Dissociation and Excitation of Molecules and Molecular Ions by Electron Impact

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Dissociation and Excitation

**DIRECT**

\[ AB^+ + e^- \rightarrow AB^+(v') + e^- \]  
\[ A + B^+ + e^- \]  
vibrational  
dissociation

**RESONANT**

\[ AB^+ + e^- \rightarrow AB^* \rightarrow AB^+(v') + e^- \]  
\[ A + B^+ + e^- \]  
vibrational  
dissociation
\[ A + B^* \]  
recombination
\[ A^- + B^+ \]  
ion-pair

**MUTUAL NEUTRALIZATION**

\[ A^- + B^+ \rightarrow A + B \]
Direct Processes

Vibrational excitation

Dissociative excitation

A + B

A* + B

A + B^+
Direct Processes

- Quantum chemistry calculations to determine potential energy curves
- Electron scattering calculations to determine T-matrix

\[
\sigma_{v \rightarrow k_v} (E) = \frac{k_v}{k_0} \int \left| \int \chi_v (R) f (E_0; R, \Omega) \chi_{k_v} (R) dR \right|^2 \frac{d\Omega}{4 \pi}
\]

\[
\sigma (E_0) = \frac{4 \pi}{k_0^2} \sum_{ll'm} \int \left| \chi_v (R) T_{ll'm}^{\Gamma \Gamma'} (R) \right|^2 dR
\]

δ-function approximation

\[
\sigma (E_0) = \sum_{ll'm} \int \sigma (E_0; R) \chi_v (R)^2 dR
\]
Complex Kohn Variational Method

Variational Functional for the T-Matrix (scattering amplitude)

\[
[T^{\Gamma_0}] = T^{\Gamma_0} - 2 \int \Psi_\Gamma (H - E) \Psi_{\Gamma_0} \\
\delta[T] = 0
\]

Trial wave function for the N+1 electron system

\[
\Psi_{\Gamma_0} = \sum_i A\{\Phi_\Gamma (r_1 \cdots r_N) F_{\Gamma \Gamma_0} (r_{N+1})\} + \sum_\mu d_{\mu}^{\Gamma_0} \Theta_\mu (r_1 \cdots r_{N+1})
\]

exchange  target  continuum  Correlation and Polarization

Continuum functions are further expanded in combined basis of Gaussians and continuum functions

\[
F_{\Gamma \Gamma_0} (r) = \sum_i c_i^{\Gamma \Gamma_0} \varphi_i (r) + [j_l (k_r r) \delta_{l0} \delta_{m0} + T_{l0mn0} h^+_l (k_r r)] Y_{l,m} (\hat{r}) / r
\]
HeH⁺ Direct Dissociative Excitation

FIG. 3. Total \( \chi^3 \Pi \rightarrow \chi^1 \Sigma^+ \) excitation cross section calculated at \( R = 0.77 \) Å. The inset shows measured dissociative exc cross sections for HeH⁺ (Ref. [1]) under low-extraction conditions where no hot bands are present.

FIG. 4. Total excitation cross section, averaged over the vibrational motion of ground state.
H$_3^+$ Direct Dissociative Excitation
Resonant vs Non-Resonant Collisions

- Electronic energy must be transferred into nuclear motion to produce vibrational excitation
- Non-resonant Collisions
  - 1800 times difference in mass
  - Electron collision time scale different from molecular vibration time scale
  - Inefficient transfer
- Resonant Collisions
  - Electron collision time commensurate with molecular vibration
  - Electron collision drives dissociation and vibration
Resonant Processes

Vibrational excitation

Dissociative excitation and recombination
Method of Attack

Split the problem into two parts:

Electron scattering at fixed nuclear geometries
  Calculate position and lifetime of the shape or Feshbach resonances

Nuclear dynamics during the resonant collision
  Calculate the quantum molecular dynamics leading to vibrational excitation or dissociative attachment/recombination
Position and Autoionization Width are determined by Breit-Wigner fit of the Eigenphase Sum

HeH⁺ Π Symmetry

Resonance peak gives a position and width: A complex energy for the resonance $E(R) = E_r - i\Gamma/2$ which can be understood qualitatively as:

$$|\Psi(r,t)|^2 = |\Psi(r)e^{-iEt}|^2 = |\Psi(r)|^2 e^{-\Gamma t}$$
Some working equations...

\[(E - K_R - V_{res}) \xi_v = \left(\frac{\Gamma(R)}{2\pi}\right)^{\frac{1}{2}} \eta_v(R)\]

Local complex potential or “Boomerang” model

\[V_{res}(R) = E_{res}(R) - i \frac{\Gamma(R)}{2}\]

Nonlocal potential model

\[V_{res}(R, R') = E_{res}(R)\delta(R - R') - i\pi \sum_{\nu}^{open} U_{\nu}(k_{\nu}, R)U_{\nu}(k_{\nu}, R')\]

\[U_{\nu}(k_{\nu}, R) = \left(\frac{\Gamma(R)}{2\pi}\right)^{\frac{1}{2}} \eta_v(R)\]
More working equations…

\[ H_{\text{Res}} = K_R + V_{\text{res}} \]

**Scattering amplitude**

\[ T_{f,i}(E) = \left| \Phi_{\text{final}} \left| \frac{1}{E - H_{\text{res}}} \right| \Phi_{\text{initial}} \right| \]

\[ \Phi_{\text{initial}} = \left( \frac{\Gamma(R)}{2\pi} \right)^{1/2} \eta_v(R) \]

**Cross section**

\[ \sigma_{f,i}(E) = \frac{4\pi^3}{k^2} \left| T_{f,i}(E) \right|^2 \]

\[ \frac{k^2(R)}{2} = E_{\text{res}} - E_{\text{tar}} \]
Local Complex Potential or “Boomerang” model for Resonant Vibrational Excitation in 1D (diatomics)

Time-dependent formulation \( \Phi_{\text{initial}}(R) = \left( \frac{\Gamma(R)}{2\pi} \right)^{1/2} \chi_i(R) \)

\[
T_{f,i}(E) = -i \int e^{iE_t} \langle \Phi_{\text{final}} | \Psi_t \rangle dt \\
_0^\infty
\]

with

\[
\Psi_t = e^{-iH_{\text{anion}}t} |\Phi_{\text{initial}}\rangle
\]
Example: $\text{He}_2^+$ Dissociative Recombination
He$_2^+$ Dissociative Recombination: Effect of Vibration

Including indirect

Direct
He$_2^+$ Dissociative Recombination: Isotope Effect
Example: HeH$^+$ Dissociative Excitation
Example: HeH$^+$ Dissociative Excitation

Example: HD$^+$ ion-pair channel
Example: HD$^+$ final states
Example: HD$^+$ ion-pair channel
HeH$^+$ New calculations
Ion-pair
$\text{H}_2$

Ion-pair $^1\Sigma_g^+$
$H_2$

Ion-pair $^1\Sigma_u$
At large $R$

$(1\sigma_g)^2 + (1\sigma_u)^2 \propto 1s_A(1)1s_B(2) + 1s_A(1)1s_B(2)$

bonding ground state

$(1\sigma_g)^2 - (1\sigma_u)^2 \propto 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)$

ion-pair state

• Construct

$$\langle \Phi_{IP} | H_{el} | \Phi_i \rangle$$

To obtain ion-pair curve

$$\langle \Phi_{IP} | H_{el} | \Phi_{IP} \rangle$$

To obtain couplings
Future Plans

• Continue studies of resonant vibrational and dissociative excitation in HeH$^+$
  – Study effects of target vibrational excitation
  – Study effects of isotopic substitution

• Include direct dissociative excitation

• Mutual Neutralization in He$^+$ H$^-$ collisions

• Final state distributions, HeH$^+$ and H$_2^+$
  – Include ion-pair channel

• Possible collaborative work on He$_2^+$