

Light-Induced Molecular Potentials

Christof Wunderlich,* Esther Kobler, Hartmut Figger, and Theodor W. Hänsch

Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany

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We investigate the dissociation dynamics of molecules exposed to intense laser fields that induce electronic Rabi frequencies comparable to the frequency of nuclear vibration. A fast, mass selected beam of the simply structured model molecule Ar_2^+ was prepared in low vibrational levels and crossed with a dye laser beam (532 nm, $\leq 5 \times 10^{12}$ W/cm²). The absolute number of photofragments has been measured as a function of intensity. A clear experimental signature of light-induced potential curves is observed: enhanced dissociation by tunneling through a light-induced potential barrier. This is deduced from a quantitative comparison with theoretical predictions. [S0031-9007(97)02785-3]

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With the advent of intense, short pulse lasers numerous experimental and theoretical investigations have explored a new regime of light-matter interactions. Exposing atoms to intense laser light led to the discovery of fascinating new phenomena, of which above threshold ionization and high harmonic generation are two well-known examples [1]. Additional nuclear degrees of freedom in molecules promise a wealth of new phenomena to be explored and studies of the dissociation and ionization dynamics of neutral molecules have revealed interesting effects particular to molecules [2].

When describing the molecule-light interaction in a dressed state model, i.e., when the light field is explicitly included into the Hamiltonian, the change of nuclear dynamics due to the light field can be conveniently visualized as arising from light-induced molecular potential curves (LIP) [4]. The shape of these light-induced potentials can be controlled by varying the parameter settings (intensity, frequency) of the laser field. Detailed theoretical investigations have been inspired by this intuitive physical model making intriguing predictions regarding the dynamics of molecules exposed to laser fields [4,5]. For example, stabilization against dissociation and enhanced dissociation by tunneling through a light-induced potential barrier are two sides of the same coin when making use of this model.

In neutral molecules various ionization and dissociation pathways exist when exposed to intense fields. Experimentally, these are not always easily disentangled and have impeded the conclusive identification of phenomena that can be attributed to LIP [2]. It is advantageous to use simply structured molecular ions, e.g., the "model molecules" H_2^+ or Ar_2^+ to isolate these new phenomena from other processes. However, if a molecular ion is prepared by the same laser pulse that is used to probe it, the advantage of using such a simple two-electronic-state molecule is not evident [2,6]. Various groups try to circumvent the problems arising from preparing and probing H_2^+ in one and the same laser pulse by ionizing H_2 in a first pulse and then to probe H_2^+ in an intense field [7].

For the experimental study presented in this Letter we have chosen Ar_2^+ that can be adequately described, like H_2^+ , using only two electronic states ($A^2\Sigma_u^+$ and $D^2\Sigma_g^+$) at the intensities used in this experiment. These two states are coupled in a light field by an electric dipole moment $d \approx r/2$ (in atomic units, r being the internuclear separation). The strong, nonperturbative coupling induces large electronic Rabi frequencies $\omega_R = (d \cdot \vec{E}_0)/\hbar$ and thus leads to nonlinear light-molecule interaction (\vec{E}_0 is the electric field). This transition moment dominates the dynamics in a light field, as has been recognized in a theoretical study by Bandrauk and Sink who investigated the photodissociation of Ar_2^+ in intense laser fields [8]. Later, the behavior of this molecule in a strong radiation field has been treated by Pegarkov and Rapoport [9]. Recently, time-dependent calculations on Ar_2^+ helped to shed more light on the dynamics in intense fields [10]. For H_2^+ numerous theoretical studies have explored its behavior in strong fields [5].

The simple structure of Ar_2^+ together with well controlled experimental conditions employing a mass selected molecular beam allows for an unambiguous interpretation of the present photofragmentation study. New effective potential curves formed in an intense laser field leave a clear fingerprint on the dissociation probability. In particular, tunneling through a light-induced potential barrier can for the first time be unambiguously identified through a quantitative comparison with theoretical predictions.

In order to illustrate the concept of LIP, we will consider the model case of the diatomic molecule Ar_2^+ . The two relevant electronic states are characterized by a bonding ($A^2\Sigma_u^+$) and an antibonding ($D^2\Sigma_g^+$) potential curve, respectively. Exposing this molecule to laser light of frequency ω_L shifts the energy of the lower, bonding potential curve by $\hbar\omega_L$, if the interaction between molecule and electromagnetic field is described in a dressed state representation. Thus, the two diabatic potential curves shown as dashed lines in Fig. 1 cross at the internuclear distance, r_X , where they are coupled resonantly by the light field. After diagonalizing the electronic Hamiltonian, a 2×2 matrix with the electronic eigenvalues as a function of

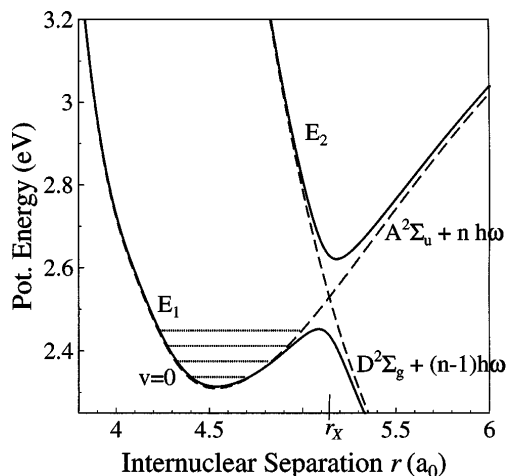


FIG. 1. Light-induced adiabatic potential curves (solid lines) in Ar_2^+ at a laser wavelength of 532 nm and intensity of $5 \times 10^{11} \text{ W/cm}^2$. Dashed lines symbolize diabatic potential curves, arising from the ground state $A^2\Sigma_u^+$ and the antibonding $D^2\Sigma_g^+$ state. Dotted lines indicate the positions of diabatic vibrational levels.

the internuclear distance on the diagonal places and the dipole interaction (proportional to \sqrt{I} , I being the laser intensity) on the off-diagonal places, one obtains adiabatic potential curves E_1 and E_2 (solid lines in Fig. 1) [4]. The characteristic features of these new electronic states can be changed by varying the frequency and intensity of the laser field. Increasing the frequency, for example, moves the avoided crossing to a smaller internuclear distance r_x . The “gap” between the adiabatic curves can be given a desired size by adjusting the intensity of the light field.

In this configuration, three regions of rovibrational energy can be distinguished for which LIP predict intriguing phenomena for the net absorption of one photon (see, for instance, [3,4]). First, for a vibrational level below the potential barrier of the lower adiabatic potential, E_1 (e.g., $v = 0$ in Fig. 1), the nuclei are still bound. However, with increasing light intensity the barrier is more and more suppressed and the probability for tunneling through it becomes appreciable. Second, some levels with vibrational energy above the avoided crossing exhibit an increased dissociation probability due to the presence of the gap between E_1 and E_2 (e.g., $v = 9$, not shown in Fig. 1). And third, diabatic levels far above the avoided crossing may become trapped in the upper of the light-induced electronic states, E_2 , and thus stabilize in an intense field.

The rate of dissociation, R , can be determined, for example, by applying the well-known Landau-Zener formula [11] to this curve crossing problem. However, this formula can be applied only when the vibrational energy lies above the avoided crossing. Zhu and Nakamura have derived modified expressions of the Landau-Zener formula that are valid over a wide range of coupling strengths and for all vibrational energies [12]. Calculating the transmission probability, p , of a particle through the adiabatic po-

tential system and dividing p by the vibrational period, τ , yields the rate of dissociation, R . As long as the relative change in intensity, $|\frac{dI}{dt}/I|$, is much smaller than $1/\tau$, the rate R obtained from LIP is well defined. This is always the case for the pulses employed in this experiment.

Alternatively, R can be obtained from Fermi’s golden rule (FGR) for one-photon absorption ($A^2\Sigma_u^+ \xrightarrow{\hbar\omega} D^2\Sigma_g^+$): $R_{\omega,v,K} = \sigma_{\omega,v,K} I / \hbar\omega$, where σ represents the cross section for excitation from a given rovibrational level (rotational quantum number k) of the ground electronic state $A^2\Sigma_u^+$ to the dissociative state $D^2\Sigma_g^+$ [3]. The electric transition dipole moment was obtained from measurements of the absolute cross section for photodissociation at low laser intensities and was found to be in reasonable agreement with results from *ab initio* calculations [13].

As expected, these two approaches yield the same results at low laser intensities. For $I \geq 10^{11} \text{ W/cm}^2$, however, the predictions of LIP for low lying levels deviate strongly from the golden rule result due to an increasing probability for tunneling through the diminishing potential barrier of E_1 . At an intensity of $\approx 7 \times 10^{12} \text{ W/cm}^2$ (532 nm), the potential barrier is completely suppressed and the probability, p , for dissociation of the $v = 0$ level equals 1. The dissociation rate, $R_{\omega,v,0}$, is plotted versus laser intensity in Fig. 2. Solid lines show the rate R that is predicted, if one uses LIP in the rotating wave approximation (one-photon coupling, Fig. 1) and dashed lines give for comparison the dissociation rate obtained from FGR.

The increase in dissociation probability due to tunneling can be diagnosed by measuring the number of photofragments as a function of intensity at fixed wavelength. The present experimental setup has been described elsewhere [3,14,15] and will be only briefly outlined in what follows. ($^{40}\text{Ar}^{40}\text{Ar}$) $^+$ molecules are generated in a dc discharge with a thermal distribution of the rovibrational populations [15] and formed into a mass selected fast (7.5 keV) beam. After the molecular beam

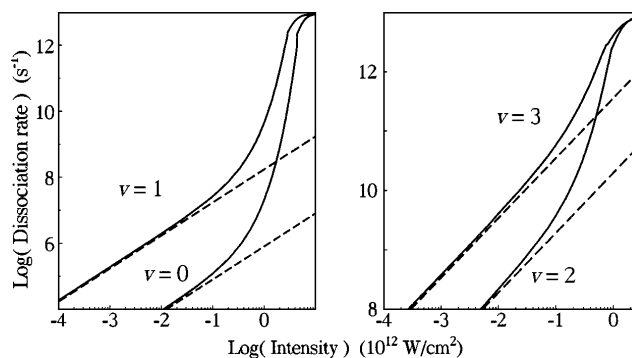


FIG. 2. Dissociation rate of Ar_2^+ as a function of laser intensity (532 nm). Dashed lines represent calculations using Fermi’s golden rule, whereas solid lines stand for a calculation using light-induced adiabatic potentials (both for one-photon absorption). (a) Vibrational quantum number $v = 0, 1$. (b) $v = 2, 3$.

has been collimated, it intersects at right angles the diffraction limited focus of a dye laser beam. Even though the laser pulse length is ≈ 30 ns, the molecules experience pulses in the picosecond region (≥ 30 ps) determined by the time needed to traverse the focal region. Charged photofragments (Ar^+ ions) and Ar_2^+ molecules are removed from the molecular beam after the interaction zone by means of electrostatic deflection plates, and Ar^+ ions are counted using a secondary electron multiplier whose detection efficiency is known.

In order to be able to observe the drastically increased dissociation rate at high intensity due to tunneling through the well of E_1 (Fig. 1), vibrational levels of Ar_2^+ above the avoided crossing ($v \geq 5$) are depopulated before the interaction with the high intensity dye laser takes place.

This is achieved by applying a properly timed low intensity ($4 \times 10^5 \text{ W/cm}^2$) Nd:YAG laser pulse at 532 nm to the molecules before they cross the second interaction zone with the dye laser. The photodissociation cross section, σ , at a fixed wavelength depends strongly on the vibrational quantum number v . The wavelength of this preparation laser is chosen such that only the populations of low lying levels remain (nearly) undepleted.

For $v = 0$, σ at 532 nm equals $2.6 \times 10^{-25} \text{ cm}^2$ and increases monotonically as a function of v until it reaches its maximum of $2.1 \times 10^{-17} \text{ cm}^2$ for $v = 6$. For this vibrational level the matrix element is largest because of a favorable Franck-Condon overlap. For even higher v , σ does not drop below 10^{-18} cm^2 (except for $v = 8, 14$; only levels with $v \leq 20$ are taken into account, since the thermal population of higher lying levels is negligible.) During the application of the Nd:YAG pulse, levels with $v \geq 5$ are therefore strongly depopulated, whereas low lying levels are hardly affected, as long as $I \times t \ll \hbar\omega/\sigma$ for small v , i.e., the dissociation probability is much less than one, with t being the interaction time. The preparation of Ar_2^+ molecules along with the experimental setup will be detailed in a longer publication [16].

Preparing Ar_2^+ in low levels is essential to obtain a clear experimental signature of tunneling through E_1 : The number of photofragments from a given vibrational level generated by the high intensity dye laser is proportional to the product of the dissociation rate and the relative population of this level. In case of a thermal distribution of the vibrational populations, this product is largest for levels in the vicinity of the potential gap ($3 \leq v \leq 7$) at a peak intensity of $5 \times 10^{12} \text{ W/cm}^2$ and still substantial for higher levels ($v \leq 15$). For these levels LIP and FGR predict essentially the same number of photofragments, even at high intensity [Fig. 3(a)] [17]. Thus, the larger number of fragments expected from LIP for low levels (tunneling) leads only to a small overall effect. However, when only low levels are populated, the distinctively larger dissociation rate predicted by LIP is clearly discernible [Fig. 3(b)].

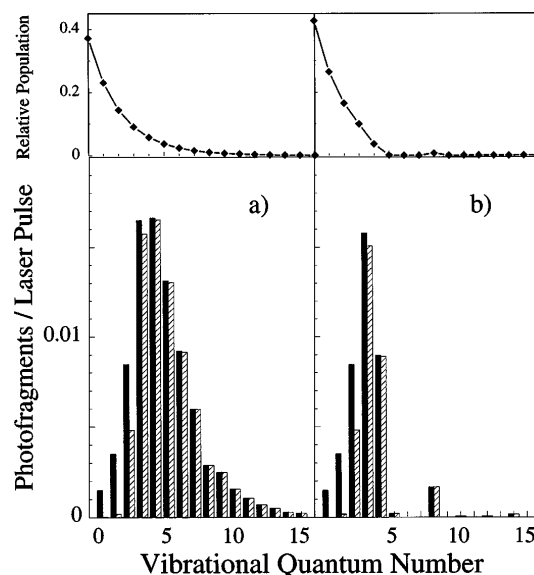


FIG. 3. Predicted number of photofragments of LIP (solid bars) and FGR (hatched bars) for individual vibrational levels ($K = 0$) at 532 nm and a peak intensity of $5 \times 10^{12} \text{ W/cm}^2$ (molecular beam radius 0.3 mm) [17]. (a) Thermal population distribution in the Ar_2^+ beam. (b) Preparation laser has been used to depopulate high levels. The graphs on top depict the initial relative populations of vibrational levels.

We will now turn to the discussion of the experimentally determined number of photofragments as a function of laser intensity under the conditions illustrated in Figs. 3(a) and 3(b), respectively.

Figure 4(a) shows the measured number of Ar^+ photofragments as a function of laser intensity at a laser wavelength of 535 nm with the initial rovibrational population being thermal (no preparation laser) [3]. The solid line in Fig. 4(a) shows the result of a computational simulation of the experiment. This simulation [3], which relies on LIP, agrees well with the experimental data. It does not involve any free parameter. Doing a simulation starting from FGR gives equally good agreement with the experimental data in this case. It is surprising to find that, even at high experimental peak intensities ($\leq 8 \times 10^{12} \text{ W/cm}^2$), the dissociation yield can be equally well described using the “classical” approach, i.e., Fermi’s golden rule for one-photon processes [3]. However, for vibrational levels in the vicinity of the potential gap and above [17], FGR and LIP predict essentially equal dissociation yields [Fig. 3(a)]: FGR predicts a large dissociation cross section because of a large Franck-Condon factor, and LIP because of the presence of the potential gap between E_1 and E_2 .

For the data depicted in Fig. 4(b) the additional Nd:YAG preparation laser is in use and therefore only low vibrational levels [Fig. 3(b)] interact with the high intensity dye laser which is set to 532 nm. In addition, the radius of the molecular beam is reduced to 0.3 mm [as compared to 0.7 mm for the data in Fig. 4(a)]. If one now uses FGR to simulate the experimental signal of

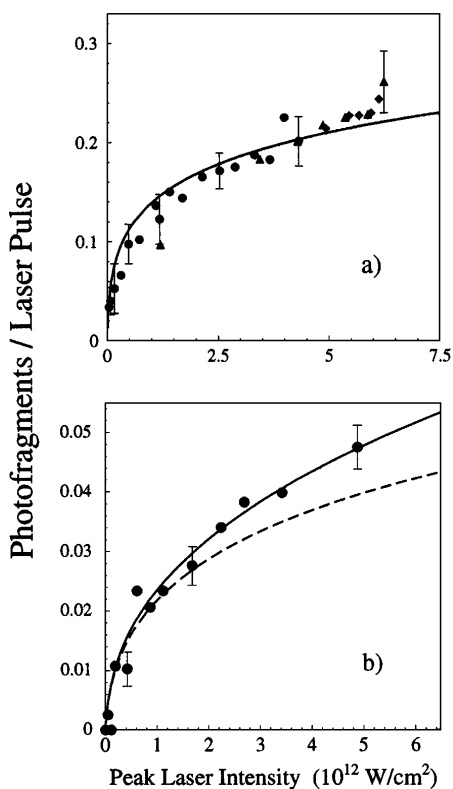


FIG. 4. Number of dissociated Ar_2^+ molecules as a function of laser intensity. Solid lines show results of computational simulations using light-induced potential curves; dashed lines stand for Fermi's golden rule. All parameters of the simulation were determined experimentally. (a) Thermal population distribution in the Ar_2^+ beam. LIP and FGR yield indistinguishable predictions. Each data point represents the average of 8000 to 20000 laser shots (535 nm). (b) Low vibrational levels only are populated. LIP predict the correct result: more photofragments due to tunneling through the barrier of E_1 . The radius of the molecular beam is reduced from 0.7 to 0.3 mm as compared to (a), averaged over 16000 shots (532 nm).

Fig. 4(b) (dashed line) one obtains a clear deviation from the data. At high intensity FGR predicts fewer photofragments than measured in the experiment. However, this quantitative comparison between experiment and theory gives very good agreement when one uses light-induced molecular potentials to simulate the data (solid line). At high intensity the probability for low lying vibrational levels to tunnel through the potential barrier of E_1 becomes appreciable and leads to an increase in the number of photofragments as is expected from LIP.

Processes other than one-photon dissociation of Ar_2^+ (multiphoton dissociation or ionization) do not interfere with the measured signal as has been shown earlier [3].

Detailed theoretical studies inspired by the intuitive physical model of light-induced molecular potentials have long predicted intriguing strong field effects. So far, there has been no conclusive experimental evidence for effects due to LIP. The data presented here give the first unam-

biguous experimental evidence for a new strong field effect arising from light-induced molecular potentials whose properties can be controlled by varying the parameters of the laser light (e.g., intensity and frequency).

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*Present address: Laboratoire Kastler Brossel, Département de Physique de l'École Normale Supérieure, 24 Rue Lhomond, F-75231 Paris Cedex 05, France.

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