

FINAL REPORT

We made excellent progress owing to the support of this grant. The principle theme was to work on photoionization of complex, asymmetric systems, both experimentally and computationally. Twenty-two publications have resulted from this support, and several more are in preparation and will be published shortly. In the interest of brevity, we note some of the highlights and themes of what has been accomplished below.

Non-Franck-Condon Vibrational Branching Ratios in Complex Systems

In the simplest view of molecular photoionization, one assumes that vibrational and photoelectron motion are decoupled, which leads to the Franck-Condon approximation. The Franck-Condon principle has two predictions that are relevant to molecular ionization: (1) vibrational branching ratios are independent of photon energy, and (2) single quantum excitations of nontotally symmetric modes are forbidden. Nonresonant and resonant processes can result in coupling molecular vibration and photoelectron motion, with the result that vibrational branching ratios become dependent on photon energy, and that forbidden vibrations can be excited.

As a first step towards the study of the photoionization of nucleobases, we began with photoelectron and theoretical studies of halothiophenes. We began these studies with 2-bromothiophene, and this system was a useful testing ground. Experimentally, we have made considerable progress on this system. In the analysis of the $X\alpha''$ ($1a_2$) $^{-1}$ state, we have identified 29 peaks resulting from the v_6 , v_7 and v_{14} vibrations and their combination bands. It turned out that the ionization dynamics were fairly complex and the effects were relatively small, so we shifted our efforts to 2-chlorothiophene. We have completed the experimental work on this system, and we anticipate publishing a joint experimental/theoretical paper on this work soon.

In addition to the halothiophenes, we also completed a similar study on acrolein, and this work was published in the *Journal of Chemical Physics*. More recently, we have completed an experimental study on photoelectron spectroscopy of the nucleobases cytosine, uracil, and thymine, and the manuscript describing this work has just been completed and will be submitted to the *Journal of Chemical Physics* shortly.

Non-resonant effects in the vibrational branching ratios of XCN, X=Br,Cl

Earlier, we experimentally and computationally studied the non-Franck-Condon vibrational effects in the photoionization of ICN leading to its ground $X^2\Pi$ state. We have now extended our computational studies to explore similar effects in

the ionization XCN (X = Cl, Br). The vibrational branching ratios for photoionization of the $X^2\Pi$ state in the XCN molecules for both non-degenerate vibrational stretching C–N and X–C modes have been computed employing the adiabatic approximation. Harmonic oscillator vibrational wave functions were used to calculate the vibrationally specific photoionization cross sections leading to the ground state of XCN^+ . In the case of the photoionization cross sections leading to the $X^2\Pi_{3/2,1/2}$ states of ICN^+ when q_1 (C–N stretching mode) or q_3 (I–CN stretching mode) are excited, significant non-Franck-Condon effects were seen at photon energies of 60–80. These differences arose from the sensitivity of the initial state orbital to the C–N bond length. In particular, the electron population in the highest occupied molecular orbital on the CN part of the ICN molecule increases as the C–N bond length increases. Similar effects have now been found in our computational study of the photoionization leading to the $X^2\Pi_{3/2,1/2}$ states of BrCN^+ and ClCN^+ . We find a breakdown of the Franck-Condon approximation due to strong geometry dependence of the transition moment coming from the geometry dependence of Cooper minima in the cross sections. This work will be published shortly.

Rescattering Photoelectron Spectroscopy

We have collaborated with the group of K. Ueda in a study of the high-field elastic rescattering processes. Experimentally, large-angle elastic differential cross sections (DCSs) were obtained for scattering of free electrons by singly charged ions of partially aligned O_2 and CO_2 molecules from an analysis of the momentum distributions of rescattering photoelectrons generated by infrared laser pulses. The extracted DCSs are in good agreement with our computed *ab initio* results, confirming the validity of the extraction procedure. Noting that the double-slit-type interference includes information about the distances between the atoms of a molecule, the results of this study has a further implication that the rescattering electron spectroscopy is indeed potentially a powerful tool for determining the structure of molecules and thus may be employed for studying chemical reactions with a temporal resolution of femto- or subfemtoseconds and with atomic spatial resolution.

A new analysis of non-Franck-Condon Effects

We have completed a study of the non-Franck-Condon effects in the valence photoionization of N_2 and CO over an extended range of energies up to 200 eV. In this study, we have developed a new method to report deviations from Franck-Condon behavior that are more informative than traditional reports of vibrational branching ratios. We have shown that the deviation of the vibrational branching ratio from the Franck-Condon value can be directly related to the logarithmic derivative of the cross section. Defining the electronic factor F as the logarithmic derivative

$$F = \frac{\sigma^{(1)}}{\sigma^{(0)}}$$

where $\sigma^{(0)}$ is the total cross section at the equilibrium geometry and $\sigma^{(1)}$ is the first derivative with respect to bond length, then F can be related to the branching ratios

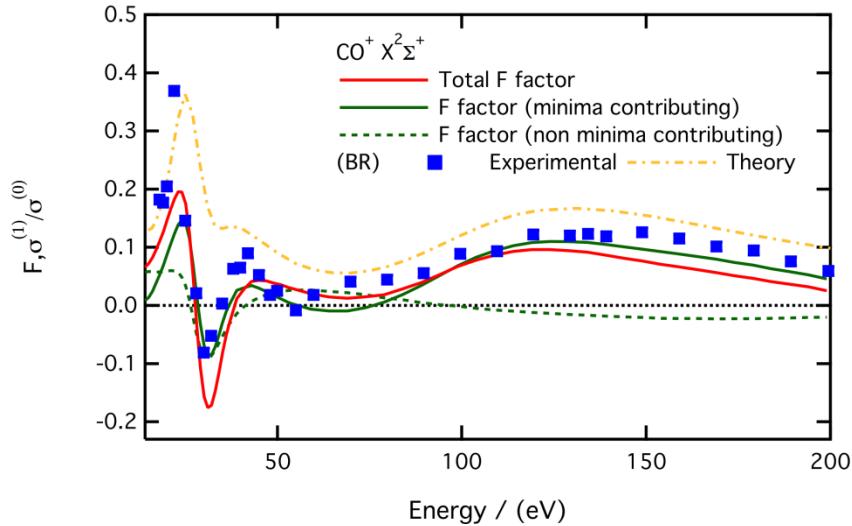
$$F = \pm \left(2 R_{l=0/0-0}^{(\text{FC})} \right)^{\frac{1}{2}} \left[\frac{R_{l=0/0-0}}{R_{l=0/0-0}^{(\text{FC})}} - 1 \right]$$

where the branching ratio is defined as

$$R_{v_j^+ \leftarrow v / v_i^+ \leftarrow v} = \frac{\sigma_{v_j^+ \leftarrow v}}{\sigma_{v_i^+ \leftarrow v}}$$

and $R_{v_j^+ \leftarrow v / v_i^+ \leftarrow v}^{(\text{FC})}$ is the branching ratio in the Franck-Condon approximation. This analysis allows for the contributions to the breakdown of the Franck-Condon approximation to be identified by partial wave.

Consider our measured and computed electronic factors in the case of the photoionization of CO leading to the $X^2\Sigma^+$ ground state of CO^+ show in the figure below.



Theoretical and experimental F factors. Experimental values were derived assuming $R^{(\text{FC})} = 0.03713$. The dot-dashed line is a complete adiabatic treatment of the branching ratios. The F factor theoretical lines are derived directly from the derivatives of the fixed-nuclei cross sections.

There are two main sources of the breakdown of the Franck-Condon approximation, geometry dependence of the orbital from which the ionization occurs and geometry dependence in the continuum. In particular, in the partial wave expansion of the photoionization matrix elements one finds energies where certain matrix elements go through zero, leading to what can be described as Cooper minima. In molecular systems where there is no corresponding atomic Cooper minima, the Cooper minima can be identified as coming from Cohen-Fano interference effects. In figure 1, we have separated out the contribution to the non-Franck-Condon deviation of the electronic factor into contributions from partial waves with Cooper minima and

contributions from those partial waves without out Cooper minima. In the figure we see that in this channel all of the deviation from the Franck-Condon value is due to partial waves with Cooper minima. In the ionization to other channels, and in particular the ionization leading to the $B\ ^2\Sigma^+$ state of CO^+ , there are substantial contributions from partial-waves without Cooper-minima the can be attributed to geometry effects in the 4σ orbital which is being ionized.

Vibrational effects in the molecular frame photoelectron angular distributions

We have also completed a study of the vibrational effects on molecular frame photoelectron angular distributions (MFPADs) in collaboration with the group of K. Ueda at Tohoku University. It was found that MFPADs for photoemission from the $\text{O}\ (1s)^{-1}$ hole in CO_2 measured in coincidence with the O^+ and CO^+ fragments, produced in the subsequent Auger decay of the core hole state, are not symmetric with respect to the reflection plane of symmetry, which is perpendicular to the molecular axis and contains the C atom. To understand the observed asymmetries, we have considered a one-dimensional vibrational model of the CO_2 system where we have only included the anti-symmetric stretch. For asymmetric geometries, i.e. when the two CO bonds have different lengths, O 1s ionization of CO_2 leads to hole states with the hole localized on the left O atom in one state and on the right O atom in the other state. Computed fixed-nuclei MFPADs from these two hole states show significant left-right asymmetries. Using a modified version of the lifetime-vibrational interference equation and the diabatic vibronic states, we then computed the dependence of the MFPAD on the lifetimes of the core holes. We could model the experimental MFPADs using computed Auger decay rates for decay to a number of CO_2^{2+} states and by assuming that decay to a directly fragmenting state leads to dissociation of the longer CO bond at the time of the decay and that decay to a double-ion state which has a minimum at the equilibrium geometry leads to predissociation with equal probability of breaking each CO bond. We have also completed a number of related MFPAD studies.

Molecular aspects of HHG: SF_6 and CF_4

A major component of our recent work has been to develop connections between molecular high harmonic generation and photoionization dynamics. The two phenomena are intimately connected, because a central aspect of high harmonic generation involves the high-field driven electron inelastically traversing the molecular framework. This is the conjugate process to photoionization. We have performed experiments on a series of molecules, including SF_6 and CF_4 . This work is done collaboratively with Kansas State researchers, primarily Profs. Carlos Trallero and C.D. Lin. It has formed the basis of a major portion of our renewal proposal, which has been funded, and is a direction that will likely dominate our future work.

Publications resulting from this grant:

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