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# Ultrafast Relaxation Dynamics of Highly-excited States in N<sub>2</sub> Molecules Excited by Femtosecond XUV Pulses

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**Abstract.** We used velocity-map-imaging to measure electronic and nuclear dynamics in N<sub>2</sub> molecules excited by a train of attosecond pulses. A time-to-space mapping of autoionization channel is demonstrated. It is found that the autoionization becomes energetically allowed when the two nuclei are still very close ( $\sim 3 \text{ \AA}$ ) and that it can be coherently manipulated by a strong femtosecond infrared pulse.

## 1 Introduction

The dynamics of photo-ionization processes in atoms and molecules plays an important role in a number of fundamental physical and chemical phenomena [1]. In particular, processes initiated by the absorption of high-energy photons, in the extreme-ultraviolet (XUV) spectral region, can have crucial implications, for example in the case of biological molecules, where a high photo-stability is always associated to ultrashort lifetimes of excited states [2]. In the last years, isolated attosecond pulses and trains of attosecond pulses have been used to measure ultrafast electron dynamics in molecules. Sub-femtosecond electron localization after attosecond excitation has been observed in H<sub>2</sub> and D<sub>2</sub> molecules [3]; control of photo-ionization of D<sub>2</sub> and O<sub>2</sub> molecules has been achieved by using attosecond pulse trains (APTs) [4,5]. Femtosecond XUV pulses have been used to investigate electron dynamics in N<sub>2</sub> molecules [6] as well as to measure autoionization processes in O<sub>2</sub> molecules [7].

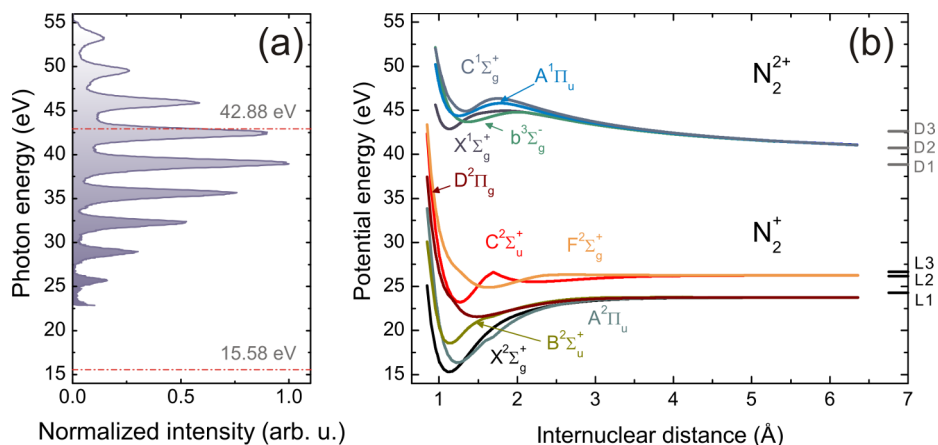
In this work we photo-ionized N<sub>2</sub> molecules with APTs and we probed the ultrafast relaxation dynamics using strong infrared (IR) pulses. APTs were produced by high-order harmonic generation (HHG) in a cell filled with krypton.

## 2 Experimental results and discussion

The bandwidth of the XUV radiation extends beyond the ionization threshold of N<sub>2</sub> at 15.58 eV, as shown in Fig. 1, up to  $\sim 55$  eV, so that the XUV photons can promote the molecular ion N<sub>2</sub><sup>+</sup> to a

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highly excited electronic state or the molecular dication  $N_2$  in a low-excited energy state (the double ionization threshold of  $N_2$  is 42.88 eV). The  $N^+$  angular distribution and yield are recorded by a velocity-map imaging spectrometer (VMIS). Three spectral features are present: (i) a sequence of closely spaced peaks at a KER below 1 eV, which can be assigned to predissociation of vibrational levels of the  $N_2^+(C^2\Sigma_u^+)$  electronic state; (ii) a band peaked at 0.9 eV, originating from direct dissociation of the  $N_2^+(F^2\Sigma_g^+)$  state to the third dissociation limit L3; (iii) a broad band with a peak at about 2.3 eV: we show that this band is primarily due to autoionization of  $N_2^{2+}$ .

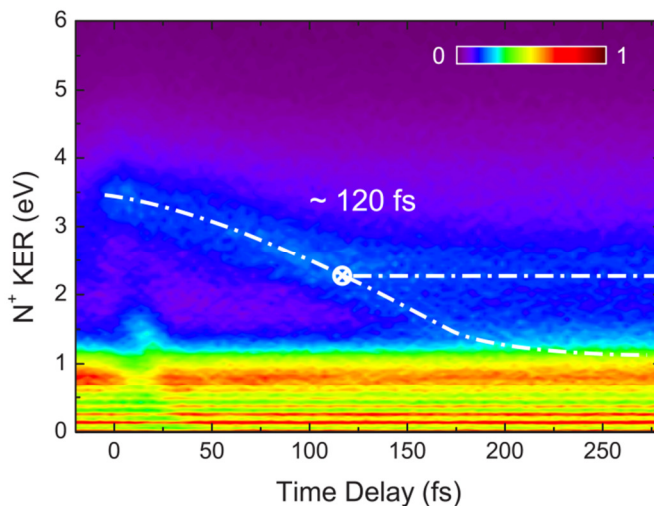


**Fig. 1.** (a) Spectrum of the XUV radiation produced by HHG in krypton. (b) Potential energy curves of the relevant electronic states of  $N_2^+$  [8] and  $N_2^{2+}$  [9] measured starting from the  $N_2(X^1\Sigma_g^+, v=0)$ .

We used a 15-fs IR pulse to probe the molecular dissociation dynamics driven by APTs. The experimental results are shown in Fig. 2. The presence of the IR pulse leads to the introduction of a new high-energy feature that extends to about 3.7 eV when the IR and XUV pulses are overlapped in time, and that decreases towards lower energies when the delay between the XUV pulse and the IR pulse is increased. Importantly, for delay times below 120 fs the IR pulse inhibits the observation of the 2.3-eV kinetic energy feature described in the previous paragraph. This behaviour is indicated by the white dash-dotted lines in Fig. 2. We postulate that these observations are due to an indirect double ionization process.

The XUV photons populate a super-excited state of the molecular ion,  $(N_2^+)^*$ , which can have an internal energy above the double photo-ionization threshold. The excited wavepacket (WP) evolves along the  $(N_2^+)^*$  potential energy curve until the inter-nuclear distance is sufficient to energetically allow autoionization, which gives rise to the band peaked at 2.3 eV measured in the  $N^+$  kinetic energy spectra in the absence of the IR probe pulse (see negative temporal delays in Fig. 2). Similarly to the case of  $O_2$  studied by Sandhu *et al.* [7], the autoionization can be inhibited by exposing the molecule to an IR pulse at short time delays. In this case the  $N_2^{2+}$  state populated by the IR pulse undergoes direct dissociation producing two  $N^+$  fragments, whose kinetic energy depends on the inter-nuclear distance at which the transition to the dication state takes place, so that the corresponding signal relaxes toward lower kinetic energies for longer time delays, following the potential energy curve of the final dication state [10]. It is noteworthy that for temporal delays between pump and probe pulses longer than 120 fs, when autoionization has become allowed, the two-color ionization process persists, as evidenced by the continued observation of a dependence of the KER on the delay between the XUV and IR pulses. This shows that the IR laser pulse can promote the autoionization of the molecule, by acting on the electron correlation that underlies the autoionization process.

An interesting result is that from the pump-probe measurements it was possible to estimate the inter-nuclear distance required for autoionization of the  $(\text{N}_2^+)^*$  state: this distance turned out to be  $\sim 3$  Å.



**Fig. 2.** Time-dependent  $\text{N}^+$  kinetic energy spectra as a function of the delay between the APT and the IR probe pulse.

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