AB INITIO MODELING: MECHANICAL AND THERMO-ELASTIC PROPERTIES OF CALCIUM CARBONATES POLYMORPHS

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INTRODUCTION

The present PhD Thesis provides a set of new computational, mechanical and thermodynamic data, aimed to provide a better characterization of calcium carbonate polymorphs, from the mineralogical, geophysical and petrographical (sedimentary and metamorphic petrography) point of view. Carbonates belong to the most abundant Earth materials, after silicates, and play an important role in the Earth's carbon cycle. Carbonates are a group of minerals in which the essential unit is the $(CO_3)^{2-}$ ion. This unit has a planar arrangement, with the carbon atom at the centre and oxygen atoms at the apices of an equilateral triangle (Zemann, 1981).

Calcium carbonate crystallizes naturally with either the calcite [$CaCO_3(I)$] or aragonite (*Pmcn*) structure. The other $CaCO_3$ polymorph is vaterite, which is metastable. The $(CO_3)^{2-}$ group is the fundamental chemical unit from which the carbonate minerals derive their identity. The other $CaCO_3$ carbonate studied in the present thesis is $CaCO_3(II)$.

For the phases studied, the geometry of each calcium carbonate polymorphs was optimized by means of *ab initio* quantum mechanical calculation CRYSTAL code (Dovesi *et al*., 2006, 2009). The choice of the exchange-correlation functionals used in the present *ab initio* quantum calculation were B3LYP (Becke, 1993) and WC1LYP (Wu & Cohen, 2006).

The vibrational modes were calculated in the quasi-harmonic approximation, and represented the eigenvalues of the mass-weighted Hessian matrix, which is nothing else than the second derivative of the potential energy as a function of coordinate displacement respect to the equilibrium position.

The bulk modulus, the thermal expansion, the specific heat, and the entropy were obtained in the limit of the quasi-harmonic approximation (Anderson, 1995), through the evaluation of the unit cell volume dependence from the frequencies of the vibrational normal modes (mode-γ of the Grüneisen's parameters) at the Γ point. The dispersion effects in the phonon spectra at various pressures were not taken into account for aragonite, but only for calcite, thanks to new version of the CRYSTAL code (Dovesi *et al*., 2009). On the other hand, the Grüneisen's parameters corresponding to the zone-centre vibrational modes can reasonably be considered representative of the whole set of parameters, due to their large number, which depends upon the number of atoms in the unit cell.

The total pressure P, at each cell volume V, and the temperature T have been obtained using thermal physics approach of (Anderson, 1995).

APPLICATIONS OF QUANTUM-MECHANICAL *AB INITIO* CALCULATION USING THE CRYSTAL CODE, THE THERMO-ELASTIC EQUATION OF STATE, AND THE THERMODYNAMIC PROPERTIES OF $CaCO_3$ POLYMORPHS

Calcite: Thermodynamic and thermo-elastic properties of (CaCO₃) calcite. An ab initio quantum-mechanical calculation

The thermodynamic calculation of total pressures, bulk modulus, thermal expansion, heat capacity, and entropy of calcite were obtained through the *ab initio* calculation of the unit cell volume dependence of the total static energy, and of the frequencies of the vibrational normal modes, at the Γ point, within the framework of the quasi-harmonic approximation. The Acoustics modes frequencies were evaluated by means of a modified Kieffer's model (Kieffer, 1979 a, b) starting from the experimental elastic constants. Moreover, an attempt to

improve the model was made by taking into account intrinsic anharmonic contributions and by correcting all of the calculated frequencies by means of the factors derived from the literature experimental data.

Starting from the optimized equilibrium geometry of the hexagonal cell of calcite ($a = b = 5.02$ Å, $c = 17.165$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 374.642$ Å^3, $E = -1.8815\cdot10^3$ Ha, at the WC1LYP level), new geometries were obtained using the CVOLOPT (constant volume optimization) keyword. These new optimized geometries correspond to a static pressures ranging from $P_{st} = -0.029$ GPa at $V = 374.642$ Å^3 (equilibrium geometry) to $P_{st} = 4.125$ GPa at $V = 352.367$ Å.

At $P_{st} = 0$ GPa, a very small difference was observed in the values of the frequencies of the vibrational modes calculated by the two different B3LYP and WC1LYP Hamiltonians (Table 1). Therefore, at high pressures all the computations of frequencies were performed by using the WC1LYP Hamiltonian only.

Table 1 - Comparison between B3LYP, WC1LYP and experimental (Hellwege *et al.*, 1970) vibrational modes at equilibrium volume of calcite

Mode	Symmetry	$\nu_{calc\ B3LYP}$	ν_{calc} WC1LYP	$\nu_{experimental}$	Δ B3LYP-experimental	Δ WC1LYP-experimental
	Vol (Å^3)	382.9129	374.64198	368.1	14.8129	6.54198
Raman						
1	E_g	159.8302	158.3299	156	3.8302	2.3299
2	E_g	283.8584	287.7434	284	-0.1416	3.7434
3	E_g	708.7351	709.836	712	-3.2649	-2.164
4	A_{1g}	1088.067	1091.5029	1086	2.067	5.5029
5	E_g	1458.5389	1435.8339	1434	24.5389	1.8339
Infrared						
6	E_u	136.0104	115.5994	102	34.0104	13.5994
7	A_{2u}	132.1876	120.8487	92	40.1876	28.8487
8	E_u	221.6146	229.6916	223	-1.3854	6.6916
9	E_u	288.3799	302.0693	297	-8.6201	5.0693
10	A_{2u}	293.6262	316.8577	303	-9.3738	13.8577
11	E_u	709.1684	710.2542	712	-2.8316	-1.7458
12	A_{2u}	869.0737	866.0317	872	-2.9263	-5.9683
13	E_u	1427.0902	1402.0681	1407	20.0902	-4.9319
Silent						
14	A_{2g}	198.2081	187.284			
15	A_{1u}	285.3215	296.4545			
16	A_{2g}	310.9397	321.5325			
17	A_{2g}	885.9733	874.2584			
18	A_{1u}	1088.4282	1091.3087			
RMS Difference		**17.514**	**10.379**			

In the investigated pressure range the majority of the vibrational modes showed frequency values which increase with pressure (*i.e.* $\gamma_j > 0$), by following nearly linear trends. Exceptions were the modes at $\nu_j = 120.85$ cm^{-1} (A_{2u}: $\gamma_j = -3.69$) and at $\nu_j = 115$ cm^{-1} (E_u: $\gamma_j = -2.81$). Vibrational modes from 150 to 300 cm^{-1} (external modes) were associated with the larger positive Grüneisen's parameters ($\gamma_{MAX} = 2.26$ at $\nu = 293.63$ cm^{-1}), except for the silent (A_{2g}) mode at 187.28 cm^{-1} having $\gamma_j \cong 0$. As concerns the internal modes (frequencies above 700 cm^{-1}), all of such parameters were in $0.2 \div 0.3$ positive range, except for the modes at 867 (A_{2u}) and 874 (A_{2g}) cm^{-1} having $\gamma_j \cong 0$.

In the Table 2a are reported the room temperature values (298 K) of bulk modulus (K_T), the thermal expansion (α), the entropy (S) and the heat capacity (C_P). The values of bulk modulus were obtained from the fitting of a BM3 EoS to the total pressure versus volume data (WC1LYP; Table 2a). The value of the bulk modulus at T = 298 K and P = 0 GPa was in good agreement (within 1σ spread) with the experimental data (columns 3 to 5 of Table 2a: Salje & Viswanathan, 1976; Bridgman, 1925; Redfern & Angel, 1999).

Table 2 - Thermodynamic properties at 298 K. Note that S was calculated in two modes: 2a) with the Kieffer model and taking into account the phonon dispersion contribution; 2b) as a function of T and P calculated at WC1LYP level. The experimental data are also reported for comparison with: 1 (Salje & Viswanathan, 1976); 2 (Staveley & Linford, 1969); 3 (Jacobs *et al.*, 1981); 4 (Gillet *et al.*, 1996); 5 (Bridgman, 1925); 6 (Redfern & Angel, 1999); 7 (Matas *et al.*, 2000); 8 (Robie *et al.*, 1979).

a

T=298 K	WC1LYP		Experimental		
	Kieffer	**Dispersion**			
K(T)	75.58		78.00[1]	73.15[5]	73.46[6]
K(P)	76.94		78.50[1]	2.99[1]	
α(K^{-1})	1.70·10^{-5}		1.77·10^5 [1]		
S(Jmole^{-1}K^{-1})	91.45	*** 91.66**	91.70[8]		
Cp(Jmole^{-1}K^{-1})	81.79		83.50[8]		

b

	WC1LYP		Experimental	
	I	**s**	**I**	**s**
K(T) (Linear fit 100÷1000 K) at different P				
0	78.56	-0.0103		-0.011[4]
				-0.008[7]
1	88.06	-0.0143		
2	98.91	-0.0167		
α (T) (Linear fit 500÷1000 K) at different P				
0	1.51·10^{-5}	9.73·10^{-9}	1.46·10^{-5} [1]	1.19·10^{-8} [1]
1	1.38·10^{-5}	8.12·10^{-9}		
2	1.26·10^{-5}	6.99·10^{-9}		

In Table 2b are presented: i) the linear fits of data calculated at WC1LYP level (column 3) concerning the bulk modulus as a function of temperature (100 ÷ 1000 K) at different pressures (0 - 2 GPa); ii) the thermal expansion as a function of temperature (500 ÷ 1000 K) at different pressures (0 - 2 GPa).

In summary, the thermodynamic properties values calculated at WC1LYP level were in a good agreement with experimental data. A better agreement between our calculated WC1LYP entropy values and the experimental ones, in all the explored 20 ÷ 1000 K temperature range, was evidenced. Our C_P data also gave a general low mean difference ($\cong$ 1 J/moleK), although we had some mismatch at 298 and 1000 K: this might imply problems in some experimental data or in the estimation of α, K_T and V, in particular at 1000 K, where we observed the largest difference. A very good agreement between the calculated and the experimental data (column 5, Table 2b; Gillet *et al.*, 1996) was observed. All our thermal expansion values were in good agreement with the experimental ones: in particular, the slopes as a function of pressure seem good up to 1200 K. The slope of thermal expansion as a function of temperature seems reasonable at 0 GPa (Salje & Viswanathan, 1976) and decrease slowly raising the pressure up to 2 GPa. This last observation disagrees with some literature statements where calcite thermal expansion slope, with respect to temperature, remains substantially constant as the pressure is raised (Gillet *et al.*, 1996). In Table 2b are summarized all the calculated thermodynamic properties, at WC1LYP level (2a) at 298 K and at different pressures (2b).

Finally, this work confirms, in general, the previous experimentally-determined thermodynamic properties of calcite (Bridgman, 1925; Staveley & Linford, 1969; Salje & Viswanathan, 1976; Robie *et al.*, 1979; Jacobs *et al.*, 1981; Gillet *et al.*, 1996; Redfern & Angel, 1999; Matas *et al.*, 2000).

Modes	B3LYP 2009	WC1LYP 2009	Carteret New	B3-Carteret	WC1-Carteret	Carteret 2009	B3-Carteret	WC1-Carteret	Frech 1980 (16 K)	B3-Frech	WC1-Frech	Frech 1980	B3-Frech	WC1-Frech	Alia 1997	B3-Alia	WC1-Alia
AG	146.59	151.96	141.5	5.09	10.46	140	6.59	11.96	145	1.59	6.96	142	4.59	9.96	143.1	3.49	8.8581
AG	163.94	169.32	161	2.94	8.32				165	-1.06	4.32	161	2.94	8.32	163.5	0.44	5.8177
AG	193.14	205.42	190	3.14	15.42	190	3.14	15.42				193	0.14	12.42	191.3	1.84	14.1204
AG	202.22	214.26	206	-3.78	8.26	205	-2.78	9.26	220	-17.78	-5.74	214	-11.78	0.26	206.4	-4.18	7.8591
AG	283.2	293.8	282	1.2	11.8	284	-0.8	9.8	292	-8.8	1.8	284	-0.8	9.8	284.8	-1.6	9.0026
AG	698.46	696.09	705.5	-7.04	-9.41	702	-3.54	-5.91				705	-6.54	-8.91	707	-8.54	-10.914
AG	851.43	840.5	854	-2.57	-13.5	853	-1.57	-12.5				853	-1.57	-12.5			
AG	1094.27	1094.1	1086.5	7.77	7.6	1085	9.27	9.1				1085	9.27	9.1	1087	7.27	7.1005
AG	1500.36	1493.72										1462	38.36	31.72	1466	34.36	27.7165
B1G	98.97	113.41	114.5	-15.53	-1.09	116	-17.03	-2.59	126(B3g)	-27.03	-12.59	123(B3g)	-24.03	-9.59	115.4	-16.43	-1.9903
B1G	169.38	175.83															
B1G	178.6	191.31	179.5	-0.9	11.81	178	0.6	13.31	184	-5.4	7.31	180	-1.4	11.31	180.6	-2	10.7059
B1G	274	282.72	271	3	11.72	272	2	10.72	266(B3g)	8	16.72	272(B3g)	2	10.72	272.3	1.7	10.4246
B1G	696.22	691.84	701.5	-5.28	-9.66	697	-0.78	-5.16				701(B3g)	-4.78	-9.16	703	-6.78	-11.163
B1G	1439.7	1436.43															
B2G	172.86	185.85							180	-7.14	5.85	190	-17.14	-4.15			
B2G	206.58	215.88							213(B2g)	-6.42	2.88	206(B2g)	0.58	9.88			
B2G	247.97	257.67	248	-0.03	9.67	248	-0.03	9.67	252(B2g)	-4.03	5.67	248(B2g)	-0.03	9.67	248.5	-0.53	9.1664
B2G	259.32	272.72	260	-0.68	12.72	260	-0.68	12.72							260.4	-1.08	12.3163
B2G	281.29	288.81							279	2.29	9.81						
B2G	710.82	709.17	716.5	-5.68	-7.33	716	-5.18	-6.83				717(B2g)	-6.18	-7.83			
B2G	913.47	904.53										907(B2g)	6.47	-2.47			
B2G	1093.35	1089.9															
B2G	1622.17	1609.88	1573.6	48.57	36.28							1574(B2g)	48.17	35.88			
B3G	96.6	106.73	110	-13.4	-3.27	111	-14.4	-4.27	118	-21.4	-11.27	112	-15.4	-5.27	106.8	-10.2	-0.0724
B3G	155.57	158.1	152	3.57	6.1	152	3.57	6.1	157	-1.43	1.1	152	3.57	6.1	153.3	2.27	4.7988
B3G	200.21	212.52															
B3G	214.37	223.11	214	0.37	9.11	215	-0.63	8.11							215.6	-1.23	7.5131
B3G	700.55	697.57				706	-5.45	-8.43				721	-20.45	-23.43			
B3G	1488.38	1486.34	1463.5	24.88	22.84	1462	26.38	24.34							1464	24.38	22.3381
N			20			19			13			22			18		
RMS Diff				13.53	13.42		8.68	10.88		11.75	8.29		16.15	14.04		11.48	11.9217
MedDev				8.07	8.64		5.48	8.49		7.4	6.05		10.32	10.93		7.37	6.4864

Table 3 - External and internal Raman active modes of Aragonite (in cm^{-1}). The computed frequencies are compared with the experimental ones: a) Carteret *et al.* (2009); b) Frech *et al.* (1980); c) Alia *et al.* (1997). As suggested by Pavese *et al.* (1992), an incorrect assignment of the symmetry, by the authors of the experimental study, cannot be excluded. Between parentheses, beside experimental frequency it is reported the different symmetry assignment given by experimentalist.

Aragonite: orthorhombic equilibrium structure and vibrational modes at point Γ (quantum mechanical calculation)

The orthorhombic cell of aragonite contains four $CaCO_3$ formula units, for a total of N = 20 atoms; its sixty vibrational modes can be classified according to the Irreducible Representations of the *mmm* point group as follows:

$\Gamma_{tot} = 9A_g + 6A_u + 6B_{1g} + 9B_{1u} + 6B_{2g} + 6B_{2u} + 9B_{3g} + 6B_{3u}$. Where: $9A_{1g} + 6B_{1g} + 6B_{2g} + 9B_{3g}$ Raman active, $8B_{1u} + 5B_{2u} + 5B_{3u}$ IR active, $6A_{1u}$ inactive and $1B_{1u}+1B_{2u}+1B_{3u}$ acoustic.

In aragonite, where eight almost independent groups can be identified (four Ca^{2+} ions and four CO_3^{2-} units), vibrational modes can be grouped into two categories, namely: external (*E*; translational and rotational type) and internal (*I*) vibrations. External vibrations involve relative translations of the eight units and librations of the carbonate ions, as a result of the freezing, within the crystal, of free translations and rotations of each single free unit. Apart few cases, in aragonite, a clear-cut distinction between translational- and rotational-type modes cannot be made; in general, the vibrations with similar frequency and same symmetry can couple to each other to give more complex modes. The internal vibrations are those modes which involve deformation of the carbonate groups.

Due to the very different strength of the intra-CO_3^{2-} and inter-ionic forces, it might be expected that E modes have lower frequencies than those associated with I modes. Inspection of the eigenvectors of the Hessian matrix and their graphical representations with the aid of Jmol (open-source Java viewer for chemical structures in 3D, http://www.jmol.org) shows that such a separation between (*E*) and (*I*) modes can indeed be made. The equilibrium geometry, the static and high frequency dielectric tensors, the Born charge tensors, the central zone phonon frequencies, and IR intensities of aragonite were calculated with the CRYSTAL code, comparing two different basis sets of increasing size and B3LYP Hamiltonian. The vibrational frequencies were compared with the experimental data and, as can be seen in Table 3, it was found an excellent agreement.

Aragonite: ab-initio quantum-mechanical calculation of aragonite at high pressure: thermodynamic properties and comparison with the experimental data

Starting from the optimized equilibrium geometry of the orthorhombic aragonite primitive cell ($a = 5.0129$ Å, $b = 8.0587$ Å, $c = 5.8529$ Å, $V = 236.44$ Å^3, $E = -3766.0212796587$ Ha, at the B3LYP level), obtained in a previous work (Pascale *et al.*, pers. comm.), new geometries were obtained for reduced volumes of the unit cell, which corresponded to pressures higher than zero. More precisely, these new optimized geometries corresponded to static pressures (1st term of formula by Anderson, 1995) ranging from $P_{st} = 0$ GPa at $V = 236.44$ Å^3 (equilibrium geometry) to $P_{st} = 28.62$ GPa at $V = 185.46$ Å^3. By expanding the cell, at volumes larger than those corresponding to the static limit, we observed a mode whose frequency was rapidly decreasing as the volume increased (soft mode); this is the A_u-mode at 35.2 cm^{-1}, for a cell volume varying from 242.15 Å^3 to 185.47 Å^3.

Such mode reached a zero value of the frequency, possibly corresponding to a zone-centre soft-mode phase transition, for a volume greater than 245 Å^3 (at the B3LYP level). For this reason it was not possible to use our calculation to predict the properties of aragonite at P = 0 GPa and T > 600 K (since, at those conditions, thermal expansion would produce calculated cell volumes larger than 245 Å^3).

All the calculated thermodynamical properties are summarized in Tables 4 (a and b). Table 4a (referring to data evaluated at T = 298 K) contains calculated values obtained by means of BM3 (column 2) and NumDeriv (column 3) methods for the following properties: bulk modulus K_T, thermal expansion α, entropy S, heat capacity (C_v and C_p). In columns 4 to 6 are reported, for comparison, some experimental values (from Martinez *et al.*, 1996; Salje & Viswanathan, 1976; Staveley & Linford, 1969).

The BM3 calculated values of the bulk modulus were in good agreement, in the whole pressure and temperature ranges considered (0 - 10 GPa and 298 ÷ 973 K), with the experimental ones, being the difference between the calculated and the experimental data less than 2 GPa. The agreement of the estimated thermal expansion coefficient [α(T)], and its temperature dependence, with the experimental data was reasonably good. In particular, the calculated value at room temperature and pressure was under-estimated by 2.3·10^{-6} K^{-1} with

respect to the experimental data, whereas the slope of the α(T) curve appeared to be over-estimated; the magnitude of such a slope decreased as the pressure increased. Concerning heat capacity (C_v and C_{pBM3}), a very good agreement with the experimental values, in the 120 ÷ 300 K temperature range, was obtained.

Table 4 - Thermodynamic properties at 298 K as a function of T (4a) and P (4b) calculated according to BM3 and NumDeriv methods. The experimental data are also reported for comparison: 1) Martinez *et al.*, (1996); 2) Staveley & Linford (1969); 3) Gillet (1993); 4) Salje & Viswanathan (1976).

a

T=298 K	BM3	NumDeriv	Experimental		
Bulk Modulus	64.67	66.84	66.78 [2]	64.81 [1]	65.66 [4]
Thermal Expansion	$6.06 \cdot 10^{-5}$	$5.88 \cdot 10^{-5}$	$6.1 \cdot 10^{-5}$ [2]	$6.5 \cdot 10^{-5}$ [1]	$6.36 \cdot 10^{-5}$ [4]
S (Jmole^{-1}K^{-1})	87.49	87.49	87.98 [2]	88[3]	78[4]
Cp(Jmole^{-1}K^{-1})	83.06	82.44	82.55 [2]		
Cv (Jmole^{-1}K^{-1})	74.96	74.96			

b

Method	BM3		NumDeriv		Experimental	
Function	I	s	I	s	I	s
P(Gpa)	Bulk Modulus as a function of Temperature (Linear fit 298÷773 K) at different pressures					
0	70.27	-0.022	75.24	-0.026	71.97	-0.02
2.5	80.49	-0.021				
5	90.91	-0.019				
7.5	101.1	-0.018				
10	111.2	-0.017				
P(Gpa)	Thermal expansion as a function of Temperature (Linear fit 298 ÷ 773 K) at different pressures					
0	$4.40 \cdot 10^{-5}$	$5.40 \cdot 10^{-8}$	$3.64 \cdot 10^{-5}$	$7.34 \cdot 10^{-8}$	$5.76 \cdot 10^{-5}$	$2.52 \cdot 10^{-8}$
2.5	$3.63 \cdot 10^{-5}$	$3.72 \cdot 10^{-8}$				
5	$3.15 \cdot 10^{-5}$	$2.61 \cdot 10^{-8}$				
7.5	$2.75 \cdot 10^{-5}$	$1.93 \cdot 10^{-8}$				
10	$2.40 \cdot 10^{-5}$	$1.54 \cdot 10^{-8}$				

On the whole, the present work confirms the values of some thermodynamic properties of aragonite, which have been experimentally determined in previous works (Stavely & Linford 1969; Salje & Viswanathan 1976; Holland & Powell, 1990; Gillet, 1993; Martinez *et al*., 1996).

The A_u mode at 35.2 cm^{-1} (at a unit cell volume of 242.15 Å^3) reached a zero value of the frequency for volumes above 245 Å^3; this could possibly corresponds to a zone-centre soft-mode phase transition (P = 0 GPa and T > 600 K conditions), which require further investigation from both the theoretical and experimental sides.

Vaterite (μ - Calcite)

The cell parameters obtained for orthorhombic vaterite were: *a* = 6.69422 Å, *b* = 8.50694 Å, *c* = 4.52341 Å, α = β = γ = 90°, *V* = 257.597 Å^3, and *E* = -3.766173·10^3 Ha, at the B3LYP level. For the *ab initio* calculations were utilized the same basis set as for aragonite BSD, and the results were then compared with the experimental results (Meyer, 1969).

The Born effective charge and dielectric tensors were obtained, with BSD and B3LYP calculations, using the CPHF method, which is available in the new test version CRYSTAL09 (Dovesi *et al.*, 2009). Diagonal elements were: xx = 2.3336, yy = 2.7939, zz = 2.5996.

The Raman vibrational modes were calculated using BSD, the same basis set as for aragonite, and B3LYP Hamiltonian. Only two exceptions were noted, namely the lowest (< 300 cm^{-1}) and the highest (> 1080 cm^{-1}) frequencies, for which the CRYSTAL calculation overestimated the experimental values as for both Raman and IR frequencies (LO-TO), by something between 7.3 and 22 cm^{-1}. The visualization of the eigenvectors of the Hessian matrix and their graphical representations with the aid of Jmol (open-source Java viewer for chemical structures in 3D, http://www.jmolorg/) showed that such a separation between *E-* and *I-*

modes could indeed be made. In such mode, the classification in internal- and external-vibrational modes of vaterite was understood. The equilibrium geometry, the static and high frequency dielectric tensors, the central zone phonon frequencies and the IR intensities of aragonite were calculated for vaterite, using the DFT (Kohn & Sham, 1965) and B3LYP Hamiltonian (Becke, 1993).

In summary, the present study shows that: i) all the properties mentioned above, can be easily and routinely obtained with the CRYSTAL code; ii) the B3LYP Hamiltonian provides very accurate vibrational frequencies for a large class of compounds, when used with a sufficiently flexible basis set, as BSD; iii) new, general, and powerful tools (such as animation, isotopic substitution), have been implemented, thus permitting an easy and automatic analysis of the atomic motion involved in each normal mode.

Calcite (II)

Starting from the experimental geometry of $CaCO_3$ (II), determined by Merrill & Bassett (1975), the structure of calcite (II) was simulated. $CaCO_3$ (II) has 5 irreducible atoms in the asymmetric unit, *i.e.* one Ca-, one C-, and 3 O-atoms. The effect of the Hamiltonians on the equilibrium geometry and total energy is shown in Table 5.

Table 5 - Geometrical parameters of $CaCO_3$ (II). The calculated values were obtained with two different functionals (B3LYP and WC1LYP) and were compared with the experimental results (Merrill & Bassett, 1975); *a*, *b*, and *c* are the lattice parameters (Å), V is the volume of the cell (Å^3), C_{ai}, C_i, $O1_i$, and $O2_i$ are the fractional coordinates of the irreducible atoms in the primitive cell, $d_{i\text{-}j}$ indicate the shortest interatomic distances (Å).

	B3LYP	WC1LYP	Experimental
E (ha)	$3.7629832 \cdot 10^3$	$3.766184 \cdot 10^3$	(Merrill & Bassett, 1975)
a	6.46320917	6.37962599	6.334
b	5.03907252	5.00426778	4.984
c	8.19823057	8.12532514	8.033
β (°)	108.026772	107.567684	107.9
ρ (g/cm^{-3})	2.615	2.684	2.77
V (A^3)	253.898004	247.305581	241.3
Ca$_x$	0.25	0.25	0.234(2)
Ca$_y$	-0.25	-0.25	0.738(2)
Ca$_z$	0.25	0.25	0.217(1)
C$_x$	0.25	0.25	0.260(8)
C$_y$	0.25	0.25	0.253(9)
C$_z$	-0.5	-0.5	0.504(3)
O1$_x$	0.38	0.38	0.380(7)
O1$_y$	0.12	0.12	0.156(3)
O1$_z$	-0.37	-0.37	0.637(3)
O2$_x$	0.12	0.12	0.134(7)
O2$_y$	0.12	0.12	0.088(4)
O2$_z$	0.37	0.37	0.381(3)
O3$_x$	0.25	0.25	0.221(6)
O3$_y$	-0.5	-0.5	0.490(4)
O3$_z$	-0.5	0.5	0.467(3)
$d_{C\text{-}O1}$	1.2878	1.2867	
$d_{Ca\text{-}O2}$	2.3910	2.3653	
$d_{Ca\text{-}C}$	3.2476	3.2224	

As can be noted, the parameters of primitive cell obtained using WC1LYP Hamiltonian, were more close to the experimental data, in comparison with those determined at the B3LYP level. According to the Irreducible Representations of the *mmm* point group it follows: $\Gamma_{tot} = 15A_g + 15A_u + 15B_g + 15B_u$ (where: $15A_g + 15B_g$ = Raman active; $15B_u$ = IR active; $15A_{1u}$ = inactive; $1B_{1u} + 1B_{2u} + 1B_{3u}$ = acoustic). The calculated vibrational frequencies of $CaCO_3$ (II) were obtained, using *ab initio* quantum mechanical calculation CRYSTAL code. As

can be noted, there is a good agreement between the frequencies calculated using B3LYP and those obtained by WC1LYP calculation.

CONCLUSIONS

The *ab initio* quantum mechanical calculation performed for the calcium carbonates polymorphs provided appropriate results both for the geometry of the crystallographic cell and for the vibrational normal modes. Therefore, it can be concluded that the CRYSTAL code is one of the best modellization method dedicated to the study of the solid phases (especially for the 3D crystalline structures), not only at the equilibrium, but, even more, under HP-HT conditions, which plays an important role in mineralogy, geophysics, petrology and materials industry.

The thermodynamical and thermo-elastic properties obtained through the vibrational normal modes, calculated with CRYSTAL code, in comparison with what stated by Debye (1912) "the frequencies in a crystal are distributed as though the solid were an isotropic elastic continuum rather than an aggregate of particles" and Einstein (1907) "all vibrational modes have the same frequency models" provide the appropriate underlying in the determination of mechanical and thermodynamical properties of the crystalline systems, such as the calcium carbonate types.

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