Available online at www.sciencedirect.com
SCIENCE DIRECT®

Chemical Physics 321 (2006) 325–336

Chemical Physics

www.elsevier.com/locate/chemphys

Light-induced molecular potentials and temperature-dependent polarization of molecular vapours in intense resonant laser fields: I. Nonperturbative theory in quasi-classical approximation

Alexander I. Pegarkov *

Department of Physics, University of Ottawa, 150 Louis Pasteur, Ottawa, Ont., Canada K1N 6N5

Received 22 June 2005; accepted 17 August 2005
Available online 3 October 2005

Abstract

The mechanism of creation of new electronic potentials and new vibration states in molecules irradiated by intense resonant laser fields is studied. The phenomena of selective orientation, delay of photodissociation, hardening and softening of intramolecular bonds are reconsidered within a model of *overexcited molecule*. It is shown that the laser-stimulated nonadiabatic dynamics of intramolecular motion can lead to unexpected alignment of molecules. The macroscopic polarization of molecular vapours irradiated by resonant lasers is analyzed. An experimental possibility to observe a *temperature-dependent manipulation* of the polarization is discussed.

PACS: 32.80.Fb; 33.80.Rv; 42.50.Hz

Keywords: Diatomic molecules; Spectra; Lasers; Molecular potentials; Polarization; Resonance processes; Nonperturbative theory

1. Introduction

Intense electromagnetic radiation, when it is in resonance with an electronic transition, considerably modifies the molecular electronic shell and couples vibration nuclear states belonging to resonant electronic states. In such a field, the laser-dressed molecular terms cross each other and their laser-induced nonadiabatic coupling changes the quantum dynamics of nuclear motion [1]. In this case, there is no reason to tell about vibration–rotation spectrum of an isolated electronic term, but one has to consider a bunch of coupled laser-dressed effective molecular terms whose energies give the electronic–vibration–rotation spectrum of a molecule irradiated by the resonant laser.

In resonant CW laser fields of weak intensity $I \ll 10^8\ \mathrm{W/cm^2}$, the laser-induced contribution to molecular spectra can be calculated by means of a perturbation theory [2,3]. If the laser field is strong enough like $10^{10}\ \mathrm{W/cm^2} \ll I \ll 10^{14}\ \mathrm{W/cm^2}$, then the laser-induced nonadiabatic spectra can be calculated within an *adiabatic perturbation theory* [4]. In the laser fields of moderate intensity, $10^8\ \mathrm{W/cm^2} < I < 10^{10}\ \mathrm{W/cm^2}$, neither perturbation theory nor adiabatic perturbation theory may be applied and various numerical approaches are widely in use [5–7]. Several years ago, it had also been demonstrated that all the three above-mentioned domains of laser intensity could be simply treated within an universal *multi-channel analytic approach* [8].

New interest to the laser-induced molecular dynamics in intense fields has recently arisen due to experimental discovery of light-induced molecular potentials [9,10] and of counterintuitive alignment of D_2 [11] and H_2^+ [12], where

---

[*] Tel.: +1 613 562 5800x6378; fax: +1 613 562 5190.
E-mail address: alexandre.pegarkov@science.uottawa.ca.

0301-0104/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2005.08.046

the light-induced potentials play the key role. The light-induced molecular potentials appeared first in theory as a useful tool to imagine the result of a radiative nonadiabatic interaction of two crossing laser-dressed molecular terms [4,13]. Unless series of experiments have been performed [9,10], it was unclear whether the light-induced molecular potentials would be of other meaning than just a simple theoretic feature. The first experimental observation of tunnelling through a potential barrier created in light-induced electronic state showed the light-induced potentials as a natural result of resonant laser–molecule interaction [9].

An 'intuitive' dynamics of molecular alignment in strong laser fields was very well established over the past five years and experimentally confirmed [14]. The 'intuitive' alignment assumes that the diatomics, intensively interacting with laser field, are mainly aligned along the E field polarization and bring a strongest contribution to ionization/dissociation yield. The counterintuitive alignment, observed in [11,12], results in strong contribution from the diatoms aligned perpendicular to the E field polarization. This means that under certain laser intensities and wavelengths the diatomic molecules, before dissociating, are aligned perpendicular to the laser field polarization where their coupling to the laser field should be zero and their ionization/dissociation yield would be invisible. Such a 'counterintuitive' alignment contradicts with traditional conception of molecular alignment and argues on incompleteness of available theory.

The counterintuitive alignment shows a possible way to use the intense laser field in order to change the macroscopic polarization of molecular vapours: if one can change the orientation of molecular axis to laser polarization vector just by changing the laser intensity, then one can keep the molecules of a vapour to be aligned predominantly along a certain spatial direction and therefore can control the macroscopic polarization of the vapour.

The first evidences of counterintuitive alignment in resonant lasers appeared more than 15 years ago in theory [15,16]. In [15], the numerical computations for laser intensities $I \sim 10^{10}$ W/cm^2 showed a nonlinear increase of photodissociation probability when the angle between molecular axis and laser field polarization was about $\pi/3$, whereas for smaller angles and even for parallel orientation the photodissociation probability decreased. In [16], it was analytically obtained that the diatomics, initially situated in different vibration states, could be aligned either parallel or orthogonal to the laser polarization vector when the laser intensity would increase over the perturbation theory limits.

The present work devotes to detailed investigation of laser-induced potentials, nonlinear effects induced by an intense laser of resonant frequency in molecular spectra, and their impact upon the counterintuitive molecular alignment. In particular, in this paper, the nonadiabatic molecular spectra in intense resonant laser field are calculated and the effects which the laser-induced intramolecular dynamics can cause in spatial molecular alignment are qualitatively discussed. The quantitative analysis was done for example of molecules Ar_2^+, Ne_2^+, Xe_2^+, Li_2. In a forthcoming paper, a quantitative picture for counterintuitive alignment of isolated molecules and temperature-dependent change of macroscopic polarization induced by intense laser field will be presented, based upon the approach of light-induced molecular potentials.

2. Nonadiabatic molecular Hamiltonian in resonant laser field

Here it is assumed that the laser pulse duration $\Delta\tau_{\text{laser}}$ is much longer than the periods of intramolecular motions like nuclear vibrations (t_{n}), electronic rotations (t_{el}), and radiative molecular transitions (t_{tran}) as well

$$\Delta\tau_{\text{laser}} \gg t_{\text{n}}, t_{\text{el}}, t_{\text{tran}}. \tag{1}$$

Then the *exact* quantum wavefunction of system "molecule + laser field" obeys the following time-independent Schrödinger equation:

$$H(\xi_a)\Psi_{\text{E}}(\xi_a) = E\Psi_{\text{E}}(\xi_a), \tag{2}$$

where $H(\xi_a)$ is the total Hamiltonian of the system and ξ_a is the complete set of molecular coordinates containing electron and nuclear variables.

The exact laser–molecule wavefunction $\Psi_{\text{E}}(\xi_a)$ may be written down in the form of following expansion over interaction-free laser field eigenfunctions and electronic-rotational eigenfunctions generating a basis

$$\Psi_{\text{E}}(\xi_a) = \sum_{NpJM\Omega} f^N_{pJM\Omega}\chi^{JM}_{p\Omega}(R;N)R^{-1}\langle\xi_a|pJM\Omega\rangle|N\rangle, \tag{3}$$

where the quantum numbers M and Ω are the projections of total angular momentum $\mathbf{J}$ onto the z-axis of space-fixed and body-fixed reference frames, p denotes the other molecular quantum numbers (excluded the vibration one), $f^N_{pJM\Omega}$ is the phase factor, dependent on all the summation quantum numbers N, p, J, M, Ω, and N designates the free laser field occupation number. $\chi^{JM}_{p\Omega}(R;N)$ depends on internuclear distance and is the full quantum-electrodynamic wavefunction of the nuclear motion in the set of intersecting electronic–rotation molecular terms dressed by the laser field (see [8] for details). The electronic–rotation basis function $\langle\xi_a|pJM\Omega\rangle$ is the following product of the Wigner function $D^J_{M\Omega}(\tilde{\alpha},\tilde{\beta},0)$, describing the molecular rotations ($\tilde{\alpha}$, $\tilde{\beta}$, $\tilde{\gamma}$ are the Euler angles of the molecular axis onto the space-fixed frame), and the relativistic wavefunction of molecular electrons $\Phi^{(\text{e})}_{p\Omega}(R,\bar{\mathbf{y}}_i,\bar{\sigma}_i)$:

$$\langle\xi_a|pJM\Omega\rangle = \left[\frac{2J+1}{4\pi}\right]^{1/2} D^J_{M\Omega}(\tilde{\alpha},\tilde{\beta},0)\Phi^{(\text{e})}_{p\Omega}(R,\bar{\mathbf{y}}_i,\bar{\sigma}_i), \tag{4}$$

where R is the internuclear distance, $\bar{\mathbf{y}}_i$ and $\bar{\sigma}_i$ are the sets of the space and spin variables of all molecular electrons in the body-fixed frame.

In this paper, only two resonant electronic terms are considered ($p = 1,2$). Such a case takes place in experiments [9–12] and is the most realistic situation for diatoms