Rabi Oscillations Between Dissociative Molecular States

Sylvie Magnier
Laboratoire de Physique Moléculaire et des Collisions, Institut de Physique, 1 boulevard Arago, Technopôle 2000, F-57078 Metz Cedex 3, France

Maurizio Persico
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, I-56126 Pisa, Italy

Naseem Rahman
Dipartimento di Scienze Chimiche, Università di Trieste, via Giorgieri 1, I-34127 Trieste, Italy
(Received 19 April 1999)

We establish for the first time the proper conditions to observe Rabi oscillations between vibrationally dissociative states belonging to different electronic terms of a diatomic molecule. We show by wave packet dynamics simulations that such a process is feasible with the molecular ion Na_2^+.

PACS numbers: 33.80.Wz, 33.80.Gj, 33.80.Rv, 42.50.Hz

Rabi oscillations, also known as optical nutation, are one of the well understood phenomena in atomic and molecular physics (see, for instance, Mandel and Wolf [1]). Their manifestation within optical fields constitutes one of the basic features of coherence and field-atom (or field-molecule) coupling in quantum physics. The experiments with two-level atomic systems, while difficult, have served to quantitatively verify the theory in various frequency regimes, including the domain of optical frequencies [2]. In this Letter, we address a related question of general interest, namely, whether the theory of Rabi oscillations can be extended to understand radiation induced transitions between continuum states. These must be high field phenomena involving atomic ionization or molecular dissociation.

For atoms, the question is reasonably straightforward. If the electromagnetic field couples two well defined autoionizing states, there is a possibility to observe Rabi oscillations. This possibility generally depends on the width of the autoionizing states: the smaller the width, the more the autoionizing state resembles a bound state embedded in a continuum, and there is nothing surprising in observing Rabi oscillations in such scenario.

For molecules, there are additional degrees of freedom. There exist the vibrational dissociative states, and transitions between such states can result in Rabi oscillations for proper potential energy curves or surfaces. Autocorrelation times for dissociating molecular wave packets are not too short, thanks to the nuclear inertia: therefore, laser pulses in the femtosecond range or even longer may be able to induce multiphoton absorption or emission before complete dissociation. Above threshold dissociation (ATD [3]) and related phenomena are then predicted to occur at moderate to high field intensities [4–7].

In this Letter we discuss the best conditions (pulse length and intensity) to observe Rabi oscillations between dissociative states, in connection with the relevant parameters of the molecular system. We also present the results of wave packet dynamics simulations which illustrate the occurrence of such a process in the Na_2^+ molecular ion. We believe that this is the first example of a Rabi oscillation between two vibrational continuum states qualitatively as well as quantitatively discussed in the literature.

In the following we establish the conditions by which a nuclear wave packet, representing a diatomic molecule, can be made to oscillate between two repulsive potential energy curves under the influence of radiation. The time-dependent molecular wave function can be written as

$$|\Psi\rangle = \sum_K \psi_K(R,t)\,|K\rangle\,, \tag{1}$$

where $|K\rangle$ is an adiabatic electronic state and R is the internuclear distance. The population of state $|K\rangle$ is given by the square norm of the associated wave packet component, $\int_0^\infty |\psi_K(R,t)|^2\,dR$.

A simplified model consists of three potentials, belonging to the electronic states $|0\rangle$, $|1\rangle$, and $|2\rangle$: $U_0(R)$ (ground state) is attractive, with equilibrium distance R_e; $U_1(R)$ and $U_2(R)$ are at least partially dissociative, in the sense that their slopes at R_e, F_1, and F_2, are negative, and the energies $U_1(R_e)$ and $U_2(R_e)$ exceed the respective dissociation energies.

A wave packet $\psi_1(R,t)$ can be created in state $|1\rangle$ by laser excitation from $|0\rangle$, at time $t = 0$. $\psi_1(R,0)$ will have approximately the same shape as the $v = 0$ vibrational eigenstate in U_0, if the exciting laser pulse is short enough. The half-width of the wave packet is $\Delta R \simeq 2(M\omega_v)^{-1/2}$, where M is the reduced mass and Ω_v is the vibrational frequency in the ground state. Therefore the energy spread of the wave packet in U_1 is $\pm\Delta R F_1 \simeq \pm 2F_1(M\omega_v)^{-1/2}$ (reflection principle [8]), which corresponds to a pulse duration of, at most, $\tau_1 \simeq \hbar(M\omega_v)^{1/2}/2F_1$. The carrier frequency of the pulse will be $\Omega_1 \simeq [U_1(R_e) - U_2(R_e)]/\hbar$.

A second pulse is meant to induce transitions between states $|1\rangle$ and $|2\rangle$. The second pulse is centered at a time t_2

after the first one, with duration τ_2 and carrier frequency Ω_2. After excitation to state $|1\rangle$ and while switching between $|1\rangle$ and $|2\rangle$, the wave packet travels downhill. If the slopes F_1 and F_2 are not too different, its center will follow the trajectory

$$R(t) \simeq R_e + \frac{F}{2M} t^2, \tag{2}$$

where $F = (F_1 + F_2)/2$. At $t = t_2$, the resonance condition requires that

$$\hbar\Omega_2 \simeq U_2(R(t_2)) - U_1(R(t_2)) \simeq U_2(R_e) - U_1(R_e) - \frac{F(F_2 - F_1)}{2M} t_2^2 . \tag{3}$$

In order to avoid interference with the first pulse [7] it is desirable to plan a two-color experiment ($\Omega_2 \neq \Omega_1$).

If the second pulse is sufficiently long and intense, it will be possible to observe Rabi oscillations between states $|1\rangle$ and $|2\rangle$. For a semiquantitative evaluation of the relevant quantities, we shall assume that the dynamics is the same as with a rectangular pulse of length τ_2 and constant intensity $I_{\rm tot}/\tau_2$: here $I_{\rm tot}$ is the integrated intensity of the pulse, related to the electric field amplitude $\mathcal{E}$ by $I_{\rm tot} = c\mathcal{E}^2\tau_2/8\pi$. The probability of being in state $|2\rangle$ at the end of the laser pulse will be

$$P_2 \simeq \frac{8\pi\mu_{12}^2 I_{\rm tot}}{8\pi\mu_{12}^2 I_{\rm tot} + \hbar^2 c\Delta\Omega_2^2\tau_2} \sin^2\left(\frac{\Omega_R\tau_2}{2}\right) \tag{4}$$

with $\Omega_R = (8\pi\mu_{12}^2 I_{\rm tot}/\hbar^2 c\tau_2 + \Delta\Omega_2^2)^{1/2}$. Here μ_{12} is the transition dipole between states $|1\rangle$ and $|2\rangle$, and $\Delta\Omega_2$ is the detuning of Ω_2 with respect to condition (3). Assuming perfect resonance ($\Delta\Omega_2 = 0$), P_2 would show maxima when

$$I_{\rm tot} = \frac{\pi\hbar^2 c}{8\mu_{12}^2\tau_2}(2n + 1)^2 \quad \text{with } n = 0, 1, 2, \ldots . \tag{5}$$

If the states $|1\rangle$ and $|2\rangle$ have two different dissociation limits, the oscillations of P_2 as a function of $I_{\rm tot}$ may be detected through the production of the corresponding atomic states. Another way to monitor the absorption of the second photon is to measure the kinetic energy of the atoms (or ions) resulting from the photodissociation [5].

Within the pulse duration the displacement of the wave packet will cause a detuning, if the frequency Ω_2 remains constant (no chirping) and the two potential curves are not exactly parallel ($F_1 \neq F_2$). At the times $t_2 \pm \tau_2/2$ (beginning and end of the pulse), the detuning will be

$$\Delta\Omega_\pm \simeq \Omega_2 - \hbar^{-1}[U_2(R(t_2 \pm \tau_2/2)) - U_1(R(t_2 \pm \tau_2/2))] \simeq \frac{F(F_2 - F_1)}{8\hbar M}\tau_2(\tau_2 \pm 4t_2) . \tag{6}$$

The Rabi oscillations will be washed out if the detuning is a large fraction of the Rabi frequency Ω_R. On the other hand, we want Ω_R of the order of π/τ_2, and this puts an upper bound on τ_2:

$$\tau_2^2(\tau_2 + 4t_2) < \frac{8\pi\hbar M}{F|F_2 - F_1|} . \tag{7}$$

Reasonable molecular parameters are $M \approx 10^4$ to 10^5 a.u. and $F \approx 10^{-2}$ a.u. The slope difference $F_2 - F_1$ may occasionally vanish, in which case long pulses will work: however, if the potential energy curves are really parallel up to long distances, Ω_2 will be resonant with an atomic transition, which should be avoided in order to perform clean molecular experiments. In most cases, F_1 and F_2 will differ by some 10%, so we shall assume $|F_2 - F_1| \approx 10^{-3}$ a.u. With these assumptions, we find that τ_2 should be shorter than about 100 fs, which is quite feasible with modern laser sources.

The required peak intensities $I_{\rm max}$ depend on the oscillator strength of the electronic transition. One can easily find systems where μ_{12} exceeds 1 a.u.: then, if one wants to observe 2 or 3 Rabi oscillations [$n = 1$ or 2 in expression (5)], $I_{\rm max} \approx 1$ TW/cm^2 should be sufficient.

We have run molecular dynamics simulations of such a process for the molecular ion Na_2^+, in the framework of a theoretical study of ATD. The molecular wave function (1) has been propagated in time under the influence of a classical radiation field with linear polarization. The radiation-molecule interaction is given by the operator $-\mu\mathcal{E}(t)$, where $\mathcal{E}$ is the electric field. The wave function propagation is done by means of the split-operator formalism implemented by Broeckhove *et al.* [9] in the TEMPO package, with a time step Δt and a grid step ΔR small enough to guarantee a good numerical accuracy ($\Delta t = 0.025, \Delta R = 0.055$ a.u.). The molecule is assumed to be in a rotationless state ($l = 0$): we have not considered the effect of molecular rotation in this exploratory study. It is well known that the gross effect of rotation on transition probabilities is a scaling of the field intensity, by a factor which depends on the quantum numbers l and m [5]. Therefore, in order to observe Rabi oscillations as a function of intensity, it is advisable to run experiments where all molecules subject to excitation are in the same rotational state, say, $l = 0$.

In this study we have used accurate potential energy functions and transition dipoles, previously determined by a model potential method [10]. The three electronic states we are interested in are $1^2\Sigma_g^+$, $1^2\Sigma_u^+$, and $2^2\Sigma_g^+$, but we take into account all close lying states (see Fig. 1).

The electric field for both laser pulses has the form

$$\mathcal{E}_i(t) = A\cos(\Omega_i t)\cos\left(\frac{\pi(t - t_i)}{2\tau_i}\right) \quad \text{for } |t - t_i| < \tau_i ,$$
$$\mathcal{E}_i(t) = 0 \quad \text{for } |t - t_i| \geq \tau_i . \tag{8}$$

The radiation intensity as a function of time is a bell-shaped curve with full width at half maximum equal to τ_i. The first pulse is centered at $t_1 = 0$, has a duration $\tau_1 = 10$ fs,

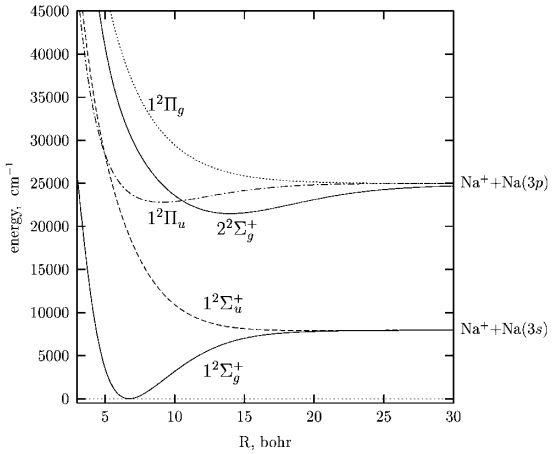

FIG. 1. Potential energy curves of Na_2^+.

and has a carrier frequency $\Omega_1 = 18\,875$ cm^{-1}, which corresponds to the absorption maximum in the one-photon $1^2\Sigma_g^+ \rightarrow 1^2\Sigma_u^+$ transition (initial vibrational state $v = 0$). The integrated intensity is 0.005 a.u., so the peak intensity is 78 GW/cm^2. The second pulse has variable intensity, duration, and frequency, and is centered at $t_2 = \tau_1 + \tau_2$, so that it follows the first one as closely as possible, without overlap.

In Fig. 2 we show the excitation spectrum obtained by varying Ω_2, with fixed second pulse intensity $I_{\text{tot}} = 0.005$ a.u. and duration $\tau_2 = 10$ fs, as in the first pulse. A more thorough study of the two-color ATD of Na_2^+ will be published elsewhere [7]. Here suffice it to say that the $1^2\Sigma_u^+$ and the $1^2\Pi_g$ states become populated during the first radiation pulse, by one- and two-photon absorption, respectively. During the second pulse two more transitions take place: $1^2\Sigma_u^+ \rightarrow 2^2\Sigma_g^+$, which is the Rabi process we are interested in, and $1^2\Pi_g \rightarrow 1^2\Pi_u$ (stimulated emission ending up into vibrationally bound states). The $1^2\Sigma_u^+$ state dissociates to Na(3s), while $1^2\Pi_g$ and $2^2\Sigma_g^+$ dissociate to Na(3p), so the production of excited sodium atoms is a clear signature of two-photon absorption. Moreover, the one-photon excitation with $\Omega_1 = 18\,875$ cm^{-1} produces atoms and ions with kinetic energies $E_K \simeq 0.68$ eV, while the two-photon process with $\Omega_2 = 12\,070$ cm^{-1}, corresponding to the maximum in the $2^2\Sigma_g^+$ absorption, yields $E_K \simeq 0.39$ eV.

The integrated intensity $I_{\text{tot}} = 0.005$ a.u. is just what is needed for a complete switch of the $1^2\Sigma_u^+$ and $2^2\Sigma_g^+$ populations with a 10 fs pulse. This value of I_{tot} can be approximately predicted by Eq. (5), given the transition dipole $1^2\Sigma_u^+ - 2^2\Sigma_g^+$, which is about 4 a.u. In order to observe Rabi oscillations, one may change the intensity of the second pulse, while keeping $\Omega_2 = 12\,070$ cm^{-1} and $\tau_2 = 10$ fs. The simulation results shown in Fig. 3a are in good agreement with the Rabi equation (4): the $1^2\Sigma_u^+$ and $2^2\Sigma_g^+$ populations undergo oscillations which depend on the square root of the intensity. The $1^2\Pi_g$ and $1^2\Pi_u$ states also exchange populations, although this transition is not resonant at this frequency.

The effect of the pulse length is seen by comparing Figs. 3a, 3b, and 3c, which show the results of simulations with variable intensity and with $\tau_2 = 10$, 20, and 40 fs, respectively. Quite clearly, also with $\tau_2 = 20$ fs almost perfect Rabi oscillations can be obtained. The only difference with respect to $\tau_2 = 10$ is a scaling of the integrated intensity by a factor $\frac{1}{2}$, as predicted by Eq. (5). Instead, in the simulation with $\tau_2 = 40$ fs (see Fig. 3c) we find that the Rabi oscillations are strongly perturbed because of the displacement of the wave packet, as previously discussed.

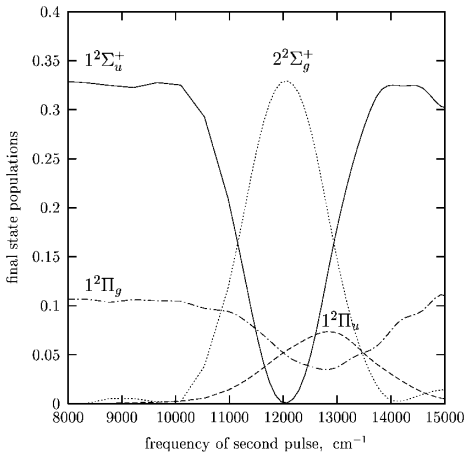

FIG. 2. Two-color excitation of Na_2^+, excited state populations as functions of the frequency of the second radiation pulse. First pulse: $\tau_1 = 10$ fs, $\Omega_1 = 18\,875$ cm^{-1}, $I_{\text{tot}} = 0.005$ a.u., $I_{\max} = 7.8 \times 10^{10}$ W/cm^2. Second pulse: same as first pulse, with variable Ω_2.

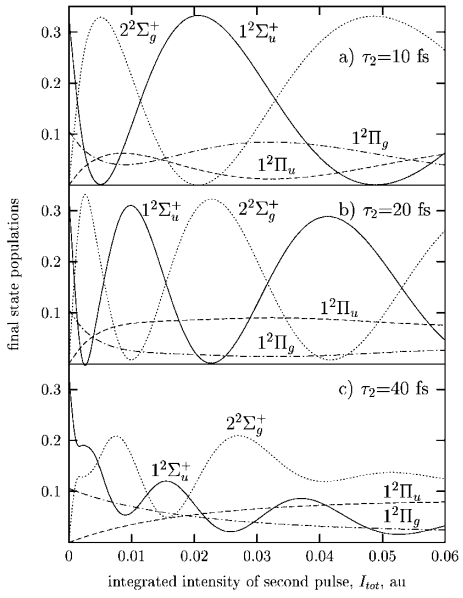

FIG. 3. Two-color excitation of Na_2^+, excited state populations as functions of the intensity of the second radiation pulse. First pulse as in Fig. 2. Second pulse: $\tau_1 = 10$, 20, and 40 fs, respectively, in (a), (b), and (c); $\Omega_2 = 12\,070$ cm^{-1}; variable I_{tot}.

In conclusion, this investigation predicts a novel effect on the basis of quantitative calculations, namely, Rabi oscillations between molecular states belonging to the dissociative continuum. The process can be experimentally observed by monitoring the electronic state and/or the kinetic energy of the product atoms. To this aim, one needs sufficiently short and intense laser pulses, depending on molecular parameters such as the slope of the dissociative potentials and the transition dipole. In particular, wave packet dynamics simulations show that pulses shorter than 40 fs and peak intensities of about 100 GW/cm^2 are needed in the case of Na_2^+. These results also show that the theory of Rabi oscillations, originally conceived for bound-bound transitions, is valuable also in understanding phenomena due to coupling between continuum states.

We thank P. Agostini and P. Van Leuven for enlightening discussions. This research was funded by the Italian MURST through the program "Theoretical models and computational methods of the structure, dynamics and spectroscopic properties of molecules and clusters."

[1] L. Mandel and F. Wolf, *Optical Coherence and Quantum Optics* (Cambridge University Press, Cambridge, 1995).
[2] M. Dagenais and L. Mandel, Phys. Rev. A **18**, 2217 (1978).
[3] N. Rahman, in *Atomic and Molecular Collisions in a Laser Field*, edited by J. L. Picqué, G. Spiess, and F. J. Wuilleumier, Journal de Physique, Colloque C1 (Editions de Physique, Les Ulis, France, 1985), Suppl. No. 1, Vol. 46, p. 249.
[4] M. Machholm and A. Suzor-Weiner, J. Chem. Phys. **105**, 971 (1996).
[5] S. Magnier, M. Persico, and N. Rahman, Chem. Phys. Lett. **279**, 361 (1997).
[6] S. Magnier, M. Persico, and N. Rahman, Laser Phys. **9**, 403 (1999).
[7] S. Magnier, M. Persico, and N. Rahman (to be published).
[8] R. Schinke, *Photodissociation Dynamics* (Cambridge University Press, Cambridge, 1993).
[9] J. Broeckhove, B. Feyen, L. Lathouwers, F. Arickx, and P. Van Leuven, Chem. Phys. Lett. **174**, 504 (1990).
[10] S. Magnier and F. Masnou-Seeuws, Mol. Phys. **89**, 711 (1996).