Study on vibrational modes by group theory and infrared spectra by DFT for calcite crystal

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The factor group symmetry analysis (FSA) method and position symmetry analysis (PSA) method are used to analyze the vibrational modes of calcite (CaCO₃) crystal, respectively. With the activated results of infrared and Raman spectra presented, strong points of each method are concluded. The infrared spectra are studied by using dynamics calculations based on density-functional theory (DFT) with the supercell model of calcite crystal. The frequencies of 27 normal modes are achieved, which are consistent with that by the group symmetry analysis very well, and fit with the experimental results better than the lattice dynamical methods.

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In the study of infrared (IR) and Raman spectra of crystal, it is very important to know which vibrational modes are optically active. The most efficient method is group theory: the factor group symmetry analysis (FSA) method and position symmetry analysis (PSA) method[1−3]. However, to our knowledge, no detailed analysis of vibrational modes of calcite crystal has been performed so far. Here, we just analyze the detailed vibrational modes by means of FSA and PSA methods, respectively.

Calcite is one of the most common minerals, representing about 4 wt.-% in earth's crust and being the part of many geological environments. The rhombohedral cell of calcite contains two CaCO₃ formula units and belongs to space group D_{3d}^6 ($R3m, n.167$, the homomorphism is D_{3d}). Calcite consists of a stacking of planar CO_3^{2-} groups and Ca^{2+} ions along the c axis of the hexagonal cell as shown in Fig. 1. There are ten atoms ($N = 10$) in a unit cell: 2Ca (9Ca per cell, one in middle of cell, the others each contributing 1/8 to the unit: $8 \times 1/8 + 1 = 2$), 2C, and 6O.

The analysis on vibrational modes can be obtained by the character reducing formula[2]

$$n_m = \frac{1}{h} \sum_R \chi(R)\chi_m(R), \qquad (1)$$

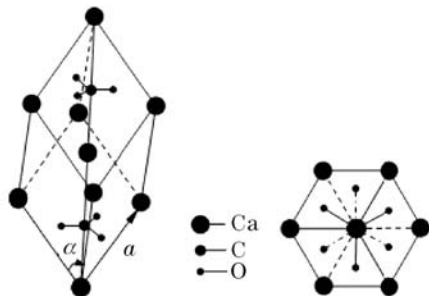$$\chi(R) = U(R) \times \omega(R), \qquad (2)$$

where n_m denotes the number of each mode, h is the order of a group, $\chi(R)$ and $\chi_m(R)$ stand for the reducible and irreducible representation characters, respectively, $U(R)$ is the number of atoms left invariant under operation R, while $\omega(R)$ is the contribute gene charactered by each atom left invariant under operation R.

In FSA, firstly, we confirm the $U(R)$ according to the operations shown in Fig. 2. 1) E operation: all the
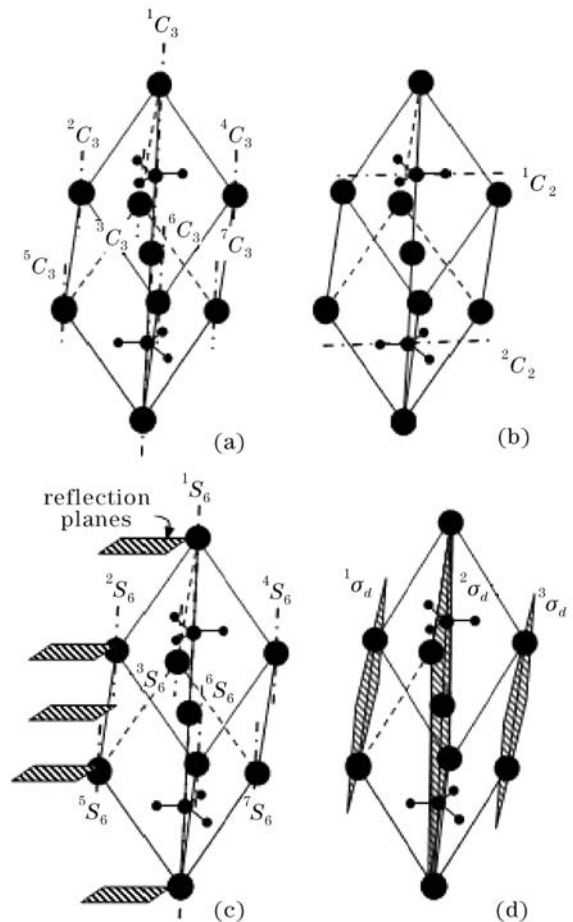

Fig. 1. Unit cell of calcite crystal structure.

Fig. 2. Unit cell of calcite showing operations.

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atoms remain unchanged, so $U(R) = 10$. 2) C_3 operation: Fig. 2(a) shows $7C_3$ axes passing through this unit cell, so $U(R) = (8 \times 1/8 + 1)\text{Ca} + 2\text{C} = 4$. 3) C_2 operation: Fig. 2(b) shows $2C_2$ axes passing through C–O, so $U(R) = 2 \times (1\text{C} + 1\text{O}) = 4$. 4) I operation: all are on the Ca atoms, so $U(R) = 2$. 5) S_6 operation: Fig. 2(c) shows the same position axes as C_3, so $U(R) = 4$. 6) σ_d operation: Fig. 2(d), $U(R) = 0$.

With Eqs. (1), (2) and the parameters listed in Table 1, the vibrational modes can be classified as $A_{1g} + 3A_{2g} + 4E_g + 2A_{1u} + 4A_{2u} + 6E_u$, the number $(3N)$ is therefore 30, and the vibrational normal modes $(3N - 3)$ are 27 except the acoustics modes $(A_{2u} + E_u)$. Among the 27 modes, A_{2u} and E_u are IR active, A_{1g} and E_g are Raman active, A_{1u} and A_{2g} are spectroscopically inactive (silent modes).

In PSA, with the triangular structure and D_{3h} molecular symmetry, using Eqs. (1), (2) and the parameters shown in Table 2, we find 12 vibrational modes of a free CO_3^{2-} ion: $A_1' + A_2' + 3E' + 2A_2'' + E''$ and $E' + A_2''$ are the translation vibrations (T), $A_2' + E''$ are the rotation vibrations (R), and the left is internal vibrations (I). Because of the S_6 site symmetry of Ca^{2+}, T modes $(A_u + E_u)$ of Ca^{2+} are found. In succession, transit these modes (for CO_3^{2-} and Ca^{2+}) to those in calcite crystal, according to the correlations in D_{3h}, D_3 and D_{3d}, S_6 and D_{3d} shown in Table 3. Considering one unit cell of calcite crystal has $2CO_3^{2-}$ and $2Ca^{2+}$ ions, 2 is multiplied to the number of modes. So in calcite crystal, the vibrational modes are CO_3^{2-}: $A_{1g} + 3A_{2g} + 4E_g + A_{1u} + 3A_{2u} + 4E_u$, Ca^{2+}: $A_{1u} + A_{2u} + 2E_u$, total: $A_{1g} + 3A_{2g} + 4E_g + 2A_{1u} + 4A_{2u} + 6E_u$.

Table 1. Irreducible and Reducible Representations Character for Calcite Crystal (D_{3d})

D_{3d}	E	$2C_3$	$3C_2$	I	$2S_6$	$3\sigma_d$	
A_{1g}	1	1	1	1	1	1	
A_{2g}	1	1	-1	1	1	-1	R_z
E_g	2	-1	0	2	-1	0	R_x, R_y
A_{1u}	1	1	1	-1	-1	-1	
A_{2u}	1	1	-1	-1	-1	1	T_z
E_u	2	-1	0	-2	1	0	T_x, T_y
$U(R)$	10	4	4	2	2	0	
$\omega(R)$	3	0	-1	3	0	1	
$\chi(R)$	30	0	-4	6	0	0	

Table 2. Irreducible and Reducible Representations Character for CO_3^{2-} (D_{3h})

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	R_z
E'	2	-1	0	2	-1	0	T_x, T_y
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E''	2	-1	0	-2	1	0	R_x, R_y
$U(R)$	4	1	2	4	1	2	
$\omega(R)$	3	0	-1	1	-2	1	
$\chi(R)$	12	0	-2	4	-2	2	

Table 3. Position Symmetry Analysis of Crystal Lattice Vibration for Calcite

Except 3 acoustics modes $(A_{2u} + E_u)$, here we can classify I modes of CO_3^{2-} to internal vibrations of calcite: $(12I)$: $A_{1g} + A_{2g} + 2E_g + A_{1u} + A_{2u} + 2E_u$. The others are external oscillations $(15E)$: $(6R)$: $A_{2g} + E_g + A_{2u} + E_u$, $(9T)$: $A_{2g} + E_g + A_{1u} + A_{2u} + 2E_u$. Obviously, the PSA gets the same results as FSA, but it can classify modes more specific.

Geometry optimization and IR spectra calculations were performed within the DFT framework, using the molecular dynamics (MD) method in the program CASTEP which is one of the only few *ab intito* codes, permitting the calculation of the vibration spectra of crystalline compounds. The suitability of CASTEP for theoretical simulation of physical-chemical properties in material study has already been reported[4−6]. But the IR spectrum calculation in CASTEP is a new development function of this code, and the superiority is also proved in this paper. In our calculation, generalized gradient approximations (GGA) for the theoretical basis of density function were chosen, and the supercell model as shown in Fig. 1 was used, while $a = 0.6375108$ nm, $\alpha = 46.07905°$[7]. Finally, the frequencies assigned with the vibrational modes analysis are got in Table 4, as predicted by group theory. And the calculated IR spectrum of calcite is reported in Fig. 3, whereas IR intensities are shown, so far the CASTEP code cannot provide the Raman intensities. Among the calculated data, the IR activity frequencies corresponding to modes are A_{2u} and E_u, and the Raman activity frequencies are A_{1g} and E_g. Because of the different strengths of the intra CO_3^{2-} and interionic force, the external modes $(1—15, < 400 \text{ cm}^{-1})$ have the lower frequencies than those associated with internal modes $(16—27, > 400 \text{ cm}^{-1})$, such a separation between external and internal modes are indeed mode.
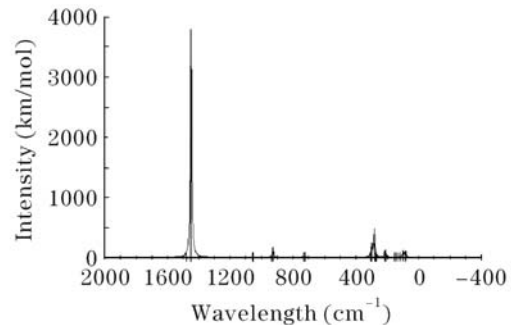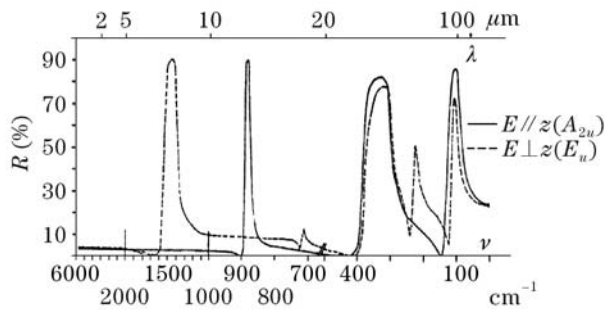

Fig. 3. Calculated IR spectra of calcite crystal.

Table 4. Comparison of Calculated (ν_{cal}) and Experimental (ν_{exp}) Vibrational Frequencies in cm^{-1}. $\Delta = \nu_{cal} - \nu_{exp}$

		ν_{cal}	ν_{exp}[10]		Δ
			IR	Raman	
E_u	1	83.83	92		−8.17
	2	99.15			7.15
A_{2u}	3	100.18	102		−1.82
E_g	4	121.25		156	−34.75
	5	137.20			−18.80
A_{2g}	6	152.20			
E_u	7	212.85	223		−10.15
	8	215.86			−7.14
E_g	9	271.16		284	−12.84
	10	272.84			−11.16
E_u	11	275.31	297		−21.69
	12	282.70			−14.30
A_{1u}	13	283.77			
A_{2u}	14	300.30	303		−2.70
A_{2g}	15	306.60			
E_g	16	721.69		712	9.69
	17	722.88			10.88
E_u	18	731.09	712		19.09
	19	732.37			20.37
A_{2u}	20	927.50	872		55.50
A_{2g}	21	933.08			
A_{1g}	22	1053.53		1086	−32.47
A_{1u}	23	1056.17			
E_u	24	1446.31	1407		39.31
	25	1448.46			41.46
E_g	26	1478.39		1434	44.39
	27	1480.87			46.87
Δ_{max}					55.50
Δ_{min}					−34.75

Fig. 4. Experimental IR spectra of calcite crystal[10].

Many papers only have reported three IR peaks (> 400 cm^{-1})[8,9], because of the restriction in measurement region of IR spectrometer of 4000—400 cm^{-1}. But our calculation breaches the restriction to get all the frequencies of normal modes. Compared with the experimental results by Hellwege *et al.*[10] (in Table 4 and Fig. 4), eight IR peaks in Fig. 3 match those in Fig. 4 very well. And E_u (24, 25) caused by symmetric C–O stretching has the strongest intensity in calculated infrared spectra, which is the feature IR peak of carbonate. As shown in Table 4, the calculated data agree well with the experimental ones, $\Delta_{max} = 55.50$ cm^{-1}, and $\Delta_{min} = -34.75$ cm^{-1}. Compared with the results from lattice dynamical methods based on parametric mode potentials: $\Delta_{max} = 43$ cm^{-1} and $\Delta_{min} = -109$ cm^{-1}[11], $\Delta_{max} = 31$ cm^{-1} and $\Delta_{min} = -110$ cm^{-1}[12], DFT is proved to be superior for simulating the infrared spectra of calcite crystal.

In conclusion, we present two methods of group theory to analyze the vibrational modes of calcite crystal. They both give 30 vibrational modes: $A_{1g} + 3A_{2g} + 4E_g + 2A_{1u} + 4A_{2u} + 6E_u$. There $A_{2u} + E_u$, A_{2u} and E_u are IR modes active, and A_{1g} and E_g modes are Raman active in the 27 normal modes. Comparing the two methods, we find that FSA has less process, but PSA can classify modes more specifically. Moreover, the IR spectrum of calcite is evaluated at DFT level by using CASTEP package. The calculation gives frequencies of the 27 normal modes. The modes of optically active frequencies match the results of group theory analysis very well. Exhilaratingly, the calculated IR spectra by DFT are in good agreement with the experimental ones, and perform better than the lattice dynamical methods based on parametric mode potentials.

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