Electron-impact excitation of molecular hydrogen: dissociation and vibrationally resolved cross sections

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Cross sections for electron scattering from H₂: before CCC (2016)

**Experiment**
- Only available for scattering from the ground state X $^1\Sigma_g^+ (v=0)$
- Good accuracy for the elastic scattering, total and ionization cross sections
- For excitation cross sections: large uncertainties, often highly inaccurate

**Theory**
- only small-size close-coupling calculations were available (R-matrix, Schwinger & Kohn variational methods, …), various DW models, impact-parameter method
  - limited to the ground state X $^1\Sigma_g^+ (v=0)$
  - highly inaccurate a few eV away from the excitation thresholds
- for scattering from excited states (vibrationally and electronically) only semiclassical impact-parameter method is available
CCC method: fixed-nuclei (FN) and adiabatic nuclei (AN) approaches

- Born-Oppenheimer approximation
- Fixed-nuclei approximation, $R = \text{fixed}$
- Diagonalization of the target Hamiltonian $H_T$ in a Sturmian (Laguerre) basis

$\Psi_i^{(+)}(x_p, x_i) = \mathcal{A} \sum_{n=1}^{N} F_n(x_p) \phi_n(x_i)$

$T_{fi}(\vec{k}_f, \vec{k}_i) = V_{fi}(\vec{k}_f, \vec{k}_i) + \sum_{n=1}^{N} \int d^3k \frac{V_{fn}(\vec{k}_f, \vec{k})T_{ni}(\vec{k}, \vec{k}_i)}{E + i0 - \varepsilon_n - k^2 / 2}$

$\sigma_{fi}(R) \propto \left| T_{fi}(R) \right|^2$
**CCC method:**
fixed-nuclei (FN) and adiabatic nuclei (AN) approaches

- Born-Oppenheimer approximation
- Fixed-nuclei approximation, $R = \text{fixed}$
- Diagonalization of the target Hamiltonian $H_T$ in a Sturmian (Laguerre) basis

\[
\Psi_i^{(+)}(x_p, x_i) = \mathcal{A} \sum_{n=1}^{N} F_n(x_p) \phi_n(x_i)
\]

- $N$-state multi-channel expansion
- Solve integral LS equation for the T-matrix

\[
T_{fi}(\vec{k}_f, \vec{k}_i) = V_{fi}(\vec{k}_f, \vec{k}_i) + \sum_{n=1}^{N} \int d^3k \frac{V_{fn}(\vec{k} f, \vec{k} i) T_{ni}(\vec{k}, \vec{k}_i)}{E + i0 - \varepsilon_n - k^2 / 2}
\]

- Cross sections

\[
\sigma_{fi}(R) \propto |T_{fi}(R)|^2
\]

- AN T-matrix

\[
T_{f \mu, iv}(E) = \int dR \ \varphi_{f \mu}(R) T_{fi}(E; R) \varphi_{iv}(R)
\]

- $\varphi_{n\mu}(R)$ are vibrational wave functions
- Vibrationally resolved cross sections

\[
\sigma_{f \mu, iv}(E) \propto |T_{f \mu, iv}(E)|^2
\]

- Single-center spherical coordinate formulation & spheroidal coordinate formulation
CCC method: PEC for molecular hydrogen

High accuracy of H₂ target states in the spheroidal formulation of CCC

![Graph showing energy levels of H₂ target states as a function of internuclear distance.](image-url)
Cross sections for electron scattering from $H_2$

**CCC:** 491, 427, 259, 92, 9-state close-coupling

- total cross section, total ionization cross section, stopping power
- elastic scattering (ICS, DCS)
- excitation cross sections (ICS, DCS) for
  - $b \quad 3\Sigma_u^+$, $a \quad 3\Sigma_g^+$, $c \quad 3\Pi_u$, $e \quad 3\Sigma_u^+$, $h \quad 3\Sigma_g^+$, $i \quad 3\Pi_g$, $j \quad 3\Delta_u$
  - $B \quad 1\Sigma_u^+$, $C \quad 1\Pi_u$, $EF \quad 1\Sigma_g^+$, $B' \quad 1\Sigma_u^+$, $D \quad 1\Pi_u$, $B'' \quad 1\Sigma_u^+$, $D' \quad 1\Pi_u$, $H \quad 1\Sigma_g^+$, $GK \quad 1\Sigma_g^+$, $I \quad 1\Pi_u$, $J \quad 1\Delta$
- dissociation into neutral fragments
- dissociative excitation of $B \quad 1\Sigma_u^+$, $C \quad 1\Pi_u$, $EF \quad 1\Sigma_g^+$, $B' \quad 1\Sigma_u^+$, $D \quad 1\Pi_u$ states
- excitations of $B \quad 1\Sigma_u^+$, $C \quad 1\Pi_u$, $EF \quad 1\Sigma_g^+$, $B' \quad 1\Sigma_u^+$, $D \quad 1\Pi_u$ states from vibrationally excited ground state $X \quad 1\Sigma_g^+ (\nu)$
- in preparation:
  - a data set of vibrationally resolved transitions $X \quad 1\Sigma_g^+ (\nu) \rightarrow B \quad 1\Sigma_u^+ (\nu')$, etc.
  - vibrational excitations of the ground electronic $X \quad 1\Sigma_g^+ (\nu)$ state via electron-impact (VCC)
  - excitation and radiative decay (ERD)
  - scattering from the metastable $c \quad 3\Pi_u (\nu=0)$ state

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e⁻-H₂ excitation ICS: B \(^1\Sigma^+_u\) - Lyman band

Oscillator Strength
- Fixed-nuclei CCC: 0.288


Janev & Miles comparisons

\[ b^3\Sigma_u^+, \ a^3\Sigma_g^+, \ c^3\Pi_u, \ e^3\Sigma_u^+, \ h^3\Sigma_g^+, \ i^3\Pi_g, \ j^3\Delta_u, \ B^1\Sigma_u^+, \ C^1\Pi_u, \ EF^1\Sigma_g^+, \ B^1\Sigma_u^+, \ D^1\Pi_u \]

Miles, Thompson, Green, J. App. Phys. 43 (1972) 678;
Janev, Reiter, Samm, JÜL-4105, Jülich, 2003

\[ \rightarrow \]

used by Ursel Fantz & Dirk Wuenderlich (Garching) in their CR model
e^−-H_2 total ionization cross section

recommended cross sections are due to Yoon et al.,
$e^{-}$-H$_2$ mass stopping power

$$-\frac{1}{\rho} \frac{dE}{dx} = \frac{N}{M} \sigma_{SP}$$

$$\sigma_{SP} = \sum_{n=1}^{N} (\varepsilon_n - \varepsilon_0) \sigma_n$$

$$= \bar{E} \sigma_{inel}$$

$\bar{E} = \frac{\sigma_{sp}}{\sigma_{inel}} = \frac{\sum_{n=1}^{N} (\varepsilon_n - \varepsilon_0) \sigma_n}{\sum_{n=1}^{N} \sigma_n}$

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E-bar from analysis of energy loss spectra

PEC for molecular hydrogen & dissociation

- repulsive first excited state $b^3\Sigma_u^+$
  - major dissociation channel at low energies

- all triplet state decay to $b^3\Sigma_u^+$ contributing to dissociation

- singlet states:
  - dissociative excitation
  - predissociation
  - excitation radiative decay dissociation
Electron-impact dissociation of H$_2$ : b $^3\Sigma_u^+$ state

Low energy (< 14 eV): AN approach is required
above 14 eV: FN approach is sufficient
Electron-impact dissociation of $H_2$: $b\;^3\Sigma_u^+$ state

New time of flight (TOF) spectrometer at California State University, Fullerton:

Old experiments: likely transmission problems for electrostatic spectrometer
Cross sections for the $b \, \Sigma_u^+$ state: experiment at California State University, Fullerton

$$R = \frac{\text{Inelastic}(b \, \Sigma_u^+)}{\text{Elastic}}$$

Cross sections for the $b \, ^3\Sigma_u^+$ state: experiment at California State University, Fullerton

$$R = \text{Inelastic}(b \, ^3\Sigma_u^+) / \text{Elastic}$$

Cross sections for the $b \ ^3\Sigma_u^+$ state: experiment at California State University, Fullerton

Electron-impact dissociation of $\text{H}_2$ : triplet states

Electron-impact dissociation of $\text{H}_2$ : singlet states

- singlet states:
  - dissociative excitation (DE)
  - predissociation (PD)
  - excitation radiative decay dissociation (ERDD)

- fully vibrationally resolved cross sections are required

$$\sigma_{f \mu, jv} (E) \propto |T_{f \mu, jv} (E)|^2$$

Have already published or submitted:
DE
ERD
$v$-$v'$ cross section data set

Electron-impact dissociation of H₂: singlet states

Electron-impact dissociation of H$_2$ to neutral fragments


Main features
- low energy dominated by the b $^3\Sigma_u^+$ state
- other triplet states make equally large contribution at the peak and above
- singlet states dominate above 50 eV:
  - At high energies (> 50 eV) the main dissociation pathway for H$_2$ is radiative decay to the ground state vibrational continuum via the B $^1\Sigma_u^+$ state.

Scattering from vibrationally excited states $X^{1\Sigma_g^+}(\nu)$


IP: semiclassical impact-parameter method – Bari group

Conclusions

- Large-scale close-coupling calculations for H₂ produced a comprehensive theoretical dataset of e-H₂ excitation cross sections
- Identified and resolved a major discrepancy for excitation of the b $^3\Sigma_{u}^+$ state in collaboration with Prof. Khakoo group (Fullerton)
- Provided first ab-initio estimates for dissociation of H₂
- in preparation: a detailed data set of vibrationally resolved cross sections for H₂
- Cross sections for isotopologues can be produced (D₂, HD, …)
- Results available from LXcat and ALADDIN databases