Mapping Molecular Orbitals with lasers

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The idea

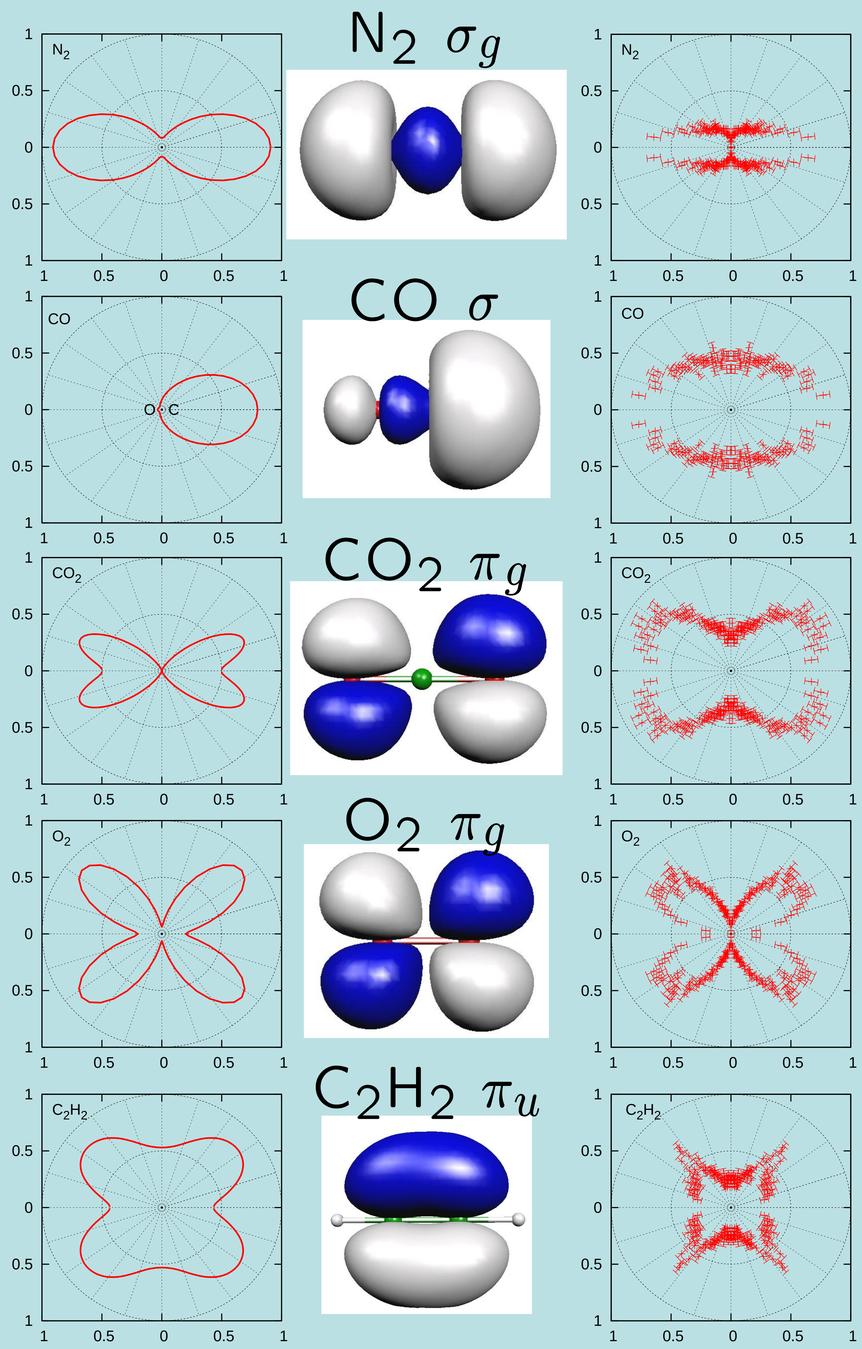
Molecular orbitals are essential theoretical constructs in modern quantum chemistry. There are few examples where these orbitals have been seen in the laboratory. Using sub-10fs lasers to double ionize the molecules and measuring the angular distributions of the fragmented ions, such molecular orbitals have been observed directly at JRM.

The essential idea is the tunneling ionization theory (see far right) where the electrons are ionized only when they are located along the laser polarization direction.

In the center we show the geometry of the molecular orbitals vs the ionization rates, and direct mapping from the observed angular distributions of the fragmented ions.

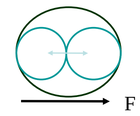
Results

Ionization rates **molecular orbital** **Experiment**



Tunneling Ionization Theory

Key Point:
Tunneling ionization rate is proportional to the electron density along the laser's electric field direction.



The W.F. in the asymptotic region

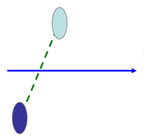
$$\psi(\mathbf{r}) = \begin{cases} C_{lm} r^{Z_c/\kappa} e^{-\kappa r} Y_{lm}(\hat{\mathbf{r}}) & \text{for atom} \\ \sum_l C_{lm} r^{Z_c/\kappa} e^{-\kappa r} Y_{lm}(\hat{\mathbf{r}}) & \text{for molecule} \end{cases}$$

The tunneling ionization rate in a static field

$$w_{stat}(F) = \sum_m \frac{B^2(m)}{2^{|m|}|m|!} \frac{1}{\kappa^{2Z_c/\kappa-1}} \left(\frac{2\kappa^3}{F}\right)^{2Z_c/\kappa-|m|-1} e^{-2\kappa^3/3F}$$

with

$$B(m) = \sum_l C_{lm}(-1)^m \sqrt{\frac{(2l+1)(l+|m|)!}{2(l-|m|)!}}.$$



The W.F. in the asymptotic region

$$\psi(\mathbf{r}) = \sum_{m'} \sum_l C_{lm} D^l_{m',m}(\hat{\mathbf{R}}) \; r^{Z_c/\kappa} e^{-\kappa r} \; Y_{lm'}(\hat{\mathbf{r}'})$$

The ionization rate in a field not along the axis

$$w(F, \hat{\mathbf{R}}) = \sum_{m'} w(F)$$

with

$$B(m') = \sum_l C_{lm} D^l_{m',m}(\hat{\mathbf{R}})(-1)^{m'} \sqrt{\frac{(2l+1)(l+|m'|)!}{2(l-|m'|)!}}$$