Extensions of Quantemol Electron Collisions (QEC) to handle isotopes and heavy elements

Greg Armstrong

Plasma Chemistry Data and Plasma Modelling Workshop
4th October 2023

Introduction to QEC

- Calculates cross sections for electron-molecule collisions.
- Molpro quantum chemistry package provides molecular target orbitals.
- Molecular R-matrix (UKRmol+) code calculates cross sections.
- Calculations set up using user-friendly GUI interface.

Introduction to QEC

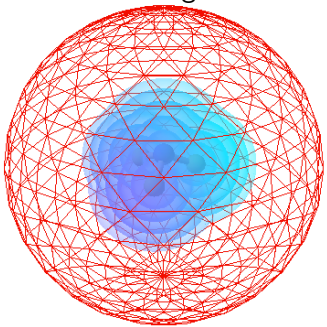
quantemol

- Calculates cross sections and rates for various collisional processes including:
  - Elastic scattering.
  - Momentum transfer.
  - Electronic, rotational, vibrational excitation.
  - Dissociative electron attachment.
  - Ionization.

R-matrix theory

- Space divided into inner, outer and asymptotic regions.
- Inner region confines the N-electron molecular target.

inner region



outer region

connection to asymptotic forms

Single outgoing electron

Exchange, correlation with inner electrons neglected

- Outer region wavefunction extends to large distances.
- Connection to asymptotic forms allows calculation of cross sections.

R-matrix theory: inner region

quantemol

- Solve $(N+1)$-electron time-independent Schrödinger equation using wavefunction expansion

$$\psi_k^{N+1} = \mathcal{A} \sum_{i,j} c_{ijk} \Phi_i^N(\mathbf{x}_1, ..., \mathbf{x}_N) \eta_{ij}(\mathbf{x}_{N+1}) + \sum_m b_{mk} \chi_m^{N+1}(\mathbf{x}_1, ..., \mathbf{x}_{N+1}).$$

- N-electron target wavefunctions $\Phi_i^N(\mathbf{x}_1, ..., \mathbf{x}_N)$ calculated using MOLPRO basis sets and orbitals.

R-matrix theory: outer region

quantemol

- Exchange and correlation with inner region electrons are neglected.
- Solve for the radial wavefunction of a single outgoing electron $(N+1)$:

$$\Psi^{N+1} = \sum_p \overline{\Phi}_p(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \frac{F_p(r_{N+1})}{r_{N+1}}.$$

- At large distances ($r_{N+1} = 100a_0$), solutions connect to asymptotic forms to calculate K and T matrices, and cross sections.

Isotope selection

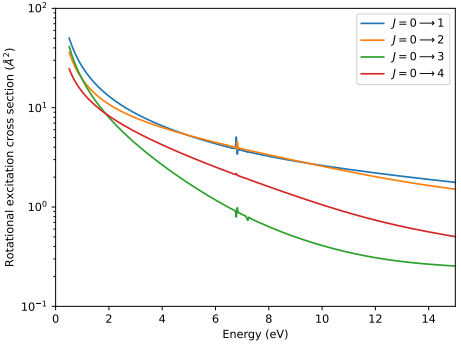
quantemol

- Isotope library now available for all elements.
- Most abundant isotope selected as default.
- Important in astrophysical applications, where major astronomical and terrestrial isotopes differ.

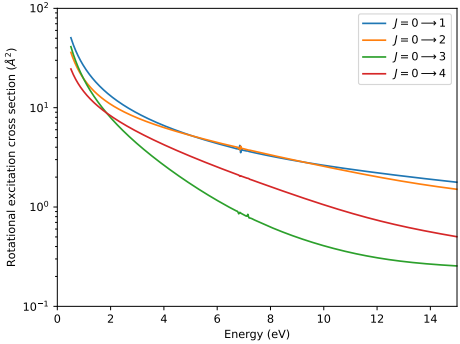
Cross sections and dipole moments for ArH^+

ArH^+ dipole moments		
$^{36}ArH^+$	$^{38}ArH^+$	$^{40}ArH^+$
2.2233	2.2319	2.240

$^{36}ArH^+$



$^{40}ArH^+$



MOLPRO basis sets for heavy elements

quantemol

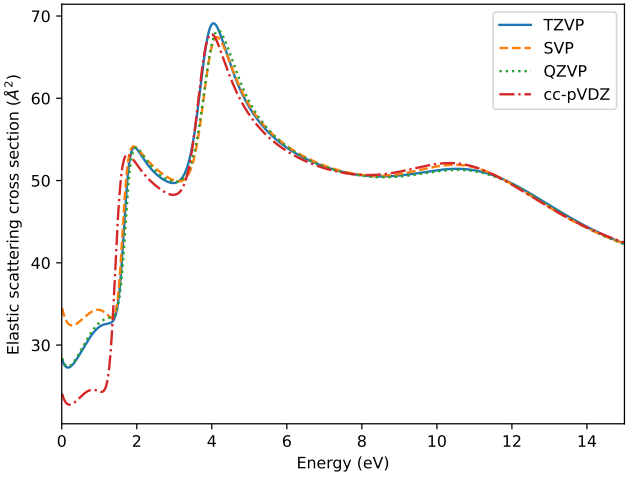
- Heavy: molecules containing elements Ar-Kr.
- Consider all-electron basis sets without core potentials.
- Dunning (cc-pVXZ) and Pople (X-YZWG) basis sets are commonly used.
- Pople basis sets only available for H-Ar.
- Include Karlsruhe bases in QEC for elements Ar-Kr.

Karlsruhe basis sets

quantemol

- Main hierarchy of Karlsruhe basis sets is:
  - def2-SVP — Split valence polarization.
  - def2-TZVP — Valence triple-zeta polarization
  - def2-QZVP — Valence quadruple-zeta polarization
- Analogous to cc-pV(D/T/Q)Z basis sets.
- Can include diffuse functions (similar to aug-cc-pVXZ).

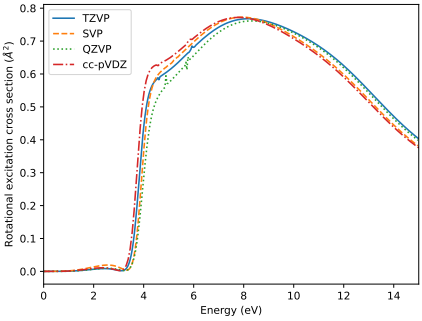
Elastic scattering cross section for $GeCl_4$



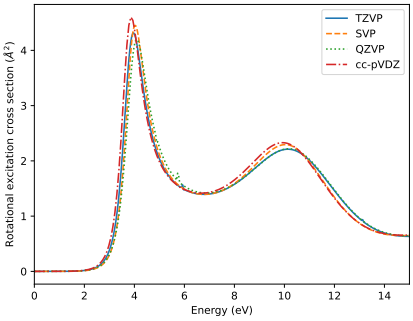
Rotational excitation cross section for $GeCl_4$

quantemol

$J = 0 \longrightarrow 1$



$J = 0 \longrightarrow 2$



Vibrational frequencies for $GeCl_4$

quantemol

$GeCl_4$				
NIST	cc-p		def2-	
(cm^{-1})	VDZ	VTZ	SVP	TZVP
396	399	404	403	407
134	126	124	130	126
453	470	472	478	475
172	171	171	175	172

Conclusions

quantemol

- Rates and cross sections can now be calculated for any isotope.
- Calculations for elements Ar-Kr can be performed using Karlsruhe basis sets.

Vibrational frequencies for $TiCl_4$

$TiCl_4$					
NIST	cc-p		def2-		
(cm^{-1})	VDZ	VTZ	SVP	TZVP	TZVPD
389	384	391	381	395	394
114	118	115	122	116	114
498	510	514	508	518	514
136	134	133	138	135	132