ARTICLE

Theoretical Study of Haloacetonitrile Anions: CH$_2$XCN$^-$ (X=F, Cl)

Xin-wen Zhang$^a$, Mei Li$^b$, Shan-xi Tian$^{a,b,*}$

$^a$. Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China

$^b$. Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on August 28, 2007; Accepted on December 20, 2007)

Haloacetonitrile anions CH$_2$XCN$^-$ (X=F, Cl) were studied by HF-SCF, Becke3-LYP, and MP2 methods together with the Dunning’s basis set aug-cc-PVTZ. The vertical electron attachments to the neutral are endothermic. The geometrically optimized CH$_2$FCN$^-$ is mainly a valence-bounded anion and CH$_2$FCN$^-\rightarrow$CH$_2$CN+F$^-$ is a nonadiabatic dissociation. This theoretical study in good agreement with the experimental results shows that the Becke3-LYP method is reasonable in describing the electronic structures of anions and dissociative attachment dynamics, while significant differences between MP2 and Becke3-LYP results are shown for the dissociation potential curves of CH$_2$CICN$^-\rightarrow$CH$_2$CN+Cl$^-$. 

Key words: Haloacetonitrile, Electron attachment, Dissociation dynamics, Electron correlation effect

I. INTRODUCTION

Anions of the molecules having large values of dipole moments ($\mu$) attract great interest of both experimental and theoretical studies, because two typical anions, the dipole-bounded and the valence-bounded, may be involved in the processes and the various fragments produced after electron-attachment can be observed [1,2]. This resonance anionic state can be reached when the electron has low impact energy. A short-lived anion may dissociate, which is usually called a dissociative attachment [2]. Whether an anion is rather stable or unstable, some questions arise as to which type (the dipole-bounded and the valence-bounded) anion might be formed; where they might be whereafter coupled or transferred, and which type of anion is correlated more strongly with the dissociation for the molecules with large $\mu$ value.

As a typical case, electron attachment to haloacetonitrile (CH$_2$XCN, X=F, Cl, Br, I) has been studied using the electron-beam [3,4] and the variable-temperature, flowing-after glow Langmuir-probe [5] techniques. In particular, Hacaloglu et al. found that five ionic products (F$^-$, CN$^-$, CFCN$^-$, CHCN$^-$, and CHFCN$^-$) were given off via a single dissociative attachment resonance at the electron energy of 0.8 eV for CH$_2$FCN, while only the Cl$^-$ ionic product was dominated for CH$_2$CICN at the low electron energy [3]. For comparison, the dominated ionic product CH$_2$CN$^-$ appeared at 2.35±0.1 eV for CH$_3$CN [6]. Competition between X$^-$ and CN$^-$ was investigated for the electron attachment to CICN and BrCN, in which two different dissociation channels, (X+CN$^-$) or (X$^-$+CN), were proposed [7]. It is well-known that the cyano group (CN) is treated as a pseudo halogen in inorganic chemistry, and it has a remarkable electron affinity (EA) value (3.82 eV) [8] which is a little larger than the halogens (EA$_F$=3.40 eV, EA$_Cl$=3.62 eV, EA$_Br$=3.36 eV) [9]. Although haloacetonitrile has a large $\mu$ value, there is an argument about which group the additional electron should be attached to. Namely, on the basis of the nature of the large EA values of cyano group and halogens, the additional electron could be attached to either of them. On the other hand, it is unclear that the low-energy electron can occupy the antibonding $\sigma^*_X$ or $\pi^*_X$ orbital in the valence-bounded anion. Unfortunately, until now there have been no $ab$ initio level calculations on the molecular properties and the energy surfaces of the haloacetonitrile anions. A theoretical study on the molecular properties and dissociation dynamics of CH$_2$FCN$^-$ and CH$_2$CICN$^-$ is reported in this work.

II. COMPUTATIONAL METHOD

It is noted that there are two different energies of electron attachment ($EEA$): vertical $EEA$ ($EEA_v$) corresponding to the vertical attachment with the neutral molecular nucleic skeleton and adiabatic $EEA$ ($EEA_a$) corresponding to the geometrically relaxed anion. An excess electron is assumed to be attached loosely in the former (the dipole-bounded) or to be bounded a little more tightly in the latter (valence-bounded anion). Therefore, using the neutral molecular equilibrium geometry ($M$), we can calculate

$$EEA_v = E_{tot}^a(M) - E_{tot}^n(M)$$

where $E_{tot}^a$ and $E_{tot}^n$ are the total energies of the anion and neutral one, respectively. $EEA_a$ including zero-point vibrational energy (ZPVE) correction can be pre-

---

*Author to whom correspondence should be addressed. E-mail: sxtian@ustc.edu.cn
predicted as

$$EEA_n = E_{tot+ZPVE}^a(A) - E_{tot+ZPVE}^n(M)$$

$$= \Delta E_e + \Delta E_n$$  \hspace{1cm} (2)

where $A$ in $E_{tot+ZPVE}^a(A)$ represents the anionic equilibrium geometry, and $\Delta E_e$ and $\Delta E_n$ are the electronic and nuclear contributions, respectively.

Similarly, the adiabatic dissociation energies ($D_a$) of anions can be calculated as the differences between the summarized energies of fragments ($F_i$, denoting the equilibrium structure) for a certain channel ($j$) and the total energy of an initial neutral molecule with ZPVE corrections

$$D_{aj} = \sum_i [E_{tot+ZPVE}(F_{ij})] - E_{tot+ZPVE}(M)$$  \hspace{1cm} (3)

Considering the direct dissociation following the electron attachment, we can calculate the direct dissociation energies ($D_d$) using the geometrical parameters of the neutral molecules

$$D_{dj} = \sum_i [E_{tot}(F_{ij}^M)] - E_{tot}(M)$$  \hspace{1cm} (4)

where $F_{ij}^M$ denotes the particular moiety in the neutral geometry. The standard counterpoise (CP) technique [10] is used for correcting basis-set-superposition errors (BSSE) in the $D_{dj}$ calculations,

$$D_{dj}^{CP} = \sum_i [E_{tot}^{*}(F_{ij}^M)] - E_{tot}(M)$$  \hspace{1cm} (5)

where $E_{tot}^{*}(F_{ij}^M)$ is calculated using the molecular basis sets.

All calculations were performed using Gaussian 98 package [11]. The Hartree-Fock self-consistent field method (HF-SCF) and the Becke’s three parameter hybrid functional method (Becke3-LYP) [12] with Dunning’s correlation consistent triple-zeta basis set augmented with diffuse functions (aug-cc-pVTZ) [13] were used for the geometrical optimizations and energy calculations. The second-order Møller-Plesset perturbation method (MP2) [14] was used for comparison with the above two methods. Although the dispersion interactions are neglected in the density functional theory methods, Becke3-LYP has been successful (or equivalent to MP2) in predicting geometries, binding energies and frequencies for many hydrogen-bonding species in which the dispersion interactions are usually considered to be extremely important [15]. Moreover, the accuracy for predicting anionic properties at the Becke3-LYP level has been demonstrated elsewhere [16,17]. All optimized geometries were confirmed to be the minima on the respective energy surfaces by the analytical frequency calculations at the HF-SCF and Becke3-LYP levels. Spin contamination was checked in the open-shell calculations. To elucidate the nature of electron attachments to CH$_2$FCN and CH$_2$ClCN, the natural charge analysis was made using the NBO 3.0 program [18] implemented in Gaussian 98. The present NBO analysis transformed the delocalized Becke3-LYP molecular orbital into localized orbital, providing insights into the chemical bonding characteristics in the neutral molecules and their anions.

III. RESULTS AND DISCUSSION

A. Electron attachment

The ground-state haloacetonitriles (CH$_2$FCN and CH$_2$ClCN), their anions, and the polyatomic fragments are shown in Fig.1 on the basis of the Becke3-LYP optimization calculations. The geometrical parameters and harmonic frequencies of the haloacetonitriles and their anions are given in Table I. For the neutral, the HF-SCF and Becke3-LYP calculations predicted the similar geometrical parameters, except for the small discrepancy ($\leq 0.036$ Å) of bond length; the harmonic vibrational frequency for each mode predicted at the Becke3-LYP level is distinctly smaller than that predicted at the HF-SCF level, indicating the different slopes of the molecular potential energy surfaces around the minima. For the anions, the discrepancies between the HF-SCF and Becke3-LYP results become more significant for CH$_2$FCN$^-$, and furthermore, the structure of anion CH$_2$ClCN$^-$ predicted at the HF-SCF level distinctly differs from that at the Becke3-LYP level. The bond CCl in this anion is predicted to be dissociated by the Becke3-LYP calculation, however, there are no significant differences between the structures of...
TABLE I Geometrical parameters ($R$ in Å and $A$ in (°)) and harmonic frequencies (cm$^{-1}$) of haloacetonitriles and anions

<table>
<thead>
<tr>
<th></th>
<th>Neutral</th>
<th>Becke3-LYP</th>
<th>MP2</th>
<th>Anion</th>
<th>Becke3-LYP</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF-SCF</td>
<td></td>
<td></td>
<td>HF-SCF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$FCN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R$(CC)</td>
<td>1.474</td>
<td>1.464</td>
<td>1.466</td>
<td>1.478</td>
<td>1.456</td>
<td>1.469</td>
</tr>
<tr>
<td>$R$(CH)</td>
<td>1.080</td>
<td>1.091</td>
<td>1.088</td>
<td>1.080</td>
<td>1.098</td>
<td>1.092</td>
</tr>
<tr>
<td>$R$(CN)</td>
<td>1.125</td>
<td>1.149</td>
<td>1.170</td>
<td>1.127</td>
<td>1.160</td>
<td>1.170</td>
</tr>
<tr>
<td>$R$(CF)</td>
<td>1.348</td>
<td>1.384</td>
<td>1.380</td>
<td>1.353</td>
<td>1.403</td>
<td>1.385</td>
</tr>
<tr>
<td>$A$(CCN)</td>
<td>178.3</td>
<td>178.6</td>
<td>178.6</td>
<td>179.3</td>
<td>166.1</td>
<td>178.6</td>
</tr>
<tr>
<td>$A$(CCF)</td>
<td>110.3</td>
<td>110.6</td>
<td>110.1</td>
<td>109.1</td>
<td>111.8</td>
<td>109.3</td>
</tr>
<tr>
<td>$A$(HCF)</td>
<td>109.2</td>
<td>108.6</td>
<td>108.8</td>
<td>109.7</td>
<td>107.4</td>
<td>109.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$ClCN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R$(CC)</td>
<td>1.463</td>
<td>1.452</td>
<td>1.456</td>
<td>1.465</td>
<td>1.380</td>
<td>1.458</td>
</tr>
<tr>
<td>$R$(CH)</td>
<td>1.076</td>
<td>1.086</td>
<td>1.086</td>
<td>1.077</td>
<td>1.076</td>
<td>1.091</td>
</tr>
<tr>
<td>$R$(CN)</td>
<td>1.126</td>
<td>1.149</td>
<td>1.171</td>
<td>1.126</td>
<td>1.168</td>
<td>1.171</td>
</tr>
<tr>
<td>$R$(CCI)</td>
<td>1.779</td>
<td>1.805</td>
<td>1.781</td>
<td>1.790</td>
<td>2.973</td>
<td>1.794</td>
</tr>
<tr>
<td>$A$(CCN)</td>
<td>178.4</td>
<td>178.7</td>
<td>178.8</td>
<td>179.9</td>
<td>178.8</td>
<td>179.4</td>
</tr>
<tr>
<td>$A$(CCI)</td>
<td>111.4</td>
<td>111.6</td>
<td>110.9</td>
<td>109.9</td>
<td>127.1</td>
<td>109.7</td>
</tr>
<tr>
<td>$A$(HCCI)</td>
<td>108.0</td>
<td>107.5</td>
<td>108.0</td>
<td>108.4</td>
<td>87.17</td>
<td>108.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ N in-plane wagging.
$^b$ CCN out-of-plane bending.
$^c$ CCN in-plane bending.
$^d$ CCF(Cl) bending.
$^e$ CH$_2$ out-of-plane wagging.
$^f$ CC, CF(Cl) stretching.
$^g$ CH$_2$ symmetric wagging.
$^i$ HCH bending.
$^j$ CN stretching.
$^k$ CH symmetric stretching.
$^l$ CH asymmetric stretching.
$^m$ Cl in-plane wagging.

 DOI:10.1088/1674-0068/21/03/255-262 ©2008 Chinese Physical Society
the neutral and the anionic CH$_2$ClCN by the HF-SCF calculations. It is interesting to compare the structural parameters and vibrational frequencies of the neutral with those of the anion predicted at the Becke3-LYP level. The bond lengths $R$(CX, X=F,Cl) and $R$(CN) are elongated and the bond angles $\angle$(CCX) are widened from the neutral to the anions. The sequence for two vibrational modes (1032.5 cm$^{-1}$, CH$_2$ out-of-plane wagging and 1061.2 cm$^{-1}$, CC, CF stretching) is reversed (943.6 cm$^{-1}$ and 988.6 cm$^{-1}$), from CH$_2$FCN to CH$_2$FCN$^-$. Due to the dissociation between Cl$^-$ and CH$_2$CN in the anion, the lowest frequency 39.85 cm$^{-1}$A$''$ is noted as Cl in-plane wagging; the other two low frequencies 168.8 cm$^{-1}$A$''$ and 171.3 cm$^{-1}$A$''$ correspond to ClCl stretching and CH$_2$ wagging. This low value of the CH$_2$ wagging frequency may be explained by the weak interactions between Cl$^-$ and CH$_2$CN (see Fig.1). The frequencies 406.3 cm$^{-1}$A$'$', 483.3 cm$^{-1}$A$'$, 602.8 cm$^{-1}$A$'$, 1015.8 cm$^{-1}$A$'$', and 1057 cm$^{-1}$A$'$ of CH$_2$ClCN$^-$ are close to those of the radical CH$_2$CN (386.9 cm$^{-1}$B$_2$, 434.2 cm$^{-1}$B$_1$, 680.7 cm$^{-1}$B$_1$, 1036.5 cm$^{-1}$B$_2$, and 1058.0 cm$^{-1}$A$_1$). It is also interesting to compare the HF-SCF and Becke3-LYP with the MP2 results. For the neutral, the results given by the MP2 calculations are a little closer to those predicted by the Becke3-LYP; while the MP2 results are closer to the HF-SCF for the anions, in particular, for CH$_2$ClCN$^-$. In general the distinct discrepancy of the anionic structures between CH$_2$FCN$^-$ and CH$_2$ClCN$^-$ predicted at the Becke3-LYP level indicates that the dissociation dynamics should be different.

In Table II, the natural charge analysis and the other electronic properties of the anions are presented together with the properties of the neutral for comparison. For the neutral, the Becke3-LYP calculations predict that the haloacetonitriles will have similar $\mu$ values vectoring from the halogen and cyano (negative) to CH$_2$ group (positive). One may notice that the negative charge of F is much larger than the Cl charge, presumably interpreted by the different intramolecular interactions between the halogen and cyano group [19]. When an electron is vertically attached to CH$_2$FCN, the CH$_2$ group is charged negatively (totally $\sim-0.914$) and only a little negative charge is added to F and N atoms that are negatively charged with almost equivalent populations, which is different from the neutral and the adiabatic anion. With the geometrical relaxation due to the electron-nuclei correlations, the negative charge on the CH$_2$ group transfers to F and N atoms in the adiabatic anion. The similar situation occurs in CH$_2$ClCN$^-$. Although the very small negative charge is still localized on the CH$_2$ group, the larger negative charge transfers to Cl; finally the Cl atom charged with a negative unit is dissociated for the adiabatic CH$_2$ClCN$^-$ anion. On the basis of the above natural charge analysis at the Becke3-LYP level, the conclusions can be derived: these vertical-attached anions can be of the dipole-bounded type; the relaxed adiabatic anion CH$_2$FCN$^-$ is still partly dipole-bounded but mainly valence-bounded $\pi_{\text{CN}}^\ast$ (negative charge increases $\sim-0.13$ on the bond CN with respect to that in the neutral); the adiabatic anion CH$_2$ClCN$^-$ can be treated as hydrogen-bonding and electrostatic bounded (C$^1-0.82974\times10^{2}\ll\text{H}^2\times(0.22557)$) cluster. Moreover, the electronic spatial extension $\langle R \rangle^2$ and dipole moment also indicate that the additional electron should be bounded in the different types, because the vertical-attached an-
ions have much larger values respective to the adiabatic anions. The extremely large \(\langle R \rangle^2\) value of the adiabatic CH\(_2\)CICN\(^−\) anion is due to the CI dissociation predicted at the Becke3-LYP level. The HF-SCF calculations predict the very large values of the \(\langle R \rangle^2\) (except for the \(\langle R \rangle^2\) of the adiabatic CH\(_2\)CICN\(^−\) anion) and the exaggeratedly large \(\mu\) values of the anions, indicating that the electron correlation is necessary to be precisely describe the electronic structures of anions.

Accordingly, the electron densities of the lowest unoccupied molecular orbitals (LUMOs) and the single occupied molecular orbital (SOMOs) of vertical-attached and adiabatic anions have been plotted in Fig.2. The HF-SCF calculations predicted the diffuse electron distributions of LUMOs of CH\(_2\)FCN and CH\(_2\)CICN and the additional electron is occupied at this diffuse orbital or is bounded diffusely, the electron distributions predicted at the Becke3-LYP level are distinctly different between the neutral LUMO and the anionic SOMO. Although the vertically-attached electron may be bounded diffusely around the CH group, the electron distribution mainly appears as the antibond \(\pi_{\text{CN}}^*\) in the SOMO of CH\(_2\)FCN (see Fig.2(a)) and as the antibond \(\sigma_{\text{CICl}}\) (actually the Cl3p in-plane orbital) in the SOMO of CH\(_2\)CICN\(^−\) (see Fig.2(b)). All differences for the anions predicted at the HF-SCF and Becke3-LYP levels may be explained by the following facts: the long-range Coulomb interactions in the HF scheme lead to the diffuse electron distributions, while the short-ranged dipole interactions can be treated well with electron correlations in the Becke3-LYP functional.

The values of \(\text{EEA}_a\) and \(\text{EEA}_n\), given by the MP2 calculations imply the contrary conclusion. Furthermore, the nucleic contributions \(\Delta E_n\) to \(\text{EEA}_n\) indicate that the geometrical relaxation owing to the electron attachment is predicted to be significant at the Becke3-LYP level. The theoretical comparison suggests that the second-order perturbation corrections to the HF wave functions in the MP2 scheme may be inadequate for these anions, and the short-ranged interactions between an attached electron and the target molecule can be reasonably described by the hybrid exchange-correlation functional. According to the anionic stability respective to the neutral [2], the present Becke3-LYP calculations predict that the CH\(_2\)FCN\(^−\) is at the shape-resonance state while CH\(_2\)CICN\(^−\) is at the Feshbach-resonance state.

### B. Dissociation dynamics

Five fragments (CHCN\(^−\), F\(^−\), CN\(^−\), CFCN\(^−\), and CHFCN\(^−\)) were observed at the collision energy of

<table>
<thead>
<tr>
<th>(\text{CH}_2\text{FCN})</th>
<th>(\text{CH}_2\text{CICN})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-SCF 56.0861</td>
<td>HF-SCF 55.6907</td>
</tr>
<tr>
<td>Becke3-LYP 21.4250</td>
<td>Becke3-LYP 16.9268</td>
</tr>
<tr>
<td>MP2 42.9655</td>
<td>MP2 38.3376</td>
</tr>
</tbody>
</table>

\(\text{EEA}_a\) and \(\text{EEA}_n\) calculated by the MP2 calculations imply the alternative conclusion. Furthermore, the nucleic contributions \(\Delta E_n\) to \(\text{EEA}_n\) indicate that the geometrical relaxation owing to the electron attachment is predicted to be significant at the Becke3-LYP level. The theoretical comparison suggests that the second-order perturbation corrections to the HF wave functions in the MP2 scheme may be inadequate for these anions, and the short-ranged interactions between an attached electron and the target molecule can be reasonably described by the hybrid exchange-correlation functional. According to the anionic stability respective to the neutral [2], the present Becke3-LYP calculations predict that the CH\(_2\)FCN\(^−\) is at the shape-resonance state while CH\(_2\)CICN\(^−\) is at the Feshbach-resonance state.
0.8 eV, with an intensity ratio 1000:250:4:3:3 [3]. The calculated \( D_a \) and \( D_d \) energies of the above dissociated processes as well as those for CH\(_2\)CICN\(^-\) are listed in Table IV. The BSSE corrections to \( D_d \) are very small (<9.36 kJ/mol) because the large basis set aug-cc-PVTZ was used throughout the calculations. The \( D_a \) values were predicted to be much smaller than the \( D_d \) values for CH\(_2\)FCN\(^-\), which is contrast to the dissociation processes of Cl\(^-\), CN\(^-\), and H from CH\(_2\)CICN\(^-\) at the Becke3-LYP level of theory. The energies \( D_d \) for two atoms dissociated from the parent anion are more than 418 kJ/mol, due to two bonds being broken. The recombination of two dissociated atoms reduces the dissociation energies significantly (see the \( D_a \) values in Table IV). Unfortunately, the strong spin contaminant ((\( S \))^2 > 0.8) was found in the MP2 calculations for the adiabatic and direct dissociations to produce F\(^-\) or Cl\(^-\). The HF-SCF calculations indicate that these dissociation processes except for CH\(_2\)CICN\(^-\)→CH\(_2\)CN+Cl\(^-\) are endothermic, which is consistent with the Becke3-LYP results. The \( D_d \) values suggest that the processes CH\(_2\)FCN\(^-\)→CH\(_2\)CN+F \(^+\) and CH\(_2\)FCN\(^-\)→CHCN\(^+\)+HF are energetically favorable with respect to the others. The observation of the higher intensity of CHCN\(^-\) with respect to that of F\(^-\) [3] perhaps suggests that the anion F\(^-\) reacts with the CH\(_2\)CN radical to produce more CHCN\(^-\).

The energetic sequence of the \( D_a \) values to produce CN\(^-\), CHCN\(^-\), and CHFCN\(^-\), given by the Becke3-LYP calculations, are in good agreement with the observations [3]. Moreover, the \( D_d \) energies to produce CN\(^-\), CHCN\(^-\), and CHFCN\(^-\) are much larger than those to produce Cl\(^-\) for CH\(_2\)CICN\(^-\) at the Becke3-LYP level. In particular, the negative \( D_d \) value (−50.75 kJ/mol) for the Cl\(^-\) fragment indicates that the process CH\(_2\)CICN\(^-\)→CH\(_2\)CN+Cl\(^-\) may be a direct (fast) dissociation while CH\(_2\)FCN\(^-\)→CH\(_2\)CN+F \(^+\) undergoes a temporary stable anionic state, at the Becke3-LYP theoretical level. Moreover, on the basis of the experimental spectra (Fig.2 in Ref.[3]), one can estimate that the appearance energy (electron energy at the half height of the integrated spectra) is about 0.4 eV for the fragments F\(^-\), CN\(^-\), and CHCN\(^-\) while this value is a little larger for CFCN\(^-\) and CHFCN\(^-\). The Becke3-LYP calculations give the \( D_d \) values: 0.345 eV (F\(^-\)), 0.435 eV (CHCN\(^-\)), 0.70 eV (CN\(^-\)), 1.093 eV (CFCN\(^-\)), and 2.03 eV (CHFCN\(^-\)). The appearance energy of Cl\(^-\) may be negative from Fig.1 in Ref.[3], supported by the \( D_d \) value (−50.75 kJ/mol, \( \sim \)-0.526 eV) in this work. In Fig.1 and Fig.2 of Ref.[3], the band shape of Cl\(^-\) differs significantly from that of F\(^-\) besides the peak positions: the former has a big tail extending to the high electron energy while the latter is a symmetric peak. This suggests that the potential energy curve for CH\(_2\)CICN\(^-\)→CH\(_2\)CN+Cl\(^-\) is decreasingly sharper than that of CH\(_2\)FCN\(^-\)→CH\(_2\)CN+F \(^+\), on the basis of the reflection principle of the potential energy curves [2,20,21]. This will be proved by the further calculations given below.

The relaxed potential energy curves are plotted in Fig.3 with the Becke3-LYP calculations by scanning bond lengths CC and CF or CCl of the neutral and anions. One can find the distinct differences between these two molecules: the dissociation energies of the CC bonds in the neutral CH\(_2\)FCN, CH\(_2\)CICN, and anion CH\(_2\)CICN\(^-\) are predicted to be extremely high, while it may be lower than 125.4 kJ/mol for CH\(_2\)FCN\(^-\) (Fig.3 (a) and (b)), the CF or CCl dissociation in anion becomes more energetically favorable than in the neutral, a temporary stable anionic state CHFCN\(^-\) exists, showing a local minimum point with an energy barrier about 6.7 kJ/mol, and a direct dissociation process is predicted along the CCl bond in CH\(_2\)CICN\(^-\), which is contrast to the increasing energies predicted.

**TABLE IV Adiabatic dissociation energies (\( D_a \) in kJ/mol) with zero-point-vibration energy (ZPVE) corrections and directed dissociation energies with the standard counterpoise for basis-set-superposition-error corrections (\( D_{d/cp} \) in kJ/mol).**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( D_{a/cp} )</th>
<th>( D_{d/cp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2\text{CFCN}^- \rightarrow \text{CHCN}+\text{HF}^a )</td>
<td>( 49.54 )</td>
<td>( 42.01 )</td>
</tr>
<tr>
<td>( \text{CH}_2\text{FCN}^- \rightarrow \text{CH}_2\text{CN}+\text{F} )</td>
<td>( 45.56 )</td>
<td>( 33.26 )</td>
</tr>
<tr>
<td>( \text{CH}_2\text{FCN}^- \rightarrow \text{CH}_2\text{F}+\text{CN}^- )</td>
<td>( 37.45 )</td>
<td>( 67.70 )</td>
</tr>
<tr>
<td>( \text{CH}_2\text{CICN}^- \rightarrow \text{CH}_2\text{CN}+\text{Cl}^- )</td>
<td>( -144.85 )</td>
<td>( 56.99 )</td>
</tr>
<tr>
<td>( \text{CH}_2\text{CICN}^- \rightarrow \text{CH}_2\text{Cl}+\text{CN}^- )</td>
<td>( -80.08 )</td>
<td>( -50.79 )</td>
</tr>
</tbody>
</table>

\(^a\) For the calculations of \( D_{d/cp} \) values, HF, HCl, and H\(_2\) are treated as two fragments rather than molecules.

DOI:10.1088/1674-0068/21/03/255-262 ©2008 Chinese Physical Society
FIG. 3 Potential energy curves calculated by the relaxed scan at the Becke3-LYP level for dissociations CX bonds (X=F,Cl) in the neutral (solid line) and the anions (broken line), for dissociations CC bonds in the neutral (solid line) and anions (broken line); the energies are calibrated by the start point. CH$_2$FCN and CH$_2$FCN$^-$ in (a) and (b), CH$_2$ClCN and CH$_2$ClCN$^-$ in (c) and (d).

by the MP2 calculations (Fig.3 (c) and (d)). However, the above analyses on the experimental spectra support the Becke3-LYP results. In Fig.3(a), another minimum point exists at about 2.2 Å on the CF curve, about 60 meV lower than the transition state and less than 10 meV lower than the separated fragments. The latter smaller energy is mostly due to electrostatic interactions between F$^--$δ$_1$····H$_2$×(+δ$_2$), which is similar to Cl$^-0.82974$····H$_2$×(+0.22557) in the anionic CH$_2$ClCN$^-$. 

IV. CONCLUSION

The molecular properties and dissociation dynamics were theoretically investigated together with analysis of the experimental spectra reported in Ref.[3]. Several different characteristics between CH$_2$FCN$^-$ and CH$_2$ClCN$^-$ are predicted by the Becke3-LYP calculations: (i) The additional electron is bounded diffusely (or dipole-bounded) in the vertical attachment, while the dipole-bounded electron may transfer to be valence-bounded (i.e. occupying $\pi_{\text{CN}}$ for CH$_2$FCN$^-$ or $\sigma_{\text{CC}}^*$ for CH$_2$ClCN$^-$), finally to form Cl$^-$ by occupying the Cl3p in-plane orbital. (ii) The vertical electron attachments to CH$_2$FCN and CH$_2$ClCN are endothermic and the geometrical relaxations of CH$_2$ClCN$^-$ lead to the exothermic dissociation CH$_2$ClCN$^-$→CH$_2$CN+Cl$^-$. (iii) Calculations of dissociation energies can qualitatively interpret the experimental spectra [3]. (iv) Further calculations of the potential energies indicate that CH$_2$FCN$^-$→CH$_2$CN+F$^-$ undergoes a temporary state and it is a nonadiabatic process, while CH$_2$ClCN$^-$→CH$_2$CN+Cl$^-$ is a typical direct dissociation process. Moreover, the HF-SCF calculations cannot give reasonable predictions for these two anions, and the distinctly different results for CH$_2$ClCN$^-$ are predicted at the Becke3-LYP and MP2 levels of theory.

V. ACKNOWLEDGMENT

This work was supported by the Program of New-Century Excellent Talents in Universities, Ministry of Education of China.