Dissociative Electron Attachment to HCN, HCCH and HCCCN

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Abstract.
Studies of polyatomic molecules show that more than one degree of freedom comes into play in the dissociative process of certain molecules upon low-energy electron collision. In many of these cases, bond breaking may only proceed if the initial symmetry of the target molecule is distorted. We have performed a multi-dimensional computational treatment of the dissociative electron attachment (DEA) to three polyatomic systems, HCN, HCCH, and HCCCN below 10 eV and compared their nuclear motion and dissociation cross section. We further investigated the isotope effect in the case of HCN and HCCH. We have adopted the same computational approach in the study of these systems. This approach consists of time-dependent wavepacket propagation where the Hamiltonian operator involves the multi-dimensional complex potential energy surfaces (PESs) of the resonant anion.

1. Introduction
Treatment of electron driven processes for polyatomics introduces challenges in comparison to diatomic molecules due to the rapid rise of computational complexity as a result of the increased number of internal degrees of freedom of the \{electron, molecule\} system. A number of theoretical studies aimed at gaining insight into the dissociative paths for polyatomic systems such as dissociative electron attachment to formic acid [1] and water [2, 3] as well dissociative recombination (DR) to HCO⁺ [4] H₃⁺ [5] and HCNH⁺ [6]. In many of these calculations, approximations have been applied to reduce the system dimensionality by restricting the nuclear motion to a subset of internal coordinates and limiting the number of electronic states involved in the computation. In this work, a comparative summary of theoretical investigations of polyatomic systems is presented. A discussion of the theoretical approaches and computational methods used in DEA to polyatomics is further provided to extend these techniques in future investigations of DEA and DR to polyatomics. This proceeding is organized as follows. First, a brief overview of the theory of DEA to polyatomics is further provided to extend these techniques in future investigations of DEA and DR to polyatomics. This proceeding is organized as follows. First, a brief overview of the theory of DEA to polyatomics applied in the present studies is outlined. Secondly, these principles are applied toward the study of specific molecules HCN, HCCH and HCCCN systems in terms of the study of dissociation mechanism and the computation of DEA cross sections.

2. Theory
Based on the early formalism put forward by O’Malley [7] and in the framework of the local complex potential approximation [8], the nuclear wave equation is given by
\[
\left[ E - K_q - E_{\text{res}}(q) + \frac{1}{2} i \Gamma(q) \right] \xi_{E \nu}(q) = \sqrt{\frac{\Gamma(q)}{2\pi}} \chi_\nu(q)
\]

(1)

where \( K_q \) is the nuclear kinetic energy operator, \( E_{\text{res}} \) is the resonance energy, \( \Gamma \) is the autoionization width, \( \chi_\nu \) stands for the initial vibrational state of the molecular target, \( \xi_{E \nu} \) represents the DEA wavefunction of the system \( E \) is the total energy of the \{electron, molecule\} system. The quantities found in Eq.(1) are expressed as a function of the variable \( q \) which represents the nuclear internal coordinates of the molecule. We further derive a time-dependent expression of this motion equation along the lines of the work of Turner and McCurdy [9]:

\[
\begin{align*}
\left[ K_q + E_{\text{res}}(q) - \frac{1}{2} i \Gamma(q) \right] \xi_\nu(q, t) &= i \partial_t \xi_\nu(q, t); \\
\xi_\nu(q, 0) &= \sqrt{\frac{\Gamma(q)}{2\pi}} \chi_\nu(q)
\end{align*}
\]

(2)

The details of this derivation are introduced elsewhere [10]. This formulation therefore, suggests a computational approach based on 2 main steps.

2.1. Resonant PESs
First, we construct the multi-dimensional PESs of the neutral target molecule and of the resonant anion formed by attachment of the incident electron. The neutral potential energy surfaces are computed using standard structure calculation methods at the multi-configuration self-consistent field and the multi-reference configuration interaction levels. The resonances parameters are computed using the Complex Kohn Variational method [11] at the electron collision energy range surrounding the DEA peaks observed experimentally. All these surfaces are expressed as a function of a suitable system of internal coordinates.

2.2. Dissociation dynamics and cross section
The Multiconfiguration Time-Dependent Hartree (MCTDH) [12] method was used to solve the time-dependent Schrödinger equation (2). We ran the nuclear dynamics using the Heidelberg MCTDH Package [13] to compute the evolution of the wavepacket representing the transient resonant state and calculate the corresponding outgoing flux. These steps leading to the DEA cross section in the case of a triatomic system are discussed in [14] and references therein.

3. Systems of interest
We focused on three polyatomic systems: HCN, HCCH and HCCCN. These molecules have linear equilibrium geometry and have an unsaturated \( \Pi \) electronic system. A low-energy (below 10 eV) incident electron is trapped by the centrifugal barrier giving rise to a \( \pi^* \)-shape resonance. This resonant state may decay via bond breaking. These molecules have been studied experimentally [15, 16, 17, 18] and authors have predicted that the DEA process involves inherent polyatomic effects.

3.1. HCN
We studied the DEA channel given by

\[
\text{HCN} \left( X^1\Sigma^+, \nu \right) + e^- (E) \rightarrow (\text{HCN})^{-\ast} \left( ^2\Pi_g \right) \rightarrow \text{CN}^- \left( ^1\Sigma, \nu' \right) + \text{H} \left( ^2S \right),
\]

The DEA process for HCN below 3 eV is shown to be dominated by a “tunneling” effect through a potential barrier in the lowest resonant surface. Inspection of the propagating wavepacket shows a slight spread along the bending degree of freedom (a broadening of about
20\% at FWHM at 6 fs). A more recent calculation \cite{19} using a more accurate resonant PES derived from a relaxed-SCF (RSCF) calculation shows a better agreement with the experiment of Allan et al. \cite{15} compared to the previous static exchange calculation \cite{20}. At the RSCF level of calculation, the trial electronic scattering wavefunction takes account of the polarization and correlation effects; the reader may refer to \cite{19} for more details about this computation.

Furthermore, the improved surface topology of HCN (due to the inclusion of the polarization and correlation effects) results in a significantly better agreement with the isotope ratio found experimentally by the same authors. Since the RSCF calculation leads to a shift of the resonance position to lower energies and to a narrowing of the autoionization widths, this results suggests that initial wavepacket undergoes a significant scaling of its amplitude by the $\sqrt{\frac{1}{2\pi}}$ factor in Eq.(1). The resulting smaller “entry amplitude” leads to an overall weaker flux of the propagating wavepacket.

Recent calculation of the DEA cross section for HCN and DCN is shown in Fig.(1) together with the experimental plots in \cite{15}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Absolute DEA cross sections for the initial angular vibrational states $\nu_i = 0, 1, 2$ and 3 and population-weighted sum at 333 K compared with experimental findings in \cite{15} for HCN (left panel) and DCN (right panel).}
\end{figure}

### 3.2. HCCCH

We treated the reaction channel given by

$$C_2H_2 \ (X^1\Sigma_g^+, \nu) + e^- (E) \rightarrow (C_2H_2)^{+} \ (3\Pi_g) \rightarrow C_2H^- \ (1\Sigma^+, \nu') + H(2S)$$

The dissociation mechanism for acetylene shows a more pronounced bending effect as the wavepacket profile along the bending dimension presents a broadening of about 45\% at FWHM at 6 fs. This indicates that the majority of the flux collected asymptotically comes from the wavepacket portion that circumvents the potential energy barrier. By calculating the population-weighted sum of the contribution of the excited angular vibrational states of acetylene, a better agreement with the experiment is obtained at 300 K in terms of isotope ratio $\frac{\sigma(C_2D^-)}{\sigma(C_2H^-)}$ at 3 eV. Despite an improved value of this isotope ratio (17.9 versus the experimental value of 14.4 \cite{21}), the absolute values of the population-weighted sum lies about 1.87 higher than the DEA absolute cross sections measured at 300 K.

Similarly to the HCN case, we considered a RSCF scattering calculation to evaluate the effect of the polarization and correlation effects on $\Gamma$ and hence the DEA cross section. We performed a RSCF calculation for 3 points around the equilibrium geometry of HCCCH and determined the average ratio between the resulting autoionization widths and those computed at the static
exchange level. The average ratio was found to be approximately $\gamma = 0.92$ indicating, as expected, a narrowing of the electron-HCCH scattering cross sections. Moreover, an average decrease of the resonance positions of approximately $\varepsilon = 0.3$ eV is observed. By applying the ratio $\gamma$ as a scaling factor to the function $\Gamma(q)$ and the value $\varepsilon$ as a shift to the potential $E_{res}(q)$ in Eq.(2), the population-weighted sum reduces to about 4.9 pm$^2$ for HCN and to 0.27 pm$^2$ for DCN. In Fig.(2), we summarize the DEA cross section results in [21] and compare with experimental finding in [16].

![Figure 2. Absolute DEA cross sections for the initial angular vibrational states $\nu_i = 0$, 1, 2 and 3 and population-weighted sum at 300 K compared with experimental findings in [15] for C$_2$H$_2$ (left panel) and C$_2$D$_2$ (right panel).](image)

One must note that this only constitutes a rough estimate of the resonance parameters, since as seen in the HCN case, a more complete (and computationally costly) description of the complex anion surface is needed to have a correct account of dissociation dynamics.

3.3. HCCCN

We took into consideration the following channels for DEA to HCCCN:

$$\text{HCCCN} (X^{1\Sigma^+}, \nu) + e^-(E) \rightarrow \text{HCCCN}^{-\nu} \rightarrow \begin{cases} \text{CCCN}^{-}(2\Sigma^+, \nu'_I) + \text{H}(2S); \text{(I)}; \\
\text{CN}^{-}(1\Sigma^+, \nu'_II) + \text{HCC}(2\Sigma^+, \nu'_III); \text{(II)}; \\
\text{HCC}^{-}(1\Sigma^+, \nu'_I) + \text{CN}(2\Sigma^+, \nu'_II); \text{(III)}; \\
\end{cases}$$

In order to account for these dissociation channels, the coupling between the two lowest resonant PESs considered for this calculation must be introduced. In fact, these complex surfaces present a conical intersection and a diabatization procedure is hence employed to construct the two diabatic states to be used in the expression of the nuclear Schrödinger equation. As such, the MCTDH approach is set to solve a system of two coupled equations of motion as detailed in [22].

Furthermore, the HCCCN molecule has been modeled as three-body system: H, (CC) and (CN) and the internal degrees of freedom considered in this calculation are given by $q = (r_1, r_2, \theta_1, \theta_2)$ as depicted in Fig.(3). The resulting DEA flux from a 3-D calculation taking into account the coordinates $r_1$, $\theta_1$ and $r_2$ ($\theta_1$ and $\theta_2$) is normalized with the experimental yield of CCCN$^-$ (CN$^-$ and CCH$^-$) anions measured by Field et al. [18] and plotted in Fig.(4).

This calculation seems to have an acceptable agreement with these measurements. The major part of the observed DEA spectrum seems to cluster in the 2-9 eV energy band with peaks in the
Figure 3. Coordinate system used in DEA dynamics calculation. In this system of internal coordinates we include the distance between the center of mass of $C_{(1)}C_{(2)}$ and the hydrogen $r_1$, the distance between the center of masses of $C_{(1)}C_{(2)}$ and CN $r_2$ and respective bending angles $\theta_1$ and $\theta_2$.

Figure 4. Normalized flux from 3-D calculations allowing the bending of the (H)-(CC)-(CN) system. Left panel: we propagate on the $A'$ resonant states (non-coupled). The dominant yields for CCH$^-$ (orange curve) and CCCN$^-$ (black curve) are about 8% and 25% of that of CN$^-$ (red curve). Other secondary peaks for each of the fragments is also observed. Right panel: we include the coupling between the $A'$ resonant states. The dominant yields for CCH$^-$ (orange curve) and CCCN$^-$ (black curve) are about 23% and 49% of that of CN- (red curve). A secondary CN$^-$ peak at 5.1 eV has a height of approximately 60% while a secondary CCH$^-$ at 6.52 eV has a height of about 10%. Both cases Experimental results of [18] are in dotted lines and follow the same color coding as the computed curves with regard to the fragment they represent.

vicinity of the main CN$^-$ maximum peak. Our calculations show that this collection of peaks is shifted to lower electron energies as the dimensionality of the system is increased, eventually approaching the experimental central value of 5.28±0.15 eV.

By introducing the coupling, the general distribution structure and the peak height ratios of the DEA flux is closer the experimental spectra; however, the positions and widths of the peaks
are altered. Hence, one can infer the existence of a trade-off between the inclusion of addition
degrees of freedom (enhancing the positions and widths of the peaks with little effect on the
fragment ratios) on one hand and the introduction of the coupling (enhancing the fragments
ratios and worsening the peaks’ positions and widths) on the other hand.

4. Discussion and Conclusion
These calculations demonstrate that the resonant anions show a propensity for deviating from
their linear geometry upon electron attachment. Molecular bending appears to drive the
dissociation dynamics and therefore, the DEA process cannot be described accurately using
a diatomic (1-D) model.

This work was organized to address incrementally larger systems. Treating the dissociative
channel in HCN leading to formation of hydrogen and the cyanide anion CN\(^-\) followed by
the DEA to acetylene to explore the breakup into hydrogen and HCC\(^-\) served as a basis for
investigation of the larger cyanoacetylene molecule and its fragmentation into CCCN\(^-\) (i.e.
production of hydrogen), CN\(^-\) and CCH\(^-\). In principle, this approach can be generalized to
other polyatomics. The practical benefit of utilizing the qualitative and quantitative dynamical
characteristics of the sub-groups is to make a well-founded choice of the reduced system of
internal coordinates appropriate for the study of the larger system (i.e. do not consider the
degrees of freedom that are unlikely to contribute significantly to the dynamics).

Therefore, relatively simple molecules (3-5 atoms) can serve as a starting point of systems
exhibiting inherent polyatomic effects. Tackling DEA and DR problems for larger polyatomic
molecules may be achieved by methodically splitting the system into groups and adding in
degrees of freedom as needed guided by information gathered from the prior studies of the
subsystems.

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