The chemical bond overlap plasmon as a tool for quantifying covalency in optical solid state materials

O.L. Malta1, R.L. Longo1, R.T. Moura jr1 and M. Lalic2
1Departamento de Química Fundamental-CCEN-UFPE-Brazil
2Departamento de Física-UFS-Brazil

Outline:
- The concept of overlap polarizability (OP)
- Testing the OP concept
- Extension to the solid state: theoretical model
- The alkali halides, \(\alpha\)-\(\text{Al}_2\text{O}_3\) and \(\alpha\)-\(\text{SiO}_2\) cases
- Concluding remarks

The concept of overlap polarizability

Origin of the subject: covalency in lanthanide compounds

Partitioning scheme for the molecular polarizability

\[ \alpha_{\text{mol}} = \sum \alpha_{\text{CB}} \]

Partitioning scheme for \(\alpha_{\text{CB}}\)

Proposition:

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\[ \alpha_{\text{A}} + \alpha_{\text{B}} + \alpha_{\text{OP}} \]

THE CASE OF A SINGLE BOND AB

\[ \alpha_{\text{OP}} = C_1 \alpha_{\text{OP}}^* \]

\[ \rho = \text{overlap integral} \]

\[ R = \text{A-B distance} \]

\[ \Delta E = \text{LUMO - HOMO} \]

\[ \alpha_{\text{OP}} \text{ force constant} \]

Overlap charge:

\[ q = q \text{ OP} \]

Postulate:

\[ q^2 = k \alpha_{\text{OP}} \]

Also

\[ q = \text{pe} \rho \]

\[ \rho = \text{overlap integral} \]

\[ p_c + p_a = \frac{c K}{2 \Delta E} \]

The concept of Ionic Specific Valence (ISV)

\[ \text{Interpretation: "Capacity" to donate charge to the formation of the chemical bond} \]

\[ V_a + V_c = 1 \]
**AN ALTERNATIVE SCALE OF COVALENCY**

\[ y = 71.466x - 0.584 \]
\[ R^2 = 0.9736 \]

**NON LINEAR EFFECTS AND COVALENCY**

\[ n = n_0 + n_1|E|^2 \]

\[ n_0 = 10^{-20} \text{eV}^{-1} \]

\[ n_1 = 10^{-20} \text{eV}^{-1} \]

**LIGAND FIELD IN LANTHANIDE COMPOUNDS**

The nature of the chemical bond is different

The ligand field:

\[ H_{LF} = \sum B_{ij}^{(n)}(0) \]

The Simple Overlap Model: effective charges \( g_{\text{eff}} \) at \( R_j/2 \)

\[ B_{ij}^{(n)} = e^2 \left( \frac{4\pi}{2n_i+1} \right)^{\frac{1}{2}} \left( \sum g_{\text{eff}}(2i) \right) \frac{v_{\text{eff}}(i)}{R_j} \]

**LANTHANIDE COMPOUNDS**

Calculation of input data:

- SMLC - II / AM1 (Sparkle Model for Lanthanide Complexes II / Austin Model 1)

\( \Delta E, R \) and \( k \)

**LANTHANIDE COMPOUNDS**

E(LUMO) - E(HOMO) → E(4f) - E(Lig. Atom)

Calculation of input data:

- SMLC - II / AM1 (Sparkle Model for Lanthanide Complexes II / Austin Model 1)
THE NEPHELAUXETIC EFFECT

The Chemical Bond Overlap Plasmon (CBOP) (a localized plasmon in the overlap region)

The Chemical Bond Overlap Plasmon (CBOP)

Extension to the Solid State

Data needed: ρ, k, and ΔE

<table>
<thead>
<tr>
<th>Chemical Bond</th>
<th>γ</th>
<th>f</th>
<th>λ</th>
<th>λ</th>
<th>n</th>
<th>ΔE</th>
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<tbody>
<tr>
<td>H2</td>
<td>0.40</td>
<td>77</td>
<td>77</td>
<td>6.5</td>
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<tr>
<td>HF</td>
<td>0.00</td>
<td>209</td>
<td>209</td>
<td>1.1</td>
<td>122</td>
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<td>HI</td>
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<td>173</td>
<td>173</td>
<td>0.6</td>
<td>90</td>
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<td>KF</td>
<td>0.06</td>
<td>177</td>
<td>177</td>
<td>0.5</td>
<td>90</td>
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</tr>
<tr>
<td>KrF</td>
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<td>177</td>
<td>177</td>
<td>0.2</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>0.06</td>
<td>177</td>
<td>177</td>
<td>0.1</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>0.10</td>
<td>177</td>
<td>177</td>
<td>0.1</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>NaI</td>
<td>0.40</td>
<td>357</td>
<td>357</td>
<td>0.02</td>
<td>71</td>
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<tr>
<td>SrF</td>
<td>0.01</td>
<td>713</td>
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<tr>
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<td>770</td>
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<tr>
<td>KI</td>
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<td>425</td>
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<td>0.01</td>
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<td></td>
</tr>
<tr>
<td>CsF</td>
<td>0.5</td>
<td>298</td>
<td>298</td>
<td>0.03</td>
<td>59</td>
<td></td>
</tr>
</tbody>
</table>
The Model

\[ S = \int \chi_M(\mathbf{r}) \chi_X(\mathbf{r}) \, d\mathbf{r} \]

distance in the crystal

\[ \rho = \left( \sum s_i^2 \right)^{1/2} \]

\[ \chi \rightarrow \text{STOs (Slater-type orbitals)} \]

Program: HyperChem 7.0

Force Constants

Model: [XM\textsubscript{6}]\textsuperscript{5+} + 242 dressed point charges + 1580 point charges

Program: Gaussian 03W – Revision B0.4

\[ \Delta E = -9.05 \times 10^{-4} - 7.14 \times 10^{-4} (\Delta X) + 0.09733 (\Delta X)^2 \]

Excitation Energies

Model: [MX] + 247 dressed point charges + 1580 point charges

Program: Gaussian 03W – Revision B0.4

\[ \text{Excited State 1: Singlet 9.2232 eV 134.43 nm  f = 0.0630} \]

\[ 6 \rightarrow 7 \quad 0.69202 \]

\[ \text{Excited State 2: Singlet 9.3227 eV 132.99 nm  f = 0.1197} \]

\[ 5 \rightarrow 7 \quad 0.69327 \]

\[ 6 \rightarrow 9 \quad 0.63690 \]

\[ 6 \rightarrow 12 \quad 0.27617 \]

Electron Energy-Loss Spectrum

\[ \sigma = \frac{2\pi^2 e^4 \hbar^2}{3m} \left( \frac{E}{E_e} \right)^2 \int_0^{\sin \theta} 0 \, d\theta \int_0^{\cos \theta} 0 \, dq \]

\[ \theta = \mathbf{k} - \mathbf{k}' \]
### Table of Estimated CBOP Energies

<table>
<thead>
<tr>
<th>Compound</th>
<th>Estimated Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>∼7.3 eV</td>
</tr>
<tr>
<td>NaF</td>
<td>∼9 eV</td>
</tr>
<tr>
<td>KF</td>
<td>∼11 eV</td>
</tr>
<tr>
<td>LiCl</td>
<td>∼13 eV</td>
</tr>
<tr>
<td>NaCl</td>
<td>∼11 eV</td>
</tr>
<tr>
<td>KCl</td>
<td>∼13 eV</td>
</tr>
<tr>
<td>LiBr</td>
<td>∼11 eV</td>
</tr>
<tr>
<td>NaBr</td>
<td>∼13 eV</td>
</tr>
<tr>
<td>KBr</td>
<td>∼15 eV</td>
</tr>
<tr>
<td>Al₂O₃ - d1</td>
<td>∼11 eV and 13 eV</td>
</tr>
<tr>
<td>SiO₂ - d1</td>
<td>∼7 eV and 9 eV</td>
</tr>
<tr>
<td>SiO₂ - d2</td>
<td>∼7 eV and 9 eV</td>
</tr>
</tbody>
</table>

### Energy-Loss Spectrum

- **First exciton (?)**
- **Interband transitions, core excitations (photoelectrons)**
- **Estimated CBOP energy: ∼7.3 eV**

### Estimated CBOP Energies

- ∼7 eV and 9 eV
Concluding remarks

$E_p$ (eV)

$\alpha_{op}$

$\text{SiO}_2$ – d1

$\text{SiO}_2$ – d2

$\text{Al}_2\text{O}_3$ – d1

$\text{Al}_2\text{O}_3$ – d2

$\text{LiF}$

$\text{NaF}$

$\text{KF}$

$\text{LiCl}$

$\text{NaCl}$

$\text{KCl}$

$64, 30, 3200$ and $4200$

COOPERATIONS:

Ana Paula Souza
Bruno Parente
Hélcio Batista
Luiz Patricia Naranjo
Patrícia Lima
Ricardo Freire
Rodrigo Albuquerque
Wagner Faustino
Renaldo Moura Jr.
(Dr. MS Students)

Alfredo M. Simas
Gilberto Sá
Petrós Santa-Cruz
Ricardo Luiz Lengo
Severino Alves Jr.
(DQF-UFPE)

Marcos A.C. Santos
Milan Lalic
(DQF-DFS)

Janina Legendziewicz
Wiesław Strok
(Wroclaw-Poland)

Luiz Dias Carlos
Filipe Almeida Paz
(Univ. Aveiro-Portugal)

CNPq, RENAMI, IMMC

Cooperation with Janina Legendziewicz, Wiesław Strok (Wroclaw-Poland) and Luiz Dias Carlos, Filipe Almeida Paz (Univ. Aveiro-Portugal).