Molecular Frame and Recoil Frame Angular Distributions in Dissociative Photoionization of Small Molecules

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Abstract. Photoelectron angular distributions in the dipole approximation can be written with respect to several different reference frames. A brief review of the molecular frame and recoil frame are given. Experimentally, one approach for obtaining such angular distributions is through angle-resolved coincidence measurements of dissociative ionization. If the system dissociates into two heavy fragments, then the recoil frame angular distribution can be measured. Computed molecular frame and recoil frame photoelectron angular distributions are compared to experimental data for the Cl 2p ionization of CH₃Cl.

1. Introduction

The theoretical description of one-photon ionization of molecules involves both representing the initial unionized state as well as the scattering state with the photoelectron leaving the system. The most detailed observable for this process is the molecular frame photoelectron angular distribution (MFPAD). One approach for measuring the MFPAD is dissociative photoionization. In this case, measured angle-resolved photoelectron-photoion coincidence measurements can then yield data which are related to the MFPAD. The main assumption connecting the measured data and the underlying MFPAD is the axial recoil approximation in which one assumes that the direction of recoil of the ionic fragments is given by the orientation of the bond that is broken at the time of the initial ionization event. When this assumption is not valid, then the coincidence experiment measures the recoil-frame photoelectron angular distribution (RFPAD), which can only indirectly be related to the underlying MFPAD.

In non-linear polyatomic molecules, when only two fragments are produced in dissociative ionization, it is not possible to measure the MFPAD and only the RFPAD is accessible even when the axial recoil approximation is valid. This is due to the additional azimuthal angle which gives the orientation of the molecule about the recoil axis. This azimuthal angle cannot be detected when only two fragments are produced, and thus the experimental data are averages over this unobserved angle.

In the present paper, we will review the different possible frames for considering photoelectron angular distributions (PADs). The expansion of these PADs in terms of one-dimensional functions of the angle between a reference axis of the molecule and the direction of emission of the photoelectron will be given. We will then consider the MFPADs and RFPADs for the photoionization of Cl 2p in CH₃Cl. The experimental results discussed here have been obtained with the so-called “vector
correlation” method [1,2] using time and position sensitive ion-electron coincidence detection, which has been developed in parallel with other powerful coincidence techniques [3].

2. Photoelectron angular distribution frames
In the molecular frame, the MFPAD for ionization by linearly polarized light can be written as a general expansion in spherical harmonics of the form:

\[ I(\theta_\kappa, \phi_\kappa, \theta_n, \phi_n) = \sum_{L,M,L',M'} A_{LML'M'} Y_{LM}(\theta_\kappa, \phi_\kappa) Y_{L'M'}(\theta_n, \phi_n) \]  

where the angles \( \theta_\kappa \) and \( \phi_\kappa \) are the polar and azimuthal angles defining the direction of emission of the photoelectron and \( \theta_n \) and \( \phi_n \) are the corresponding angles defining the direction of polarization of the light. In the dipole approximation, only low order terms in the angular expansion describing the dependence on the field orientation contribute to the sum. Additionally, for linear molecules \( M = -M' \) so that a restricted sum is obtained:

\[ I(\theta_\kappa, \phi_\kappa, \theta_n, \phi_n) = \sum_{L=0,2} \sum_{|M|=0} H_{LML'M'} \theta_{L',M'} Y_{LM}(\theta_\kappa, \phi_\kappa) Y^*_{L'M'}(\theta_n, \phi_n) \]  

Finally, this sum can be rewritten in terms of only real-valued functions to give the MFPAD of the form [4]:

\[ I^{(m)}(\theta_\kappa, \phi_\kappa, \theta_n, \phi_n) = F_{00}^{(m)}(\theta_n) + F_{20}^{(m)}(\theta_n) P_2^0(\cos \theta_n) \]
\[ + F_{22}^{(m)}(\theta_n) P_2^2(\cos \theta_n) \cos(2[\phi_n - \phi_\kappa]) \]  

The four functions of \( \theta_n \) in equation (3) contain all the information needed to describe the MFPAD for any combination of polarization directions and photoelectron emission directions. It is also worth noting that the four \( F_{L,M} \) functions can be written in terms of a wide variety of one-dimensional angular distributions. For example one can write the \( F_{L,M} \) functions in terms of the distribution, \( I_{\theta_n=0}^{\phi_\kappa-\phi_n=0} \) obtained with the light polarization parallel to the molecular axis, i.e. \( \theta_n = 0 \), the distribution, \( I_{\theta_n=90^\circ}^{\phi_\kappa-\phi_n=0} \) obtained with the light polarization perpendicular to the molecular axis, i.e. \( \theta_n = 90^\circ \), and the photoelectron in the plane defined by the field and the molecular axis, i.e. \( \phi_\kappa = \phi_n = 0 \) , and the distributions \( I_{\theta_n=90^\circ}^{\phi_\kappa-90^\circ=0} \) and \( I_{\theta_n=45^\circ}^{\phi_\kappa-45^\circ=0} \) defined in a similar fashion. The \( F_{L,M} \) functions are then given by

\[ F_{00}(\theta) = \frac{1}{3} \left[ I_{\theta_n=0} + I_{\theta_n=90^\circ}^{\phi_\kappa-90^\circ} + I_{\theta_n=90^\circ}^{\phi_\kappa-\phi_n=90^\circ} \right] \]  
\[ F_{20}(\theta) = \frac{2}{3} \left[ I_{\theta_n=0} - \frac{1}{2} I_{\theta_n=90^\circ}^{\phi_\kappa-90^\circ} - \frac{1}{2} I_{\theta_n=90^\circ}^{\phi_\kappa-\phi_n=90^\circ} \right] \]  
\[ F_{21}(\theta) = \frac{1}{3} \left[ 2 I_{\theta_n=45^\circ}^{\phi_\kappa-\phi_n=0} - I_{\theta_n=0}^{\phi_\kappa-\phi_n=0} - I_{\theta_n=90^\circ}^{\phi_\kappa-\phi_n=0} \right] \]
For ionization by circularly polarized light, the MFPAD can be written in similar functional form using the expansion in terms of real-valued functions. In that case the MFPAD is given by

$$ I^{(m)}(\theta_k, \phi_k, \theta_n, \phi_n) = F_{00}^{(m)}(\theta_k) + \frac{1}{2} \left[ F_{20}^{(m)}(\theta_k) P_2^0(\cos \theta_n) \right] \left[ \cos(\phi_k - \phi_n) \right] $$

(5)

where the direction defined by $\theta_k$ and $\phi_k$ now corresponds to the direction of propagation of the light, the $F_{LN}$ functions are identical to those obtained for the same system using linearly polarized light, and the one new function $F_{11}$ is related to the circular dichroism, with the “+” sign in equation (5) corresponding to positive helicity light and the “−” corresponding to negative helicity.

Finally, there is the case of elliptically polarized light. In that case, the full MFPAD can be written using the same $F_{LN}$ functions, however the dependence of the MFPAD on the state of the polarization of the light leads to the introduction of an additional azimuthal angle that defines the orientation of the ellipse describing the electric vector about the direction of propagation of the light [5].

For linear molecules the axial recoil approximation can breakdown in two ways. The first way occurs when the dissociation lifetime is a significant fraction of a rotational period. In this case, one must consider the rotational temperature of the target and perform the appropriate average over populated rotational states [6]. When this is done, one again obtains the same functional form as given in equations (3) and (5). The detailed comparison of the computed and measured $F_{LN}$ functions in such a case enabled us e.g. to determine the predissociation lifetime of the N$_2$O$^+$($C^2\Sigma^+$) ionic state in valence shell ionization of the N$_2$O molecule [7]. The second mechanism for the breakdown of the axial recoil approximation for polyatomic linear molecules is the possibility of bending of the molecule before or during dissociation. In this case one again retains the same functional form in the measured RFPAD [8]: the latter can then be used to determine the mean bending angle of the molecular ion, as shown in the study of dissociative photoionization of N$_2$O into the N$_2$O$^+$($B^2\Pi$) valence state[8].

For non-linear molecules in the dipole approximation, the MFPAD given in equation (1) can be also written in terms of real-valued functions:

$$ I^{(m)}(\theta_k, \phi_k, \theta_n, \phi_n) = \sum_{L=0}^{2n} \sum_{N=0}^{n} \sum_{N'=0}^{n-2} \sum_{K} F_{LNN'}^{(m)}(\theta_k) P_L^N(\cos \theta_n) \cos(N' \phi_k - N \phi_n) $$

+ \sum_{L=0}^{2n} \sum_{N=0}^{n} \sum_{N'=0}^{n-2} \sum_{K} F_{LNN'}^{(m)}(\theta_k) P_L^N(\cos \theta_n) \sin(N' \phi_k - N \phi_n) $$

(6)

involving then a larger and in principle unlimited number of $F_{LN}$ functions, as compared to the four and five $F_{LN}$ functions valid for photoionization of a linear molecule induced by linearly and elliptically polarized light, respectively. In the present paper we will consider the MFPAD for the Cl 2p ionization of CH$_3$Cl. In this system with $C_3v$ symmetry, with the C-Cl bond oriented along the $z$ axis and one of the H atoms located in the $xz$ plane, many of the terms in equation (6) are zero by symmetry, leading to the following reduced form for the MFPAD:
Here we will compare to experimental data where Cl\(^+\) and CH\(_3\)\(^+\) fragments are formed and detected in coincidence with the ejected photoelectron. In this case, assuming the validity of the axial-recoil approximation, the experimental RFPAD can be compared to the theoretical RFPAD which is obtained by averaging the MFPAD given in equation (7) over the unobserved orientation of the H atoms about the C-Cl bond. This can be obtained from the distribution given in equation (7) by averaging over the orientation of the molecular frame about the molecular axis

\[
I^m(\theta_k, \phi_k, \theta_n, \phi_n) = \sum_{L=0,2} \sum_{N=0}^L \sum_{k=0, \pm 1, \pm 2, K} F_{L,N,N+3k}^c (\theta_k) P_L^{\gamma} (\cos \theta_n) \cos \left( N + 3k \phi_k - N \phi_n \right). \tag{7}
\]

This leads to the usual form of the RFPAD in terms of the four \(F_{LN}\) functions:

\[
I^c(\theta_k, \theta_n, \phi_k - \phi_n) = \frac{1}{2\pi} \int_0^{2\pi} I^m(\theta_k, \phi_k + \gamma, \theta_n, \phi_n + \gamma) d\gamma. \tag{8}
\]

A similar form has been previously obtained for the RFPAD of the \(C_2\) molecule NO\(_2\) [9].

3. Computational Methods

The computations for the photoionization of CH\(_3\)Cl were performed using the frozen-core Hartree-Fock approximation [10] using the Schwinger variational method with Padé corrections [11]. All integrals were computed using the single-center expansion method [12] including partial waves up to \(l_{\max} = 40\) and using the position of the Cl atom as the center of expansion. The geometry was \(R(\text{C-Cl}) = 1.785\ \text{Å}, R(\text{C-H}) = 1.09\ \text{Å},\) and \(\angle \text{H-C-Cl} = 110.75^\circ\) [13]. The target was computed using an augmented correlation-consistent polarized valence triple zeta (aug-cc-pVTZ) basis set with the GAUSSIAN electronic structure code [14].

In this study we consider the ionization of the Cl 2\(p\) orbital. The present treatment does not include

\[ (2p)^{-1} A_1 \quad (2p)^{-1} E \quad (2p)^{-1} A_1 + E \]

Figure 1. MFPAD for the ionization of CH\(_3\)Cl Cl (2\(p\))\(^{-1}\) by linearly polarized light at a photon energy of 211 eV and a photoelectron kinetic energy of 5 eV. The top row of figures is for light polarized parallel to the C-Cl axis (\(\theta_n = 0^\circ\)) and the bottom row is for the light polarized perpendicular to the molecular axis (\(\theta_n = 90^\circ\)).
spin-orbit interactions, thus in the $C_{3v}$ symmetry, the $2p$ orbitals split into a non-degenerate $A_1$ orbital and a degenerate pair of orbitals of $E$ symmetry. The Koopmans’ ionization potentials (IPs) for the corresponding ion states are 218.27 eV for the $A_1$ hole state and 218.22 eV for the $E$ hole state. In the photoelectron spectrum one finds two ion states that correspond to the $^2p_{1/2}$ and $^2p_{3/2}$ atomic states of the Cl atom, with IPs of 207.9 and 206.3 eV, respectively [15]. In the full molecular symmetry there would actually be three states with symmetry $E_{1/2}$, $E_{1/2}$, and $E_{3/2}$ [16], however in this system the splitting due to the non-spherical environment (0.05 eV from Koopmans’s IPs) is much smaller than the spin orbit splitting of 2.6 eV. Thus the final states will be very close to the atomic states and one of the $E_{1/2}$ states will be nearly degenerate with the $E_{3/2}$ state. In both the $^2p_{1/2}$ and $^2p_{3/2}$ states the hole has a 1:2 ratio of probabilities for being in the $A_1$ and $E$ states so that we have computed the photoionization for the $A_1$ and $E$ states separately and just added the resulting MFPADs and RFPADs together to compare the measured angular distributions for the Cl $^2p_{1/2}$ and $^2p_{3/2}$ states. The validity of this approach is supported by the experimental observation that the RFPADs for the Cl $^2p_{1/2}$ and $^2p_{3/2}$ states are nearly identical. In all calculations, we assumed an IP of 206.3 eV and compared the computed results to the experimental results for the Cl $^2p_{3/2}$ state.

4. Results and Discussion
Preliminary experimental data for the RFPAD for CH$_3^+$ and Cl$^+$ fragmentation of CH$_3$Cl for photoionization by light with an energy of 211 eV have been previously published [17]. In the present paper we compare computed and measured RFPADs for this same process. At this energy, the primary process is the formation of either the $^2p_{1/2}$ or $^2p_{3/2}$ states of CH$_3$Cl$^+$. After the initial photoionization event, the $(2p)^{-1}$ hole state rapidly decays by an Auger process leading to a doubly (or multiply) ionized CH$_3$Cl molecule that then dissociates into two or more charged fragments that can be detected in coincidence with the initial photoelectron. Taking advantage of the multihit property of the delay-line position-sensitive detectors [18] for ion fragment detection, this situation is quite favorable to

Figure 2. A comparison of computed and measured RFPADs for the ionization of CH$_3$Cl Cl ($2p)^{-1}$ by linearly polarized light at a photon energy of 211 eV and a photoelectron kinetic energy of 5 eV. The left column of figures is for light polarized parallel to the C-Cl axis ($\theta_n = 0^\circ$) and the right column is for the light polarized perpendicular to the molecular axis ($\theta_n = 90^\circ$). The normalization is such that the total photoionization cross sections are identical.
identify and select all fragmentation channels, among which the \((\text{CH}_3^+ , \text{Cl}^+)\) channel is the dominant one [17].

In figure 1, we present the computed MFPADs separately for the \((2p)^{-1} A_1\) state and the \((2p)^{-1} E\) state and the sum of the two which then corresponds to the MFPAD for either the Cl \(2p_{1/2}\) or \(2p_{3/2}\) states. For the parallel excitation \((\theta_n = 0^\circ)\) one can clearly see the three-fold symmetry of the CH$_3$Cl molecule. If this were just the Cl atom, one would have reflection symmetry with respect to the \(xy\) plane for both the parallel polarization case shown in the top row and the perpendicular ionization shown in the bottom row of figure 1. For the parallel ionization of the \(2p\) \(A_1\) orbital there is a strong asymmetry indicating the importance of scattering in the final state in determining the form of the MFPAD. For the \(2p\) \(E\) orbitals, there is much less asymmetry for parallel ionization. This reduction in the importance of final state scattering effects with the \(2p\) \(E\) orbitals can be attributed to the fact that the C atom is in the nodal plane of the outgoing \(E\) symmetry scattered waves for ionization by light aligned along the C-Cl axis. In the MFPAD obtained from the sum of the two symmetries, presented in the right column of figure 1, the largest asymmetry is the ionization by light with the perpendicular orientation. This is also the geometry where the electrons ejected from the \(2p\) \(E\) orbitals will be able to scatter from the C atom.

In figure 2 we present a comparison of the measured and computed RFPADs. In this case, we have shown the RFPAD obtained by the detection of the CH$_3^+$ and Cl$^+$ fragments. Assuming the validity of the axial recoil approximation, the RFPAD is computed from the MFPAD shown in figure 1 by merely averaging over the orientation of the H atoms as implied by equation (8). Thus in the RFPADs one loses the information about the H atom location leading to an RFPAD with the functional form of the MFPAD of a linear molecule as given in equation (9).

From the three-dimensional plots shown in figure 2, one can see that there is a very good agreement between experiment and theory for this system. A more quantitative comparison is given in figure 3, where cuts through the three-dimensional distributions are given. The results in figure 3 indicate that the qualitative features, i.e. position of the various lobes and their relative intensity, are well reproduced by the calculations. A more quantitative comparison indicates that the computed and measured RFPADs differ by \(\sim 15\%\). In figure 3, the degree of asymmetry with respect \(xy\) plane can also be clearly seen. For ionization parallel to the C-Cl axis there is weak asymmetry, whereas for the perpendicular ionization the asymmetry is somewhat stronger.
5. Conclusion
Generalizing our previous work on molecular frame photoemission for linear molecules in the dipole approximation, we have presented the functional form of the MFPAD for non-linear molecules using an expansion in terms of real-valued functions. When the molecule breaks into two fragments, the corresponding RFPAD takes the same the form as that of the MFPAD for linear molecules. We have seen that the relatively simple FCHF treatment of the Cl $2p$ photoionization of CH$_3$Cl gives an RFPAD that agrees quite well with the measured RFPAD for the fragmentation in CH$_3^+$ and Cl$^+$ fragments. The asymmetry of the RFPAD with respect to the $xy$ plane is seen to give an indication of the strength of the final state scattering effects in the RFPAD. This level of agreement should allow for the further investigation of other fragmentation pathways in this system. By a comparison of computed and measured RFPADs for such processes, one may be able to infer additional information about the dissociation dynamics of the CH$_3$Cl$^+$ ion.

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