Real-Time Dynamics of Electron Localization Observed in a Dissociating Molecule

Irina A. Bocharova[1], Maia Magrakvelidze[1], Sankar De[1], I.V. Litvinyuk[1,2]

[1]*J.R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506, USA*
[2]*Centre for Quantum Dynamics, Griffith University, Nathan, QLD 4111*

Abstract

In a pump-probe experiment, we measured dependence of yields and kinetic energies for symmetric $N^{2+} + N^{2+}$ (2,2) and asymmetric $N^{3+} + N^{+}$ (3,1) dissociation channels of N_2^{4+} on time delay between few-cycle 800 nm pump and probe pulses. We observe that the asymmetric (3,1) channel is produced only for delays of up to 20 fs and completely suppressed for longer delays. The symmetric (2,2) channel is efficiently produced for all studied delays. We interpret that observation as an indication that the unpaired electron in dissociating N_2^{3+} is completely localized on one of the ions after 20 fs.

Keywords: pump-probe; electron localization; Coulomb explosion; molecular dynamics

Introduction

When a diatomic molecule dissociates, the end result is a pair of well-separated non-interacting atomic fragments. One intriguing question is: when during dissociation do the electrons choose a specific nucleus as their final location? In general, electron delocalization (sharing) between the two centers results from interaction of degenerate localized (atomic) states, which causes energy splitting between symmetric (*gerade*) and anti-symmetric (*ungerade*) combinations (molecular orbitals) of these states. Energy lowering due to electron sharing is the basis of chemical bonding. The energies of *gerade* and *ungerade* delocalized orbitals depend on internuclear separation, and the states become degenerate for infinitely separated identical atoms. For a certain intermediate distance, that energy difference becomes smaller than the coupling between the delocalized states (either due to an external field or non-adiabatic contribution from nuclear motion) and localized eigenstates will result. When the molecule dissociates in the presence of an intense laser field, it is the laser electric field that couples molecular *gerade* and *ungerade* states and causes electron localization. Accordingly, electron localization can be controlled through employing asymmetric electric fields (either via short pulses with stable carrier-envelope phase [Kling et al. 2006] or via various two-color schemes) with an electron ending up preferentially at a chosen side. Electron localization is known to play an important part in the process of charge-resonance enhanced ionization (CREI, [Zuo and Bandrauk 1995]). CREI at a critical distance is a well-established mechanism of double ionization of hydrogen molecules, and it is expected to also operate in larger diatomic molecules, though there is still very little direct evidence in support of this expectation. Here we present the first direct time-resolved measurement of dynamics of the electron localization process performed in a pump-probe experiment with few-cycle laser pulses. We conclude that in a dissociating N_2^{3+} molecule interacting with a strong laser field the unpaired electron is localized after approximately 20 fs when the internuclear distance reaches about twice the neutral molecule bond length.

Materials and methods

The experiments were conducted at J.R. Macdonald Laboratory, Physics Department, Kansas State University in Manhattan, Kansas. Figure 1 presents schematic of the experimental setup. The few-cycle pulses were generated by compressing the output of a multi-pass Ti:sapphire amplifier (800 nm, 30 fs, 1 mJ) with an Ar-filled hollow-core fiber compressor to yield 7.5 fs 450 μJ pulses, whose duration was verified with frequency-resolved optical gating (FROG). The pulses were split into two replicas with variable delay using a computer controlled Mach-Zehnder interferometer. The pump and probe pulses were focused by an on-axis spherical mirror (f = 75 mm) on a supersonic jet of N_2 inside a uniform-electric-field ion momentum imaging spectrometer. Full 3D momenta of all resulting ion fragments were measured. Various dissociation channels were identified by looking for ion pairs with near-zero total momentum. The kinetic energy release (KER) spectra were calculated for each channel and plotted vs. the varying time delay between pump and probe pulses in form of 3D histograms.

Results and discussion

We measured and compared time-dependent KER spectra for N_2^{4+} molecular ions dissociating into either symmetric $N^{2+} + N^{2+}$ (2, 2) or asymmetric $N^{3+} + N^{+}$ (3, 1) final channels. The first (pump) pulse ionizes the neutral molecule and initiates its dissociation. The second (probe) pulse acts on the dissociating molecular ions to ionize them even further until the final charge state is reached. Starting with N_2^{3+} the molecular ions are completely

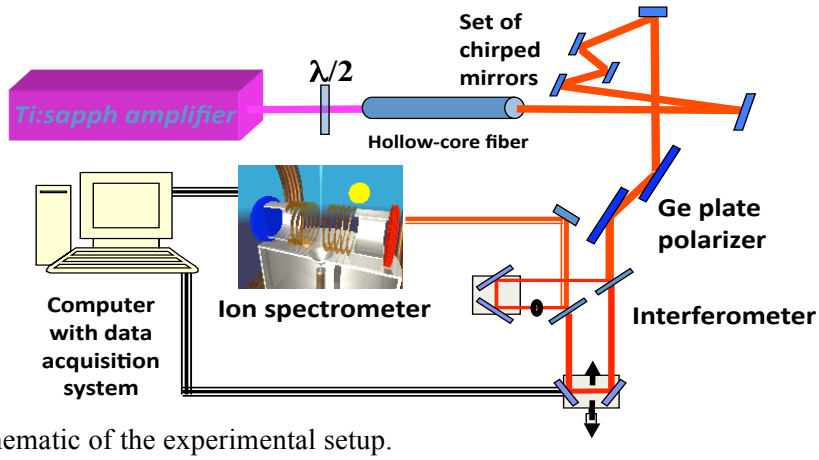

Figure 1. Schematic of the experimental setup.

dissociative (no stable or quasi-stable molecular ions exist) and starting with N_2^{4+} they can dissociate into different channels with both fragments being charged. Figure 2 presents the time-dependent KER spectra for (2, 2) and (3, 1)

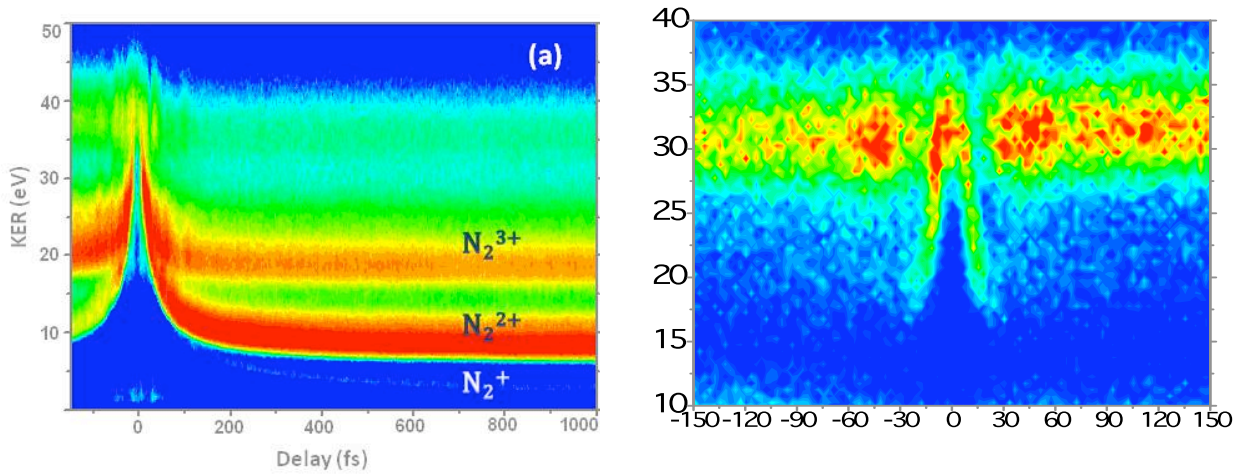

Figure 2. Time-dependent KER spectra for $N^{2+} + N^{2+}$ (left panel) and $N^{3+} + N^{+}$ (right panel) dissociation channels. Pump pulse peak intensity is 8×10^{14} W·cm^{-2}, probe pulse peak intensity is 15×10^{14} W·cm^{-2}.

dissociation channels. The characteristic decrease in KER with increasing time delay reflects the time evolution of the internuclear distance (Coulomb energy) during dissociation taking place in three possible intermediate molecular ions. We focus our interest on dissociation of N_2^{3+} intermediate ion. It can be thought of as a pair of N^{2+} atomic ions sharing a single unpaired electron. At some point during dissociation this unpaired electron will localize on one of the atoms yielding N^{2+}+ N^{+}. After such localization is complete, any further strong-field ionization of this system will produce only the symmetric (2, 2) channel, simply because the ionization potential of N^{+} is much lower than that of N^{2+}. However, when a non-localized electron is removed, the asymmetric (3, 1) channel can also be expected. Figure 1 shows that the (2, 2) channel is efficiently produced for all studied delays, while the (3, 1) channel is only seen for delays of less than 20 fs. That observation indicates that in dissociating N_2^{3+} the unpaired electron becomes localized after 20 fs. The lowest total kinetic energy of the fragments in (3, 1) channel puts the internuclear distance at which the localization takes place at about twice the bond length of the neutral molecule. That is consistent with a commonly estimated value for the critical distance for CREI.

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References
Kling M. et al. (2006) Science **312**, 246
Zuo T. and Bandrauk A.D. (1995) Phys. Rev. A **52**, R2511