Ultrafast absorption of intense x rays by nitrogen molecules

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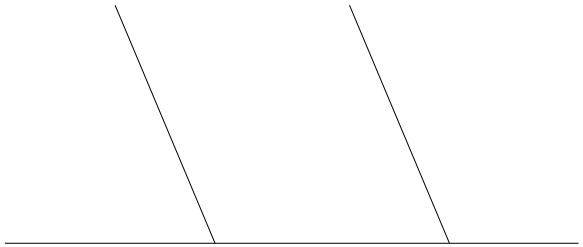
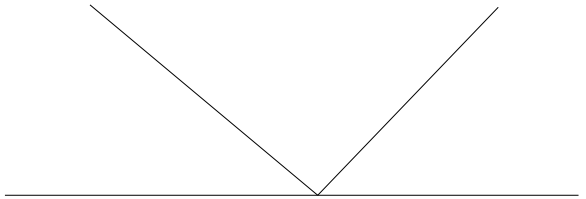
Interaction of intense x rays with atoms

- Assume x-ray intensity at 1 keV photon energy of 10^{17} W / cm^2
- Ponderomotive potential: U_p = 0.01 eV
- Keldysh parameter for neon *K* edge at 870.2 eV: $\gamma = \sqrt{I_p / (2 U_p)} = 174$
- **Simultaneous** two-photon processes small
- **Sequential** two-photon absorption significant (**nonlinear** process due to core-hole decay)



Sequential



Simultaneous

X-ray interaction with atoms

- Time-dependent interaction of x-rays described by **rate-equation model**
- **One-x-ray-photon absorption cross sections** from nonrelativistic one-electron approximation with the Los Alamos National Laboratory Atomic Physics Codes
- **Auger and x-ray fluorescence decay widths** from Dirac-Hartree-Slater (DHS) method
- **LCLS pulses** modeled as
  - Temporally: Gaussian function; no need for spiky SASE pulses
  - Spatially: Gaussian beam; cross section has FWHM major and minor axes of 2.2 and 1.2 µm; longitudinally long Rayleigh length and thus a small variation over the interaction volume

C. Buth, J.-C. Liu, M. H. Chen, J. P. Cryan, L. Fang, J. M. Glownia, M. Hoener, R. N. Coffee, N. Berrah, Phys. Rev. A (submitted)
M. Hoener *et al.*, Phys. Rev. Lett. 104, 253002 (2010)

Rate-equation model for a nitrogen atom

- Restrict to ***K*-shell** electrons
- X-ray absorption by a **nitrogen atom** is described by the rate equations for the **ground state depopulation**

$$\frac{\mathrm{d}}{\mathrm{d}t}P_{223}(t)=-\sigma_{223}P_{223}(t)J_{\mathrm{X}}(t)$$

- the formation of a **single core hole**

$$\frac{\mathrm{d}}{\mathrm{d}t}P_{123}(t)=\left(\sigma_{123\leftarrow 223}P_{223}(t)-\sigma_{123}P_{123}(t)\right)J_{\mathrm{X}}(t)-\Gamma_{123}P_{123}(t)$$

- and the production of a **double core hole**

$$\frac{\mathrm{d}}{\mathrm{d}t}P_{023}(t)=\left(\sigma_{023\leftarrow 123}P_{123}(t)-\sigma_{023}P_{023}(t)\right)J_{\mathrm{X}}(t)-\Gamma_{023}P_{023}(t)$$

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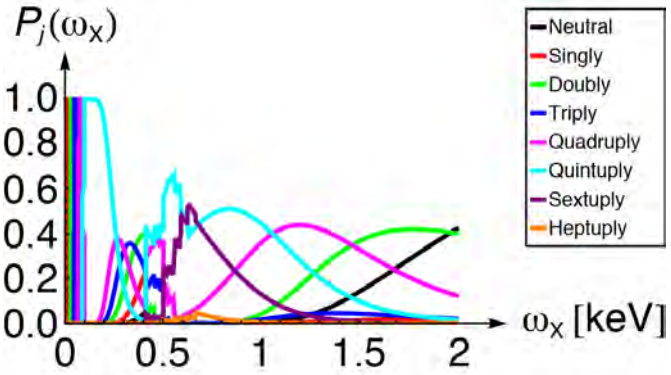
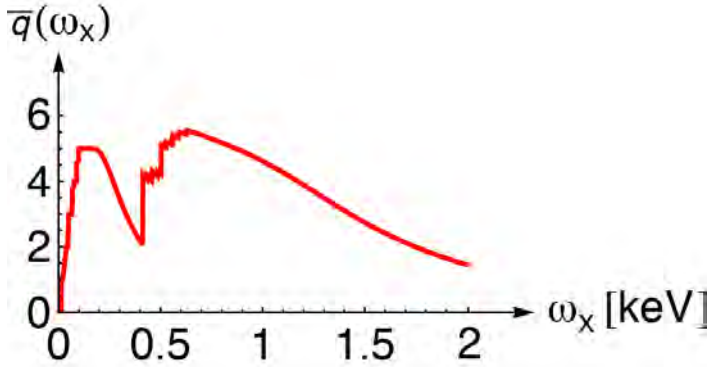
Ion yields of a nitrogen atom

- **Full** atomic rate-equation model
- Charge-state probabilities for a Gaussian 2 fs pulse (FWHM) at 1.1 keV photon energy $P_j = \sum_{l+m+n=7-j} P_{lmn}(\infty)$





- Ion yields $Y_j = \frac{P_j}{1-P_0}$
- Average charge state $\bar{q} = \sum_{j=1}^{7} j\ Y_j$

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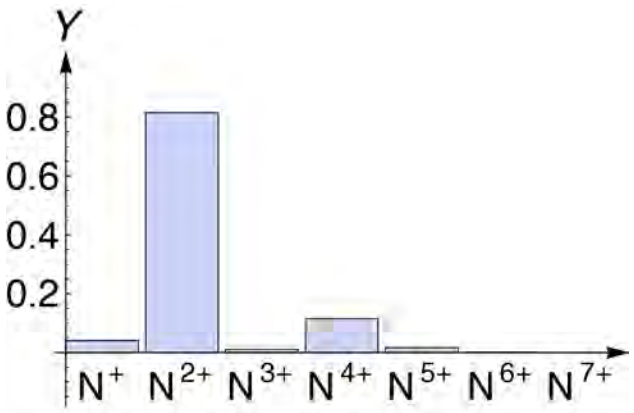
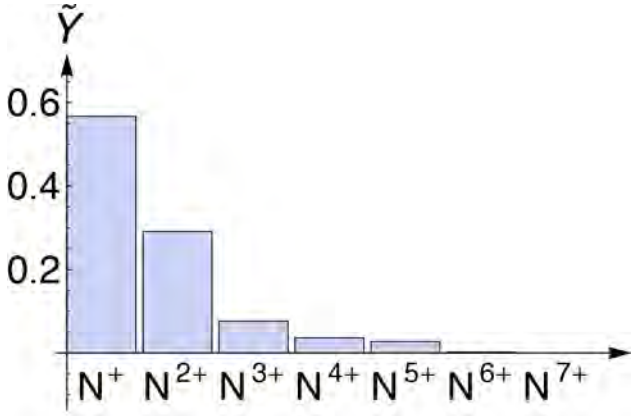
Atomic versus molecular ion yields

- Atomic ion yields **differ** significantly from molecular ion yields
- At 280 fs pulse duration, 0.26 mJ pulse energy, 1.1 keV photon energy

Atomic model



Experiment with molecule



- Reason for differences: two **molecular fragmentation channels**

$$N_2^{2+} \rightarrow N + N^{2+}$$
$$N_2^{2+} \rightarrow N^{+} + N^{+}$$

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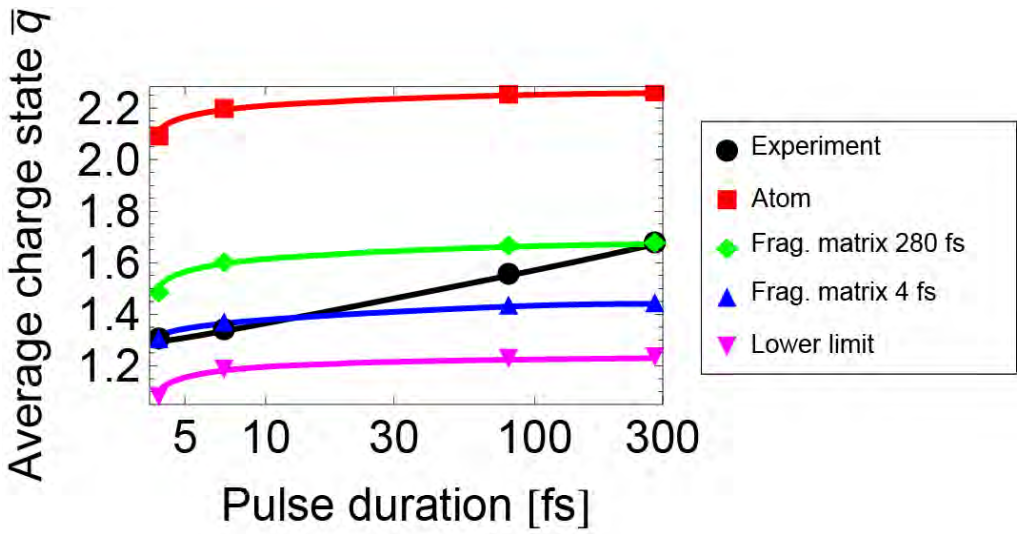
Heuristic models for molecular ion yields

- **Modeling N_2 as an N atom**: strong approximation
- **Lower-limit ion yields**: equal sharing of total charge of molecule upon breakup
- **Molecular fragmentation matrix**: assume a fixed relation between molecular ion yields and atomic ion yields:

$$\begin{pmatrix} N^{+} \\ \vdots \\ N^{7+} \end{pmatrix}_{mol} = \boldsymbol{F}_{frag} \begin{pmatrix} N^{+} \\ \vdots \\ N^{7+} \end{pmatrix}_{atom}$$



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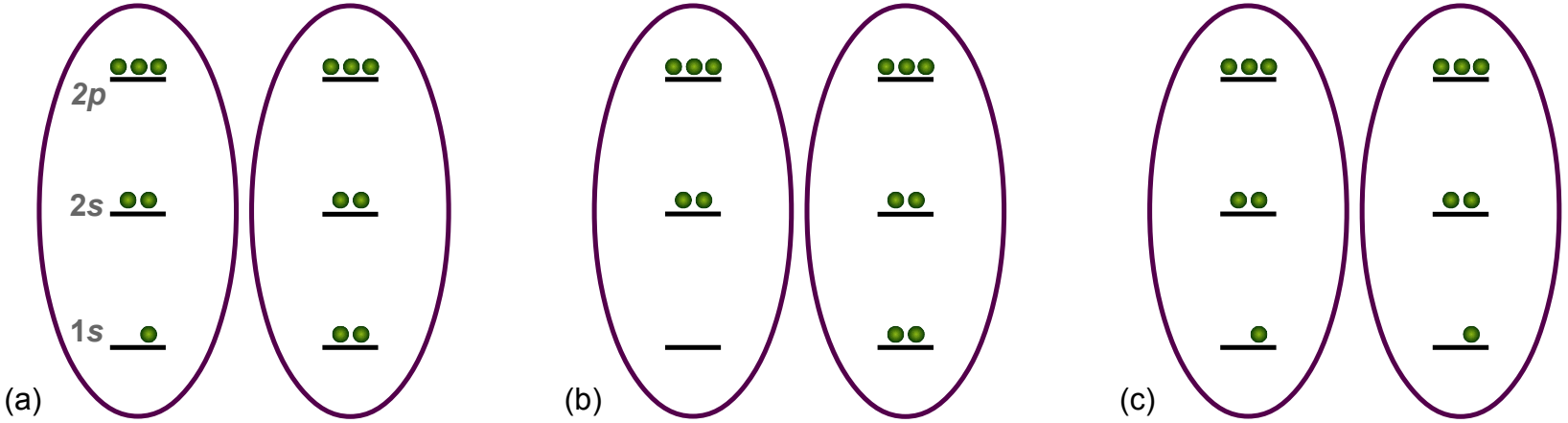
Single and double core holes



Single core hole (SCH)

Doubly-depleted core orbital of one atom:

Single-site double core hole (ssDCH)

Two core holes localized to two different atoms:

Two-site double core hole (tsDCH)

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X-ray interaction with molecules

- Molecular cross sections and decay widths are approximated by the corresponding atomic quantities
- Treat atoms in a molecule **independently**
- Charge states of a **nitrogen molecule** are deduced from the atomic model:

$$P_{223}(t)\,P_{223}(t),\quad 2\,P_{123}(t)\,P_{223}(t),\quad P_{123}(t)\,P_{123}(t),\quad P_{023}(t)\,P_{223}(t)$$

- Building on this basis, a combination of atomic rate equations with dedicated molecular channels can be devised: molecular rate equations
- Incorporate by phenomenological constants to treat molecular breakup
- **Which are the dominant molecular channels?**

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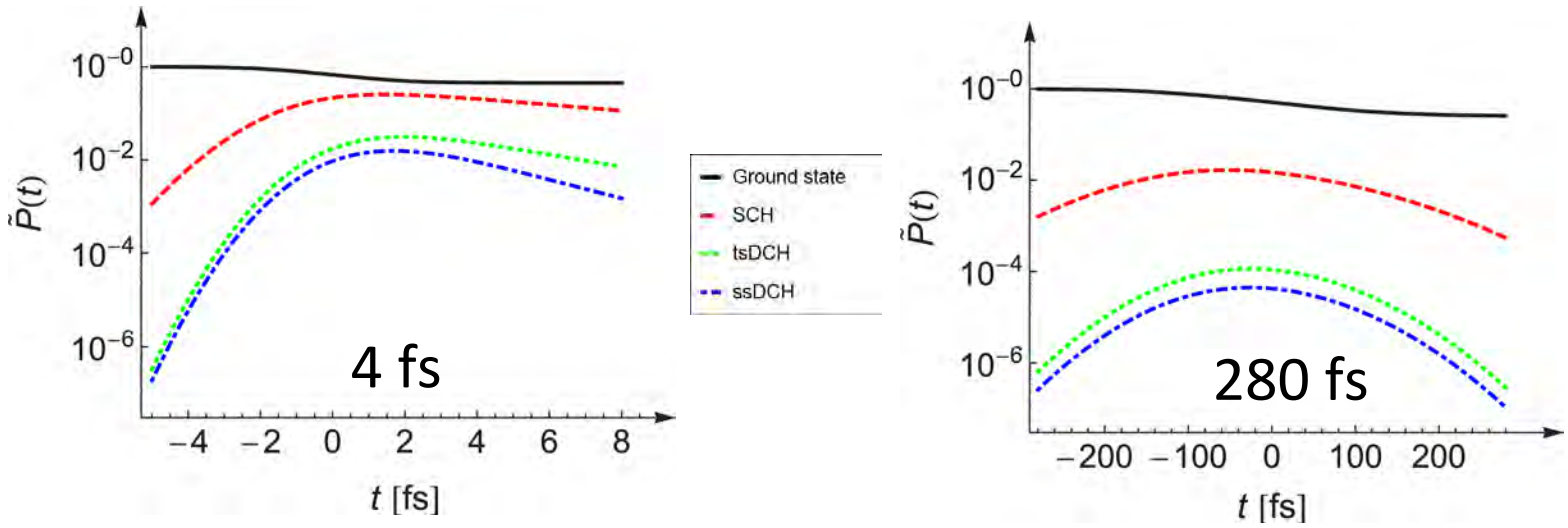
Double-core holes in a nitrogen molecule

- Only **1*s* orbital** in nitrogen
- The probabilities $\tilde{P}(t)$ to find N_2 during the x-ray pulse in its ground state, with SCH, a tsDCH, and a ssDCH
- **Predominantly** contribution of SCH
- Influence of tsDCH and ssDCH is **small**



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Molecular rate equations

- **Phenomenological** molecular rate-equation model based on following elemental processes:

  (1) metastable N_2^{2+} are formed by SCH Auger decay; introduces a time scale: molecular dication may fragments into two atomic ions prior absorbing more x rays

  (2) N_2^{3+} is formed by further valence ionization by x rays; dissociates into $N_2^+ + N_2^{2+}$

  (3) N_2^{3+} with a SCH or N_2^{2+} with a DCH lead to N_2^{4+} via Auger decay on a much faster time scale than molecular fragmentation; importance of SCH versus DCH depends on x-ray intensity

  (4) for even higher charge states, we essentially with independent atoms which are treated as atomic fragments

$$N_2 \xrightarrow{\gamma} N_2^+ \xrightarrow[\text{Auger decay}]{} N_2^{2+} \rightarrow N^+ + N^+$$
$$\rightarrow N + N_2^{2+}$$

$$N_2 \xrightarrow{\gamma} N_2^+ \xrightarrow[\text{Auger decay}]{} N_2^{2+} \xrightarrow{\gamma} N_2^{3+} \xrightarrow[\text{Auger decay}]{} N_2^{4+} \rightarrow N_2^{2+} + N_2^{2+}$$

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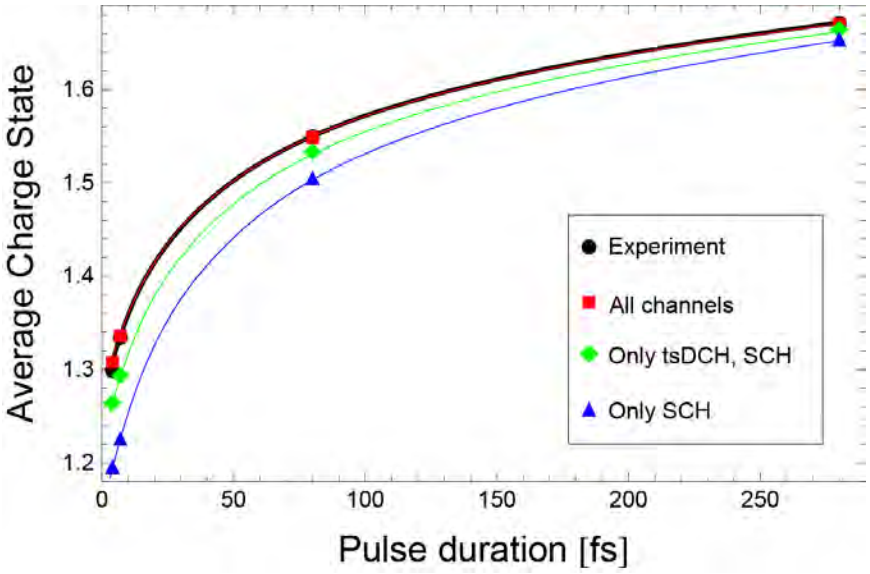
Molecular processes responsible for frustrated absorption

- Model captures **only** essential physics
- Need to **adjust** nominal pulse energy, i.e., 0.26mJ: 38% (280fs), 30% (80 fs), 16 % (7 fs) and for 0.15 mJ: 24 % (4 fs)
- Impact of DCHs small; dip caused predominantly by charge redistribution due to molecular fragmentation



J.-C. Liu, C. Buth (unpublished)

Conclusion

- **Sequential** two-photon absorption prevailing mechanism
- Ion yields from a rate-equation model for nitrogen
- **Impact of DCHs small**
- Frustrated absorption caused **predominantly** by charge redistribution due to molecular fragmentation

Acknowledgment

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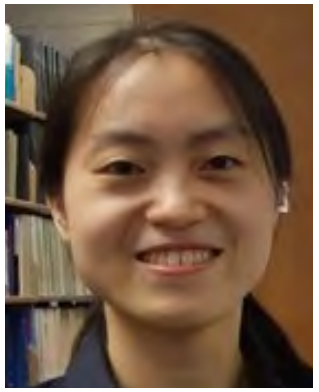

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