ADIABATIC EXCITATION OF MULTILEVEL BAND SYSTEMS ☆

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We show that the multiple-photon excitation (MPE) of multiplet systems can be described more accurately using the adiabatic than the sudden approximation for many experimentally important cases.

Among the numerous aspects of the multiple-photon excitation (MPE) of polyatomic molecules by infrared laser light [1] that have resisted explanation up to the present time, few have been more difficult to explain quantitatively using the current theories [1(a), 2] than the multiple-photon dissociation (MPD) of SF_6 and other molecules at very low intensities, the most striking example of which is the MPD observed [3] in the beam of a continuous-wave CO_2 laser. Theories of MPE using an effective-states basis and the sudden approximation [2,4] tend to describe MPE as the result of multiphoton resonances [2,5], which are too narrow at low field strengths to provide a plausible explanation of the excitation of SF_6 even to three quanta of excitation ($\upsilon_3 = 3$), much less to dissociation. Further, an isolated multiphoton resonance can result at most in a time-averaged excitation probability of 1/2 in the upper state [2]. While we make no pretense of solving the problem of MPE at low intensities, we show in this communication that excitation of a multilevel system with successive dense "bands" of levels (fig. 1) using a slowly (adiabatically) increasing optical field can lead to nearly complete *inversion* of the population from the ground state to a sublevel of the highest band. Further, numerical estimates for a system of interest (a subset of the $\upsilon_3 = 0$ and $\upsilon_3 = 1$ levels of SF_6) indicate that in fact it is the adiabatic approximation, not the sudden approximation, that is the more nearly satisfied in many cases of interest in experimental studies of MPE in real molecules. Our findings complement and extend those of Kuz'min and Sazonov [6], who have studied adiabatic inversion in a very highly idealized system consisting of a ladder of nondegenerate states.

Since the appropriateness of the adiabatic as opposed to the sudden approximation is a central point in this work, we begin with a brief discussion of the criterion for validity of the adiabatic approximation in the context of MPE. We then show analytically and numerically that adiabatic inversion is to be expected in many cases when a $(1, N)$ system is excited by a laser frequency that lies within the band of upper levels, and present numerical results that illustrate the adiabatic inversion of a $(1, N, N')$ system. We conclude with a few remarks on the circumstances under which an adiabatic inversion, which for an isolated molecule exists only while

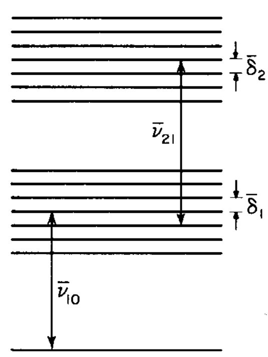

Fig. 1. Excitation of a $(1, N, N')$ system.

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the laser field is turned on, may be converted into real excitation persisting after the pulse has been turned off.

To analyze the validity of the adiabatic approximation, consider the rotating-wave Schrödinger equation for a multilevel system driven by a quasimonochromatic laser field $E(t) = E_0(t) \cos \omega t$,

$$\mathrm{d}c/\mathrm{d}t = \mathrm{i}H^{\mathrm{eff}}c, \quad (1)$$

where c is a column vector each of whose components is the Schrödinger-picture probability amplitude of a state $|mA\rangle$ of the multilevel system, times a time-dependent phase factor ([7], eq. (3)). The effective hamiltonian H^{eff}, which has been given in [8], eq. (1), is of the form

$$H^{\mathrm{eff}} = \Delta + (2\hbar)^{-1} E_0 \mu, \quad (2)$$

where Δ is a diagonal matrix containing the detunings from resonance, $\Delta_{mA} = m\omega - \hbar^{-1} E_{mA}$, and μ is the matrix of dipole transition moments. If the field envelope E_0 is increased sufficiently slowly from its initial value of zero (at $t = -\infty$) to a finite value, the system will remain in that eigenstate $|\lambda_0\rangle$ of H^{eff} that envolves continuously from the initial state $|m_0A_0\rangle$. In the multilevel adiabatic-following approximation (MLAFA) one assumes that the state vector of the system is $|\lambda_0\rangle$ for a finite rate of change of the field envelope E_0. The condition that the probability amplitude of any of the other dressed states $|\lambda_i(E_0)\rangle$ $(i \neq 0)$ be small compared to that of $|\lambda_0(E_0)\rangle$ is ([9], p. 753)

$$a_{0i}(E_0) \approx |\alpha_{0i}/\omega_{0i}| \ll 1, \quad (3)$$

where $\omega_{0i}(E_0) = \lambda_0(E_0) - \lambda_i(E_0)$; $\lambda_i(E_0)$ is the eigenvalue of H^{eff} corresponding to the dressed state $|\lambda_i(E_0)\rangle$; and

$$\alpha_{0i}(E_0) = \langle\lambda_0(E_0)|\mathrm{d}H^{\mathrm{eff}}/\mathrm{d}t|\lambda_i(E_0)\rangle/\omega_{0i}(E_0). \quad (4)$$

From (2), $\mathrm{d}H^{\mathrm{eff}}/\mathrm{d}t = (\dot{E}_0/E_0)(H^{\mathrm{eff}} - \Delta)$ for a laser pulse of fixed frequency and time-varying amplitude. For the purpose of estimating the validity of the MLAFA according to (3), we take the pulse risetime τ_{p} as an estimate of $(\dot{E}_0/E_0)^{-1}$. The criterion for validity of the MLAFA is therefore

$$|\langle\lambda_0(E_0)|\Delta|\lambda_i(E_0)\rangle|[\tau_{\mathrm{p}}(\omega_{0i}(E_0))^2]^{-1} \ll 1. \quad (5a)$$

(Note that the detuning matrix Δ is not diagonal in the dressed-states basis.) For a two-level system, explicit evaluation of eqs. (3)–(4) leads to the condition $|\dot{\Omega}\Delta| \ll |\omega_{0i}|^3$ for validity of the MLAFA (where $\Omega = \mu_{0i}E_0/2\hbar$); the latter condition has been derived previously by Crance using a different method [10]. Although (5) is in a convenient form for numerical evaluation for a multilevel system, analytical evaluation is difficult in general. In the limit of weak fields, for which $|\Omega_{i0}| \equiv |E_0\langle m_iA_i|\mu|m_0A_0\rangle|(2\hbar)^{-1} \ll |\Delta_{m_iA_i}|$, first-order perturbation theory gives $\langle\lambda_0|\Delta|\lambda_i\rangle \approx -\Omega_{i0}$ (as long as $\Omega_{i0} \neq 0$). To order E_0, $\omega_{0i} \approx -\Delta_{m_iA_i}$. The criterion for validity of the MLAFA in a weak field is therefore

$$|\Omega_{i0}|[\tau_{\mathrm{p}}\Delta^2_{m_iA_i}]^{-1} \ll 1 \quad \text{(weak field)}, \quad (5b)$$

which is surely satisfied whenever $|\Delta_{m_iA_i}|\tau_{\mathrm{p}} \gg 1$ since $|\Omega_{i0}\Delta^{-1}_{m_iA_i}| \ll 1$. Criterion (5b) for a *multilevel* system is consistent with, and generalizes, the weak-field adiabaticity criterion previously obtained from an exact solution for a two-level system driven by a semiexponential pulse [11].

For strong fields the situation is more complex because of the possibility of avoided crossings of the dressed energy levels for some values of E_0. In the case of a system consisting of three levels ($|0\rangle$, $|1\rangle$ and $|2\rangle$), an avoided crossing can occur between the dressed states $|\lambda_0\rangle$ and $|\lambda_2\rangle$ that evolve adiabatically from $|0\rangle$ and $|2\rangle$ if the laser frequency is tuned between the one-photon and two-photon resonance frequencies. If we assume that the intermediate state $|1\rangle$ is only weakly populated at the avoided crossing, then the splitting $\omega_{02} \approx 2\Omega_{01}\Omega_{12}/\Delta_1$ at the crossing; i.e. ω_{02} is twice the so-called "two-photon Rabi frequency" [12]. The avoided crossing occurs when $\Delta_2 = \lambda_0 \approx -\Omega^2_{01}/\Delta_1$, i.e. when the (01) Rabi frequency is the geometric mean of the upper-and intermediate-level detunings. Further, $\langle\lambda_0|\Delta|\lambda_2\rangle \sim -\Delta_2$. The criterion for adiabaticity in this case is therefore

$$|\Delta_1/(4\Omega^2_{12}\tau_{\mathrm{p}})| \ll 1 \quad \text{(avoided crossing)}, \quad (5c)$$

where Ω_{12} is evaluated at the field strength for which the crossing occurs. For example, if $\mu_{01} \sim \mu_{12}$, then (5c) and the relation $\Omega^2_{01} \approx -\Delta_1\Delta_2$ (at the crossing) imply that the criterion for adiabaticity is $\Delta_2\tau_{\mathrm{p}} \gg 1/4$: i.e. the critical time scale in this case is established by the detuning of the upper level.

We turn to a discussion of adiabatic inversion of a $(1, N)$ system consisting of the lower two sets of levels in fig. 1. As is well known, the eigenvalue equation for this system is [13] $\lambda = \Sigma^N_{(i=1)}\Omega^2_i(\lambda - \Delta_{1i})^{-1}$. The component along $|1j\rangle$ of the eigenvector corresponding to

λ is given by

$$b_j(\lambda) = \Omega_j(\lambda - \Delta_{1j})^{-1}\, b_0(\lambda). \qquad (6)$$

For low fields such that

$$|\Omega_j| \ll |\Delta_{1,i\pm 1} - \Delta_{1i}|, \qquad (7)$$

the eigenvalues are $\lambda \approx 0$ and $\lambda \approx \Delta_{1i}$. For higher fields the dressed level $|\lambda_0\rangle$ correlated with the ground state $|0\rangle$ is repelled by the manifold of levels $|\lambda_{1i}\rangle$. If the detuning Δ_0 of the ground level (which we take as $\equiv 0$) lies *outside* the manifold of upper-level detunings Δ_{12}, then the mutual repulsion of $|\lambda_0\rangle$ and the manifold of $|\lambda_{1i}\rangle$ as E_0 is increased, together with the fact that all but two of the dressed-state energies are trapped between successive detunings $[\Delta_{1i}, \Delta_{1,i\pm 1}]$, have the consequence that at sufficiently high fields the $(1,N)$ system closely resembles a two-level system. However, if $\Delta_0(\equiv 0)$ is *within* the manifold $\{\Delta_{1i}\}$, then the repulsion of λ_0 by most of the upper levels $|\lambda_{1i}\rangle$ as E_0 is increased will lead to an avoided crossing of $|\lambda_0\rangle$ with some dressed level $|\lambda_{1j}\rangle$, with the consequence that $\lambda_0 \to \Delta_{1j}$ as $E_0 \to \infty$. It is this avoided crossing that leads to adiabatic inversion of a $(1,N)$ system when the laser frequency is tuned within the band of upper levels.

To analyze the avoided crossing and to evaluate the adiabaticity criterion 5(a), let $\lambda_{11} = \Delta_{1j} + \eta_j$, where we expect that $|\eta_j| \ll |\Delta_{1,j\pm 1} - \Delta_{1,j}|$ for high fields. From (6a) we find that

$$\eta_j \approx \mu_j^2 (E_0/2\hbar)^2\, [\Delta_{1j} - (E_0/2\hbar)^2 K_j]^{-1}, \qquad (8)$$

where $K_j = \Sigma_{(i\neq j)}\, \mu_i^2 (\Delta_{1j} - \Delta_{1i})^{-1}$. Speaking crudely, for fields for which the Rabi frequency is large compared to the spacing of upper levels, i.e.,

$$|\Omega_j| \gg |\Delta_{1,j\pm 1} - \Delta_{1,j}|, \qquad (9)$$

K_j will be the dominant term in the denominator of (8), since Δ_{1j} is nearly zero. Thus the crossing occurs when $|\Omega_j| \sim |\Delta_{1,j\pm 1} - \Delta_{1,j}|$. The asymptotic value of η_j is $\eta_j^{(a)} \sim -\mu_j^2/K_j$. The probability amplitude of the upper state $|1j\rangle$ in this case, is from (6), $b_j(\lambda_0) \approx (\Omega_j/\eta_j)\, b_0(\lambda_0)$, so that the population in $|1j\rangle$ is large provided that $|\Omega_j| \gg |\eta_j|$. The inversion is most nearly complete for a given E_0 when $|1j\rangle$ is located at the edge of the manifold (fig. 2). If we let $j = N$, $\mu_i = \mu$ and $\Delta_{1,i+1} - \Delta_{1,i} = \delta$ (independent of i), and then approximate $K_N \approx (\mu^2/\delta) \ln N$, we find the asymptotic $\eta_N = \lambda_{1N} - \Delta_{1N}$ to be $\eta_N^{(a)} \approx -\delta/\ln N$. The asymptotic upper-state probability amplitude is $b_N(\lambda_0) \sim -(\mu E_0/(2\hbar\delta))\,(\ln N)\, b_0(\lambda_0)$; the ratio of the Rabi frequency to the level spacing and the logarithm of the number of upper states are thus the dominant parameters in determining the degree of inversion.

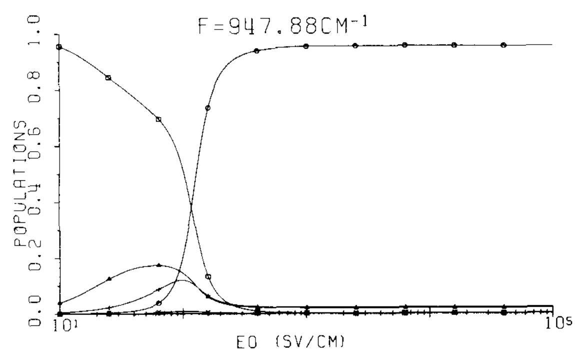

Fig. 2. Populations in the sublevels $|1j\rangle$ of a (1, 5) system for which the upper-level spacing is $\delta/2\pi c$ = 0.1 cm^{-1}; the transition dipole moments are $\Sigma\, \mu_i^2 = (4 \times 10^{-19}$ st C –cm (esu))^2 □: $|0,0\rangle$ state; ○: $|1,1\rangle$ state.

An evaluation of the adiabatic criterion (5a) using $|\omega_{01}| \sim \delta$ and $|\langle\lambda_0|\Delta|\lambda_{1j}\rangle| \sim |\Delta_{1N}|/2$ (which are valid for a state at the edge of the manifold $\{\Delta_{1i}\}$) leads to the criterion

$$\tau_p \delta \gg 1/2 \qquad (10)$$

for adiabatic inversion of the levels $|0\rangle$ and $|1N\rangle$ by increasing E_0. To see whether this criterion is satisfied in MPE experiments, consider the excitation of clusters of levels with a given value of R in the $v_3 = 1$ state of SF_6. The spacing between clusters is $\delta/2\pi c$ 300–500 MHz; typical pulse lengths $\tau_p \sim$ 50–100 ns thus easily satisfy (10), and even for the subpulses of length $\tau_p \sim 1$ ns in a typical self-mode locked CO_2 TEA laser pulse one finds $\delta\tau_p \sim 1$. The critical field strength at which an avoided crossing occurs in $v_3 = 1$ of SF_6 is $E_0 \sim 2\hbar\delta/\mu \sim 10$ sV cm^{-1}, corresponding to an intensity $I \sim 10^4$ W cm^{-2}, which is quite modest in comparison with intensities often used in MPE experiments. By contrast, the critical field strength for adiabatic inversion of a $v = 2$ level with an intermediate-state detuning $\Delta_1 \sim 2$ cm^{-1} and an upper-state detuning $\Delta_2/2\pi \sim 500$ MHz, which exemplifies the situation envisaged in [6], is $E_0 \sim 200$ sV cm^{-1}, corresponding to the much higher intensity $I \sim 4 \times 10^6$ W cm^{-2}. Thus the phenomenon of adiabatic inversion of $(1,N)$ systems must be taken seriously in studies of MPE in real systems.

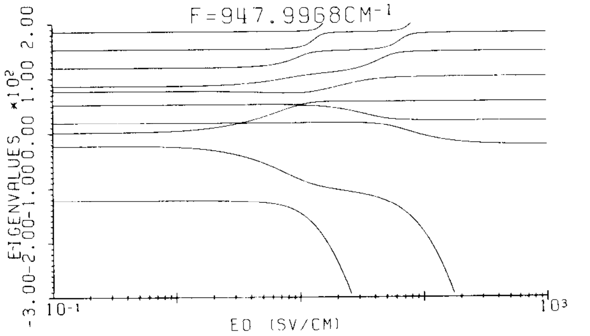

Fig. 3. Dressed-state eigenvalues λ of a (1, 3, 6) system as functions of the laser field amplitude E_0, showing avoided crossings. Parameters were (see fig. 1) $\bar{\nu}_{10}$ = 948.000 cm^{-1}; $\bar{\nu}_{21}$ = 947.985 cm^{-1}; $\bar{\delta}_1$ = 0.01 cm^{-1}; $\bar{\delta}_2$ = 0.0033 cm^{-1}; $\Sigma\mu_i^2 = (4 \times 10^{-19}$ esu$)^2$; and $\omega/2\pi c$ = 947.98 cm^{-1}.

Similar phenomena of adiabatic inversion occur in $(1,N,N')$ systems, as is illustrated for a (1, 3, 6) system in figs. 3 and 4. In fact, one expects adiabatic inversion to be a general phenomenon for multilevel "band" systems, and to occur at field strengths of the order of magnitude indicated by (7) whenever the laser frequency ω is such that $n\hbar\omega$ lies within the nth band. In SF_6 early calculations suggested [14] and recent work has confirmed [15] that a sequence of such resonantly connected "bands" exists up to high levels of excitation ($v_3 \sim 10$). Similar patterns of nearly resonant excitation have been found or conjectured in other molecules [1]. Further, the vibrational quasi-continuum that has been invoked to explain many features of MPE is usually assumed [5] to afford a resonant transition at any laser frequency near the $v = 0 \rightarrow v = 1$ transition frequency; the $(1,N,N',...)$ system is a model of such a system. Therefore one expects adiabatic inversion to be a commonplace phenomenon in multilevel systems and for laser pulses that satisfy (10). As is illustrated in fig. 4, avoided crossings can lead to partial de-excitation (as well as to excitation) to the highest band of a multilevel system. This situation was not forseen in previous work [6]. In fig. 5 we show the quantity $|\langle\lambda_0|\Delta|\lambda_i\rangle|\omega_{i0}^{-2}$, which by (5a) must be short compared to the laser pulse length for the (1, 3, 6) system of figs. 3 and 4. Evidently all but the shortest pulses that have been used in MPE experiments easily satisfy the adiabatic criterion for the parameters of the model (1, 3, 6) system, which though arbitrary are of a realistic order of magnitude.

A true adiabatic inversion of the kind we have described cannot persist if the laser pulse is also turned off adiabatically, for then the system will simply remain in the level $|\lambda_0\rangle$, which approaches the ground state as $E_0 \rightarrow 0$. However, the adiabatic approximation will be violated when (10) is no longer obeyed. In polyatomic molecules, one expects the level spacing δ to be a *decreasing* function of vibrational energy; thus (10) may be satisfied for low-lying vibration-rotation states but not for higher levels. In these circumstances the excitation of the higher levels more nearly resembles sudden than adiabatic excitation, and some population will remain excited after the laser pulse is turned off. Of course, if a molecule adiabatically excited to high levels dissociates or undergoes a collision during the laser pulse, the energy deposited adiabatically is not returned to the laser field as $E_0 \rightarrow 0$.

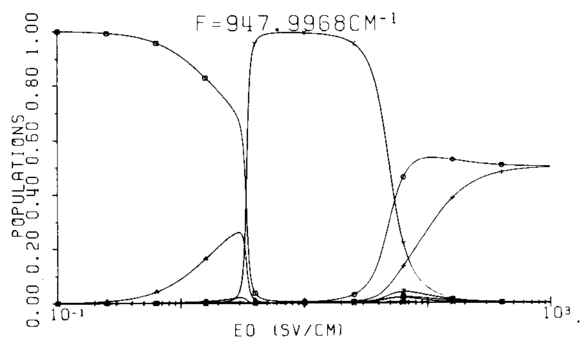

Fig. 4. Populations of the sublevels of a (1, 3, 6) system as functions of the field amplitude E_0, illustrating the excitation first of v = 2 and subsequently v = 1. □: ground state; Y: |2, 6⟩ state; ○: |1, 1⟩ state; +: |1, 3⟩ state.

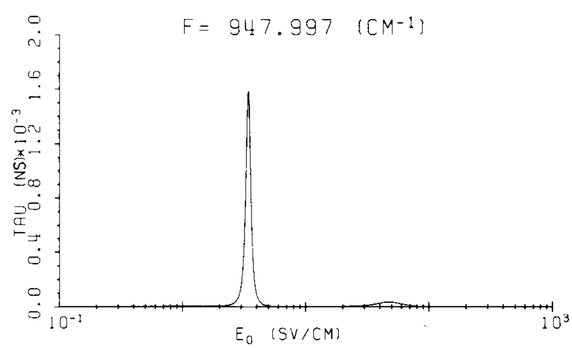

Fig. 5. The quantity $T_p \equiv |\langle\lambda_0|\Delta|\lambda_i\rangle|\omega_{0i}^{-2}$ as a function of laser field amplitude E_0 for the (1, 3, 6) system of figs. 3 and 4. By (5a), the adiabatic approximation is obeyed for pulses that are long compared to T_p.

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