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Vibrational analysis of L-serine using the density functional theory*

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In this paper, we present a computational study of L-serine using ab initio molecular dynamics simulation based on density functional theory (DFT) within the ultrasoft pseudopotentials and generalized-gradient approximation. Taking into account the intermolecular interactions, we can indeed simulate the features of the experimental results very well for L-serine zwitterions in its solid state. The vibrational spectrum of L-serine performed by DFT was in excellent agreement with our previous inelastic incoherent neutron scattering spectra measured at 20K for L-serine in the 10–200meV region on HET spectrometers at ISIS, Rutherford Appleton Laboratory.

Keywords: density functional theory, molecular dynamics, inelastic incoherent neutron scattering
PACC: 7115M, 7115Q, 2540F, 6320D

1. Introduction

Amino acids are the building blocks of proteins. It has been demonstrated that in the liquid or the solid phase most amino acids exist as the zwitterions (NH_3^+–CH (–*R*)–COO^-), and interact with the surrounding molecules through hydrogen bondings, while with the intermolecular bonds being not present in the gas state, they exhibit the neutral form (NH_2–CH (–*R*)–COOH). Their Raman, IR, inelastic neutron scattering spectra in the solid phase have been measured extensively.[1−8] Many ab initio simulations of these spectra have also been reported.[9−12] Nevertheless, most vibrational spectra of amino acids in the solid state have not been assigned satisfactorily by means of ab initio method levels based on the isolated neutral molecular or the isolated zwitterions, lack of intermolecular interactions.

Although recently density functional theory (DFT)[13] has been used extensively to investigate the electronic structure, bonding and spectroscopic properties of solid, both in bulk form[14−17] and at surfaces,[18−20] simulations of the vibrational spectra of large molecular in the solid phase by using DFT method are few in the literature. The main reason is that the high computational cost is needed to obtain adequate precision.

In this paper considering the intermolecular interactions, long-range interactions, by using ab initio DFT molecular dynamics (MD) simulations we present a theoretical simulation of the vibrational spectrum of L-serine (L-: left hand) in the solid state obtained by our previous inelastic incoherent neutron scattering (IINS) study.[21]

Serine (Ser) is one of the non-essential amino acids and most commonly found in proteins along with glycine and leucine. X-ray diffraction[22−24] studies indicate that the crystal structure of L-serine is stabilized by a three-dimensional network of hydrogen bonds. The amino group forms hydrogen bonds of lengths 2.84, 2.87 and 2.89Å respectively with the carboxyl group of the neighbouring molecular, and also the hydroxyl group forms a hydrogen bond of length 2.92Å with the other adjacent hydroxyl group.[24] Its

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Raman, IR and neutron scattering spectra and their assignments have been published in several papers, along with ab initio calculations.[25−28] Here for comparison we show the result of Ref.[28], which is an ab initio simulation of IINS spectra in Hartree–Fock (HF) level based on isolated zwitterions.

2. Computational details

The first-principle calculations were carried out by using the Vienna ab initio simulation package (VASP)[29,30] which is designed to perform ab-initio quantum mechanical MD simulations using psedopotentials and a plane wave basis set. In this work the structure obtained from the neutron diffraction[24] for L-serine was used as a starting structure. Due to the limitation of our computer calculation speed and the large size molecules, in this simulation we only choose one unit cell, which consists of four molecules as depicted in Fig.1. All the atomic degrees of freedom were relaxed using VASP with the ultra-soft Vanderbilt pseudopotentials.[31] In this pseudopotential approach, the pseudopotential represents the effective interaction of the valence electrons with the atomic cores, and only the valence electrons are treated explicitly. The generalized gradient approximation (GGA)[32] by Perdew and Wang (PW91)[33] for the exchange-correlation energy is used to give good description of the hydrogen bonding in L-serine. The GGA is crucial for the accurate treatment of the hydrogen bond.[34] The PW91 form has also been tested extensively for various intermolecular interactions including hydrogen bonding.[35] Kohn–Sham orbits are expanded in plane waves up to a relatively high kinetic energy cutoff of 400eV, because the hydrogen atoms require a larger number of plane waves for describing localization of their charges in real space. The Monkhorst–Pack scheme[36] with $2\times2\times4$ k-points grid mesh has been used for integration in the Brillouin zone. Fermi level is smeared by the Gaussian method[37] with a width of 0.2eV. The geometry optimization is stopped when energy convergence is less than 0.0001eV per atom. Within this scheme we find excellent agreement between the theoretical and experimental[24] structural parameters.

After the system was energy-minimized, ab initio molecular dynamics simulation was performed at constant temperature. All the atoms were allowed to move according to the forces calculated from the converged electronic structure. The temperature of 50K was maintained by scaling velocities. Time step of 1fs was used. Typically, the system was equilibrated for 1ps, and the trajectories have been calculated for 4ps, with a time step of 1fs. The vibrational spectra for hydrogen atoms were obtained by performing Fourier transformation of velocity autocorrelation functions,[19] recorded in our MD trajectories. The vibrational spectra (i.e. phonon density of states (PDOS)) can be obtained by

$$\mathrm{DOS} = \int_0^\infty \exp(-\mathrm{i}wt)\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle \mathrm{d}t, \qquad (1)$$

where

$$\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle = \frac{1}{N}\sum_{i=1}^{N}\langle \boldsymbol{v}_i(t)\cdot\boldsymbol{v}_i(0)\rangle.$$

Integration in Eq.(1) was performed using a time step of 30fs for a duration of 4ps after the initial equilibration.

3. Results and discussion

3.1. Optimized geometries

It is believed that the Gaussian program package is more suitable for simulations of isolated molecules, due to lack of intermolecular H-bonding. Moreover, in many calculated reports about amino acids molecules it has been demonstrated that the MP2 and B3LYP levels predict molecular structure more accurately than the HF level.[38−41] Therefore, although Ref.[28] obtained the zwitterion geometric form of the L-serine molecule, its result is still not of good quality because of using the HF level. In our calculations we worked out the crystal structure of L-serine by considering the intermolecular interactions and using the Vienna ab initio simulation package, VASP.

L-serine crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell.[24] The experimental values of the lattice constants are a=8.599Å, b=9.348Å, and c=5.618Å. The crystal structure for the unit cell of L-serine and the heavy atom label are shown in Fig.1.

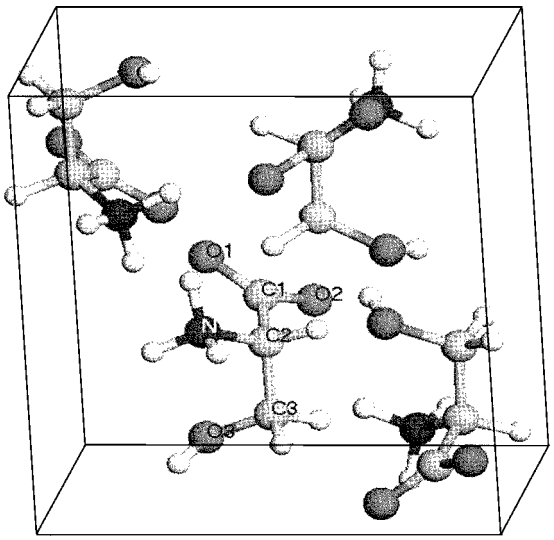


Fig.1. The structure of L-serine, space group $P2_12_12_1$. The unit cell has four serine molecules.

The optimized lattice constants a=8.479Å, b=9.296Å, and c=5.594Å are consistent well with the experimental values. Table 1 summarizes bond lengths, bond angles and torsion angles among the heavy atoms obtained by this work based on DFT method, the HF results[16] and the neutron diffraction.[24] The values in bracket are the differences among the calculated ones and the neutron diffraction results. It can be seen from the table that our results of the minimized crystal structure of L-serine agree with the neutron scattering results very well. Concerning bond lengths, the most differences in our work are smaller than those in the HF, except for the C1-O1 and C2-C3 bonds. Taking account of intermolecular interactions, our calculated values of the bond angles and torsion angles are very close to its experimental values. All the angular deviations in our work are not more than 3°, much smaller than those in the HF (see Table 1).

Table 1. Optimized structural parameters of L-serine for the heavy atoms. The bond lengths are in angstroms; angles and the dihedral angles are in degrees.

	Present work	HF[b)]	Expt.[a)]
Bond lengths/Å			
C1-O1	1.260 (0.020)	1.234 (0.006)	1.240
C1-O2	1.275 (0.028)	1.208 (0.039)	1.247
C1-C2	1.526 (0.001)	1.571 (0.044)	1.527
C2-N	1.483 (0.002)	1.503 (0.018)	1.485
C2-C3	1.523 (0.013)	1.516 (0.006)	1.510
C3-O3	1.436 (0.003)	1.401 (0.032)	1.433
Bond angles/(°)			
C2-C1-O1	118.55 (0.2)	112.3 (6.1)	118.4
C2-C1-O2	116.01 (0.3)	114.9 (1.4)	116.3
O1-C1-O2	125.44 (0.2)	132.8 (7.6)	125.2
C1-C2-N	111.85 (1.1)	104.1 (6.7)	110.8
C3-C2-N	110.28 (0.6)	110.6 (0.9)	109.7
C1-C2-C3	112.36 (0.2)	113.7 (1.1)	112.6
C2-C3-O3	111.91 (1.7)	110.0 (0.2)	110.2
Torsion angles/(°)			
O1-C1-C2-C3	122.78 (0.9)	141.0 (17.3)	123.7
O2-C1-C2-N	179.00 (2.9)	–159.0 (19.1)	–178.1
O2-C1-C2-C3	–56.29 (1.5)	–38.5 (16.3)	–54.8
C1-C2-C3-O3	–64.85 (2.6)	–61.3 (1.0)	–62.3
N-C2-C3-O3	60.74 (0.8)	55.4 (6.1)	61.5

[a)] From neutron diffraction study of L-serine on the solid phase.[24]

[b)] From an ab initio simulation in the HF level.[28]

3.2. Vibrational frequencies

In our previous paper[21] we presented a series of inelastic incoherent neutron scattering (IINS) spectra of L-serine measured on HET spectrometer at ISIS in the region from 10 to 130 meV (see Fig.2(a)). In this paper we also show the extra IINS spectra in the region from 130 to 200 meV obtained at the same beam line in Fig.2(b). For comparison, the IINS vibrational frequencies of L-serine measured by Pawlukojc *et al*[28] measured on TFXA spectrometer at ISIS are

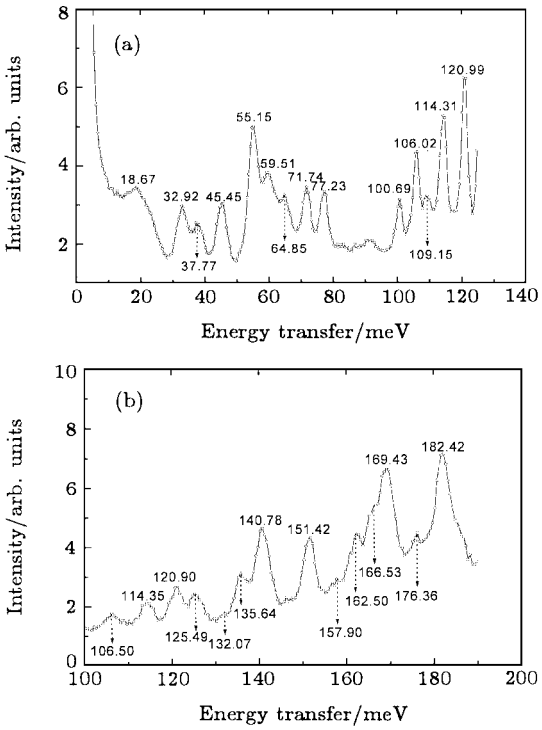


Fig.2. Plot of IINS spectra below 20 K for L-serine: (a) in the region from 10 to 130 meV; (b) in the region from 100 to 200 meV.

also listed in Table 2. Since the HET spectra suffers poor resolution at the low energy transfers, the peaks at 61.25 meV in TFXA spectra are absent in our HET spectra. On the contrary, the two peaks at 100.69 and 109.15 meV in HET spectra are not observed in TFXA spectra. Therefore our HET results provide more details about the vibrational dynamics of L-serine.

Figure 3 shows our calculated vibrational spectrum obtained by performing Fourier transformation of velocity autocorrelation functions resulted from the ab initio MD. We list our calculated and observed frequencies for the L-serine in Table 2. The observed

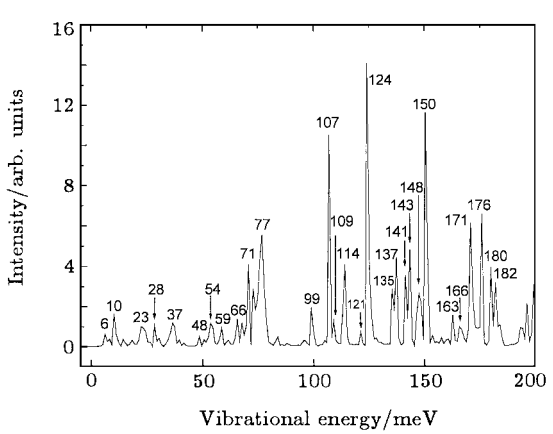


Fig.3. Calculated vibrational spectra for the L-serine in the region from 0 to 200 meV.

frequencies by Pawlukojc *et al*[28] are also shown in Table 2 for comparison. Table 2 shows that the largest peak shift is 4.7meV in our calculation, much smaller than that in HF (13.9meV).

Table 2. Vibrational energies for L-serine (in units of meV).

This work		Ref.[28]	
Calculated	IINS	RHF/ 6-311++G**	IINS
6.14(0.7)	18.67	7.44(0.6)	6.82
10.05(2.4)		13.51(1.1)	12.40
23.15(0.8)		24.30(0.4)	23.93
28.23(4.7)	32.92	34.59(2.2)	32.36
36.63(1.1)	37.77	35.96(1.1)	37.07
48.35(2.9)	45.45	43.15(1.7)	44.88
53.83(1.3)	55.15	68.69(13.9)	54.80
58.53(1.0)	59.51	–	58.89
–	–	–	61.25
65.55(0.7)	64.85	57.53(7.1)	64.60
70.65(1.1)	71.74	61.50(9.9)	71.42
76.71(0.5)	77.23	72.90(4.0)	76.87
99.00(1.7)	100.69	–	–
107.01(1.0)	106.02	100.30(6.0)	106.26
108.95(0.2)	109.15	–	–
114.03(0.3)	114.35	103.78(10.5)	114.31
121.07(0.2)	120.90	113.69(7.8)	121.51
124.21(1.3)	125.49	120.89(4.7)	125.60
135.18(3.1)	132.07	128.70(4.0)	132.66
137.29(1.7)	135.64	131.18(6.2)	137.38
141.41(0.6)	140.78	136.14(5.1)	141.22
150.39(1.0)	151.42	144.44(7.4)	151.88
156.48(1.4)	157.90	157.58(0.8)	158.33
162.51(0.0)	162.50	162.79(0.9)	163.66
166.04(1.1)	166.53	164.78(3.0)	167.75
170.72(1.3)	169.43	166.76(2.6)	169.36
175.61(0.8)	176.36	168.99(7.6)	176.55
179.71(0.1)	–	172.09(7.7)	179.78
181.67(0.8)	182.42	179.78(3.2)	183.00

Since vibrational frequencies are very sensitive to the structure of molecules studied, the discrepancies of vibrational frequencies are also from the geometric difference. Table 1 shows a slightly larger difference for the bond lengths C1-O1 (0.020Å), C1-O2 (0.028Å) and C2-O3 (0.013Å) between our optimized geometry and the neutron diffraction results. Based on the assignment of vibrational spectrum in Ref.[28], the computed frequencies of 28.23, 48.35 and 135.18 meV arising from the C1-C2-N_{bend}, N-C2-$C3_{bend}$ and C_1O_{str} modes are corresponding to the observed frequencies of 32.92, 45.45 and 132.07 meV in our IINS spectrum respectively. Since the calculated O1 and O2 atoms are away from C1 atom compared to experimental ge-

ometry (see Table 1), it causes the C1-C2-N_{bend} bend easily, thus the calculated frequency of C1-C2-N_{bend} is shifted to lower energy, at 28.23 meV, as compared to the experimental value of 32.92 meV. For N-C2-$C3_{bend}$ vibration, the calculated C2-C3 bond length 1.523Å is longer than the experimental value 1.510Å. This makes the N-C2-$C3_{bend}$ vibration stronger, and the calculated frequency is shifted from 45.45 meV to high energy of 48.35 meV. Because the calculated bond lengths of C1-O1 (1.260Å) and C1-O2 (1.275Å) are longer than the measured values[24] of 1.240Å and 1.247Å respectively, it is also much easier to understand the red shift of the C1=O stretching mode. Except for those discrepancies stated above, our PDOS carried out by DFT method is in good agreement with the experimental IINS spectra.

4. Conclusion

In summary, taking into account the intermolecular interactions we have obtained the vibrational spectrum of L-serine by using ab initio MD simulations based on DFT method. The optimized geometries and vibrational spectra of L-serine performed by DFT are in excellent agreement with the neutron diffraction and our previous inelastic neutron scattering results. We have reproduced satisfactorily the main features of the experimental results for L-serine zwitterions in its solid state.

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