A Tale of Two Atoms or Studies of HeH: DR, VE, DE, RIP, PI, MN, …

Ann E. Orel
Asa Larson

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Studies of HeH/HeH$^+$

- Calculated accurate potential energy curves
  - Ion states
  - Neutral states
  - Autoionizing states
- Calculated autoionization widths
  - Complex Kohn variational method
- Calculated non-adiabatic coupling elements between all neutral states including the autoionizing states
  - Analytic non-adiabatic couplings from MESA
Level of Calculation

• Structure
  – Basis set
    • He aug-cc-pVQZ
    • H aug-cc-pVTZ
    • Extra diffuse functions to describe 3d states
    • 106 functions total
    • Full CI
  – Results
    • Reproduced asymptotic energies to roughly 200cm$^{-1}$
    • Reproduced crossing points of ion-pair curve to tenths of atomic units
Level of Calculation

• Non-adiabatic coupling elements
  – Same basis
  – Lowest 10 orbitals from MCSCF
  – Full CI in 10 orbitals, doubles outside

• Results
  – Reproduced full CI energies
Level of Calculation

• Scattering
  – Same basis
  – 10 Natural orbitals
  – Full CI in 10 orbitals, singles outside

• Results
  – Shifted energies, but relative to ion same energies as full CI
Problems being studied

- Direct Dissociative Excitation
- Resonant Excitation
  - Vibrational
  - Dissociative
  - Ion-pair formation
- Dissociative Recombination
  - Direct
  - Indirect
- Mutual Neutralization
- Penning Ionization
Resonant Processes

Vibrational excitation

Dissociative excitation and recombination
Local complex potential
or “Boomerang” model

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

Nonlocal potential model

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

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

\[U_{\nu}(k_{\nu}, R) = \left( \frac{\Gamma(R)}{2\pi} \right)^{1/2} \eta_{\nu}(R)\]

Some working equations…

\[\frac{k^2(R)}{2} = E_{res} - E_{tar}\]
More working equations...

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

Scattering amplitude

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

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

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)

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

Time-dependent formulation

\[ T_{f,i}(E) = -i \int_{0}^{\infty} e^{iE_t t} \langle \Phi_{\text{final}} | \psi_t \rangle dt \]

with

\[ \psi_t = e^{-iH_{\text{anion}} t} |\Phi_{\text{initial}}\rangle \]

Example: \( \text{N}_2 \)
HeH$^+$ Dissociative Excitation
Josefine Soder

HeH$^+$ and HeH Resonant States

Energy (eV) vs. Bond Distance (bohr)

- $^1\Sigma$
- $^3\Sigma$
- Resonance

He$^+$ + H → He$^*$ + H
He + H$^+$
HeH$^+$ Dissociative Excitation (OLD)

Resonant Curves

Electronic resonant states of HeH of $^2\Sigma^+$ symmetry
Autoionization Widths

Autoionization width of resonant states of HeH of \( ^2\Sigma^+ \) symmetry

Internuclear distance (\( a_0 \))

Autoionization width (au)
Resonant Dissociative Excitation ($v=0$)
Resonant Dissociative Excitation
Effect of vibration

![Graph showing cross section vs. energy for different vibrational levels (v=0, v=1, v=2).]
HeH$^+$
Direct Dissociative Excitation

Energy (eV) vs. Bond Distance (bohr)

$^1\Sigma$
$^3\Sigma$

He$^+$ + H
He + H$^+$
Direct Processes

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

\[
\sigma_{v \rightarrow k_v}(E) = \frac{k_v}{k_0} \int \int \chi_v(R) f(E_0; R, \Omega) \chi_{k_v}(R) dR \left| \sum_{l'l'm} \frac{1}{k_0^2} \int \chi_v(R) T_{l'l'm}^{TT'}(R) \right|^2 \frac{d\Omega}{4\pi}
\]

\[
\sigma(E_0) = \sum_{l'l'm} \int \sigma(E_0; R) \chi_v(R)^2 dR
\]

$\delta$-function approximation
Fixed Nuclei Cross Section

R=1.45 Bohr

Energy (eV)

Cross Section (Atomic Units)
HeH$^+$ Direct Dissociative Excitation

Effect of Resonances

Cross Section (cm$^2$)

Energy (eV)

$^3\Sigma$

$^3\Sigma$

Total
Resonances??

- First set of resonances ~25eV
  - Lie between first \((^3\Sigma)\) and second \((^1\Sigma)\) state of the ion
  - Dominate configuration \(H + He^*\)
  - Branching dominate to \(H^+\) and He
- First set of resonances ~35eV
  - Dominate configuration \(H^* + He^*\)
  - Could produce \(He^+\) and H
HeH$^+$ and HeH Resonant States

- $^1\Sigma$
- $^3\Sigma$
- Resonances
- Resonance

Energy (eV) vs. Bond Distance (bohr)

- He$^*$ + H$^*$
- He$^+$ + H
- He$^*$ + H
- He + H$^+$
Direct Dissociative Excitation

$v=0$

Cross section (cm$^2$)

Energy (eV)
HeH$^+$ Direct Dissociative Excitation

Effect of Initial State Vibration

Cross Section (cm$^2$)

Energy (eV)

$v=0$

$v=1$

$v=2$
Direct Dissociative Excitation

Comparison to Experiment ($v=0$)

- Expt
- Theory
- Theory (1991)

Cross Section ($\text{cm}^2$)

- $3\times10^{-17}$
- $2.5\times10^{-17}$
- $2\times10^{-17}$
- $1.5\times10^{-17}$
- $1\times10^{-17}$
- $5\times10^{-18}$
- $0$

- $10$
- $15$
- $20$
- $25$
- $30$
- $35$
- $40$
HeH⁺ New calculations
Ion-pair
Electronic resonant states of HeH of $^{2}\Sigma^{+}$ symmetry

Energy (H)

Internuclear distance ($a_0$)
Non-Adiabatic Couplings

Electronic resonant states of HeH of $^2\Sigma^+$ symmetry
No autoionization

Mutual Neutralization - Preliminary

Sifiso Nkambule
Future Plans

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

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

• Continue studies of direct and indirect dissociative recombination in HeH$^+$
  – Final state distributions
  – Include ion-pair channel
  – Study effects of target vibrational excitation
  – Study effects of isotopic substitution