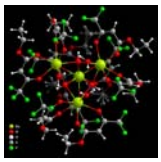
NanoSpain 2008

DQF



THE CHEMICAL BOND OVERLAP PLASMON AS A TOOL FOR QUANTIFYING COVALENCY IN OPTICAL SOLID STATE MATERIALS

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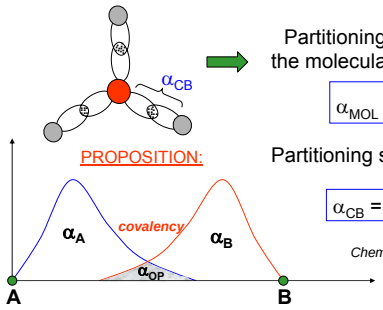
OUTLINE:

- *The Concept of Overlap Polarizability (OP)*
- *Testing the OP Concept*
- *Extension to the Solid State:* theoretical model
- *The Alkali Halides, α-Al_2O_3 and α-SiO_2 Cases*
- *Concluding Remarks*

The concept of overlap polarizability

Origin of the subject: *covalency in lanthanide compounds*



Partitioning scheme for the molecular polarizability

$\alpha_{MOL} = \Sigma\alpha_{CB}$

Partitioning scheme for α_{CB}

$\alpha_{CB} = \alpha_A + \alpha_B + \alpha_{OP}$

Chem.Phys.282, 21 (2002)

DEFINITION

Quantum mechanical expression for the polarizability (zero field) :

$$\alpha = 2e^2 \sum_n \frac{\langle a|\hat{r}|n\rangle\langle n|\hat{r}|a\rangle}{(E_a - E_n)}$$

$|a\rangle$ and $|n\rangle$ { • molecular states with energies E_a and E_n • complex linear combination of atomic orbitals

Partitioning scheme

$\alpha = \Sigma\alpha_{cores} + \Sigma\alpha_{OP}$

THE CASE OF A SINGLE BOND AB

$\Rightarrow \alpha_{OP} = c_1\alpha^*_{OP}$ $(C_1 \cong 1)$

where $\alpha^*_{OP} = \frac{e^2\rho^2R^2}{2\Delta E}$ { ρ = overlap integral; R = A-B distance; ΔE = LUMO - HOMO

- **The overlap charge:** $A^+ + B^- \rightarrow A—B$

Postulate: $q^2 = k\alpha_{OP}$ also $q = pe\rho$

force constant

$p_c + p_a$

THE CASE OF A SINGLE BOND AB

$$p_c + p_a = R\sqrt{\frac{c_1 k}{2\Delta E}}$$

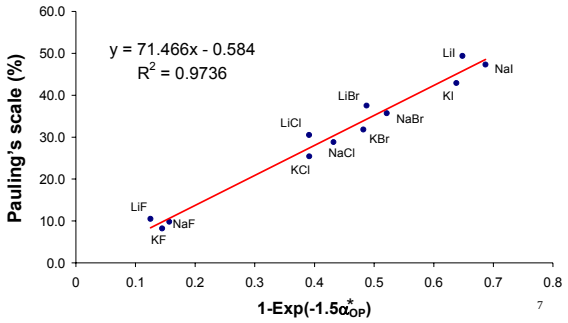
- **The Concept of Ionic Specific Valence (ISV)**

$v_a = p_a / \sqrt{c_1}$ and $v_c = p_c / \sqrt{c_1}$

Interpretation: "Capacity" to donate charge to the formation of the chemical bond

$V_c + V_a \sim 1$

• AN ALTERNATIVE SCALE OF COVALENCY



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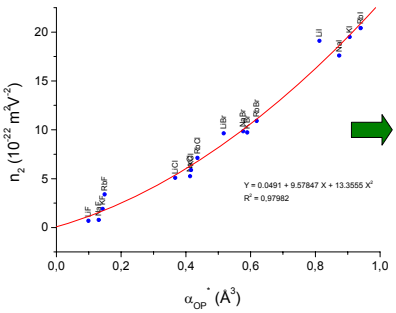
• NON LINEAR EFFECTS AND COVALENCY



$n = n_0 + n_2|E|^2$

Solid	n_2 ($10^{-22}m^2V^{-2}$)	
	Theory	Exp.
BeO	3,38	4,92
MgO	4,25	4,89
MgF_2	1,21	0,49
CaF_2	1,38	1,07
SrF_2	0,85	1,30

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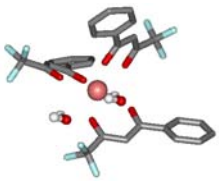
• **LIGAND FIELD IN LANTHANIDE COMPOUNDS**

The nature of the chemical bond is different

The ligand field : $H_{LF} = \sum_{n,m,i} B_m^n C_m^{(n)}(i)$

The Simple Overlap Model : effective charges $g_j e\rho_j$ at $\vec{R}_j / 2\beta$



$$B_m^n = e^2\left(\frac{4\pi}{2n+1}\right)^{1/2}\langle r^n\rangle\sum_j g_j\rho_j(2\beta_j)^{n+1}\frac{Y_m^{n*}(\Omega_j)}{R_j^{n+1}}$$

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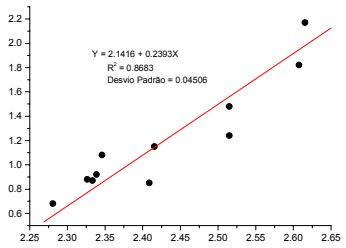
LANTHANIDE COMPOUNDS

• **Overlap Charge** : $q = (g_c + g_a)e\rho$

Assumptions : $g_c << g_a$ and $g_a = v_a$ (ISV) !



$$g_j = R_j\sqrt{\frac{k_j}{2\Delta E_j}}$$

main relation fundamental aspect

Chem. Phys. Lett. **331**, 519 (2000)

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LANTHANIDE COMPOUNDS

In this case

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)

⇩

ΔE , R and k

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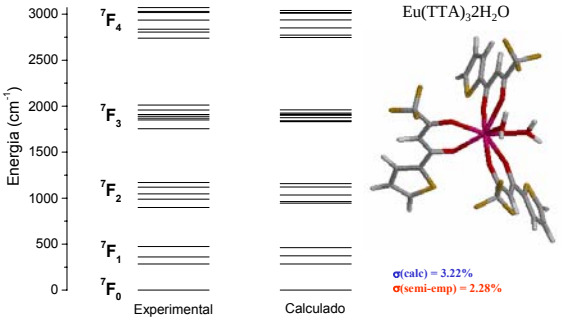
LANTHANIDE COMPOUNDS



Átomo ligante =	O2	O3	O7	O8	O12	O13	O44	O45
VIE =	0.84	0.85	0.84	0.85	0.84	0.85	0.88	0.91
g(semi-emp) =	0.88	0.88	0.88	0.88	0.88	0.88	1.48	1.48

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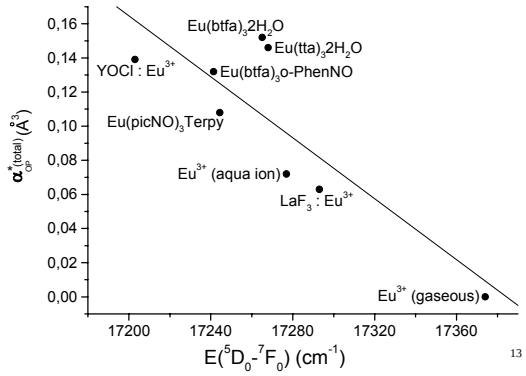
THE NEPHELAUXETIC EFFECT



The Chemical Bond Overlap Plasmon(CBOP)

(a localized plasmon in the overlap region)

Absorption

$$f = \frac{2\, m\, \omega_0}{3\, \hbar\, e^2}\mu^2$$

$$\omega_0 = \sqrt{\frac{k}{m}}$$

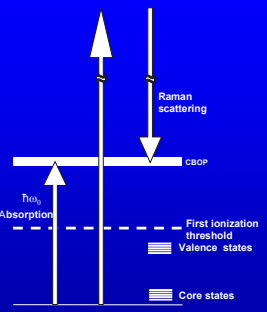
$$m = v\rho m_e$$

Raman scattering

$$\sigma = \frac{4\pi\omega\omega_S^3}{c^4}\alpha_S^2$$

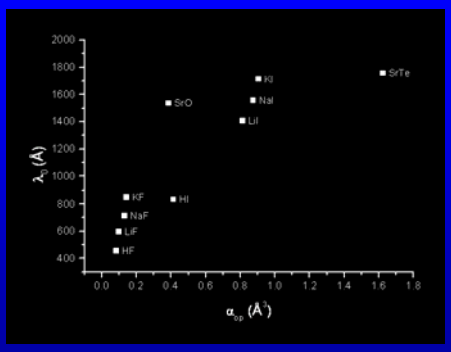
$$\alpha_S^2 \cong \left(\frac{\Delta E}{\hbar\omega}\right)^4 \alpha_{OP}^2 (\hat{e}_\omega \cdot \hat{e}_{\omega_1})^2$$

Chem.Phys.Lett.406, 192 (2005)

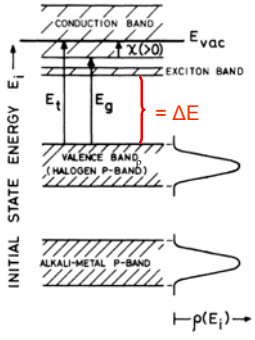


Chemical Bond	λ_0	f	λ	λ_x	σ	λ_ρ
LiF	596	**0.03**	199	298	**0.5**	391
LiI	1408	**0.10**	469	704	**7.1**	328
NaF	713	**0.02**	238	357	**0.4**	368
NaI	1558	**0.08**	519	777	**5.5**	342
KF	850	**0.01**	283	425	**0.2**	314
KI	1714	**0.06**	571	856	**3.8**	368
SrO	1537	**0.01**	513	770	**0.2**	297
SrTe	1756	**0.12**	585	877	**3.3**	302
HF	456	**0.06**	152	228	**5.1**	-
HI	833	**0.21**	278	417	**13.3**	-

λ in Å and σ in 10^{-26} cm^2

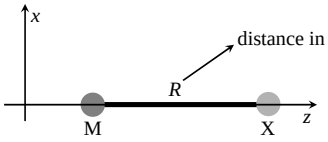


Extension to the Solid State



Data needed:
ρ, k and ΔE

The Model



$$\rho = \left(\sum_i S_i^2 \right)^{1/2}$$

$$S = \int \chi_M(1)\chi_X(1)\, d\tau$$

s and p_z

overlap

EHT

	Li *s*	Li p_z
F *s*	0.21501	0.34045
F p_z	–0.06986	–0.09832

$\chi \rightarrow$ STOs (Slater-type orbitals)

Program: HyperChem 7.0

Force Constants

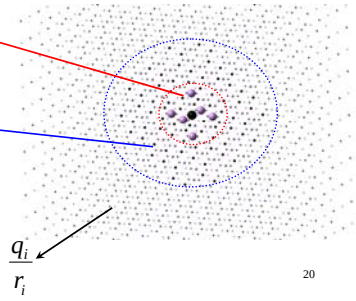
Model: $[XM_6]^{5+}$ + 242 dressed point charges +1580 point charges

Program: Gaussian 03W – Revision B0.4

quantum system:
B3LYP/6-311+G(d)
geometry optimization

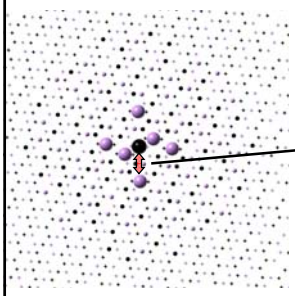
$$\frac{q_i}{r_i} + Ae^{-\alpha r_i}$$

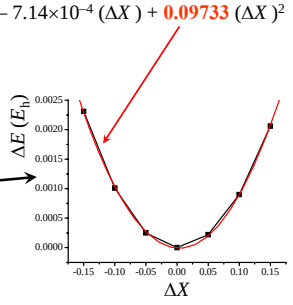
q_i = ±1 (fixed)
A and α adjusted
to reproduce the
crystal structure



Force Constants

$\Delta E = -9.05\times10^{-6} - 7.14\times10^{-4}\,(\Delta X) + \mathbf{0.09733}\,(\Delta X)^2$





Excitation Energies

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

Program: Gaussian 03W – Revision B0.4

quantum system:
B3LYP/6-311+G(d)
geometry optimization

$$\frac{q_i}{r_i} + Ae^{-\alpha r_i}$$

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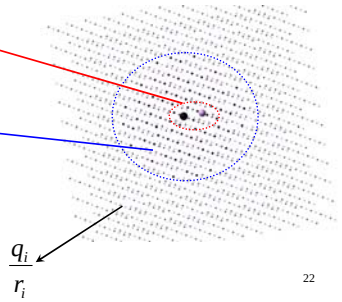
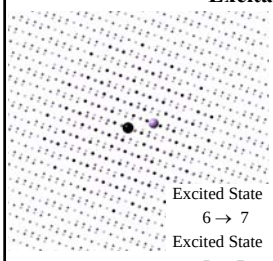


Excitation Energies

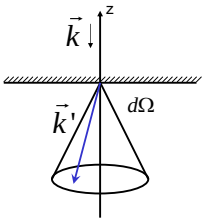


ΔE

TD-B3LYP/6-311+G(d)

Excited State 1: Singlet 9.2232 eV 134.43 nm f = 0.0630
6 → 7 0.69202
Excited State 2: Singlet 9.3227 eV 132.99 nm f = 0.1197
5 → 7 0.69327
Excited State 3: Singlet 9.3227 eV 132.99 nm f = 0.1197
4 → 7 0.69327
Excited State 4: Singlet 10.9207 eV 113.53 nm f = 0.0004
6 → 8 0.10678
6 → 9 0.63690
6 → 12 0.27617

Electron Energy-Loss Spectrum



CBOPch arg e = evρ

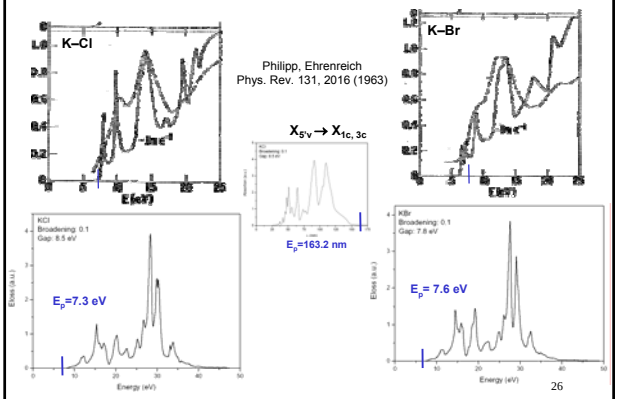
$$H_{int} = \frac{e^2 v\rho}{|\vec{r}' - \vec{r}|} = e^2 v\rho \sum_{L,M} \left(\frac{4\pi}{2L+1} \right) \frac{r'^L}{r^{L+1}} Y^*_{L,M}(\Omega') Y_{L,M}(\Omega)$$

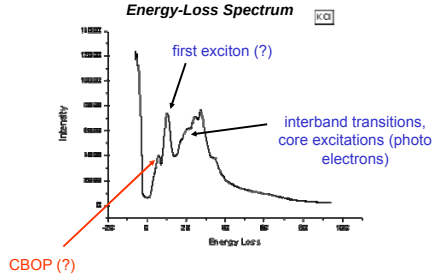
$$|i\rangle = |\vec{k},0\rangle \qquad |f\rangle = |\vec{k}',1\rangle$$

$$\langle f|H_{int}|i\rangle \cong e^2 v\rho \frac{4\pi}{3} \frac{\mu_{OR}}{e} \left\langle \vec{k}' \left| \frac{Y_{1,M}(\Omega)}{r^2} \right| \vec{k} \right\rangle$$

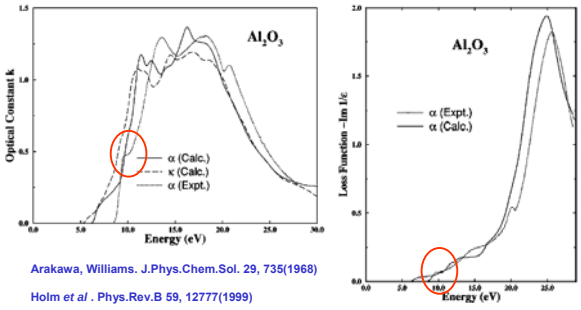
$$\sigma = \frac{2\pi^2}{3\hbar^2} \frac{e^4 v^2 \rho^4 R^2 m}{E_c} \int_{\theta_i}^{\theta_f} \frac{\cos^2\theta_q \sin\theta_q}{(1-\cos\theta_q)} d\theta_q \qquad \vec{q} = \vec{k} - \vec{k}'$$

	λ_o(Å)	f	σ_S (10^{-26} cm^2)	λ_i(Å)	λ_S(Å)	Ep(eV)	σ_{Loss} (10^{-23} cm^2)	α_{op}
LiF	958	0.014	1.06	125	144	12.8	0.30	0.16
NaF	1011	0.012	0.22	417	711	12.2	0.27	0.18
KF	1108	0.011	0.20	417	670	11.0	0.25	0.20
LiCl	1551	0.034	6.70	125	136	8.0	1.6	0.57
NaCl	1559	0.040	3.00	417	570	8.0	2.0	0.65
KCl	1630	0.037	2.40	417	561	7.6	2.0	0.71
LiBr	1657	0.033	3.30	417	558	7.4	1.6	0.64
NaBr	1692	0.033	2.80	417	554	7.3	1.7	0.70
KBr	1691	0.036	2.10	417	554	7.3	2.0	0.77
Al_2O_3 – d1	1065	0.211	0.0036	417	686.7	11.6	64.41	2.58
Al_2O_3 – d2	937.5	0.17	0.013	417	752.7	13.2	30.65	1.34
SiO_2 – d1	1753	2.80	1.64	417	548	7.0	3178	15.79
SiO_2 – d2	1371	5.58	1.41	417	600	9.0	7676	8.21





estimated CBOP energy: ~7.3 eV



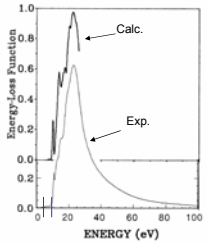
Arakawa, Williams. J.Phys.Chem.Sol. 29, 735(1968)

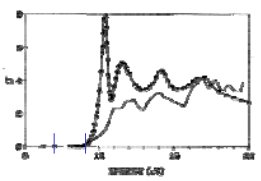
Holm *et al* . Phys.Rev.B 59, 12777(1999)

Estimated CBOP energies: ~11 eV and 13 eV

SiO_2 α-quartz

	λ_o(Å)	f	σ_S (10^{-26} cm^2)	λ_i(Å)	λ_S(Å)	Ep(eV)	σ_{Loss} (10^{-23} cm^2)	α_{op}
SiO_2 – d1	1753	2.80	1.64	417	548	7.03	3178	15.79
SiO_2 – d2	1371	5.58	1.41	417	600	8.99	7676	8.21

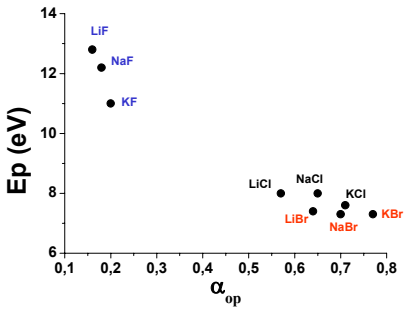




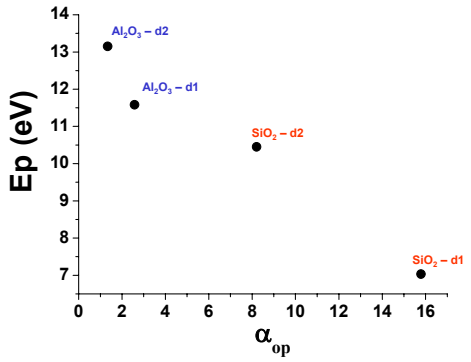
Calculated optical conductivity σ.

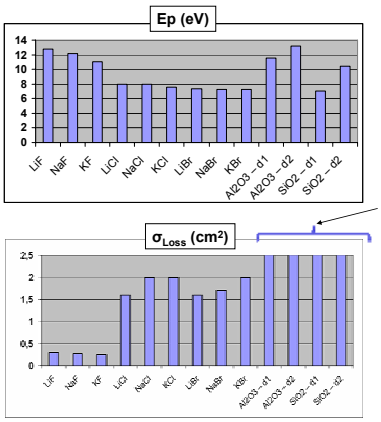
Estimated CBOP energies: ~7 eV and 9 eV

Concluding remarks



Concluding remarks





64, 30, 3200 and 4200

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