Normal mode analysis on the relaxation of an excited nitromethane molecule in argon bath

Albert Wagner (Argonne National Laboratory)
Luis A. Rivera-Rivera (Texas A&M University) *

Outline

• Motivation
• Methods
  - MD calculations
  - post processing normal mode decomposition
• Results for CH$_3$NO$_2$ in an Ar bath
  - IVR vs. collisional relaxation
  - mode-specific vibrational and rotational decay

* Now at Ferris State University, Big Rapids, MI
Advanced internal combustion engine designs reach high enough pressures (~500 atm) that compromise the isolated binary collision approximation foundation of kinetics models.

- At low pressure, molecules undergo *isolated binary collisions*
  - Relaxation or reaction rates *proportional* to pressure

- At high pressure, molecules undergo collisions with *multiple partners* molecules and bath gas can cluster
  - Relaxation or reaction rates may *not be proportional* to pressure

- *Explicit molecule/bath-gas trajectories studies* of breakdown of isolated binary collision approximation.
Method: Molecular Dynamics

LAMMPS code with 3D periodic boundary conditions

1000 trajectories of 1 excited molecule in bath of 1000 Ar atoms at given T,P

Initial conditions were obtained in four steps:
(1) Determination of the equilibrium volumes at 300 K for the eight pressures studied
(2) Selection of microcanonical phase space points for the internal degrees of freedom of the excited molecule
(3) Equilibration of the Ar bath around the molecule, with the molecule held rigid and stationary during equilibration
(4) Assignment of thermal translational velocities to the molecule.
Method: Forces and Results

FORCES:

CH$_3$NO$_2$:

Sorescu, Rice, and Thompson

\[ V = \sum \{ \text{Morse stretches,} \]
\[ \text{harmonic bond angles,} \]
\[ \text{cosine dihedral angles} \} \]
\[ \leq \text{adjusted to selected} \]
\[ \text{experimental properties} \]

Ar-Ar:

\[ V = A \exp(-R/b) - C/R^6 \]
\[ \leq \text{adjusted to} \]
\[ \text{experimental potential} \]

Ar-H,O,N:

\[ V = A \exp(-R/b) - C/R^6 \]
\[ \leq \text{parameters by combination rules} \]
\[ \text{for O-O, N-N, H-H parameters} \]
**Method: Forces and Results**

**FORCES:**

**CH$_3$NO$_2$:**

Sorescu, Rice, and Thompson  

\[
V = \sum \{\text{Morse stretches, harmonic bond angles, cosine dihedral angles}\}
\]

\[\leq \text{adjusted to selected experimental properties}\]

**Ar-Ar:**

\[V = A \exp(-R/b) - C/R^6\]

\[\leq \text{adjusted to experimental potential}\]

**Ar-H,O,N:**

\[V = A \exp(-R/b) - C/R^6\]

\[\leq \text{parameters by combination rules for O-O, N-N, H-H parameters}\]


**RESULTS (JCP 142, 014303 (2015))**

CH$_3$NO$_2$: 50 kcal in vib/rot; Ar 300K bath

![Graph showing E(t) vs. Time (ps) with curves for E$_{vib}$, E$_{rot}$, and E$_{trans}$ with a peak at 100 atm.](attachment:image.png)
Method: Forces and Results

FORCES:

CH$_3$NO$_2$:

Sorescu, Rice, and Thompson

$V = \sum \{ \text{Morse stretches, harmonic bond angles, cosine dihedral angles} \}$

<= adjusted to selected experimental properties

Ar-Ar:

$V = A \exp(-R/b) - C/R^6$

<= adjusted to experimental potential

Ar-H,O,N:

$V = A \exp(-R/b) - C/R^6$

<= parameters by combination rules for O-O, N-N, H-H parameters


RESULTS (JCP 142, 014303 (2015))

CH$_3$NO$_2$: 50 kcal in vib/rot; Ar 300K bath

![Graph showing the relationship between energy and time for various conditions.]
**Method: Forces and Results**

**FORCES:**

CH$_3$NO$_2$: 50 kcal in vib/rot; Ar 300K bath

Sorescu, Rice, and Thompson  

\[ V = \sum \{ \text{Morse stretches, harmonic bond angles, cosine dihedral angles} \} \]
<= adjusted to selected experimental properties

Ar-Ar:

\[ V = A \exp(-R/b) - C/R^6 \]
<= adjusted to experimental potential

Ar-H,O,N:

\[ V = A \exp(-R/b) - C/R^6 \]
<= parameters by combination rules for O-O, N-N, H-H parameters  
Method: Forces and Results

**FORCES:**

**CH$_3$NO$_2$:**

Sorescu, Rice, and Thompson

\[ V = \sum \{\text{Morse stretches,} \]
\[ \text{harmonic bond angles,} \]
\[ \text{cosine dihedral angles}\} \]

\[ \leq \text{adjusted to selected} \]
\[ \text{experimental properties} \]

**Ar-Ar:**

\[ V = A \exp(-R/b) - C/R^6 \]

\[ \leq \text{adjusted to} \]
\[ \text{experimental potential} \]

**Ar-H,O,N:**

\[ V = A \exp(-R/b) - C/R^6 \]

\[ \leq \text{parameters by combination rules} \]
\[ \text{for O-O, N-N, H-H parameters} \]
\[ \text{as in Sorescu et al. } J. \text{ Phys. Chem. B} \text{ **1997**, } *101*, 798 \]

**RESULTS (JCP 142, 014303 (2015))**

**CH$_3$NO$_2$:** 50 kcal in vib/rot; Ar 300K bath
Method: Separation of Vibrational, Rotational Energies

Rhee & Kim formulation for mode specific energy analysis [JCP 107, 1394 (1997)]

- Defines two angular velocities

  Instantaneous: \( \omega = I^{-1} \cdot (X \otimes \frac{dX}{dt}) \)

  Eckart-conditioned equilibrium: \( \omega_r = I_r^{-1} \cdot (X_e \otimes \frac{dX}{dt}) \)
  where \( I_r \) has products of \( X^*X_e \)

- Decomposes \( \frac{dX}{dt} = v + u + (\omega_r \otimes X) \)
  where \( v = \) vibrational velocity
  \( u = (\omega - \omega_r) \otimes X \) (vib. angular motion)

- Decomposition of energy
  \( E_{vib} = (1/2) v \cdot v + (1/2) u \cdot u + \text{Potential Energy} \)
  \( E_{rot} = (1/2) \omega_r \cdot I \cdot \omega_r \)
  \( E_{vibrot} = u \cdot (\omega_r \otimes X) \)

Our additional derivations

- Kinetic energy of \( E_{vib} \) decomposed ONLY into vibrational normal modes
- \( E_{rot}, E_{vibrot} \) decomposed into BOTH vibrational and rotational normal modes

Post processing of \( E_{vib}, E_{rot}, E_{vibrot} \) into vib. and rot. normal mode components

- Above analysis of kinetic energy using archived atomic velocities and positions
- Assumption: Vibrational mode’s share of kinetic and potential energy are equal
Results: IVR vs. Vibrational Collisional Relaxation

- \[
\frac{[\text{Evib}(i,t) - E_\infty]}{\sum_j [\text{Evib}(j,t) - E_\infty]} = \text{Fraction of the total excess vibrational energy at time } t \text{ that belong to the } i\text{th mode (equal for all modes at } t = 0, 1/15)\]

- Collisional relaxation mode-specifically removes vibrational energy
  IVR equalizes vibrational energy in all the modes

- plot \[
\frac{[\text{Evib}(i,t) - E_\infty]}{\sum_j [\text{Evib}(j,t) - E_\infty]} \text{ scaled by } 1/2^{i-1}\]

<table>
<thead>
<tr>
<th>CH₃-NO₂</th>
<th>Hindered Rotor: 117 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>Symmetric Stretch: 2961 cm⁻¹</td>
</tr>
</tbody>
</table>

- \[
\frac{[\text{Evib}(i,t) - E_\infty]}{\sum_j [\text{Evib}(j,t) - E_\infty]} = 1/15 \]
  IVR > collision rates
- \[
\frac{[\text{Evib}(i,t) - E_\infty]}{\sum_j [\text{Evib}(j,t) - E_\infty]} = \sim 1/15 \]
  IVR \sim collision rates
- \[
\frac{[\text{Evib}(i,t) - E_\infty]}{\sum_j [\text{Evib}(j,t) - E_\infty]} <,> 1/15 \]
  IVR < collision rates
Results: mode-specific Evib decay

- mode-specific decay is pressure dependent
- pressure dependence mostly due to changing number of collision
  number of collision is proportional to density*Time = ρ*Time
Results: mode-specific Evib decay

- mode-specific decay is pressure dependent

- pressure dependence mostly due to changing number of collision
  number of collision is proportional to density*Time = \( \rho \times \text{Time} \)

- additional non-linear effects (e.g., multiple collision events) will not be discussed
Results: mode-specific Evib decay

mode-specific decomposition of Evib(t)

Class 1:
- 10 modes
- ~single exponential decay
- all ~same rate
Results: mode-specific Evib decay

mode-specific decomposition of Evib(t)

Class 1:
- 10 modes
- ~single exponential decay
- all ~same rate

Class 2:
- 3 modes
- ~single exponential decay
- all ~same faster rate
**Results: mode-specific Evib decay**

mode-specific decomposition of Evib(t)

Class 1:
- 10 modes
- ~single exponential decay
- all ~same rate

Class 2:
- 3 modes
- ~single exponential decay
- all ~same *faster* rate

Class 3:
- 2 modes
- *poly*exponential decay
- rate slows with depleted energy
Results: mode-specific Erot, Evibrot decay

ROTATIONAL mode-specific decomposition of Erot(t)

- All modes have an early fast relaxation
- mode 2 relaxes somewhat faster (rotation perpendicular to C-N-O-O plane)
- relaxation nearly complete

• no early relaxation effect
• mode 3 has biggest share (rotation about C-N axis)
• relaxation not nearly complete
Results: mode-specific Erot, Evibrot decay

VIBRATIONAL mode-specific decomposition of Erot(t)

- Order of magnitude smaller effect with only 5 vibrational modes important
- mode 1 (hindered rotation) biggest effect
In Rhee & Kim formulation

• Vibrational normal modes are components of $E_{vib}$, $E_{rot}$, and $E_{vibrot}$
• Rotational normal modes are only components of $E_{rot}$ and $E_{vibrot}$

For $CH_3NO_2$

• IVR begins to lose out against collisional relaxation at $\sim$50atm.

• Polyexponential behavior mainly in hindered rotor and $CH_3$ symmetric stretch.
Acknowledgments

- The Laboratory for Molecular Simulation at Texas A&M University for providing support and computer time.