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

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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.

Quantum chemistry methods &

Coupled-cluster singles, doubles and non-iterative triples - CCSD(T) 
State Averaged Complete Active Space Self-consistent Field Method (SA-CASSCF) followed by Multi-reference 2nd-order Perturbation Theory (CASPT2 for dynamical electron correlation) 
Douglas-Kroll-Hess model Hamiltonian for the scalar relativistic effects 
CASSCF/RASSI - State Interaction method to identify the (excited) states
Active space: combinations of valence-shell Aos - Cs[5s, 5p, 6s, 5d]; H[1s]; Active electrons: 10(neutral), 9(cation), 11(anion);

Goals

The results of a 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 \( \omega \) [cm\(^{-1}\)] 
- First anharmonicity correction \( \omega_X \) [cm\(^{-1}\)] 
- Excitation energies \( T_e \) (low-lying states) [cm\(^{-1}\)] 
- Oscillator strengths \( f \)
- Dissociation energies \( D_e \) [cm\(^{-1}\)]

Computational details

- Software: GAMESS-US (CCSD(T)) \(^1\), MOLCAS 7.8 (CASPT2) \(^2\)
- CCSD(T) step: frozen orbitals on Cs in CCSD(T) in 1s - 4d shells, completely renormalized variant of the CC method due to Piecuch & coworkers \(^3\)
- SA-CASSCF: computational symmetry point group \( C_{2v} \), inactive orbitals 13a\(10b\), active orbitals 8a\(6b\), active electrons: 10(neutral), 9(cation), 11(anion)
- States: \( \Sigma, \Lambda, \Pi, \Delta \) (neutral), \( \Sigma, \Lambda, \Pi, \Delta \) (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 \( \Sigma^+ \Sigma \) CsH

<table>
<thead>
<tr>
<th>Source</th>
<th>( R_e ) [Å]</th>
<th>( \omega_X ) [cm(^{-1})]</th>
<th>( \omega ) [cm(^{-1})]</th>
<th>( D_e ) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exper.</td>
<td>2.494</td>
<td>891</td>
<td>12.9</td>
<td>14.791</td>
</tr>
<tr>
<td>CR-DMrg*</td>
<td>2.590</td>
<td>856</td>
<td>11.6</td>
<td>13.373</td>
</tr>
<tr>
<td>CR-CCTQ</td>
<td>2.516</td>
<td>882</td>
<td>13.0</td>
<td>15.253</td>
</tr>
<tr>
<td>CR-CCTQ</td>
<td>2.519</td>
<td>891</td>
<td>15.1</td>
<td>13 937</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ground and 1st excited state</th>
<th>( \Lambda^+ ) [Å]</th>
<th>( \omega ) [cm(^{-1})]</th>
<th>( T_e ) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X ( \Sigma^+ )</td>
<td>2.519</td>
<td>891</td>
<td>15.1</td>
</tr>
<tr>
<td>A ( \Sigma^+ )</td>
<td>3.751</td>
<td>150</td>
<td>17.083</td>
</tr>
</tbody>
</table>

Most important doublet states for CsH\(^+\) (quartets are unbound)

<table>
<thead>
<tr>
<th>Method</th>
<th>( R_e ) [Å]</th>
<th>( \omega ) [cm(^{-1})]</th>
<th>( \omega_X ) [cm(^{-1})]</th>
<th>( D_e ) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASPT2</td>
<td>2.671</td>
<td>693</td>
<td>16.5</td>
<td>(-10 500)</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>2.668</td>
<td>706</td>
<td>15.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Summary

- CsH\(^+\): CCSD(T) and DK-CASPT2 data give the equilibrium distances \( R_e \), harmonic frequencies \( \omega \) and anharmonicities \( \omega_X \) 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 Cs2 molecule.

Acknowledgement

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References


Figures

- CsH\(^+\) states, far UV (~140nm or ~9-10 eV)
- \( X^2\Sigma^+ \) CsH properties [Å, cm\(^{-1}\)]
- Most important doublet states for CsH\(^-\) (quartets are unbound)

Dunham analysis, using 6th degree polynomial fit.