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REGULAR ARTICLE

Role of Excited States in Asymmetric Harmonic Emission

Liqiang Feng[1†] and Tianshu Chu[1,2,*]

[1]*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China, P. R. 116023*

[2]*Institute for Computational Sciences and Engineering, Laboratory of New Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, Qingdao University, Qingdao, China, P. R. 266071*

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Abstract: Role of excited states is theoretically studied in the asymmetric harmonic generation from quasi-asymmetric molecule LiH^{3+}. The calculated energies and time-dependent populations on the relevant electron states demonstrate that there is the laser-induced electron transfer between the ground state and the first few excited states, which is responsible for the observed multiple frequencies enhancements on the harmonic emission process. In addition, such electron transfer process is very likely to be general for the quasi-asymmetric molecules, as suggested by calculations for LiH^{3+} at different internuclear distances and with different central frequencies, pulse intensities, carrier-envelope phases, pulse durations as well as for the other quasi-asymmetric molecule BeH^{4+}.

AMS subject classifications: 35Q41, 78A10, 81V55

Key words: High-order harmonic generation, quasi-asymmetric molecules, laser-induced electron transfer

1 Introduction

*Corresponding author. *Email addresses:* tschu@dicp.ac.cn, tschu008@163.com (T.-S. Chu),
†*Email address*: lqfeng@dicp.ac.cn (L.-Q. Feng)

With the development of the laser technology, the interaction between the intense laser pulses and the atoms [1,2] or the molecules [3,4] becomes an issue of wide interest and has received a lot of attention. High-order harmonic generation (HHG) as one of the most important nonlinear phenomena has been investigated for many years due to its potential applications in the generation of coherent UV attosecond pulses [5, 6] and in the time-resolved dynamics measurement of the atomic/molecular structure [7].

Currently, the HHG process can be described by the semiclassical recollision model [8] that consists of three steps: tunnel ionization-acceleration-recombination where both ionization and recombination processes occurred on the ground electronic state. Very recently, it has been found that, for some quasi-asymmetric molecules with permanent dipoles and multiple centers such as HeH^{2+} [9,10], not only the ground state but also the excited states can be recorded by harmonic emission, especially by the lower order harmonics. For instance, Bian *et al* found that there is one electron transfer process between the 1sσ ground state and the 2pσ excited state of HeH^{2+} on the harmonic emission process [11]. Chen *et al* discovered that there are two characteristic electron trajectories on each cycle harmonic emission caused by the general ground state and the excited state [12]. However, it remains unclear whether this excited state effect is the general characteristics of the quasi-asymmetric molecules.

Thus, in this paper, to work out the above issue as well as for better understand the excited state effect on the asymmetric molecules, we carried out a time-dependent Schrödinger equation (TDSE) investigation on the asymmetric harmonic emission from the two quasi-asymmetric molecules of LiH^{3+} and BeH^{4+}. Atomic units (a.u.) are used throughout this paper unless stated otherwise.

2 Computational aspects

In our numerical simulations, the HHG spectra are obtained by solving the time-dependent Schrödinger equation [13-18]. Here, we assume that the molecule is aligned along the laser polarization direction. Thus, the Hamiltonian is given by $H = \left[-\partial^2/\partial x^2 + V(x) + xE(t)\right]$. Here, $V(x) = -Z_1/\sqrt{(x+R_1)^2+a} - Z_2/\sqrt{(x-R_2)^2+a}$ is the Coulomb potential, which can be described by the soft-core parameters (a=0.223 for LiH^{3+} and a=0.1249 for BeH^{4+}). Z_1 and Z_2 are the effective charges of the two nuclei (Z_1=3, Z_2=1 for LiH^{3+} and Z_1=4, Z_2=1 for BeH^{4+}) and R is the internuclear distance with $R_1=[Z_2/(Z_1+Z_2)]R$ and $R_2=[Z_1/(Z_1+Z_2)]R$. The laser field is expressed as: $E(t)=E\exp[-4\ln(2)t^2/\tau^2]\cos(\omega_0 t+\phi)$, where E, ω_0, τ and ϕ denote the amplitude, the frequency, the pulse duration and the carrier-envelope phase (CEP) of the laser pulse. Further, the harmonic spectrum ($S(\omega)$) is obtained by Fourier transforming the dipole

acceleration a(t), $S(\omega)=\left|\frac{1}{\sqrt{2\pi}}\int_0^T a(t)e^{-i\omega_0 t}dt\right|^2$, where a(t) is obtained by means of Ehrenfest's theorem [19]: $a(t)=\left\langle\phi(x,t)\left|-\frac{\partial V(x)}{\partial x}+E(t)\right|\phi(x,t)\right\rangle$ ($\phi(x,t)$ is the time-dependent wave function). The detail theoretical method can be found in previous investigations [13-18].

3 Results and discussion

Figure 1 shows the HHG spectrum of the LiH^{3+} molecule at the internuclear distance R=2.0 a.u. The laser field is chosen to be 5fs/800nm, I=1.0×10^{15}W/cm^2 (I=E^2 is the pulse intensity) and ϕ=0°. Clearly, except for the general characteristic on the harmonic emission process, that is the ultrabroad plateau between the maximum cutoff energy and the second maximum cutoff energy and the predicted maximum cutoff energy $E_{max}=I_p+3.17U_p$, where I_p is the ionization potential and $U_p=e^2E^2/4m_e\omega^2$ is the ponderomotive energy of the free electron, the most important phenomenon of this asymmetric harmonic emission is the multiple frequencies enhancements in the low harmonic orders. Particularly, there are four intense resonant peaks (the intensities of these peaks are enhanced by at least one order of magnitude in comparison with the plateau) respectively around the 36th, the 52nd, the 63rd and the 72nd harmonic orders. According to the former investigations about the HeH^{2+} molecule, we know that these resonant peaks are caused by the laser-induced electron transfer between the ground state and the excited states [11,20]. In **Figure 2,** we tentatively provide the physical reason behind the electron transfer process. First, the electron (green dot) may be excited to the excited states by the 1st, the 2nd pathways (that is, directly excitation from the ground state to the excited states) or the 3rd pathway (that is, indirectly excitation from the low excited state to the high excited state). Then, due to the permanent dipole of this asymmetric molecule, these excited states may have a very long lifetime [21], which further causes a comparable population on these excited states. When the laser field changes its direction part of the electron populated on the excited states may transit back to the ground state and emits photons (the 4th pathway in **Figure 2**). Due to this, a strong resonant peak would appear around the harmonic corresponding to the E_{ES}-E_{GS} energy gap with E_{GS} and E_{ES} the energies of the ground state and the excited states.

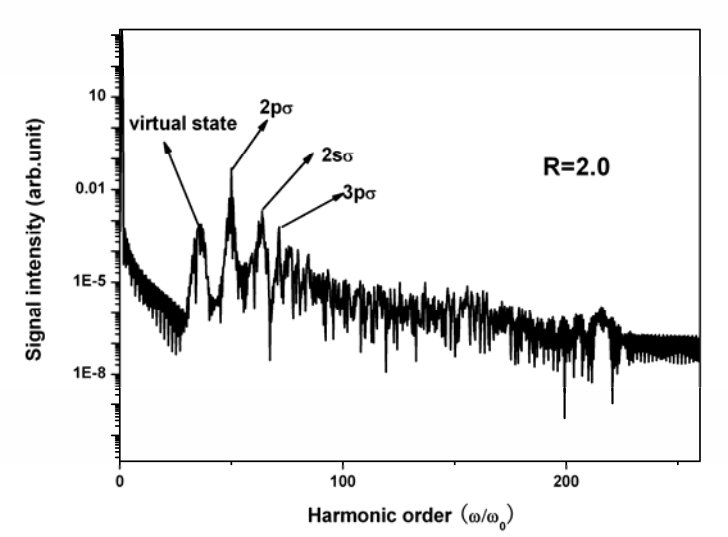

Figure 1: HHG spectrum from LiH^{3+} at internuclear distance R=2.0a.u. The laser field is chosen to be 5fs/800nm with $I=1.0\times10^{15}W/cm^2$ and $\phi=0°$.

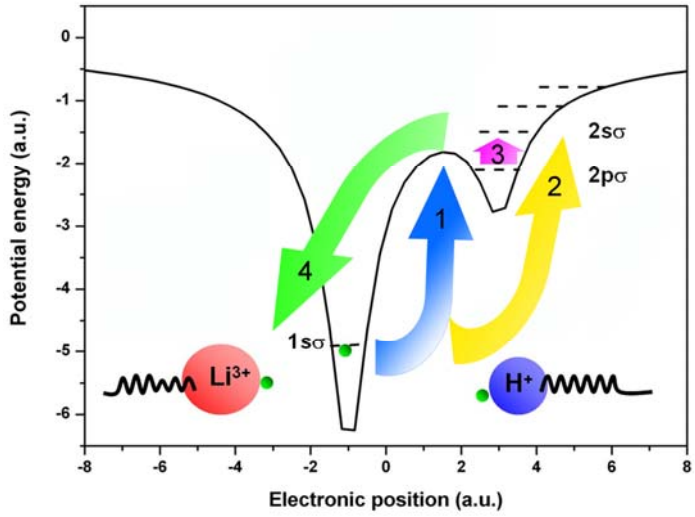

Figure 2: An illustrative scheme of the laser induced electron transfer between the ground state and the excited state.

Table 1 shows the undressed energies of the first few electronic states, along with the energy data taken from refs. 22-23. Clearly, our calculated results are in quantitative agreement with the experimental data or other accurate theoretical results except for the appearance of an additional virtual state (VS). From analyzing the energies of these

electronic states, we can see that the resonant peaks around the 36th, the 52nd, the 63rd and the 72nd harmonic orders agree well with the energy differences between the virtual state and the 1sσ ground state, between the 2pσ state and the 1sσ state, between the 2sσ state and the 1sσ state and between the 3pσ state and the 1sσ state. In **Figure 3**, we present the time-dependent populations of the electron on the 1sσ, the 2pσ, the 2sσ and the 3pσ states along with the laser profile. The figure shows that the electron transfer occurs predominately at the time when the laser field changes its direction, and the transfer intensity to the excited state has the following order: 2pσ>2sσ>3pσ, which is responsible for the intensity differences of the above resonant peaks. We note that the 1st resonant peak (around the 36th) is not considered in the above population analysis due to it corresponds to the virtual state which does not exist in a real system.

Table 1: Electronic energies (in a.u.) of LiH^{3+} at R=2.0a.u. The energies inside the brackets are experimental data or other accurate theoretical results taken from refs.[22, 23].

R	$E_{1s\sigma}$	E_{VS}	$E_{2p\sigma}$	$E_{2s\sigma}$	$E_{3p\sigma}$	E_{VS}-$E_{1s\sigma}$	$E_{2p\sigma}$-$E_{1s\sigma}$	$E_{2s\sigma}$-$E_{1s\sigma}$	$E_{3p\sigma}$-$E_{1s\sigma}$
2.0	-5.004	-2.97	-2.042	-1.41	-0.902	$35.7\omega_0$	$52\omega_0$	$63.2\omega_0$	$72.04\omega_0$
	(-5.002)		(-2.001)	(-1.452)	(-0.869)		$(52.6\omega_0)$	$(62.3\omega_0)$	$(72.5\omega_0)$

From the above analyses, we see that the excited states play an important role in the asymmetric harmonic emission. However, whether the excited state effect is the general characteristic of the quasi-asymmetric molecules still remains unanswered. To elucidate this issue, we further calculated and examined the asymmetric HHG spectra of LiH^{3+} with different internuclear distances and different laser parameters as well as the HHG spectrum of one other asymmetric molecule BeH^{4+}

Table 2: Electronic energies (in a.u.) of LiH^{3+} at R=3.0a.u. and 4.0a.u. The energies inside the brackets are experimental data or other accurate theoretical results taken from refs [22,23]. (Here the virtual state is not taken into account)

R	$E_{1s\sigma}$	$E_{2p\sigma}$	$E_{2s\sigma}$	$E_{3d\sigma}$	$E_{3p\sigma}$	$E_{2p\sigma}$-$E_{1s\sigma}$	$E_{2s\sigma}$-$E_{1s\sigma}$	$E_{3d\sigma}$-$E_{1s\sigma}$	$E_{3p\sigma}$-$E_{1s\sigma}$
3.0	-4.82	-1.81	-1.42		-0.724	$52.8\omega_0$	$59.7\omega_0$		$71.9\omega_0$
	(-4.83)	(-1.67)	(-1.37)		(-0.783)	$(55.4\omega_0)$	$(60.7\omega_0)$		$(71\omega_0)$
4.0	-4.743	-1.52	-1.41	-1.06	-0.745	$56.6\omega_0$	$58.5\omega_0$	$64.5\omega_0$	$70.2\omega_0$
	(-4.75)	(-1.48)	(-1.32)	(-1.17)	(-0.724)	$(57.4\omega_0)$	$(60.2\omega_0)$	$(62.8\omega_0)$	$(70.7\omega_0)$

Figures 4(a) and **(b)** show the HHG spectra of LiH^{3+} at other two internuclear distances of R=3.0 a.u. and 4.0 a.u., respectively. The laser field is the same as that in **Figure 1.** Clearly, the intense resonant peaks remained for these two internuclear distances. From analyzing

the energies of the electronic states shown in **Table 2**, we can see that these resonant peaks are also caused by the electron transfer between the ground state and the first few excited states (i.e. 2pσ, 2sσ, 3pσ, and 3dσ states). The HHG spectra for internuclear distances other than the ones shown here are quite similar, thus, we did not show them in the present article. From **Figure4**, we found that the resonant peaks are independent of the internuclear distance.

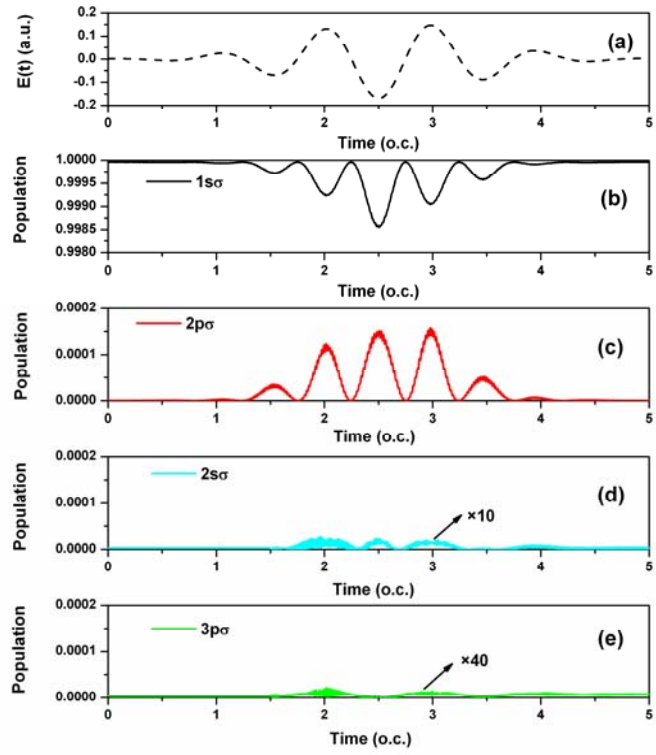

Figure 3: (a) The profile of the laser field used in the present calculation. **(b)-(e)** The time-dependent populations of the electron on the 1sσ, 2pσ, 2sσ and 3pσ states, respectively.

Figures 5(a)-(d) respectively show the HHG spectra of LiH^{3+} with different central wavelengths (λ_0=400nm-700nm with I=1.0×10^{15}W/cm^2, τ=5fs, and ϕ=0^o, **Figure 5(a)**), and with different pulse intensities (I=5.0×10^{14}W/cm^2, 1.5×10^{15}W/cm^2, 2.0×10^{15}W/cm^2 with λ_0=800nm, τ=5fs, and ϕ=0^o, **Figure 5(b)**), as well as with different pulse durations (τ=6fs, 10fs with λ_0=800nm, I=1.0×10^{15}W/cm^2, and ϕ=0^o, **Figure 5(c)**), and also with different CEPs (ϕ=30^o, 60^o, 90^o, 150^o with λ_0=800nm, I=1.0×10^{15}W/cm^2, and τ=5fs, **Figure 5(d)**). The internuclear distance is chosen to be R=2.0a.u. in all of the above calculations. It shows that the four resonant

peaks (1-4), corresponding to the VS, the 2pσ, the 2sσ, and the 3pσ states, are permanent in these calculated spectra, suggesting the excited state effect is sensitive to the laser parameters.

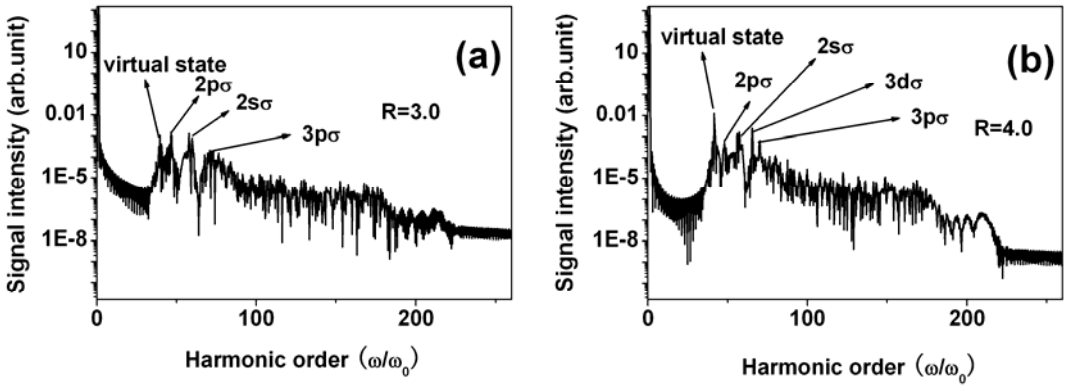

Figure 4: (a) and **(b)** The HHG spectra from LiH^{3+} at internuclear distances R=3.0a.u. and 4.0, respectively. The laser field is the same as that in **Figure 1**.

Figure 6 shows the HHG spectrum of the quasi-asymmetric molecule BeH^{4+}. Here, the internuclear distance is chosen to be R=5.0a.u. and the laser field is the same as that in **Figure 1**. Clearly, there are also several intense resonant peaks in the low harmonic orders caused by the laser-induced electron transfer. Through analyzing our calculated energies of the electronic states of BeH^{4+} listed in **Table 3**, we identify that these peaks are caused by the electron transiting back from the first few excited states (i.e. 2pσ, 2sσ, 3dσ and 3dπ states) to the 1sσ ground state. Moreover, by studying the HHG spectra at different internuclear distances and with different laser parameters (which are not shown in this paper), we found that the low harmonic enhancement phenomenon is also insensitive to laser parameters and internuclear distance for the BeH^{4+} system. As of now, through the above analyses (**Figures 4-6**) and together with the previously similar findings for HeH^{2+} in refs [11,20], we can deduce that the excited state effect, in other words, the appearance of the resonant peaks which are caused by the laser-induced electron transfer between the ground state and the excited states, is very likely a general phenomenon on the asymmetric harmonic emission.

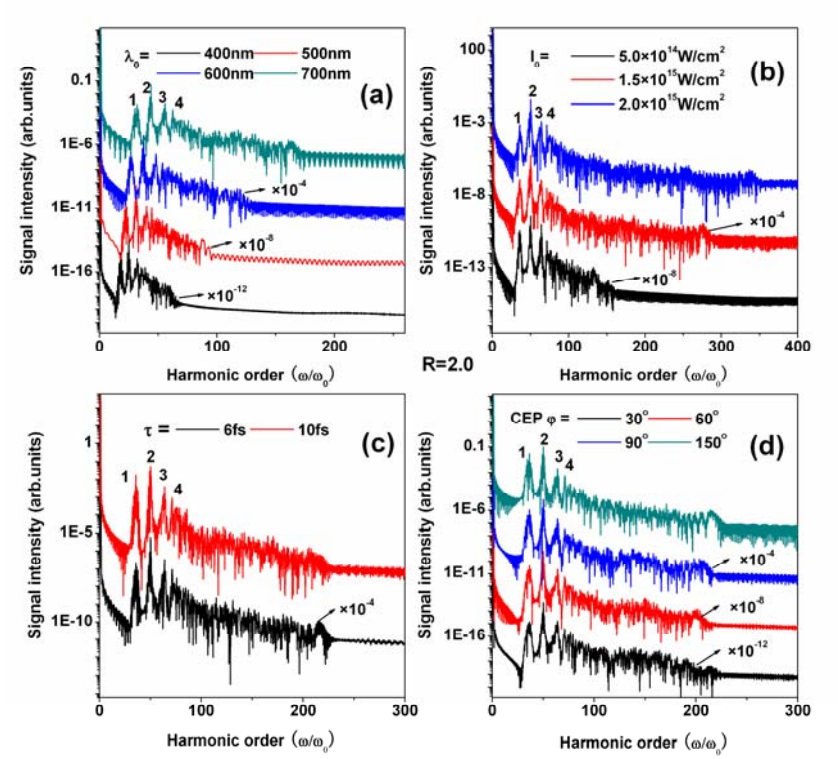

Figure 5: The HHG spectra from the LiH^{3+} at (a) different wavelengths (λ_0=400nm-700nm), (b) different pulse intensities (I_0=5.0×10^{14}W/cm^2, 1.5×10^{15}W/cm^2 and 2.0×10^{15}W/cm^2), (c) different pulse durations (τ=6fs and 10fs), (d) different CEPs (ϕ=30^o, 60^o, 90^o, and 150^o). The other parameters are the same as those in Figure 1**.** The peaks 1-4 are corresponding to the VS, the 2pσ, the 2sσ, and the 3pσ states, respectively.

Table 3: Electronic energies (in a.u.) of BeH^{4+} at R=5.0a.u. The energies inside the brackets are experimental data and other accurate theoretical results taken from refs [22]. (Here the virtual state is not taken into account)

R	$E_{1s\sigma}$	$E_{2p\sigma}$	$E_{2s\sigma}$	$E_{3d\sigma}$	$E_{3d\pi}$	$E_{2p\sigma}$-$E_{1s\sigma}$	$E_{2s\sigma}$-$E_{1s\sigma}$	$E_{3d\sigma}$-$E_{1s\sigma}$	$E_{3d\pi}$-$E_{1s\sigma}$
5.0	-8.17	-2.31	-2.21	-1.49	-1.21	102.9ω_0	104.6ω_0	117.3ω_0	122.2ω_0
	(-8.2)	(-2.23)	(-2.17)	(-1.358)	(-1.127)	(104.8ω_0)	(105.8ω_0)	(120.1ω_0)	(124.2ω_0)

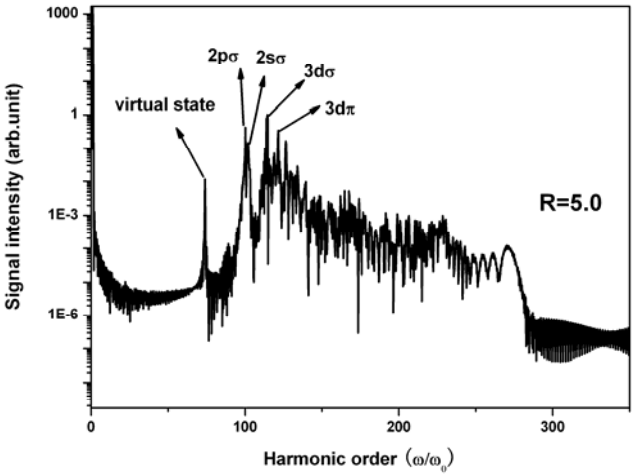

Figure 6: The HHG spectrum from BeH^{4+} at internuclear distance R=5.0a.u. The laser field is the same as that in **Figure 1**.

4 Conclusion

We have theoretically investigated the role of the excited states in the asymmetric harmonic emission from the quasi-asymmetric molecule LiH^{3+}. An interesting phenomenon has been observed on the asymmetric harmonic spectra, which can not be found for atoms or symmetric molecules: that is the multiple frequencies enhancements, i.e., the appearance of the resonant peaks, in the low harmonic orders. Through the detailed analyses of the electronic energies and the electronic states populations, we found that these harmonics enhancements are caused by the laser-induced electron transfer between the ground state and the first few excited states. By examining the calculated harmonic spectra of LiH^{3+} at different internuclear distances and with different laser parameters as well as the harmonic spectra of the other asymmetric molecule BeH^{4+}, we demonstrated that the excited state effect, i.e., the appearance of several resonant peaks, is insensitive to both asymmetric molecular structure and laser field. Thus, we deduced that this phenomenon might be general for quasi-asymmetric charged molecules. It is note that because of this excited state effect, the harmonics, generated from ground state (excited state) and recombined with the excited state (ground state), will have a phase difference with the harmonics obtained by electron ionization and recombination with the same state. This phase difference will lead to a destructive interference structure on the harmonic emission, which can be used to generate the complex attosecond laser pulses [9] or to illuminate some inherent features for the

asymmetric system, i.e. the interference minimum on the harmonics [11], and the asymmetric ionization [12] etc.

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