Thermodynamic properties of Cu-O-H phases from first-principles calculations

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Goals of the present study

- Calculate, from first principles, the thermodynamic properties of known Cu(I) compounds with oxygen and hydrogen.
- Perform a computational search for other stable or metastable configurations of Cu, H, and O that could be products of copper corrosion.
- Analyze the thermodynamic stability of copper and its compounds in the oxygen-free water environment.

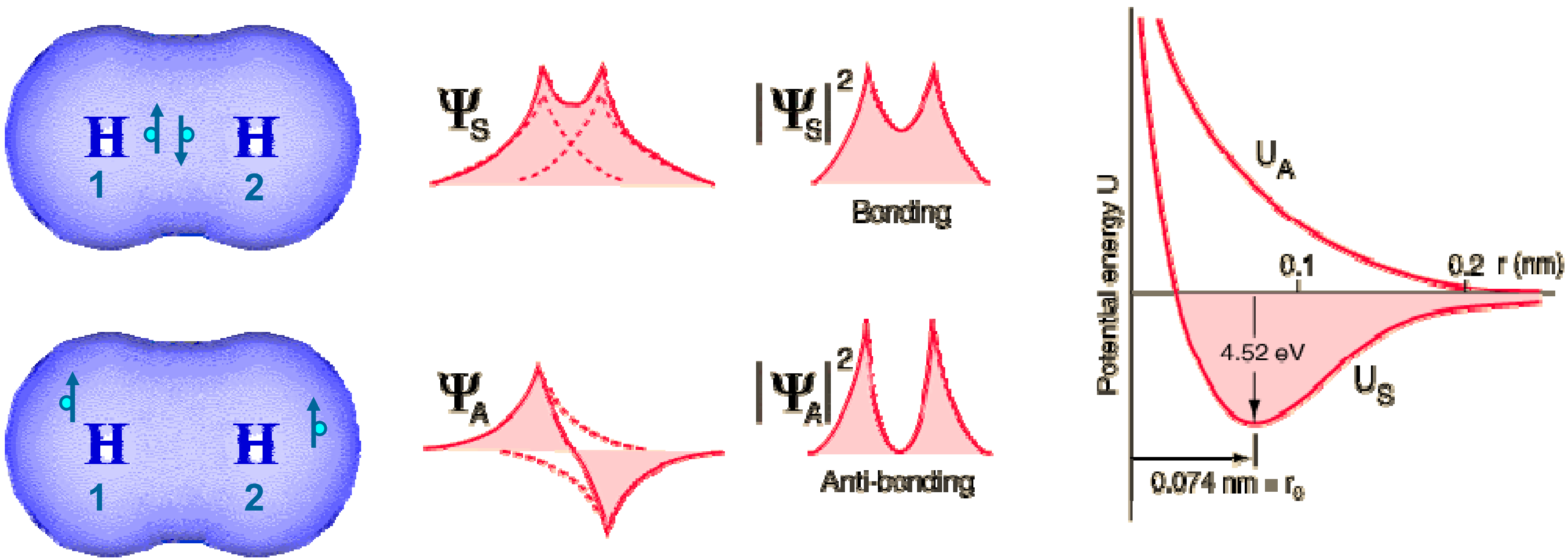
Method

QUANTUM-ESPRESSO

Ultra-soft pseudopotentials (Vanderbilt)
Density functional approximation: GGA (PBE)
Linear response theory (Baroni *et al.*)

The H_2 molecule

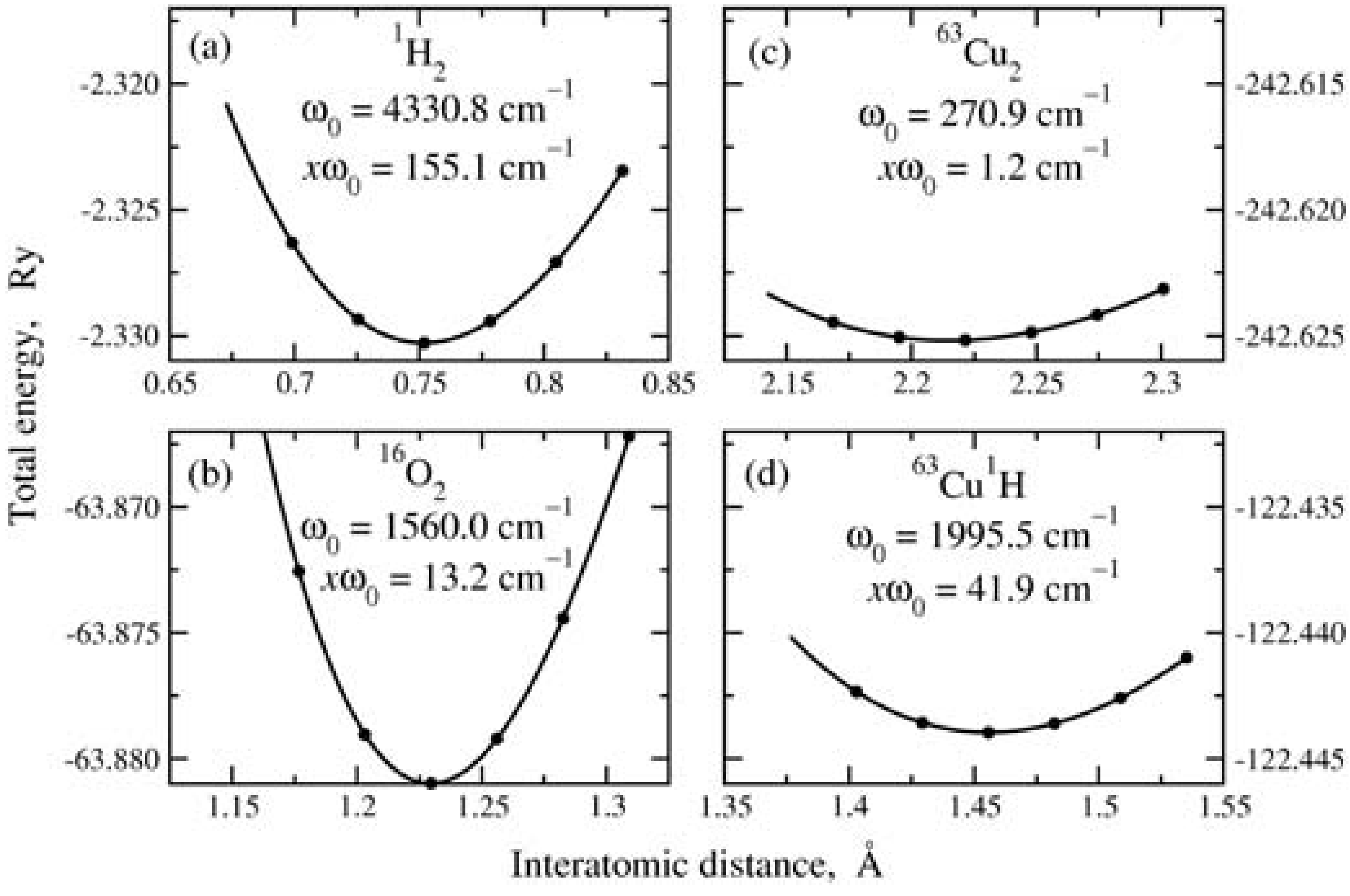
Stable state: Paired spins, symmetric



Unstable state: Unpaired spins, antisymmetric

Vibrational properties of dimer molecules

Fit: $$U(r) = C + D\left[\exp\left(-2\alpha\frac{r-r_0}{r_0}\right) - 2\exp\left(-\alpha\frac{r-r_0}{r_0}\right)\right]$$



Vibrational properties of dimer molecules

Spectrum: $$E = C - D + \hbar\omega_0\left(n+\frac{1}{2}\right) - \hbar x\omega_0\left(n+\frac{1}{2}\right)^2$$

Zero-point energy: $$\mathrm{ZPE} \approx \frac{1}{2}\hbar\omega_0 - \frac{1}{4}\hbar x\omega_0$$

Dimer	Data source	r_0 (Å)	ω_0 (cm^{-1})	$x\omega_0$ (cm^{-1})	ZPE (cm^{-1})
$^{1}H_2$	**This work**	**0.7517**	**4330.76**	**155.14**	**2126.59**
	Exp. [1]	0.7414	4401.21	121.34	2179.30
$^{16}O_2$	**This work**	**1.2294**	**1560.09**	**13.22**	**776.74**
	Exp. [1]	1.2075	1580.19	11.98	787.38
$^{63}Cu_2$	**This work**	**2.2149**	**264.55**	**1.02**	**135.14**
	Exp. [1]	2.2197	270.89	1.21	
$^{63}Cu^{1}H$	**This work**	**1.4557**	**1941.26**	**37.51**	**987.30**
	Exp. [1]	1.4626	1995.54	41.90	

[1] K. K. Irikura, *Experimental vibrational zero-point energies: Diatomic molecules* , J. Phys. Chem. Ref. Data **36**, 389 (2007).

Energy units and accuracy

$$1000\ \text{cm}^{-1} \cong 0.124\ \text{eV} \cong 12.0\ \text{kJ/mol}$$

Table 2: Absolute error (eV) of some density functional approximations in predicting the dissociation energy of small molecules [2].

Molecule	LDA	GGA(PBE)	BLYP	PKZB
H_2	+0.16	–0.21	–0.00	+0.22
OH	+0.77	+0.15	+0.14	+0.06
H_2O	+1.49	+0.09	+0.01	–0.09
O_2	+2.36	+1.01	+0.64	+0.47

[2] S. Kurth, J.W. Perdew, and P. Blaha, *Molecular and solid-state tests of density functional approximations: LSD, GGAs, and Meta-GGAs*, Inlt. J. Quantum Chem. **75**, 899 (1999).

Modeling the free energy of pure substances H_2(g) and O_2(g):

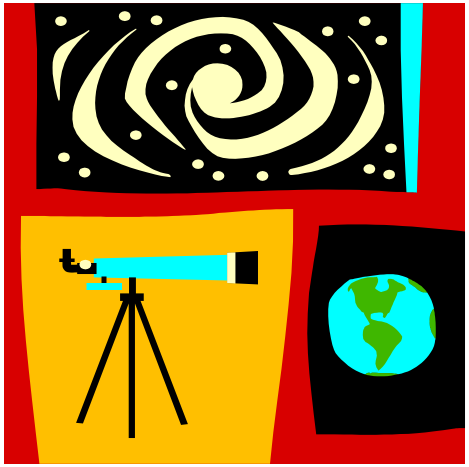
1. Compute the energies of isolated H and O atoms.
2. Use experimental dissociation energies to get the energies of H_2 and O_2.
3. Add the vibrational and rotational contributions in order to model finite-temperature properties.

Known copper(I) compounds with oxygen and hydrogen

- Cu_2O (cuprite structure)
- Red copper oxide
- First semiconductor-based device (copper oxide rectifier)

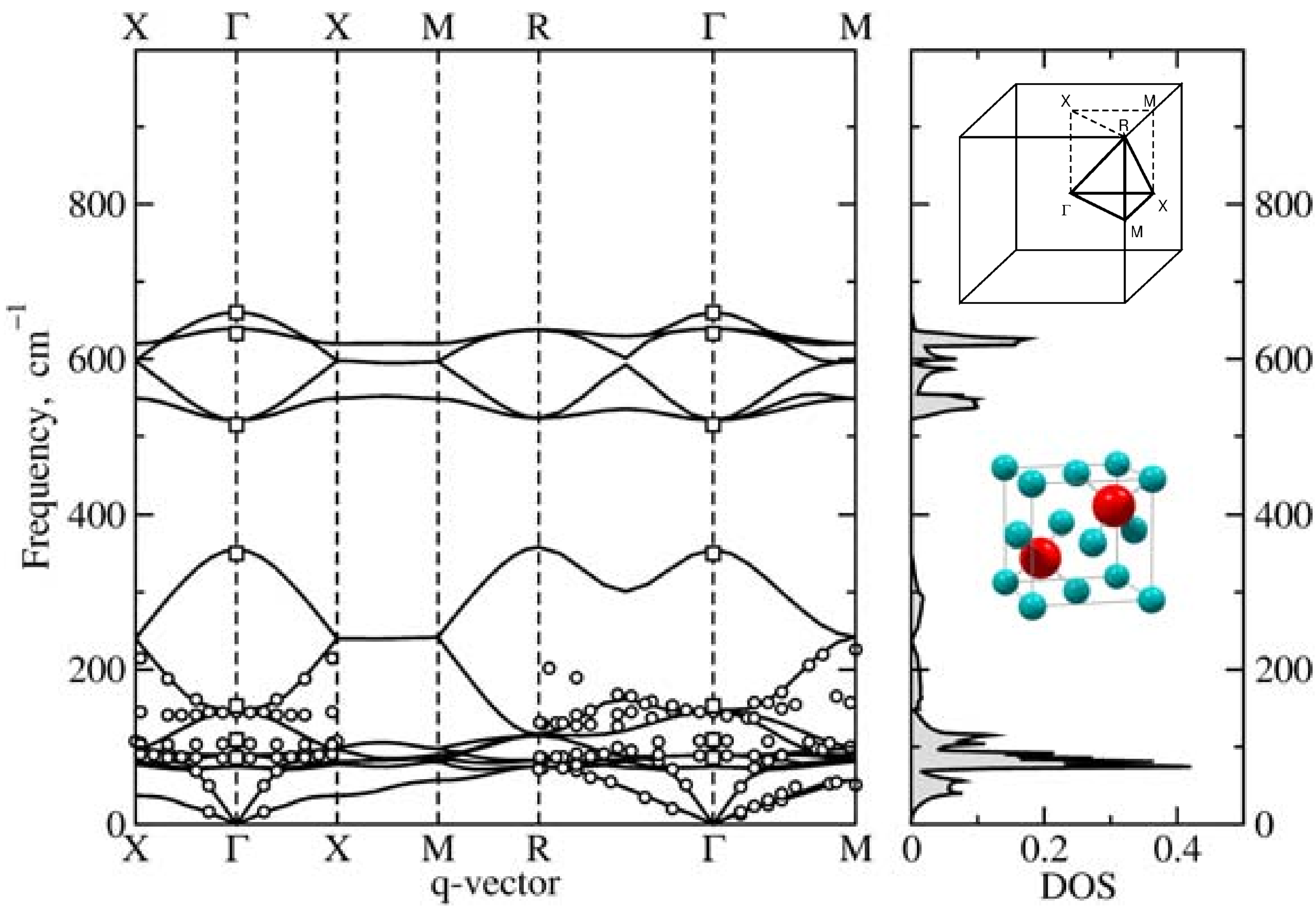
Cu^+ O^{2-}

- CuH (wurtzite structure)
- First known hydride
- Unstable (explosive)
- CuH molecules in interstellar gas

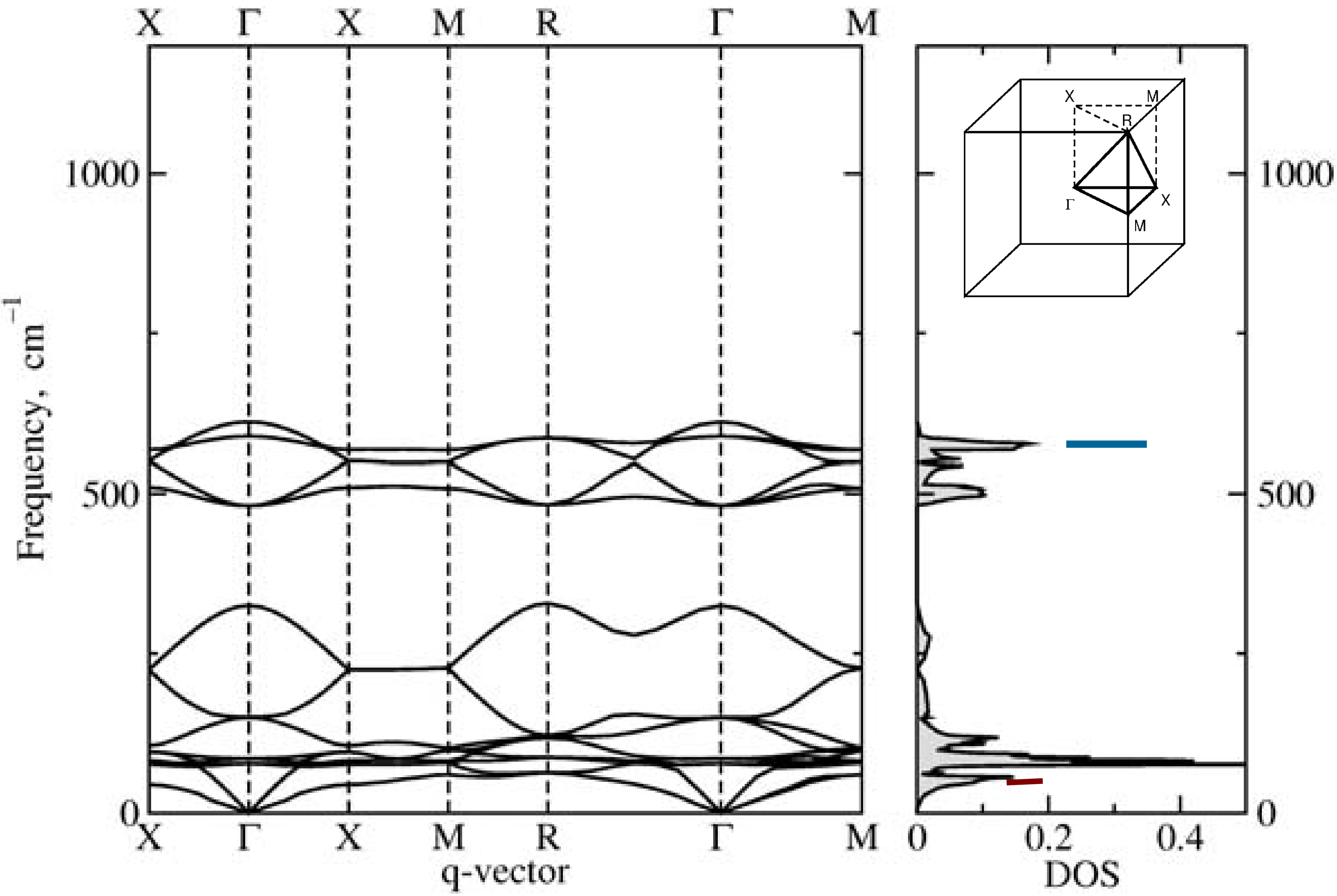


Cu^+ H^-

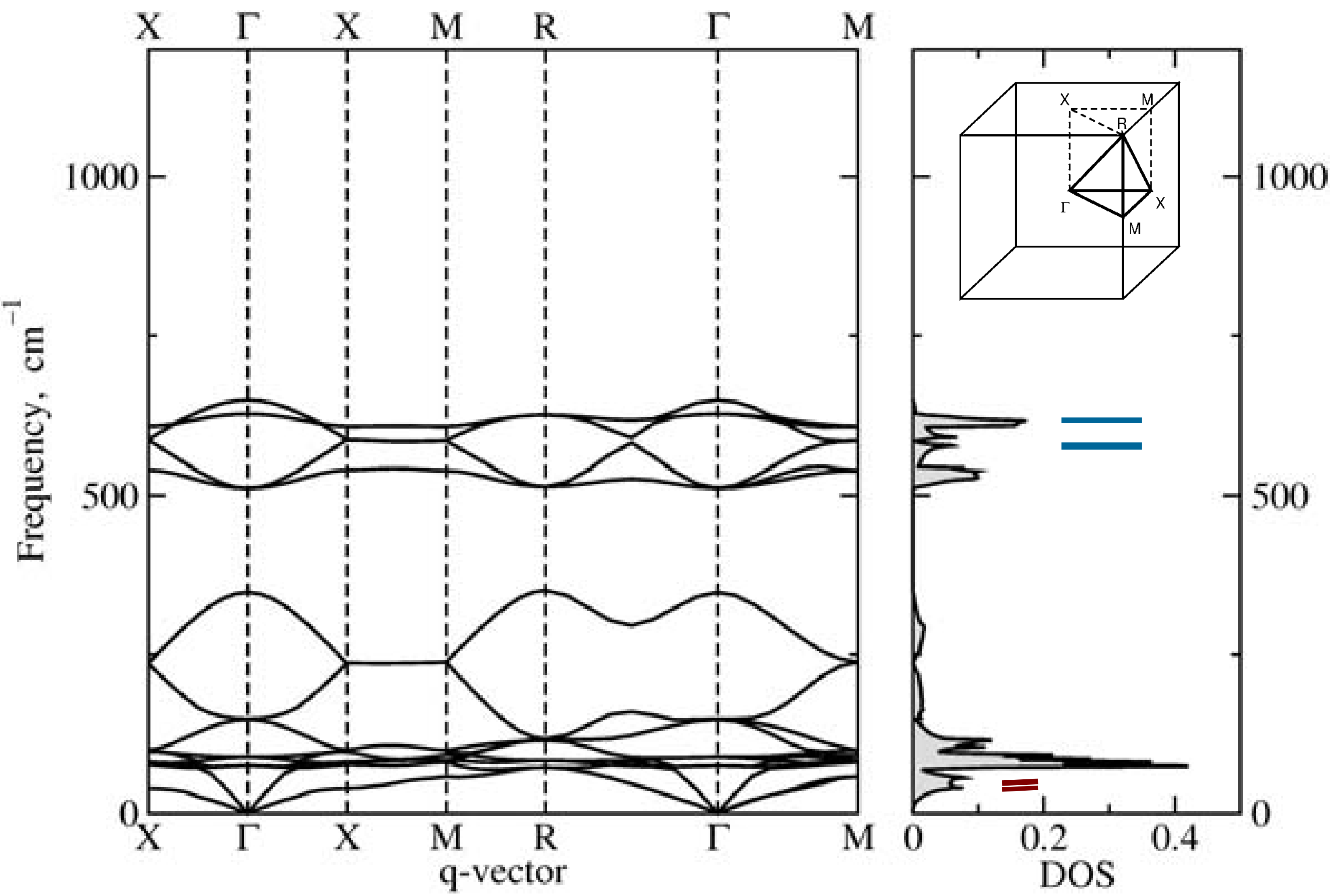
Phonon spectrum of Cu_2O



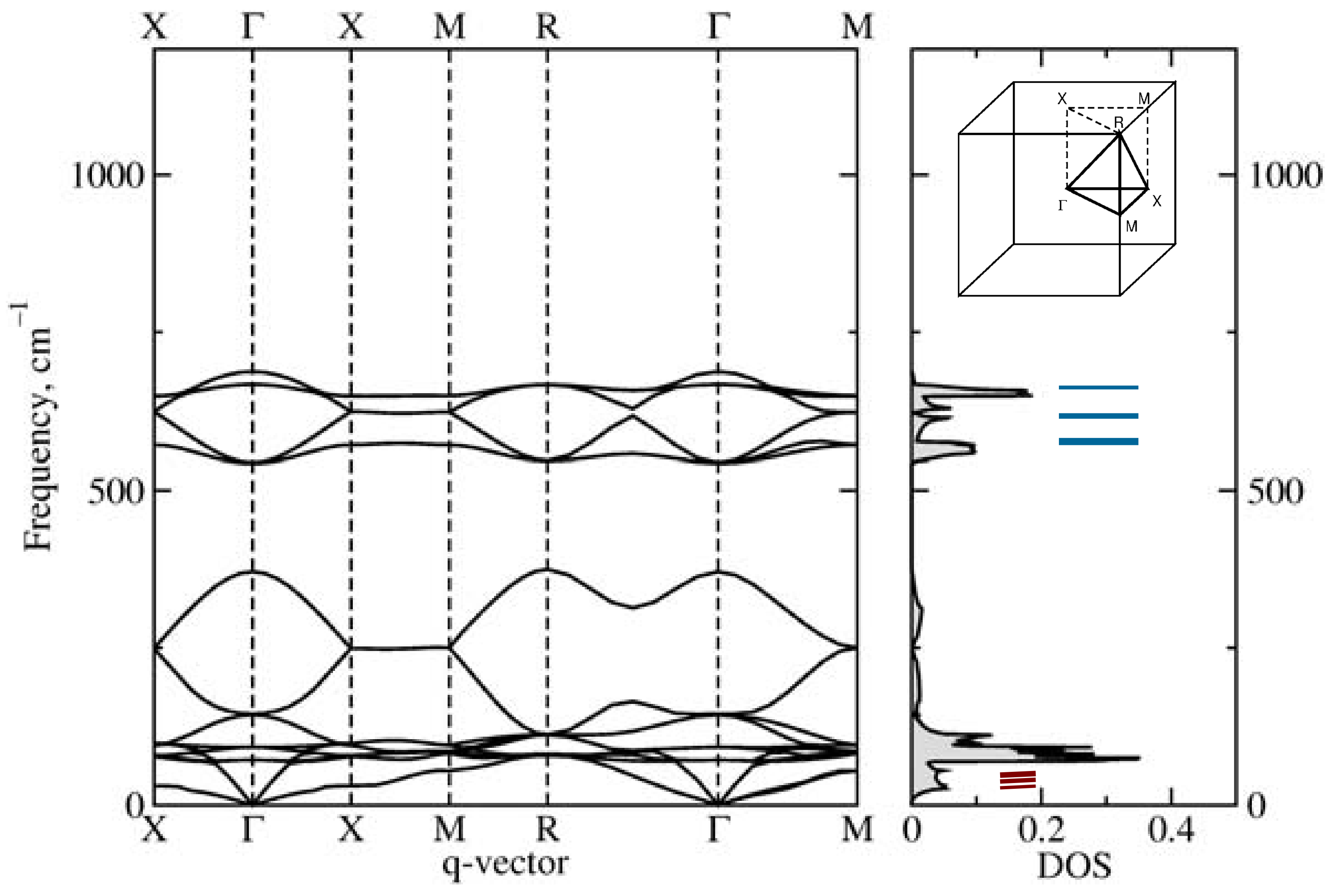
Phonon spectrum of Cu_2O



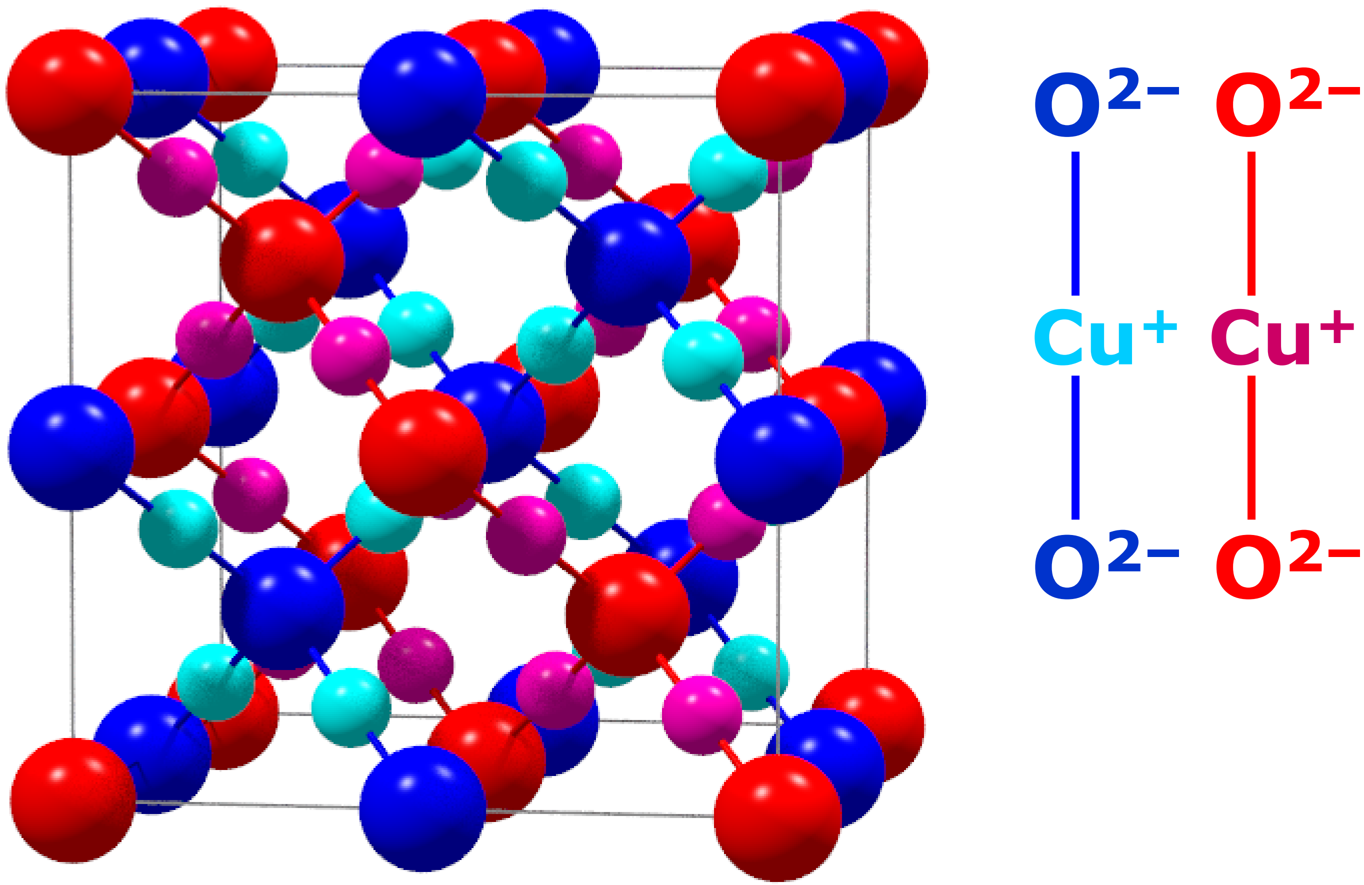
Phonon spectrum of Cu_2O



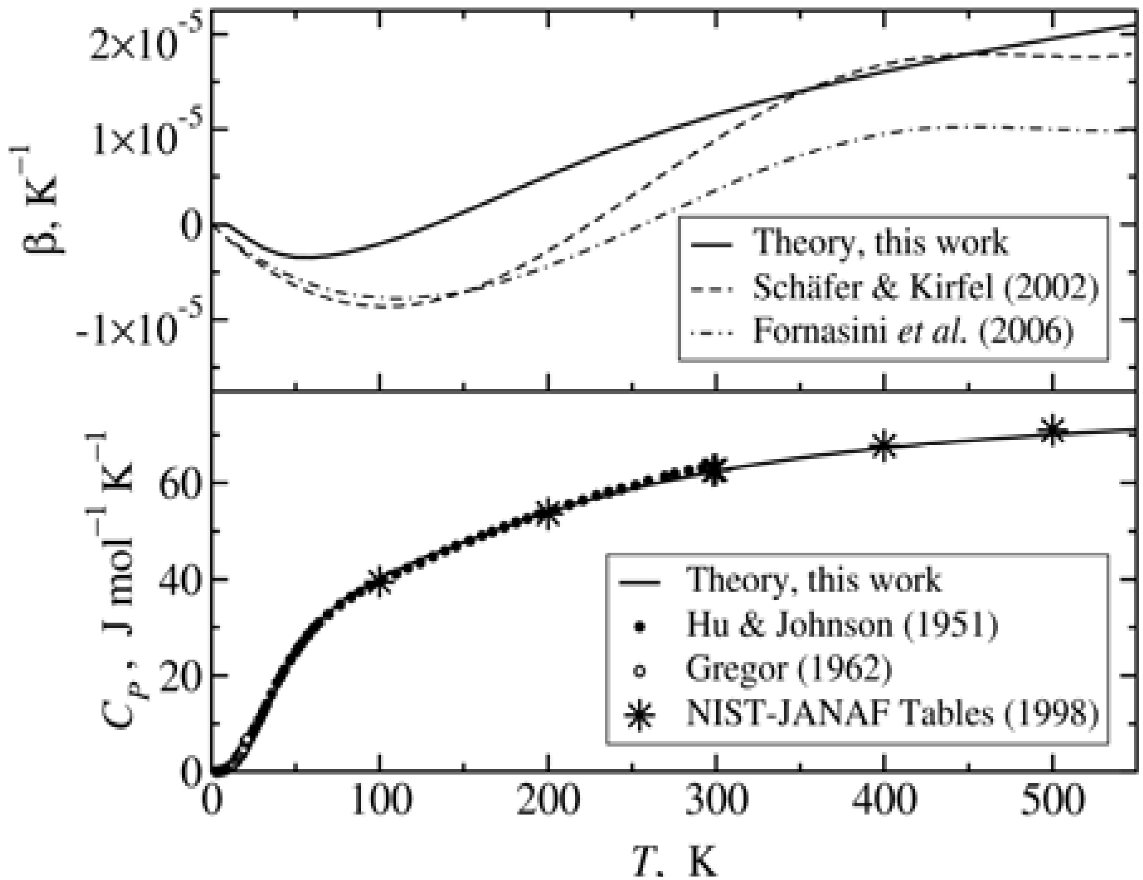
Phonon spectrum of Cu_2O



Cuprite: copper(I) oxide



Thermodynamic properties of Cu_2O



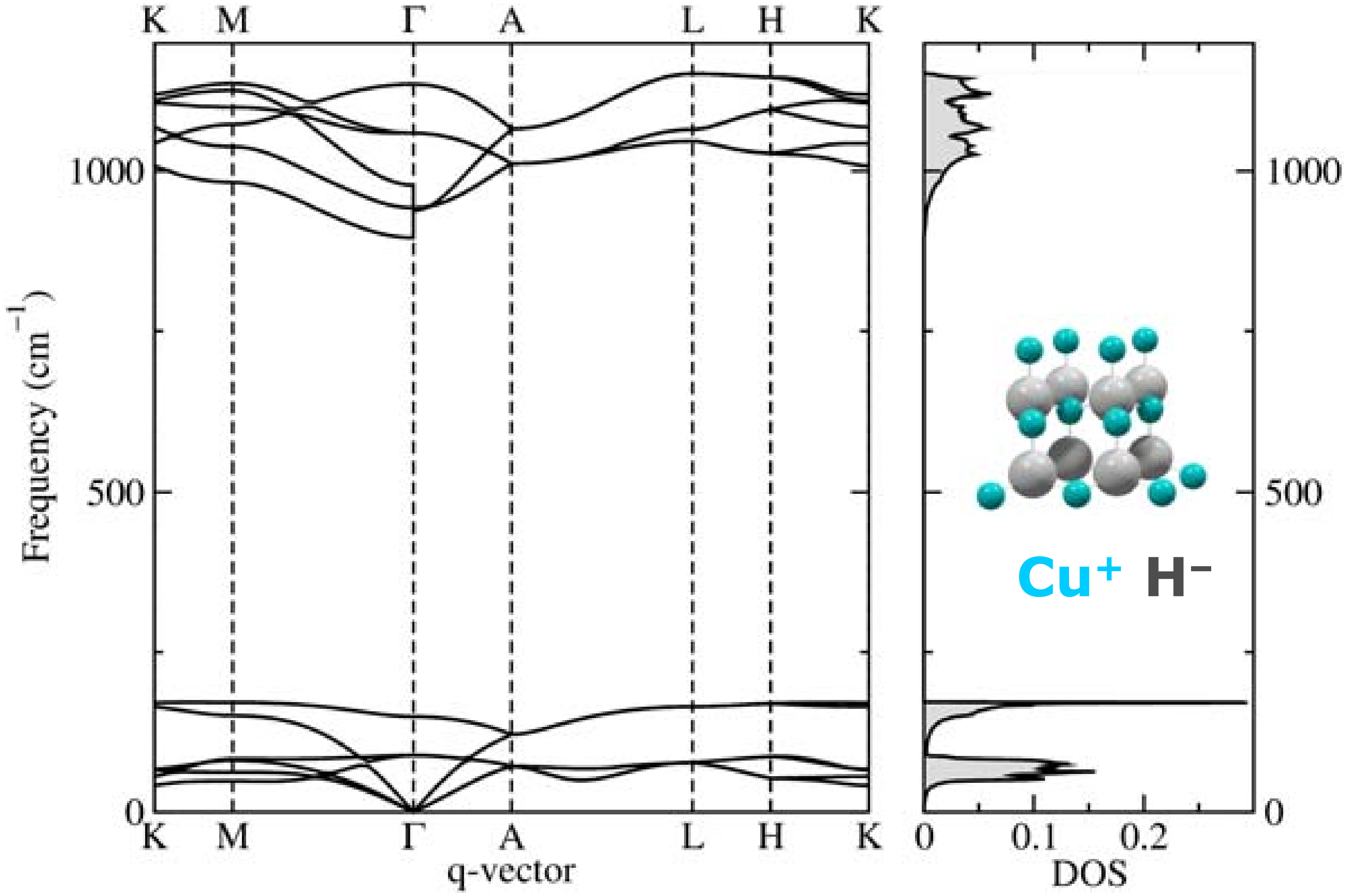
$$E_0 = U_0 + \frac{1}{2}\int_0^\infty \hbar\omega g(\omega) d\omega$$

$$C_V = k_B \int_0^\infty \left(\frac{\hbar\omega}{2k_B T}\right)^2 \frac{g(\omega)d\omega}{\sinh^2(\hbar\omega/2k_B T)}$$

$$E(T) = E_0 + \int_0^\infty \frac{\hbar\omega g(\omega) d\omega}{\exp(\hbar\omega/k_B T) - 1}$$

$$F(T) = U_0 + k_B T \int_0^\infty \log\left[2\sinh(\hbar\omega/ 2k_B T)\right] d\omega$$

Phonon spectrum of CuH



Experimental infrared spectra of CuH

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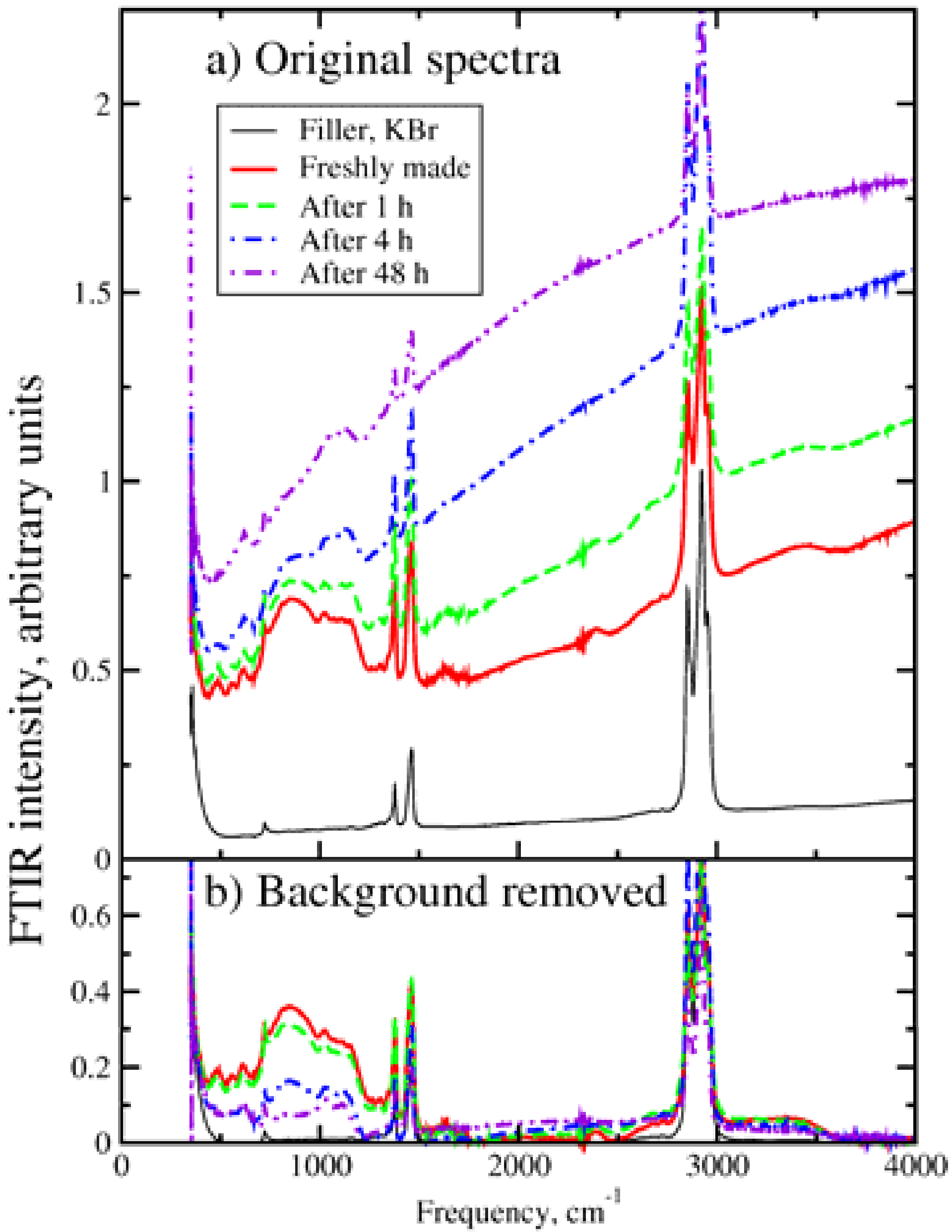
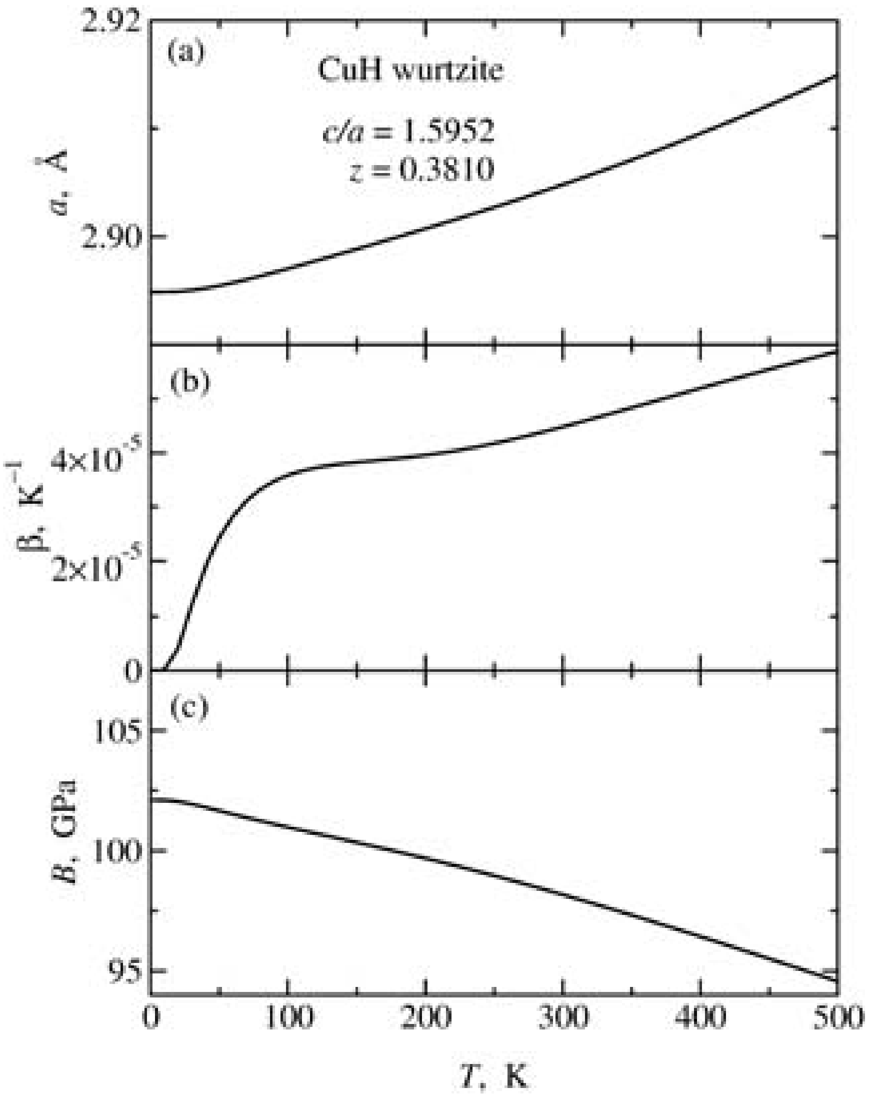
I. L. Soroka and M. Boman

Chemical synthesis and Fourier-transform infrared (FTIR) spectroscopy of CuH:

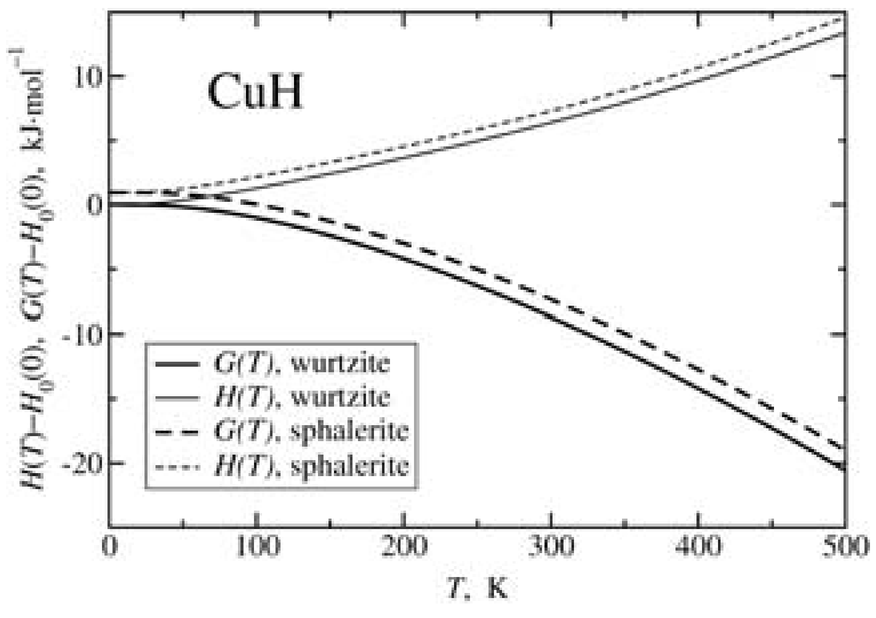


Thermodynamic properties of CuH

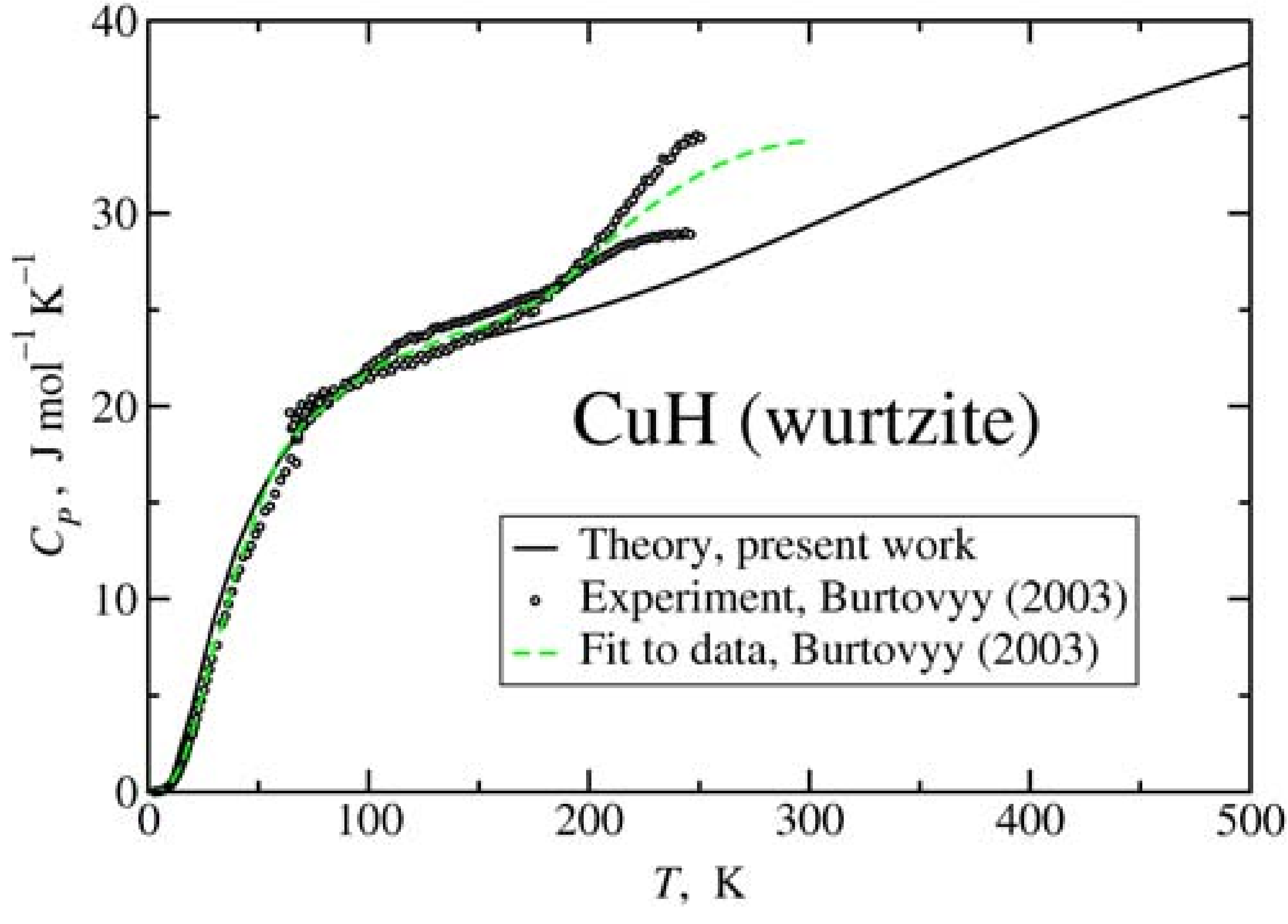


Experiment: a=2.89 Å c/a=1.595

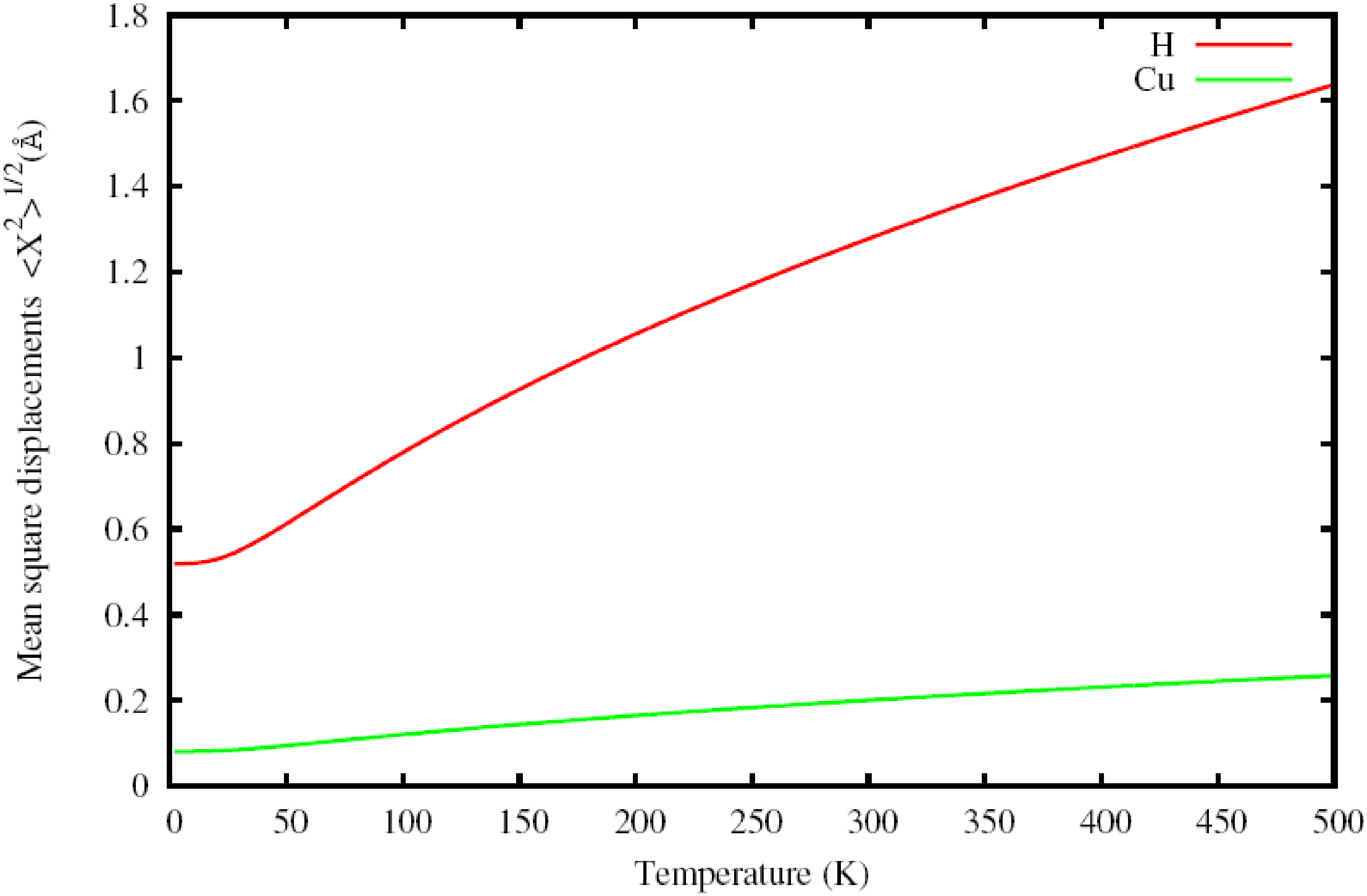
X-ray: H. Müller and A.J. Bradley, J. Chem.Soc. (1926), p. 1669.
Neutrons: J.A. Goedkoop and A.F. Andersen, Acta Cryst. **8**, 118 (1955).



Thermodynamic properties of CuH



Mean-square-root displacements of ions in CuH



Thermodynamic stability

$$2\text{Cu(cryst.)} + 1/2\cdot O_2(g) \rightarrow Cu_2O\text{(cryst.)}$$
$$\Delta G = G(Cu_2O) - 2\cdot G(Cu) - 1/2\cdot G(O_2)$$

Table 3: Enthalpy and free energy of formation (kJ/mol) of some stable and metastable copper compounds.

Substance	Data source	$\Delta H(0)$	$\Delta H(298.15)$	$\Delta G(298.15)$
Cu_2O	**This work**	**–160.6**	**–161.9**	**–140.9**
	NIST-JANAF [3]	–169.0	–170.7	–147.9
CuO	**This work**	**–146.0**	**–148.0**	**–144.7**
	NIST-JANAF [3]	–153.8	–156.1	–128.3
CuH(wurtzite)	**This work**	**+39.5**	**+36.7**	**+50.9**
	Exp. [4]		+27.5	+54.0
	Exp. [5]		+55.1	+80.5

[3] M.W. Chase, *NIST-JANAF Thermochemical Tables. Fourth Edition. Part II, Cr-Zr* (American Institute of Physics, New York, 1998).

[4] R. Burtovyy, E. Utzig, and M. Tkacz, *Studies of the thermal decomposition of copper hydride*, Thermochimica Acta **363**, 157-163 (2000).

[5] R. Burtovyy, D. Włosewicz, A. Czopnik, and M. Tkacz, Heat capacity of copper hydride, Thermochimica Acta **400**, 121—129 (2003).

What is the product of corrosion?

NyTeknik

Av: Lars Anders Karlberg
Publicerad 6 april 2009 10:08

Corrosion of Copper by Water

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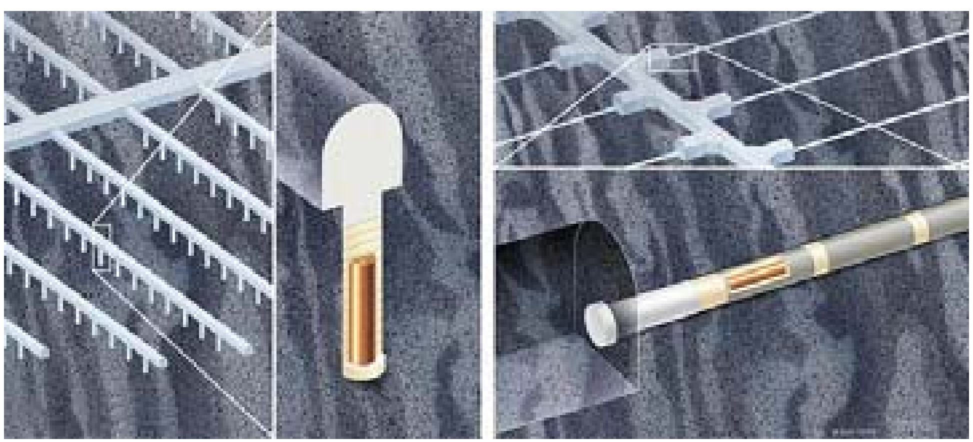
[c]Advanced Nuclear Technology, SE-751 83, Uppsala, Sweden

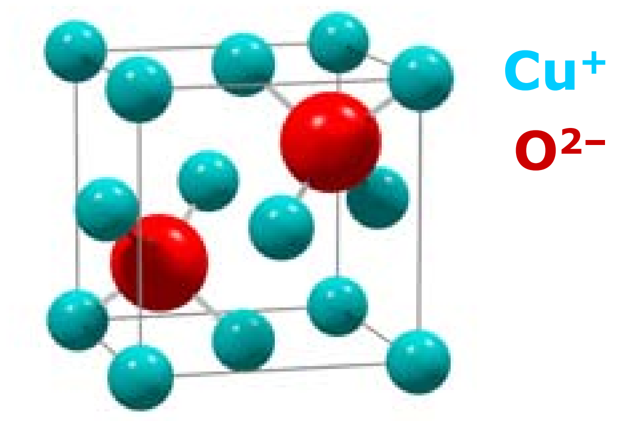
$$Cu + yH_2O \rightarrow H_xCuO_y + (2y - x)H_{ads}$$

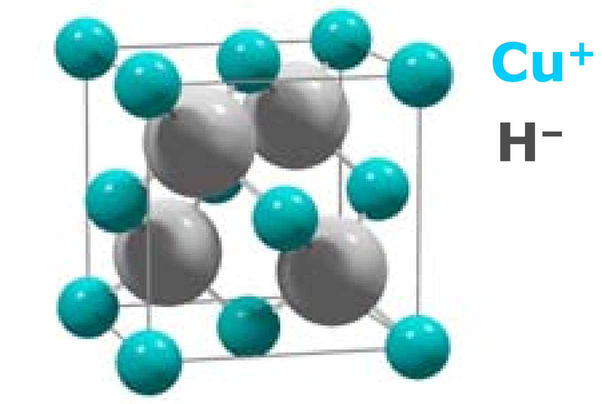


Search strategy

- Consider Cu^{+}, O^{2-}, H^{-}, and H^{+} ionic species.
- Require global charge neutrality and local coordination in accordance with Pauling's rule, in order to get saturated chemical bonds.
- Impose no symmetry and fully relax each structure.
- Compute the phonon spectrum to get the zero-point energy and finite-temperature properties.

1. Oxy-hydride?





Cu_4O_2 (cuprite)
$a = 4.217$ Å

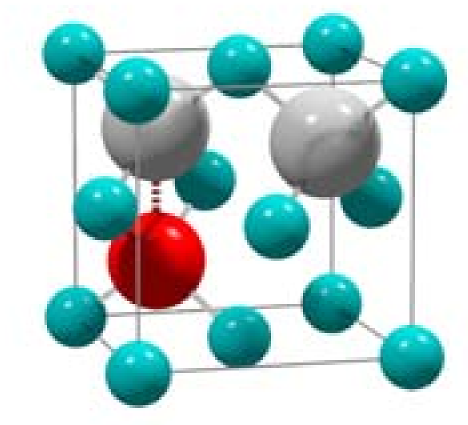
Cu_4H_4 (sphalerite/zincblende)
$a = 4.063$ Å

Similarities:

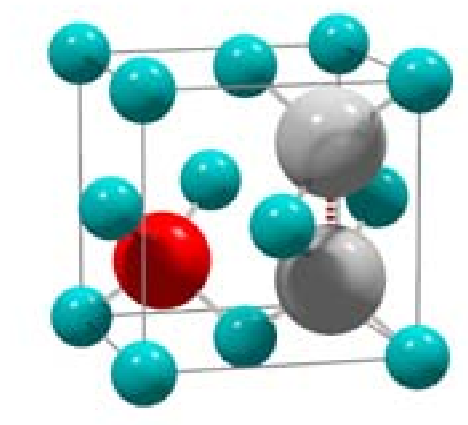
1. Cu^+ sublattice is fcc
2. Anions are in the tetrahedral interstitial positions

Crystal structure of oxy-hydride?

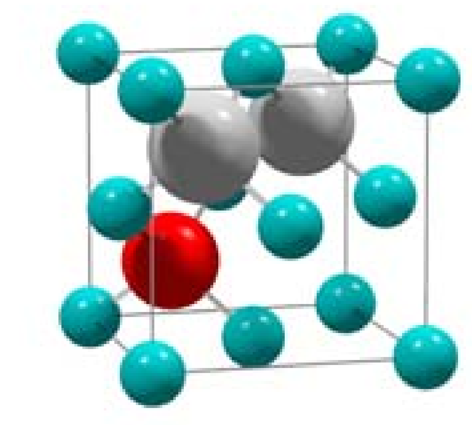
$Cu_4O_1H_2$



Configuration 1



Configuration 2



Configuration 3

Structure motif:

1. Cu^+ sublattice is fcc
2. Anions are in the tetrahedral interstitial positions

Phonon spectrum of $Cu_4O_1H_2$ (Cnf.3)

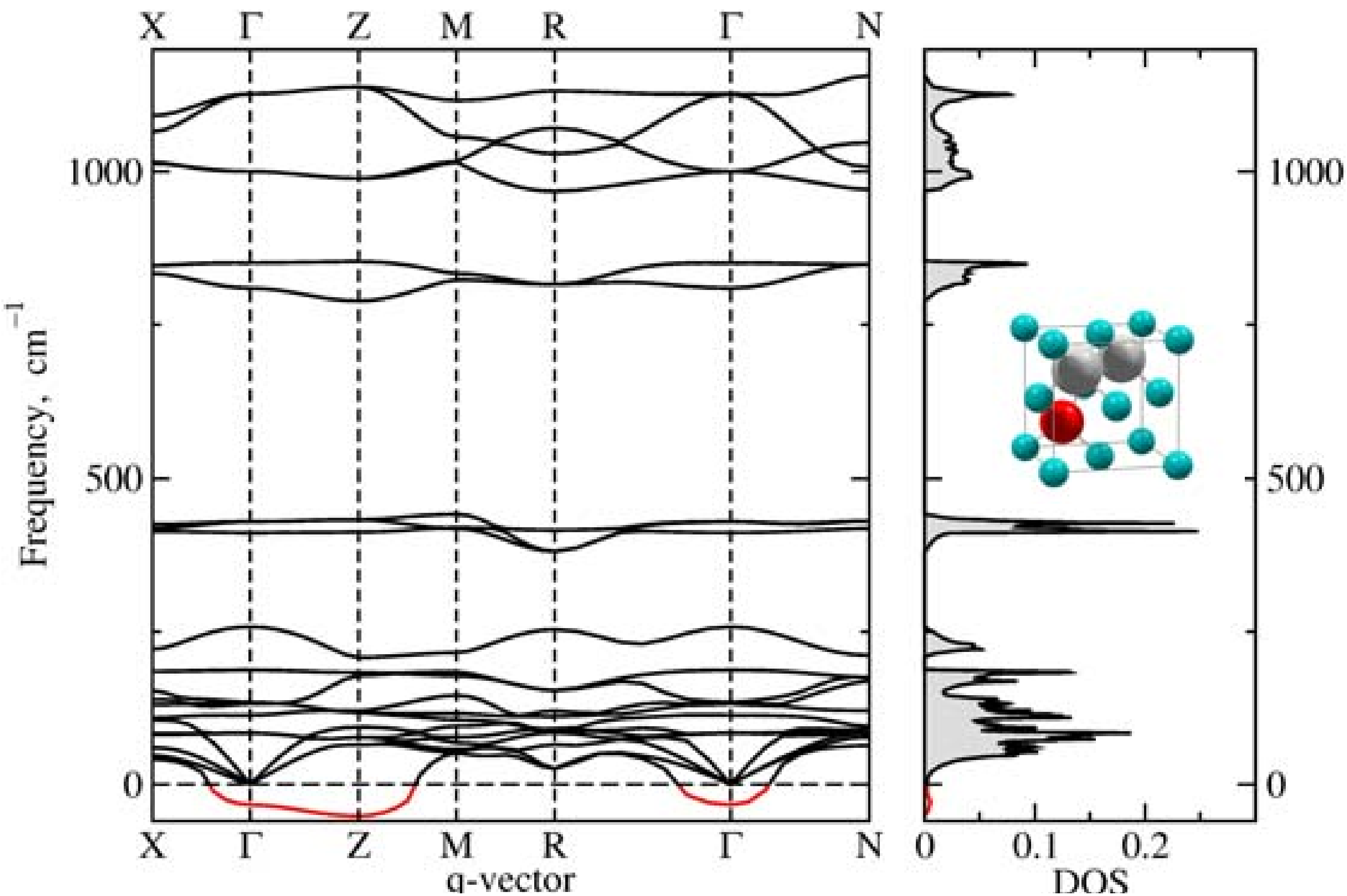


Figure 2.10: Phonon spectrum and density of states (DOS) in copper oxy-hydride Cu_4H_2O in the fully-relaxed atomic Configuration 3, with the lattice parameters $a = 4.225$ Å and $c = 3.821$ Å ($c/a = 0.904$). The notations for q-vectors are as follows: $\Gamma = \frac{\pi}{a}(0, 0, 0)$; $X = \frac{\pi}{a}(1, 0, 0)$; $Z = \frac{\pi}{a}(0, 0, \frac{a}{c})$; $M = \frac{\pi}{a}(0, 1, \frac{a}{c})$; $R = \frac{\pi}{a}(1, 1, \frac{a}{c})$; $N = \frac{\pi}{a}(1, 1, 0)$. Imaginary phonon frequences are shown as negative values and indicated by red color.

Instability of an oxyhydride

Table 4: Enthalpy and free energy of formation (kJ/mol) copper(I) oxide, hydride, and oxyhydride.

Substance	Data source	$\Delta H(0)$	$\Delta H(298.15)$	$\Delta G(298.15)$
Cu_2O	This work	−160.6	−161.9	−140.9
CuH(wurtzite)	This work	+39.5	+36.7	+50.9
Cu_4H_2O, conf. 2	This work	−11.7	−17.7	+30.1
Cu_4H_2O, conf. 3	This work	−30.6	−35.6	+17.2

$$Cu_4O_1H_2 \rightarrow Cu_2O + 2CuH$$

is a strongly exothermic reaction:

$$\Delta H(0\ \mathrm{K}) = -\ 51.0\ \mathrm{kJ/mol}$$

$$\Delta H(\mathrm{RT}) = -\ 53.0\ \mathrm{kJ/mol}$$

$$\Delta G(\mathrm{RT}) = -\ 56.2\ \mathrm{kJ/mol}$$

2. Copper(I) hydroxide?

<u>Geometry of a CuOH molecule:</u>

|Cu–O| = 1.77 Å

|O–H| = 0.98 Å

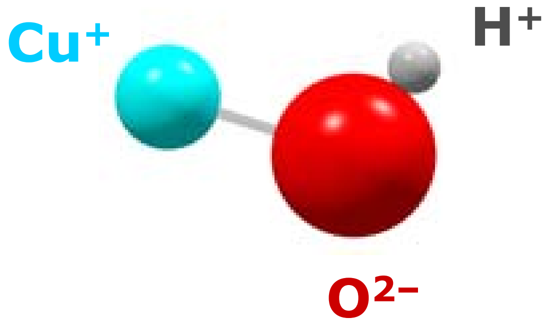
∠Cu–O–H = 106.7°

<u>Vibration modes:</u>

631 cm^{-1} Cu–OH stretching

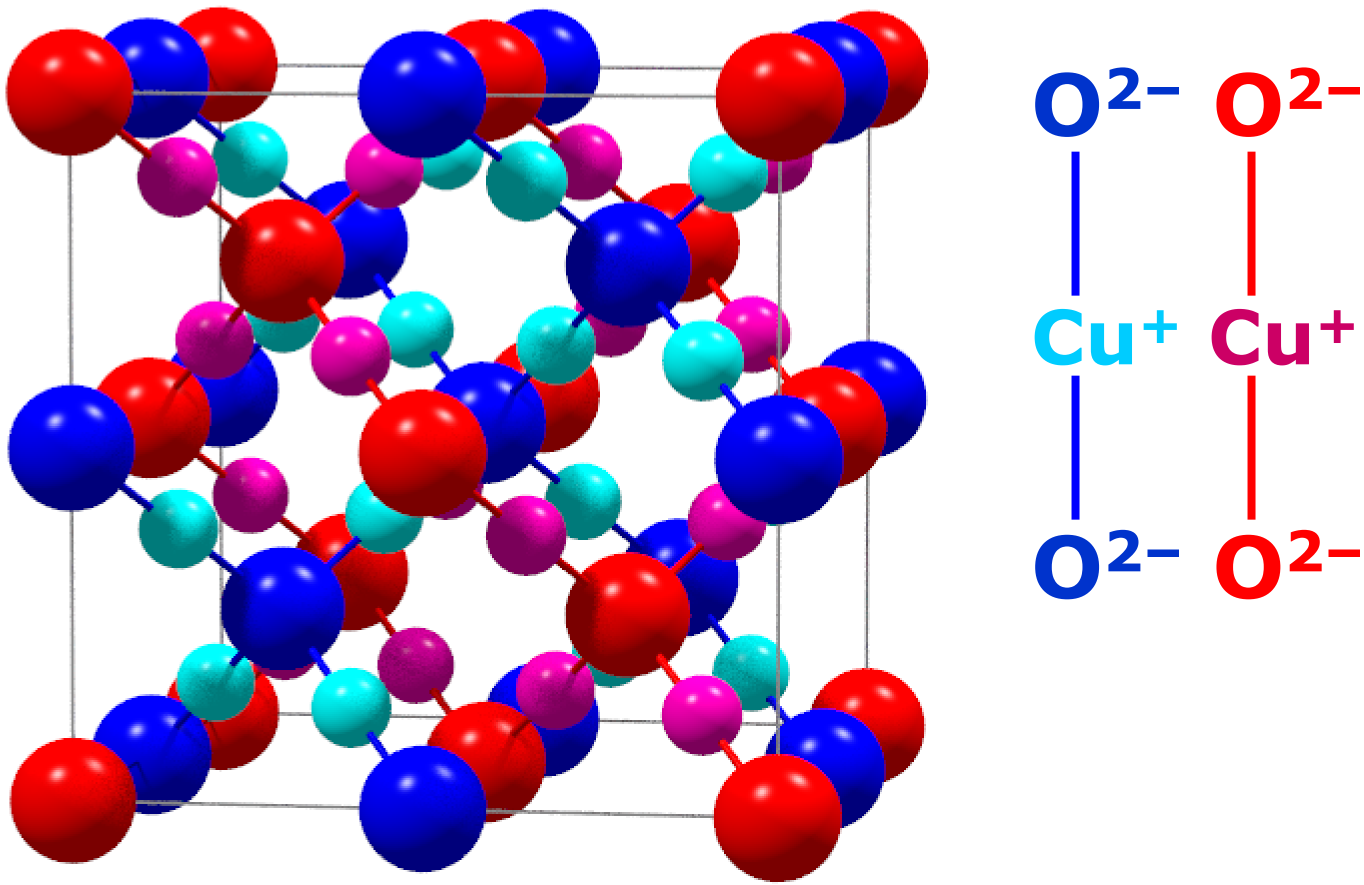
819 cm^{-1} O–H bending

3704 cm^{-1} O–H stretching

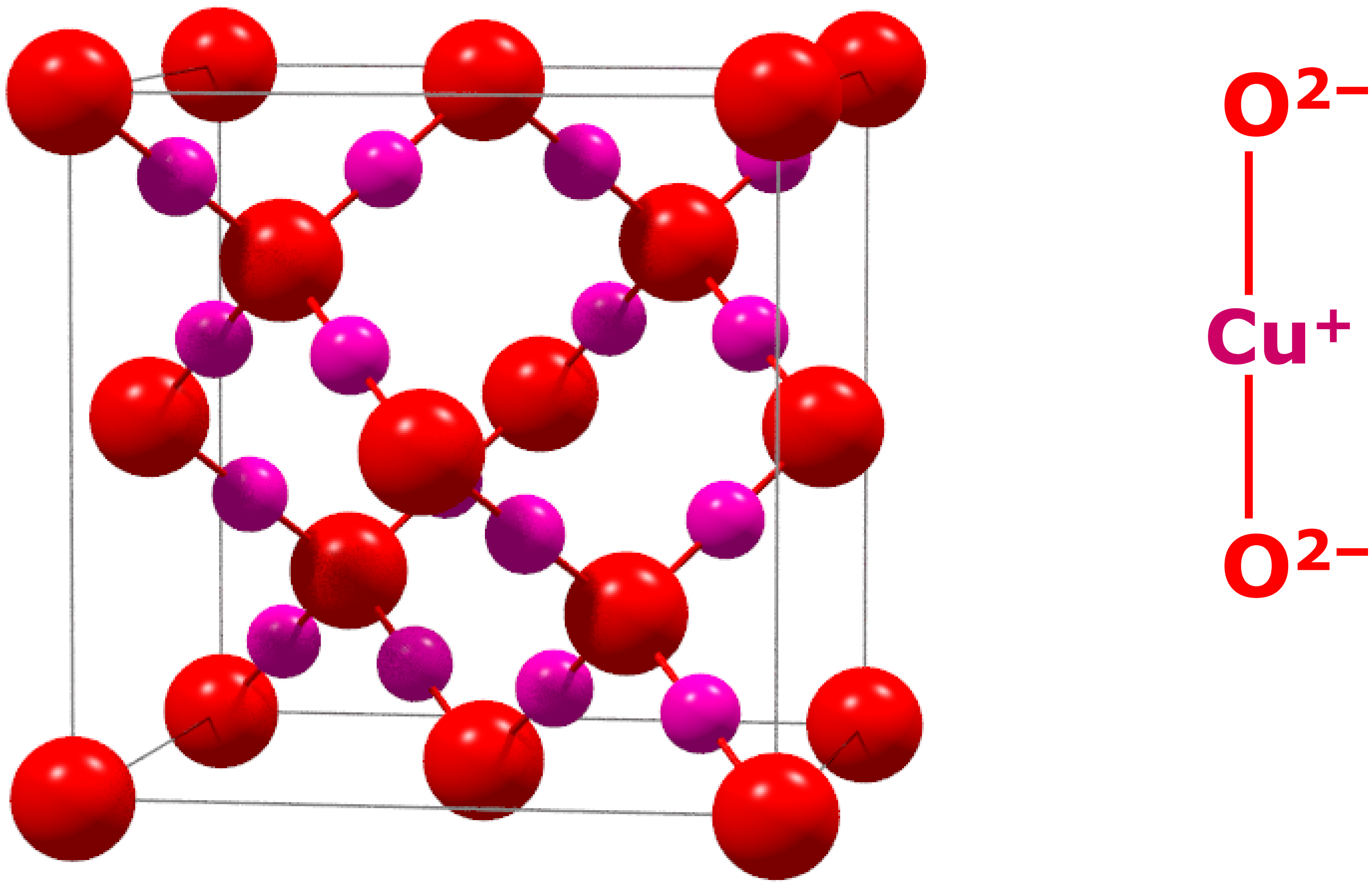


Let us build a solid out of the CuOH molecules, making it as stable as possible.

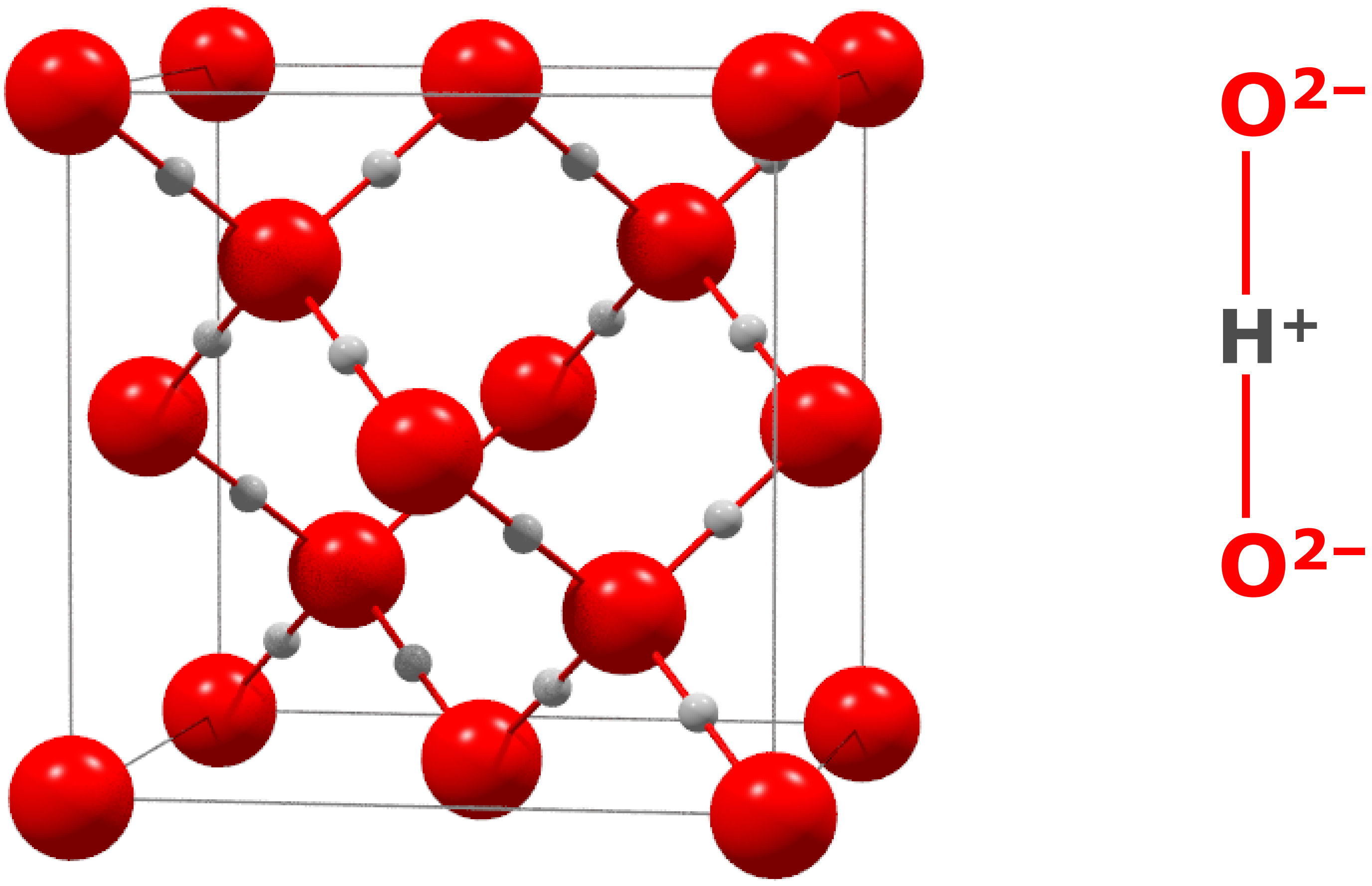
From cuprite to ice (Ic)



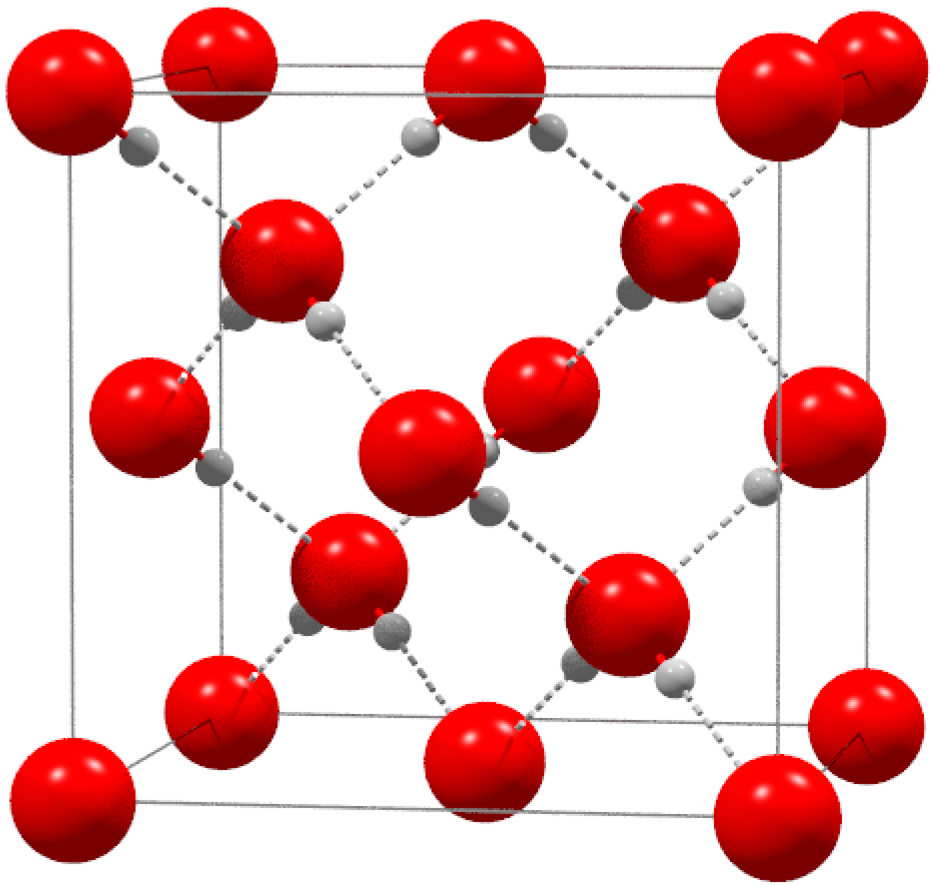
From cuprite to ice (Ic)

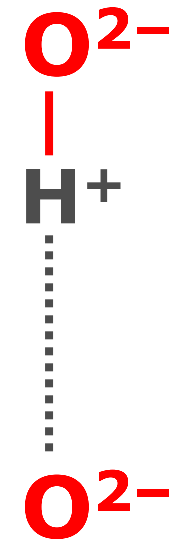


From cuprite to ice (Ic)



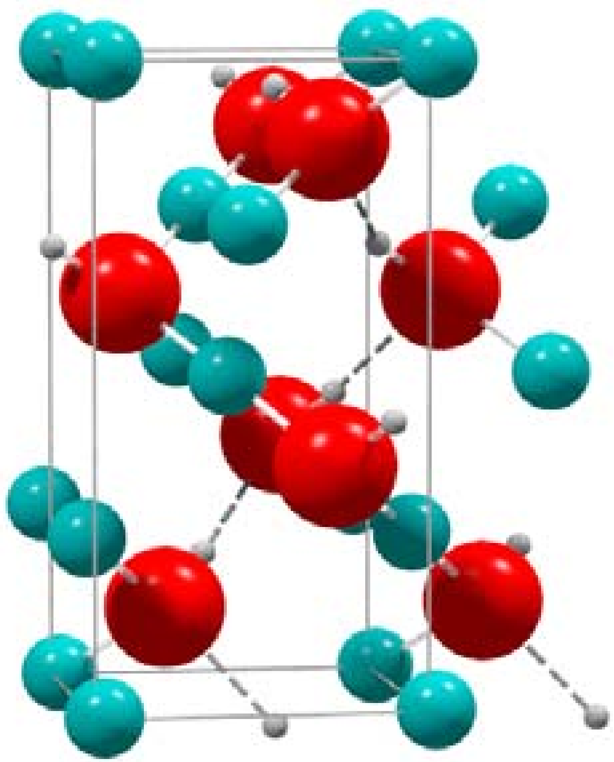
From cuprite to ice (Ic)



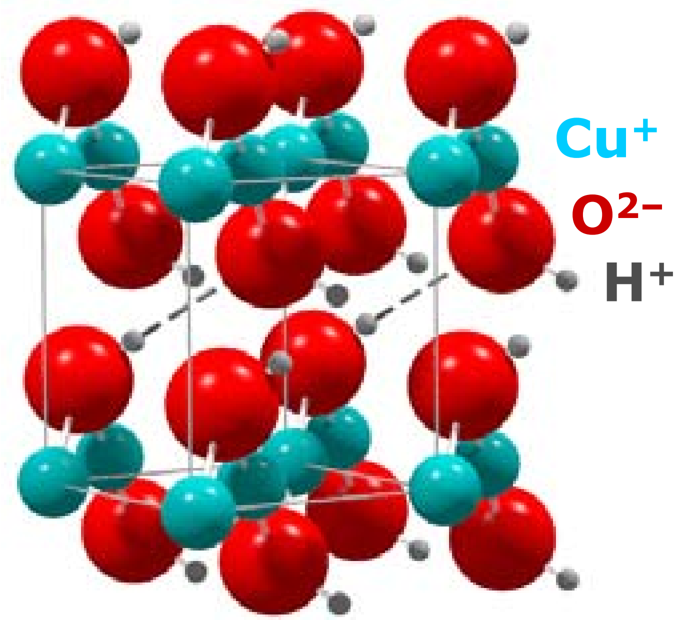


Crystal structure of copper(I) hydroxide?

CuOH – “cuprice”

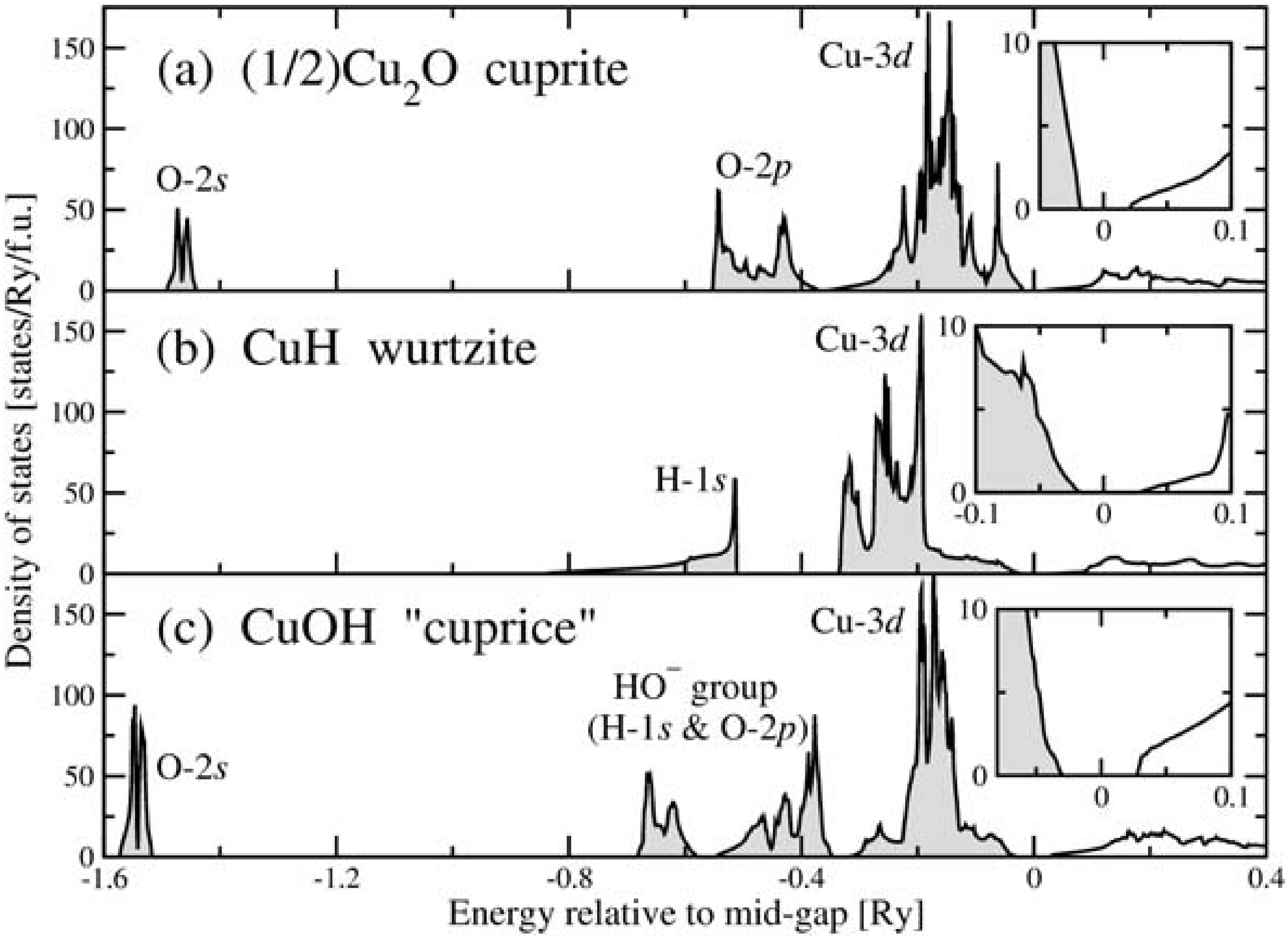


Configuration 1

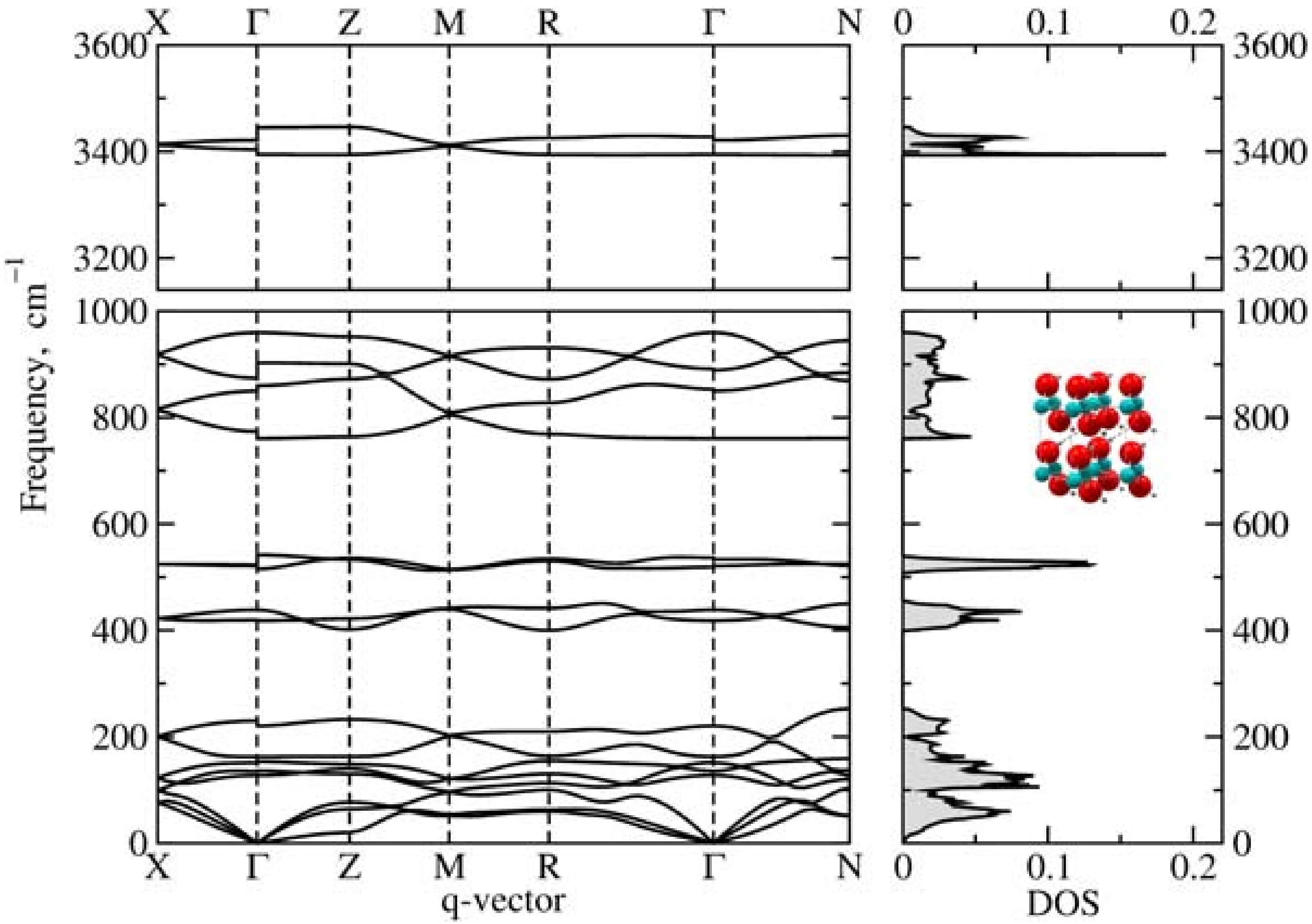


Configuration 2

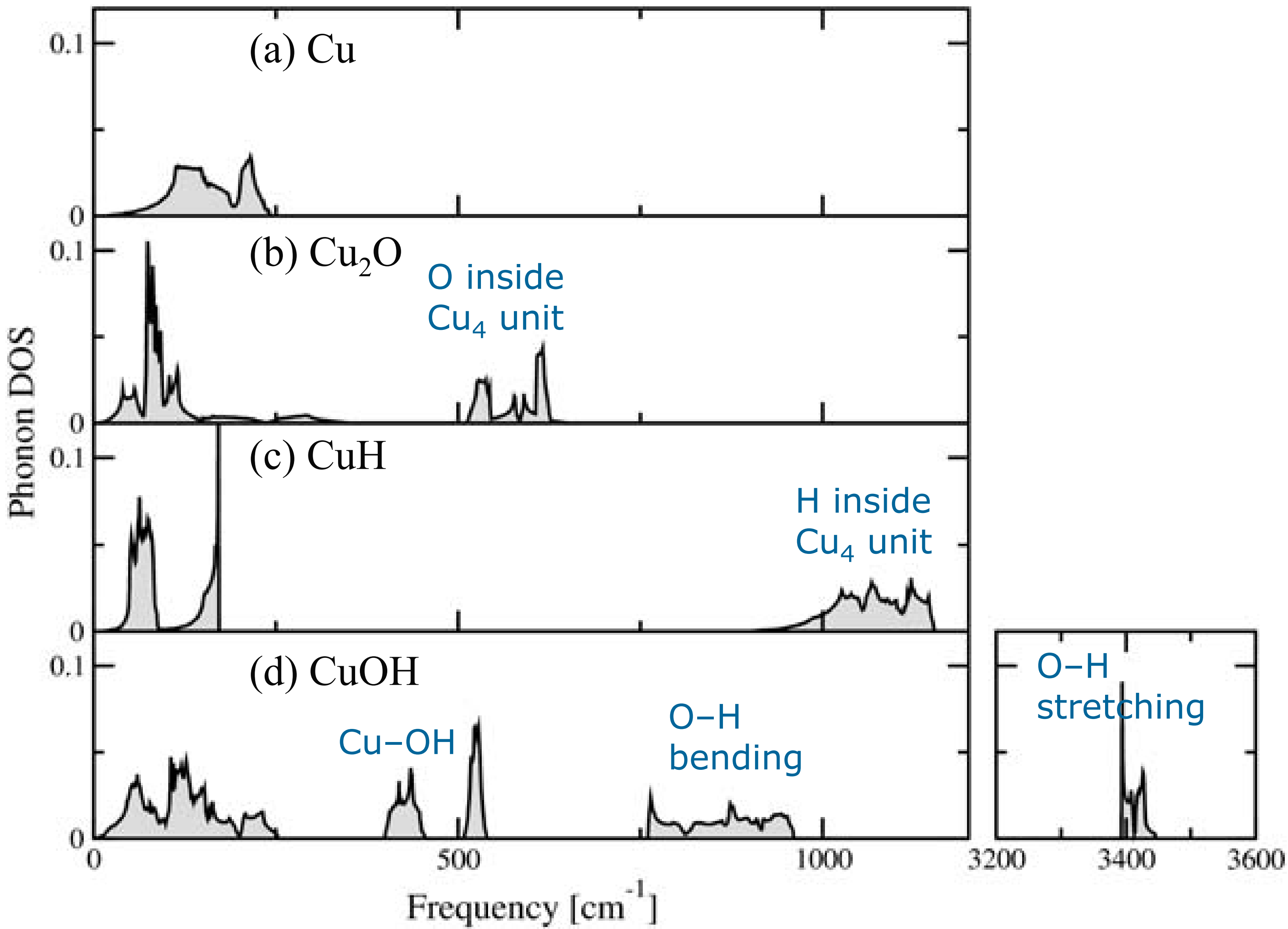
Electronic spectra of solid Cu_2O, CuH, and CuOH



Phonon spectrum of CuOH (Cnf.2)



Vibrational spectra of solid Cu, Cu_2O, CuH, and CuOH



Thermodynamic properties

Table 5: Enthalpy and free energy of formation (kJ/mol) copper(I) oxide, copper(I) hydroxide, and water.

Substance	Data source	$\Delta H(0)$	$\Delta H(298.15)$	$\Delta G(298.15)$
Cu_2O	This work	–160.6	–161.9	–140.9
CuOH, conf. 1	This work	–195.4	–199.8	–160.8
CuOH, conf. 2	This work	–196.5	–200.8	–158.2
H_2O(liq.)	NIST-JANAF [3]	–	–285.8	–237.1

1. CuOH is unstable with respect to condensation:

$$2CuOH \rightarrow Cu_2O + H_2O$$

ΔH = –46.1 kJ/mol
ΔG = –56.4 kJ/mol

2. Corrosion of copper by water is energetically unfavorable

$$H_2O + 2Cu \rightarrow Cu_2O + H_2$$

ΔH = +123.9 kJ/mol
ΔG = +96.3 kJ/mol

$$2H_2O + 2Cu \rightarrow 2CuOH + H_2$$

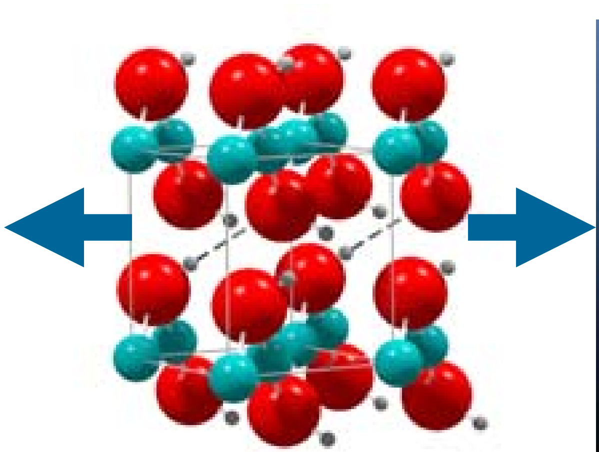
ΔH = +170.0 kJ/mol
ΔG = +152.7 kJ/mol

Conclusions

Cuprite is the champion of stability among Cu(I) compounds.

Cuprice (CuOH) is only metastable…

and decomposes onto cuprite and water.



Corrosion of copper by water is not confirmed.

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SNIC

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O. Peil, A.V. Ruban, and
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