International Journal of Modern Physics B
Vol. 30 (2016) 1650079 (13 pages)

DOI: 10.1142/S021797921650079X

First-principles studies of pure and fluorine substituted alanines

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Received 20 August 2015
Revised 19 December 2015
Accepted 28 January 2016
Published 25 May 2016

This paper communicates the structural, electronic and optical properties of L-alanine, monofluoro and difluoro substituted alanines using density functional calculations. These compounds exist in orthorhombic crystal structure and the calculated structural parameters such as lattice constants, bond angles and bond lengths are in agreement with the experimental results. L-alanine is an indirect band gap insulator, while its fluorine substituted compounds (monofluoroalanine and difluoroalanine) are direct band gap insulators. The substitution causes reduction in the band gap and hence these optically tailored direct wide band gap materials have enhanced optical properties in the ultraviolet (UV) region of electromagnetic spectrum. Therefore, optical properties like dielectric function, refractive index, reflectivity and energy loss function are also investigated. These compounds have almost isotropic nature in the lower frequency range while at higher energies, they have a significant anisotropic nature.

Keywords: Alanine; structural properties; DFT; energy band profiles; optical spectra.

PACS numbers: 31.15.E-, 42.70.-a, 61.82.Ms, 71.15.Mb, 77.22.-d

1. Introduction

Amino acids are organic compounds having basic building block of proteins.[1] Amino acids contain acid and amine functional groups. Out of the 500 amino acids[2] the

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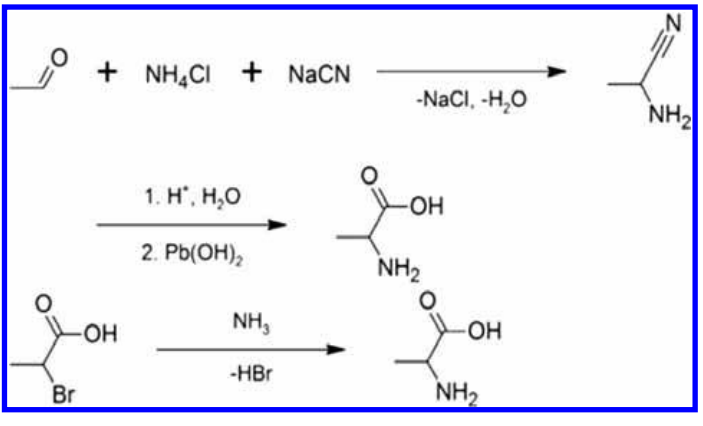
human body needs only 20 of them. Some of them are essential and are obtained from dietary sources while others are nonessential and can be synthesized by the body. Alanine is nonessential, nonpolar and the first ever synthesized amino acid[3] and is one of the most abundant amino acids in natural proteins.[4] It is found in a wide variety of foods like seafood, dairy products, eggs, gelatin, nuts, seeds, soy, whey, brewer's yeast, brown rice, corn, legumes, whole grains and meats.[5]

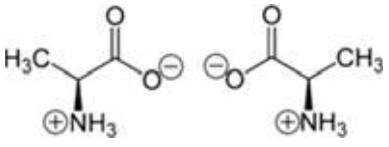
Strecker in 1850 prepared alanine via the cyanohydrin reaction from acetaldehyde and ammonia with hydrocyanic acid and subsequent hydrolysis by HCl. The reaction is given the name Strecker reaction as shown below[6]:



L-alanine was first crystallized by Barnal[7] and its isolation from natural sources, i.e., silk and ovalbumin, was described by Schutzenberger as early as 1875.[8] Alanine has promising nonlinear, optical, elastic, piezoelectric and dielectric properties[9,10] and has applications in laser technology, optical communication, data computing technologies and radiotherapy.[11–13]

Change in the alanine cycle is linked to the development of type II diabetes.[5] It boosts up the immune system by producing antibodies and provides energy to muscles, brain and central nervous system. Alanine has close links to metabolic pathways such as glycolysis, gluconeogenesis and the citric acid cycle. It also arises together with lactate and generates glucose from protein via the alanine cycle.[8]

Alanine is optically active and mostly the L-isomer is found in nature. It is a naturally occurring chiral amino acid with the empirical formula $C_3H_7NO_2$(2-aminopropaionic acid).[3,8] Its molecular mass is 89.09 $g \cdot mol^{-1}$, melting point is 314–316°C, solubility is 166.5 g/l and pH is 6. It occurs in orthorhombic crystal structure and is colorless. The carbon atom of alanine is bound with a methyl group making it one of the simplest α-amino acids with respect to molecular structure. The methyl group of alanine is nonreactive and is not directly involved in protein synthesis.[3,14,15] The carboxyl group that donates the proton, which is gained by the ammine group to become ammonium, is called Zwitterion.[16] This is a double ion and this ionization is caused by water as shown in Fig. 1.



(a) (b)

Fig. 1. Zwitterionic forms of L-alanine. (a) (S)-Alanine and (b) (R)-Alanine.

In the present paper, structural, chemical, electronic and optical properties of L-alanine (CH_3CHNH_2COOH), monofluoroalanine (CH_2FCHNH_2COOH) and difluoroalanine (CHF_2CHNH_2COOH) are investigated using density functional calculations. The substitution of fluorine in L-alanine has a significant effect on the physical properties of L-alanine.

2. Material and Methods

In the present study, L-alanine, monofluoroalanine and difluoroalanine are investigated using full potential linearized augmented plane waves (FP-LAPW) method as implemented in the WIEN2k package.[17] For exchange and correlation energy, the generalized gradient approximation (GGA) is used. For the accurate band gap and optical properties of the compounds, the modified Becke–Johnson (mBJ) exchange potential is used as an additional potential to GGA.[18] In the full potential scheme, the potential and charge density are expanded by spherical harmonics inside the nonoverlapping spheres (muffin-tin spheres) and by plane wave basis set in the remaining space of the unit cell (interstitial region). For the wavefunction expansion inside the atomic spheres, the value of l is confined to $l_{\max} = 10$ and for the interstitial nonspherical part $l_{\max} = 6$. The muffin-tin radii for constituent atoms are selected in such a way that no charge leakage from the core occurs and the total energy is converged. For the wavefunction in the interstitial region, the plane wave cutoff value of $K_{\max}$ is $8/R_{\mathrm{MT}}$, while the charge density is Fourier expanded up to $G_{\max} = 14$ Ry. The Brillouin zone integration is performed using a mesh of 2000 k-points, and convergence is checked through self-consistency.

3. Structural Properties

To investigate the ground state structural properties of L-alanine, CH_3CHNH_2COOH, CH_2FCHNH_2COOH and CHF_2CHNH_2COOH optimizations are performed for each unit cell in orthorhombic structure with the space group $P2_12_12_1$(No. 19).[19] The structural parameters are evaluated using the fitted Birch–Murnaghan equation of states as reported in our previous work.[20] The calculated lattice constants (a, b and c) for CH_3CHNH_2COOH, CH_2FCHNH_2COOH and CHF_2CHNH_2COOH are listed in Table 1. It is clear from the table that our theoretical results are in agreement with the reported experimental results[19,21,3,22] for CH_3CHNH_2COOH and CH_2FCHNH_2COOH, respectively, while no literature

Table 1. Lattice parameters (Å) of L-alanine (CH_3CHNH_2COOH), monofluoroalanine (CH_2FCHNH_2COOH) and difluoroalanine (CHF_2CHNH_2COOH).

Compounds	Present results	Experimental	Other theoretical
L-alanine (CH_3CHNH_2COOH)			
a (Å)	6.06136	6.032,[b] 6.0095[a]	6.0272[f]
b (Å)	12.5776	12.343,[b] 12.339[a]	12.3412[f]
c (Å)	5.72790	5.7840,[b] 5.7904[a]	5.782[f]
Monoflouroalanine (CH_2FCHNH_2COOH)			
a (Å)	6.146648		5.90[c]
b (Å)	12.57760		13.85[c]
c (Å)	5.727900		5.75[c]
Diflouroalanine (CHF_2CHNH_2COOH)			
a (Å)	6.14450		
b (Å)	12.5733		
c (Å)	5.57410		

[a]Ref. 22, [b]Ref. 9, [c]Ref. 24 and [f]Ref. 2.

Table 2. Bond lengths (Å) of L-alanine, monoflouroalanine and difluoroalanine.

Compounds	Present results (Å)	Experimental (Å)	Other (Å)
L-alanine (CH_3CHNH_2COOH)			
$N–H_{(1)}$	1.0424	0.95[b]	1.069,[e] 1.042[f]
$C_{(1)}–C_{(2)}$	1.5448	1.525[b]	1.53,[d] 1.536[f]
$N–H_{(3)}$	1.04631	1.048[e]	1.03,[d] 1.047[f]
$N–H_{(2)}$	1.0664	0.88[b]	1.065[f]
$C_{(1)}–O_{(2)}$	1.2590	1.256,[b] 1.258[f]	1.22,[d] 1.185[f]
$C_{(1)}–O_{(1)}$	1.2810	1.247,[b] 1.242[f]	1.301[f]
$C_{(2)}–H_{(4)}$	1.1013	0.98,[b] 1.093[f]	1.1,[d] 1.088[f]
$C_{(3)}–H_{(7)}$	1.0982	0.99,[b] 1.082[f]	1.086[f]
$C_{(3)}–H_{(6)}$	1.0992	0.98,[b] 1.081[f]	1.088[f]
$N–C_{(2)}$	1.4918	1.491,[b]1.487[f]	1.45,[d] 1.488[f]
Monoflouroalanine (CH_2FCHNH_2COOH)			
$C_{(3)}–F_{(1)}$	1.4297		1.41[c]
$C_{(3)}–H_{(2)}$	1.1024		
$C_{(3)}–H_{(3)}$	1.1024		
$C_{(3)}–C_{(2)}$	1.5250		1.51[c]
$C_{(1)}–N$	1.4828		
$C_{(1)}–C_{(2)}$	1.5424		1.54[c]
$C_{(1)}–O_{(1)}$	1.2629		
$C_{(1)}–O_{(2)}$	1.2706		
Diflouroalanine (CHF_2CHNH_2COOH)			
$C_{(3)}–F_{(1)}$	1.4058		
$C_{(3)}–F_{(2)}$	1.4074		
$C_{(3)}–H_{(5)}$	1.1011		
$C_{(3)}–C_{(2)}$	1.5345		
$C_{(2)}–C_{(1)}$	1.5512		
$C_{(1)}–O_{(1)}$	1.2512		
$C_{(1)}–O_{(2)}$	1.2743		

[b]Ref. 9, [c]Ref. 24, [d]Ref. 13, [e]Ref. 16 and [f]Ref. 22.

Table 3. Bond angles (θ°) of L-alanine, monoflouroalanine and difluoroalanine.

Compounds	Present calculated (deg)	Experimental (deg)	Others (deg)	% Error
L-Alanine (CH_3CHNH_2COOH)				
$H_{(5)}$–$C_{(3)}$–$H_{(6)}$	108.31	108.9,[e] 108.36[g]	108.4,[f] 108.14[g]	0.54
$C_{(1)}$–$C_{(2)}$–N	110.00	110.3,[b] 110.05[g]	112,[d] 110.98[g]	0.27
$C_{(1)}$–$C_{(2)}$–$C_{(3)}$	112.40	111.5,[b] 111.0[g]	117,[d] 110.32[g]	0.80
$O_{(1)}$–$C_{(1)}$–$O_{(2)}$	126.03	125.6[b]	128[d]	0.34
Monoflouroalanine (CH_2FCHNH_2COOH)				
$C_{(3)}$–F–$H_{(6)}$	108.82		106[c]	
$C_{(1)}$–$C_{(2)}$–N	110.09		—	
$C_{(1)}$–$C_{(2)}$–$C_{(3)}$	109.12		121[c]	
$O_{(1)}$–$C_{(1)}$–$O_{(2)}$	126.81		127[c]	
Diflouroalanine (CHF_2CHNH_2COOH)				
$C_{(3)}$–$F_{(1)}$–$F_{(2)}$	106.63			
$C_{(1)}$–$C_{(2)}$–N	109.98			
$C_{(1)}$–$C_{(2)}$–$C_{(3)}$	108.92			
$O_{(1)}$–$C_{(1)}$–$O_{(2)}$	126.81			

[b]Ref. 9, [c]Ref. 24, [d]Ref. 13, [e]Ref. 25, [f]Ref. 16 and [g]Ref. 22.

is available on CHF_2CHNH_2COOH. The geometrical parameters (bond lengths) of the compounds are listed and compared with the available literature in Table 2. The presently calculated bond lengths are in good agreement with the experimental and theoretical calculated results. The bond angles of the three compounds are given and compared in Table 3. The calculated bond angles are in agreement with the experimental results. The difference between our result and other theoretical data[13] of C–C–C is because that the reported work based on local density approximation overestimated the C–C–C bond. The calculated bond lengths of L-alanine are in agreement with the experimentally measured values, those of monofluoroalanine are compared with the theoretical results and no data is available for the bond lengths of difluoroalanine. All hydrogen atoms of $NH_2^+$of alanine molecule are involved in hydrogen bonding with the carboxylic group of another alanine molecule ($N–H\cdots O$), with bond lengths of 2.83, 2.85 and 2.81 Å.[3,23] The unit cell of alanine contains four Zwitterionic molecules ($NH_3C_2H_4CO^-$), linked by three-dimensional network of hydrogen bonds of unequal strength.[3]

In order to investigate the bonding nature of these compounds, the electronic charge densities are plotted in Fig. 2. It is obvious from the figure that the energy states are strongly overlapped and distributed along the C–C, C–H, C–O, N–H and C–N. Hence, these bonds are strongly covalent in nature with bond lengths shown in Table 2, which are in agreement with experimentally reported data.[16,19,24] The difference in electronegativities of the constituent atoms C (2.5), N (3), H (2.1), O (3.5) and F (4) also shows that there is a covalent bond between C–C, C–H, C–O, N–H and C–N. It is clear from Fig. 2 that the charge density is greater towards F atom which shows that the bond between C–F is polar. As F atom is substituted

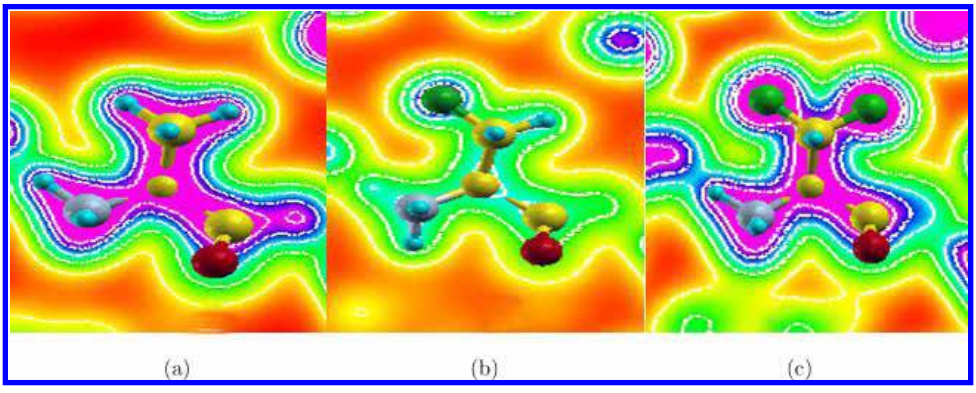


Fig. 2. (Color online) Electron densities of (a) L-alanine ($C_3H_7NO_2$), (b) monofluoroalanine ($C_3H_6FNO_2$) and (c) difluoroalanine ($C_3H_5F_2NO_2$).

in L-alanine to form monofluoro and difluoroalanines, the electron densities shifted from carboxylic carbon towards the beta carbon, as shown in Figs. 2(a)–2(c). It is due to the more electronegative nature of F atom.

4. Electronic Properties

The electronic properties of materials are described in terms of energy band gaps and density of states (DOS). Calculation of the electronic band gaps is a key investigating tool for understanding most of the physical properties of materials that are directly or indirectly related to the electronic band structure. The calculated energy band structures for each compound are shown in Fig. 3. The figure shows that these compounds are wide band gap materials and therefore are insulators. The calculated band gap of L-alanine is 5.0 eV whereas its experimental band gap

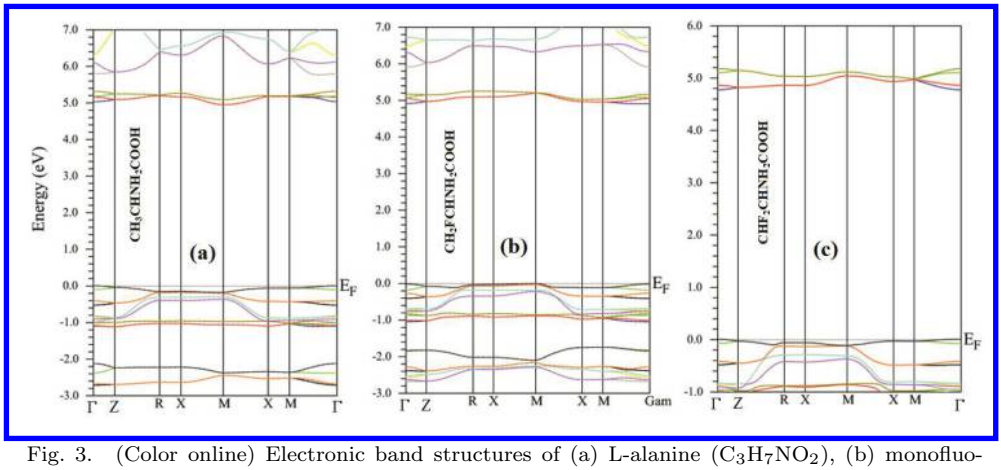


Fig. 3. (Color online) Electronic band structures of (a) L-alanine ($C_3H_7NO_2$), (b) monofluoroalanine ($C_3H_6FNO_2$) and (c) difluoroalanine ($C_3H_5F_2NO_2$).

is 5.02 eV (see Ref. 25), that reflects the effectiveness of our model. The nature of the band gap of L-alanine is indirect at symmetry line Γ–M. Substituting hydrogen by fluorine, the band gap transforms from indirect to direct and reduces in number. The calculated band gaps of CH_2FCHNH_2COOH and CHF_2CHNH_2COOH are 4.8 and 4.7 eV, respectively, and both have direct band gap nature at Γ–Γ symmetry line. This transformation of L-alanine from an indirect to direct band gap materials is of high importance, because indirect band gap materials weakly respond to electromagnetic radiations due to the fact that their conduction band minima and the valence band maxima occur at different symmetry lines of the Brillouin zone. Consequently, phonons are involved in the inter-band transitions of electrons, which is a weak process as compared to a two-body event, i.e., electron and photon. Therefore, in optoelectronic technology direct band gap materials dominate over the indirect band gap materials.

To explain the detailed roles of different orbitals in the energy band structure, the total and partial DOSs are calculated and shown in Fig. 4. The core states are low energy electrons having high binding energies and the valence states are

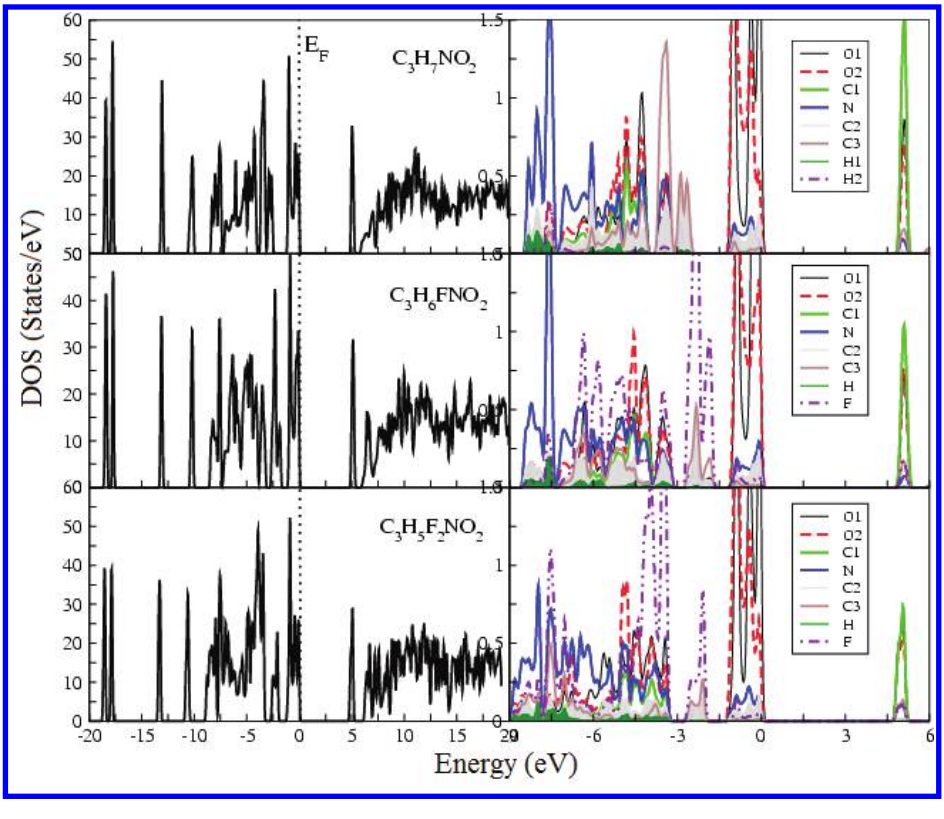


Fig. 4. (Color online) Total and partial DOSs of L-alanine ($C_3H_7NO_2$), monofluoroalanine ($C_3H_6FNO_2$) and difluoroalanine ($C_3H_5F_2NO_2$).

high energy electrons with low binding energies. The partial DOS (Fig. 4) shows three different regions in the valence band. The lower energy region (−9–−3 eV) is contributed by hybridized states of N-p, C1-p, C2-p, C3-p, O1-p, O2-p, H-s and F-p. The maximum peak in this region is from N-p which decreases with fluorine substitution. The next contribution comes from C2-p. The energy region around −3–−2 is contributed by the mixed energy states of C2-p, C3-p, H2-s and F-p. The maximum peak comes from C3-p which goes on decreasing with fluorine substitution. These energy states also shift towards the Fermi level with F substitution which results in shrinkage and direct band gap. The top of the valence band is contributed by hybridized states of O1-p, O2-p, N-p and C2-p. In the conduction band, the probable empty energy states for electronic transition are dominated by C1-p, O1-p and O2-p states.

5. Optical Properties

Optical properties provide information about the internal character of the material. It shows the optical response of the material to electromagnetic radiations. To

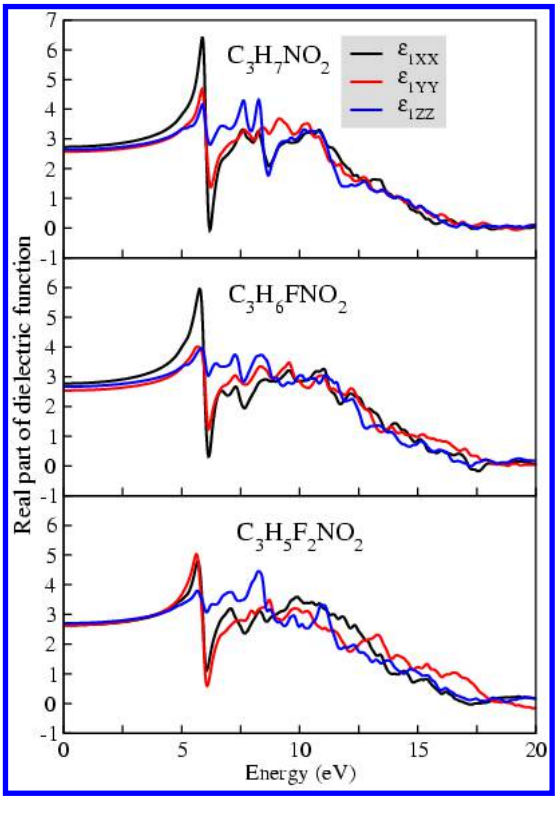


Fig. 5. (Color online) Real parts of the dielectric functions of L-alanine ($C_3H_7NO_2$), monofluoroalanine ($C_3H_6FNO_2$) and difluoroalanine ($C_3H_5F_2NO_2$).

identify the optoelectronic behaviors of L-alanine, $C_3H_6FNO_2$ and $C_3H_5F_2NO_2$ for various technological devices, frequency-dependent optical parameters like dielectric functions, refractive indices, reflectivities and energy loss functions are calculated.

The dielectric function $\varepsilon(\omega)$ of a material depends on the electronic band structure and its exploration by optical spectroscopy is a powerful method in the determination of the overall optical behavior of a compound.[26] It is the sum of the real part ($\varepsilon_1(\omega)$) and the imaginary part ($\varepsilon_2(\omega)$). The real part of the dielectric function tells about polarization and the ability of a material to allow electromagnetic radiations and is presented in Fig. 5 for the three compounds. It is clear from the figure that the values of static dielectric functions ε_0 (at zero frequency limit) of 2.5 are almost the same for all the three compounds. There is a slight increase in these values when F is substituted by H. The real part of the dielectric function increases with the increase in energy and reaches to the maximum at 6 eV, beyond this energy it gradually decreases and reaches below unity after 15 eV. The peak points are at 5, 4.8 and 4.7 eV for L-alanine, $C_3H_6FNO_2$ and $C_3H_5F_2NO_2$, respectively. They are closely related to their band gaps. From the plot, it is obvious that at low energies the compounds are transparent till 5 eV, but above 5 eV

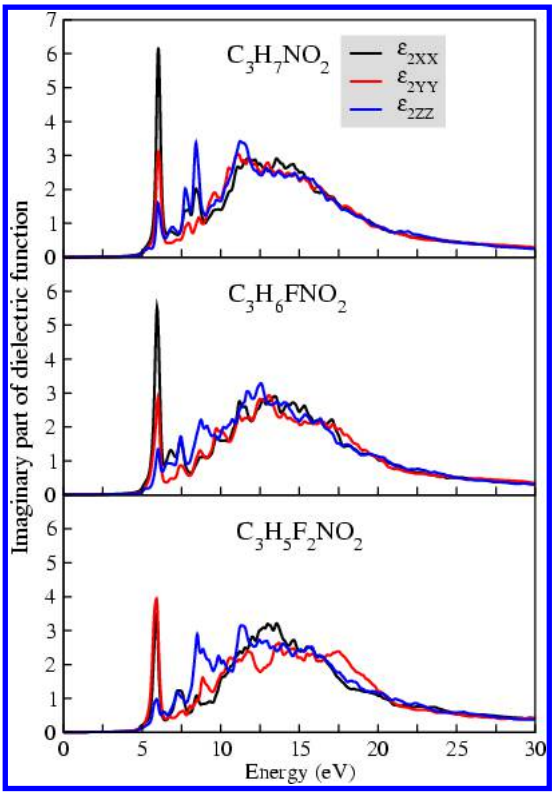


Fig. 6. (Color online) Imaginary parts of the dielectric functions of L-alanine ($C_3H_7NO_2$), monofluoroalanine ($C_3H_6FNO_2$) and difluoroalanine ($C_3H_5F_2NO_2$).

energies the compounds strongly respond to light. This polarization is strong till 5.8 eV, then decreases with small fluctuations and beyond 15 eV there is a minimum response.

The calculated imaginary parts of the dielectric functions for alanine, $C_3H_6FNO_2$ and $C_3H_5F_2NO_2$ in the energy range 0–30 eV are shown in Fig. 6. The onsets of the spectra are at 4.96, 4.70 and 4.56 eV for alanine, $C_3H_6FNO_2$ and $C_3H_5F_2NO_2$, respectively. These points are the measures of the optical gaps of the corresponding materials. The absorption of a material can be described from the imaginary part of the dielectric function plot. The maximum absorption occurred in the ultraviolet (UV) region, i.e., sensitive to UV radiation, so their possible applications will be in optoelectronic devices such as photocells, temperature sensor, optical waveguide and photovoltaic cells.[27,9]

The frequency-dependent refractive index is one of the key parameters for the optical description of dielectric materials. The calculated refractive indices for $C_3H_7NO_2$, $C_3H_6FNO_2$ and $C_3H_5F_2NO_2$ in the energy ranges 0–20 eV are plotted in Fig. 7. The figure reveals that at zero frequency limits, the refractive indices slightly increase with the substitution of F and remain constant up to 4.9 eV for all

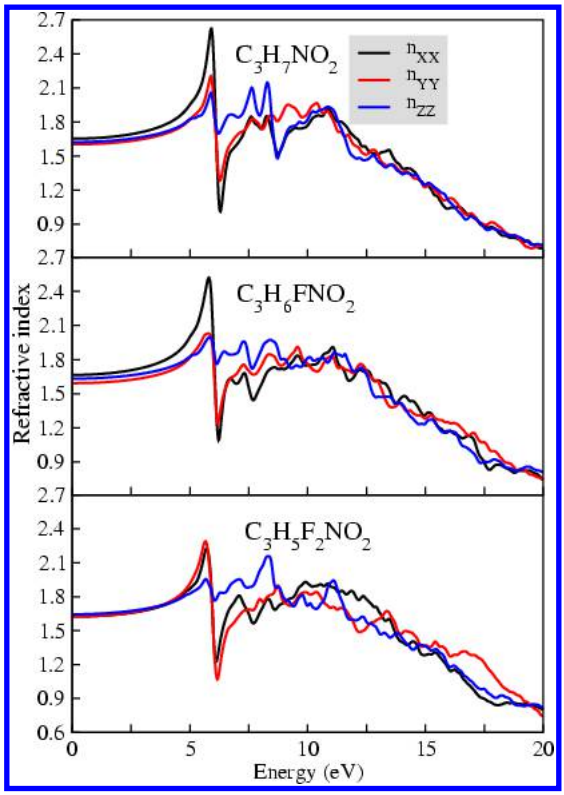


Fig. 7. (Color online) Refractive indices of L-alanine ($C_3H_7NO_2$), monoflouroalanine ($C_3H_6FNO_2$) and diflouroalanine ($C_3H_5F_2NO_2$).

the three compounds. They reach to maximum values at 5.4 eV, then they decline and remain constant till 12 eV. The maximum peaks of the refractive indices are due the first transition of electron from the valence band to conduction band, which is a direct transition. There is an inverse relation between the zero frequency limit of the refractive index and band gap of a semiconductor, consequently, wider band gap semiconductors have lower refractive indices. Beyond 12 eV, the refractive index becomes less than unity because the materials can no longer act as transparent ones at higher energies and their refractive indices drops below unity, where they absorb or reflect high energy photons. The wider band gap of L-alanine makes it transparent up to 5 eV. However, by substituting fluorine by hydrogen the refractive index decreases but its width increases.

Electron energy loss spectroscopy (EELS) is used for the investigation of different aspects of materials, for example, the number and type of atoms being struck by the beam and the elastically scattered and nonscattered electrons. Energy loss functions for the compounds of L-alanine, monofluoroalanine and difluoroalanine are shown in Fig. 8. This shows that at low energies no energy losses occur and the higher energies outside the transparency region provoke polarization which causes

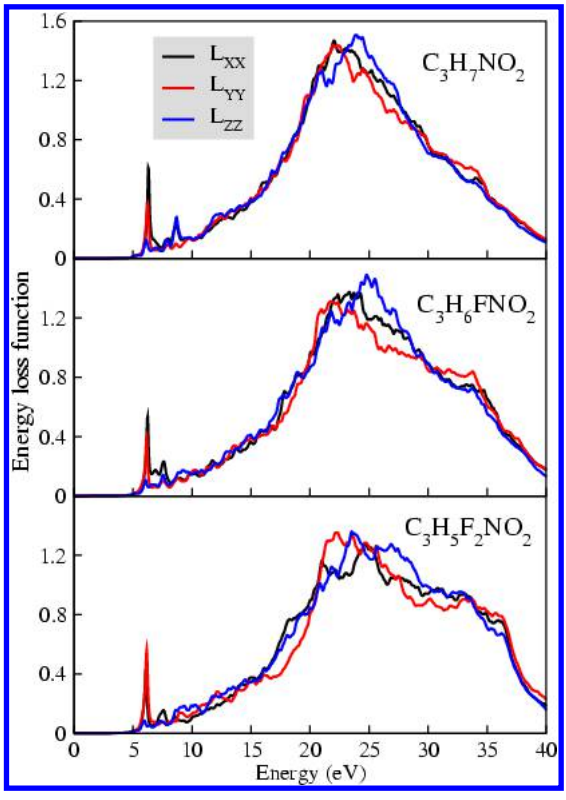


Fig. 8. (Color online) Energy loss functions of L-alanine ($C_3H_7NO_2$), monofluoroalanine ($C_3H_6FNO_2$) and difluoroalanine ($C_3H_5F_2NO_2$).

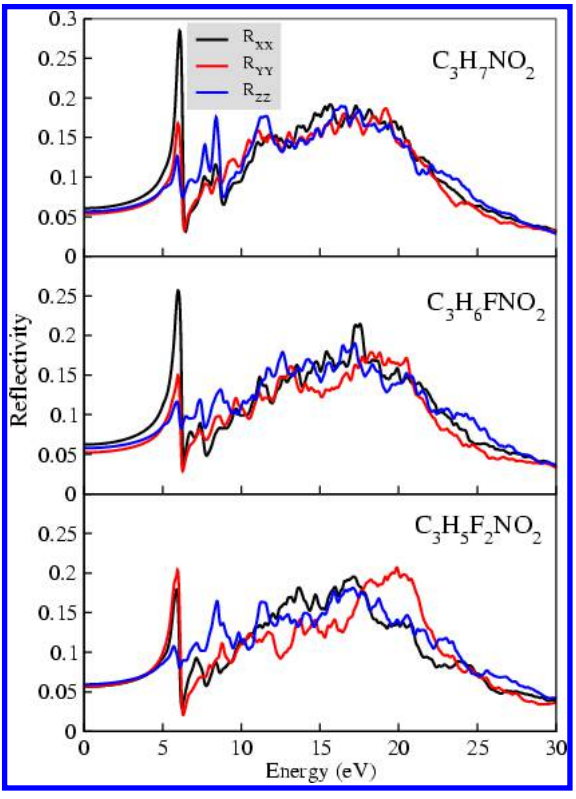


Fig. 9. (Color online) Reflectivities of L-alanine ($C_3H_7NO_2$), monoflouroalanine ($C_3H_6FNO_2$) and diflouroalanine ($C_3H_5F_2NO_2$).

scattering with an associated increase in the propagation loss. With increasing energies, energy loss function increases and reaches to the maximum at 25 eV. This corresponds to plasma resonance and the corresponding frequency is called plasma frequency, above which the material exhibits metallic behavior whereas below it the material shows dielectric properties.

Incident photon-dependent optical reflectivity is the measure of reflection of incident light by the material. The reflectivities of the three compounds, namely L-alanine, monofluoroalanine and difluoroalanine, are presented in Fig. 9. It is clear from the plots that the reflectivities of the compounds at low energies are low, i.e., 0.06, but abruptly increase at 4.3 eV. At this energy, the reflectivities are 0.27 for alanine, 0.25 for monofluoro substituted alanine and 0.21 for difluoro substituted alanine.

6. Conclusion

In summary, the structural and optoelectronic properties of L-alanine, monofluoroalanine and difluoroalanine are investigated using FP-LAPW method. The struc-

tural parameters are consistent with experimentally and theoretically reported results. The bond nature in these compounds is covalent because the electronic density is distributed over all the atoms of the molecules. The L-alanine is an indirect band gap insulator and optically inactive, it is transformed into optically active materials by substituting fluorine by hydrogen. The critical points in the imaginary part of the dielectric function confirm the band gaps. Optical properties reveal that maximum absorption of these compounds occurs in UV region. They can be efficiently used as optoelectronic materials for UV applications.

References

1. D. L. Nelson and M. M. Cox, *Lehninger Principles of Biochemistry*, 3rd edn. (Butterworth Publishing, New York, 2000).
2. I. Wagner and H. Musso, *Angew. Chem, Int. Ed. Engl.* **22**, 816 (1983).
3. A. H. Reshak *et al.*, *J. Mater. Chem.* **21**, 17219 (2011).
4. P. P. Kumar, *Arch. Appl. Sci. Res.* **3**, 290 (2011).
5. H. R. Sreepad, *Int. J. Res. Pharm. Biomed. Sci.* **3**, 797 (2012).
6. E. C. Kendall and B. F. McKenzie, *Org. Synth.* **1**, 21 (1929).
7. J. D. Barnal, *Z. Kristallogr.* **78**, 363 (1931).
8. J. P. Greenstein and M. Winitz, *The Chemistry of the Amino Acids*, Vol. 3 (R. E. Krieger, Malabar, 1984), pp. 1819–1840.
9. Z. Tylczynski, A. Sterczynska and M. Wiesner, *J. Phys., Condens. Matter.* **23**, 355901 (2011).
10. A. H. Reshak *et al.*, *J. Mater. Sci., Mater. Electron.* **23**, 1922 (2012).
11. R. J. Mani *et al.*, *Int. J. Adv. Sci. Tech. Res.* **3**, 162 (2013).
12. Z. P. Zagorski and K. Sehested, *J. Radioanal. Nucl. Chem.* **232**, 139 (1998).
13. S. Olsson *et al.*, *Phys. Med. Biol.* **47**, 1333 (2002).
14. M. Varadhalakshmi, S. Muruganand and S. Palaniswamy, *Int. J. Res. Pharm. Biomed. Sci.* **3**, 1 (2012).
15. R. J. Mani and P. Selvarajan, *Indian J. Appl. Res.* **3**, 446 (2013).
16. I. Degtyarenko *et al.*, *J. Comput. Theor. Nanosci.* **5**, 277 (2007).
17. P. Blaha *et al.*, WIEN2k: An augmented plane wave plus local orbitals program for calculating crystal properties, University of Technology, Vienna, Austria (2001).
18. F. Tran and P. Blaha, *Phys. Rev. Lett.* **102**, 226401 (2009).
19. W. Q. Wang, *Surf. Sci.* **512**, 379 (2002).
20. I. Khan *et al.*, *Comput. Mater. Sci.* **77**, 145 (2013).
21. H. R. Sreepad *et al.*, *AIP Conf. Proc.* **1512**, 836 (2013).
22. Z. Zheng and W. Fan, *J. Biol. Phys.* **38**, 405 (2012).
23. E. Pauwels *et al.*, *Phys. Chem. Chem. Phys.* **12**, 8733 (2010).
24. I. Nilsson, A. E. Johnson and G. V. Heijne, *J. Biol. Chem.* **278**, 29389 (2003).
25. M. Z. S. Flores *et al.*, *Phys. Rev. B* **77**, 115104 (2008).
26. I. Khan *et al.*, *Physica B* **406**, 2509 (2011).
27. F. Akhtar and J. Podder, *Res. J. Phys.* **6**, 31 (2012).