RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 52, NUMBER 4 OCTOBER 1995

Charge-resonance-enhanced ionization of diatomic molecular ions by intense lasers

T. Zuo and A. D. Bandrauk

Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

(Received 12 April 1995)

We study the ionization of the H_2^+ molecular ion in intense, short-pulse laser fields by numerically solving the three-dimensional time-dependent Schrödinger equation as a function of internuclear distance R. Anomalously high ionization for the molecular ion at large internuclear separations is observed for orientations parallel to the linearly polarized laser field. The ionization rate is found to exhibit maxima at large R, exceeding the atom limit by an order of magnitude. This is attributed to transitions between pairs of charge-resonant states which are strongly coupled by the field in diatomic molecular ions. The effect is shown to also occur in higher odd-charge diatomic molecular ions and can be attributed to field-induced nonadiabatic transitions between the charge-resonant states and electron tunneling suppression by the instantaneous Stark field of the laser.

PACS number(s): 33.80.Eh, 33.90.+h, 33.15.−e, 42.50.Hz

As high-power laser sources have become widely available in modern laboratories in recent years, there has been growing interest in the study of atoms and molecules interacting with intense laser fields. Among the most extensively studied phenomena, both experimentally and theoretically, is the process of intense laser ionization of atoms (for a review, see, e.g., [1]). Intense laser ionization of atoms is now reasonably well understood, especially, in the high-intensity and long-wavelength regime characterized by the Keldysh parameter $\gamma<1$ (γ is the ratio of laser frequency to the laser peak electric field in atomic units). The ionization of atoms can then be described as a process of electron tunneling out of the combined field of the attractive Coulomb potential and the classical instantaneous laser electric field to reach the continuum. This model can be described quantitatively by the Keldysh-Faisal-Reiss theory [2,3] and is believed to also work for molecular systems at equilibrium nuclear separations [4].

For a molecule that is subjected to short, intense laser pulses, molecular dynamics (dissociation) is accompanied by ionization [5]. At high intensities ($I>10^{14}$ W/cm^2) such that the ionization process is generally faster than the dissociation process, it is useful to study molecular ionization for fixed internuclear separations. In this Rapid Communication we investigate in detail the process of ionization of the simplest diatomic ion, H_2^+, in a short pulse of linearly polarized, intense laser field as a function of the internuclear separation R by solving the three-dimensional (3D) time-dependent Schrödinger equation. Our results have reconfirmed that the ionization rate strongly depends on the internuclear separation as predicted before [6,7]. Our finding is that the rate is greatly enhanced at intermediate to large internuclear separations (from $R\simeq 5$ a.u. to $R\simeq 12$ a.u.) for H_2^+ in a 10^{14}-W/cm^2, $\lambda=1064$-nm laser field. These rates exceed the rate of the separated-atom limit, namely, that of the hydrogen atom by one order of magnitude under the same laser conditions. The reason for this anomalously high ionization rate, which we call CREI (see below) can be deduced from an analysis of H_2^+ ionization in a dc field. We wish to show in this work that the ionization enhancement is a consequence of two factors: (1) There exists a pair of charge-resonant (CR) states that are strongly coupled to the electromagnetic field at large R; this guarantees a sufficient population in the upper instantaneous field-modified CR states by nonadiabatic laser excitations; and (2) the sum of the Coulomb fields from the two nuclear centers at intermediate separations is altered by the static instantaneous laser field, thus freeing the upper field-induced autoionizing states compared to the corresponding atomic case. This allows a more efficient and faster ionization of the population in these upper levels.

The ground state, $1\sigma_g$, and the first excited state, $1\sigma_u$, of H_2^+ have been characterized as CR states and were first discussed by Mulliken [8]. Such pairs of CR states have an important property, i.e., the dipole moment between them diverges linearly as $R/2$ for large R where the charge distributions of the two states become almost the same (charge resonance) and their energies become nearly degenerate [7,9]. As a consequence, the CR states play a crucial role in many photophysical and photochemical processes, such as the creation of laser-induced bound states [9], molecular above-threshold photodissociation [9], even and odd harmonic generation in H_2^+ [7], etc. We will see that the CR states are also responsible for the anomalously high ionization of H_2^+ at intermediate-to-large R, which in this paper we refer as charge-resonance-enhanced ionization, CREI.

Figure 1 shows the calculated ionization rates of H_2^+ as a function of internuclear separation R for a 1×10^{14}-W/cm^2, 1064-nm, linearly polarized laser field. These rates are calculated using our previous method of solving the 3D time-dependent Schrödinger equation for H_2^+ with fixed internuclear separation [6,7]. The laser field is turned on linearly in five optical cycles (17.5 fs) and then kept constant. The norm of the wave function decays exponentially due to the removal of the continuum electron at the boundaries of the numerical grid. The rate Γ is then obtained by fitting the norm to the formula $|\psi(t)|^2=\exp(-\Gamma t)|\psi(0)|^2$.

It is seen in Fig. 1 that the ionization rate Γ is low at the equilibrium internuclear separation ($R=2$ a.u.) due to the large ionization potential $I_p=30$ eV [7]. In this region, the molecular ion ionizes just like an atom [4]. When R increases to intermediate-to-large internuclear separations ($5<R<12$ a.u.), however, the rate increases rapidly, exceed-

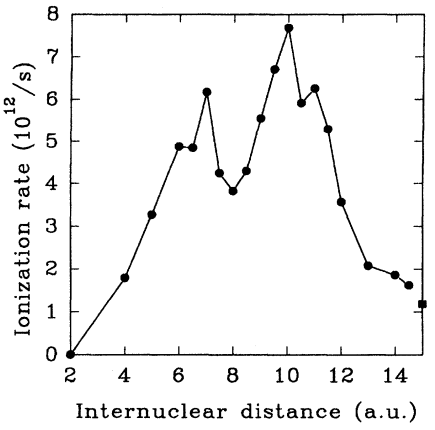

FIG. 1. Ionization rate of the H_2^+ molecular ion in 10^{14}-W/cm^2, 1064-nm, linearly polarized laser fields (five-cycle linear rise). The square on the right vertical axis marks the ionization of the hydrogen atom.

ing that of the hydrogen atom by one order of magnitude, although I_p is always larger than that of the atom (13.6 eV). We have already reported examples of such large ionization rates in [7] for selective R in previous studies of harmonic generation. Clearly the simple picture in which Γ is more or less a monotonic function of I_p according to the Ammosov-Delone-Krainov theory [3] (without intermediate resonances, a typical case for long-wavelength excitation) no longer applies. In fact, two prominent peaks are observed: one at $R_1=7$ a.u., the other at $R_2=10$ a.u. We will show next that the peak at R_2 is due to the CR-state-induced above-barrier ionization and that at R_1 it is due to a symmetry-breaking localization of the electron in one of the two Coulomb wells of H_2^+. It is these two peaks that are typical of CREI.

Given the remarkable success of the model of instantaneous dc-field tunneling ionization for the long-wavelength laser ionization of atoms [10], it is useful to examine the ionization of H_2^+ in a dc field following the ideas of Codling and Frasinski [11]. In Figs. 2(a)–2(c) we plot the effective (Coulomb plus dc field) potential along with the two lowest autoionizing (tunneling) states in such a potential for $R=6$ a.u., $R=10$ a.u., and $R=14$ a.u., respectively. The dc field strength is taken to be the peak strength of the 1×10^{14}-W/cm^2, 1064-nm laser field. The two autoionizing states marked by $1\sigma_-$ and $1\sigma_+$ are calculated numerically from the static Hamiltonian (in atomic units)

$$H=H_0+E_0z, \tag{1}$$

where H_0 is the zero-field Hamiltonian of H_2^+, and E_0 is the strength of the dc field, which is assumed to be along the z axis. Using the numerical techniques described by [12] we not only obtain the energy levels $1\sigma_-$ and $1\sigma_+$ but also their complex linewidths $\Gamma_{+(-)}$, or equivalently the (auto)ionization rates that are also indicated in Fig. 2. It is worth noting that the energy difference between the two autoionizing states is E_0R at large R, indicating that they are mainly evolved from the field mixing of the bare $1\sigma_u$ and $1\sigma_g$ (initially field-free) states of H_2^+ (which are degenerate at large R [7]). The resulting states become essentially the atomic states $1s_a$ and $1s_b$ localized on each proton or in each well. From Figs. 2(a)–2(c) we can now see why the autoionization rate of the upper level $1\sigma_+$ has a maximum at the intermediate nuclear separation $R=10$ a.u.. This is due to the fact that the middle (inner) barrier between the two nuclei frees the $1\sigma_+$ level at around $R=10$ a.u. This is shown in Fig. 2(b). The upper level $1\sigma_+$ lies just above the inner barrier, is unstable therefore, and ionizes very quickly. Furthermore, the strong coupling of the CR states to the external field at large R ($E_0R/2$) guarantees that the population of the upper level $1\sigma_+$ is substantial (our calculations show that for $R=10$ a.u. it is almost equal to that of the lower level) after the time of the dc field turn-on (35 fs in our calculation); i.e., the strong coupling of the CR states and the rapid ramp of the dc field populates the upper level $1\sigma_+$ and also keeps it from "flowing" to the lower level because of the destruction of the tunneling by the Stark effect, E_0R. For an adiabatic turn-on (a very long time with respect to the inter-well-tunneling time) of the dc field, no population would exist in the upper level after the turn-on. Adiabatic localization in the

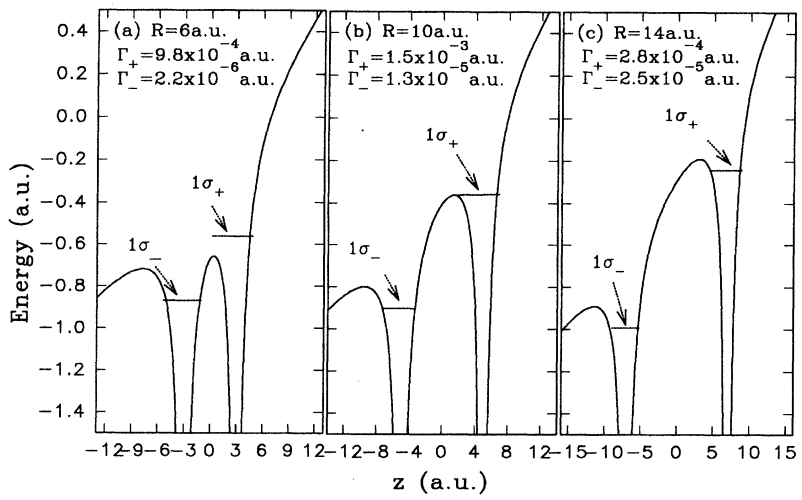

FIG. 2. Lowest two dc-field-induced levels of H_2^+, $1\sigma_+$ and $1\sigma_-$, in the effective potential $V_c(R)+E_0z$. The strength of the dc field is $E_0=0.0533$ a.u. ($I=1\times10^{14}$ W/cm^2).

lower level is thus prevented by the oscillation of the field, as seen next. For the smaller internuclear separation ($R=6$ a.u.), the (auto)ionization rate of the upper level is found to be somewhat smaller. This is due to the fact that although the upper $1\sigma_+$ level still is above the inner barrier, the left outer barrier becomes comparable and broad, leading to slower ionization. Furthermore, we are dealing with the 3D system, so confinement in the transverse direction is another factor. Also in this case ($R=6$ a.u.) the coupling E_0R of the CR states to the external field is not as strong as that of $R=10$ a.u., resulting in the upper level being less populated (about 40% from our calculation). In this case the total ionization depends more on the much slower process of the lower $1\sigma_-$ level electron tunneling out of the outer barrier. For very large internuclear separation [$R=14$ a.u., Fig. 2(c)], both the inner barrier (the barrier confining the upper $1\sigma_+$ level) and the outer barrier (the barrier confining the lower $1\sigma_-$ level) approach the limit of the separated atom, the hydrogen atom case, even though our calculations show that the upper level is efficiently populated. This results in a total ionization rate close to the hydrogen rate (Fig. 1) as a result of barrier confinement. For small R (<6 a.u.), the upper $1\sigma_+$ level again becomes trapped by the left (smaller R) barrier, thus decreasing substantially the ionization rate again. Our results therefore confirm the original ideas of Codling and Frasinski [11]. It is therefore only around some intermediate-to-large R, where both the conditions, namely (1) sufficient population of the upper $1\sigma_+$ level through nonadiabatic excitation and (2) lowering of both inner and outer barriers, are satisfied that one can expect a substantial amount of fast ionization from the upper level.

We now turn to Fig. 1, the nonstatic, i.e., 1064-nm laser field ionization of H_2^+. It can be expected that the oscillation of the laser electric field alternates the position of the instantaneous $1\sigma_+$ upper level and lower $1\sigma_-$ level at the laser frequency, thus always inducing nonadiabatic excitation (in the context of the above-dc-field treatment) needed for the enhanced ionization, i.e., CREI. The electron distributions of the two wells decay alternatively, following the laser oscillation. This has been clearly observed in our calculations. In Fig. 1 we have also noticed a lower peak at $R=7$ a.u.. This is attributed to laser-induced (symmetry-breaking) electron localization. The electron localization and its implications in two-level systems have been previously studied by several groups [7,13,14]. It is known that H_2^+ at relatively large R can be reasonably represented by a two-level system consisting of only the $1\sigma_g$ and $1\sigma_u$ states. For large R we have previously shown [7] that the difference in $1\sigma_g$ and $1\sigma_u$ state populations behaves as [see also Fig. 11, Ref. [7(b)]]

$$|c_g(t)|^2-|c_u(t)|^2=J_0(2\Omega_R/\omega)+2\sum_{k=1}^{\infty}J_{2k}(2\Omega_R/\omega)\cos(2k\omega t), \qquad (2)$$

where the J's are Bessel functions, $\Omega_R=E_0R/2$ is the Rabi frequency, and ω is the laser frequency. In fact, $\omega_0 J_0(2\Omega_R/\omega)$ is the energy difference of the dressed (Floquet) states, with ω_0 the energy difference of the two bare states [14]. Clearly at zeros of J_0 there is a maximum charge asymmetry, i.e., the electron prefers to stay at one well rather than the other, leading to the breaking of the inversion symmetry and thus allowing, e.g., strong even-order harmonic generation [7]. This is known as laser-induced electron localization due to tunneling suppression. The second time-dependent term in Eq. (2) corresponds to the electron following of the field at multiple frequencies $k\omega$, which in the long-wavelength limit can be viewed as alternation of the upper and lower levels, $1\sigma_u$ and $1\sigma_g$, i.e., a linear combination of the $1\sigma_u$ and $1\sigma_g$ molecular orbitals or alternatively $1s_a$ and $1s_b$ atomic orbitals. For the parameters $R=7$ a.u., laser intensity $I=1\times10^{14}$ W/cm^2, and wavelength $\lambda=1064$ nm, the argument of J_0, $2\Omega_R/\omega$ (=8.7 a.u.) is very close to the third zero ($x=8.6$) of the zero-order Bessel function $J_0(x)$, thus suggesting electron localization. The electron localization is confirmed in our full 3D time-dependent calculation. Figure 3 shows the probability of one of the wells, $|\langle 1s_a|\psi(t)\rangle|^2$ (normalized, see figure caption) during the interaction with the laser field for several internuclear separations. It is seen that at $R=7$ a.u. maximum (about 12%) localization occurs as compared with other R's. Since it is the dominance of the (instantaneous) upper $1\sigma_+$ level ionization over the tunneling between the two wells that enhances the ionization, the electron localization that results from suppression of the inter-well-tunneling increases further the ionization at $R=7$ a.u. We emphasize that the term "electron localization" used in this paper indicates the tendency of an electron to spend more time in one well (see caption of Fig. 3), i.e., where the electron probability is unequal in the wells.

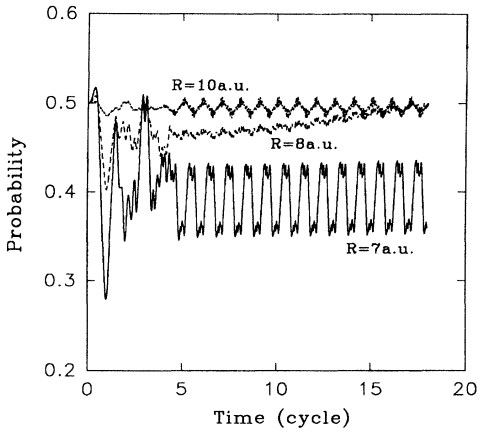

FIG. 3. Relative probability of an electron in one of the wells, calculated from the formula $P_a=|\langle 1s_a|\psi(t)\rangle|^2/[|\langle 1s_a|\psi(t)\rangle|^2+|\langle 1s_b|\psi(t)\rangle|^2]$, where $\psi(t)$ is the time-dependent wave function and $|1s_{a\ (b)}\rangle$ is the hydrogen orbital sitting at $R/2$ ($-R/2$).

Since the CR states exist not only in the H_2^+ molecular ion but also in higher odd-charge molecular ions, one can therefore expect tunneling ionization to show up in higher-charge systems [15]. We have extended our numerical calculations to a three-charge one-electron system A_2^{3+}, where A represents an atomiclike ion with two positive charges and the model high-charge molecular ion consists of two such double-charge centers separated by R_A and a single electron. CREI is again observed with the maximum ionization occurring at the position where R_A is large, to allow efficient upper

CR state population while satisfying the requirement that the σ_+ level be above the inner barrier created by the two-center Coulomb potential. For the He_2^{3+} system in a 5×10^{15}-W/cm^2 dc field, our calculations predict the maximum ionization occurring at $R_A=5$ a.u., i.e., $R_{A2}\simeq R_2/Z$, where Z is the nuclear charge.

In conclusion, the intense field ionization of diatomic molecular ions is qualitatively different from the ionization of atoms or their ions. H_2^+ in the long-wavelength, high-intensity laser field limits manifests anomalously high ionization rates at intermediate and large internuclear separations, which we call CREI. The presence of CR states that are strongly coupled to the external electromagnetic field at large R leads to a strong nonadiabatic excitation [on the time scale of the laser oscillations, Eq. (2)], keeping nearly half of the electron distribution in the vicinity of each of the two Coulomb centers, due to the destruction of tunneling between the wells by the instantaneous Stark effect of the laser field. In the dc field tunneling picture of long-wavelength, high-intensity laser ionization, the electron in the upper field-induced well (Fig. 2) has a much higher probability of ionizing than the electron in the separated-atom limit (lower well). Symmetry-breaking electron localization can also play an important role in intense laser ionization of diatomic molecular ions and this produces a second ionization maximum at smaller R. Current experimental results on intense field ionization of molecules [16] indicate in general the presence of Coulomb explosions, with fragments having less kinetic energy than that predicted by direct vertical ionization. Clearly the ionization rates obtained in the present work, which shows that large ionization occurs at specific large internuclear distances, play an important role by allowing Coulomb explosions to occur at larger R than the initial equilibrium distance [5], i.e., the molecule stretches during the initial part of the laser pulse until it reaches the critical distance where the ionization rate is enhanced by CREI. Our results show that odd-charge ions will have in general a critical intermediate distance for Coulomb explosions. This is also predicted recently by the one-dimensional time-dependent calculation of [15] for diatomic ions, which gives approximately the same critical distance for H_2^+ as ours, in spite of larger ionization rates compared with our 3D time-dependent results. Further calculations at shorter wavelength and higher intensities [17] give smaller critical distances, in agreement with experiments [16].

Note added. It recently came to our attention that a one-dimensional model, which also allows one to predict the critical ionization distance for multielectron dissociative ionization, has been proposed in Ref. [18].

We thank P. Corkum for discussions concerning tunneling ionization and S. Chelkowski for discussions.

[1] M. Gavrila, *Atoms in Intense Laser Fields* (Academic Press, New York, 1992).

[2] L. V. Keldysh, Sov. Phys. JETP **20**, 1307 (1965); F. H. M. Faisal, J. Phys. B. **6**, L89 (1973); H. R. Reiss, Phys. Rev. A. **22**, 1786 (1980).

[3] M. V. Ammosov, N. B. Delone, and V. P. Krainov, Sov. Phys. JETP **64**, 1191 (1986).

[4] S. L. Chin, Y. Liang, J. E. Decker, F. A. Ilkov, and M. V. Ammosov, J. Phys. B **25**, L249 (1992).

[5] S. Chelkowski, T. Zuo, O. Atabek, and A. D. Bandrauk, Phys. Rev. A **52**, 2977 (1995).

[6] S. Chelkowski, T. Zuo, and A. D. Bandrauk, Phys. Rev. A **46**, 5342 (1992).

[7] (a) T. Zuo, S. Chelkowski, and A. D. Bandrauk, Phys. Rev. A **48**, 3837 (1993); (b) **49**, 3943 (1994).

[8] R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939).

[9] A. D. Bandrauk, *Molecules in Laser Fields* (Marcel Dekker, New York, 1993), Chap. 3; A. Giusti-Suzor, F. H. Mies L. F. DiMauro, E. Charron, and B. Yang, J. Phys. B **28**, 309 (1995).

[10] P. B. Corkum, N. H. Burnett, and F. Brunel, Phys. Rev. Lett. **62**, 1259 (1989).

[11] K. Codling and L. J. Frasinski, J. Phys. B **26**, 783 (1993).

[12] M. R. Hermann and J. A. Fleck, Jr., Phys. Rev. A **38**, 6000 (1988).

[13] R. Bavli and H. Metiu, Phys. Rev. Lett. **69**, 1986 (1992).

[14] M. Yu. Ivanov, P. B. Corkum, and P. Dietrich, Laser Phys. **3** 375 (1993).

[15] T. Seideman, M. Yu. Ivanov, and P. B. Corkum (unpublished).

[16] M. Schmidt, D. Normand, and C. Cornaggia, Phys. Rev. A **50**, 5037 (1994).

[17] S. Chelkowski and A. D. Bandrauk (unpublished).

[18] J. H. Posthumus, L. J. Frasinski, A. J. Giles, and K. Codling, J. Phys. B **28**, L349 (1995).