

Associative Detachment data for $H^{-} + H \rightarrow H_{2} + e^{-}$



EDITORIAL in Phys. Rev. A 83, 040001 (2011)

Policy Statement on Uncertainty Estimates

It is not unusual for manuscripts on theoretical work to be submitted without uncertainty estimates for numerical results. In contrast, papers presenting the results of laboratory measurements would usually not be considered acceptable for publication in Physical Review A without a detailed discussion of the uncertainties involved in the measurements. For example, a graphical presentation of data is always accompanied by error bars for the data points. The determination of these error bars is often the most difficult part of the measurement. Without them, it is impossible to tell whether or not bumps and irregularities in the data are real physical effects, or artifacts of the measurement. Even papers reporting the observation of entirely new phenomena contain enough information to convince the reader that the effect being reported is real. The standards become much more rigorous for papers claiming high accuracy.....

EDITORIAL in Phys. Rev. A 83, 040001 (2011)

Provision of benchmark results intended as reference data or standards of comparison with other less accurate methods.

It is primarily papers in (this) category that require a careful assessment of the theoretical uncertainties

Guidelines for Uncertainty Estimates for Theoretical Atomic, Molecular Data

Hyun Chung, Bas J. Braams,International Atomic Energy AgencyK. Bartschat, A.G. Csaszar, G.W.F. Drake, T. Kirchner, V. Kokoouline, J Tennyson

Uncertainty Quantification (UQ) for: 1.Structure calculations: atoms and molecules 2.Electron collision calculations: atoms and molecules 3.Charge transfer calculations

J. Phys. D: Appl. Phys., 49, 363002 (2016) (Topical Review).

Theoretical Atomic & Molecular Calculations

- Underlying equations "completely known" (Dirac, 1929)
- But not (analytically) soluble!
- Problem is therefore model construction + numerics
- No culture of uncertainty analysis



Focal Point method: WD Allen, HF Schaeffer III et al

Base model (BM): High accuracy calculation

- + (Small) corrections, assumed additive
- •BM+larger basis
- •BM+improved correlation
- •BM+relativistic effects

•etc

Table 2

Ab initio contributions to the dissociation energies of $H_2^{16}O$ and $HD^{16}O$. All values are in cm⁻¹. Results of the previous *ab initio* studies [8,30] are given for comparison. Uncertainties, where available, are given in parenthesis. Signed contributions are additive corrections. Contributions A to H are nuclear-mass independent, all others are nuclear-mass dependent (MD).

		Ref. [8]	Ref. [30]	This work
Α	CCSD(T) frozen core	43957(52)		43956(6)
В	Core correlation CCSD(T)	+77		+81(2)
C	All-electron CCSD(T) [=A + B]	44034	+13424	44037(6)
D	Higher-order correlation	-7	-25	-52(3)
E	Full CI value [=C + D]	44027	44 000	43985(7)
	MRCI+Q value			43984(60)
F	Scalar relativistic correction	-53	-50	-53(3)
G	QED (Lamb shift) correction			+3(1)
Н	Spin-orbit effect		-65	-69.4(1)
I	Angular momenta coupling. OH			+31.5(0)

Dissociation threshold of $H_2^{18}O$:

Validating ab initio calculations by state-selective triple-resonance spectroscopy DS Makarov, MA Koshelev, NF Zobov & OV Boyarkin, Chem. Phys. Lett. 627, 73 (2015)

-	Barren and a search and a searc			
Р	Sum spin effects, OD [=H + O]			-51.3(1)
Q	BODC, HDO			+26.9(0.5)
R	ZPE HDO			-4023.0(0)
S	ZPE OD			+1350.8(0.5)
т	Net ZPE, HDO [=R + S]			-2672.2(0.5)
U	Non-adiabatic contributions			0(1)
v	Total MD, H ₂ O [=I + K+N + U]			-2721(1)
W	Total MD, HDO [=O + Q+T + U]			-2627(1)
	$D_0(H_2O)$ Calc. [=E + V]	41187(52)	41116	41145(8)
*	$(Obs - Calc) D_0(H_2O)$	-42	+30	+1
	$D_0(HDO)$ Calc. [=E + W]			41238(8)
*	(Obs – Calc) D ₀ (HDO)			+2
	$\Delta \text{calc} = D_0(\text{H}_2\text{O}) - D_0(\text{HDO}) [=\text{V-W}]$			-93.4(0.9)
	$\Delta obs = D_0(H_2O) - D_0(HDO)$			-93.8(0.3)
*	$\Delta obs - \Delta calc$			-0.5

Computed dissociation energy of water



How much light does one molecule of CO₂ absorb?





Orbiting Carbon Observatory: OCO-2

Monitoring:

- Changes in CO₂ concentration
- Sources and sinks of CO₂
- Requires CO_2 line intensities better than 0.5% accurate



A spectral line



Molecular spectra for atmospheric species

- Line positions Measured very accurately
- Line intensities
- Line profile

Often measured to only 5 – 10% Voigt profile +

As stored in databases such as HITRAN

General scheme of solution



Born-Oppenheimer approximation.

Solve the electronic problem, obtaining Potential Energy Surface V(<u>R</u>) and Dipole Moment Surface $\mu(\underline{R})$.

Use V(<u>R</u>) for the motion of the nuclei.

From $\mu(\underline{\mathbf{R}})$ and nuclear-motion wavefunctions calculate line intensities.

L. Lodi and J. Tennyson, J. Phys. B: At. Mol. Opt. Phys. **43**, 133001 (2010)

Method: Spectrum from the "first-principles"



What we need is:

- < i | <u>µ</u> | f >
- < i | initial wavefunction
- | f > final wavefunction
- $\underline{\mu}$ dipole moment surface

Calculating transition dipoles and intensities

$$\mathbf{S} = |\langle \mathbf{i} | \underline{\mu} | \mathbf{f} \rangle|^2 = |/\Psi_i^* \underline{\mu} \Psi_f d\tau|^2$$

- < i | initial wavefunction
- | f > final wavefunction

µdipole moment

Intensity $\boldsymbol{\alpha}$ to dipole squared

$$I(T) = 4.16237933 \times 10^{-19} \nu / \text{cm}^{-1} \frac{S / \text{Debye}^2}{O} \left[\exp\left(\frac{-E_{lower}}{kT}\right) - \exp\left(\frac{-E_{upper}}{kT}\right) \right]$$

Q is the partition function

Accurate molecular wavefunctions for CO₂

Electronic problem

- 1. Hartree-Fock "Orbital approximation"
- 2. Electron correlation configuration interaction
- 3. Core correlation
- 4. Higher-order correlation Davidson correction
- 5. Scalar relativistic correction "MVD1"
- 6. Quantum Electrodynamics(QED) Lamb shift
- 7. Spin-orbit coupling

8. Born-Oppenheimer failure
 9. Born-Oppenheimer failure

diagonal off-diagonal

10. Nuclear motion

vibration-rotation

method used variational variational variational perturbation theory 1st order perturbation theory 1st order perturbation theory Not needed for CO₂

 1^{st} order perturbation theory Small for CO₂, neglected

variational (effectively exact)

Ab initio dipole moments

Compute as Expectation Value (EV): $\langle \psi | e r | \psi \rangle$ Using Finite Field (FF): change in energy in small electric field

•Same by Hellmann-Feynman theorem

- •FF 3 5 times more expensive
- •FF can include perturbative effects (eg relativistic effects)
- •FF seems more accurate

Use finite field method

L. Lodi and J. Tennyson, J. Phys. B: At. Mol. Opt. Phys. **43**, 133001 (2010)

12 FACTORS: ab initio dipole moments

Born-Oppenheimer

- 1. Number of points 200 ->2000++
- 2. MRCI , MOLPRO
- 3. All electrons / core-valence (CV)
- 4. Highest basis set aug-cc-pCV6z
- 5. Complete Basis Set extrapolation
- 6. Optimized (higher) active space (CAS) very important **Corrections**
- 7. Adiabatic (DBOC) 8.Relativistic (MVD1, Gaunt (Breit),)
- 9. Quantum electroddyamics (QED)
- 10. Spin-orbit (SO)
- 11. Vibration non-adiabatic
- 12. Rotational non-adiabatic
- Factor 13:

small contribution important (cancels CV?) assumed small assumed small assumed small assumed small **Fitting**

Lots

Important

5z seems converged

not needed

Dipole moment of water at equilibrium

Contribution Val	ue (a.u.)	Uncertainty (a.u.)
Nonrelativistic, all electron	0.7310	0.0005
Relativistic correction	-0.0017	0.0001
Vibrational averaging	0.0001	0.0001
Final value for the ground-state dipole	0.7294	0.0006
Experimental value (Clough et al, 1973)	0.7296	0.0002

L. Lodi, R.N. Tolchenov, J. Tennyson, A.E. Lynas-Gray, S.V. Shirin, N.F. Zobov, O.L. Polyansky, A.G. Csaszar, J. van Stralen & L. Visscher, J. Chem. Phys., **128**, 044304 (2008)

Also

L. Lodi, J. Tennyson and O.L. Polyansky, J. Chem. Phys., 135, 034113 (2011)

Scatter factor, ρ

Compute line intensity 4 ways:

- PES1, DMS1
- PES2, DMS1
- PES2, DMS2
- PES1, DMS2
- $\rho = S_{max}/S_{min}$

If $\rho < \rho_{critical}$ line is stable: uncertainty from best DMS If $\rho > \rho_{critical}$ line is unstable: use data from elsewhere

Choice of ρ_{critical} remains an issue

CO₂ (11102) – (00001): J-localized instability



CO₂ scatter factors with intensity



E Zak, J Tennyson OL Polyansky, L Lodi, NF Zobov, SA Tashkun &VI Perevalov, JQSRT, 177, 31 (2016)

High-Accuracy CO₂ Line Intensities Determined from Theory and Experiment



OL Polyansky, K Bielska, M Ghysels, L Lodi, NF Zobov, JT Hodges & J Tennyson, Phys Rev Letts 114, 243001 (2015)

CO₂ (20012 - 00001) band near 2 μ m



New measurements: J Brunzendorf et al (Braunschweig) J T Hodges et al (NIST) L Gianfrani et al (Naples) All agree within 0.3% (0.1% on average)

Line intensities of ¹²C¹⁶O₂



Need for sub-percent accuracy of line intensities

OCO-2 Space Mission:

sources, sinks and migrations of atmospheric CO2

TCCON, NDACC: influence of CO₂ on climate change, validation of results from space missions Fossil fuel emission, geological history radioactive ¹⁴C, other isotopes: ¹⁷O, ¹⁸O





UQ in molecular structure calculations.

- Still not the norm: usual is validation against experiment
 Many cases of fortuitous cancellation "Right answer for the wrong reasons"
- UQ now possible for high accuracy studies

UQ in scattering calculations.

- Target properties (energy levels, polarizability, dipole) associated with quality of wavefunctions used.
- Model contributions, including:
 - treatment of N-electron target vs. (N + 1)-electron collision problem
 - accounting for the nuclear motion effects
- Numerical uncertainty

Quantities in collisional studies for which UQ should routinely be provided include:

- threshold energies;
- cross sections and/or appropriate rates;
- positions and widths of key resonances ;
- other observables such as branching ratios

1. Target model

Dipoles if non-zero (and other target moments)

Rotational excitation, elastic scattering, electronic excitation

Cross section $\alpha \mu^2$

So uncertainty approx 2 $\Delta \mu$ / μ

2. Codes, Formalism, numerical approximations R-matrix, Schwinger, Kohn, etc

- Code comparisons: generally satisfactory
- Numerical approximations (grids, basis set truncation, etc):

Generally well-understood and not major source of error

Models not methods

Model vs Method

Eg Resonances in electron – H_3^+ (in eV)

Method	Schwinger		R-matr	R-matrix		
	Orel	& Kulander (1993)	Faure	& Tennyson (2002)		
	E _{res}	Γ	E_{res}	Γ		
² E'	9.1	0.64	9.12	0.64		
² A ₁ '	10.3	0.18	10.14	0.19		
² A ₂ '	~11.2		11.11	0.09		

- Different methods: similar answers for same model
- Results very dependent on the model

R-matrix with Pseudostates Method (RMPS) Polarizability of H_3^+ (in a.u.)

States in close-coupling expansion	$\alpha_{parallel}$	$\alpha_{perpendicular}$
6 (physical target states)	-3.2848	-0.0638
28 (E_{cut} = 33.47 eV)	-3.4563	-2.0893
64 (E _{cut} =45 eV)	-3.5247	-2.2093
152 (E _{cut} =132 eV)	-3.5336	-2.2480
Accurate <i>ab initio</i> value	-3.5978	-2.2454

Mean polarizability of H₂O (in a.u.)



M Jones & J Tennyson, J. Phys. B, 43, 045101 (2010)

Reliable treatment of polarisation effects is biggest problem in low-energy electron-molecule collision calculations

3. Scattering models

- Usually the major source of (unquantified) uncertainty
- UQ

Repeat with variety of models Systematic study eg using pseudo-state methodology Benchmark problems: eg N_2 and dipolar system

Low-energy electron collision processes

Rotational excitation

 $AB(N'') + e \longrightarrow AB(N') + e$

Vibrational excitation

 $AB(v"=0) + e \longrightarrow AB(v') + e$

Dissociative recombination/Dissociative attachment $AB + e \longrightarrow A + B$

> Electronic excitation $AB + e \longrightarrow AB^* + e$ Impact dissociation $AB + e \longrightarrow A + B + e$ Impact ionisation (e,2e) $AB + e \longrightarrow AB^+ + e + e$

Increasing Energy

Elastic scattering AB + e --AB + e

 Treated well theoretically. Theory MUST be used to correct measured cross sections for electron – polar molecules.

> Rotational excitation $AB(N'') + e \longrightarrow AB(N') + e$

• Calculated rotational excitation cross sections seem reliable. Need more experimental data for comparison.

Close-coupling with pseudostates: electrons

Target representation: Many physical states + pseudostates Interaction: polarisation via coupling between target (pseudo)states

$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_i b_{j,k} \phi_j^{N+1}$$

 ϕ_i^N Complete Active Space CI + single excitations to pseudo-orbitals ϕ_j^{N+1} (CAS-CI)^{N+1}

+ occupation of pseudo-orbitals

Captures: All polarisation effects, state coupling, ionisation

Resonances? All (+ pseudo-resonances at high energy)

Energy range: Above ionisation

Other comments: Converged treatment of polarisation

Computationally expensive

RMPS is R-matrix method; designed to treat many electrons

Similar in spirit to convergent close-coupling

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Underlying equations "completely known" (Dirac, 1929)

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Jonathan Tennyson

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