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Tracking Hole Localization in K-shell and Core-Valence Excited Acetylene Photoionization via Body-Frame Photoelectron Angular Distributions

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Asymmetry in the molecular-frame photoelectron angular distributions (MFPAD) from core-hole or core-valence excited polyatomic targets with symmetry-equivalent atoms can provide direct evidence for core-hole localization. Using acetylene as an example, we contrast the small asymmetry that can be seen in direct core-level ionization, due to the competition between two competing pathways to the continuum, with ionization from core-valence excited HCCH, which offers the prospect of observing markedly greater asymmetry.

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I. INTRODUCTION

Ever since Bagus and Schaefer [1] first observed that a considerably lower self-consistent field energy could be obtained for a core-hole ionized state of O_2^+ by relaxing the restriction that the orbitals have g or u symmetry, the subject of core-hole localization in molecules possessing symmetry-equivalent atoms has continued to attract the attention of theorists and experimentalists. For diatomic molecules, the question of whether core ionization creates a $1s$ hole in one of the atoms or a delocalized hole that preserves the symmetry of the molecule is still being debated. Indeed, experiments in which photoelectrons and Auger electrons produced by core ionization were measured in coincidence in the molecular frame demonstrated that in some cases the K-hole behaves like a localized state while in others as a delocalized one, depending on the angle of detection [2].

The situation in polyatomic molecules with symmetry-equivalent atoms is more straightforward, since the presence of asymmetric vibrational modes leads to a vibronic coupling between g and u states and the rapid localization of an initially created K-hole on a single atom [3]. Evidence for this mechanism has been seen in the case of acetylene, where there is rich vibrational fine structure in the $C(1s)^{-1} \rightarrow \pi^*$ band that is well described by a theoretical model which treats vibronic coupling in both the core and valence orbital spaces with broken-symmetry orbitals [4].

It has also been suggested that the asymmetry observed in molecular-frame K-shell photoelectron angular distributions (MFPADS) in molecules with symmetry-equivalent atoms provides direct evidence for core-hole localization. MFPADS for $O(1s)^{-1}$ ionization in CO_2 [5] and $C(1s)^{-1}$ ionization in HCCH [6], measured in coincidence with ion fragments that are produced after fast Auger decay into an asymmetric dissociation channel (e.g. $O^+ + CO^+$ in CO_2 and $H^+ + C_2H^+$ in HCCH), show definite asymmetry which has been ascribed to a localization of the core-holes at geometries away from the symmetric equilibrium geometry. If Auger decay leading

to asymmetric dissociation is fast relative to vibrational motion, then the memory of the instantaneous geometry at the moment of photon absorption is retained and imprinted on the asymmetric dissociation channel. However, it must be pointed out that, in the case of CO_2 , asymmetry in the MFPAD is also observed for $C(1s)^{-1}$ ionization when measured in coincidence with the $O^+ + CO^+$ ion fragmentation channel [7, 8]. Asymmetry associated with core-hole localization is a mute point in that case, since there is only a single carbon atom in the target. The observed asymmetry was quantitatively reproduced by considering the geometry dependence of the fixed-nuclei MFPADS which, when convoluted with the zero-point vibrational motion, explained the observed distributions [9]. So a question that naturally arises is to what extent core-hole localization enhances the geometry dependence of the MFPADS and, if it does, why the asymmetry observed in CO_2 for $O(1s)^{-1}$ ionization and in HCCH for $C(1s)^{-1}$ ionization is not markedly larger than that seen for $C(1s)^{-1}$ ionization in CO_2 , which it is not. That question will be addressed here for the case of HCCH.

We will also examine an alternative, and potentially more decisive, way of using outer-valence MFPADS to observe hole localization in a small polyatomic, again using the acetylene molecule to illustrate the idea. An experiment would proceed in two steps. In the first step, a short X-ray pulse is used to excite, but not ionize, a core-valence state ($1s \rightarrow \pi^*$) below the carbon K-edge. Such a state typically lives for ~ 6 fsec before it Auger decays, during which time the hole can localize on one of the carbon atoms. A second UV pulse then ionizes the excited π^* valence electron before Auger decay can occur. If the angular distribution of the resulting photoelectrons is measured in the molecular frame in coincidence with ions produced in an asymmetric dissociation channel, a strong left/right asymmetry should be observed.

The outline of this paper is as follows. In the following section, we give a brief description of calculation of MFPADS using the complex Kohn formalism. In Section III, we describe the electronic structure calculations we

performed to determine the target core-valence excited states. Our calculated MFPADs are presented in Sec. IV. We conclude with a brief discussion.

II. THEORY

A. Molecular-frame photoionization cross sections

Photoionization cross sections in the molecular frame can be constructed from the matrix elements

$$I_{\Gamma_0}^{\mu} = \langle \Psi_{\Gamma_0}^{-} | r_{\mu} | \Psi_0 \rangle, \quad (1)$$

where r_{μ} is a component of the dipole operator, which we evaluate here in the length form,

$$r_{\mu} = \begin{cases} z, & \mu = 0 \\ \mp (x \pm iy) / \sqrt{2}, & \mu = \pm 1 \end{cases}. \quad (2)$$

$$\psi_{\Gamma_0}^{-}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{l_0 m_0} i^{l_0} \exp(-i\delta_{l_0}) Y_{l_0 m_0}^*(\hat{\mathbf{k}}) \psi_{k, \Gamma_0 l_0 m_0}^{-}(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (3)$$

with the Coulomb phase shift δ_{l_0} defined as

$$\delta_{l_0} = \arg \Gamma(l_0 + 1 - iZ/k). \quad (4)$$

The cross section, differential in the angle of photoejection and photon polarization relative to the fixed body-frame of the molecule, is then given by

$$\frac{d^2\sigma}{d\Omega_{\hat{k}, \Gamma_0} d\Omega_{\hat{\epsilon}}} = \frac{8\pi\omega}{3c} |I_{\hat{k}, \Gamma_0, \hat{\epsilon}}|^2, \quad (5)$$

where ω is the photon energy, c is the speed of light and the amplitude $I_{\hat{k}, \Gamma_0, \hat{\epsilon}}$ is given by

$$I_{\hat{k}, \Gamma_0, \hat{\epsilon}} = \sqrt{\frac{4\pi}{3}} \sum_{\mu l_0 m_0} i^{-l_0} e^{i\delta_{l_0}} I_{\Gamma_0}^{\mu} Y_{1\mu}(\hat{\epsilon}) Y_{l_0 m_0}(\hat{k}). \quad (6)$$

At low photoelectron energies, molecular MFPADs reflect a competition between favored electron ejection along the direction of photon polarization or into regions favored by molecular environment, tempered by optical selection rules. To fill in the gaps dictated by optical selection rules, it is convenient to present the computational results at a particular nuclear geometry through an MFPAD integrated over all photon polarization directions [10]. This is obtained from Eqs. (5) and (6) by using the orthonormality of the spherical harmonics $Y_{1\mu}(\hat{\epsilon})$:

$$\int \frac{d^2\sigma}{d\Omega_{\hat{k}} d\Omega_{\hat{\epsilon}}} d\Omega_{\hat{\epsilon}} = \frac{8\pi\omega}{3c} \frac{4\pi}{3} \sum_{\mu} \left| \sum_{l_0 m_0} I_{\Gamma_0}^{\mu} Y_{l_0 m_0}(\hat{k}) \right|^2. \quad (7)$$

$\Psi_{\Gamma_0}^{-}$ is the final-state wave function for production of photoions in a specific cation state Γ_0 and Ψ_0 is the initial state wave function of the neutral N electron target. To construct an amplitude that represents an ionization process for a specific value of photoelectron momentum, \mathbf{k} , measured in the molecular body-frame, we expand $\Psi_{\Gamma_0}^{-}$ in partial waves:

Eq. (7) is the incoherent sum of the MFPADs over the three components of the dipole operator. This quantity must have the symmetry of the target cation state.

B. Complex Kohn method

To compute the final state wave function $\psi_{k, \Gamma_0 l_0 m_0}^{-}$, which describes the photoelectron escaping in the field of the residual molecular ion, we use the complex Kohn variational method [11, 12]. In the present study, the wave function $\psi_{k, \Gamma_0 l_0 m_0}^{-}$ is expressed as

$$\begin{aligned} \psi_{k, \Gamma_0 l_0 m_0}^{-} &= \hat{A}(\chi_{\Gamma_0} F_{\Gamma_0}^{-}) + \sum_i d_i^{\Gamma_0} \Theta_i \\ &\equiv P\Psi + Q\Psi, \end{aligned} \quad (8)$$

where is χ_{Γ_0} the final $(N-1)$ -electron ionic state, $F_{\Gamma_0}^{-}$ is the photoelectron continuum wavefunction, \hat{A} is the antisymmetrization operator and the Θ_i are N -electron correlation terms built from square-integrable functions.

In the Kohn method, the channel function $F_{\Gamma_0}^{-}$ is further expanded in terms of square-integrable functions plus numerical continuum functions as:

$$\begin{aligned} F_{\Gamma_0}^{-} &= \sum_i c_i^{\Gamma_0} \phi_i(r) + \\ &\sum_{lm} \sqrt{\frac{2}{\pi}} [f_l(k_{\Gamma}, r) \delta_{l l_0} \delta_{m m_0} \delta_{\Gamma \Gamma_0} + \\ &T_{ll_0 m m_0}^{\Gamma \Gamma_0} h_l^{-}(k_{\Gamma}, r)] Y_{lm}(\hat{r}) / (k_{\Gamma} r), \end{aligned} \quad (9)$$

where $T_{l_0 m m_0}^{\Gamma_0}$ are elements of the \mathbf{T} -matrix, ϕ_i is a set of orthonormal (Cartesian-Gaussian) functions and f_l and h_l^- are partial-wave continuum radial functions, behaving asymptotically as regular and incoming Coulomb functions:

$$f_l(k_\Gamma, r \rightarrow \infty) \longrightarrow \sin(k_\Gamma r + \frac{Z}{k_\Gamma} \ln 2k_\Gamma r - \frac{\pi l}{2} + \delta_l)$$

$$h_l^-(k_\Gamma, r \rightarrow \infty) \longrightarrow \exp(-i(k_\Gamma r + \frac{Z}{k_\Gamma} \ln 2k_\Gamma r - \frac{\pi l}{2} + \delta_l)).$$
(10)

By construction, the functions ϕ_i , as well as the continuum functions f_l and h_l^- , are chosen to be orthogonal to the molecular orbitals used to expand the initial target Ψ_0 and final ion state χ_{Γ_0} . This constitutes a strong orthogonality constraint which must be relaxed by the inclusion of appropriate penetration terms Θ_i for every target molecular orbital that is not doubly occupied.

III. BODY-FRAME ACETYLENE PHOTOIONIZATION

At its linear equilibrium geometry, neutral acetylene is nominally described by the electronic configuration $1\sigma_g^2 1\sigma_u^2 3\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_4^4$ and, in linear geometry near equilibrium, by $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$. The X-ray absorption spectrum below the carbon K-edge at 291.1 eV is dominated by an intense peak at 285.8 eV [13] which results from promotion of a $1\sigma_g$ (2σ) electron into the antibonding $1\pi_g^*$ ($2\pi^*$) orbital. In the symmetric equilibrium nuclear configuration, the two equivalent C 1s sites give rise to quasi-degenerate core orbitals ($1\sigma_g$, $1\sigma_u$) split by ~ 110 meV and thus a pair of core-valence Π^* excited states of g and u symmetry, one dipole-allowed (${}^2\Pi_u$) and one dipole-forbidden (${}^2\Pi_g$) from the ground-state. We turn our attention first to carbon K-shell ionization from neutral ground-state acetylene.

A. K-shell Photoionization

Adachi *et al.* [6] observed asymmetry in the MFPADs for HCCH K-shell ionization when the photoelectrons were measured in coincidence with fragment ions in the $\text{H}^+ + \text{CCH}^+$ dissociation channel. The measured asymmetry was largest ($\sim 10\%$) when the photon polarization was coincident with the molecular axis and, not surprisingly, vanished for perpendicular polarization. The observed asymmetry was attributed to core-hole localization. They argued that memory of the core-hole position in the ionized state can be communicated to the final dissociative state since the core-hole hopping time they calculated ($\tau_h \sim 40$ fs) was much greater than the Auger lifetime ($\tau_{life} \sim 7$ fs).

We have calculated the MFPADs for K-shell photoionization of HCCH using the formalism outlined above.

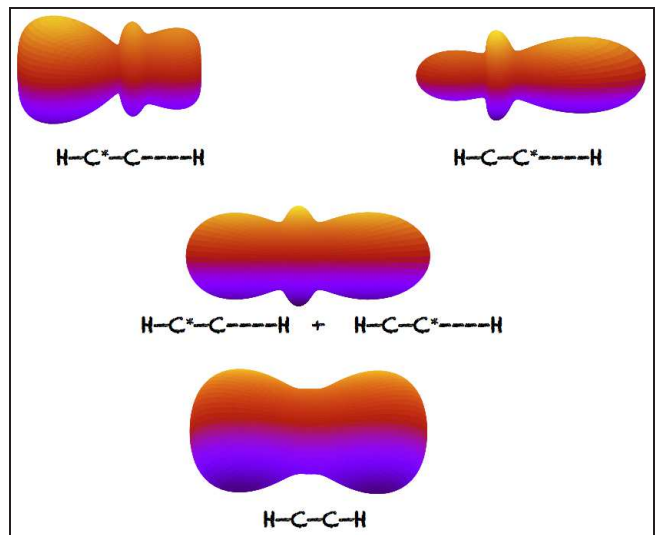


FIG. 1: (Color online) HCCH carbon $1s^{-1}$ MFPADs at 4 eV photoelectron energy averaged over photon polarization direction. Top: $1\sigma^{-1}$ and $2\sigma^{-1}$ components at RMS asymmetric stretch geometry; asterisks label the carbon atom with the core-hole. Middle: total MFPAD at asymmetric stretch geometry. Bottom: total MFPAD at equilibrium geometry. The MFPADs were rescaled to the same maximum magnitude.

The calculations were carried out in a two-state coupled channel approximation using single-configuration wave functions for the $1\sigma^{-1}(1\sigma_g^{-1})$ and $2\sigma^{-1}(1\sigma_u^{-1})$ carbon $1s$ core-hole states constructed with neutral self-consistent field molecular orbitals. The molecular orbitals were expanded in a Gaussian basis of 9s, 6p and 1d carbon functions contracted to 5s, 4p, 1d and 10s, 3p on the hydrogens, contracted to 5s, 3p. For the complex Kohn scattering calculations, the basis was augmented with additional diffuse functions - 3s, 1p on the carbons and 2s, 2p on the hydrogens. The calculations were done in linear geometry at an asymmetric configuration, using RMS values for the CH bond distances in the $\nu = 0$ asymmetric stretch mode, and at equilibrium geometry as well. At the asymmetry geometry, the carbon 1σ and 2σ molecular orbitals are completely localized on the two carbon atoms. The results are shown in Fig. 1.

Evidently, the individual MFPAD components at asymmetric geometry display marked asymmetry, with increased propensity for photoelectron ejection on the side of the molecule where the core-hole is localized. These components of the total MFPAD represent two quasi-degenerate paths to the continuum. When summed, however, the resulting MFPAD shows only a small left/right asymmetry. The totally symmetric MFPAD at equilibrium geometry is also shown for comparison.

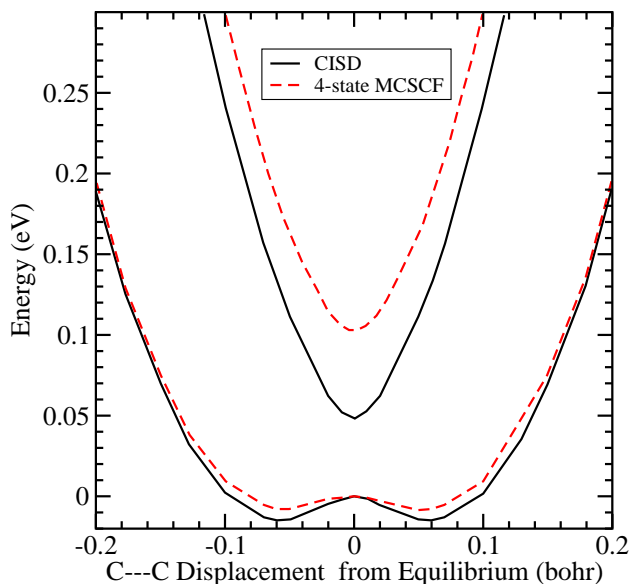


FIG. 2: (Color online) Potential energy curves of the C $1s-\pi^*$ states of HCCH in linear geometry with the C–C distance fixed at its ground-state equilibrium value of 2.273 bohr. Results are shown for 4-state-averaged MCSCF and multi-reference CISD calculations.

B. Core-Valence Photoionization

We turn next to photoionization of the core-valence Π^* states of acetylene. To characterize these states, we first carried out multi-reference configuration-interaction (MRCI) calculations, again restricting the calculations to linear geometries. A molecular orbital basis for these calculations was obtained by starting with a self-consistent field (SCF) calculation on neutral HCCH in an asymmetric linear geometry, which breaks the g/u symmetry of the orbitals. The orbitals from this calculation were then used as a starting guess for a state-averaged multi-configuration self-consistent field (MCSCF) calculation on the doubly degenerate core-valence excited Π^* states. The MCSCF calculations were finally followed by a multi-reference singles and doubles configuration-interaction (CISD) calculation, using the four MCSCF configurations (ie. $\Pi_{x,y}^{*,lower}$ and $\Pi_{x,y}^{*,upper}$) as reference configurations, with the restriction that there be at least one vacancy in either the 1σ or 2σ orbitals. MCSCF/CISD calculations were then carried out for a range of asymmetric stretch linear geometries, keeping the C–C distance fixed and using the MCSCF results from one geometry as a starting guess for the next. This procedure produced smooth adiabatic potential energy curves for the $1s-\pi^*$ states with localized C $1s$ orbitals. The calculations were carried out using an augmented, correlation-consistent, polarized valence triple zeta basis with 11s, 6p, 3d, 2f functions on the carbons contracted to 5s, 4p, 3d, 2f and 6s, 3p, 2d on the hydrogens contracted to 4s, 3p, 2d. Results using this basis are plotted in Fig. 2. We find

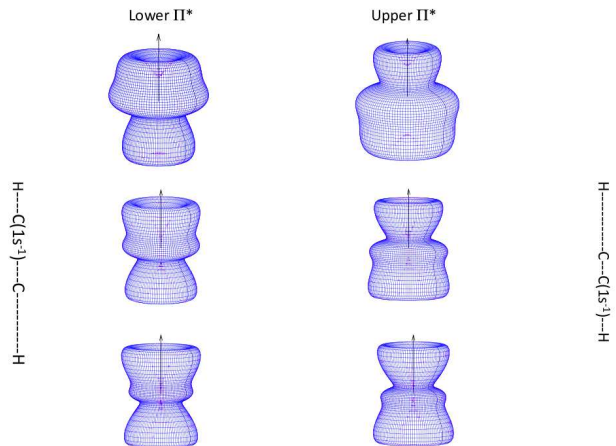


FIG. 3: (Color online) MFPADs for the lower (left) and upper (right) Π^* states of HCCH at a C–C displacement of 0.06 bohr. MFPADs are averaged over all photon polarization directions and summed over degenerate components for each state. Results are for photoelectron energies of 2 eV (top), 4 eV (middle) and 6 eV (bottom).

that the CISD calculations show a splitting of ~ 0.05 eV between the lower (dipole-allowed) and upper (dark) Π^* states at the symmetric equilibrium geometry of ground-state HCCH. It is noteworthy that about the shallow potential wells in the lower state with minima near C–C displacements of ± 0.06 bohr, the $1s$ hole localizes on the carbon atom opposite the stretched CH bond, while for the upper state at the same geometries the reverse is true. We also carried out similar calculations using the smaller basis previously described for core-hole ionization and found very similar results. Therefore, for the complex Kohn results, we used the smaller basis. The target $1s-\pi^*$ states for the photoionization calculations were carried out with single-configuration broken symmetry states constructed using natural orbitals from the CISD calculations.

MFPADs for both the lower and upper Π^* states were calculated using single-configuration target neutral and ion states constructed from a common set of natural orbitals from the lower or upper Π^* states, respectively. The MFPADs were averaged over all photon polarization directions and summed over the two degenerate components of each state. Figure 3 shows the results obtained for a C–C displacement of 0.06 bohr. A pronounced left/right asymmetry in the MFPADs is to be noted. The asymmetry tracks the position of the localized C $1s$ hole and is thus reversed for the lower and upper states.

Only the lower adiabatic Π^* state is dipole-allowed from the ground state of HCCH. However, we must address the possibility that the dark upper state could be

populated by vibronic interactions, which would then weaken the expected left/right asymmetry in the observed distributions since the asymmetry in the MFPADs for the lower and upper states would, when summed, cancel each other. To address this effect, it is convenient to work in the diabatic representation, for which we use a two-state model in a simplified one-dimensional picture considering only the asymmetric stretch nuclear coordinate R [14, 15]. The diagonal adiabatic potential matrix \mathbf{H}^a , whose elements are the computed lower and upper Π^* states, can be transformed into a diabatic potential matrix \mathbf{H}^d , whose diagonal elements are the diabatic potentials and the off-diagonal elements are the electronic coupling elements. The transformation is given by

$$\mathbf{H}^d = \mathbf{M}^{-1} \mathbf{H}^a \mathbf{M} \quad (11)$$

with

$$\mathbf{M} = \begin{bmatrix} \cos \gamma(R) & -\sin \gamma(R) \\ \sin \gamma(R) & \cos \gamma(R) \end{bmatrix} \quad (12)$$

The rotation angle $\gamma(R)$ can either be parametrized by following, for example, the procedure given by Roos, Orel and Larson [15] or it can be evaluated *ab initio* from the computed non-adiabatic coupling P_{12} using the relation [14]

$$\gamma(R) = \int_R^\infty P_{12}(R') dR' . \quad (13)$$

The computed diabatic potential curves and electronic coupling elements are shown in Fig. 4.

We used a two-state finite-element discrete variable representation method [16] to solve numerically for the vibrational wave functions using the computed potential energy curves and electronic couplings. Fig. 5 shows the probability density for the lowest vibrational levels computed in the diabatic representation. We note that the states are well localized over the left/right wells, so that MFPADs from these states should show the predicted asymmetry.

IV. DISCUSSION

Using the acetylene case as an example, we have shown how two different classes of MFPADs, when measured in coincidence with an asymmetric fragment ion channel following Auger decay, can be used to observe core-hole localization in polyatomic molecules with symmetry-equivalent atoms. In the case of direct core-level photoionization, the presence of two dipole-allowed pathways to the continuum corresponding to electron ejection from quasi-degenerate core orbitals partially obscures the observed asymmetry in the total cross section. A potentially clearer picture of hole localization is obtained in a two-step process where an X-ray photon is first used to prepare a core-valence excited state and a second UV

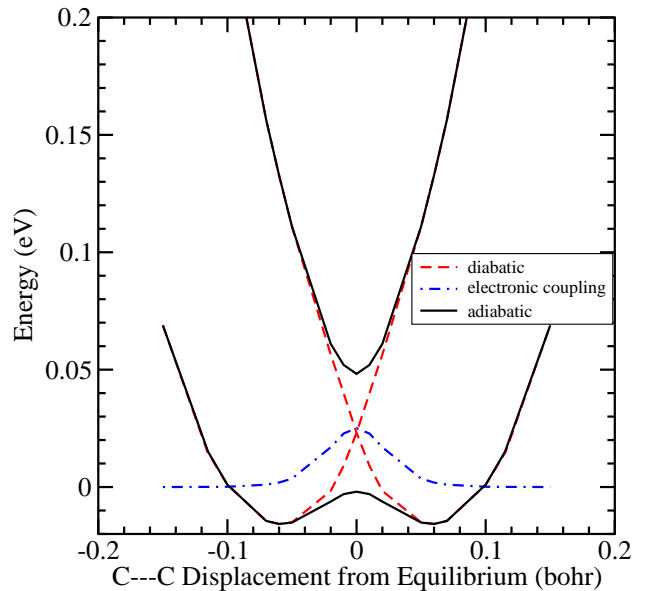


FIG. 4: (Color online) Diabatization of computed CISD potential energy curves, following the treatment of ref. [15]

photon is then used to ionize the species. The dark state can be suppressed by monitoring the ionization from the lowest vibrational levels of the core-excited states, since they are well localized and their MFPADs have marked left/right asymmetry.

The prospect for experimental observation of the effects discussed here will depend on the availability of short X-ray and UV pulse sources at the desired wavelengths and the ability to overlap these pulses in space and time. With pulses of 10 fs or longer, the effective bandwidths are less than 0.5 eV, so the shapes of the MFPADs should not be obscured by bandwidth issues. Some effort would be required to eliminate sources of background electrons of the same energy as the photoelectrons produced by sequential X-ray absorption and UV ionization. The C $1s^{-1}\pi^*$ state of acetylene lies at 285.8 eV and is the only strong X-ray absorption feature below the carbon K-edge at 291.1 eV. For the ionizing UV pulse, one would probably want to choose a laser frequency in the window between 6 and 8 eV - a range readily accessible by harmonic generation with an IR source - where there are no strong absorption bands in neutral acetylene and where the photionization signal from the Π^* excited molecule is expected to be large. While a proposed experiment would no doubt be challenging, it should be feasible with the next generation of free electron laser light sources.

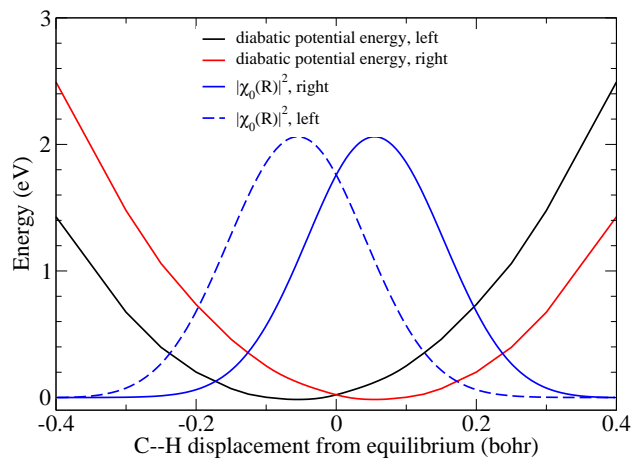


FIG. 5: (Color online) Vibrational $\nu = 0$ probability densities from two-state diabatic model.

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