Shakeup Excitation during Optical Tunnel Ionization

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Shakeup of a two-electron system is investigated in the strong infrared laser field limit, both theoretically and experimentally. During tunnel ionization the electron shakes up a second electron to an excited bound state. Theoretically, a complete analytical theory of shakeup in intense laser fields is developed. We predict that shakeup produces one excited σ_u ${D_2}^+$ state in $\approx 10^5$ ionization events. Shakeup is measured experimentally by using the molecular clock provided by the internuclear motion. The number of measured events is found to be in excellent agreement with theory.

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The dominant contribution to nonsequential ionization of atoms in strong laser fields is recollision. The first electron is ionized, accelerated in the laser field, and kicks out a second electron during recollision [1]. The dominant contribution to nonsequential ionization of atoms in x-ray pulses is shakeoff. The first electron is ionized by absorbing one x-ray photon and shaking off a second electron on its way out [2].

Little is known about the role of shakeoff and shakeup in the strong field regime, although shakeoff was originally suggested to be the dominant mechanism in strong field double ionization [3]. In this Letter the gap is closed. Shakeup (SU) in strong laser fields is investigated experimentally and theoretically. Shakeup is used here as the generic term for all excitations generated by the ionizing electron on its way out. SU in atoms and small molecules is expected to be weak. Our analysis is driven by the fact that SU is bound to become prominent in larger molecules, where the energy spacing between ground and excited states becomes small.

Experimentally, we report the first observation of shakeup excitation during strong field ionization. The measurement is done in D_2. SU creates charged ions at a distance close to the internuclear distance of the neutral molecule. In this way a signature at the high energy end of the kinetic energy spectrum of the ionic fragments is created, from which SU can be identified. A ratio of SU excitation of σ_u to tunnel ionization of 2×10^{-5} is measured in D_2. Deuterium was chosen for a number of reasons. First, all excited states of ${D_2}^+$ are relatively simple and therefore allow a clean identification of shakeup. Second, as a two-electron system, electron-electron correlation effects can be calculated without too many approximations, facilitating the theoretical analysis.

On the theoretical side, we develop an analytical theory of shakeup in strong laser fields that is in excellent agreement with experiments. The SU excitation process proceeds in two stages referred to as SU1 and SU2 here. In the terminology of x-ray double ionization, SU1 and SU2 correspond to the SU and the two-step one photon (TS1) processes, respectively. SU1: the two-electron wave function contains components of all one electron states. Each of these components can lead to tunneling, resulting in regular ionization for the ground state and in shakeup for the excited state component. SU2: On its way out the electron creates an electric dipole field that causes nonadiabatic transitions to excited states. Our theory complements existing theoretical work on atomic SU1 [4] and determines for the first time the value of the dipole-induced SU2 contribution. SU2 is found to be the dominant mechanism in D_2.

The theoretical analysis is performed in two steps. SU1 is governed by the part of the wave function under the barrier up to the classical birth point at which the electron penetrates the barrier. Tunneling takes place in a fraction of the laser period so that the quasistatic molecular Ammosov-Delone-Krainov (MO-ADK) theory [5,6] can be applied. SU2 takes place after the electron has been born in the continuum and is calculated using a time-dependent, Keldysh-type method [7].

Following MO-ADK [6] we find the ionization rate for SU1 as

$$w_j = \sum_{m'} \frac{B_j^2(m')}{2^{|m'|} \mid m' \mid !} \frac{1}{\kappa_j^{2/\kappa_j - 1}} \left(\frac{2\kappa_j^3}{F}\right)^{2/\kappa_j - |m'| - 1} e^{-2\kappa_j^3/3F}, \tag{1}$$

where the laser electric field is denoted by F, l and m are the angular and magnetic quantum numbers, respectively, and $B_j(m') = \sum_l C_{lj} D^l_{m'm} Q(l, m')$ with $D^l_{m'm}$ and $Q(l, m')$ defined in Ref. [6]. The index $j = 0, 1$ refers to the ionic σ_g and σ_u states, respectively. The coefficient C_{lj} is obtained from matching the tunneling wave function under the barrier to the corresponding, field-free, asymptotic components of D_2 σ_g. We find $C_{00} = 2.5$ and $C_{01} = 1.6$. Terms with $l > 0$ are negligible for D_2. Further, $\kappa_j = \sqrt{2I_{pj}}$, where $I_{pj} = (I_g - I_j)$ is the ionization potential of D_2, I_g

is the binding energy of the D_2 σ_g state, and I_j is the binding energy of the ${D_2}^+$ states. The difference to conventional ionization is that tunneling depends on the eigenstate the remaining electron ends up after ionization. For $j = 0$, the bound electron remains in the ground state and conventional ionization takes place. For $j = 1$, the second electron gets bound in the ionic σ_u state. Shakeup results from the fact that the D_2 wave function contains components of all single electron bound states, which is a manifestation of its correlated nature. The ionization rates for regular and shakeup ionization are different, as the ionization potential and the coefficient C_{lj} depend on the final ionic bound state.

The second contribution, SU2, is calculated by a Keldysh-type approach that yields the two-level equations

$$\begin{aligned} i\frac{da_0}{dt} &= I_0 a_0(t) - \mu F_d(t) a_1(t), \\ i\frac{da_1}{dt} &= I_1 a_1(t) - \mu F_d(t) a_0(t), \end{aligned} \tag{2}$$

for the ${D_2}^+$ molecule in the field of the electron leaving the ion after ionization. Here, $a_0(t)$ and $a_1(t)$ are the probability amplitudes of the field-free σ_g and σ_u ${D_2}^+$ states. The term $\mu F_d = \mu \mathbf{x}/|\mathbf{x}|^3$ is the dipole contribution to the interaction between tunneling and bound electrons. For the sake of simplicity we assume that the laser electric field and therewith the trajectory of the tunneling electron are parallel to the z axis. Then, $\mu = \mu_0 \cos(\varphi)$ is the dipole component along $\hat{z}$, φ is the angle between the z axis and the molecular axis, and μ_0 is the dipole moment along the molecular axis. The dipole moment in the plane perpendicular to the molecular axis is zero for homonuclear diatomic molecules. The electric field $F_d = 1/d^2$, where d measures the distance of the ionized electron from the center of the molecule. The electron is born at time t_0 at the classical turning point $d_0 = R/2\cos(\varphi) + I_{p0}/F(t_0)$ and is then accelerated by the laser field following the trajectory $d(t) = d_0 + F(t_0)(t - t_0)^2/2$.

The coupled Eqs. (2) are solved by diagonalization. We use the standard transformation $(a_0, a_1) = \hat{U}(b_0, b_1)$ [8], where $U_{11} = U_{22} = \cos(\xi)$ and $U_{21} = -U_{12} = \sin(\xi)$. Further, $\xi = -(1/2)\arctan[\Omega(t)/\Delta]$, $\Omega(t) = 2\mu F_d(t)$ is the Rabi frequency, and $\Delta = I_1 - I_0$. Finally, b_0, b_1 are the probability amplitudes of the adiabatic eigenfunctions, dressed by the dipole field F_d of the escaping electron. Adiabatic means that Eqs. (2) are diagonalized and solved exactly in the limit of a time-independent field F_d. In this limit no shakeup occurs. However, for a time-dependent field, as a result of the time derivative of $\hat{U}$ in the Schrödinger equation, off-diagonal elements always exist and are responsible for nonadiabatic transitions. SU2 is given by the probability for a nonadiabatic, dipole-induced excitation times the ionization probability which is

$$v_1(t_0) = w_0(t_0)\left|\int_{t_0}^{\infty}\frac{d\xi}{dt}e^{i\phi(t_0,t)}dt\right|^2, \tag{3}$$

with $\phi(t_0, t) = \int_{t_0}^{t}[\Delta^2 + \Omega(t')^2]^{1/2}dt'$. Equation (3) presents a general expression for nonadiabatic transitions. SU ionization takes place in the weak field limit, $\Omega \ll \Delta$. In this limit, integration of (3) yields

$$v_1(t_0)=w_0(t_0)\left|\frac{\mu}{\Delta d_0^2(t_0)}+\frac{\mu\Delta}{2F(t_0)d_0(t_0)}[\Lambda(\xi)+\Lambda(-\xi)]\right|^2, \tag{4}$$

where $\Lambda(\xi) = (1 - 1/\xi)\exp(\xi)E_1(\xi)$, $\xi(t_0) = \Delta[2d_0(t_0)/F(t_0)]^{1/2}$, and $E_1(\xi) = \int_{\xi}^{\infty} dt\exp(-t)/t$ is the tabulated exponential integral. For negative ξ the principal value of E_1 has to be taken.

Our analysis reveals the following intuitive picture of SU2. When the tunneling electron is born at t_0, the bound electron is in the adiabatic ground state dressed by the dipole electric field, which contains components of the field-free, excited states. However, the population of the field-free excited states is only virtual. In the limit, where the ionized electron is removed infinitely slowly from the ion, the remaining bound electron will make an adiabatic transition from the dipole-field dressed to the dipole-field-free ground state; i.e., the bound electron will remain in the ground state. In reality, the ionized electron leaves the nucleus with finite velocity and nonadiabatic transitions take place, which are the source of SU2.

The theory has been tested by experiments relying on the concept of the "molecular clock." First ionization will set in motion a nuclear wave packet on the ground state potential energy surface of ${D_2}^+$. The potential surfaces

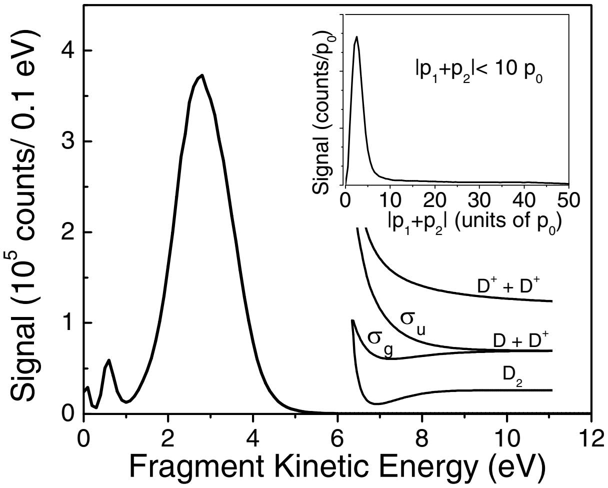

FIG. 1. The main figure shows the measured distribution of correlated D^+ fragments resulting from irradiating D_2 with 3×10^{14} W/cm^2, circularly polarized light. The upper right figure shows the momentum sum for the two fragments. The pair was considered coincident if the sum of momenta was less than $10p_0$, with $p_0 = e^2/\hbar$ the atomic unit of momentum. The potential energy diagram for D_2 is in the lower right. The laser pulse will singly ionize D_2, leaving ${D_2}^+$ in the σ_g state. Shakeup will leave ${D_2}^+$ in the excited σ_u state, resulting in greater kinetic energy release.

of D_2 and of its ions are shown in the inset of Fig. 1. This motion is well known from theory and experiment [9]. If an electronic excitation of ${D_2}^+$ were to occur at some later time, the excited molecule would ionize and dissociate, with fragment kinetic energy directly reflecting the time delay between ionization of D_2 and excitation of ${D_2}^+$. That allows us to distinguish instantaneous excitation of ${D_2}^+$, taking place at the internuclear separation of the neutral molecule, from delayed excitation and ionization of ${D_2}^+$, which may happen at later times and larger distances, characteristic of enhanced ionization [10] or recollision [9]. We assume that the most likely state of ${D_2}^+$ to be excited is σ_u, the lowest energy excited state. If the σ_u state is populated at the time of ionization and the molecule dissociates on that potential energy surface, the fragment kinetic energy (≈ 9 eV) will reflect the internuclear separation of the D_2 ground state.

The extremely low probability of such events would prevent their observation over the noise background if we could only detect a single ion fragment. Fortunately, during dissociation on the σ_u surface of ${D_2}^+$ the remaining electron will ionize as the molecule passes the enhanced ionization region. The second ionization step has little influence on the fragment kinetic energy. Most importantly, this process produces a pair of correlated deuterons, which can be detected in coincidence. Conservation of momentum introduces a severe constraint that allows us to dramatically improve the signal to noise ratio for detection of deuterons resulting from double ionization of D_2. We estimate that such momentum-correlated detection allows us to confidently observe events with relative probability higher than 10^{-6} in respect to single ionization.

The experiment used 40 fs, 800 μJ pulses produced by a Ti:sapphire regenerative amplifier operated at 500 Hz. To remove any contribution from recollision, the pulses were circularly polarized. The pulses were focused inside a vacuum chamber (background pressure 10^{-9} Torr) by an $f/2$ on-axis parabolic mirror ($f = 50$ mm) on a beam of deuterium molecules. We estimate our focal spot diameter and confocal parameter to be 5 and 100 μm, respectively.

The molecular and laser beams intersected orthogonally inside a uniform acceleration time-of-flight mass spectrometer and were mutually perpendicular to the time-of-flight axis. The molecular beam was heavily skimmed such that its width along the laser beam propagation direction was 40 μm FWHM. This ensured that few molecules were outside the high intensity region of the laser focus.

Ions were accelerated by the uniform electric field onto a time- and position-sensitive delay line anode detector. This detector, in conjunction with a multichannel, multihit time-to-digital converter, allowed simultaneous measurement of both ion arrival times (with 500 ps resolution) and positions in the detector plane (with 250 μm resolution) for up to 16 ion impacts per laser pulse. From the time and position data, the three-dimensional initial velocity vector was computed for each detected ion. The recoil momentum distribution of surviving ${D_2}^+$ ions was measured to determine the intensity at which molecules ionized, as described previously [11].

Figure 1 represents the kinetic energy distribution of all detected deuterons at 3×10^{14} W/cm^2 intensity. The enhanced ionization [10] peak at 3 eV per fragment dominates the kinetic energy distribution. The smaller bond softening [12] peak is seen at 0.6 eV. For double-hit events the total (sum) momentum for each deuteron pair was histogrammed (inset to Fig. 1). The peak at low total momentum represents true coincidences, since momentum conservation requires that the momenta of the two deuterons must sum to zero. The high momentum tail of the distribution comes from accidental coincidences, i.e., when deuterons from two different molecules are detected within one event. In our analysis we define a correlated double hit as having a total momentum in the range of (0–10)p_0 to safely include all possible single molecule events. Here $p_0 = e^2/\hbar$ is the atomic unit of momentum. About 15% of all events were correlated double hits, reflecting the 50% detection efficiency for the first deuteron and the 30% efficiency of detecting the second fragment.

The histograms of kinetic energy (per fragment) of all correlated events at two different laser intensities are shown in Fig. 2. The kinetic energy was calculated in the center-of-mass frame for each molecule. At

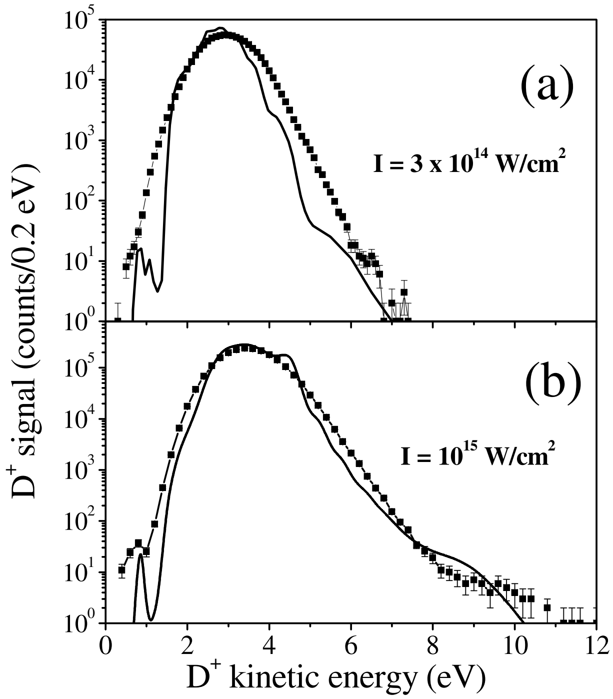

FIG. 2. The dots represent the experimental measurement of kinetic energy release per D_2 fragment, shown with a log scale. The solid curve is the calculation. Two laser intensities are shown. Only for the higher intensity of 10^{15} W/cm^2 is there evidence of shakeup events above 8 eV. The measured branching ratio is 2×10^{-5}.

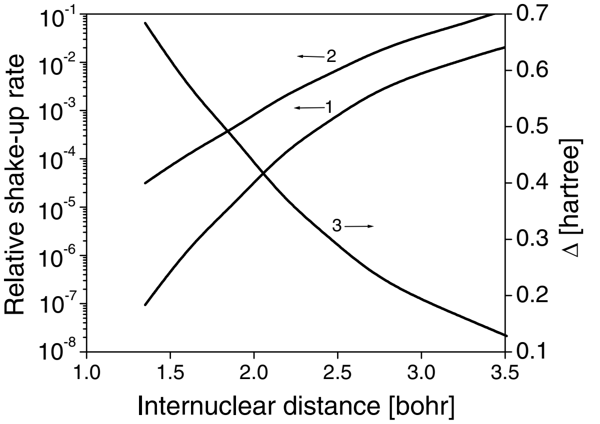

FIG. 3. Relative shakeup rates in D_2 as a function of internuclear distance. Curve 1 (SU1) depicts w_1/w_0; see Eq. (1). Curve 2 (SU2) depicts v_1/w_0; see Eq. (4). The rates have been averaged over φ, the angle between the laser electric field and the molecular axis. Shakeup is calculated at the intensity 8×10^{14} W/cm^2. Curve 3 shows Δ, the energy difference between the ionic σ_g and σ_u states of ${D_2}^+$.

3×10^{14} W/cm^2 [Fig. 2(a)] we observe no correlated events with fragment energies near 9 eV, with the high energy tail of the enhanced ionization peak extending to 7.5 eV. Only a single event with fragment energies above 7.5 eV was observed, and its kinetic energy (14 eV per fragment) was too high to attribute it to D_2 excitation. Thus at this intensity we can impose an upper limit on the probability of instantaneous excitation to be less than 10^{-6}.

However, at 10^{15} W/cm^2 we do see a distinct high energy band at around 9 eV extending beyond the edge of the enhanced ionization peak [Fig. 2(b)]. Though the number of counts is small, it is statistically significant and allows us to estimate the branching ratio between the ground and first excited state of ${D_2}^+$ to be about 2×10^{-5}. At this intensity the single ionization of D_2 is saturated and raising the intensity even further would not increase the probability of excitation.

The kinetic energy of the fragments was calculated by solving the nuclear wave packet propagation on the σ_g and σ_u ${D_2}^+$ surfaces [13]. Ionization and shakeup populate the two ionic surfaces according to the rates (1) and (4). Nonadiabatic population transfer, caused due to the launching of the wave packet, presents a numerical artifact and is filtered. Ionization of ${D_2}^+$ is calculated by using numerically determined ionization rates [14]. The numerical results are found to be in excellent agreement with experiment; see Fig. 2.

The excellent agreement between theory and experiment allows us to determine parameter regimes in which SU will make a dominant contribution to nonsequential, correlated ionization. From the inspection of Eqs. (1) and (4) it becomes clear that SU has to be significant for large molecules, where the energy spacing between the levels becomes small. As a clean measurement in large molecular systems is not straightforward, we suggest the following experiment. The decreasing energy spacing can be emulated by using dissociating wave packets of diatomic molecules, for which the internuclear distance increases and the energy spacing decreases. In Fig. 3, SU1 and SU2 are plotted versus internuclear distance of D_2. At an internuclear distance of 3.5 bohrs the level spacing is ≈ 3 eV, which is a typical value found in complex molecules. The ratio of tunneling to SU ionization becomes $\approx 10^{-1}$. This reveals the dominant contribution of SU to the ionization of large molecules. SU2 is larger than SU1 over the whole parameter range and therefore presents the leading shakeup mechanism.

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