THE PROJECTION METHOD IN THE MOLECULAR FRAME ANGULAR DISTRIBUTION

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Molecular photoionization is one of the simplest reactions yet it provides a wealth of information about molecules and thus has continuously received a remarkable level of interest. With the advent of new-generation synchrotron sources and multiple coincidence techniques, studies of the inner-shell photoionization in free molecules are rapidly developing. The reaction procedure is usually treated as several independent sequential steps:

hν + AB	→	AB+* + e- (Photoelectron)
AB+*	→	AB++ + e- (Auger electron)
AB++	→	A+ + B+ (Coulombic explosion)
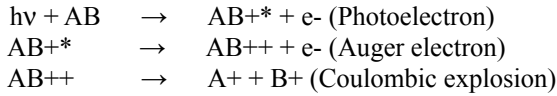
Molecular frame photoelectron angular distribution MFPAD provide a dynamical window of photoelectron emission as it is scattered off in the anisotropic potential of the molecule. The interference pattern showed by MFPAD is like a photograph that the molecule is illuminated from inside.

One established experimental approach to obtain the molecular frame photoionization information is to make angle resolved photoelectron-photoion coincidence measurements in dissociative photoionization. By using position sensitive detector in electron/ion TOF, as shown in Fig. 1, we can measure the time of flight and the position (t,x,y) of electron/ion that arrive the detector. The momenta of particles can be reconstructed from the measured (t,x,y) by flying path analysis. With axial recoil approximation, the measured electron-ion correlation shows photoelectron angular distribution in molecular frame MFPAD.

Fig.1. Schematic drawing of measurement. The momentum of particles are calculated from (x,y,t).

The MFPAD is a function of the direction of the photoelectron emission, the molecular axis orientation, the direction of the light propagation and the light polarization. In the dipole approximation, the dependence of the MFPAD on the parameters that define the light is greatly simplified compared to the general case. As shown in Fig.2, the MFPAD is now only function of the angle of the light polarization with respect to the molecular axis θ_n^{lab}, the photoelectron emission with respect to the molecular axis θ_e, and dihedral angle ϕ_e. The expression is written as [1]:

$$I\left(\theta_e, \phi_e, \theta_n^{lab}\right) = F_{00}^{(m)}\left(\theta_e\right) + F_{20}^{(m)}\left(\theta_e\right) P_2^0\left(\cos\theta_n^{lab}\right)$$
$$+ F_{21}^{(m)}\left(\theta_e\right) P_2^1\left(\cos\theta_n^{lab}\right)\cos\phi_e$$
$$+ F_{22}^{(m)}\left(\theta_e\right) P_2^2\left(\cos\theta_n^{lab}\right)\cos 2\phi_e$$
$$F_{JN}^{(m)}\left(\theta_e\right) = \sum_{J'} C_{J'JN}^{(m)} P_{J'}^N\left(\cos\theta_e\right)$$

Fig.2. The molecular reference frame

There are a number of possible approaches for obtaining the $F_{JN}^{(m)}$ functions from relative angle-resolved photoelectron – photoion coincidence measurements. If the full 4π angular distributions of the photoelectron and ion recoil directions have been measured, then it is possible to use the projection method [2] to obtain $F_{JN}^{(m)}$. The projection method relies on the fact that the expansions in equation are in terms of orthogonal polynomials.

$$F_{JN}^{(m)}\left(\theta_e\right) = \frac{(2J+1)(J-N)!}{2\pi\left(1+\delta_{N,0}\right)(J+N)!} \int_0^\pi \sin\theta_n^{lab}\, d\theta_n^{lab} \times$$

$$\int_0^{2\pi} d\phi_e\, I\left(\theta_e, \phi_e, \theta_n^{lab}\right) P_J^N\left(\cos\theta_n^{lab}\right)\cos\left(N\phi_e\right)$$

Here, we use the photoionization of NO above N 1s ionization threshold as the example to show how projection method works.
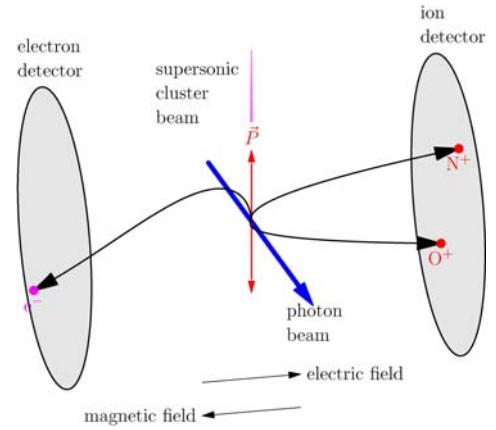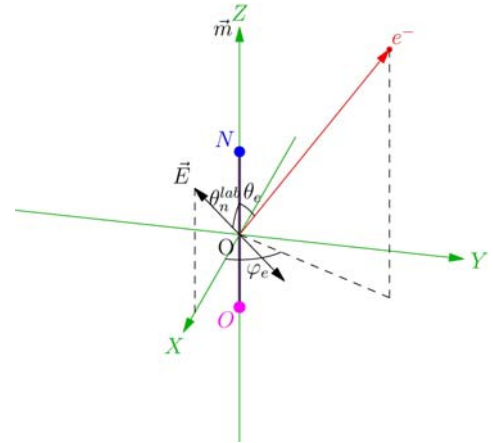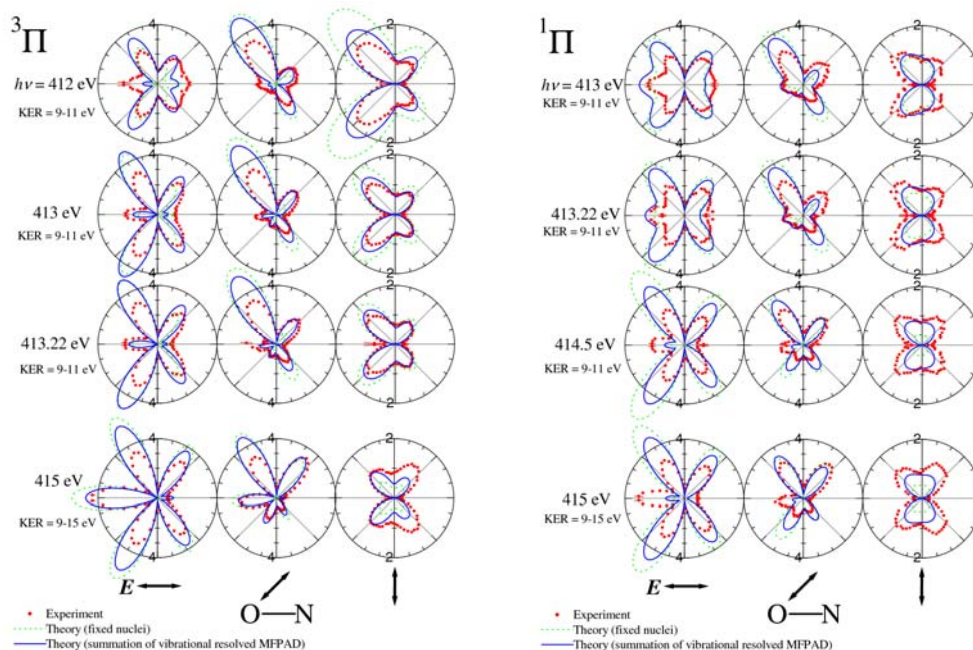
Fig. 3. The MFPADs of NO molecular above N 1s threshold, compared with ab-initio calculation.

The ground state of NO is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi\ X^2\Pi$. Ionization of N 1s electron will lead to $2\sigma 2\pi\ ^3\Pi$ and $2\sigma 2\pi\ ^1\Pi$.

In the ab-initio calculations, The F_{JN} functions are computed using the multichannel Schwinger configuration interaction (MCSCI) method [3], in which the initial and final bound state wavefunctions are described using configuration interaction (CI) wavefunctions. The orbitals used in the CI wavefunctions are the natural orbitals obtained from a complete-active-space self-consistent-field (CASSCF) calculation of the ground state of the NO+ molecule where all orbitals were active, including the core orbitals. Thus there were six σ orbitals and two π orbitals in the calculation. The one-electron basis set was the aug-cc-pVTZ basis set of Dunning and co-worker. The results presented here were obtained from a fixed nuclei calculation where the bond length R(NO) was taken to be 1.15077 °A, and a sum of vibrational sublevels, respectively.

From the F_{JN} functions obtained, we obtained one dimensional MFPADs, as shown in Fig. 3. It can be seen that the multiplet-specific behavior is not very dramatic. The agreement between measurement and calculation is quite good. In general, the value calculated with vibration motion considered are closer to the measured one than those without consideration of vibration motion considered

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