Molecular Properties of Neutral and Charged CsH in the Context of the Heating and Current Drive Systems

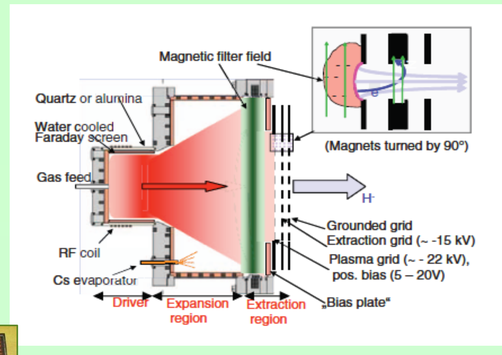
Ivan Černušák[a], Ján Škoviera[a], Vladimír Kellö[a] , Miroslav Urban[a,b]

[a]*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia*
[b]*Institute of Material Science, MTF Slovak University of Technology, 917 24 Trnava, Slovakia*

Motivation

The neutral beam injection (NBI) system for ITER is based on the negative H/D ion source with the Caesium-enhanced surface conversion of atoms. NBI with stable ion current is an important part of ITER (plasma heating). Cs chemistry in NBI is rather complex and accurate molecular data on Cs compounds are still missing. The knowledge of Cs chemistry and dynamics can help to minimize unfavorable compound formation with impurities in the background plasma. Experimentally (at IPP Garching), the quality of the plasma is monitored by Optical Emission Spectroscopy probe in VIS region .

Goals



The results of an comprehensive *ab initio* study of the molecular structure and spectroscopic properties of neutral and charged caesium hydrides include:

- Equilibrium distances R_e [Å]
- Harmonic frequencies ω_e [cm^{-1}]
- First anharmonicity correction $\omega_e x_e$ [cm^{-1}]
- Excitation energies T_e (low-lying states) cm^{-1}]
- Oscillator strengths f_{12}
- Dissociation energies D_e [cm^{-1}]

Quantum chemistry methods &

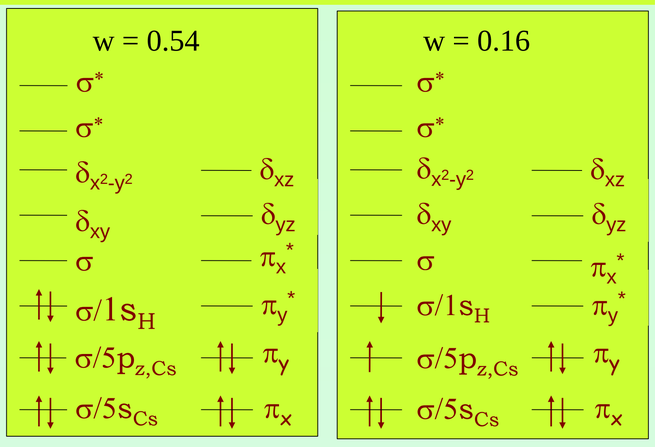
Computational details

- Coupled-cluster singles, doubles and non-iterative triples - CCSD(T) [1]
- State Averaged Complete Active Space Self-consistent Field Method (SA-CASSCF) followed by Multi-reference 2nd-order Perturbation Theory (CASPT2 for dynamical electron correlation) [2]
- Douglas-Kroll-Hess model Hamiltonian for the scalar relativistic effects
- CASSCF/RASSI - State Interaction method to identify the (excited) states
- AO – to – MO basis: ANO-RCC – Large, relativistic, all electron
- ANO-RCC Large: Cs [12s10p8d4f2g] and H[6s4p3d1f]

- Software: GAMESS-US (CCSD(T))[1], MOLCAS 7.8 (CASPT2) [2]
- CCSD(T) step: frozen orbitals on Cs in CCSD(T) in 1*s* - 4*d* shells, completely renormalized variant of the CC method due to Piecuch & coworkers [3] ;
- SA-CASSCF: computational symmetry point group C_2, inactive orbitals 13a⊕10b, active orbitals 8a⊕6b, active electrons: 10(neutral), 9(cation), 11(anion);
- States: $^1\Sigma$, $^1\Delta$, $^1\Pi$, $^3\Sigma$, $^3\Delta$, $^3\Pi$ (neutral), $^2\Sigma$, $^2\Delta$, $^2\Pi$, $^4\Sigma$, $^4\Delta$, $^4\Pi$ (ions);
- Active space: combinations of valence-shell Aos - Cs[5s, 5p, 6s, 5d]; H[1s];
- Spectroscopic properties – Dunham analysis, using 6th degree polynomial fit.

Results

Two most dominant configurations $X^1\Sigma^+$ CsH



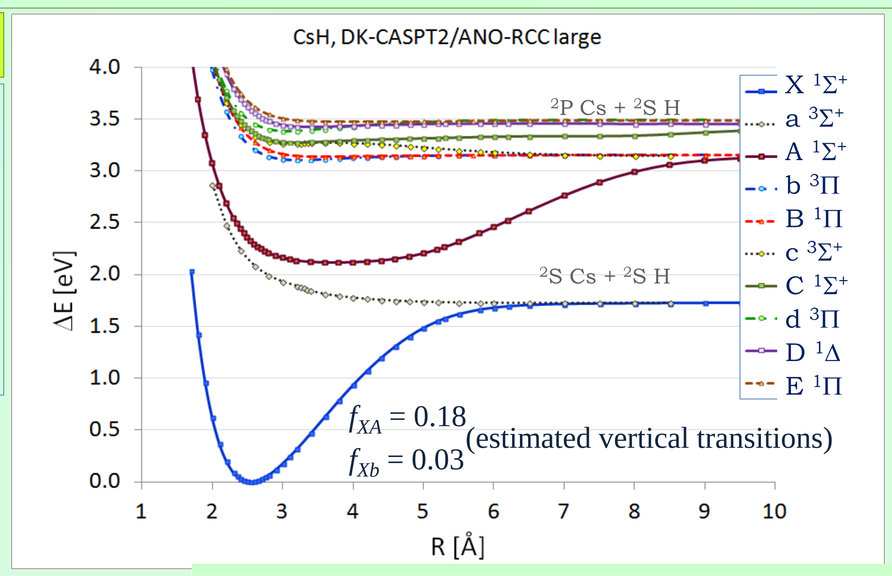
Spectroscopic properties of $X^1\Sigma^+$ **CsH**, [Å, cm^{-1}]

Source	R_e	ω_e	$\omega_e x_e$	D_e
Exper.	2.494	891	12.9	14 791
dk-DMRG[4]	2.590	856	11.6	13 373
dk-CCSD(T)[4]	2.516	882	13.0	-
CI[5]	2.371	-	-	15 253
DK-CASPT2	2.519	891	15.1	**13 937**
CR-CCSD(TQ)	2.503	893	13.9	(14 066)

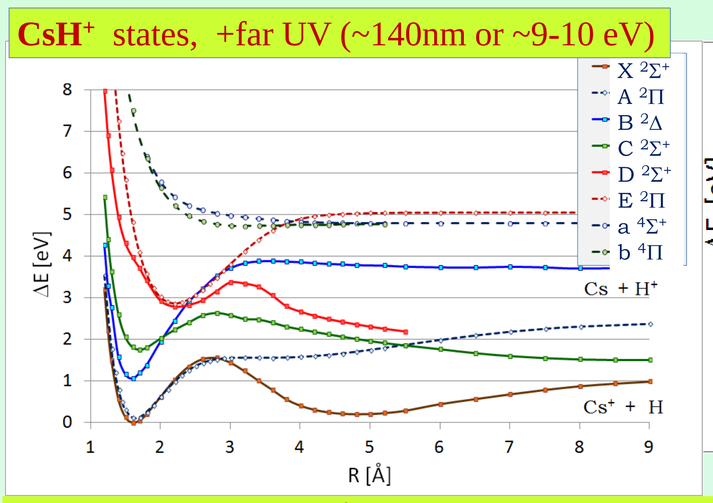
Ground and 1st excited state [Å, cm^{-1}]

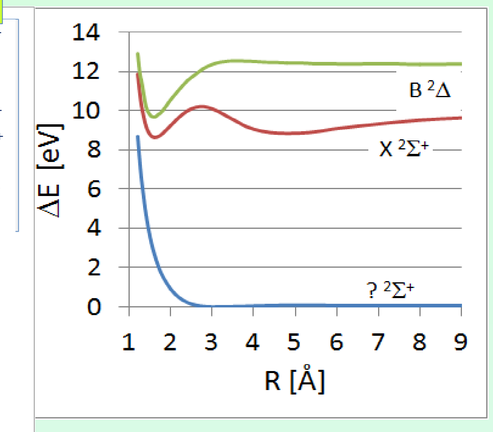
DK-CASPT2	R_e	ω_e	$\omega_e x_e$	T_e
X $^1\Sigma^+$	2.519	891	15.1	0
A $^1\Sigma^+$	3.751	150	-20.0*	17 083**

* $\omega_e y_e$ = -6.1 [cm^{-1}] ** **λ = 585 nm**



CsH$^+$ states, +far UV (~140nm or ~9-10 eV)

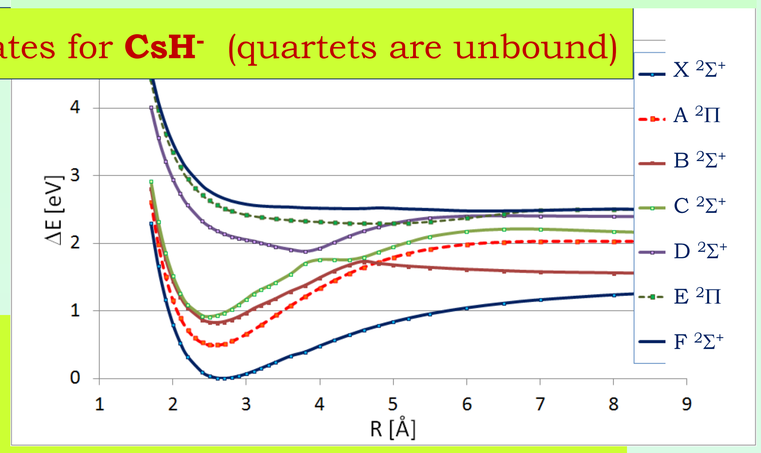




CsH$^+$	R_e [Å]	ω_e [cm^{-1}]	$\omega_e x_e$ [cm^{-1}]	D_e [cm^{-1}]
Semiemp.[6]	3.249	-	-	242
CIPSI[7]	3.164	-	-	653
DK-CASPT2	3.096	(293)	(58)	480-670
	essentially unbound			
next (excited) $^2\Sigma^+$ state				
DK-CASPT2	1.615	2119	62	~8200

$IP_{?^2\Sigma^+ \leftarrow X^1\Sigma^+}$ = 5.49eV, CsH$^+$ unstable/metastable

Most important doublet states for **CsH$^-$** (quartets are unbound)



$X\,^2\Sigma^+$ CsH$^-$ properties [Å, cm^{-1}]

Method	R_e	ω_e	$\omega_e x_e$	D_e
CASPT2	2.671	693	18.5	(~**10 500**)
CR-CCSD(T)	2.668	706	15.5	-

CsH$^-$ – data for excited states [Å, cm^{-1}]

State	R_e	ω_e	$\omega_e x_e$	D_e	T_e
A $^2\Pi$	2.558	828	13.7	~16 292	3 976
B $^2\Sigma^+$	2.578	805	16.7	~10 477	6 630
C $^2\Sigma^+$	2.480	971	29.3	(~16 500)	7 356

$EA_{DK\text{-}CASPT2}$ = 0.21eV, stability comparable to neutral

Summary

- CsH: CCSD(T) and DK-CASPT2 data give the equilibrium distances (R_e), harmonic frequencies (ω_e) and anharmonicities $\omega_e x_e$ very close to the experiment.
- CsH$^+$: the lowest calculated state is predicted to be unbound, the next (metastable) state lies too high to be seen by Optical Emission Spectroscopy probe in VIS region.
- CsH$^-$: relatively low electron affinity (of CsH), the "decent" dissociation energy (125.6 kJ/mol) is of the same order as the stability of the neutral (167.5 kJ/mol) .
- **Work in progress**: Spin-orbit splittings, predictions of the possible transition in optical (VIS) region, similar study on Cs_2 molecule.

ACKNOWLEDGEMENT: This work was supported by SRDA (APVV-0059-10), EUROATOM FU07-CT-2007-00051; "Centre of Excellence on Green Chemistry Methods and Processes (CEGreenI)"ERDF (ITMS 26240120001

References

1. a) M.W.Schmidt, et al. J. Comput. Chem., **14**, 1347 (1993); b) M.S.Gordon, M.W.Schmidt pp. 1167-1189, in "Theory and Applications of Computational Chemistry" C.E.Dykstra, G.Frenking, K.S.Kim, G.E.Scuseria (Eds), Elsevier, Amsterdam, 2005.
2. F. Aquilante et al. J. Comput. Chem. **31**, 224 (2010).
3. a) P. Piecuch et al. *Theor. Chem. Acc.* **112,** *349* (2004); b) P. Piecuch P and M. Wloch, *J. Chem. Phys.* **123,** *224105* (2005); c) P. Piecuch et al. *Comput. Phys. Commun.* **149,** *71* (2002).
*4. G. Moritz, A. Wolf, M. Reiher, J.Chem.Phys.***18**,*123* (2005).
5. W. Zrafi et al., J. Phys. B: At. Mol. Opt. Phys. **39**, *3815* (2006).
6. L. von Sentpaly et al., Chem.Phys. Lett. **93**, *555* (1982).
7. M. Aymar J. Deiglmayr, O. Dulie, Can. J. Phys. **87**, *543.* (2009).