Autler-Townes Splitting in the Multiphoton Resonance Ionization Spectrum of Molecules Produced by Ultrashort Laser Pulses

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We report for the first time the proper conditions to observe Autler-Townes splitting (ac-Stark splitting) from vibrationally coherent states belonging to the different electronic terms of a diatomic molecule. Wave packet dynamics simulations demonstrate that such a process is feasible by multiphoton resonance ionization of the molecule Na_2 with a single ultrashort intense laser pulse. With the ultrahigh time resolution of a femtosecond laser pulse, one can directly measure the absolute value of the transition dipole moment between any kinds of molecular states by this kind of Autler-Townes splitting, which is a function of the internuclear distance R.

PACS numbers: 33.80.–b, 42.50.–p

Atomic Autler-Townes (AT) splitting has been observed on a radio-frequency transition for a long time [1], but AT splitting in a gas-phase molecule has only recently been investigated [2–6]. Quesada *et al.* [2] reported the transition dipole moment of H_2 by measuring the ratio of AT splitting to the electric field strength. Qi *et al.* demonstrated that the transition dipole moment of the lithium dimer could be measured by AT splitting using cw triple resonance spectroscopy [5,6]. AT splitting on the Na atom [7] and a semiconductor [8] with an ultrashort intense pulse have also been explored recently [8]. But, perhaps, because of the relatively small size of the typical molecular transition dipole moment, few papers reported any result about molecular AT splitting on vibrationally coherent states with an ultrashort laser pulse.

In this Letter, with multiphoton ionization wave packet dynamics simulations, we demonstrate that one can observe AT splitting in the photoelectron spectrum with a proper single laser pulse and a prototype dimer Na_2. Because of the direct relation of AT splitting with the local transition dipole moment and the intensity of the electric field, AT splitting can be used to precisely measure, in principle, the peak intensity of the laser pulse if the transition dipole moment is known, which is not easy to accurately determine. On the other hand, one can also measure the internuclear-distance R-dependent local transition dipole moment by AT splitting with a properly localized wave packet if the intensity of the ultrashort laser pulse is known.

Along with the development of the ultrashort laser pulse, real-time molecular dynamics has been directly observed and many new phenomena have been investigated [9–13] and will be discovered. In explanation and foreseeing the experimental results, quantum wave packet dynamics simulations play the central role [14–18]. In order to entail the excitation of a local coherent wave packet with the common available femtosecond laser

system, one must choose the target molecule characterized by small vibrational energy. From this point of view, the sodium dimer is an excellent prototype molecule [12,16–18], also for its detailed information of potential energy curves and that of its single cation [19,20]. Therefore we employed a model of the sodium dimer with three electronic states in this Letter to establish the picture of AT splitting of coherent molecular states: the ground state $|X\rangle$ ($1^1\Sigma_g^+$), the double minimum state $|S\rangle$ ($2^1\Sigma_u^+$), and the ionic ground state $|I\rangle$ ($1^2\Sigma_g^+$) [16]. We ignore the rotational degree of freedom in our study. The relevant potential energy curves are shown in Fig. 1, as is the laser interaction process. The laser is centered at 340 nm in this work. We note here that the objective of this exploratory study is to show us the concept of the novel molecular AT splitting which is out from coherent wave packets, and the possible participation of electronic states other than the selected ones here is neglected. In actual experiments, one may find other systems more suitable for observing this novel physical phenomenon.

The time-dependent Schrödinger equation is numerically solved for the vibrational wave functions χ_X, χ_S, and χ_I in the three electronic states which are coupled by a laser field with the split-operator fast-Fourier transform technique. The ionization continuum is traditionally discretized into a band of quasicontinuum levels in terms of the electron eigenstates $|E\rangle$ containing the core and free electron. The states are labeled according to the kinetic energy of the ejected electron:

$$|\psi_I(R, t)\rangle = \sum_1^N \chi_I(R; E_n, t)|E_n\rangle, \qquad (1)$$

where E_1 and E_N are the smallest and largest energies which can be transferred to the electron, respectively, and R is the internuclear distance. $\chi_I(R; E_n, t)$ are the vibrational wave functions of Na_2^+, corresponding to the emission of an electron with kinetic energy E_n. This leads
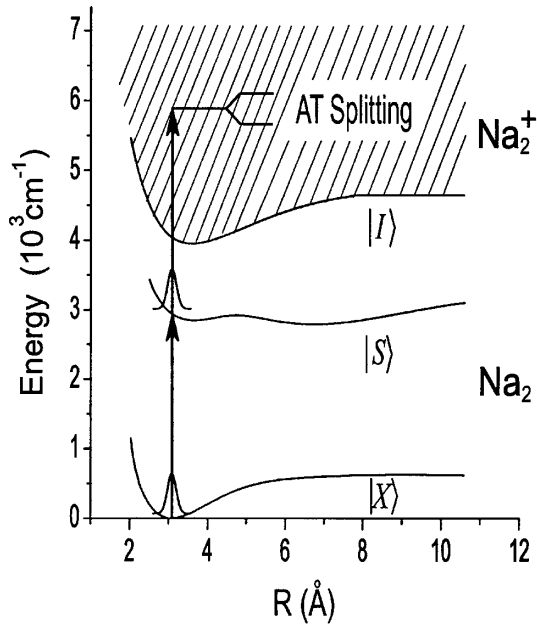
FIG. 1. Potential energy curves of the electronic states involved in the direct two-photon resonant photoionization of the sodium dimer. The arrows are the excitation energy of the laser pulse, centered at 340 nm.

to a Hamiltonian matrix of $(N + 2)(N + 2)$, including the two neutral states and the ionization quasicontinuum N levels. N is typically set to 40 in this work. It is time consuming to treat the ionization continuum with this model for diagonalizing the Hamiltonian matrix, but easy and accurate [15,21–23].

The laser field of frequency ω is described by $F(t)E_0 \cos(\omega t)$, with $F(t)$ being the pulse shape which is chosen to be a $\exp(-4\ln 2 \cdot t^2/T^2)$ Gaussian function and E_0 being the peak intensity. The time-dependent Schrödinger equation is solved with the condition that the molecule is initially in its electronic and vibrational ground state of energy ε_0.

The time-dependent population of the first excited state is obtained from the numerical calculation

$$P_S = \int dR|\chi_S(R, t)|^2 \qquad (2)$$

and the electron spectra, defined as

$$P_I(E_n) = \lim_{t \to \infty} \int dR|\chi_I(R; E_n, t)|^2.$$

The transition dipole moment μ_{XS} between the neutral states is given its *ab initio* value from Ref. [24]. Employing the Condon approximation, μ_{XS} is set to the value at the equilibrium position in the ground state. The transition dipole moment μ_{SI} between $|S\rangle$ and $|I\rangle$ states is set to $1/20$ of μ_{XS} [21]. Consistent with the model expanding the ionization continuum in a set of orthogonal polynomials, varying μ_{SI} by a factor of 10 essentially

does not affect the construction of the final electron spectra [25]. We furthermore assumed the dipole moment being independent of the electron energy E, and we do not apply the rotating wave approximation.

Figure 2 displays the electron spectra calculated within the quantum wave packet model detailed above using the three potential curves of Fig. 1 and a $T = 20$ fs pulse (FWHM) with intensities of $1.0I_0$, $2.5I_0$, and $5.0I_0$ ($I_0 = 1.0 \times 10^{11}$ W cm^{-2}). Also, the time evolution of the population in the $|S\rangle$ state of the molecule is shown. The dash-dotted line is the shape function $F(t)$ of the pulse. For an intensity of $1.0I_0$ the electron distribution is a smooth function of energy peaked around 2.286 eV, which is simply $\varepsilon_0 + 2\hbar\omega - V_I(R_0)$, $\hbar\omega$ being the photon energy and $V_I(R_0)$ the potential of the $|I\rangle$ state at the equilibrium distance of the ground neutral state.

The one-peak appearance of the spectrum splits into two symmetric humps progressively with increasing strength of the electric field. Figure 3 shows the different evolutions of the photoelectron spectra with the laser intensities of $1.0I_0$ and $5.0I_0$, corresponding to the top and bottom plots displayed in Fig. 2. We will show that, neglecting the vibrational motion, the pattern in the electronic spectrum can be regarded as another kind of Autler-Townes splitting which comes from two strongly coupled vibrational coherent states evolving along their own molecular electronic potential curves.
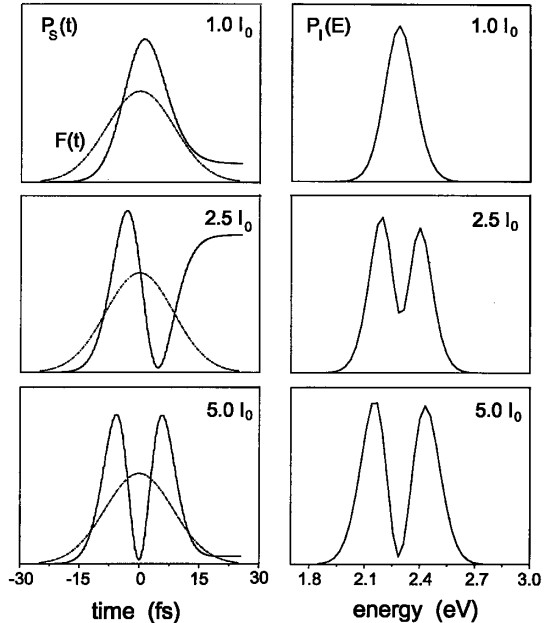

FIG. 2. Left panels: $|S\rangle$-state population (full line) obtained with three pulse intensities as indicated ($I_0 = 1.0 \times 10^{11}$ W cm^{-2}). The dot-dashed lines display the temporal variation of the envelope function of the laser pulse of width 20 fs. Right panels: Corresponding photoelectron spectroscopy simulated within the quantum multiphoton ionization wave packet description.
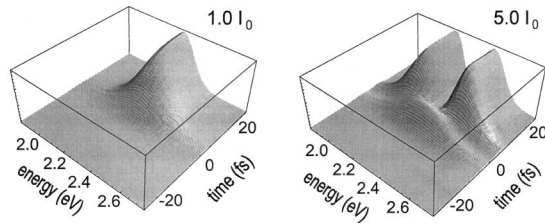
FIG. 3. The comparison of the temporal evolutions of the photoelectron spectra obtained with different electric field strengths (the conditions are the same as those of the corresponding ones of Fig. 2). After more than two perfect Rabi floppings arise, the spectrum splits into two completely separate peaks—AT splitting appears.

FIG. 4. Same as Fig. 2 but for an intensity of $6.5I_0$ ($I_0 = 1.0 \times 10^{11}$ W cm^{-2}) and a rectanglelike pulse with steep edges. The energy between doublets agrees exactly to the value, 0.44 eV, of the Rabi frequency.

It is known that an ultrashort laser pulse of 20 fs creates wave packets in the $|S\rangle$ electronic state which are coherent superpositions of the vibrational eigenstates. During field-molecule interaction on this time scale, the $|S\rangle$-state wave packet has no time to move away from the initial region where they are resonantly coupled by the laser field. The resonant region ΔR is located around the equilibrium position R_0 in the electronic ground state where $\hbar\omega$ equals the energy difference between the potentials of the two electronic states. Therefore the process of the field-molecule interaction can be regarded as that of a two-level laser-atom interaction, and the corresponding levels are of energies $V_X(R_0)$ and $V_S(R_0)$, respectively. In terms of the traditional explanation of ac-Stark splitting in the dressed-state picture, the doublet structure arises whenever there is a sufficient Rabi oscillation between a pair of intermediate resonant states during the ionization process [7,26]. Therefore we can expect that the energy difference between these two peaks displayed in Fig. 2 equals the Rabi frequency $\Omega = \mu_{XS} \cdot E_0$. In the spectra calculated with the laser field strength of $5.0I_0$, the splitting is 0.276 eV, and the corresponding Rabi frequency is 0.385 eV for μ_{XS} is 3.76 a.u. Considering the time-dependent shape of the laser field, the energy splitting agrees well with the Rabi frequency. With a stronger strength of the electric field, we can expect the energy splitting to be nearer to the Rabi frequency. If an intense 20 fs rectanglelike pulse with steep leading and tailing edges is applied, the amplitude of the ac-Stark split is expected to agree exactly with the Rabi frequency. The numerical spectra shown in Fig. 4 verify our prediction. The electric field strength of the rectanglelike pulse is $6.5I_0$, i.e., 4.3×10^{-3} a.u., therefore the Rabi frequency is 0.44 eV. The numerical result displays the energy splitting as exactly 0.44 eV.

The vibrationally coherent AT splitting shares many features of the traditional one. It also has its special characteristics because of the ultrashort excitation. Such as, first, it is obvious that it comes from dressed eigenstates of vibrational wave packets, and second, the splitti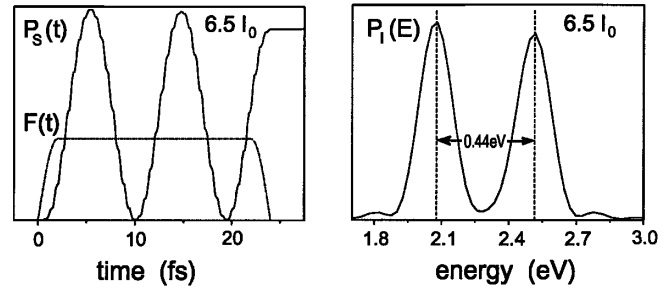ng of the spectrum is not sensitive to the photon energy of the laser field, for the large bandwidth of the laser pulse is capable of exciting many vibrational levels at the same time and so on. This novel phenomenon is worth investigating further both with theory and experiment.

If there are three resonant states involved in the multiphoton ionization, we expect that the photoelectron spectra generated by a short and intense enough laser pulse are characterized by three peaks, according to our developed concept for the traditional concept of ac-Stark splitting [27]. In fact, the experiments on multiphoton three-state resonance ionization with an ultrashort intense laser pulse have been carried out by several groups on the alkali dimer [10,25,28]. Therefore it is surprising that no reports have appeared until now on AT splitting of vibrational coherent states. One possible reason is that the FWHM of the commonly available electric field pulse is typically 80 fs. With this much longer pulse of 80 fs, the vibrational motion of the wave packets cannot be neglected. The excited wave packet moves away from the resonance region during laser-molecule interaction and the "perfect" Rabi oscillation does not arise any more. Figure 5 displays the spectrum and the time-dependent population of the $|S\rangle$ state obtained with a Gaussian pulse of 80 fs and $0.8I_0$. The spectrum is similar to that of the nonresonance case of the traditional ac-Stark splitting: the spectrum no longer consists of two symmetric peaks,
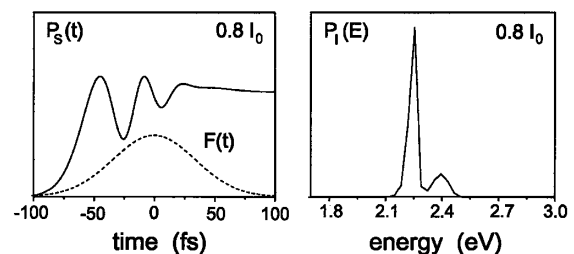

FIG. 5. Same as Fig. 2 but for an intensity of $0.8I_0$ ($I_0 = 1.0 \times 10^{11}$ W cm^{-2}) and a pulse width of 80 fs. The Rabi oscillations are not complete, like that of the nonresonant two-level system, and the spectrum arises with a predominant narrow peak at 2.26 eV and a small one at 2.4 eV.

but one predominant and another vanishing. We might ignore the much weaker peaks in our analysis of the experimental results. Another reason might be the spatial inhomogeneity of the laser field in practice. The inhomogeneity smears out the trough between the peaks and only a much broadened spectrum is observed [10]. In this sense, it should be more practical to observe this new molecular AT splitting with two pulses [4].

In Ref. [25] the same kind of complex ionization spectrum on the sodium dimer was theoretically reported, but was not profoundly investigated and regarded as the result of a certain interference. This might be another reason as to why no experimental results have been reported on this new kind of AT splitting.

Even if the rotational motion of the molecule has been ignored in our numerical simulation, the effect of experimental inhomogeneity of the rotational distribution of the molecules on the coherent vibrational AT splitting cannot be neglected in practice. This also accounts for the fact that this kind of AT splitting has not been observed during the past years. This issue is not considered in this Letter but is worth investigating further with theory to see what is the rotation-inhomogeneity effect, although there are experimental ways to get around the rotational inhomogeneity [29].

In summary, we have shown that the AT splitting comes from the vibrationally coherent states belonging to different electronic potential energy curves in the molecular multiphoton resonance ionization spectra and can be observed with a single ultrashort intense laser pulse. It results from efficient Rabi oscillation within the resonant region during the laser-molecule interaction. It is important to keep in mind that only a short enough pulse can be used or the vibrational motion of the molecule washes out the splitting. This kind of AT splitting shares many features of the traditional AT splitting and it could be used to measure the R-dependent transition dipole moment or the intensity of the laser field.

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