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17 - 28 May 2010

From Supported Clusters to Nanocatalysis
Part II

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Spring College on Computational Nanoscience, Trieste, May 18, 2010

FROM SUPPORTED CLUSTERS TO NANOCATALYSIS

CO on MgO: lessons from 25 years of interplay between theory and experiment

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Università Milano-Bicocca, Milan (Italy)

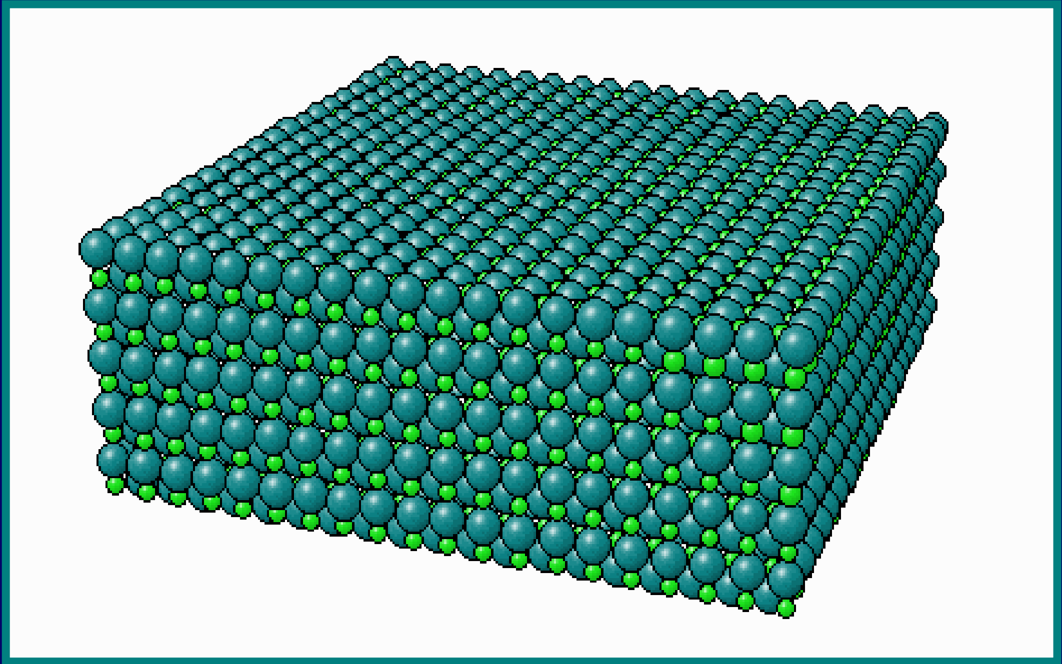
Part I – Nanocatalysis: supported clusters, particles, and model systems

Part II - CO on MgO: lessons from 25 years of interplay between theory and experiment

Part III – New phenomena: metal clusters on ultra-thin oxide films

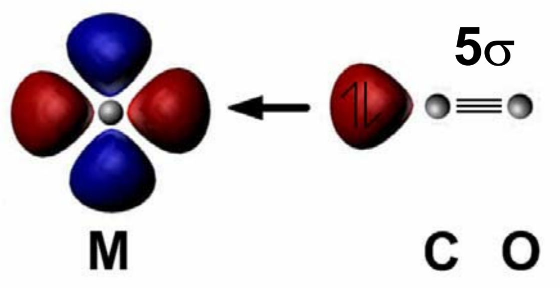
CO: one of the simplest gas-phase molecules

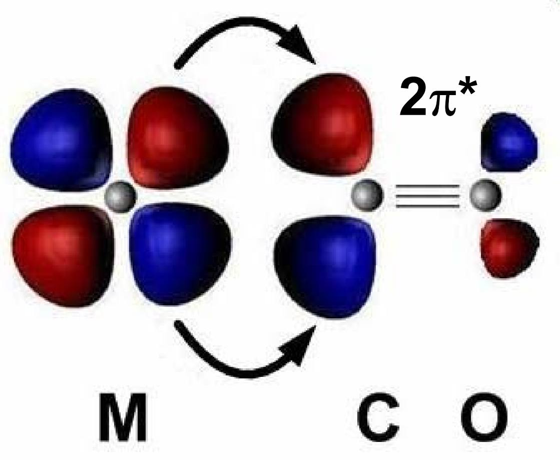
MgO: a cubic, ionic, unreconstructed oxide

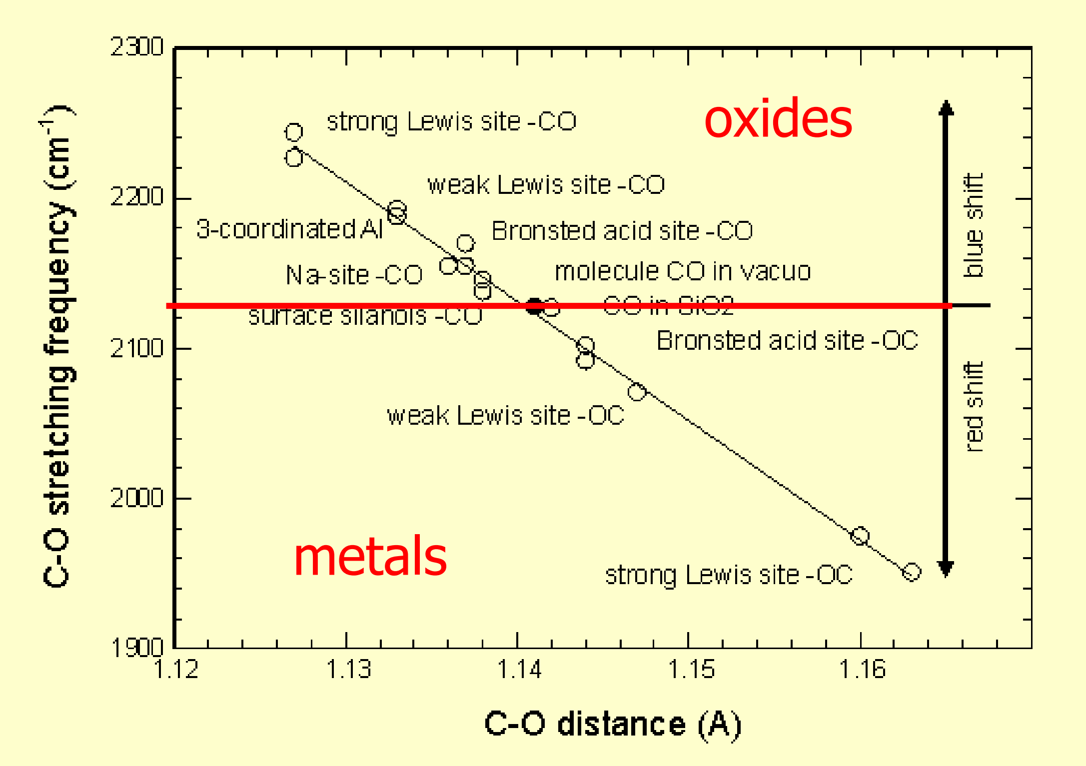


CO adsorption on MgO: in principle, one of the simplest solid-gas interactions one can imagine

CO as a probe molecule (the Blyholder model)



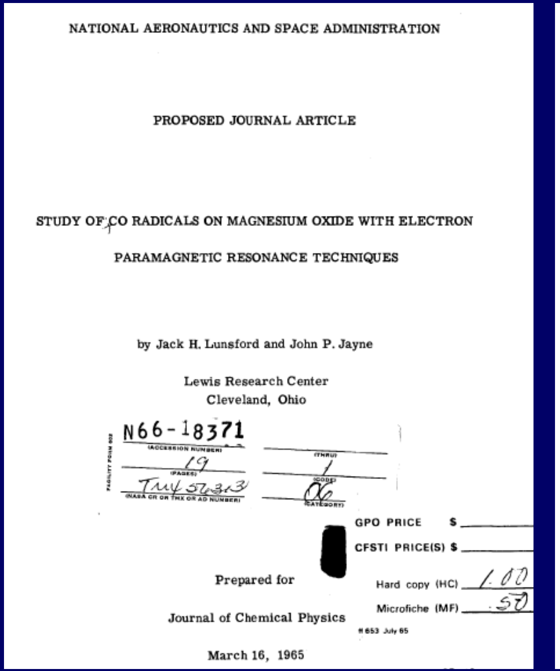




The first experiments at NASA (1965)

CO adsorbed on polycrystalline MgO leads to formation of paramagnetic species (characteristic signal in EPR) - J.H. Lusford and J.P. Jayne, J. Chem. Phys. 44 (1966) 1492

Original interpretation: 2e$^-$ donated from CO 5σ to the surface & 1e$^-$ back-donated from the surface to the CO 2π*



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

PROPOSED JOURNAL ARTICLE

STUDY OF CO RADICALS ON MAGNESIUM OXIDE WITH ELECTRON PARAMAGNETIC RESONANCE TECHNIQUES

by Jack H. Lunsford and John P. Jayne

Lewis Research Center
Cleveland, Ohio

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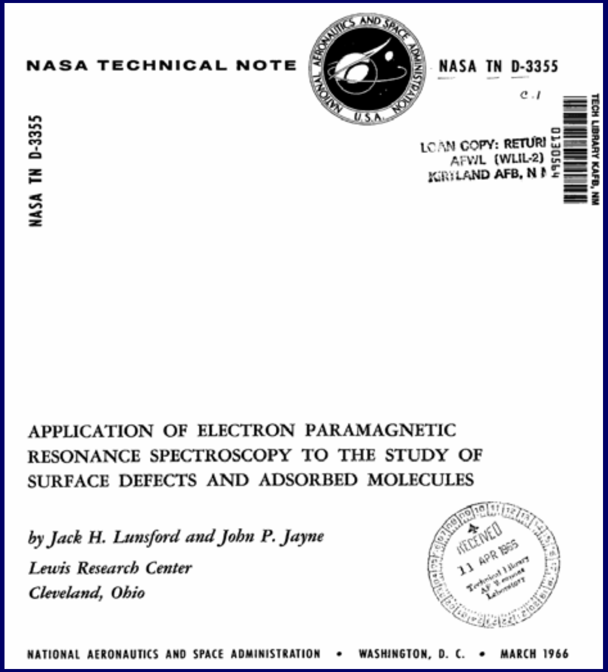
March 16, 1965



NASA TECHNICAL NOTE

NASA TN D-3355

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NASA TN D-3355

APPLICATION OF ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY TO THE STUDY OF SURFACE DEFECTS AND ADSORBED MOLECULES

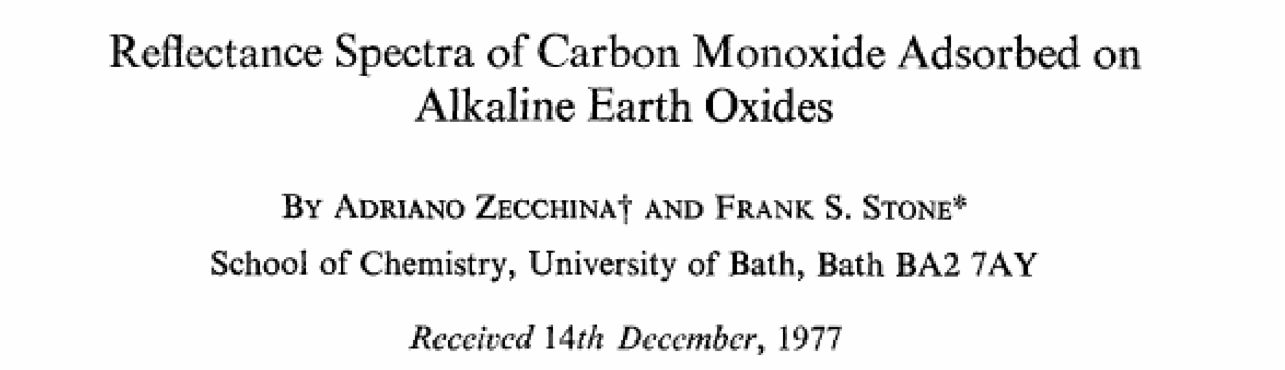
by Jack H. Lunsford and John P. Jayne

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1966

3. Approximately 5 percent of the carbon monoxide that adsorbs on magnesium oxide forms a paramagnetic species. The anisotropic g values and hyperfine constants along with the concepts for bonding in metal carbonyls indicate that this radical is a linear molecule with the unpaired electron in a π-antibonding orbital.

1970's: the work of Zecchina and Stone



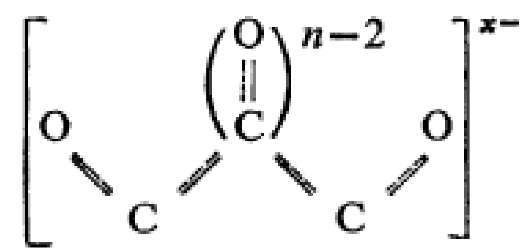
Reflectance Spectra of Carbon Monoxide Adsorbed on
Alkaline Earth Oxides

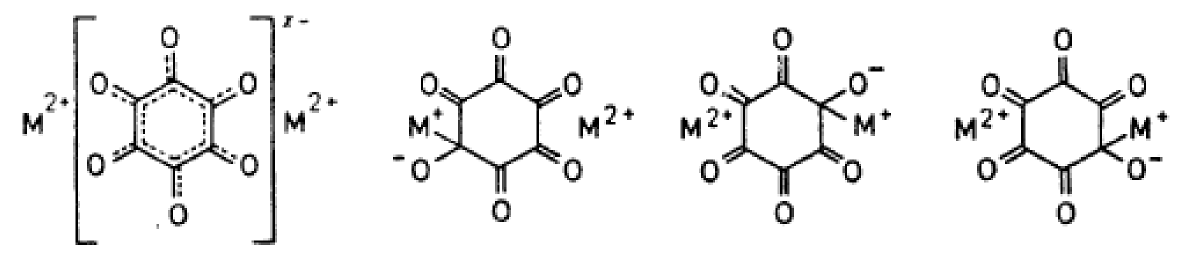
By Adriano Zecchina† and Frank S. Stone*
School of Chemistry, University of Bath, Bath BA2 7AY

Received 14th December, 1977

A. Zecchina

Charge transfer from MgO to CO further supported by experiment showing formation of dimers and oligomers formula $(CO)_2^{2-}$ and $(CO)_n^{x-}$ $(n > 2)$.
A. Zecchina and F.S. Stone, J. Chem. Soc. Faraday I 74 (1978) 2278





Early experiments on MgO powders suggested high chemical reactivity with carbon monoxide

More experiments (1978-1985)

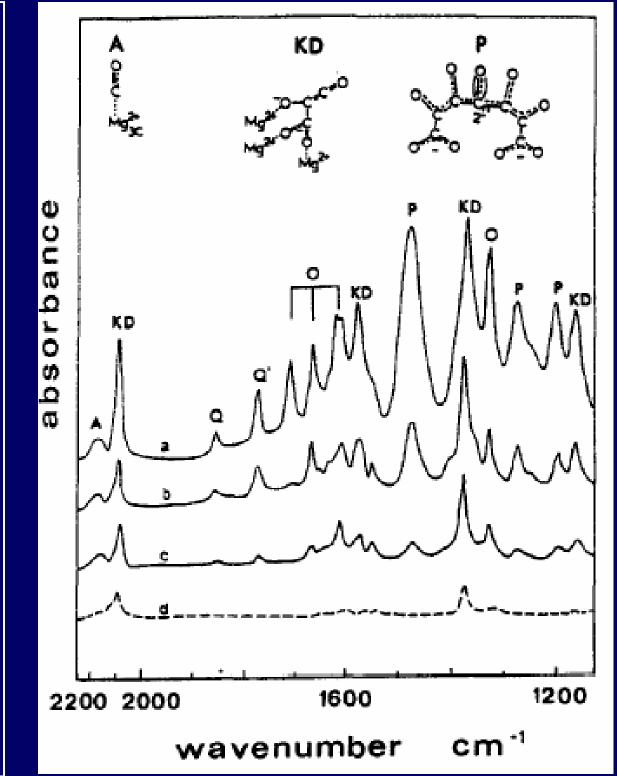
IR on MgO powders at 77K

Beside low-frequency values, also high frequency peak observed in IR spectra

$\Delta\omega_e(CO) = +9\ cm^{-1}$ (positive shift, contrary to metals!)

CO normal to the surface

E. Escalona et al., Faraday Discuss. Chem. Soc. 80 (1985) 183



Adsorption isotherms

$D_e \approx 0.15$ eV (but how reliable is this D_e? high pressure measurements and powder samples)

S. Furuyama et al., J. Phys. Chem. 82 (1978) 1028

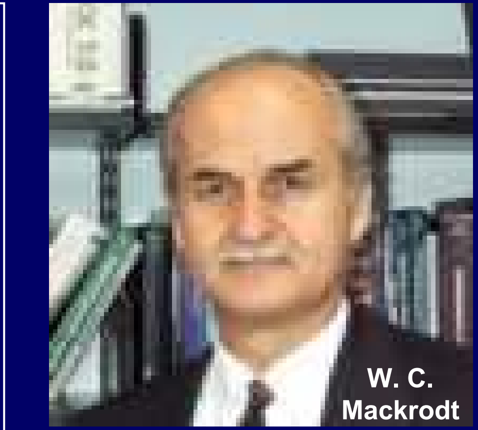
E.A. Pauskshtis et al., React. Kinet. Catal. Lett. 16 (1981) 93

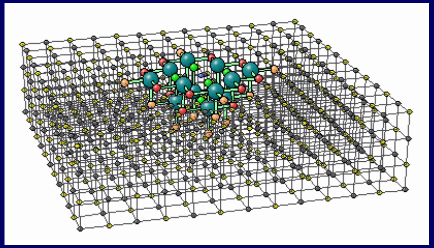
CO on MgO

Theory comes in (1984)

- Bonding mode: CO or OC?
- Hartree-Fock calculations on MgO clusters embedded in point charges (PCs)
- C-down CO on Mg^{2+} is preferred
- bonding is weak $D_e \approx 0.39$ eV

E.A. Colbourn and W.C. Mackrodt, Surf. Sci. 143 (1984) 391





PERIODIC MODELS AND LOCAL MODELS OF SOLIDS AND SURFACES

band structure theory

periodic supercell

repeated in three-dimensions

typical size of a cell 50-100 atoms

models high concentration of defects or adsorbates

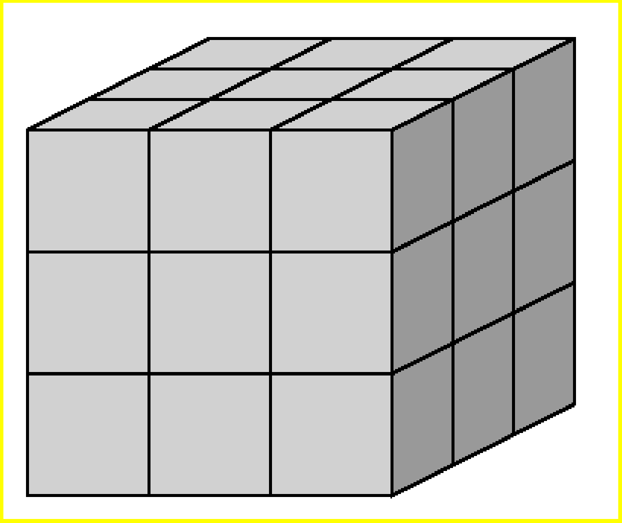
molecular orbitals theory

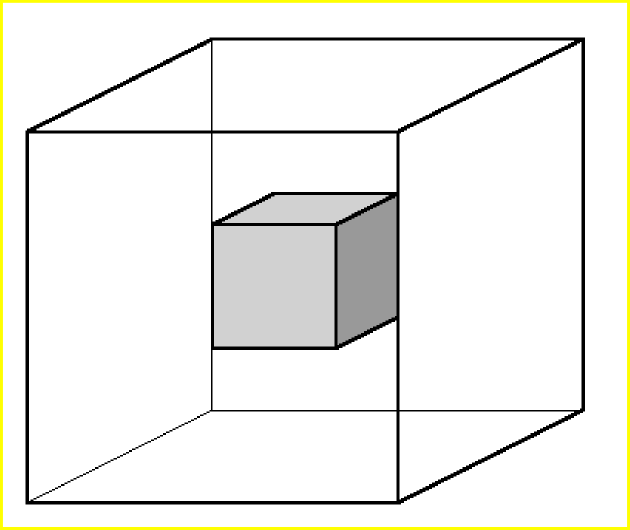
clusters of atoms

solid state effects from embedding

typical size of a cluster 30-80 atoms

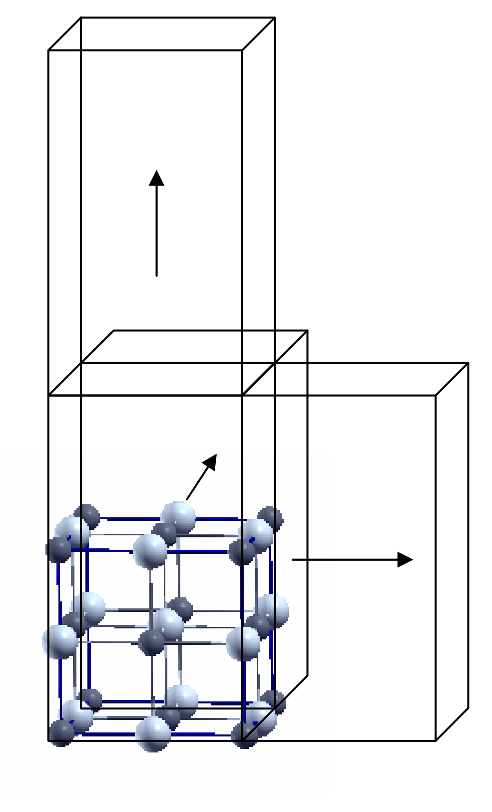
models isolated defects or adsorbates

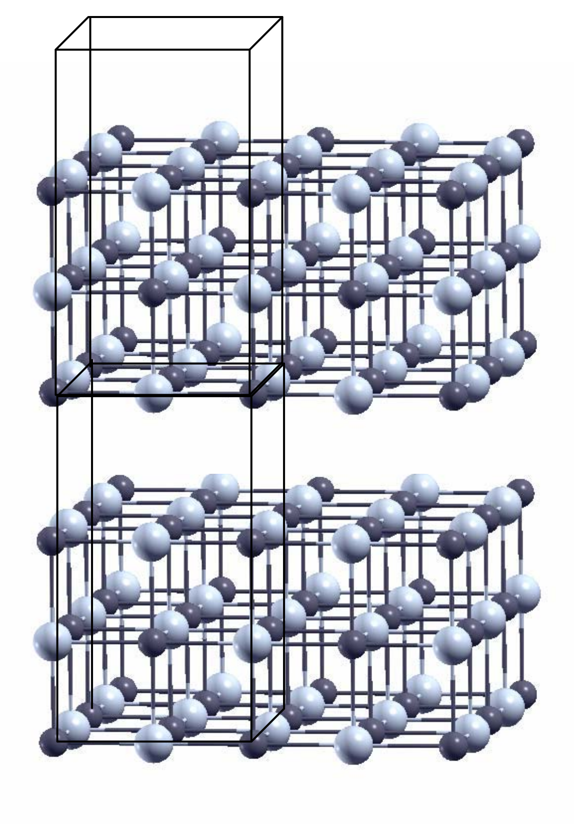




PERIODIC MODELS FOR SURFACES

SLAB SUPERCELLS OF CUBIC SYSTEM





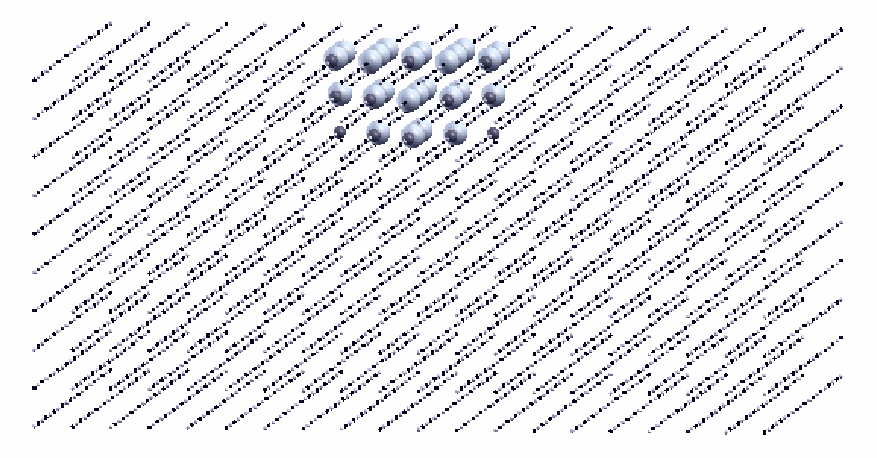
- size 100 or more atoms (depending on concentration of adsorbates on surface
- thickness 3 -10 layers depending on material
- convergence of properties must be checked!
- vacuum region of ca. 10 Å to avoid spurius interaction with bottom layer
- some codes allow 2D periodicity which does not require vacuum region

CLUSTER MODELS

GROUP OF ATOMS IN EMBEDDING
simulating solid state effects

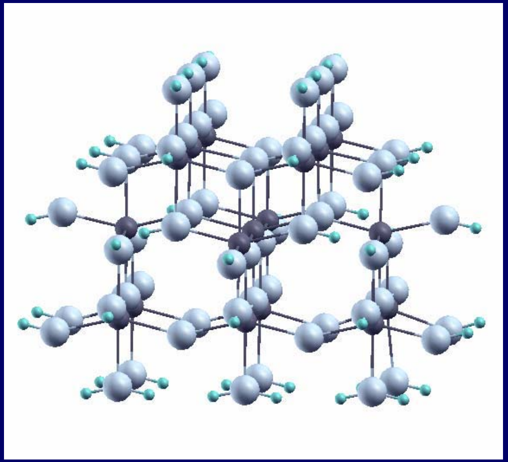
POINT CHARGES

WATER OR OH GROUPS



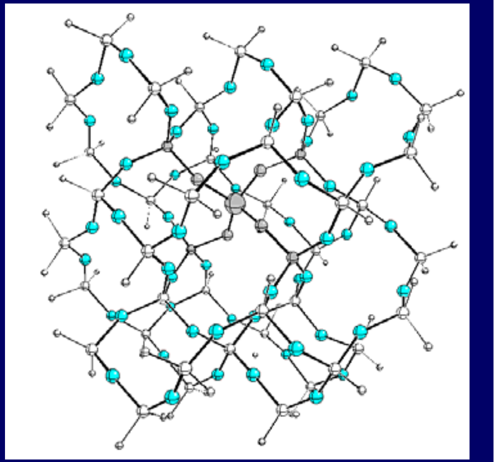
MgO CaO ecc..

IONIC



TiO_2

MIXED



SiO_2

COVALENT

- check convergence of the Madelung potential at the defect or adsorption site
- avoid spurius effect at the QM/PC interface

- avoid spurius effect at the cluster border
- QM/MM approach

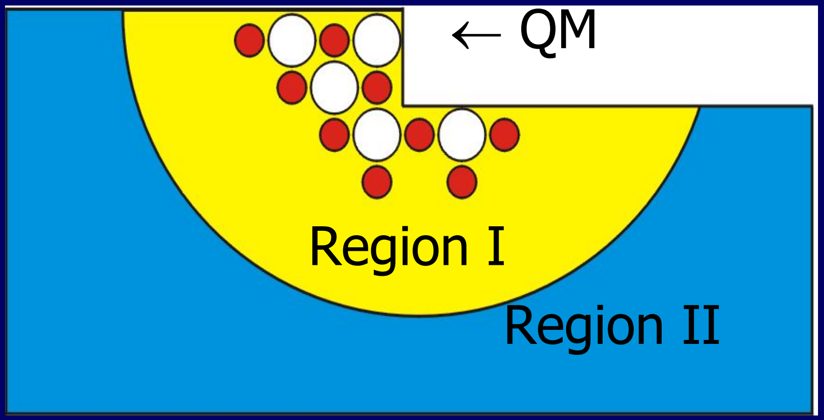
Cluster model better for charged and low-symmetry centers

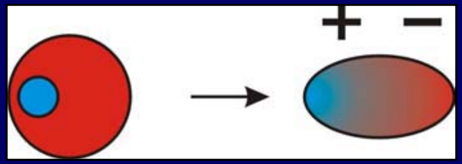
CLUSTER MODELS: MORE SOPHISTICATED EMBEDDING FOR IONIC SOLIDS

Shell Model Embedding

Finite aggregate of atoms embedded in external potential

- Stoichiometric quantum-mechanical (QM) cluster
- Embedding (1): Effective core potentials
- Embedding (2): polarizable shell-model embedding (Region I)
- Embedding (3): Madelung potential through large array of PCs (Region II)



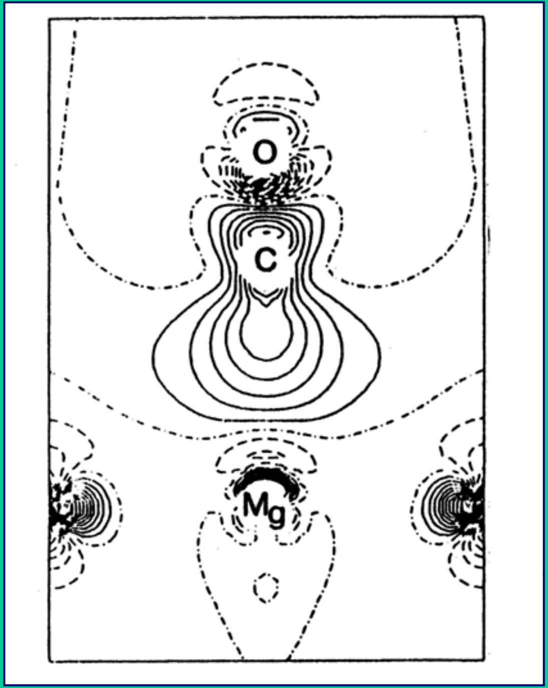


Shell-model: every ion described by two point charges connected by a spring **dipolar response** of the ions included

Shell and core positions optimized in a self consistent way

P. SUSHKO, A. SHLUGER: GUESS CODE

Periodic Hartree-Fock enters in scene (1987)



CRYSTAL code (Torino) periodic Hartree-Fock calculations D_e = 0.15-0.33 eV (at coverage $\theta = 1$)

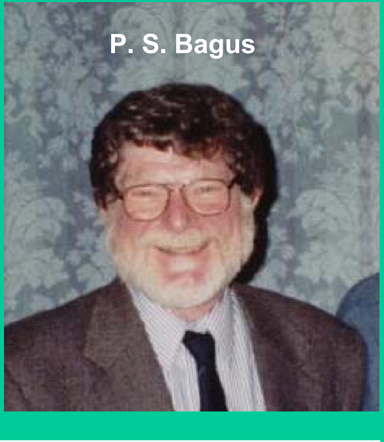
R. Dovesi et al., Surf. Sci. 186 (1987) 267; C. Pisani et al, Surf. Sci. 216 (1989) 489

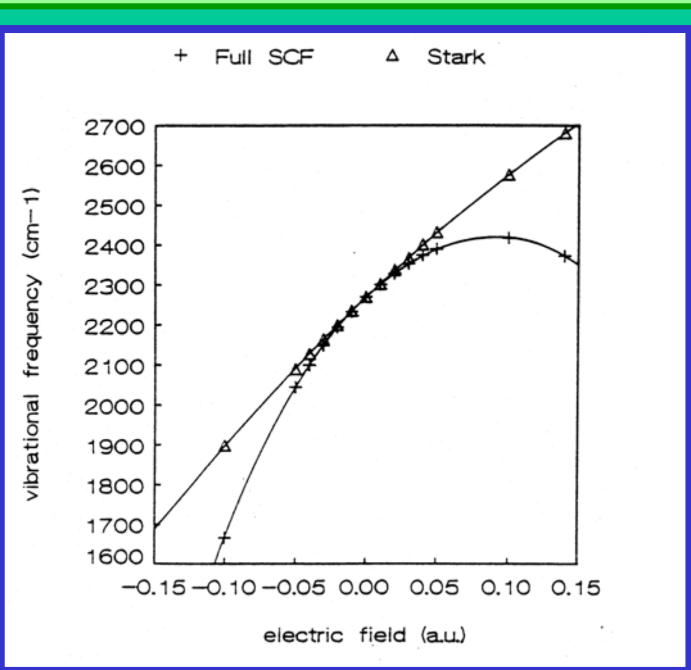
Bond: electrostatic + polarization of CO 5σ lone pair

New cluster models and methods of analysis (1991)

Hartree-Fock (HF) calculations on clusters + PCs show that small positive $\Delta\omega_e$(CO) arises from surface electric field & “wall effect” (repulsion with rigid surface)

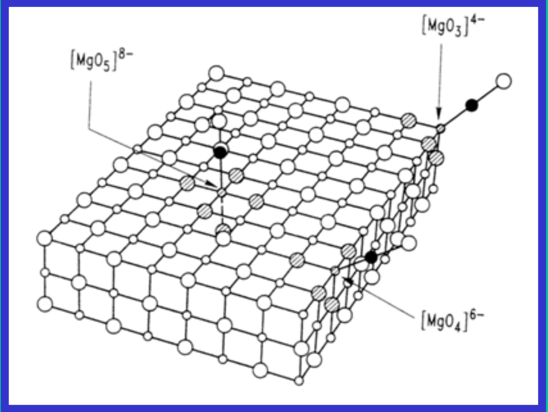
Pacchioni, Cogliandro, Bagus, Surf. Sci. 255 (1991) 344; Int. J. Quant. Chem. 42 (1992) 11150


P. S. Bagus



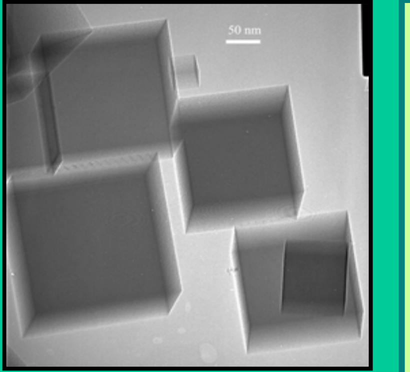
- a direct relationship between the surface electric field intensity and $\Delta\omega_e$(CO) is found
- reinforces the idea of a largely electrostatic interaction of CO with ionic substrates

Role of low-coordinated Mg^{2+} sites (1992)



- Theory: electrostatic interaction allows to rationalize IR spectra; $\Delta\omega_e(CO)$ larger when CO is bound at low-coordinated Mg^{2+} sites

- on low-coordinated sites also D_e is larger



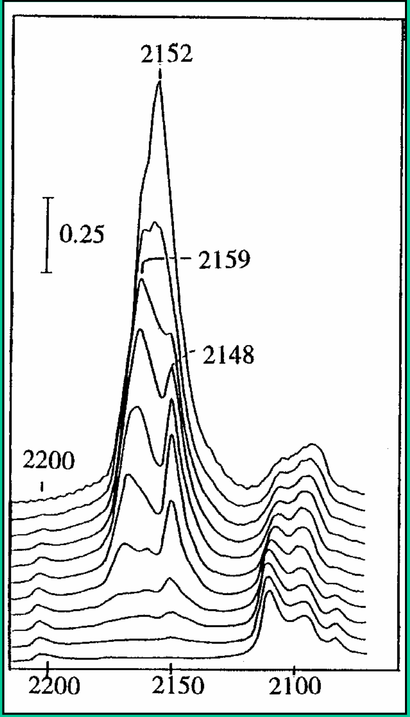
MgO smoke: Nano-sized cubes with high surface area

- HF predicts $\Delta\omega_e(CO)$ of +31, +55, and +97 cm^{-1} for CO adsorbed on terrace, step and corner sites.

Pacchioni et al., Surf. Sci. 275 (1992) 450

- Experiment: ω shifts are larger in absolute value but similar in trend to those measured for CO on various sites of MgO smokes, +9, +21, and +57 cm^{-1}

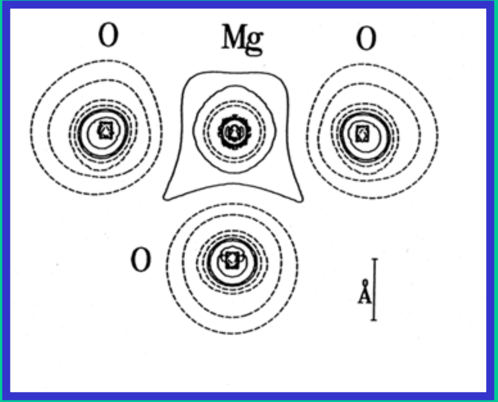
Marchese et al., Surf. Sci. 269/270 (1992) 135



The turn of Density Functional Theory (1992-1994)

LDA on clusters+PCs $\Rightarrow D_e \approx 0.56$ eV & $\Delta\omega$(CO) = +54 cm^{-1}! indication of charge transfer from CO 5σ to surface (totally different from previous analysis)

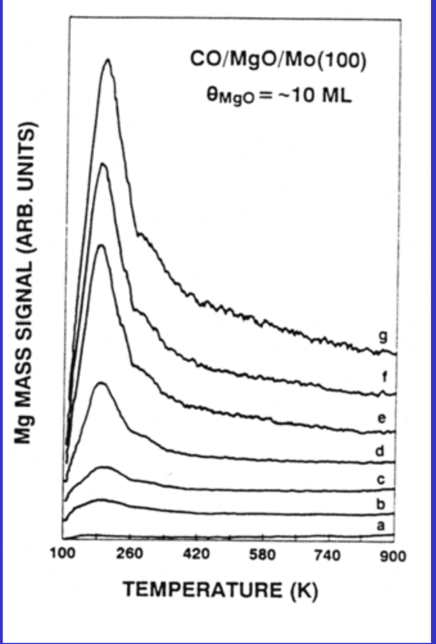
K. Neyman and N. Rösch, Chem. Phys. 168 (1992) 267



Comparison of HF and DFT reveals a less ionic description of MgO in LDA as compared to Hartree-Fock

G. Pacchioni, K. Neyman, N. Rösch, J. El. Spectr. Rel. Phenom. 69 (1994) 13

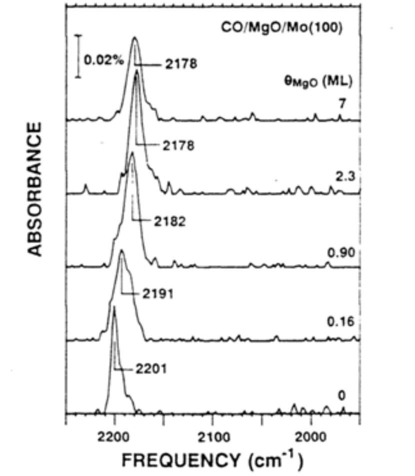
From MgO powders to thin films: a new field (1992)



New method to study oxides in UHV: ultra-thin films. The way to “clean”, defect-free, ideal surfaces

CO/MgO/Mo(100): TPD

The temperature programmed desorption (TPD) spectra show the presence of a single peak at 180 K corresponding to a CO heat of adsorption of 0.43-0.46 eV



CO/MgO/Mo(100): FT-IR

CO adsorbed on seven monolayers of MgO shows a frequency of 2178 cm^{-1}, with a ω shift with respect to free CO of +35 cm^{-1}

He et al. Surf. Sci. 261 (1992) 164

MgO powders versus thin films (1992)

ultra-thin MgO films grown on Mo(100) in UHV:

TPD ⇒ $D_e \approx 0.43$ eV & IR ⇒ $\Delta\omega_e$(CO)= +35 cm^{-1}

He et al., Surf. Sci. 261 (1992) 164

therefore

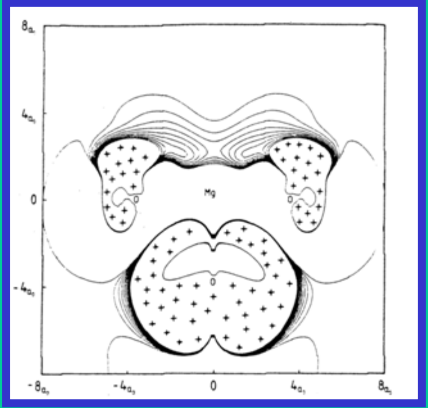
- D_e(CO) on thin films ≈3 times larger than on MgO powders
- $\Delta\omega_e$(CO) ≈ 3-4 times larger than on MgO powders

Conclusion: polycrystalline MgO defect rich (thin films assumed to be defect free from LEED, XPS, etc.)

Theory fails to reproduce experiment (1994)

Improved model: embedded (AIMP+PCs) cluster calculations

Nygren et al., J. Chem. Phys. 100 (1994) 2010, Mejias et al., Surf. Sci. 327 (1995) 59



AIMPs embedding is shown to be important to avoid unphysical polarization of O^{2-} & Mg^{2+} ions at the cluster edge

$\Downarrow$

more accurate description of charge density and electrostatic potential of the MgO surface

Attempt to reproduce He et al. binding energy of 0.4 eV. But … $D_e \approx 0.01$ eV after inclusion of basis set superposition error (BSSE) and electron correlation !

Theoretical methods come to an agreement (1995)

- New DFT cluster calc. with GGA & BSSE ⇒ $D_e \approx 0.09$ eV

Neyman, Rösch et al., Chem. Phys. Lett. 246 (1995) 546

- All cluster calculations, HF+corr or DFT-GGA, predict a very weak bonding for CO on MgO < 0.1 eV (disagree with experimental results of He et al., $D_e \approx 0.4$ eV)

- New calculated $\Delta\omega_e$ of +20 cm^{-1} for step site, and of +60 cm^{-1} for corner site consistent with IR spectra for MgO smokes (but disagree with $\Delta\omega_e$ = +35 cm^{-1} assigned to CO molecules on terrace sites by He et al.)

Pelmenschikov et al., J. Phys. Chem. 99 (1995) 97

Problem with theory or problem with experiment?

Tentative explanations of disagreement

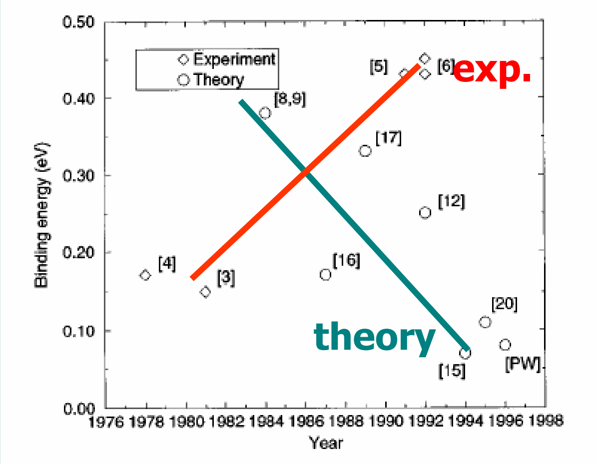
- The results (1995) indicate that

theory gives D_e < 0.1 eV, UHV exp. > 0.4 eV

theory gives $\Delta\omega$ < 10 cm^{-1}, UHV exp. > 30 cm^{-1}

- Various tentative explanations are proposed (special surface relaxation, attractive CO-CO dipole interactions, etc.)

Failure of computational approaches (1996)



The discrepancy between theory and experiment becomes embarassing

Improvement in the calculations leads to larger disagreement with experiment (and viceversa)

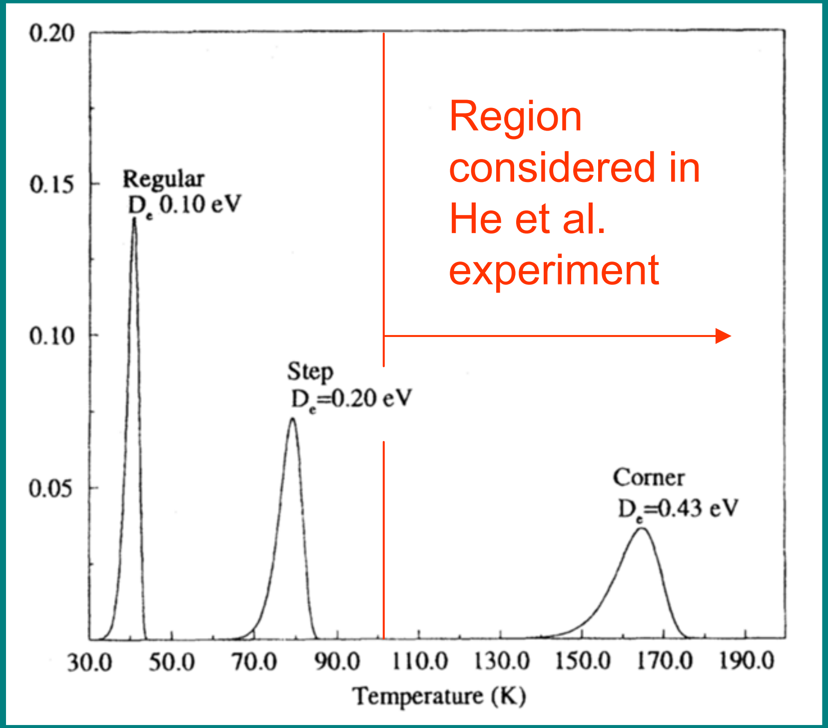
Are cluster models inadequate?

Could the experiment be misinterpreted? (1996)

Reinterpretation of the experiment of He et al. (new analysis of the TPD spectra and on accurate cluster model)

Ab initio correlated results show D_e of 0.08, 0.18 and 0.48 eV for CO adsorbed on terraces, steps, and corners. For same sites $\Delta\omega_e$ is +9, +27, and +56 cm^{-1}.

From computed adsorption energies 3 peaks expected in TPD spectrum at 40 K (terrace), 80 K (step), and 160 K (corner)



M. Nygren and L. G. M. Pettersson,
J. Chem. Phys. 105 (1996) 9339

Only one peak at 180 K seen in TPD by He et al.

Theory challenges experiment (Erice, 1996)

For the first time the fact that the MgO thin films grown on a metal substrate in UHV are defect-free is questioned in an explicit way. The active sites in CO adsorption may be low coordinated Mg cations, probably located at step or corner sites

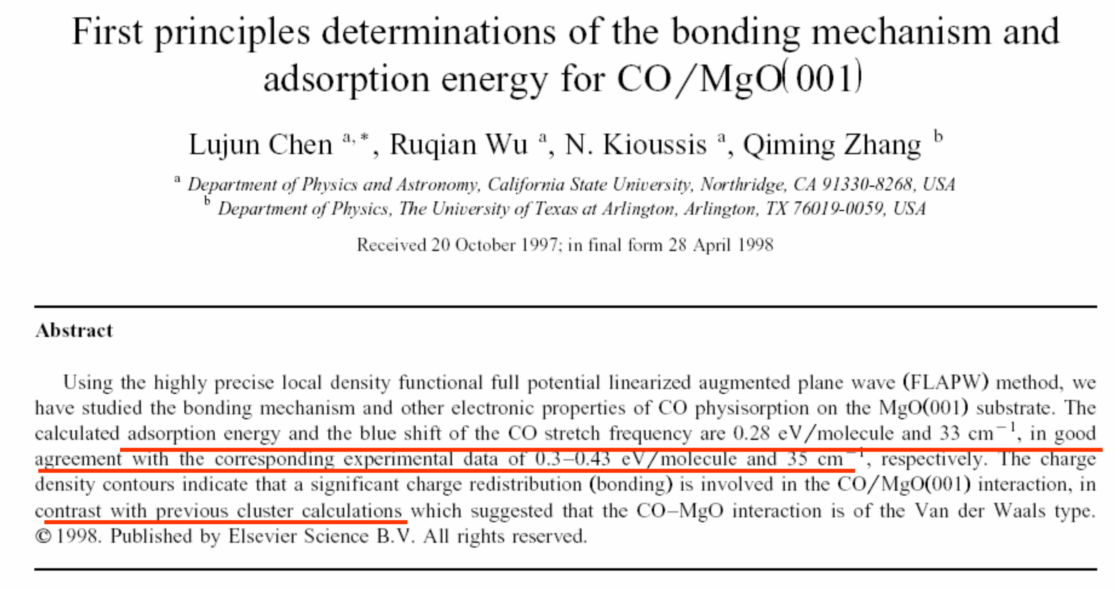
suggestion to experimentalists: look at TPD spectrum on single crystal MgO (100) surface
(not an easy experiment to do)

Nothing happens for the next two years …

New theory contradicts old theory (1998)

Summer ’98: a new study “solves” the problem

Periodic LDA gives D_e = 0.28 eV and $\Delta\omega_e$= +33 cm^{-1}, in “good agreement with the He et al. experiment”



First principles determinations of the bonding mechanism and adsorption energy for CO/MgO(001)

Lujun Chen [a,*], Ruqian Wu [a], N. Kioussis [a], Qiming Zhang [b]

[a] *Department of Physics and Astronomy, California State University, Northridge, CA 91330-8268, USA*
[b] *Department of Physics, The University of Texas at Arlington, Arlington, TX 76019-0059, USA*

Received 20 October 1997; in final form 28 April 1998

Abstract

Using the highly precise local density functional full potential linearized augmented plane wave (FLAPW) method, we have studied the bonding mechanism and other electronic properties of CO physisorption on the MgO(001) substrate. The calculated adsorption energy and the blue shift of the CO stretch frequency are 0.28 eV/molecule and 33 cm^{-1}, in good agreement with the corresponding experimental data of 0.3–0.43 eV/molecule and 35 cm^{-1}, respectively. The charge density contours indicate that a significant charge redistribution (bonding) is involved in the CO/MgO(001) interaction, in contrast with previous cluster calculations which suggested that the CO–MgO interaction is of the Van der Waals type.

Chen et al., Chem. Phys. Lett. 290 (1998) 255.

The paper states that previous studies failed because of “inherent approximations [in cluster calculations], e.g. limitations of the Gaussian LCAO, boundary effects, and embedding problems”

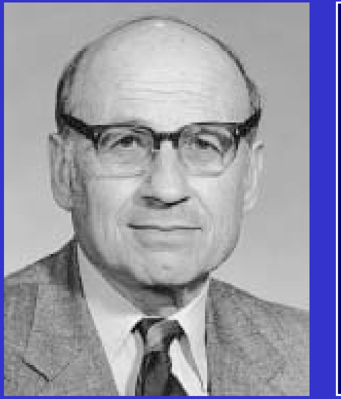
Consequences of this work, IF CORRECT, are dramatic

What would be the consequences of Chen's work (1998)

- LDA excellent for weak interactions
- GGA inadequate to study adsorption on oxide surfaces
- Gaussian basis not appropriate
- Cluster models cannot be used
- MgO thin films are defect free

Theory is in a very bad position if is unable to describe CO adsorption on MgO

Nobel Prize in Chemistry 1998

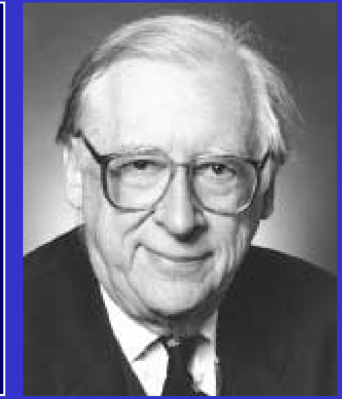


⇐ Walter Kohn

DFT

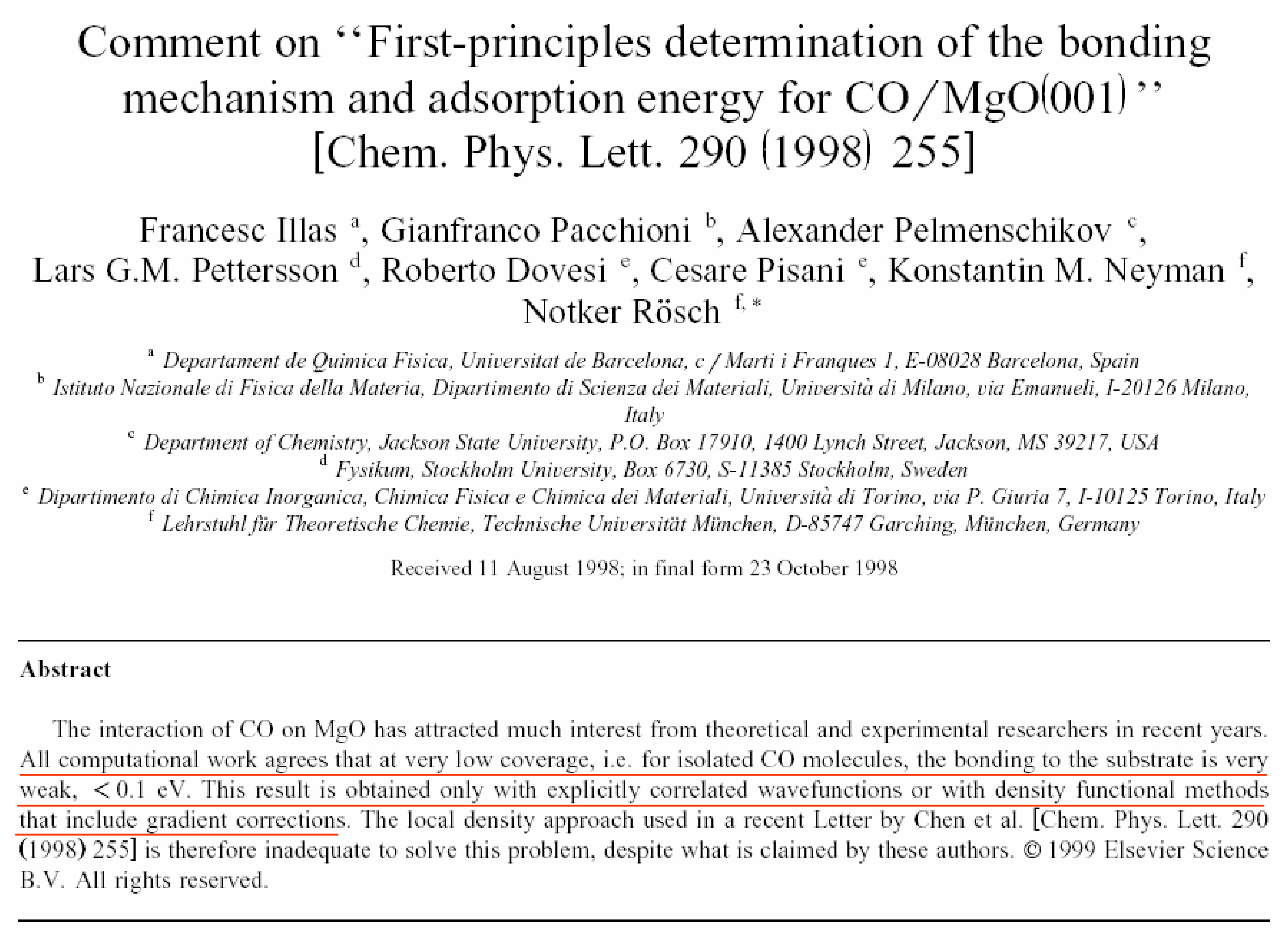
John Pople ⇒

Quantum chemistry



A comment to CPL is worth reading

Chem. Phys. Lett. 306 (1999) 202



Comment on "First-principles determination of the bonding mechanism and adsorption energy for CO/MgO(001)" [Chem. Phys. Lett. 290 (1998) 255]

Francesc Illas [a], Gianfranco Pacchioni [b], Alexander Pelmenschikov [c],
Lars G.M. Pettersson [d], Roberto Dovesi [e], Cesare Pisani [e], Konstantin M. Neyman [f],
Notker Rösch [f, *]

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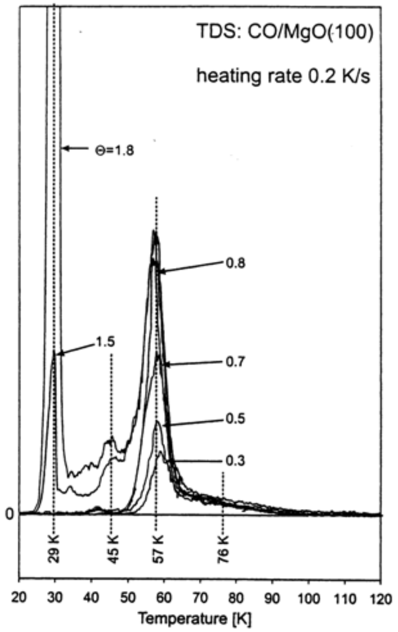
Received 11 August 1998; in final form 23 October 1998

Abstract

The interaction of CO on MgO has attracted much interest from theoretical and experimental researchers in recent years. All computational work agrees that at very low coverage, i.e. for isolated CO molecules, the bonding to the substrate is very weak, < 0.1 eV. This result is obtained only with explicitly correlated wavefunctions or with density functional methods that include gradient corrections. The local density approach used in a recent Letter by Chen et al. [Chem. Phys. Lett. 290 (1998) 255] is therefore inadequate to solve this problem, despite what is claimed by these authors. © 1999 Elsevier Science B.V. All rights reserved.

The conclusive experiment (1997-1999)
TPD of CO on MgO single crystal

Careful experiment planned in the laboratory of H.J. Freund (Fritz-Haber Institut, Berlin) in the summer of 1997. A new experimental setup is designed to measure the adsorption energy of NO and CO molecules on MgO single crystal surfaces. Wichtendahl et al., Surf. Sci. 423 (1999) 90, Phys. Stat. Sol. (a) 173 (1999) 93.



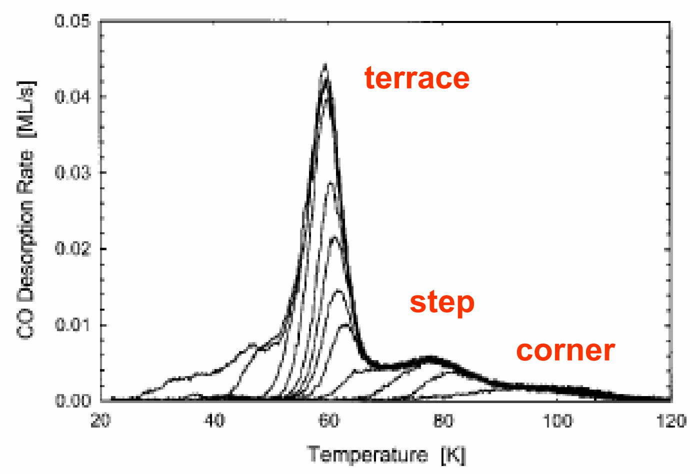
TDS for CO on UHV-cleaved MgO(001) shows multi-layer desorption at 29 K and, for small coverages, a desorption peak at T = 57 K (terrace sites) and a broad feature at 76 K (defect sites).

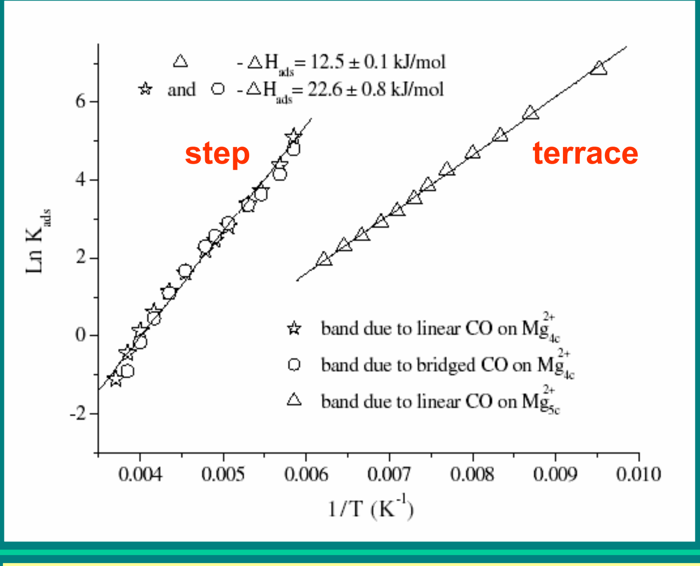
CO/MgO(100) adsorption energy: D_e = 0.14 eV!

fully consistent with theoretical analyses from cluster calculations (and with previous measurements on powders!)

More recent CO/MgO studies (2000-2004)

- New TPD spectra on good quality MgO thin films; D_e = 0.18 eV; at very low coverage desorption occurs only from defects – Z. Dohnalek et al. J. Phys. Chem. B 105 (2001) 3747





- Measurements of K_{eq} for adsorption as function of T allows new estimate of D_e on powders: 0.13 eV (terrace), 0.23 eV (steps) – G. Spoto, A. Zecchina et al. Surf. Sci. 540 (2003) L605, G. Spoto, A. Zecchina et al. Prog. Surf. Sci. 76 (2004) 71

- Theoretical analysis of bonding based on various methods shows that D_e is still underestimated; reason: dispersion forces are not properly included in currently used DFT methods. CO binds to MgO(100) mainly through dispersion forces - A. Damin, P. Ugliengo et al. Surf. Sci. 479 (2001) 255

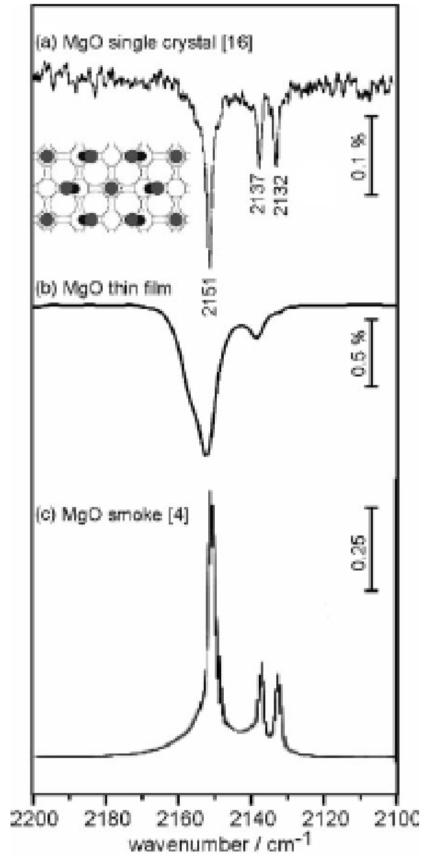
MgO single crystals, thin films and powders (2006)

CO adsorption on the surface of MgO(0 0 1) thin films

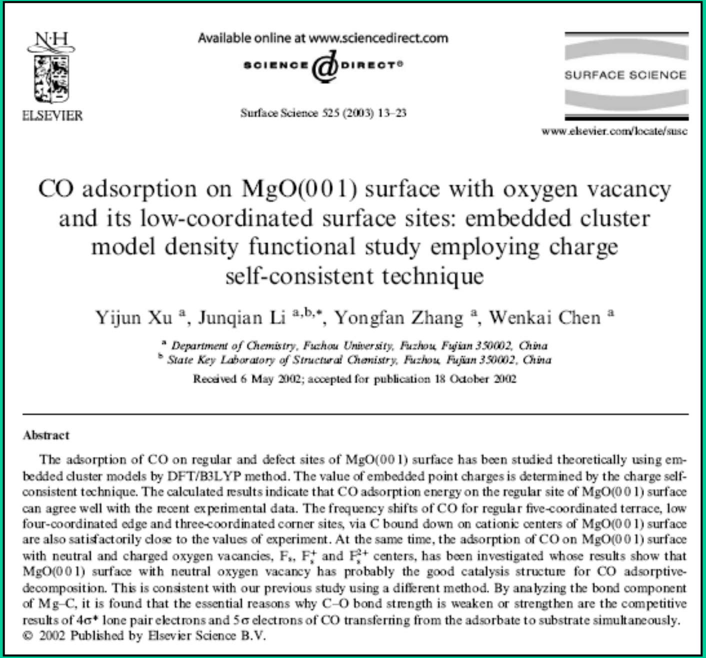
Martin Sterrer *, Thomas Risse, Hans-Joachim Freund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

The IR data obtained on thin films are in perfect agreement with similar data obtained on MgO single crystal and MgO powders, except for the higher surface roughness of MgO thin films – M. Sterrer, T. Risse, H.-J. Freund, Appl. Catal. A 307 (2006) 58



CO on MgO: benchmark for theory (2003-2007)



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Surface Science 525 (2003) 13–23
SURFACE SCIENCE
www.elsevier.com/locate/susc

CO adsorption on MgO(001) surface with oxygen vacancy and its low-coordinated surface sites: embedded cluster model density functional study employing charge self-consistent technique

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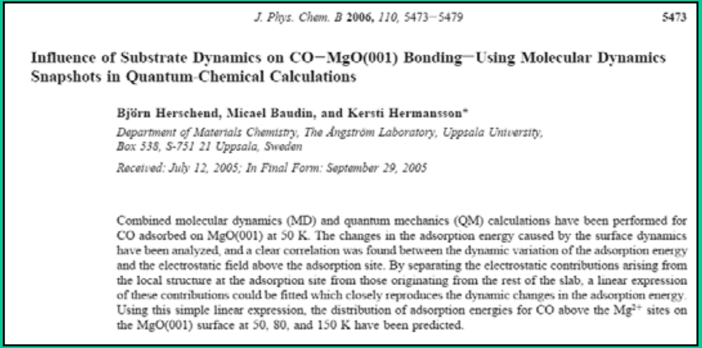
Received 6 May 2002; accepted for publication 18 October 2002

Abstract

The adsorption of CO on regular and defect sites of MgO(001) surface has been studied theoretically using embedded cluster models by DFT/B3LYP method. The value of embedded point charges is determined by the charge self-consistent technique. The calculated results indicate that CO adsorption energy on the regular site of MgO(001) surface can agree well with the recent experimental data. The frequency shifts of CO for regular five-coordinated terrace, low four-coordinated edge and three-coordinated corner sites, via C bound down on cationic centers of MgO(001) surface are also satisfactorily close to the values of experiment. At the same time, the adsorption of CO on MgO(001) surface with neutral and charged oxygen vacancies, F_s, F_s^+ and F_s^{2+} centers, has been investigated whose results show that MgO(001) surface with neutral oxygen vacancy has probably the good catalysis structure for CO adsorptive-decomposition. This is consistent with our previous study using a different method. By analyzing the bond component of Mg–C, it is found that the essential reasons why C–O bond strength is weaken or strengthen are the competitive results of 4σ* lone pair electrons and 5σ electrons of CO transferring from the adsorbate to substrate simultaneously.



J. Phys. Chem. B **2006,** *110,* 5473−5479 **5473**

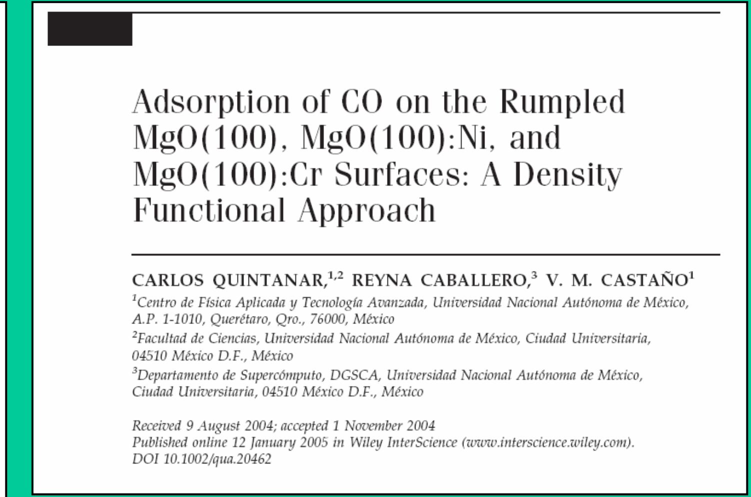
Influence of Substrate Dynamics on CO−MgO(001) Bonding−Using Molecular Dynamics Snapshots in Quantum-Chemical Calculations

Björn Herschend, Micael Baudin, and Kersti Hermansson*

Department of Materials Chemistry, The Ångström Laboratory, Uppsala University, Box 538, S-751 21 Uppsala, Sweden

Received: July 12, 2005; In Final Form: September 29, 2005

Combined molecular dynamics (MD) and quantum mechanics (QM) calculations have been performed for CO adsorbed on MgO(001) at 50 K. The changes in the adsorption energy caused by the surface dynamics have been analyzed, and a clear correlation was found between the dynamic variation of the adsorption energy and the electrostatic field above the adsorption site. By separating the electrostatic contributions arising from the local structure at the adsorption site from those originating from the rest of the slab, a linear expression of these contributions could be fitted which closely reproduces the dynamic changes in the adsorption energy. Using this simple linear expression, the distribution of adsorption energies for CO above the Mg^{2+} sites on the MgO(001) surface at 50, 80, and 150 K have been predicted.



Adsorption of CO on the Rumpled MgO(100), MgO(100):Ni, and MgO(100):Cr Surfaces: A Density Functional Approach

CARLOS QUINTANAR,[1,2] REYNA CABALLERO,[3] V. M. CASTAÑO[1]

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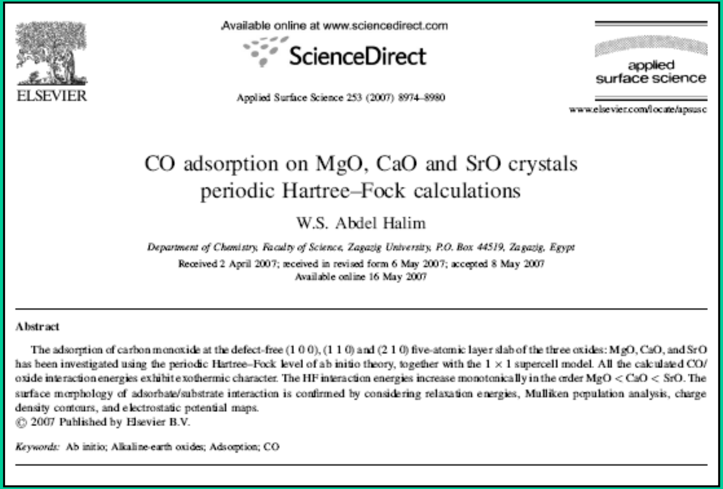
Published online 12 January 2005 in Wiley InterScience (www.interscience.wiley.com).
DOI 10.1002/qua.20462



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Applied Surface Science 253 (2007) 8974–8980
applied surface science
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CO adsorption on MgO, CaO and SrO crystals periodic Hartree–Fock calculations

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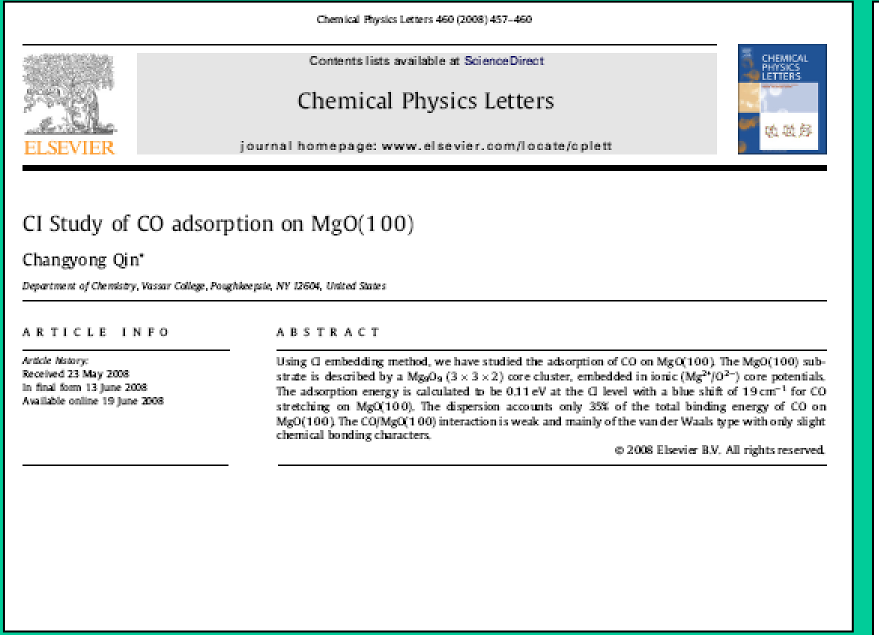
Available online 16 May 2007

Abstract

The adsorption of carbon monoxide at the defect-free (1 0 0), (1 1 0) and (2 1 0) five-atomic layer slab of the three oxides: MgO, CaO, and SrO has been investigated using the periodic Hartree–Fock level of ab initio theory, together with the 1 × 1 supercell model. All the calculated CO/oxide interaction energies exhibit exothermic character. The HF interaction energies increase monotonically in the order MgO < CaO < SrO. The surface morphology of adsorbate/substrate interaction is confirmed by considering relaxation energies, Mulliken population analysis, charge density contours, and electrostatic potential maps.

Keywords: Ab initio; Alkaline-earth oxides; Adsorption; CO

CO on MgO: benchmark for theory … (2008)



Chemical Physics Letters 460 (2008) 457–460

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CI Study of CO adsorption on MgO(100)

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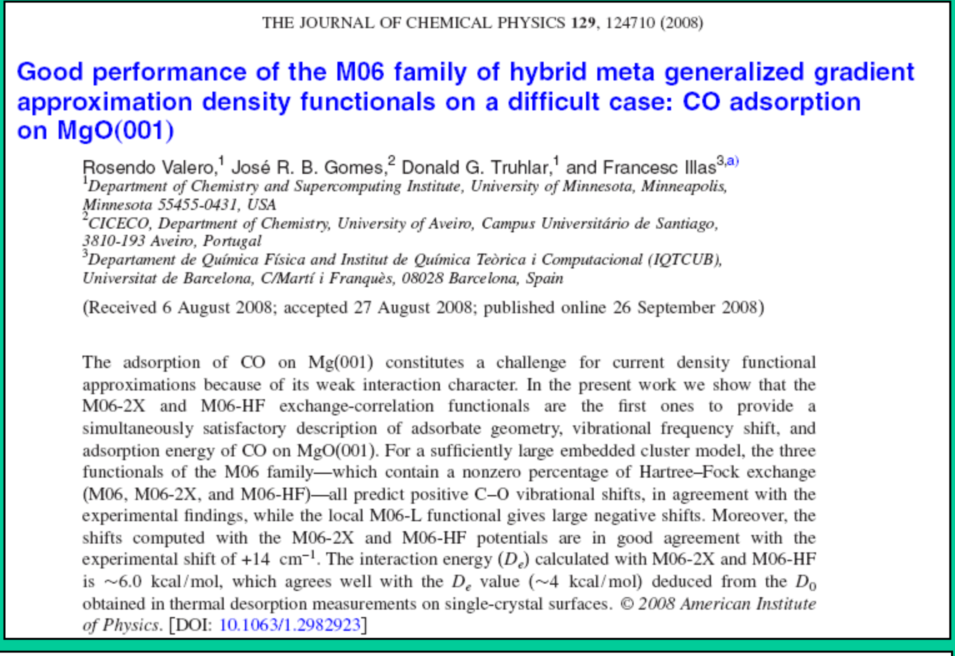
ABSTRACT

Using CI embedding method, we have studied the adsorption of CO on MgO(100). The MgO(100) substrate is described by a Mg_9O_9 (3 × 3 × 2) core cluster, embedded in ionic (Mg^{2+}/O^{2-}) core potentials. The adsorption energy is calculated to be 0.11 eV at the CI level with a blue shift of 19 cm^{-1} for CO stretching on MgO(100). The dispersion accounts only 35% of the total binding energy of CO on MgO(100). The CO/MgO(100) interaction is weak and mainly of the van der Waals type with only slight chemical bonding characters.



THE JOURNAL OF CHEMICAL PHYSICS **129**, 124710 (2008)

Good performance of the M06 family of hybrid meta generalized gradient approximation density functionals on a difficult case: CO adsorption on MgO(001)

Rosendo Valero,[1] José R. B. Gomes,[2] Donald G. Truhlar,[1] and Francesc Illas[3,a)]
[1]*Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, USA*
[2]*CICECO, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*
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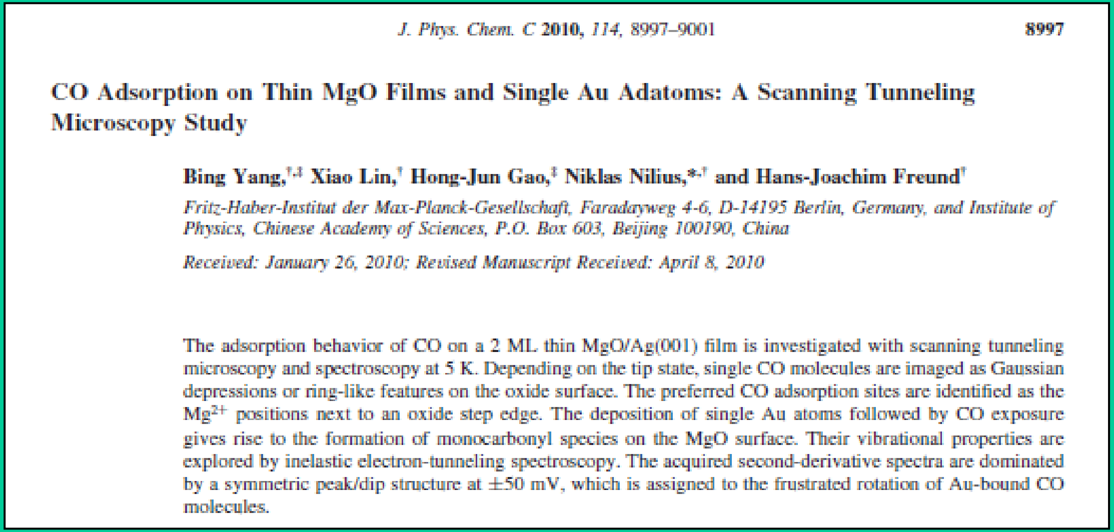
(Received 6 August 2008; accepted 27 August 2008; published online 26 September 2008)

The adsorption of CO on Mg(001) constitutes a challenge for current density functional approximations because of its weak interaction character. In the present work we show that the M06-2X and M06-HF exchange-correlation functionals are the first ones to provide a simultaneously satisfactory description of adsorbate geometry, vibrational frequency shift, and adsorption energy of CO on MgO(001). For a sufficiently large embedded cluster model, the three functionals of the M06 family—which contain a nonzero percentage of Hartree–Fock exchange (M06, M06-2X, and M06-HF)—all predict positive C–O vibrational shifts, in agreement with the experimental findings, while the local M06-L functional gives large negative shifts. Moreover, the shifts computed with the M06-2X and M06-HF potentials are in good agreement with the experimental shift of +14 cm^{-1}. The interaction energy (D_e) calculated with M06-2X and M06-HF is ~6.0 kcal/mol, which agrees well with the D_e value (~4 kcal/mol) deduced from the D_0 obtained in thermal desorption measurements on single-crystal surfaces. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2982923]

… and experiment (2010)



J. Phys. Chem. C **2010**, *114*, 8997–9001 **8997**

CO Adsorption on Thin MgO Films and Single Au Adatoms: A Scanning Tunneling Microscopy Study

Bing Yang,[†,‡] Xiao Lin,[†] Hong-Jun Gao,[‡] Niklas Nilius,[*,†] and Hans-Joachim Freund[†]

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Received: January 26, 2010; Revised Manuscript Received: April 8, 2010

The adsorption behavior of CO on a 2 ML thin MgO/Ag(001) film is investigated with scanning tunneling microscopy and spectroscopy at 5 K. Depending on the tip state, single CO molecules are imaged as Gaussian depressions or ring-like features on the oxide surface. The preferred CO adsorption sites are identified as the Mg^{2+} positions next to an oxide step edge. The deposition of single Au atoms followed by CO exposure gives rise to the formation of monocarbonyl species on the MgO surface. Their vibrational properties are explored by inelastic electron-tunneling spectroscopy. The acquired second-derivative spectra are dominated by a symmetric peak/dip structure at ±50 mV, which is assigned to the frustrated rotation of Au-bound CO molecules.

CO on MgO: What did we learn?

- Experimental studies on polycrystalline oxides are important and useful also for oxide surfaces prepared in UHV

- Thin MgO films epitaxially grown on metal substrates contain a larger density of defects than one could think based on other characterization methods (now clear also from STM images)

- Modern accurate wave function based methods including correlation effects and density functional theory based methods including gradient corrections provide a powerful tool to complement experiment and help in solving problems in surface and material science

- Be careful when you compare theory with experiment. Make sure that you are talking of the same thing! Only trust “very good agreement with experiment” when theory is good and experiment is good (many examples in the literature of “good agreement” with wrong experiments …)

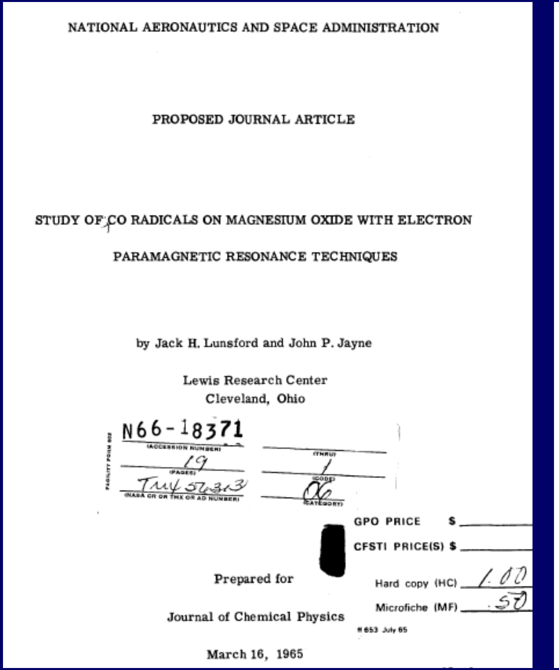
- MgO is probably the best characterized oxide and can now be used to test new methods and techniques

What about Lunsfords' experiments ?

CO adsorbed on polycrystalline MgO leads to formation of paramagnetic species (characteristic signal in EPR) - J.H. Lusford and J.P. Jayne, J. Chem. Phys. 44 (1966) 1492

J. H. Lunsford

Original interpretation: $2e^-$ donated from CO 5σ to the surface & $1e^-$ back-donated from the surface to the CO $2\pi^*$



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

PROPOSED JOURNAL ARTICLE

STUDY OF CO RADICALS ON MAGNESIUM OXIDE WITH ELECTRON PARAMAGNETIC RESONANCE TECHNIQUES

by Jack H. Lunsford and John P. Jayne

Lewis Research Center
Cleveland, Ohio

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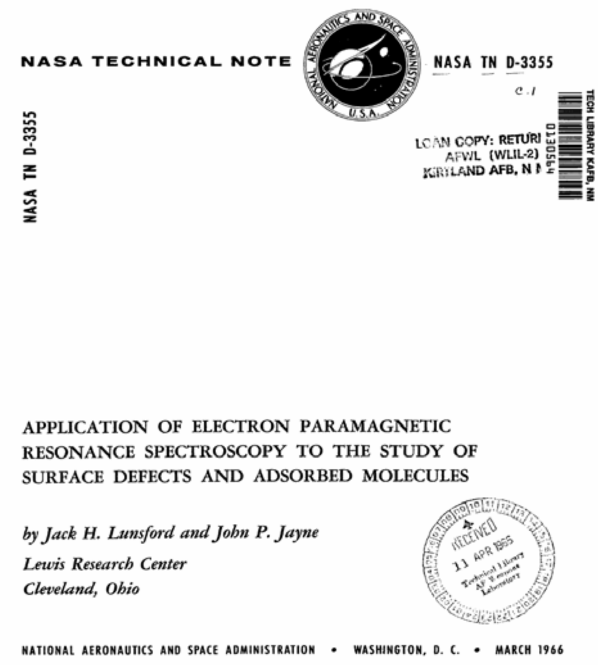
March 16, 1965



NASA TECHNICAL NOTE

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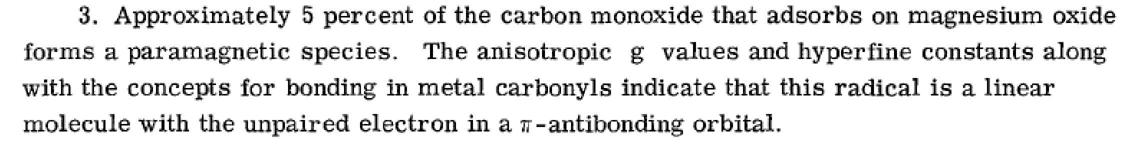
NASA TN D-3355

APPLICATION OF ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY TO THE STUDY OF SURFACE DEFECTS AND ADSORBED MOLECULES

by Jack H. Lunsford and John P. Jayne

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1966

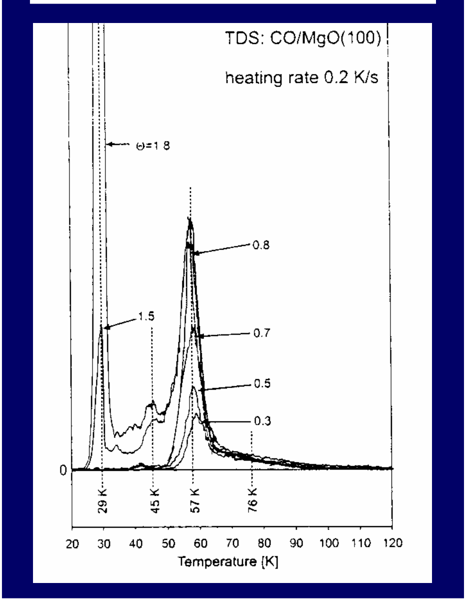


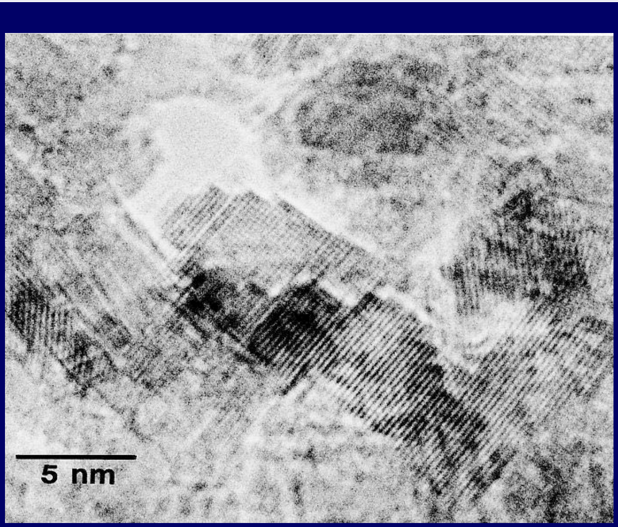
3. Approximately 5 percent of the carbon monoxide that adsorbs on magnesium oxide forms a paramagnetic species. The anisotropic g values and hyperfine constants along with the concepts for bonding in metal carbonyls indicate that this radical is a linear molecule with the unpaired electron in a π-antibonding orbital.

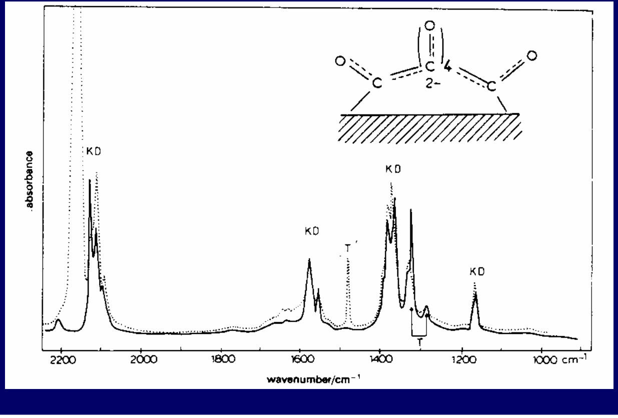
Different reactivity of oxide surfaces with different morphologies: CO on MgO

CO on single crystal MgO, no reactivity at all and adsorption occurs only below 57 K

(Freund 1998)

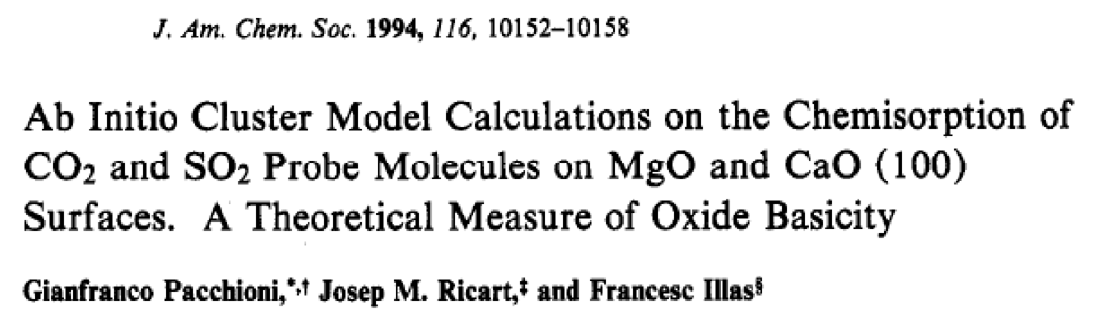






CO on polycrystalline MgO, complex radical anions form at 60 K! (Zecchina 2004)

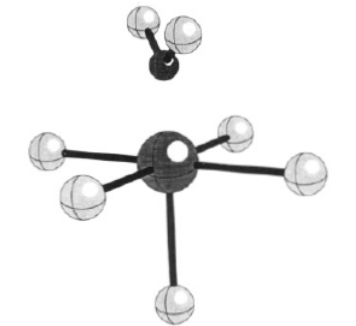
Surface basicity: an important aspect of the chemical activity of oxide surfaces

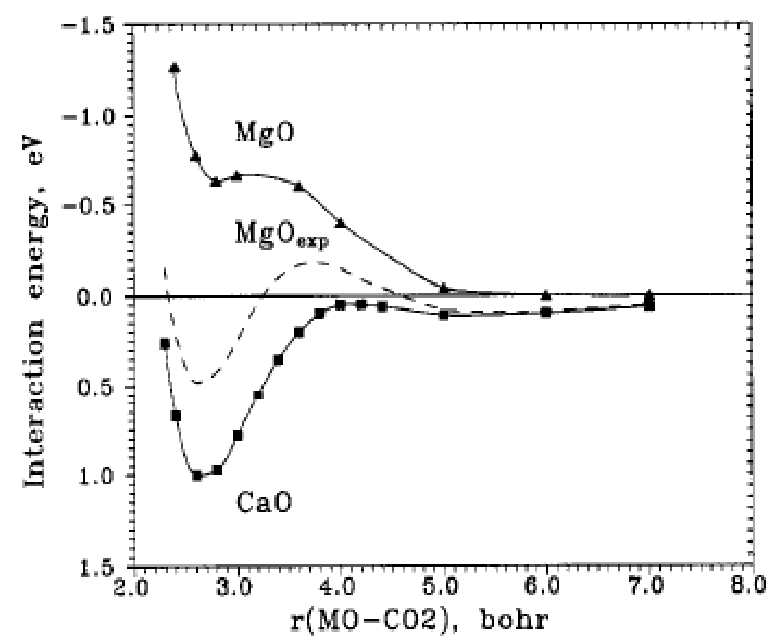


J. Am. Chem. Soc. **1994,** *116,* 10152–10158

Ab Initio Cluster Model Calculations on the Chemisorption of CO_2 and SO_2 Probe Molecules on MgO and CaO (100) Surfaces. A Theoretical Measure of Oxide Basicity

Gianfranco Pacchioni,[*,†] Josep M. Ricart,[‡] and Francesc Illas[§]





Terrace sites: MgO does not bind CO_2, CaO does

Direct correlation with Madelung potential (MP): high MP (MgO) weak basicity of O^{2-}, low MP (CaO) strong O^{2-} basicity

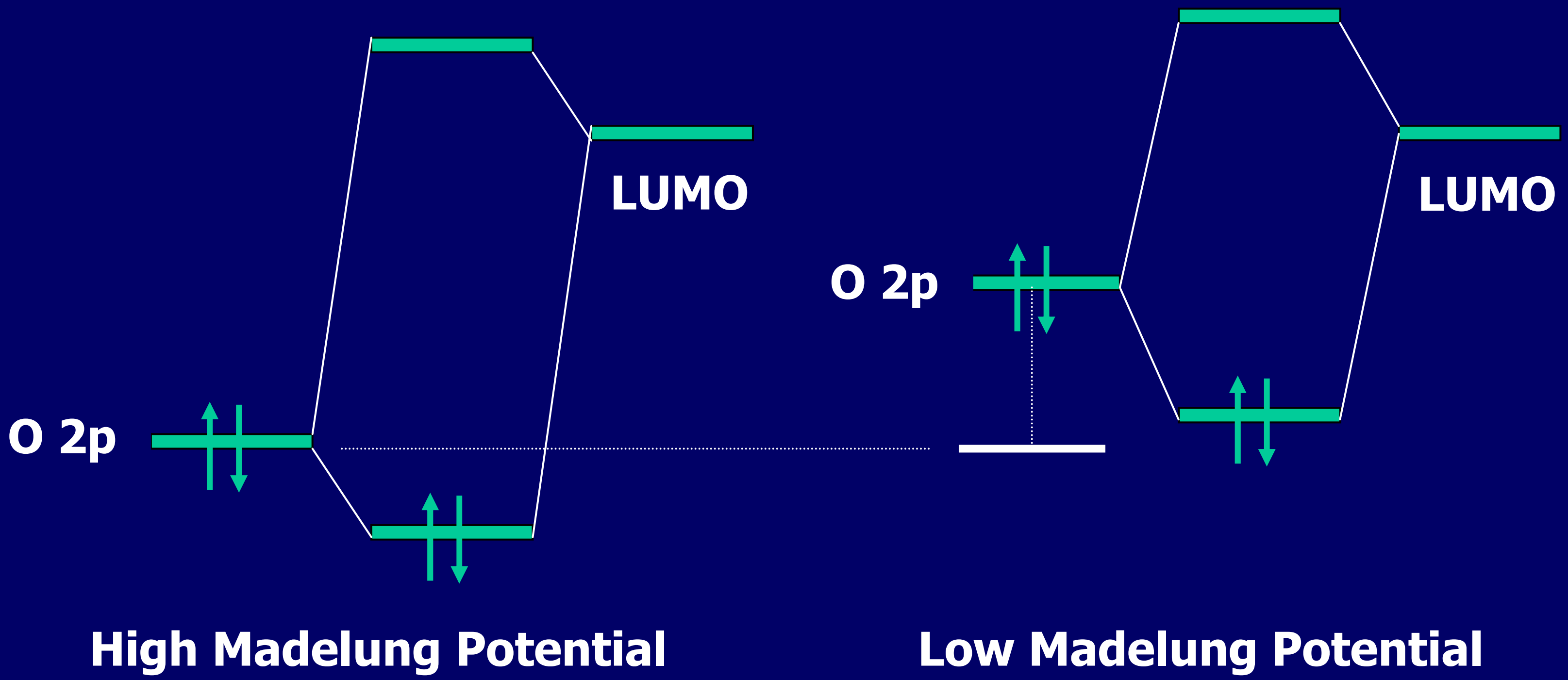
Different reactivity of CO_2 with MgO and CaO later confirmed by direct experimental evidence

Surface basicity and Madelung potential

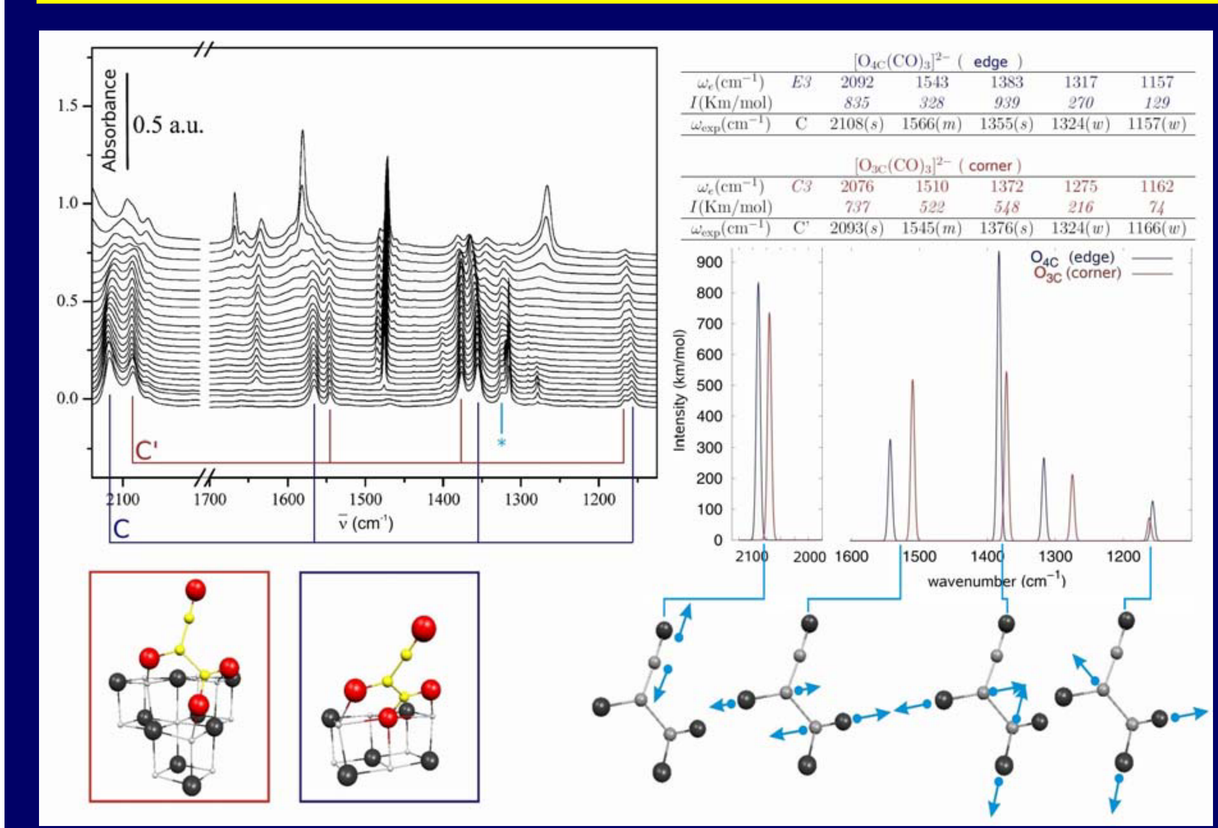
$O^{-}(g) + e^{-} \rightarrow O^{2-}(g)$ reaction unfavorable

O^{2-} ion unstable in gas-phase (where it dissociates into O^{-} + e)

O^{2-} stabilized in ionic crystals (e.g. MgO) by Madelung potential



Formation of $[C_nO_{n+1}]^{2-}$ species on polycrystalline MgO



$[O_{4C}(CO)_3]^{2-}$ (edge)

ω_e(cm^{-1})	*E3*	2092	1543	1383	1317	1157
I(Km/mol)		*835*	*328*	*939*	*270*	*129*
ω_{exp}(cm^{-1})	C	2108(s)	1566(m)	1355(s)	1324(w)	1157(w)

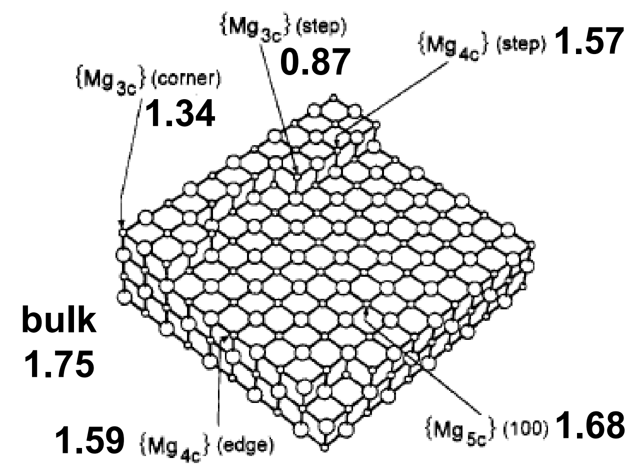
$[O_{3C}(CO)_3]^{2-}$ (corner)

ω_e(cm^{-1})	*C3*	2076	1510	1372	1275	1162
I(Km/mol)		*737*	*522*	*548*	*216*	*74*
ω_{exp}(cm^{-1})	C'	2093(s)	1545(m)	1376(s)	1324(w)	1166(w)

CO reacts with basic low-coordinated O^{2-} sites (low MP)

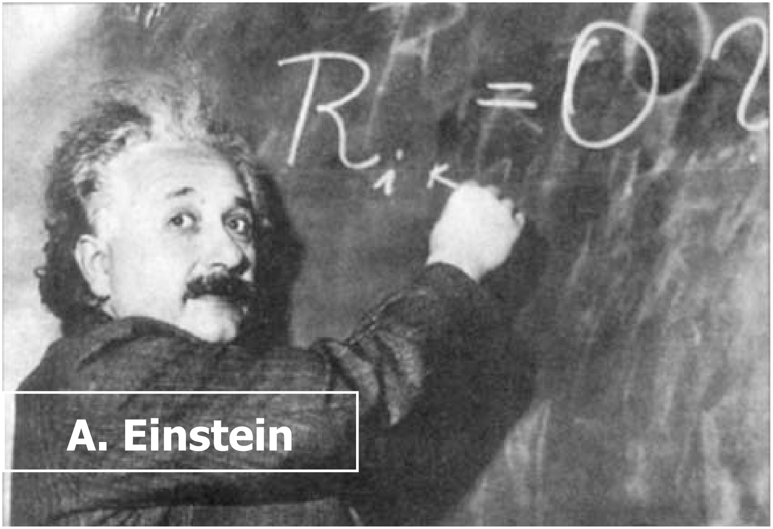
$[O(CO)_{n-1}]^{2-} + CO \rightarrow [O(CO)_n]^{2-}$

Up to 5 CO molecules react at very low T (77 K)



Spoto et al. Prog. Surf. Sci. (2004); Finazzi, Di Valentin, GP, Surf. Sci. (2006).

THEORY AND PRAXIS



A. Einstein

Theory is when we know everything but nothing works

Praxis is when everything works but we do not know why

We always end up by combining theory with praxis: nothing works and we do not know why…

END OF LECTURE 2

Surface Review and Letters, Vol. 7, No. 3 (2000) 277–306

QUANTUM CHEMISTRY OF OXIDE SURFACES: FROM CO CHEMISORPTION TO THE IDENTIFICATION OF THE STRUCTURE AND NATURE OF POINT DEFECTS ON MgO

GIANFRANCO PACCHIONI*
Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca,
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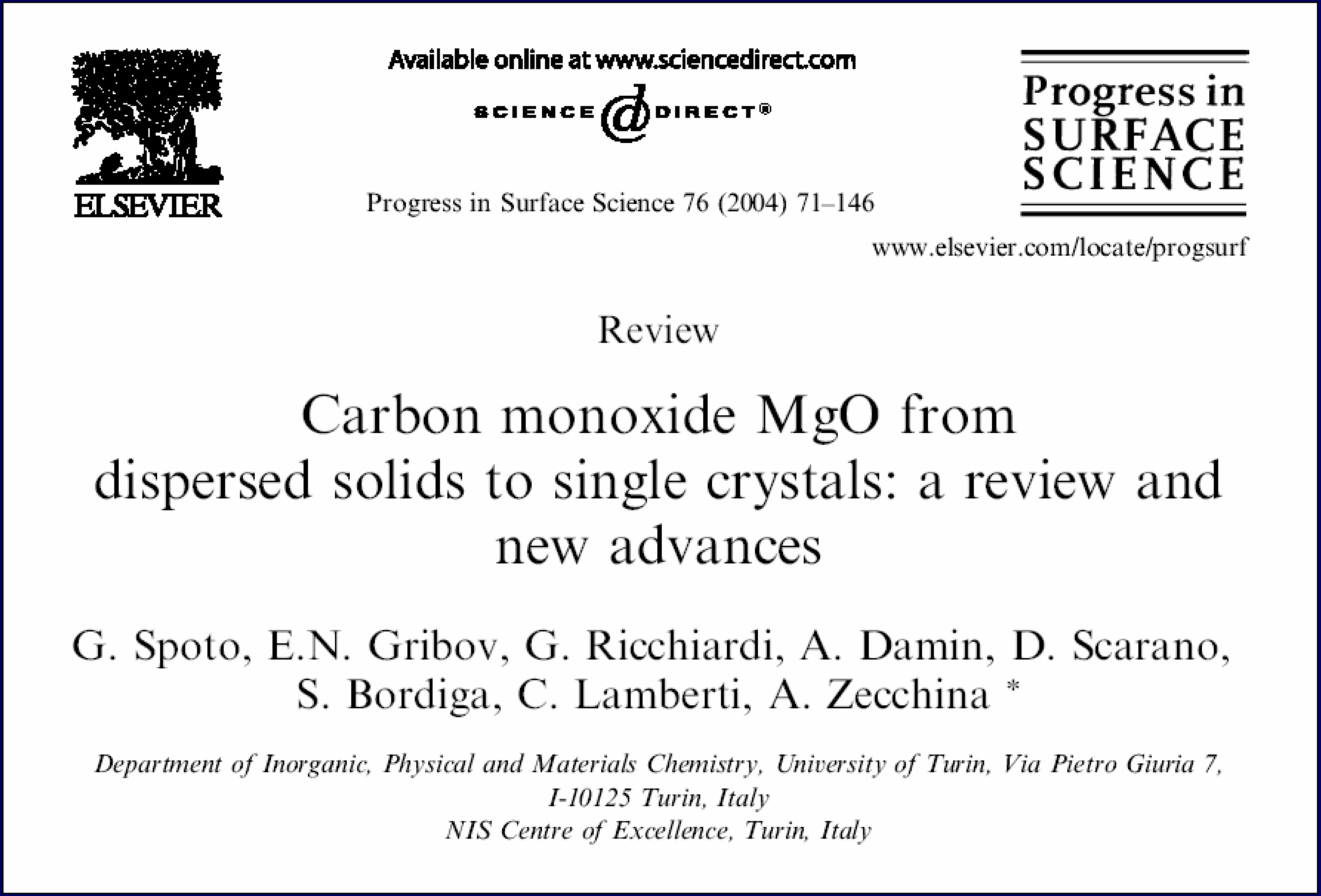

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Review

Carbon monoxide MgO from dispersed solids to single crystals: a review and new advances

G. Spoto, E.N. Gribov, G. Ricchiardi, A. Damin, D. Scarano,
S. Bordiga, C. Lamberti, A. Zecchina *

Department of Inorganic, Physical and Materials Chemistry, University of Turin, Via Pietro Giuria 7,
I-10125 Turin, Italy
NIS Centre of Excellence, Turin, Italy

ELECTRONIC STRUCTURE METHODS

Time-independent Schrödinger Equation

$$H \Psi = E \Psi$$

Born-Oppenheimer Approximation:
separation of electronic and nuclear motion

$$H_{el} (r,R) \Psi_{el} (r,R) = E_{el} (r,R) \Psi_{el} (r,R)$$

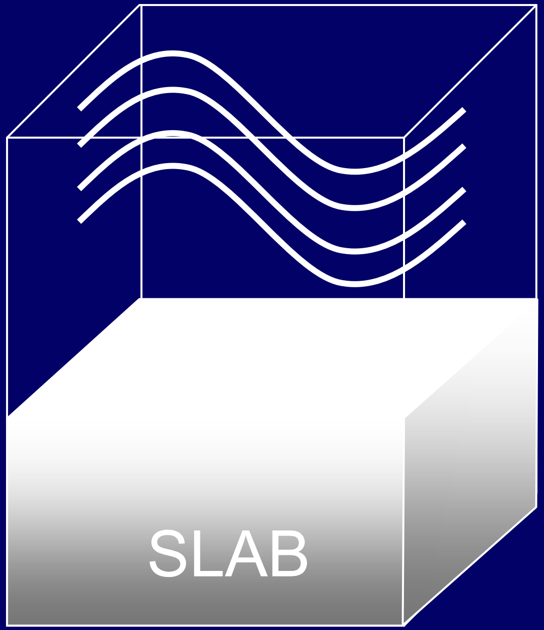
The electronic problem can be solved for nuclei which are momentarily clamped to fixed positions in space

Ψ_{el} is the N-electrons wavefunction which can be expressed in terms of one-electron wavefunctions φ expanded in a basis of known functions or basis set (in principle no approx.)

BASIS SETS: PLANE WAVES

for periodic calculations:

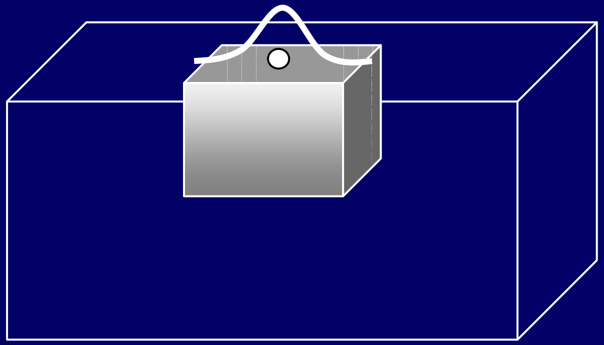
$$\varphi(k,r) = \sum_{G} c(k+G)\,\frac{1}{\sqrt{\Omega}}\,e^{i(k+G)\cdot r}$$

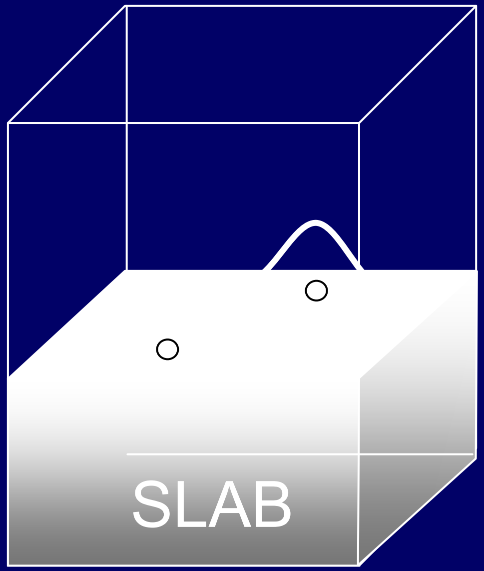


- satisfy Bloch’s theorem
- basis set functions are independent of atomic positions
- plane waves basis set must fill both atomic slab and vacuum region
- use of pseudopotentials

BASIS SETS: GAUSSIAN ATOMIC FUNCTIONS

for cluster but also periodic calculations:





$$\varphi_i\,(r) = \sum c_{pi}\,\chi_p^{GTO}\,(r)$$

$$\chi^{GTO}\,(r) = (x-A_x)^k\,(y-A_y)^l\,(z-A_z)^m\,e^{-\alpha r^2}$$

- basis set functions centered at atomic positions
- no basis set functions in the vacuum region
- all electron basis sets or
  pseudopotentials + valence electron basis sets
- split-valence basis sets to describe valence states
- diffused functions for anionic species
- polarization functions
- excellent to describe local atomic properties

METHODS: FROM HF TO DFT

Hartree-Fock HF (HF, UHF)

$$E_{HF} = E_{NUCL} + \langle hP \rangle + 1/2 \langle PJ(P) \rangle - 1/2 \langle PK(P) \rangle$$

E_{NUCL}	nuclear repulsion energy
P	density matrix
$\langle hP \rangle$	one-electron term
$1/2\langle PJ(P) \rangle$	classical Coulomb repulsion term
$-1/2\langle PK(P) \rangle$	exchange energy (exact in HF)

HF: no electron correlation

Correlation effects may be included through CI, PT or DFT

Kohn-Sham formulation of DFT (LDA, LSDA)

$$E_{KS} = E_{NUCL} + \langle hP \rangle + 1/2 \langle PJ(P) \rangle + E_X + E_C$$

$E_X[P]$	exchange functional
$E_C[P]$	correlation functional

HF special case: $E_X[P] = -1/2\langle PK(P) \rangle$; $E_C = 0$

DFT COMPUTATIONAL CODES : MOST COMMON ONES

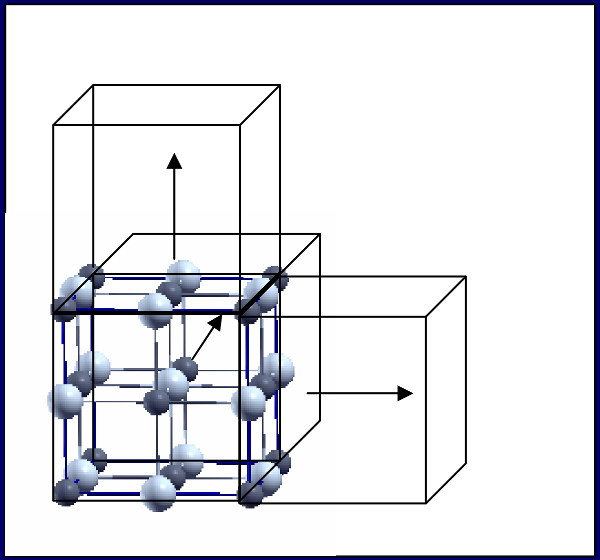
- GAUSSIAN03 cluster calculation with gaussian atomic basis set
  HF, POST-HF, DFT, hybrid DFT
  www.gaussian.com
- GUESS interfaced to GAUSSIAN cluster + shell model embedding
  www.cmpm.ucl.ac.uk/~ayg/group/home.html
- CRYSTAL06 periodic calculations with gaussian atomic basis set
  HF, DFT, hybrid DFT
  www.crystal.unito.it
- Quantum-espresso
  PWSCF plane-wave pseudopotential periodic calculations
  DFT, DFT+U
  Car-Parrinello MD ab initio molecular dynamics
  www.democritos.org
- VASP plane-wave pseudopotential periodic calculations
  DFT, DFT+U, Hybrid DFT (PBE0, HSE)
  http://cms.mpi.univie.ac.at/vasp
- CASTEP plane-wave pseudopotential periodic calculations DFT
  www.castep.org
- DACAPO plane-wave pseudopotential periodic calculations DFT
  https://wiki.fysik.dtu.dk/dacapo/Dacapo
- ……..

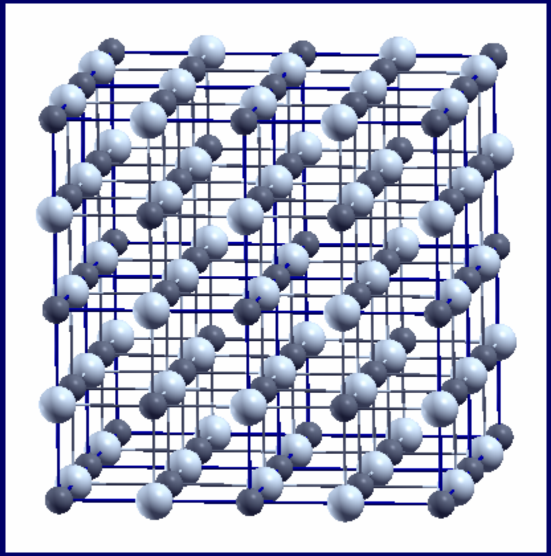
WHAT ONE CAN COMPUTE (2010)

CALCULATIONS	EXPERIMENTS
geometries	XRD
adsorption energies	TPD
thermodynamics	calorimetry
electronic structure	UPS, EELS
TD-DFT	optical abs. spectra
vibrations, phonons	IR, Raman, HREELS
EPR parameters	EPR spectroscopy
core level shifts	XPS
Integrated local DOS	STM imaging
kinetics (TS theory)	surface reactivity
molecular dynamics	(T dependence, kinetic constants)
……	……

PERIODIC MODELS FOR BULK

BULK SUPERCELLS OF CUBIC SYSTEM





- size 100 or more atoms
- neutral supercells (or background charge)
- spurious or incorrect effects may be observed for too small supercells
- k-point sampling of the Brillouin zone in reciprocal space must be done with care (size of the supercell)