

Radiation Generated by the Ultrafast Migration of a Positive Charge Following the Ionization of a Molecular System

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(Received 23 November 2010; published 31 January 2011)

Electronic many-body effects alone can be the driving force for an ultrafast migration of a positive charge created upon ionization of molecular systems. Here we show that this purely electronic phenomenon generates a characteristic IR radiation. The situation when the initial ionic wave packet is produced by a sudden removal of an electron is also studied. It is shown that in this case a much stronger UV emission is generated. This emission appears as an ultrafast response of the remaining electrons to the perturbation caused by the sudden ionization and as such is a universal phenomenon to be expected in every multielectron system.

DOI: 10.1103/PhysRevLett.106.053001

PACS numbers: 33.20.-t, 42.65.Re, 82.39.Jn

If a multielectron system is ionized, a question of fundamental importance is, how do the remaining electrons react? How does the created hole change its form and position as time proceeds due to the interaction with the remaining electrons, and, of course, what is the time scale of these changes? More than 10 years ago it was shown [1] that after ionizing a molecule the many-body effects alone can beget rich ultrafast electron dynamics such that the hole created upon ionization can migrate throughout the system on the time scale of only few femtoseconds. Since the mediator of the process is the electron correlation and the electron relaxation, in order to distinguish it from the nuclear-dynamics-driven charge transfer, this phenomenon was termed charge migration. The charge migration after ionization of the valence shell has been theoretically studied in different molecules [2–5]. In some specific, but not rare, cases the hole initially created on one end of the molecule was found to oscillate to the other one and back within just a few femtoseconds. Being usually much faster than the nuclear motion, the charge migration following ionization can thus be computed neglecting the nuclear dynamics, as long as one is interested in what happens within the time interval during which this ultrafast process takes place. Clearly, at later times the coupling to the nuclear dynamics will start to play a role and it has to be considered. However, before the nuclear dynamics start to perturb the picture, the charge migration represents a charge oscillating throughout the molecule and, thus, the molecule itself can be seen as an oscillating dipole. It is well known that an oscillating dipole emits radiation. The natural question is then, what is the emitted radiation and how strong is it?

In this Letter we show that the charge migration phenomenon generates a characteristic infrared (IR) radiation and compute the spectrum of this emission. In addition, we study the fundamental question of what will happen if the ionization is performed extremely fast and obtain surprising

results. We would like to note here that although it might appear academic, approaching the limit of sudden ionization is conceivable in view of the rapid development of the attosecond laser pulse techniques (see, e.g., Refs. [6,7]).

The total power of the radiation emitted by a moving charge as a function of time can be calculated via the well-known Larmor formula (see, e.g., Ref. [8]), which in atomic units reads

$$P(t) = \frac{2}{3c^3} |\ddot{\vec{D}}(t)|^2, \quad (1)$$

where $\ddot{\vec{D}}(t)$ is the second time derivative of the dipole moment

$$\vec{D}(t) = \langle \Psi(t) | \hat{D} | \Psi(t) \rangle \quad (2)$$

and c is the speed of light. The spectrum of the emitted radiation can be obtained by substituting in Eq. (1) $\ddot{\vec{D}}(t)$ by its Fourier transform.

Let us take a realistic showcase example, the molecule 3-methylen-4-penten-*N,N*-dimethylamine (MePeNNA), for which we showed in a recent work that after an outer-valence ionization a strong charge migration takes place [5]. Our many-body calculations showed that the outer-valence part of the ionization spectrum of the molecule consists of two ionic states, one at about 7.9 eV and one at about 8.4 eV (see Ref. [5] and Fig. 3 below). These two states can be simultaneously populated via a laser pulse with photon energy centered between the two states and a bandwidth sufficient to embrace both of them. Since the states are about 0.5 eV apart, one needs a pulse with duration of about 1 fsec, ideally even shorter. Subfemtosecond pulses are already available (see, e.g. [9]), and, thus, a simultaneous population of the two states is experimentally achievable. Of course, if the two ionization channels are open, they will interfere. A similar situation was realized experimentally and discussed in

Refs. [10,11]. Our calculations showed [5] (see also Fig. 3 below) that, due to the many-body effects, each of the two ionic states is a strong mixture of two one-hole (1h) configurations, $(\text{HOMO})^{-1}$ and $(\text{HOMO} - 1)^{-1}$ (here the superscript “ -1 ” denotes that the corresponding molecular orbital has one fewer electron). The highest occupied molecular orbital (HOMO) of MePeNNA is localized on the chromophore moiety of the molecule, while the HOMO $- 1$ on the N terminal (see Fig. 1). A constructive interference between the two ionization channels will lead to a localization of the initial hole on the chromophore, while a destructive one will lead to a localization of the charge on the N terminal. Let us take the ionic state prepared by the constructive interference, i.e., a hole localized on the chromophore, and see what will be the succeeding electron dynamics. Such an initial state can be prepared, e.g., by an intense positively chirped broadband laser pulse [12] or by a π pulse. For computing the charge migration we use elaborated many-body *ab initio* methods only. A detailed description of the methodology is given elsewhere [2,4].

The hole density of the molecule MePeNNA after creating the initial hole on the chromophore is shown in Fig. 1. The hole density is given by the difference between the electronic densities of the system before and after the ionization [1,2]. It is clearly seen that immediately after the ionization the hole starts to oscillate between the “left” and the “right” moiety of the system with a period of about 7.5 fsec. These oscillations will be gradually distorted by the coupling to the nuclear degrees of freedom. The slower nuclear dynamics will eventually trap the charge on one of the two sites. However, the nuclear dynamics time scale is such that the hole will have time to perform a few, nearly perfect oscillations before the nuclear motion will distort

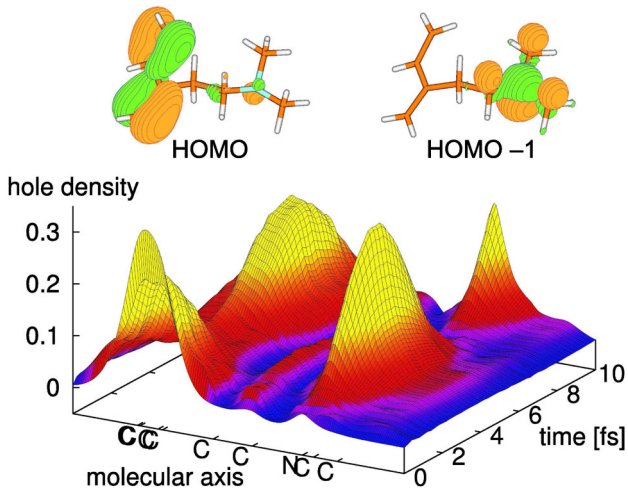


FIG. 1 (color online). Hole density along the molecular axis of the molecule MePeNNA as a function of time after a localized ionization of the chromophore. The molecular axis is chosen to pass through the longest spatial extension of the molecule. The Hartree-Fock HOMO and HOMO $- 1$ of the molecule are also shown.

the picture. Thus, within the first few periods this charge migration process will represent an oscillating dipole.

In order to compute the time-dependent dipole moment of the cationic MePeNNA after the ionizing pulse is over, one can use the following, in principle exact, expansion of Eq. (2):

$$\vec{D}(t) = \sum_{I,J} x_I^* \langle I | \hat{D} | J \rangle x_J e^{-i\omega_{IJ}t}, \quad (3)$$

where $|I\rangle$ is a complete set of cationic eigenstates, $x_I = \langle I | \Phi_i \rangle$ is the transition amplitude with respect to the initially prepared nonstationary cationic state $|\Phi_i\rangle$, and $\omega_{IJ} = E_J - E_I$ is the difference between the corresponding cationic eigenenergies. If the parameters of the ionizing pulse are chosen as discussed above, only the first two states will be populated and will give a nonzero contribution to the expansion (3). The components of the time-dependent dipole moment computed via Eq. (3) are shown in the upper panel of Fig. 2. By taking the second time derivative of the dipole moment and Fourier transforming it, one obtains the spectrum of the emission generated by the oscillating charge shown in the lower panel of Fig. 2.

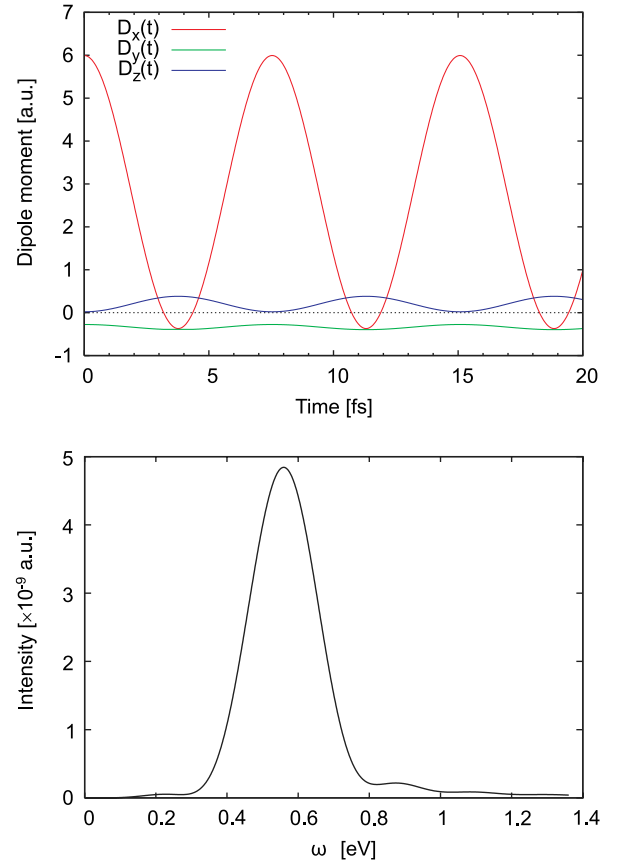


FIG. 2 (color online). Components of the time-dependent dipole moment (upper panel) and the emission spectrum (lower panel) generated by the charge migration process initiated by a localized ionization of the chromophore site of the molecule MePeNNA.

We see that the spectrum consists of a single peak at about 0.55 eV corresponding to the oscillation period of 7.5 fsec. This emission is probably measurable. The total energy emitted during 10 fsec radiation from a single molecule is $\sim 2.3 \times 10^{-9}$ eV. For density of $\sim 10^{18}$ molecules/cm³, a typical density used in high-harmonic generation gas chambers [13], and interaction volume of $\sim 10^{-7}$ cm³ [13], the charge migration will generate ~ 115 IR photons. Not long ago, the IR emission caused by the charge separation step of the phototransduction process of bacteriorhodopsin was successfully measured [14]. We would like to note that since the charge migration generates a characteristic radiation, the experimental observation of such an emission will be a direct proof for existence of the phenomenon of charge migration.

Let us now discuss the situation when the ionization is performed extremely fast, ideally infinitely fast. Of course, one cannot in practice remove an electron suddenly in the literal sense, but we have to note that attosecond laser pulses are already available and maybe in the not-so-distant future one will be able to approach this limit also experimentally in the following sense. It will suffice that the electron is removed such that during the process of ionization the other electrons do not have time to react. The time needed for the other electrons to respond to a sudden creation of a hole is about 50 asec [15] (see also Ref. [16]). It was shown [15] that this time is universal, i.e., it does not depend on the particular system, and as such appears as the time scale of the electron correlation. Thus, in practice, sudden ionization is equivalent to ionization performed faster than the electron correlation. If the ionization is performed faster than the electron correlation, one may assume that the electron is removed from a single molecular orbital, being a result of an independent particle model. The Hartree-Fock (HF) approximation provides the best independent particle theory to describe the ionization since the many-body corrections to the ionization energies begin to contribute at a higher order of perturbation theory than with other choices of approximations [17]. That is why we may assume that the initial hole created upon sudden ionization is described favorably by a HF orbital. On the other hand, if the sudden ionization has to be performed with a laser pulse, it has to be extremely short, ideally shorter than 50 asec. We would like to note that isolated pulses with duration of about 80 asec are already available [18]. Such pulse will have a very broad band allowing the population of a large number of ionic states of the system. Thus, many ionic states $|I\rangle$ will contribute to the expansion (3). In addition, with such pulses one will probably not be able to address a particular HF orbital. In principle, all valence HF orbitals will participate, and one will have to know how to separate the signal coming from the ionization out of the desired orbital.

Let us assume, for the moment, that one can remove an electron from a particular HF orbital and see what will happen. As an example we will take again the molecule

MePeNNA and will remove an electron from its HOMO, which, as we discussed above, is localized on the chromophore (see Fig. 1). The ionization spectrum of the molecule, calculated via Green's function methodology [19], is shown in Fig. 3. The $(\text{HOMO})^{-1}$ contributions to the ionic states are shown in dark gray (red) in the figure. We see that apart from the two states already discussed above, the configuration $(\text{HOMO})^{-1}$ contributes also to a large number of ionic states spread over a large energy range (see the inset of Fig. 3). Thus, a sudden removal of an electron from the HF HOMO will create a superposition of a large number of ionic states weighted by the corresponding transition matrix elements. The time-dependent dipole moment created by such initial wave packet is shown in the upper panel of Fig. 4.

We see that apart from the strong oscillation with a period of about 7.5 fsec, the components of the dipole moment show small wiggles on a time scale of only few tens of attoseconds. These, of course, come from the coupling between states separated by tens of eV. Although small, these variations of the dipole moment generate a strong emission in the UV range. This can be clearly seen in the lower panel of Fig. 4, where the emission generated by the charge migration following sudden ionization of the HF HOMO of the molecule is shown. We see that the spectrum spreads up to about 50 eV with the most intense emission in the range 10–25 eV. The intensity of this UV emission is 2 orders of magnitude stronger than the IR radiation produced by the 7.5 fsec oscillations of the charge between the two ends of the molecule. The latter is shown in the inset of the lower panel of Fig. 4 together with the emission produced by the initial state constructed as a superposition of the two lowest in energy states, as discussed above and shown in Fig. 2. Interestingly, the white noise generated by the contribution of a large number of ionic states

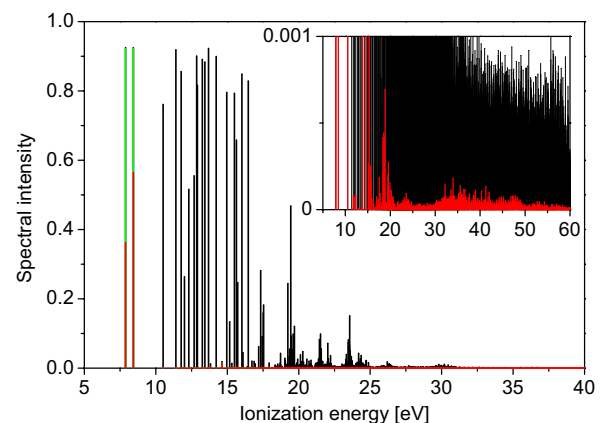


FIG. 3 (color online). Ionization spectrum of the molecule MePeNNA computed using the *ab initio* many-body Green's function method. The contributions of the 1h configuration $(\text{HOMO})^{-1}$ to the cationic states is given in dark gray (red). The contribution of the $(\text{HOMO} - 1)^{-1}$ configuration in the first two ionic states is shown in light gray (green). The inset is a zoom of the same plot.

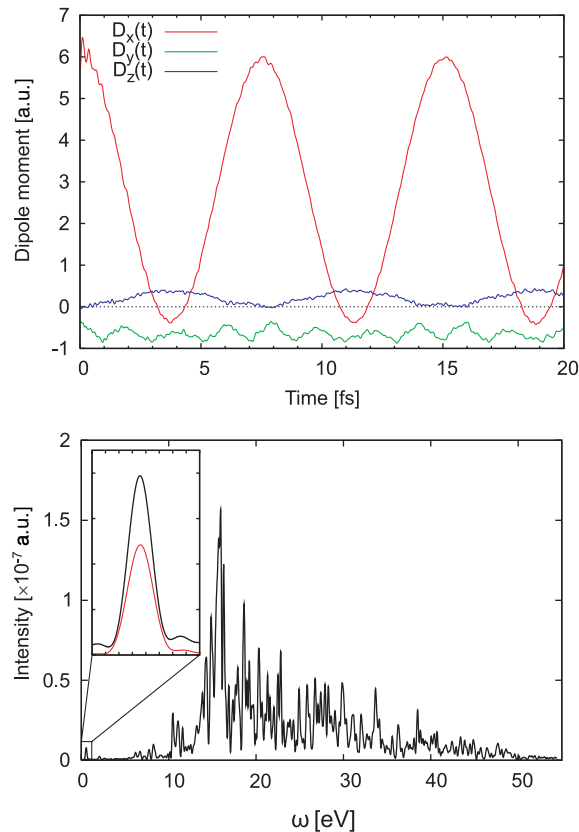


FIG. 4 (color online). Components of the time-dependent dipole moment (upper panel) and the emission spectrum (lower panel) after sudden removal of an electron from the HF HOMO of the molecule MePeNNA. Comparison with the emission spectrum reported in Fig. 2 is shown in the inset.

introducing a superposition of a large number of different frequencies gives rise to a substantial increase of the IR emission produced by the 7.5 fsec charge oscillation.

We have to emphasize that the UV emission generated by the attosecond variations of the hole charge is not inherent only to the cases when a strong charge migration within the molecule is observed. These variations appear as a result of the electronic correlation present in the cation and as such will accompany any sudden ionization of a many-electron system, irrespective of the succeeding dynamics. Removing an electron from each valence HF orbital will lead to an emission in the UV range similar to the one shown in Fig. 4. Thus, exposing the system to an ultrashort pulse will generate an UV emission which will be a superposition of the emission spectra coming from the ionization of each individual HF orbital.

In conclusion, we demonstrated that the purely electronic phenomenon of ultrafast charge migration following ionization of a molecular system generates a characteristic radiation. Since the charge migration typically represents charge oscillations with a few femtoseconds period, the generated emission is in the IR range. Encouraged by the successful measurement of the emission produced by the nuclear-dynamics-driven charge transfer in

bacteriorhodopsin [14], we believe that the emission generated by a purely electron-correlation-driven charge migration could be measurable. That is why we advocate here experimental efforts in this direction. Because of the fact that the charge migration produces a characteristic radiation, the observation of such IR emission would be a direct experimental proof for the charge migration phenomenon. We also studied the situation when the initial ionic wave packet is produced by a sudden removal of an electron and found out that in this case a much stronger UV emission is generated. Moreover, this emission appears as an ultrafast response of the remaining electrons to the perturbation caused by the sudden ionization and as such is a universal phenomenon to be expected in every multielectron system irrespective of the succeeding electron dynamics.

We hope that our results will trigger future experimental studies on the fascinating subject of ultrafast charge migration and ultrafast ionization.

The authors thank André Bandrauk for enlightening discussions. This research was supported in part by the National Science Foundation under Grant No. NSF PHY05-51164 and by the DFG.

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- [1] L. S. Cederbaum and J. Zobeley, *Chem. Phys. Lett.* **307**, 205 (1999).
- [2] J. Breidbach and L. S. Cederbaum, *J. Chem. Phys.* **118**, 3983 (2003).
- [3] H. Hennig, J. Breidbach, and L. S. Cederbaum, *J. Phys. Chem. A* **109**, 409 (2005).
- [4] A. I. Kuleff, J. Breidbach, and L. S. Cederbaum, *J. Chem. Phys.* **123**, 044111 (2005).
- [5] S. Lünemann, A. I. Kuleff, and L. S. Cederbaum, *J. Chem. Phys.* **129**, 104305 (2008).
- [6] F. Krausz and M. Ivanov, *Rev. Mod. Phys.* **81**, 163 (2009).
- [7] M. Nisoli and G. Sansone, *Prog. Quantum Electron.* **33**, 17 (2009).
- [8] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1999), 3rd ed.
- [9] G. Sansone *et al.*, *Science* **314**, 443 (2006).
- [10] O. Smirnova *et al.*, *Nature (London)* **460**, 972 (2009).
- [11] O. Smirnova *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 16 556 (2009).
- [12] J. Cao, C. J. Bardeen, and K. R. Wilson, *Phys. Rev. Lett.* **80**, 1406 (1998).
- [13] B. Shan, A. Cavalieri, and Z. Chang, *Appl. Phys. B* **74**, S23 (2002).
- [14] G. I. Groma *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 7971 (2004).
- [15] J. Breidbach and L. S. Cederbaum, *Phys. Rev. Lett.* **94**, 033901 (2005).
- [16] A. I. Kuleff and L. S. Cederbaum, *Phys. Rev. Lett.* **98**, 083201 (2007).
- [17] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1989).
- [18] E. Goulielmakis *et al.*, *Science* **320**, 1614 (2008).
- [19] J. Schirmer, A. B. Trofimov, and G. Stelter, *J. Chem. Phys.* **109**, 4734 (1998).