Front. Phys., 2013, 8(1): 34–38
DOI 10.1007/s11467-013-0281-4

RESEARCH ARTICLE

Fluorescence emission from excited molecular ions in intense femtosecond laser fields

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Received December 16, 2012; accepted January 7, 2013

Strong fluorescence emissions were observed for nitrogen, carbon monoxide, and carbon dioxide molecules in intense femtosecond laser fields. These emissions can be assigned to the transitions of the molecular ions from the excited electronic states to the ground electronic states. The formation mechanisms were discussed and the lifetimes were measured for these excited molecular ions in intense laser fields.

Keywords tunneling ionization, molecular orbital, fluorescence

PACS numbers 42.50.Hz, 34.50.Gb, 33.50.Dq

1 Introduction

Ions are ubiquitous in space and can be generated through cosmic radiation, UV rays, X-rays, shock waves as well as high-energy particle collisions. In a recent article, Larsson, Geppert and Nyman reviewed the gas-phase ion chemistry in extraterrestrial space [1]. Molecular ions have been discovered in the atmospheres of some planets and their satellites in 1930s [2]. They play an important role in the cosmic chemistry, such as the origin of life on Earth. Due to the importance of molecular ions in the atmosphere, the ionization of molecules has attracted much attention in laboratory in the past few decades. The formation mechanism and decay dynamics of molecular ions were extensively studied with electron bombardment [3], photoionization [4, 5], discharge [6], Penning ionization [7], fast ion collision [8], charge transfer [9] and so on.

Recently, chirp pulse amplifier technology has made ultra-intense and ultra-short laser available in laboratory. Dynamic processes become a hot topic for molecules in such intense laser fields [10]. These studies indicate that tunneling ionization is a fundamental process for molecules in intense laser fields. According to Molecular Ammosov–Delone–Krainov (MO-ADK) model [11], the ionization rate decays exponentially on the electron binding energy. Therefore, it is always assumed that the electron in the highest occupied molecular orbital (HOMO) is firstly removed and the molecular ion is always in its ground electronic state. However, some evidences suggest that not only the HOMO, but also the lower-lying molecular orbitals, are involved in the process of tunneling ionization [12–17]. Correspondingly, the molecular ions are in the ground electronic state as well as excited electronic states in intense laser fields. Very recently, we provide direct evidences that lower-lying molecular orbitals are involved in the tunneling ionization of molecules by probing the fluorescence emission from the molecular ion in the excited electronic state [18].

In this article, we report the observation of fluorescence emission of N_2^+, CO^+ and CO_2^+ that are generated in intense femtosecond laser fields. The formation mechanisms are discussed and lifetimes are measured for these excited molecular ions.

2 Experimental

The experiments were performed using a Ti:sapphire laser amplifier with a repetition rate of 1 kHz. The pulse duration is 35 fs and central wavelength is 800 nm. The laser pulses are focused into a vacuum chamber by using a convex lens with focus length of 150 mm. The peak intensity of the laser pulse is estimated by measuring

the focusing size. The vacuum chamber is pumped by a magnetically-levitated molecular turbo pump backed by a dry scroll pump. The gas sample is introduced into the vacuum chamber through a capillary with an inner diameter of 100 μm and a length of 300 mm. By adjusting the pressure of the capillary inlet end, the pressure of the vacuum chamber is controlled to be less than 1×10^{-3} mbar when the gas sample is introduced. The fluorescence signals generated in the laser–molecule interaction are collected by a combination of one spherical mirror and one convex lens and then sent into a monochromator followed by a photo-multiplier tube (PMT R585, Hamamatsu, Japan). The output analog signals of the PMT are sent to a 2-GHz dual-channel data acquisition card (CS22G8, GAGE, USA) and recorded by a computer for analysis.

The fluorescence detection is much less efficient than the mass spectroscopy. High gas density is usually required for fluorescence measurement. In our experiment, the fluorescence spectra are recorded with a typical pressure of several 10^{-4} mbar. The laser-molecule interaction is very complicated in intense laser fields. Therefore, we have to ensure that excited molecular ion is produced by direct laser excitation and the fluorescence signal comes from unimolecular reaction. Figure 1(a) shows the fluorescence intensity with wavelength at 391 nm as a function of the gas pressure in the reaction chamber. The fluorescence emission comes from the (0, 0) band of $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$. Within the pressure range between 3×10^{-5} mbar and 1×10^{-3} mbar, the fluorescence intensity shows a linear dependence on the gas pressure. The linear pressure dependence of the fluorescence intensity demonstrates that the excited molecular ion $N_2^+(B^2\Sigma_u^+)$ is produced by direct laser excitation and the fluorescence signal comes from unimolecular reaction [19]. Figure 1(b) shows the fluorescence lifetime of $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$ as a function of the gas pressure.

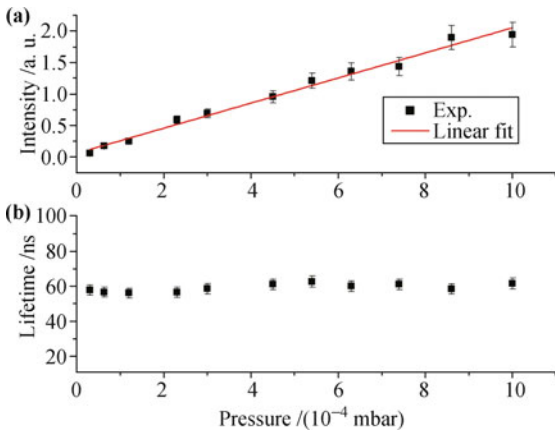

Fig. 1 **(a)** Fluorescence intensity and **(b)** fluorescence lifetime of the (0, 0) band of $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$ as a function of the gas pressure in the reaction chamber.

Here, the fluorescence lifetime represents the time the molecule stays in its excited electronic state and is obtained by fitting the fluorescence signal with an exponential decay. The results show that the fluorescence lifetime is almost constant within the pressure range we have measured. The independence of the pressure demonstrates that the collision-induced decay can be neglected for $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$, which has a lifetime of about 60 ns in intense femtosecond laser fields.

3 Results and discussion

Figure 2 shows the fluorescence spectra of N_2, CO and CO_2 irradiated by 800 nm, 35 fs laser pulses with an intensity of 1.5×10^{15} W/cm^2. The spectra were recorded over the wavelength range between 200-500 nm and not calibrated by the detecting system. According to the molecular parameters listed in Table 1, it is predicted that the (0, 0) band locates at 1109 nm and 391 nm for the emission of $N_2^+(A^2\Pi_u - X^2\Sigma_g^+)$ and $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$, 490 nm and 219 nm for $CO^+(A^2\Pi - X^2\Sigma^+)$ and $CO^+(B^2\Sigma^+ - X^2\Sigma^+)$, 351 nm and 289 nm for $CO_2^+(A^2\Pi_u - X^2\Pi_g)$ and $CO_2^+(B^2\Sigma_u^+ - X^2\Pi_g)$. In combination with previous reports [7, 9], the spectra shown in Fig. 2 can be assigned to $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$, $CO^+(A^2\Pi - X^2\Sigma^+)$, $CO^+(B^2\Sigma^+ - X^2\Sigma^+)$, $CO_2^+(A^2\Pi_u - X^2\Pi_g)$, and $CO_2^+(B^2\Sigma_u^+ - X^2\Pi_g)$, respectively, with the (0,0) bands being marked by a red star. It should be mentioned that there mixed some fluorescence from $CO^+(B^2\Sigma^+ - A^2\Pi)$ in the spectrum of CO^+. In the present measurement, the chamber pressure was kept to 4×10^{-4} mbar when the corresponding gas sample was introduced into the chamber and the molecular ion has been confirmed through direct laser excitation. The electronic configurations are

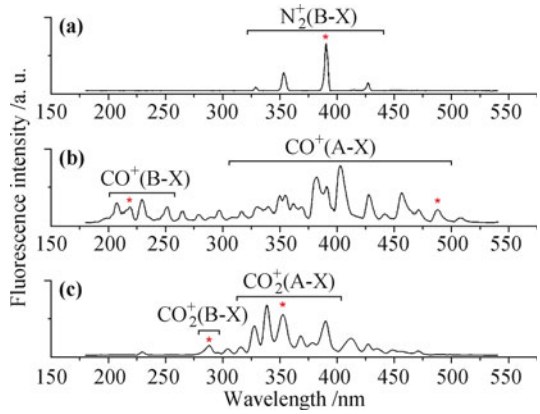

Fig. 2 Fluorescence spectra of **(a)** N_2, **(b)** CO and **(c)** CO_2 irradiated by 800 nm, 35 fs laser pulses with an intensity of 1.5×10^{15} W/cm^2. The spectra were recorded over the wavelength range between 200–500 nm and not calibrated by the detecting system. The (0, 0) bands are marked by red stars.

$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$, $KK(3\sigma)^2(4\sigma)^2(1\pi)^4 \cdot (5\sigma)^2$ and $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2 \cdot (1\pi_u)^4(1\pi_g)^4$ for neutral N_2, CO and CO_2 molecules, respectively. The removal of one electron from HOMO will leave the molecular ion in the ground electronic state (the X state). The removal of one electron from the lower-lying orbital will leave the molecular ion in the excited electronic state. For example, the removal of one electron from HOMO-1 creates the molecular ion in the first excited electronic state (the A state).

In intense laser fields, the molecular ion can be produced when an electron is stripped away through absorbing proper amount photons or tunneling effect. The Keldysh parameter $\gamma = \sqrt{I_p/(2U_p)}$ is always used to determine the ionization mechanism, where I_p is the molecular ionization potential, U_p is the ponderomotive potential and also the quiver energy of a free electron in an oscillating field [20]. When $\gamma \geqslant 1$, the ionization is in the multi-photon regime and the molecule is ionized by absorbing several photons simultaneously. Otherwise, the ionization is in the tunneling regime and the molecule is ionized through tunneling effect. The ionization potential, the Keldysh parameter, and the electronic configuration are listed in Table 1 for all the three molecules studied here. It can be seen that even for the lower-lying orbitals, the Keldysh parameter is much less than unity. The results indicate that the excited molecular ion is produced through tunneling ionization from lower-lying orbitals.

Tunneling ionization is highly complicated for molecules in intense laser fields. The ionization rate is determined not only by the electron binding energy, but also the symmetry of the ionizing molecular orbital. According to MO-ADK model [11], the ionization rate decays exponentially on the electron binding energy. Therefore, it is always assumed that the HOMO electron is firstly removed by the laser electric field and the molecular ion is in the ground electronic state. However, the energy difference is small for valence electrons in adjacent molecular orbitals. For example, the binding energies of neutral N_2 molecules are 15.58 and 17.07 eV for HOMO and HOMO-1, respectively. The energy difference is only 1.49 eV. The structure observed in the high harmonic spectra suggests that the molecule may be ionized through tunneling from several orbitals simultaneously [12, 14]. Due to the complicated generation processes of high harmonic in intense laser fields, sophisticated theories and accurate measurements are required to separate the contribution of lower-lying orbital to the tunneling current in intense laser fields. In addition to the energy difference, the electron in different molecular orbitals exhibits different symmetries relative to the molecular axis. According to MO-ADK model, the ionization rate is also determined by the symmetry of the ionizing molecular orbitals [11]. For example, the HOMO of N_2 molecules is σ_g and the maximum electronic density is in the direction parallel to the molecular axis. As a result, when the laser electric field is parallel to the molecular axis, the ionization rate is maximal and the molecular ion is in the ground electronic state. In contrast, the HOMO-1 of N_2 molecules is π_u and the maximum electronic density is in the direction perpendicular to the molecular axis. Correspondingly, when the laser electronic state is perpendicular to the molecular axis, the ionization rate is maximal and the molecular ion is in the first excited electronic state. Such angle-dependent ionization has been verified by experimental observations and theoretical calculations [21, 22].

The fluorescence emission shown in Fig. 2 directly demonstrates that multiple molecular orbitals are simultaneously involved in the process of tunneling ionization and molecular ions are not only in the ground electronic state, but also in the excited electronic states. The excited molecular ion will decay to its ground electronic state through emitting a photon of light. In the present measurement, we do not observe the emission of

Table 1 Electronic configurations, ionizing molecular orbital symmetry, binding energies, corresponding electronic state of the molecular ion, ionization potential (I_p), as well as the Keldysh parameter (γ) for N_2, CO and CO_2 molecules in intense laser fields. All data are taken from online NIST chemistry database except γ is calculated accordingly.

Electronic configuration	Ionizing molecular orbital symmetry	Binding energy/eV	Electronic state	I_p/eV	γ
N_2	HOMO (σ_g)	15.58	$X^2\Sigma_g^+$	15.58	0.30
$KK(\sigma_g 2s)^2(\sigma_u 2s)^2$	HOMO-1 (π_u)	17.07	$A^2\Pi_u$	16.70	0.31
$(\pi_u 2p)^4(\sigma_g 2p)^2$	HOMO-2 (σ_u)	21.00	$B^2\Sigma_u^+$	18.75	0.32
CO	HOMO (σ)	14.01	$X^2\Sigma^+$	14.01	0.28
$KK(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$	HOMO-1 (π)	17.66	$A^2\Pi$	16.54	0.30
	HOMO-2 (σ)	21.92	$B^2\Sigma^+$	19.67	0.33
CO_2	HOMO (π_g)	13.77	$X^2\Pi_g$	13.77	0.28
$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2$	HOMO-1 (π_u)	19.70	$A^2\Pi_u$	17.30	0.31
$(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$	HOMO-2 (σ_u)	20.27	$B^2\Sigma_u^+$	18.06	0.32

$N_2^+(A^2\Pi_u - X^2\Sigma_g^+)$ because the wavelength of the emission is beyond the spectral response of our fluorescence detection system. In previous experiments, cold target recoil ion momentum spectroscopy (COLTRIMS) is always used to study tunneling ionization of molecules in intense laser fields [23]. It is known that COLTRIMS can provide accurate yields as well as kinetic energy of reaction products. But it is not sensitive to the internal state of the detected ion and cannot disentangle the molecular ion in different electronic states. Fluorescent spectroscopy provides the upper and lower states of observed transitions. Thus we can determine the internal quantum state of molecular ion and separate different molecular orbitals' contribution to the tunneling ionization by measuring the fluorescence spectra of the excited molecular ion in intense laser fields. If we use a femtosecond laser pulse to align molecules and another femtosecond laser to ionize the aligned molecules, then we can acquire the ionization rate of lower lying orbitals as a function of the alignment angle between the molecular axis and the laser polarization through measuring the fluorescence from aligned molecules. In combination with some theoretical simulations, the symmetry might be imaged for lower-lying molecular orbitals. Such investigation is being carried out in our laboratory.

Figure 3 shows the fluorescence decay for the (0, 0) band of (a) $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$, (b) $CO^+(A^2\Pi - X^2\Sigma^+)$ and $CO^+(B^2\Sigma^+ - X^2\Sigma^+)$, (c) $CO_2^+(A^2\Pi_u - X^2\Pi_g)$ and $CO_2^+(B^2\Sigma_u^+ - X^2\Pi_g)$. Fitting with an exponential decay, the lifetimes were determined to be 60 ns, 700 ns, 60 ns, 109 ns and 120 ns, for $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$, $CO^+(A^2\Pi - X^2\Sigma^+)$, $CO^+(B^2\Sigma^+ - X^2\Sigma^+)$, $CO_2^+(A^2\Pi_u - X^2\Pi_g)$, and $CO_2^+(B^2\Sigma_u^+ - X^2\Pi_g)$, respectively. These results are consistent with previous reports except $CO^+(A^2\Pi - X^2\Sigma^+)$

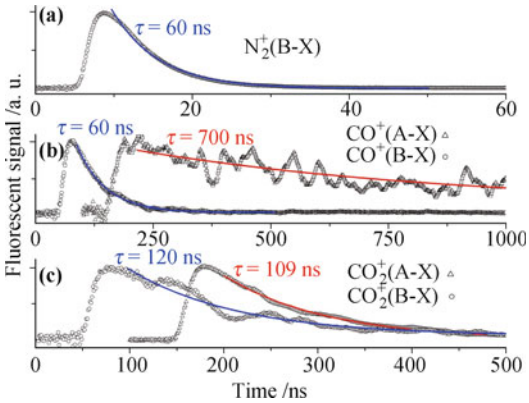

Fig. 3 Fluorescence decay for the (0, 0) band of **(a)** $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$, **(b)** $CO^+(A^2\Pi - X^2\Sigma^+)$ and $CO^+(B^2\Sigma^+ - X^2\Sigma^+)$, **(c)** $CO_2^+(A^2\Pi_u - X^2\Pi_g)$ and $CO_2^+(B^2\Sigma_u^+ - X^2\Pi_g)$. The intensities are normalized with the peak heights. Scattered points are experimental data and colored solid lines are theoretical fitting. The $CO^+(A^2\Pi - X^2\Sigma^+)$and $CO_2^+(A^2\Pi_u - X^2\Pi_g)$ are shifted right by 100 ns for visual convenience.

[24–26]. The lifetime of $CO^+(A^2\Pi - X^2\Sigma^+)$ is 700 ns in our measurement, which is much shorter than the values of 2–3 μs reported by Holland and Maier [3]. The large difference might come from the collision-induced decay. The chamber pressure in our experiment is three orders of magnitudes higher than that in the experiment of Holland and Maier [3] and reaches several 10^{-4} mbar. In the laser-molecule interaction zone, the pressure is even higher. Under this experimental condition, the collision time is probably several hundred nanoseconds. Therefore, the collision-induced decay can be neglected when the lifetime of the excited molecular ion is near 100 ns. However, the collision-induced decay might play a significant role when the lifetime of the excited molecular ions is longer than 1 μs. As a result, the lifetime of $CO^+(A^2\Pi - X^2\Sigma^+)$ is greatly shortened in the present measurement.

4 Summary

Multiply charged ions have some unique properties and may participate in fusion plasmas and planetary ionospheres as an important media. In a recent themed issue "Multiply charged ions in the gas phase", various aspects are reviewed for the physics and chemistry of multiply charged ions [27]. Intense laser fields provide a convenient tool for generating multiply charged ions in the laboratory. However, the internal quantum state of the multiply charged ions is scarcely studied for these charged ions [19]. In the present measurement, we observed strong fluorescence emissions of the excited molecular ions generated in intense laser fields. The results demonstrate that ionization from lower-lying orbitals is a general aspect for molecules in intense laser fields. The excited molecular ions thus formed will decay to their ground electronic states through emitting photons. Fluorescence spectroscopy can determine the internal quantum state of molecular ions and is therefore a viable approach of separating different lower-lying orbitals to the contribution of tunneling ionizations for molecules in intense laser fields.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grants Nos. 61178019, 11134001, and 11121091) and New Century Excellent Talents from Ministry of Education of China.

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