Semi-Classical Dynamics Studies of the Photodissociation of ICN\(^{-}\) and BrCN\(^{-}\)

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Quantum Dynamics Calculations on ICN$^-$ and BrCN$^-$

Quantum Dynamics Calculations on ICN$^-$ and BrCN$^-$

<table>
<thead>
<tr>
<th>Product</th>
<th>I$^-$ + CN</th>
<th>Br$^-$ + CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Branching</td>
<td>96</td>
<td>34</td>
</tr>
</tbody>
</table>

Quantum Dynamics Calculations on ICN⁻ and BrCN⁻

Branching and CN Rotation

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<tr>
<td>Branching</td>
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<tr>
<td>%E_{CN,rotation}</td>
<td>20</td>
<td>12</td>
</tr>
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</table>

ICN$^-$-(Ar)$_n$ Photodissociation

Experimental Photoproducts of ICN$^-$-(Ar)$_n$ Dissociation using 2.5 eV Photons

- Extend the theoretical studies of the ICN$^-$ and BrCN$^-$ to the ICN$^-$-(Ar)$_n$ and BrCN$^-$-(Ar)$_n$ clusters
- Investigate the photodissociation processes of the clusters with classical dynamics instead of quantum dynamics calculations

ICN$^-$($\text{Ar}$)$_n$ Photodissociation

Experimental Photoproducts of ICN$^-$($\text{Ar}$)$_n$ Dissociation using 2.5 eV Photons

Classical Dynamics Questions

✧ How well does the classical mechanics with surface hopping reproduce the branching calculated in the quantum dynamics?

✧ How is the energy distributed among the various degrees of freedom?

✧ Is there evidence in the bare anion of possible recombination?

✧ Investigate the photodissociation processes of the clusters with classical dynamics instead of quantum dynamics calculations

| Differences between the Calculations in the Quantum and Classical Dynamics |
|-------------------------------------------------|-----------------|-------------------------------------------------|
| **Quantum**                                     | **Classical**   |
| 1. CN Stretch Fixed at the equilibrium distance | Harmonic oscillator approximation of $r$ |
| 2. Definition of $\theta$ for $J = 0$          | Isotropic       | Restricted in a plane                          |
Semi-Classical Dynamics Initiated on $^2\Pi_{1/2}$ State

Average Product Branching and Energy Distribution
Semi-Classical Dynamics Initiated on $^2\Pi_{1/2}$ State

Average Product Branching and Energy Distribution

Product Branching

- Product branching depends on the calculations and representation
Semi-Classical Dynamics Initiated on $^2\Pi_{1/2}$ State

Average Product Branching and Energy Distribution

- Product branching depends on the calculations and representation
- Energies partitioning in the quantum and classical dynamics are different
Semi-Classical Dynamics Initiated on $^2\Pi_{1/2}$ State

**Average Product Branching and Energy Distribution**

**Questions on the Classical Dynamics Results:**

- Why are there differences in the classical and quantum dynamics?
- How can we understand these differences?
- What will be a better approach to the problem and what can be learned about the system?

- Product branching depends on the calculations and representation.

- Energies partitioning in the quantum and classical dynamics are different.
Treatment of Bend in the Dynamics Calculations

- **Quantum**: the bend motion is defined relative to spherical coordinates.
- **Classical**: the bend motion is constrained to a plane.
- **Consequence**: differences in the energy distributions or even the branching ratios in the dynamics.
Treatment of Bend in the Dynamics Calculations

- **Quantum**: the bend motion is defined relative to spherical coordinates.

- **Classical**: the bend motion is constrained to a plane

- **Consequence**: differences in the energy distributions or even the branching ratios in the dynamics.

- Perform the quantum dynamics calculations with constraint on the molecular motion to a plane.

- How will the branching ratios and energy distributions change?
Quantum Dynamics Calculations with Planar Approximations

Average Product Branching and Energy Distribution

Product Branching

- The product branching changes
- Increase in translational energy
- Decrease in rotational energy

Energy Distribution

CD = Classical Dynamics; QD = Quantum Dynamics
Quantum Dynamics Calculations with Planar Approximations

Average Product Branching and Energy Distribution

Constraining the molecular motion to a plane changes the product branching and energy partitioning!!!

The treatment of the bend in the classical and quantum dynamics leads to differences in the branching ratios and energy distributions

- The product branching changes
- Increase in translational energy
- Decrease in rotational energy

CD = Classical Dynamics; QD = Quantum Dynamics
Classical Dynamics: A Closer Look at the Dissociation of ICN$^-$

Selected trajectory runs Starting on the $^2\Pi_{1/2}$ State

Anionic fragments undergo multiple collision along the trajectory
ICN\(^-\)(Ar)\(_n\) Photodissociation

Experimental Photoproducts of ICN\(^-\)(Ar)\(_n\) Dissociation using 2.5 eV Photons

Number of Parents Argon Atoms (n)  Number of Parents Argon Atoms (n)
Number of Parents Argon Atoms (n)

Possible stabilization of the longer lived bare anions upon solvation leading to recombined product.

Summary

- Comparing the classical dynamics with surface hopping with the quantum dynamics calculations:
  - Branching ratios depend on the representation used in the calculations.
  - Energy is transferred from rotation to translation

- Treatment of the bend motion leads to differences in the energy distributions and branching ratios
  - Confirmed by performing quantum dynamics calculations with planar approximation to the bend motion

- The dissociation process in the classical dynamics show some anions undergo multiple collisions before dissociating.
  - Solvation may stabilize these anions and lead to recombined products
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