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Coherence versus incoherence in stepwise laser excitation of atoms and molecules*

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We discuss multistep resonant photoionization of atoms and photodissociation of molecules. We derive a condition under which induced atomic or molecular coherence can always be neglected, allowing accurate analysis of the multiphoton process by simple rate equations. The condition is realizable in practice, and consistent with large ionization and dissociation rates.

The simplicity of the population-rate-equation (PRE) approach to atomic excitation phenomena is a strong justification for its widespread use. In the case of resonant multilaser ionization these population rate equations are easily written and solved. For example, the four-laser case is illustrated in Fig. 1, and the appropriate PRE's are

$$\dot{n}_1 = -R_1(n_1 - n_2) + n_2/\tau_{21}, \tag{1}$$

$$\dot{n}_2 = R_1(n_1 - n_2) - R_2(n_2 - n_3) - \frac{n_2}{T_2} + \frac{n_3}{\tau_{32}}, \tag{2}$$

$$\dot{n}_3 = R_2(n_2 - n_3) - R_3(n_3 - n_4) - \frac{n_3}{T_3} + \frac{n_4}{\tau_{43}}, \tag{3}$$

$$\dot{n}_4 = R_3(n_3 - n_4) - R_4 n_4 - \frac{n_4}{T_4}. \tag{4}$$

The populations of the levels of the atom are denoted n_1, n_2, etc. The rates of stimulated emission and absorption are denoted R_1 for the first transition, R_2 for the second, and so on, with R_4 denoting the stimulated rate for excitation into the continuum at which point ionization is considered to be complete. The time parameters arise from spontaneous radiative decay, collisions of various kinds, and other lifetime- and coherence-limiting phenomena. For example, $1/\tau_{32}$ is the rate at which spontaneous processes take population from level 3 to level 2, whereas $1/T_3$ is the total rate (including $1/\tau_{32}$) for population to leave level 3. Obviously $1/\tau_{32}$ and $1/T_3$ are related by a branching ratio. The rate of change of the total population, $\dot{n}_T = \dot{n}_1 + \dot{n}_2 + \dot{n}_3 + \dot{n}_4$, is not zero for two reasons: because the atoms that are ionized are not counted in the four equations; and because the levels in the diagram may decay to relatively metastable levels which are not even drawn, allowing population to become more or less permanently lost.

It is easy to solve Eqs. (1)–(4), even for arbitrary values of the parameters and arbitrary initial populations. What is not easy, is to decide whether or not the equations should be solved at all. Because of the tunability and very narrow bandwidth of dye lasers, every step upward in the atomic excitation ladder can, in practice, be stimulated strongly, coherently, and on resonance. There is then the possibility of coherence among the transitions, for example of periodic pulsations in the level populations. In this case the rate equations (1)–(4) are inapplicable and must be supplemented in the well-known way with more elaborate atomic operator or density matrix equations that contain "off-diagonal" information. From the standpoint of practical solvability, this supplementation is a backward step of major proportion. For an N-level ladder the number of equations is no longer N but more nearly N^2. In a thorough calculation where one might want to take separate account of hyperfine components of levels, as well as of any metastable levels that might act as population sinks, the number of separate transitions could easily exceed 10 or 20.

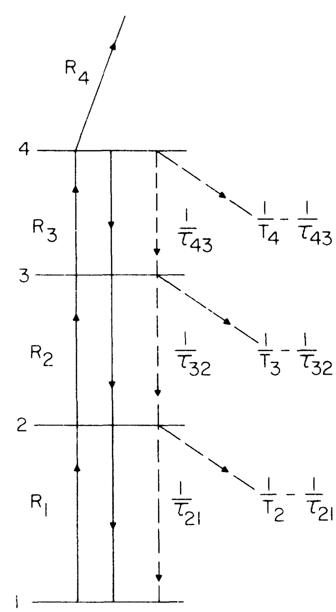

FIG. 1. Four-laser ionization of an atom. The solid lines signify laser-induced emission and absorption; and the dotted lines signify decay and loss transitions independent of laser power.

The difference between N and N^2 would then be very significant.

The question therefore arises, are there any circumstances in which the rate equations can be used with confidence to study multistep excitation chains, even if the exciting lasers have very narrow bandwidths, have high intensities, and are tuned to resonance with the several transitions in the ladder? A closely related question was considered by Wilcox and Lamb,[1] whose principal interest was in low-power situations. In ionization and dissociation experiments, on the other hand, the high-power limit applies to most of the transitions of interest. That is, the stimulated transition rate dominates all of the incoherent and spontaneous relaxation rates acting on most of the level populations. Still, as we show below, rate equations can provide a complete description of the transition dynamics under certain frequently met conditions, even in the high-power limit.

For reference, we recall the expression for the stimulated transition rate appropriate to a monochromatic laser of frequency ω_L interacting with an atomic transition having transition frequency ω_A and linewidth Γ (Ref. 2):

$$R = \sigma(\omega_L, \omega_A)\Phi \ , \tag{5}$$

Φ being the photon flux and $\sigma(\omega_L, \ \omega_A)$ the absorption cross section,

$$\sigma(\omega_L, \ \omega_A) = \frac{4\pi^2\omega_L d^2}{\hbar c}\,\frac{\Gamma}{2\pi}\,\frac{1}{(\omega_L - \omega_A)^2 + \frac{1}{4}\Gamma^2} \ . \tag{6}$$

By the photon flux we mean the number of photons/cm^2 sec in the laser beam. For definiteness the experiment can be thought of as being carried out with crossed atomic beam and laser beams, in which case the linewidth Γ is due mainly to processes that remove populaticn from one or the other of the two levels that define the transition, and is hardly influenced at all by Doppler broadening. It is the stimulated transition rate R that enters population rate equations such as Eqs. (1)–(4); and it is the R's that are responsible for the growth of population in levels 2, 3, ..., at the expense of level 1, in all such PRE's.

In general PRE's do not, of course, provide a complete description of any excitation process. Their structure is suitable only for processes in which the populations change monotonically. It is well known that nonmonotonic pulsations of level populations can occur if an atom is subjected to intense coherent nearly resonant radiation. These population pulsations occur at the Rabi rate.[3] This Rabi rate is related to the field-dipole interaction energy divided by $\hbar$. If we denote by d the transition dipole matrix element, and let $\mathcal{E}$ be the amplitude of the laser field:

$$\vec{E}(z, t) = \hat{x}\mathcal{E}(e^{i(\omega_L t - kz)} + \text{c.c.}), \tag{7}$$

then the general expression for Ω, the Rabi rate, is

$$\Omega = [(2d\mathcal{E}/\hbar)^2 + (\omega_L - \omega_A)^2]^{1/2}. \tag{8}$$

It is important to note that at resonance ($\omega_L = \omega_A$) the Rabi rate (8) is *linear* in the laser-field amplitude, and so is physically quite different from the stimulated absorption rate (5), which is proportional, via the photon flux, to the *square* of the field amplitude.

We now derive[4] a simple connection between the Rabi rate Ω, and the usual stimulated rate R, that will allow some general conclusions to be drawn about the relevance of PRE's even in the case of strong coherent excitation. First of all, let us agree to consider only on-resonance laser light. This maximizes R, and minimizes Ω, for a given laser strength. In this case,

$$R = (8\pi\omega_L d^2/\hbar c \Gamma)\Phi \tag{9}$$

and

$$\Omega = 2d\mathcal{E}/\hbar \, . \tag{10}$$

However, since

$$\hbar\omega_L\Phi = (c/2\pi)\mathcal{E}^2 \ ,$$

we immediately find the relation (Allen and Eberly, Ref. 2)

$$R = \Omega^2/\Gamma \ . \tag{11}$$

Relation (11) has a number of interesting features. It shows, for example, that the Rabi population pulsation rate is the geometric mean of the stimulated transition rate and the absorption linewidth. Its greatest significance, however, lies in the restriction it places on R. Obviously $R > \Omega$ only if $\Omega > \Gamma$. However, it is just when $\Omega > \Gamma$ that population pulsations occur.[5] And when population pulsations occur, PRE's (built around the stimulated rates R) are no longer adequate to describe the excitation process. That is, one has smooth monotonic population flow through the levels of the atom (and valid PRE's) only when R is small,[6] small in the sense that $R < \Omega$ (i.e., $\Omega < \Gamma$).

There is a practical question associated with the results of the preceding paragraph. It would not be easy to operate a fully coherent multilaser ionization or dissociation process, say, for the purpose of isotope selection, because the phases of the several lasers would be difficult to control very well. Thus the very highest rates of population movement from level 1 to level 2, from 2 to 3, and so on, which arise from fully coherent interactions with the lasers, are at present practically unavailable.

On the other hand, multiphoton transitions leading to ionization or dissociation have a feature not found in more-common multilaser optical pumping processes. This feature is the effective irreversibility of the final step. There is effectively no recombination from the ionized or dissociated stage. That being the case, the last transition (step 4 in Fig. 1) can be stimulated as strongly as desired without producing Rabi cycling in the transition. Thus the final step can always be treated by a rate equation, with a rate as large as desired. We show below that this feature is sufficient to permit population rate equations to be used to describe all of the lower transitions as well, so long as the laser powers are high enough. In other words, contrary to what might have been expected, very high laser powers, as specified below, can be used to guarantee both the existence of high ionization or dissociation rates and the strict absence of Rabi cycling, making a PRE analysis of the process completely valid.

Let us arrange first of all for the lasers to be powerful enough so that the stimulated rates R_1, R_2, etc., dominate the various decay rates $1/\tau_{21}$, $1/T_2$, etc. That is, all four lasers saturate their respective transitions. Next let us further arrange the laser powers so that we have

$$R_4 > R_3 > R_2 > R_1. \tag{12}$$

Under the condition expressed by relation (12) the laser that induces the last step on the ladder may have to be several orders of magnitude more powerful than the first laser. This is because the cross section (6) appropriate to a high-lying optical transition in an atom can be orders of magnitude smaller than the cross section for a ground-state transition. This restriction is not nearly so severe if, for example, the level we have labeled 4 is a high-lying Rydberg-like level and infrared or microwave photons are being used to induce transition 4.

The useful feature of (12), as far as the question asked in the third paragraph goes, is that the answer to that question is definitely yes. The PRE's will be completely adequate, no population pulsations will occur, and the fully coherent off-diagonal equations will carry no additional information. In order to show this we need only rearrange some of the material given above. (A more-detailed treatment is given in the Appendix.) The linewidth of the nth transition is provided by the incoherent processes affecting the transition. In our case, lifetime-limiting effects are the dominant sources of incoherence, and the main limit on the lifetime of the nth transition is provided by the rapid removal of population from its upper level by the laser that is pumping the $(n+1)$st transition. Recall that we assume that spontaneous effects can be ignored compared with the high-power stimulated effects. Thus we can write $\Gamma_n = R_{n+1}$. This combines with (11) and (12) to give the simple inequality

$$\Gamma_n = R_{n+1} > R_n = \Omega_n^2/\Gamma_n. \tag{13}$$

This last relation is of course equivalent to

$$\Gamma_n^2 > \Omega_n^2 . \tag{14}$$

If we interpret ">" to mean greater by a factor of 4 or 5, then (14) says $\Omega \lesssim \Gamma$ and any population pulsations will be insignificant, as claimed. The conclusion is therefore as stated above, namely, that when the stimulated transitions dominate all others, and when the stimulated rates are ordered according to (12), then all of the coherent Rabi oscillations are damped. Coherent processes can safely be neglected in the transition chain leading to ionization or dissociation.

A few remarks may be appended to the conclusion reached in relation (14). The first is to mention again that the conclusion depends only on the intensities of the lasers used. Coherence-exhibiting features of the transitions will simply be overwhelmed if the laser powers are high enough, no matter how coherent or near to resonance they are. Further, the inequality chain assumed in (12) has a practical consequence as well as the theoretical consequence expressed in (14). The practical consequence of (12) is that no bottlenecks can develop in the ionization chain. It is always more probable for an atom to be stimulated further up than to be stimulated back down. Of course, it is just this fact, acting through the relation (11) between stimulated and Rabi rates, that guarantees the result given in (14). That is, the probability of going upward out of a given pair of levels is just too high to permit the atom to undergo even one Rabi cycle between the levels.

Note that all of these conclusions rest on the implicit assumption that the last transition, in our case the fourth, is known *a priori* to be well described by a PRE. If Rabi cycling occurred in the fourth transition, relation (12) would be meaningless. Fortunately, it is just in the cases of ionization and dissociation that our implicit assumption is most reasonable, since it is equivalent to the neglect of recombination transitions.

Finally, we must point out clearly that, although we have shown that complex and reasonably realistic situations do exist in which high-power and very coherent laser beams do not produce coherent interactions with an atom (situations do exist in which PRE's may be used from the beginning), we have made a number of assumptions that do not permit our conclusion to be extrapolated too widely. Most of these assumptions are stated in the text, but an important one not stated explicitly is that the ionization ladder is climbed step by step and always on resonance. Another one is that any level degeneracies can be ignored completely.

We thank J. I. Davis and B. W. Shore for a conversation in which the right questions were asked.

APPENDIX

In the text above Eq. (13) we claim that under the conditions stated it is unnecessary to consider the full set of off-diagonal as well as diagonal density matrix or operator equations. Relation (14) is a crude indication that our claim is valid. A much better indication may be thought desirable, so we provide it here.

We want to establish not only that the set of N^2 fully coherent equations describing transitions in an N-level atom can be replaced by the N equations for the "diagonal" population variables, if the laser powers are high enough, but also that the phenomenological rate constants that enter the population equations are the ones we have used in the text. In order to do this we simply write the N^2 equations, and show that most of them are superfluous in the high-power regime, no matter how coherent and close to resonance the laser fields are.

A central feature of our argument was its step-by-step character. That is, we isolated the nth transition in the excitation chain and discussed it separately. We will not do that here, to guard against the possibility that such isolation introduces error. However, we will discuss an atom with one fewer energy level. This has the dual advantage of somewhat greater simplicity, as well as greater familiarity. In fact, the fully coherent three-level equations do not need to be derived, but can be taken from other references.[7] Thus in the following analysis we have discarded level 1. In the end we compare our results with the corresponding results of PRE's, (2)–(4), with all references to level 1 removed, i.e., with $R_1 = 1/T_2 = 0$.

The nine equations for the three upper transitions shown in Fig. 1 are

$$\dot{n}_2 = \tfrac{1}{2}\Omega_2 v_{23} + n_3/\tau_{32}\,, \tag{A1}$$

$$\dot{n}_3 = -\tfrac{1}{2}\Omega_2 v_{23} + \tfrac{1}{2}\Omega_3 v_{34} - n_3/T_3 + n_4/\tau_{43}\,, \tag{A2}$$

$$\dot{n}_4 = -\tfrac{1}{2}\Omega_3 v_{34} - n_4/T_4 - R_4 n_4, \tag{A3}$$

$$\dot{u}_{23} = -\Delta_{23} v_{23} + \tfrac{1}{2}\Omega_3 v_{24} - (1/2T_3) u_{23}, \tag{A4}$$

$$\dot{v}_{23} = \Delta_{23} u_{23} + \Omega_2(n_3 - n_2) - \tfrac{1}{2}\Omega_3 u_{24} - (1/2T_3) v_{23}, \tag{A5}$$

$$\dot{u}_{34} = -\Delta_{34} v_{34} - \tfrac{1}{2}\Omega_2 v_{24} - \tfrac{1}{2}(1/T_3 + 1/T_4 + R_4) u_{34}\,, \tag{A6}$$

$$\dot{v}_{34} = \Delta_{34} u_{34} + \tfrac{1}{2}\Omega_2 u_{24} - \tfrac{1}{2}(1/T_3 + 1/T_4 + R_4) v_{34} + \Omega_3(n_4 - n_3), \tag{A7}$$

$$\dot{u}_{24} = -\Delta_{24} v_{24} - \tfrac{1}{2}\Omega_2 v_{34} + \tfrac{1}{2}\Omega_3 v_{23} - \tfrac{1}{2}(1/T_4 + R_4) u_{24}, \tag{A8}$$

$$\dot{v}_{24} = \Delta_{24} u_{24} + \tfrac{1}{2}\Omega_2 u_{34} - \tfrac{1}{2}\Omega_3 u_{23} - \tfrac{1}{2}(1/T_4 + R_4) v_{24}\,. \tag{A9}$$

In these equations, written using the rotating-wave approximation (RWA), the n's have the same meaning as in Eqs. (2)–(4) of the text. The u's and v's are the several transition-operator amplitudes, in-phase and in-quadrature, respectively, with the two laser fields. The laser fields are assumed to be tuned within the nonoverlapping Doppler lines of the two transitions, and Δ_{ij} is the small amount by which an individual transition line under the Doppler curve is out of resonance with the appropriate laser. The possibility of fully coherent interaction of the laser fields with the atom means that the two Rabi rates Ω_2 and Ω_3 enter these equations, and not the stimulated absorption rates R_2 and R_3 of Eqs. (2)–(4). As in the text we ignore recombination of the ionized or dissociated state back down into level 4, with the result that there is no Rabi rate Ω_4.

When there is no recombination from the ionized or dissociated state, then the final step (transition 4 in Fig. 1) can be made arbitrarily fast without risk of Rabi cycling simply by turning up the power of the laser responsible for the transition. We assume this has been done, and we assume $\Omega_3 > \Omega_2$, so that we can make use of the inequalities:

$$R_4 \gg \Omega_3 \gg \Omega_2 \gg \Delta_{34}, \Delta_{24}, 1/T_3,\ 1/T_4\,. \tag{A10}$$

These inequalities are another way of stating the assumption in the text that the stimulated laser-induced processes are all more rapid than any of the spontaneous relaxation processes. In addition we have here chosen to order the laser powers in a way consistent with Eq. (12). With Eq. (A10) applied to Eqs. (A1)–(A9) we can begin treating the problem stated in the text with a fully coherent analysis instead of with heuristic notions based on the relative size of the Rabi rate Ω and the poorly defined linewidth Γ. Note that (apart from R_4 itself) the coherent equations (A1)–(A9) do not even have a quantity indentifiable as a linewidth associated with either transition 2 or transition 3 after (A10) has been invoked to eliminate the relaxation rates from the equations.

When (A10) is invoked, any population reaching level 4 is instantly ionized. Thus the population in level 4 is always negligible, and the off-diagonal variables connected to level 4 should be very small. A formal integration of Eqs. (A6)–(A9) leads to this same conclusion, and shows that the quasisteady amplitudes of these variables are

$$u_{34} \cong 0, \tag{A11}$$

$$v_{34} \cong (2\Omega_3/R_4)(n_4 - n_3), \tag{A12}$$

$$u_{24} \cong (\Omega_3/R_4)v_{23}\ , \tag{A13}$$

$$v_{24} \cong -(\Omega_3/R_4)u_{23}. \tag{A14}$$

After substituting (A11)–(A14) into the remaining equations of motion, we find

$$\dot{n}_2 = \tfrac{1}{2}\Omega_2 v_{23}\ , \tag{A15}$$

$$\dot{n}_3 = -\tfrac{1}{2}\Omega_2 v_{23} + (\Omega_3^2/R_4)(n_4 - n_3)\ , \tag{A16}$$

$$\dot{n}_4 = -(\Omega_3^2/R_4)(n_4 - n_3) - R_4 n_4\ , \tag{A17}$$

$$\dot{u}_{23} = -(\Omega_3^2/2R_4)u_{23}\ , \tag{A18}$$

$$\dot{v}_{23} = \Omega_2(n_3 - n_2) - (\Omega_3^2/2R_4)v_{23} \tag{A19}$$

Note that the rate Ω_3^2/R_4 appears in Eqs. (A18) and (A19) as a coherence-destroying rate. That is, both off-diagonal variables u_{23} and v_{23} are exponentially damped at the rate Ω_3^2/R_4.

Now we may observe that, if the laser fields are strong enough, and under the assumption (A10), then the coherence-destroying rate Ω_3^2/R_4 can be made to dominate both (A18) and (A19). Very quickly u_{23} and v_{23} will relax to the quasisteady and very small values

$$u_{23} \cong 0, \tag{A20}$$

$$v_{23} \cong 2\Omega_2(\Omega_3^2/R_4)^{-1}(n_3 - n_2). \tag{A21}$$

When these solutions are substituted into the remaining equations of motion we find

$$\dot{n}_2 = -\Omega_2^2(\Omega_3^2/R_4)^{-1}(n_2 - n_3)\ , \tag{A22}$$

$$\dot{n}_3 = \Omega_2^2(\Omega_3^2/R_4)^{-1}(n_2 - n_3) - (\Omega_3^2/R_4)(n_3 - n_4)\ , \tag{A23}$$

$$\dot{n}_4 = (\Omega_3^2/R_4)(n_3 - n_4) - R_4 n_4\ . \tag{A24}$$

It is apparent that the $3\times3=9$ equations with which we started the Appendix have been reduced to only three. The three are population rate equations and can be compared with the PRE's (2)–(4) in the text in the limit that the spontaneous relaxation terms can be ignored everywhere (a limit used in the text and in the Appendix on the assumption that all transitions are well saturated). The correspondence between (A22)–(A24) and (2)–(4) is exact if the following identification of rates is made:

$$R_2 \equiv \Omega_2^2(\Omega_3^2/R_4)^{-1} = \Omega_2^2/R_3\ , \tag{A25}$$

$$R_3 \equiv \Omega_3^2/R_4\ . \tag{A26}$$

Note that (A25) and (A26) constitute a rederivation of Eq. (11) in the text, but with the linewidth Γ now clearly identified.

Thus we find three things in Eqs. (A22)–(A26). First, it is now clear that our assertion in the text is valid: if the laser powers are high enough and ordered according to (12), then the ionization or dissociation dynamics will be accurately described by PRE's. Second, the threshold for the validity of this assertion comes when the Rabi rate of a given transition is exceeded by any population-removing or coherence-destroying rate operating on the transition. And third, when the laser power is very high, the relevant incoherent rate is just the stimulated transition rate of the strongest transition directly coupled to the given transition.

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[1]L. R. Wilcox and W. E. Lamb, Jr., Phys. Rev. 119, 1915 (1960). Appendix I of this paper formalizes the technique used in the preceding paper [W. E. Lamb, Jr. and T. M. Sanders, Jr., Phys. Rev. 119, 1901 (1960)] to examine the rate-equation question. It is in the Lamb-Sanders paper, at the end of Sec. 2, that the physical conditions required to justify their conclusions are most clearly stated: "For the validity of the (rate) equations it was necessary to assume (1) the rotating field approximation, and (2) that the population difference $(\sigma_{aa} - \sigma_{bb})$ was slowly varying. These assumptions are valid for a steady-state experiment unless excessive rf is used." In their language it is just the case of excessive rf that interests us in the present paper.

[2]See, for example, any of a wide range of texts for discussions of stimulated transition rates and absorption cross sections, including E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., London, 1935); E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1961); L. Allen and J. H. Eberly, *Optical Resonance and Two Level Atoms* (Wiley, New York, 1975), Sec. 6.3 and Eq. (6.19).

[3]For a discussion of coherent population oscillations see A. Yariv, *Quantum Electronics*, 2nd ed. (Wiley, New York, 1975), p. 379; M. Sargent, M. O. Scully, and W. E. Lamb, Jr., *Laser Physics* (Addison-Wesley, Reading, Mass., 1974), Secs. 2.1 and 2.4; L. Allen and J. H. Eberly, Ref. 2, Sec. 3.3.

[4]L. Allen and J. H. Eberly, Ref. 2, Sec. 6.3; and M. Sargent, M. O. Scully, and W. E. Lamb, Jr., Ref. 3, Sec. 2.4.

[5]Population pulsations are absent when $\Omega < \Gamma$ because Γ is the effective damping rate for such pulsations. See M. Sargent *et al.*, Ref. 4, Sec. 2.4.

[6]This explains the appearance of proposals to use co-

herent processes (not describable by PRE's) in laser isotope separation, where the greatest possible ionization or dissociation rate is sought. That is, higher transition rates are achieved by higher laser powers, but as soon as the laser power is high enough so that $R > \Omega$, then the transition rate R is a misleading parameter because then the PRE's are invalid. In other words, if $R > \Omega$ then $\Omega > \Gamma$ and population pulsations will dominate the physics, so that one must take coherent effects seriously and employ them to advantage if possible.

[7]Three-level-atom equations have been analyzed recently, for example, by R. G. Brewer and E. L. Hahn [Phys. Rev. A 11, 1641 (1975)]. They consider the case in which the spontaneous relaxation rates $1/T_3$, $1/\tau_{43}$, etc., make important contributions to the dynamics.