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Theory of Laser-Pulse-Induced Molecular Dynamics: Gas-Phase Molecular Collisions and Adbond Dynamics

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THEORY OF LASER-PULSE-INDUCED MOLECULAR DYNAMICS: GAS-PHASE MOLECULAR COLLISIONS AND ADBOND DYNAMICS

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INTRODUCTION

A semiclassical study presented here indicates that a sufficiently short and intense pulse can be much more effective in inducing a collisional radiative transition than cw radiation or a long pulse, although the intensity must not be too high because the Rabi oscillation can bring down the probability. For the situation of a molecule physisorbed on a crystalline surface and irradiated by a laser, a master equation approach, used to describe the time evolution of the population of the vibrational adbond levels, shows that for high intensities laser-induced vibrational excitation is the same for pulsed and cw lasers.

GAS-PHASE MOLECULAR COLLISIONS

Most theoretical and experimental work in the past on the subject of molecular collisions occurring in the presence of a laser field has been concerned with the case in which the field consists of continuous wave (cw) radiation. In this case the colliding molecules are influenced by the laser radiation during both the incoming and outgoing trajectories. If, however, the laser field consists of a pulse whose duration is shorter than the collision time (for a typical collision time of 10^{-11} - 10^{-12} s, one must have a (sub)picosecond pulse), only a part of the collision process occurs in the presence of the laser field. The outcome of the collision therefore may be significantly diffarent depending whether the laser radiation is cw or pulsed. The difference shows up strongly in particular for collision processes involving an electronic transition that occurs via curve crossing, as we have shown in our earlier work.[1,2] Below we give a brief description of such a transition taking place in the presence of laser radiation, with special attention to the effect of the temporal duration of the laser radiation. An experimental study of this effect has recently been reported.[3]

Let us consider an electric-dipole transition induced by collision that occurs in the presence of laser radiation. Within the semiclassical two-state formalism, the Schrödinger equation yields the following coupled equations for the probability amplitudes $c_1(t)$ and $c_2(t)$ for the two states 1 and 2 being considered:[4]

$$i\hbar \frac{dc_1(t)}{dt} = H_{11}c_1 + H_{12}c_2 \tag{1a}$$

$$i\hbar \frac{dc_2(t)}{dt} = H_{21}c_1 + H_{22}c_2 \quad , \tag{1b}$$

where H_{11} and H_{22} represent adiabatic potential curves in the dressed-molecule representation for the two states 1 and 2 which, we assume, cross at a certain internuclear distance $R = R_c$ (i.e., $H_{22}(R_c)-H_{11}(R_c) = 0$), the interaction term H_{12} is given by $H_{12} = -\vec{\mu}\cdot\vec{E}_0/2$, $\vec{\mu}$ is the transition moment, and $\vec{E}_0$ is the electric field amplitude of the laser radiation. The transition probability 1 → 2 is obtained by solving the coupled equations (1a) and (1b) with the initial conditions $|c_1(0)| = 1$ and $c_2(0) = 0$. These equations, however, cannot be solved analytically in general because the matrix elements H_{ij} vary with time in a complicated manner for a realistic collision system. One therefore must rely on either approximate or numerical solutions. Here we present results of approximate calculations based on the Landau-Zener method along with results of numerical calculations.

Perhaps the simplest approximate solution to Eqs. (1) is provided by the Landau-Zener model. The model assumes that the transition is localized in a narrow neighborhood of the crossing point R_c over which $H_{22} - H_{11}$ varies linearly with R and H_{12} remains constant. The transition probability as the system passes through the crossing point R_c is then given by

$$P = 1 - \exp(-p) \tag{2a}$$

where

$$p = 2\pi[H_{12}(R_c)]^2/\hbar v\gamma[1 - (\frac{b}{R_c})^2]^{\frac{1}{2}} \quad , \tag{2b}$$

b is the impact parameter, γ is the slope of $|H_{22}-H_{11}|$ vs. R at R_c, and v is the relative velocity of the colliding partners at R_c. If the collision occurs in the presence of a short pulse so that the system is illuminated on the way in or out only, the transition probability is given by $P_s = P$. On the other hand, if the system is illuminated both on the way in and out as is the case for cw radiation or a long pulse, the transition probability is given by $P_{cw} = 2P(1-P)$. To exhibit clearly the intensity dependence of the transition probability, we note that p is proportional to I and let $p = \beta I$.

Then the short-pulse probability and cw probability are given respectively by

$$P_s = 1 - \exp(-\beta I) \tag{3a}$$

$$P_{cw} = 2\exp(-\beta I)[1-\exp(-\beta I)] \tag{3b}$$

where, for the case of a short pulse, a square pulse of intensity I is assumed.

In Table 1 we give the Landau-Zener probabilities P_s and P_{cw} for different values of I and b for the case $R_c = 9.5$, $v = 1.83\times10^{-4}$, $\gamma = 0.002$ and $\mu = 3$ (all quantities are expressed in atomic units), assuming that the laser beam is linearly polarized in the direction of the relative velocity v of the colliding partners and that the transition moment $\vec{\mu}$ is parallel to the internuclear axis as in a $\Sigma - \Sigma$ transition. The probability P_{cw} as a function of the intensity I exhibits the well-known single-peak structure of the Landau-Zener model, whereas P_s monotonically increases with I. As a result, P_{cw} and P_s differ significantly at high I for which $\beta I \gg 1$. Thus, according to the Landau-Zener model, a short pulse can be much more effective than cw radiation or a long pulse in inducing a transition, if the pulse intensity is sufficiently high.

Table 1. The cw probability P_{cw} and short-pulse probability P_s calculated using the Landau-Zener model.

b(a.u.)	I(W/cm^2)	10^8	5×10^8	10^9	5×10^9	10^{10}	5×10^{10}	10^{11}	5×10^{11}
1	P_{cw}	0.053	0.23	0.37	0.39	0.13	0.00	0.00	0.00
	P_s	0.027	0.13	0.24	0.74	0.93	1.00	1.00	1.00
5	P_{cw}	0.045	0.20	0.33	0.43	0.18	0.00	0.00	0.00
	P_s	0.023	0.11	0.21	0.69	0.90	1.00	1.00	1.00

In order to check the accuracy of the data presented in Table 1, we also have calculated the transition probability by numerically integrating Eqs. (1). For this calculation, we have assumed that the potential curves satisfy

$$H_{22} - H_{11} = 3\exp(-0.737R) - 0.0027\ , \tag{4}$$

which yields $R_c = 9.5$ and $\gamma = 0.002$. We have also assumed a straight-line constant velocity (= v) trajectory for simplicity of calculation and have chosen $v = 1.83 \times 10^{-4}$ and $\mu = 3$, as before. The result of our calculation is summarized in Table 2. Comparison of Tables 1 and 2 indicates that the Landau-Zener model yields relatively accurate probabilities at low intensities, but the model fails at high intensities ($I > 10^{11}$ W/cm^2). This is mainly due to the inability of the Landau-Zener model to correctly describe the Rabi oscillation of the molecular system at a high laser intensity.[2] Since P_s decreases due to the Rabi oscillation as I is increased beyond ~10^{11} W/cm^2, there is a finite range of the intensity over which a short pulse is much more effective than cw radiation. For the model system being considered, this range is 10^{10} - 10^{11} W/cm^2.

Table 2. The cw probability P_{cw} and short-pulse probability P_s calculated by numerical integration of Eqs. (1).

b(a.u.) \ I(W/cm^2)		10^8	5×10^8	10^9	5×10^9	10^{10}	5×10^{10}
1	P_{cw}	0.056	0.24	0.39	0.39	0.21	0.15
	P_s	0.029	0.14	0.27	0.73	0.88	0.92
5	P_{cw}	0.034	0.17	0.28	0.41	0.13	0.13
	P_s	0.019	0.091	0.17	0.71	0.93	0.93

b(a.u.) \ I(W/cm^2)		10^{11}	5×10^{11}	10^{12}	5×10^{12}	10^{13}	3×10^{13}
1	P_{cw}	0.24	0.39	0.44	0.48	0.48	0.50
	P_s	0.86	0.73	0.68	0.60	0.61	0.54
5	P_{cw}	0.23	0.40	0.46	0.49	0.48	0.47
	P_s	0.87	0.72	0.64	0.58	0.61	0.63

In view of the recent experimental study[3] of the short-pulse effect considered here, we show in Table 3 the total number N_t of transitions per target atom per unit pulse energy, an experimentally observable quantity, for different values of the pulse duration and intensity. Although this quantity was obtained by integrating the Landau-Zener probability over impact parameter, the data shown in the table is expected to be accurate since the Landau-Zener model yields accurate probabilities at the values of I considered here. As can be seen from the table, there is very little difference between long and short pulses at 10^8 - 10^9 W/cm^2. The difference, however, shows up at 10^{10} W/cm^2, as a noticable jump in N_t is seen in going from 10 to 1 ps (the collision time of the system being considered is ~ 2.5 ps).

Table 3. Total number of transitions per target atom per unit pulse energy (in arbitrary units).

$I(W/cm^2)$ \ pulse duration (ps)	1000	100	10	1	0.1
10^8	19.8	19.8	19.9	20.2	20.2
10^9	15.1	15.1	15.7	18.5	18.5
10^{10}	1.45	1.57	2.81	8.75	8.84

In conclusion, the results of our calculations summarized in Tables 1, 2 and 3 indicate that a short pulse can be much more effective in inducing a collisional radiative transition than cw radiation or a long pulse. This short-pulse effect becomes significant if the pulse intensity is sufficiently high that the probability of transition at the crossing point is high (~ 1). On the other hand, the intensity must not be too high because the Rabi oscillation can bring down the probability to a low value at an extremely high intensity.

ADBOND DYNAMICS

Level Populations

We now turn to consider a molecule physisorbed on a crystalline surface and irradiated by a laser. Due to the weak van der Waals bond, the admolecule has a series of vibrational states for the motion perpendicular to the surface. Under certain conditions it is reasonable to assume that a laser, with frequency ω_L, is in reasonance with only one pair of these levels, say $|g\rangle$ and $|e\rangle$. The transition frequency is $\omega_{eg} = \omega_e - \omega_g > 0$; the detuning is defined as $\Delta = \omega_L - \omega_{eg}$. Relaxation of the adbond occurs due to its interaction with the lattice vibrations of the substrate. In the Markov approximation, this is described through the occurrence of rate constants a_{nk} in a set of first-order differential equations for the level populations and coherences of the reduced density operator of the adbond, the so-called master equation.[5-10]

For pulsed lasers with a pulse duration Δt short compared to the relaxation times (= the inverse rate constants) of the adbond, the latter can be neglected during the pulse. Then, the time evolution during the pulse is given by the optical Bloch equations,[10]

$$\begin{aligned}
\frac{dR_1(t)}{dt} &= \Delta R_2(t) \\
\frac{dR_2(t)}{dt} &= -\Delta R_1(t) + \Omega_p(t)R_3(t) \\
\frac{dR_3(t)}{dt} &= -\Omega_p(t)R_2(t) \quad ,
\end{aligned} \tag{5}$$

where $\Omega_p(t) = \vec{\mu}.\vec{E}_0(t)/\hbar$ is the time-dependent Rabi frequency; $\vec{E}(t) = \vec{E}_0(t)\cos(\omega_L t)$ is the electric field amplitude of the laser, with slowly-varying envelope $\vec{E}_0(t)$; and μ again is the transition dipole moment. The real-valued quantities R_i are defined by the populations of and coherences between the two adbond levels coupled by the laser, in the rotating frame, according to[10]

$$
\begin{aligned}
R_1 &= \bar{P}_{ge} + \bar{P}_{eg} \\
R_2 &= -i\,(\bar{P}_{ge} - \bar{P}_{eg}) \\
R_3 &= P_e - P_g \quad .
\end{aligned}
\tag{6}
$$

The total exciting effect up to time t of a laser is characterized by

$$\theta(t) = \int_{\infty}^{t} dt'\, \Omega_p(t') \quad . \tag{7}$$

Here, we are only interested in the effect of a complete laser pulse, so that the integral can be taken over a single pulse to give a time-independent parameter θ. Let R_1°, R_2° and R_3° be the values just before the pulse.[10] Then, for zero-detuning, the values right after the pulse are given by[10]

$$
\begin{aligned}
R_1(\Delta t) &= R_1^\circ \\
R_2(\Delta t) &= R_2^\circ\cos(\theta) + R_3^\circ\sin(\theta) \\
R_3(\Delta t) &= R_3^\circ\cos(\theta) - R_2^\circ\sin(\theta) \quad ,
\end{aligned}
\tag{8}
$$

where the start of the pulse is taken as zero point of time, and Δt is the pulse duration. We shall only consider the situation of maximal excitation, which is obtained for $\theta = \pi$, the so-called π-pulses.

Instead of a single pulse, we shall consider a series of equally spaced π-pulses, with interval time t_p and pulse duration $\Delta t << t_p$. Assume that the system is initially in thermal equilibrium, i.e., $R_1 = 0$, $R_2 = 0$ and $R_3 = R_3(eq)$. Then, after a π-pulse, R_1 and R_2 are zero again, but R_3 is changed into its opposite: $R_3(\Delta t) = - R_3(eq)$. Between two consecutive pulses the adbond evolves in time through its relaxation against the lattice vibrations. This process can be described by a master equation.[5-9] In the present situation only the populations have to be considered. However, unlike the coupling with the laser, transitions to and from all vibrational states are possible. With the result of the laser pulse as initial condition, the formal solution of the master equation is ($\Delta t \leq t \leq t_p$),

$$\underset{\sim}{P}(t) = \underset{\sim}{P}(eq) + e^{-Wt}\{\underset{\sim}{P}(\Delta t) - \underset{\sim}{P}(eq)\} \quad , \tag{9}$$

where W is the matrix formed by the transition rate constants a_{nk} and has elements

$$W_{nm} = \sum_k a_{nk}\delta_{nm} - a_{mn} \quad . \tag{10}$$

$\underset{\sim}{P}(t)$ is the vector formed by the populations $P_n(t)$, and $\underset{\sim}{P}(eq)$ refers to the thermal equilibrium distribution, given by $W \underset{\sim}{P}(eq) = 0$.

After a number of pulses have passed, the adbond will reach a quasi-steady state, wherein the time evolution of the populations is the same in each interval t_p (see Fig. 1). Then, combining Eqs. (8) and (9), two sets

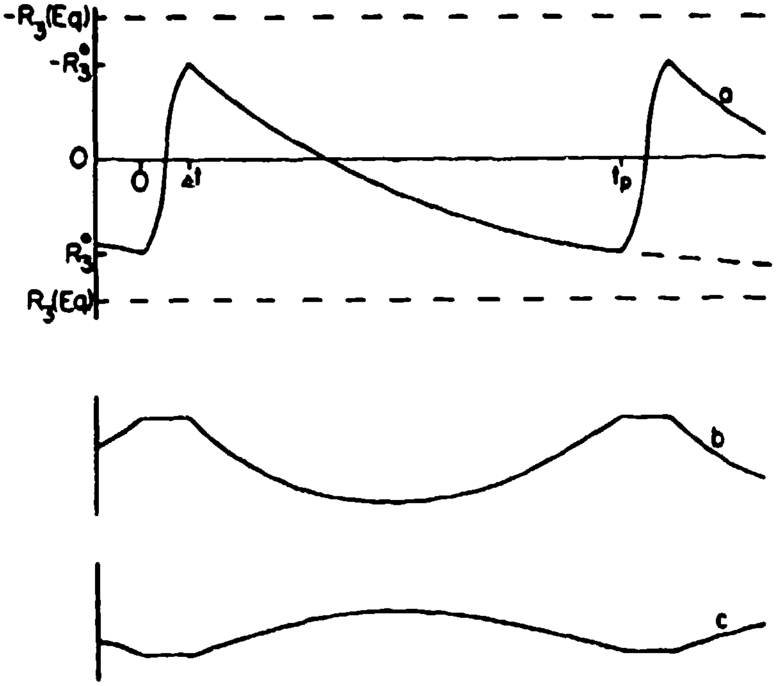

Fig. 1. Schematic drawing of the time evolution of the level occupations for a pulse sequence in the quasi-steady state. Curve a represents R_3; curve b gives $P_g + P_e$; and curve c gives P_n for any other level $n \neq e$ or g.

of equations are obtained, which together determine the constants $P_n(\Delta t)$ in terms of the rate constants a_{nk} and the interval time t_p:

$$\underset{\sim}{P}(t_p) = \underset{\sim}{P}(eq) + e^{-Wt_p} \{\underset{\sim}{P}(\Delta t) - \underset{\sim}{P}(eq)\} \tag{11}$$

$$\begin{aligned} P_n(t_p) &= P_n(\Delta t) = P_n^\circ \quad (n \neq e,g) \\ P_g(t_p) &= P_e(\Delta t) = P_g^\circ \\ P_e(t_p) &= P_g(\Delta t) = P_e^\circ \quad . \end{aligned} \tag{12}$$

For a continuous wave laser, the Rabi-frequency is a constant, Ω_{cw}. Now, the relaxation processes cannot be neglected during the interaction with the laser. The rate constants a_{nk} give rise to additional terms in the optical Bloch equations, in a way analogous to their occurence in the master equation.[11,12] After some time a true steady state will be reached, in which the populations are determined by

$$\sum_k a_{nk} P_n(\infty) = \sum_k a_{kn} P_k(\infty) \quad (n \neq e,g)$$

$$\sum_k a_{gk} P_g(\infty) = \sum_k a_{kg} P_k(\infty) - \frac{1}{2} \frac{\Gamma_{eg}}{\frac{1}{2}\Gamma_{eg}^2 + 2\Delta^2} \{P_g(\infty) - P_e(\infty)\} \tag{13}$$

$$\sum_k a_{ek} P_e(\infty) = \sum_k a_{ke} P_k(\infty) + \frac{1}{2} \frac{\Gamma_{eg}}{\frac{1}{2}\Gamma_{eg}^2 + 2\Delta^2} \{P_g(\infty) - P_e(\infty)\} \quad ,$$

where $\Gamma_{eg} = \sum_k \{a_{ek} + a_{gk}\}$, and the steady-state values are denoted by $P_n(\infty)$.

Pulsed Laser Versus Continuous Wave Laser

To compare the effect of a pulse train with the effect of a continuous wave (cw) laser on the dynamics of some system, a criterion is needed to compare both lasers. Below two possible criteria will be defined. First, it is required that both lasers have equal average power. Because the Rabi-frequency, $\Omega(t)$, is proportional to the electric field of the laser, the intensity is proportional to $\Omega^2(t)$. Performing the time-average for a series of π-pulses then gives:[11]

$$\Omega_{cw}^2 = \pi^2/(\Delta t \; t_p) \quad . \tag{14}$$

A second possible criterion is to require the average dissipation from both lasers to be equal. This leads to[11]

$$(P_g^\circ - P_e^\circ)/t_p = (\Omega_{cw}^2/\Gamma_{eg})(P_g(\infty) - P_e(\infty)) \quad , \tag{15}$$

where P_g°, P_e°, $P_g(\infty)$ and $P_e(\infty)$ follow from Eqs. (11)-(13).

The efficiency of a pulsed laser over a cw laser to induce some process (e.g., desorption or chemical reaction) will be different for each process. Here we restrict ourselves to the effect on the population of the upper one of the two levels coupled by the laser for a two-level system. A more extensive discussion is given elsewhere.[11] Let us define the efficiency ε as the ratio of the average excited level population $P_e(av)$ under pulsed laser irradiation to the steady state population $P_e(\infty)$ under cw laser irradiation. For a two-level system, Eqs. (11)-(13) are easily solved.[11] We are interested in the situation where the laser-induced population is substantially larger than the equilibrium thermal occupation of the levels. Then, neglecting the latter, the efficiency is[11]

$$\varepsilon = \frac{2}{(1 + e^{-\Gamma t_p})} \frac{(1 - e^{-\Gamma t_p})}{\Gamma t_p} \frac{\frac{1}{2}\Gamma^2 + \Omega_{cw}^2}{\Omega_{cw}^2} \quad . \tag{16}$$

For a given integrated intensity of one pulse, the average intensity of the pulse train is proportional to t_p^{-1}. Then a definition for a strong/weak pulsed laser is $\Gamma t_p \lessgtr 1$. Analogously a strong/weak continuous wave laser is defined by (Ω^2_{cw}/Γ^2) being much larger/smaller than one.

Using these definitions, it follows from Eq. (16) that $\epsilon = 1$ in the strong laser limit. This can easily be understood when it is realized that both for the pulsed laser and the cw laser the system is then continuously driven into saturation ($R_3 = 0$). Using criterion 1 (Eq. (14)) leads to

$$\epsilon = \frac{1 - e^{-\Gamma t_p}}{1 + e^{-\gamma t_p}} \, \frac{\Gamma^2 + 2\Omega^2_{cw}}{\Gamma^2} \, \frac{\Gamma \Delta t}{\pi^2} \, . \tag{17}$$

In the weak laser limit this gives $\epsilon = \Gamma\Delta t/\pi^2 \ll 1$, and thus ϵ can be made arbitrarily small by decreasing the pulse duration Δt. The explanation is that the intensity of the pulsed laser is proportional to $\Omega_p^2 \Delta t$, whereas the exciting effect is only proportional to $\Omega_p \Delta t$. Decreasing Δt, while $\Omega_p^2 \Delta t$ is held constant, will decrease $\Omega_p \Delta t$ too. For a cw laser both the intensity and the exciting effect are proportional to Ω^2_{cw}. The latter can be regarded as the limiting form of a pulsed laser with $\Delta t \to \infty$, and therefore will give the most efficient form of excitation.

For criterion 2, $\epsilon = 1$ is obtained, independent of the laser power. This result reflects the fact that the energy flow into the substrate (is absorbed energy) is proportional to the average occupation of the excited level and not on how P_e varies in time.[11,13]

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REFERENCES

1. H. W. Lee and T. F. George, J. Phys. Chem. 83:928 (1979).
2. H. W. Lee and T. F. George, Phys. Rev. A, in press.
3. T. Sizer II and M. G. Raymer, Phys. Rev. Lett. 56:123 (1986).
4. H. W. Lee and T. F. George, Phys. Rev. A 29:2509 (1984).
5. S. Efrima, L. Jedrzejek, K. F. Freed, E. Hood, and H. Metiu, J. Chem. Phys. 79:2436 (1983).
6. Z. W. Gortel, H. J. Kreuzer, P. Piercy, and R. Teshima, Phys. Rev. B 27:5066 (1983).
7. B. Fain and S. H. Lin, Surf. Sci. 147:497 (1984).
8. H. F. Arnoldus, S. van Smaalen, and T. F. George, Phys. Rev. B 34:6902 (1986).
9. H. F. Arnoldus, S. van Smaalen and T. F. George, Adv. Chem. Phys., in press.
10. L. Allen and J. H. Eberly, "Optical Resonance and Two-level Atoms," Wiley, New York (1975).
11. S. van Smaalen and T. F. George, Surf. Sci. 183:263 (1987).
12. W. H. Louisell, Quantum Statistical Properties of Radiation Wiley, New York (1973), Ch. 6.
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