

Induced nonadiabatic transitions in molecules

V. A. Kovarskiĭ, A. V. Belousov, É. P. Sinyavskiĭ, and O. Yu. Keloglu

(Submitted 30 April 1985)

Zh. Eksp. Teor. Fiz. **89**, 1552–1557 (November 1985)

Induced nonradiative nonadiabatic molecular transitions are considered which are activated by dipole-active vibrations interacting with low-frequency laser radiation. The populations of a two-level electron system interacting with “hot” vibrations are calculated by the nonequilibrium density matrix technique. The time dependence of the populations is shown to be determined by the nonmonotonic time dependence of the nonadiabatic transition probabilities.

1. INTRODUCTION

Recent experiments on the interaction of infrared laser pulses with molecules have led to the observation of induced nonradiative transitions (NT), in which the laser-excited vibrations induce electron transitions between two electron-vibrational terms. According to Refs. 1 and 2, such induced “inverse nonradiative transitions” should be accompanied by luminescence whose intensity and time profile are determined by the induced NT probability and the dependence of the latter on the properties of the laser pulse. Unlike ordinary “cold” nonradiative transitions, induced NT’s are vibrationally “hot” due to the interaction of dipole-active molecular vibrations with the infrared laser radiation, and the hot vibrations participate in the nonadiabatic transition.³ Two cases can occur in practice—either the selection rules break down, or else they forbid a direct interaction of an electron with the dipole-active vibrations. In the latter case one must analyze the anharmonic coupling between the dipole-active vibration and other vibrational modes interacting directly with the electron. For simplicity, in what follows we will limit ourselves to the case when direct electron-vibrational (e-V) interaction is allowed.

The selective excitation of dipole-active vibrations was discussed in Ref. 4, where it was shown that the threshold for complete randomization of the molecular vibrations must lie above the dissociation threshold for a given mode. For the nonradiative transitions of interest to us, the nonadiabatic region [in which term crossings (quasiintersections) occur] must thus lie below both the dissociation threshold and the threshold for total randomization of the molecular vibrations.

In the theory of nonradiative transitions, the role of the accepting modes is played by fully symmetric vibrations which are coupled to the electrons much more strongly than other vibrations, which promote the transition but are not fully symmetric.⁵ However, the promoting modes are much more important in induced nonradiative transitions, because their effective coupling constant with the electrons contains vibrational occupation numbers which depend on the pumping intensity.

Below we develop a theory of induced nonadiabatic NT’s based on the nonequilibrium density matrix technique.

2. BALANCE EQUATIONS AND EXPRESSION FOR THE INDUCED NONRADIATIVE TRANSITION PROBABILITIES

We consider a molecule with two electron terms 1 and 2 such that the optical transitions between them form an electron-vibrational (e-V) absorption band. The incompletely symmetric mode Q is assumed to be dipole-active, and both it and the completely symmetric mode q contribute to the halfwidth of the band. When IR laser radiation of resonant frequency ω_0 and field amplitude

$$F(t) = f(t)F_0 \sin \omega_0 t$$

excites the molecules, the Q mode is excited and its contribution to the NT may be greater than for the “cold” fully symmetric mode q (here $f(t)$ specifies the form of the laser pulse). The induced nonradiative transitions may thus compete, and we will see below that under certain conditions they may be much more probable than ordinary nonradiative transitions. The Hamiltonian for the e-V system is of the form

$$H = H_Q + H_q + \sum_{i=1}^2 \varepsilon_i \hat{n}_i - \sum_{i=1}^2 \hat{n}_i (\omega^2 q_i^0 q_i + \Omega^2 Q_i^0 Q_i) - eF(t)Q + V_{12} \hat{r}_+ + V_{21} \hat{r}_-. \quad (1)$$

Here H_Q and H_q are the Hamiltonian for the uncoupled Q and q modes; $\Omega^2 Q_i^0$ and $\omega^2 q_i^0$ are the coefficients of the e-V interaction function for the i th electron state; Ω and ω are the frequencies of modes Q and q respectively; the ε_i are the energies of the electron terms. The last two terms in (1) define the nonadiabaticity operator \hat{L} , where for simplicity we set $V_{12} = \text{const}$. The operators \hat{n}_i and \hat{r}_\pm are related to the Pauli matrices σ_α ($\alpha = 1, 2, 3$) by

$$\hat{n}_{1,2} = \frac{1}{2} \pm \sigma_3, \quad \hat{r}_\pm = \sigma_1 \pm \sigma_2.$$

The populations n_1, n_2 of the electron levels are given by

$$n_{1,2}(t) = \text{tr} \{ \hat{n}_{1,2} \rho(t) \}.$$

Here the nonequilibrium density matrix $\rho(t)$ satisfies the Liouville equation with total Hamiltonian $H + H_T$, where H_T describes the other vibrational modes of the polyatomic molecule and their anharmonic coupling to modes Q and q .

We carry out the usual unitary shift transformation⁶

inside the trace operator to select a multiphoton vertex:

$$\tilde{L} = U^+ \tilde{L} U = \pi_{12} V_{12} \hat{r}_+ + \pi_{21} \hat{r}_- V_{21}. \quad (2)$$

Here we have written

$$\pi_{12} = \exp \left\{ \frac{i}{\hbar} [(Q_1^0 - Q_2^0) P + (q_1^0 - q_2^0) p] \right\}, \quad (3)$$

where P and p are the momentum operators for the Q and q modes. We limit the analysis to second order in adiabatic perturbation theory, i.e., the equations of motion for the populations n_1, n_2 will be considered to second order in the nonadiabaticity operator \tilde{L} . (It is easy to see that the off-diagonal elements of the density matrix give corrections to n_1, n_2 which are of higher order in \tilde{L} .)

In the Markov approximation we find

$$\begin{aligned} \dot{n}_1(t) &= W_{21}(t) n_2(t) - W_{12}(t) n_1(t), \\ \dot{n}_2(t) &= -\dot{n}_1(t). \end{aligned} \quad (4)$$

Here $W_{12}(t)$ and $W_{21}(t)$ are the probabilities for an induced nonradiative transition from term 1 to 2 and from term 2 to 1 per unit time:

$$\begin{aligned} W_{12}(t) &= \frac{|V_{12}|^2}{\hbar^2} \cdot 2 \operatorname{Re} \int_0^\infty d\tau \exp \{ -i(\bar{\epsilon}_2 - \bar{\epsilon}_1) \tau / \hbar - \Gamma \tau \} \\ &\quad \times \langle \pi_{12}(t) \pi_{12}^+(t-\tau) \rangle_0, \end{aligned} \quad (5)$$

$$\begin{aligned} W_{21}(t) &= \frac{|V_{12}|^2}{\hbar^2} \cdot 2 \operatorname{Re} \int_0^\infty d\tau \exp \{ i(\bar{\epsilon}_2 - \bar{\epsilon}_1) \tau / \hbar - \Gamma \tau \} \\ &\quad \times \langle \pi_{12}^+(t-\tau) \pi_{12}(t) \rangle_0, \end{aligned}$$

where we write

$$\begin{aligned} \langle A \rangle_0 &= Z^{-1} \operatorname{Sp} \{ A \exp [-\beta (H_Q + H_q + \tilde{H}_T)] \}, \\ \tilde{H}_T &= U^+ H_T U, \quad \pi_{12}(t) = S^+(t, 0) \pi_{12} S(t, 0), \end{aligned} \quad (6)$$

and the evolution operator $S(t, 0)$ satisfies the equation

$$i\hbar S(t, 0) = [H_Q + H_q - eF(t)Q + \tilde{H}_T] S(t, 0), \quad S(0, 0) = 1. \quad (7)$$

Equation (4) is valid for $\Gamma \equiv \Gamma_1 \gg \Gamma_{\parallel}$, where Γ is the transverse relaxation constant for the excited electron state.

It is convenient to carry out the averaging in Eqs. (5) under the assumption that the vibrations described by H_T randomly modulate the frequencies Ω and ω of modes Q and q (Ref. 7). We will assume that Ω and ω form a random Gaussian process,⁷ i.e.,

$$\Omega(t) = \Omega + \delta\Omega(t), \quad \omega(t) = \omega + \delta\omega(t),$$

where

$$\langle \Omega(t) \rangle = \Omega, \quad \langle \omega(t) \rangle = \omega, \quad (8)$$

$$\langle \delta\Omega(t) \delta\Omega(0) \rangle = K_1(t), \quad \langle \delta\omega(t) \delta\omega(0) \rangle = K_2(t)$$

and the process is uncorrelated, so that H_T has a dense spectrum: $K_{1,2}(t) = (\gamma_{1,2}/2)\delta(t)$ (this is the situation in Sec. 3, where we discuss the experimental results). The brackets in (8) indicate an average over different instances of the random process $\delta\Omega, \delta\omega$, while γ_1^{-1} and γ_2^{-1} are the relaxation times for modes Q and q , respectively. The calculations for

other model functions (e.g., $K_{1,2}(t) = K_{1,2}^0 \times \exp(-\gamma_{1,2}|t|)$) are similar to the ones given below and will be omitted.

We can use Eqs. (6)–(8) to transform the correlation functions in (5) and obtain

$$\langle \pi_{12}(t) \pi_{12}^+(t-\tau) \rangle_0 = \exp \{ iA^{1/2} \Phi_t(\tau) + G(\tau) + g(\tau) \}, \quad (9)$$

where

$$\Phi_t(\tau) = R(t) \sin \omega_0 t - R(t-\tau) \sin \omega_0 (t-\tau),$$

$$R(t) = -d_Q F_0 \int_0^t d\tau f(t-\tau) \exp(-\gamma_1 \tau / 2), \quad (10)$$

$$\begin{aligned} G(\tau) &= A [(1 + \bar{N}) (\exp \{ -i\Omega\tau - \gamma_1 |\tau| / 2 \} - 1) \\ &\quad + \bar{N} (\exp \{ i\Omega\tau - \gamma_1 |\tau| / 2 \} - 1)], \end{aligned}$$

$A = (Q_1^0 - Q_2^0)^2$ is the Stokes loss parameter, and d_Q and \bar{N} are the transition dipole moment and the Planck occupation number for the Q mode. The expression for $g(\tau)$ follows from $G(\tau)$ with

$$\begin{aligned} A \rightarrow a = (q_1^0 - q_2^0)^2, \quad \bar{N} \rightarrow \bar{n} = [\exp(\hbar\omega/kT) - 1]^{-1}, \\ \gamma_1 \rightarrow \gamma_2, \quad \Omega \rightarrow \omega. \end{aligned}$$

With Eqs. (9) and (10), the induced NT probability (5) at resonance $\omega_0 \approx \Omega$ becomes

$$W_{12}(t) = \sum_s J_s^2(\rho_F(t)) W_s, \quad \rho_F(t) = A^{1/2} |R(t)|, \quad (11)$$

[we have assumed in deriving (11) that $\tau_0 \gg \Gamma^{-1}$, where τ_0 is the length of the laser pulse]. Here $J_s(x)$ is the Bessel function, and the partial NT probability W_s is the contribution from s quanta of the laser-excited vibration:

$$\begin{aligned} W_s &= \frac{|V_{12}|^2}{\hbar^2} \cdot 2 \operatorname{Re} \int_0^\infty d\tau \exp \left[\frac{i}{\hbar} (\bar{\epsilon}_2 - \bar{\epsilon}_1 - s\hbar\omega_0) \tau \right. \\ &\quad \left. + G(\tau) + g(\tau) - \Gamma\tau \right]. \end{aligned} \quad (12)$$

The transition moment d_Q becomes “smeared out” among the various closely spaced vibrational levels,⁸ and we may assume that d_Q is a random function with a Gaussian distribution. For large Stokes losses,

$$\begin{aligned} A(1+2N_t) > 1, \quad a(1+2\bar{n}) \gg 1, \\ N_t \equiv \bar{N} + 1/4 | \bar{R}(t) |^2, \quad \bar{R} = R \langle d_Q \rangle / d_Q, \end{aligned}$$

where $\langle d_Q \rangle$ is the average transition dipole moment for

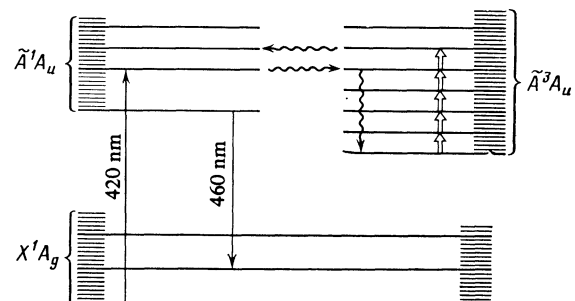


FIG. 1. Diagram showing levels and transitions for diacetylene.⁹

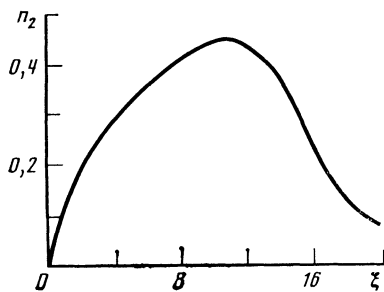


FIG. 2. Population n_2 as a function of time $\xi = t/\tau_0$ for $f(t) = \exp(-t/\tau_0)$ for CO_2 laser energy density $E = 0.6 \text{ J/cm}^2$ (τ_0 is the length of the laser pulse).

mode Q , we readily find the expression

$$\bar{W}_{12}(t) = \frac{(2\pi)^{1/2} |V_{12}|^2}{\hbar^2 \omega_0} \left[a(1+2\bar{n}) \frac{\omega^2}{\omega_0^2} + A(1+2N_i) \right]^{-1/2} \exp \left[-\frac{(\bar{\varepsilon}^2/\hbar - \bar{\varepsilon}_1/\hbar + A\omega_0 + a\omega)^2}{2A\omega_0^2(1+2N_i) + 2a(1+2\bar{n})\omega^2} \right] \quad (13)$$

for the induced NT probability from (11) by averaging over the Gaussian fluctuations in the dipole moment.

Expressions (11)–(13) for the induced nonradiative transition probability determine the populations after substitution in (4):

$$n_2(t) = \int_0^t dt' W_{12}(t') \exp \left\{ -\int_{t'}^t d\tau (W_{12}(\tau) + W_{21}(\tau)) \right\}, \quad (14)$$

$$n_1(0) = 1, \quad n_2(0) = 0, \quad n_1(t) + n_2(t) = 1.$$

3. COMPARISON OF THEORY WITH EXPERIMENT

It will be of interest to compare the above theory with experimental results on induced nonradiative transitions for diacetylene and benzophenone molecules excited by a pulsed CO_2 laser.^{9–11} According to Ref. 9, a nonadiabatic transition is selectively excited in these molecules, and the threshold for dissociation via mode Q and the threshold for total randomization both lie above the quasiintersection level for the singlet and triplet terms. In addition, because these molecules contain many atoms the Hamiltonian H_T has a dense vibrational spectrum. The stimulated fluorescence $I_{f1}(t)$ observed in Ref. 9 from the singlet states was due to multiphoton excitation of the triplet molecular state (Fig. 1) followed by transfer of excitation to the singlet levels. The time behavior $I_{f1}(t)$ was nonmonotonic and peaked after the short laser pulse had terminated (Fig. 2). Under the experimental conditions in Ref. 9, the populations n_1 and n_2 were determined

primarily by rapid multiphoton transitions between the levels, so that $I_{f1}(t) \propto n_2(t)$. Figure 2 shows the theoretical dependence $n_2(t)$ for benzophenone calculated from (13), (14) with

$$\langle d_Q \rangle = 5 \cdot 10^{-3} \text{ D}, \quad \gamma_1 = 3 \cdot 10^{-6} \text{ s}^{-1},$$

$$a = 10, \quad A = 1, \quad \hbar\omega = 0.07 \text{ eV},$$

$$\hbar\Omega = 0.12 \text{ eV}, \quad \bar{\varepsilon}_2 - \bar{\varepsilon}_1 = 0.26 \text{ eV},$$

$$|V_{12}|^2/\hbar^2\omega_0 = 3 \cdot 10^8 \text{ s}^{-1}.$$

The increased relaxation time noted in Refs. 9–11 for mode Q ($\gamma_1 \sim 10^6 \text{ s}^{-1}$) is chiefly responsible for the time lag of $I_{f1}(t)$ relative to the laser pulse. The agreement between theory and experiment is fully satisfactory.

We note in closing that if the molecules are excited by continuous radiation, the induced nonadiabatic transition probabilities become independent of time and are given by the familiar expressions for multiphoton transitions with the equilibrium vibrational occupation numbers \bar{N} replaced by $\tilde{N} = \bar{N} + (F_0/\hbar\gamma)^2$. The NT probability increases with field strength F_0 , and for the above parameter values $W_{12}(\tilde{N})/W_{12}(\bar{N}) \sim 10$.

We are indebted to E. E. Nikitin for some valuable comments concerning Eq. (4).

¹R. V. Ambartsumyan, G. N. Makarov, and A. A. Pureskii, Zh. Eksp. Teor. Fiz. **28**, 646 (1978).

²V. S. Dolzhikov, V. N. Lokhman, N. V. Chekalin, and A. N. Shabanov, Kvantovaya Elektron. (Moscow) **5**, 648 (1978) [Sov. J. Quantum Electron. **5** 373 (1978)].

³V. A. Kovarskii and S. A. Baranov, Zh. Eksp. Teor. Fiz. **71**, 2033 (1976) [Sov. Phys. JETP **44**, 1067 (1976)].

⁴V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and A. M. Prokhorov, Dokl. Akad. Nauk SSSR **263**, 1336 (1982) [Sov. Phys. Dokl. **27**, 331 (1982)].

⁵E. S. Medvedev and V. I. Osherov, Teoriya Bezyzluchatel'nykh Perekhodov v Mnogatomnykh Molekulakh (Theory of Nonradiative Transitions in Polyatomic Molecules), Nauka, Moscow (1983).

⁶V. A. Kovarskii, Mnogokvantovye Perekhody (Multiphoton Transitions), Shtinitsa, Mishinev (1974).

⁷S. Mukamel, J. Ross, and I. Oppenheim, Phys. Rev. **A17**, 1988 (1978).

⁸V. M. Akulin and A. N. Dykhne, Zh. Eksp. Teor. Fiz. **73**, 2098 (1977) [Sov. Phys. JETP **46**, 1099 (1977)].

⁹N. A. Borisevich, S. I. Blinov, A. V. Dorokhin, G. A. Zaleskaya, and A. A. Kotov, Izv. Akad. Nauk SSSR, Ser. Fiz. **43**, 394 (1979).

¹⁰N. A. Borisevich, S. I. Blinov, A. V. Dorokhin, G. A. Zaleskaya, and A. A. Kotov, Dokl. Akad. Nauk SSSR **241**, 801 (1978) [Sov. Phys. Dokl. **23**, 575 (1978)].

¹¹G. A. Zaleskaya, Zh. Prikl. Spektrosk. **32**, 34 (1980) [Opt. Spectrosc. (USSR) **32**, 18 (1980)].

Translated by A. Mason