to

$$\lambda_0\underset{\epsilon_1\rightarrow 0}{\rightarrow}\mathbf{Z}_0-\frac{(\mu_1\epsilon_1)^2}{\hbar\Delta_1-\mathbf{Z}_0}. \quad \text{(A8)}$$

We obtain from Eqs. (A8) and (18) that

$$\mathbf{Z}_0\overset{\epsilon_1\rightarrow 0}{\rightarrow}\sum_k\frac{(\mu_k\epsilon_2)^2}{\mathbf{Z}_0+\hbar\Delta_k}. \quad \text{(A9)}$$

It follows from Eqs. (A8) and (22) that

$$U_{0,0}\overset{\epsilon_1\rightarrow 0}{\rightarrow}\left\{1-\left(\frac{\mu_1\epsilon_1(\mathbf{Z}_0-\hbar\Delta_1)}{(\mathbf{Z}_0-\hbar\Delta_1)^2+(\mu_1\epsilon_1)^2}\right)^2+\sum_k\left(\frac{\mu_k\epsilon_s(\mathbf{Z}_0-\hbar\Delta_1)}{(\mathbf{Z}_0-\hbar\Delta_1)(\mathbf{Z}_0+\hbar\Delta_k)+(\mu_1\epsilon_1)^2}\right)^2\right\}^{-1/2}, \quad \text{(A10)}$$

and unless $\hbar\Delta_1=\mathbf{Z}_0$ we have that

$$U_{0,0}\underset{\epsilon_1\rightarrow 0}{\rightarrow}\left\{1+\sum_k\left(\frac{\mu_k\epsilon_2}{\mathbf{Z}_0+\hbar\Delta_k}\right)^2\right\}^{-1/2}. \quad \text{(A11)}$$

It follows from Eqs. (A10) and (22) that

$$U_{0,1}=U_{0,0}\frac{\mu_1\epsilon_1}{\lambda_0-\hbar\Delta_1}\underset{\epsilon_1\rightarrow 0}{\rightarrow}0. \quad \text{(A12)}$$

[1] For a recent review, see e.g., M. Shapiro and P. Brumer, Int. Rev. Phys. Chem. **13**, 187 (1994); P. Brumer and M. Shapiro, Sci. Am. **272 (3)**, 56 (1995).

[2] J. Oreg, F. T. Hioe, and J. H. Eberly, Phys. Rev. A **29**, 690 (1984).

[3] U. Gaubatz, P. Rudecki, M. Becker, S. Schiemann, M. Külz, and K. Bergmann, Chem. Phys. Lett. **149**, 463 (1988); U. Gaubatz, P. Rudecki, S. Schiemann, and K. Bergmann, J. Chem. Phys. **92**, 5363 (1990); J. R. Kuklinski, U. Gaubatz, F. T. Hioe, and K. Bergmann, Phys. Rev. A **40**, 6741 (1989); B. W. Shore, K. Bergmann, J. Oreg, and S. Rosenwaks, *ibid.* **44**, 7442 (1991); K. Bergmann and B. W. Shore, in *Molecular Dynamics and Spectroscopy by Stimulated Emission Pumping*, edited by H. L. Dai and R. W. Field (World Scientific, Singapore, 1994).

[4] G. Coulston and K. Bergmann, J. Chem, Phys. **96**, 3467 (1992).

[5] B. W. Shore, J. Martin, M. P. Fewell, and K. Bergmann, Phys. Rev. A **52**, 566 (1995).

[6] C. Liedenbaum, S. Stolte, and J. Reuss, Phys. Rep. **178**, 1 (1989).

[7] B. Broers, H. B. van Linden van den Heuvell, and L. D. Noordam, Phys. Rev. Lett. **69**, 2062 (1992).

[8] J. S. Melinger, S. R. Gandhi, A. Hariharan, J. X. Tull, and W. S. Warren, Phys. Rev. Lett. **68**, 2000 (1992); J. S. Melinger, S. R. Gandhi, A. Hariharan, D. Goswami, and W. S. Warren, J. Chem. Phys. **101**, 6439 (1994).

[9] M. Takatsuji, Phys. Rev. A **4**, 808 (1971).

[10] D. Grischkowsky and M. M. T. Loy, Phys. Rev. A **12**, 1117 (1975); D. Grischkowsky, M. M. T. Loy, and P. F. Liao, *ibid.* **12**, 2514 (1975).

[11] R. P. Feynman, F. L. Vernon, Jr., and R. W. Hellwarth, J. Appl. Phys. **28**, 49 (1957).

[12] C. E. Carroll and F. T. Hioe, Phys. Rev. Lett. **68**, 3523 (1992).

[13] T. Nakajima, M. Elk, J. Zhang, and P. Lambropoulos, Phys. Rev. A **50**, R913 (1994).

[14] M. Shapiro (unpublished).

[15] M. Shapiro, J. Chem. Phys. **101**, 3849 (1994).

[16] R. Loudon, *The Quantum Theory of Light*, 2nd ed. (Clarendon, Oxford, 1983).

[17] A. Vardi and M. Shapiro, J. Chem. Phys. **104**, 5490 (1996).