6 Non-Coulomb Explosions of Molecules in Intense Laser Fields

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Summary. Polyatomic molecules undergo neutral dissociation in moderate intense laser fields. As a typical molecule species, methane has been studied in the laser intensity of $10^{12} - 10^{13}$ W/cm$^2$ of a Ti-sapphire laser ($\lambda = 800\text{nm}$). The fragments of electronically excited CH ($A \ ^2\Delta$, $B \ ^2\Sigma$, $C \ ^2\Sigma^+$) and H ($n = 3$), where $n$ is the principal quantum number, are observed in the fluorescence spectrum. It is interesting that the same products were found in the synchrotron radiation previously, where the XUV photons of $10^{-22} - 22.5\text{eV}$ were used. The above phenomena show that the fragmentation in the intense laser field through multiphoton absorption and in the synchrotron radiation through single XUV photon absorption are due to the excitation and dissociation of super-excited states, which have more energy than the ground state of molecular ion.

6.1 Introduction

There is a growing interest in the study of molecular behavior in intense laser fields. Being a relatively new field in molecular science, strong laser field-molecule interaction, especially dissociation of molecules, is very promising from many points of view including controlling chemical reaction [1]. In this paper, the intense femtosecond laser we refer to is the most popular femtosecond Ti-sapphire laser whose wavelength is around 800nm.

When a molecule is placed in a strong laser field, the field applies a force to both the electrons and the atomic cores of the molecule, all the internal degrees of freedom of a molecule can be influenced [2–5]. Electrons of the molecule are affected by the intense laser pulse immediately. Some abnormal phenomena thus appear. In the “moderate” laser intensity of $10^{13} - 10^{14}$ W/cm$^2$, molecules are usually first tunnel ionized [6–8]. The swinging of the ionized electron in the alternative laser field may cause a re-scattering effect. The effect would result in high harmonic generation (HHG) [9], above-threshold ionization (ATI) [10], and double ionization (DI) of molecules [11].

Atomic cores of a molecule may also be affected by such intense laser pulse. Immediately after the ionization, the molecule may dissociate in a strong laser field. The phenomenon is usually explained by Coulomb explosion (CE) [12]. Beyond the laser intensity of $3 \times 10^{14}$ W/cm$^2$, doubly or multiply charged
molecular ions can be generated. Driven by the intra-molecular Coulomb repulsive force, the ionic skeleton undergoes CE, yielding ionic products. The product species are detected by mass spectroscopic techniques in most cases [13–15].

However, neutral fragments of molecules yielded in intense laser fields have also been found recently, even at the relatively “low” laser intensity of $10^{13}$ W/cm$^2$ [16–18]. Fluorescence spectroscopy was used to detect neutral fragments, which could not be detected by mass spectroscopy. Since “low” intensity laser could not produce multiple charged ions, the appearance of the neutral products cannot be explained by the CE of multiply charged ions. Therefore, a new mechanism is needed to explain the neutral fragmentation of molecules at relatively low laser intensity.

It is interesting to compare the fluorescence spectra obtained in the intense laser fields to those appearing in synchrotron radiation (SR). The spectra recorded in both cases are analogous to each other. This implies that the final products are yielded from the parent molecules with similar mechanisms. The single photon energy of about 15eV used in the SR is almost equal to the total energy of ten laser photons which a typical molecule absorbs in the multiphoton excitation regime. It is therefore strongly suggested that the neutral dissociation of molecules in intense laser fields and that in SR have a common mechanism, that is, the dissociation of the super-excited molecule, whose energy is higher than the first ionization potential of the molecule.

López-Martens et al. have studied the dissociation of NO$_2$ under the intensities between 3 and 20TW cm$^{-2}$ by femtosecond two-color fluorescence depletion spectroscopy [19,20]. The dependence of the NO ($A\ 2\Sigma^+ \rightarrow X\ 2\Pi^+$) fluorescence intensity on the laser intensity suggests that a parent molecule NO$_2$ is excited to an electronically excited state by absorbing three 3.1eV (400nm) photons, and dissociates into NO ($A\ 2\Sigma^+$) and O ($^3$P). Moreover, the authors suggest that this state has a “3s$\sigma^2\Sigma^+$ Rydberg state character” and is located “0.5eV below the first ionization threshold.” So the dissociative state discussed in these two papers cannot be considered as a super-excited state, which we focus on in this paper.

The purposes of this paper are: (1) to introduce a new type of fragmentation induced by relatively moderate laser intensity ($10^{12}$–$10^{13}$ W/cm$^2$), and (2) to propose a mechanism to explain the neutral dissociation of super-excited molecule after the laser excitation.

### 6.2 Fluorescence Detections

The high power femtosecond laser system consists of a Ti:Sapphire oscillator (Spectra Physics, Maitai), a regenerative amplifier (Spectra Physics, Spitfire) and a two-pass Ti:Sapphire amplifier. The laser beam is focused, using a 100cm focal length lens, into a cell with a CaF$_2$ input window containing gases with a variable pressure of 3–50torrs. The fluorescence emitting