The calculation of active Raman modes of α-quartz crystal via density functional theory based on B3LYP Hamiltonian in 6–311+G(2d) basis set[†]

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Abstract. We obtained an approximation of the force field of α-quartz crystal using a new idea of applying density functional theory [J Purton, R Jones, C R A Catlow and M Leslie, *Phys. Chem. Minerals* **19**, 392 (1993)]. Our calculations were based on B3LYP Hamiltonian [A N Lazarev and A P Mirgorodsky, *Phys. Chem. Minerals* **18**, 231 (1991)] in 6−311+G(2d) basis set for $H_{16}Si_7O_6$ cluster and included a unit cell of the lattice. The advantage of our method is the increase in the speed of calculations and the better adaption of simulation results with the experimental data.

Keywords. Density functional theory; Raman; cluster models; normal modes; Hessian matrix; quartz.

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1. Introduction

In the last decade, density functional theory (DFT) has probably become the most important tool in the field of applied computational chemistry [1–5]. Most of the exchange-correlation functionals currently used [6–11], including the exceedingly popular Becke 3-parameter-Lee–Yang–Parr (B3LYP) [12] hybrid functional [8,13,14] were developed more than ten years ago. Yet these first-generation functionals have a number of chemically important weaknesses. The physicists had done many studies for several years to find a coherent, systematic and secure method for deriving the main parameters and other dynamical properties such as specific heat and dielectric constant and other useful applications. Half a century has passed since the first theoretical viewpoints on the quantitative and qualitative properties of crystalline lattices were presented (for example, Bloch study [15] on periodic potentials). In this paper we examined the latest advances in enlarged quantum mechanics using computer algorithms and for that we presented a

[†]Dedicated to the memory of late Dr Majid Shahryari.

Table 1. Principal parameters of quartz lattice at 300 K [19].

| a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
4.9134	4.9134	5.4052	90.00	90.00	120.00

suitable approximation about the properties of systematic lattices, such as quartz with triangular lattice in room temperature via some considerations [16–18]. In table 1, we present principal parameters of quartz lattice at 300 K which has trigonal system and the schematic structure of α-quartz is shown in figure 1.

For infinite cells, researchers have used coherent cluster method for breaking the close infinite lattice structure. A good answer is not expected from complete incoherence of small cluster force fields. It is used for getting accurate answers. Also, corresponding calculations need more time, it is necessary to have supercomputers and it is costly to use algorithms which are not meant for large clusters of lattices. Therefore, clustered calculations by using small chosen clusters are important.

The cluster selected for this research is $H_{16}Si_7O_6$, which consists of constitutive unit cells of quartz atoms. For targeted silicon atoms, valance band is being completed at the open end of the cluster by hydrogen.

2. An overview of the α-quartz sample

α-quartz is a very important electrical and optical crystal with fascinating physical properties, such as piezoelectricity [21–23], optical activity [24–26], birefringence [27,28], and optical transmission in ultraviolet region. This crystal finds applications in electrical and optical devices such as quartz resonators, transducers, wave plates, optical rotators and compensators [27]. The physical properties of α-quartz are found to depend on the
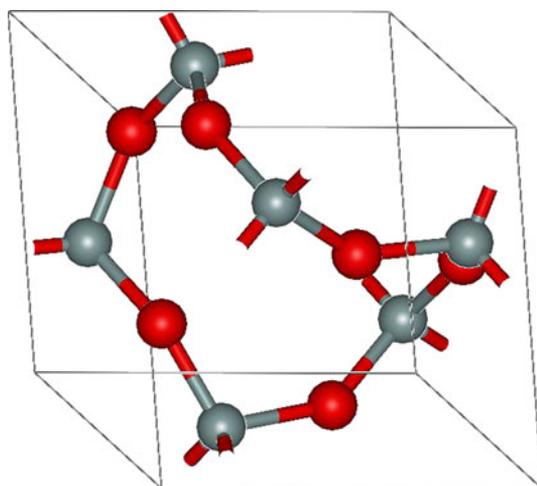
Figure 1. Crystal structure of α-quartz [20].
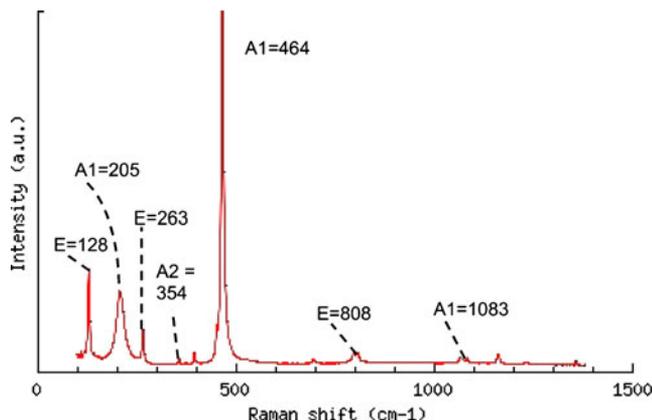
Figure 2. Raman spectrum of α-quartz at 300 K [30].

impurities. α-quartz is an optically active crystal, in which the plane of vibration of the incident light has a continuous rotation as the incident light propagates along the optical axis [29].

3. Active modes in Raman spectra

Only the active oscillations change in elliptical polarizations; in basis of Raman spectra which inclusively change in elliptical polarization. The greater difference in the value of polarization will cause more scattering; thereupon it creates the results in higher peaks of Raman spectra. In the case of lattice oscillations of quartz, four modes, as completely polar from A1 symmetry, and three modes of E symmetry have the highest value of Raman scattering. In figure 2 we observe an experimental spectrum of quartz at 300 K. The studied peaks in this paper are distinct and the value of oscillation frequency is exact. These are shown in figure 2.

4. Cluster calculations in the new method

Figure 3 shows the $H_{16}Si_7O_6$ cluster which was used for calculation in this article. It is important to know that the values for intermolecular distances and available link degrees in this cluster are similar to the values of the actual quartz lattice.

In this new method the process of calculations of the studied distinct atoms in oscillations is used for obtaining effective elastic constant. In straight method which was used in the study of the molecular structure, we calculated the Hessian matrix of atomic displacements in generalized coordinates, then we obtained the frequency values [31], and the direction of normal oscillation modes, therefore eigenvectors of this matrix is also expressed by
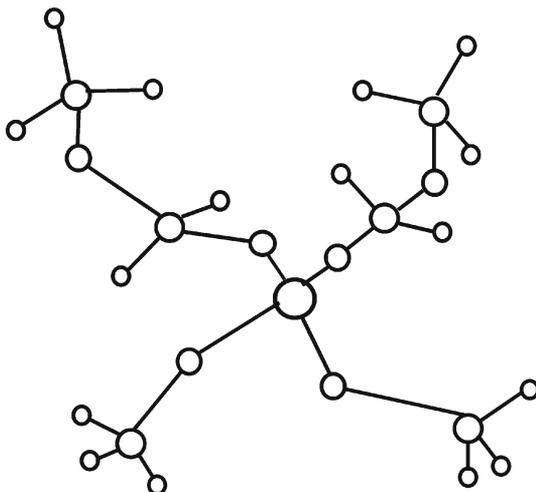
$$\omega^2 x_j = \sum_k H_{j,k} x_k a, \tag{1}$$

Figure 3. $H_{16}Si_7O_6$ cluster.

where H is the Hessian matrix, x_j is the generalized coordinate and ω is the dependent frequency of the jth oscillation. As we mentioned, the usual method for obtaining proper results for infinite structures like molecules and ions has many applications, but when we apply these methods to infinite structures, we encounter a serious problem: these methods are not applicable in the case of lattices because lattices have infinite dimensions. So, we used these methods in selected clusters. Because of the small dimensions of these clusters compared to the actual lattice, there will be aberrations in force field in the lattice [32] and there will be natural errors compared to the experimental values. However, directions of eigenvectors of Hessian matrix [30] in clusters differ from directions of actual lattice because of the free displacement of clusters and also because of the effective force field aberrations. In the calculations presented in this paper, correction of these directions coincides with the direction of actual lattice oscillation. We accomplish the calculations which are derived from the effective force field. The results were obtained from the change applied in the effective force on selected atom in small displacement which is used for reaching the dependent oscillation frequency. A smaller value of this displacement has been chosen to avoid anharmonicity compared to the displacement of actual lattice. Thus, with some changes in the calculations, we could obtain a correct value of dependent errors of cluster dimension. The reason of this is that the direction changes are deleted; however, this important parameter has an exclusive role in the value of errors.

5. Results and discussions

We used density functional theory based on B3LYP Hamiltonian for calculating the force field of $H_{16}Si_7O_6$ cluster. The base used in these calculations was 6-311+G(2d) which has the dependent polarity of d orbital and also first order of perturbation in quantum

Table 2. Comparison of results of calculation for active Raman modes of quartz obtained by our method and the observed frequency of ref. [23].

Symmetry type	Observed frequency (cm^{-1})	Calculated frequency (cm^{-1})	Relative error (%)
A1	1083.0	1115.9	3
E	808.6	817.2	1
A1	463.6	460.2	0.7
A1	354.3	350.5	1.1
E	263.1	267.9	1.8
A1	205.6	200.1	2
E	128.0	122.8	4

calculations that is dependent and available for the interactions of atomic orbitals. For completing our calculations we used the software entitled Gaussian 03W, and also Vibratz software for finding the oscillation direction in infinite lattice of quartz [33,34].

Table 2 demonstrates the observed results of seven active modes in Raman spectrum gained from this method. Experimental values of Raman spectroscopy [19,30], and also, values of the relative errors in comparison to the observed values are given in table 2. For comparison, we have presented in table 3, the previous works with average value of errors. Finally, for showing better results of different methods, we plotted figures 4 and 5 for understanding the different results of calculations which included our calculated results in comparison to the observed spectrum values from tables 2 and 3 and we could

Table 3. Comparisons of the results in different references and with our calculated results.

Observed frequency (cm^{-1})	Calculated frequency[a] (cm^{-1})	Calculated frequency[b] (cm^{-1})	Calculated frequency[c] (cm^{-1})	Calculated frequency[d] (cm^{-1})
1083	1115	1218	1152	1123
808.6	817	833	848	762
463.66	460	584	493	469
354.3	350	428	347	372
263.1	268	334	268	235
205.6	200	230	201	201
128.0	123	171	142	113
Relative error (%)	1.94	19.7	4.95	4.21

[a]The results obtained in this research.
[b]Results of calculation for H_4SiO_4 and $H_6Si_2O_7$ clusters in 6-31G(d) basis set [15].
[c]Results of calculation for $H_{12}Si_5O_{16}$ cluster, by using half-experimental calculations [1].
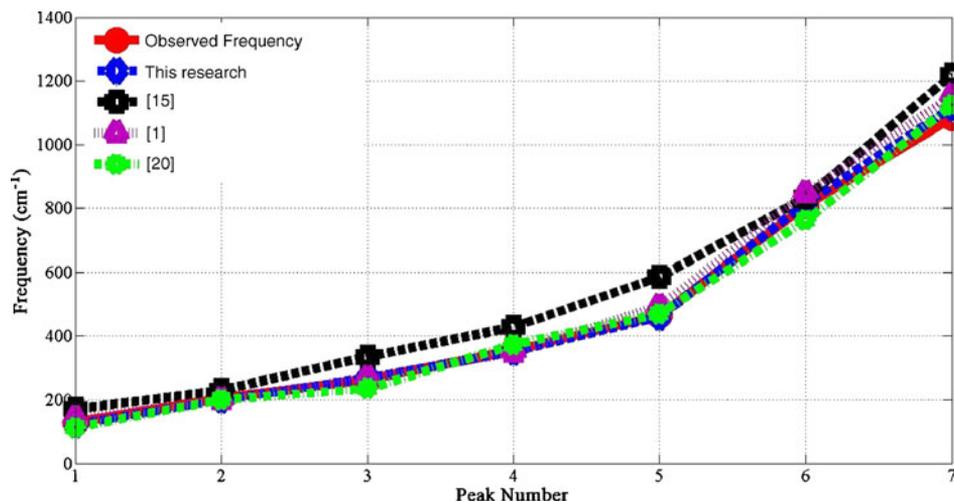[d]Results in ref. [20].

Figure 4. Plots of numerical values for different calculations by comparing with observed frequencies.

show that our calculations are in good agreement with the observed values of spectrum for α-quartz sample.

6. Conclusion

• Observed results from seven active modes in Raman spectrum generated from the density functional theory based on B3LYP Hamiltonian in $6-311+G(2d)$ basis set
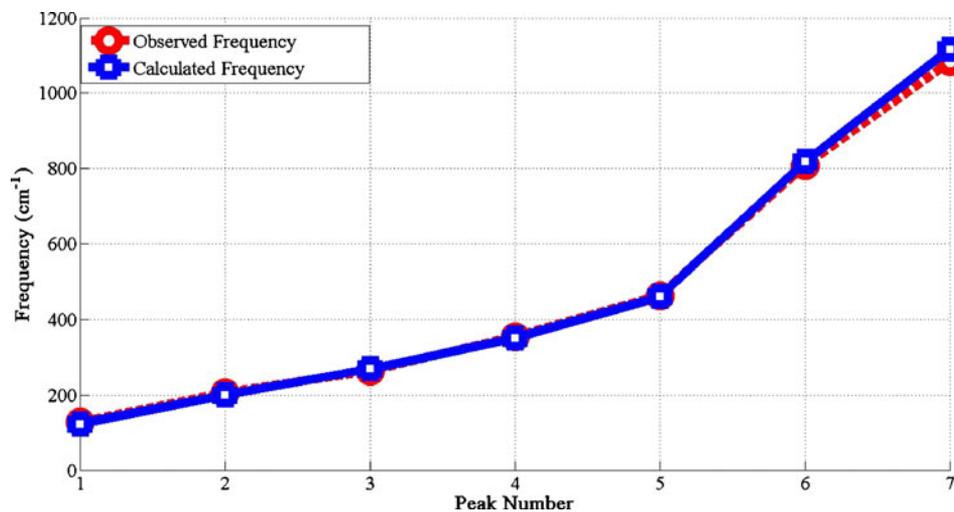

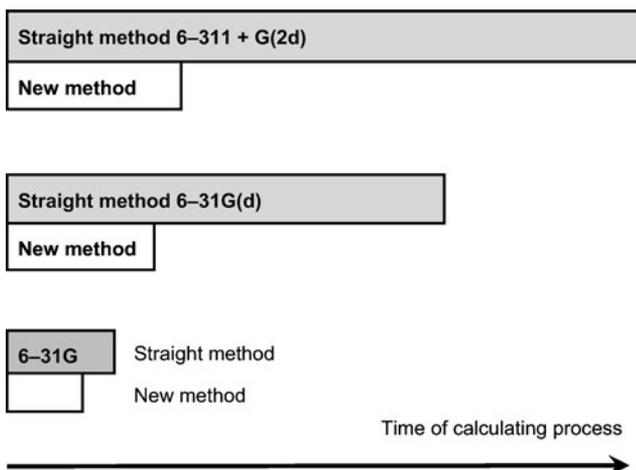**Figure 5.** Plots of calculated frequencies in this paper and the observed frequencies.

Figure 6. Relative time for calculation using 6−31G, 6−31G(2d) and 6−311+G(2d) processes. Gray box shows the time for standard calculation and white box shows the time for calculation using the new method.

has more compatibility compared to the experimental results. These are shown in figures 4 and 5. We can see that the corresponding curve of this research is the best curve which is closer to the observed frequency curve, i.e., our new calculated method is closer to the observed frequency curve. These results are showing the corrected patterns in the displacements of directions which are used for obtaining the force constant. In this study, calculations are used for obtaining the value of force field produced from clusters. It shows that the value of aberrations of the previously observed results about the oscillation's frequency depends on the aberrations of oscillation direction with errors of force field cluster.

- One advantage of this method is the high speed of calculation compared to the normal methods (nearly 300% to 500%) which is very important. Figure 6 shows the schematic image of our aim.

Acknowledgements

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