Investigation of chemical effect on the absorption parameters for some selected indium complex at 59.54 keV photon energy

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Abstract. In this work, the mass attenuation coefficients, molecular, atomic and electronic cross sections, effective atomic numbers and electron densities of some selected indium complexes such as $C_5H_{10}InNO_9$, $C_3H_6InNO_9$ and $C_9H_{10}InNO_9$, were determined with experimentally and theoretically using transmission geometry at 59.54 keV photon energy which emitted from ^{241}Am annular source. The results were compared with the theoretical calculations which obtained from the WinXCOM program. Also, the results were interpreted based on some chemical parameters such as energy gap, ionization energy, electron affinity, hardness, chemical potential, electronegativity and global electrophilicity values of malonate, 2,2 dimethylmalonate and phenylmalonate which were calculated using the density functional theory (DFT/B3LYP).

1. Introduction

Indium is a soft and silvery metal. It is an important part of corrosion resistant mirror surface, solar panels, nuclear reactors and touch screens. The mass attenuation coefficient, molecular, atomic and electronic cross sections, effective atomic number and electron density are the basic quantities required in determining the penetration of X-ray or gamma photons in a material. These parameters are used in X-ray fluorescence surface chemical analysis, radiation physics, dosimetric computations for health physics, elemental analysis, basic studies of nuclear physics, etc. In composite materials such as soil, plastic, complex, alloy, the atomic number cannot be represented uniquely across the entire energy region, as in the case of elements, by a single number. This number is defined as effective atomic number in composite materials. The electron density is defined as the numbers of electrons per unit mass.

There are several studies in the literature about the mass attenuation coefficients, effective atomic numbers and electron densities [1-9]. İçelli et al [1] determined the molecular, atomic, electronic cross sections and effective atomic numbers for some boron compounds and the trommel sieve waste using an extremely narrow-collimated-beam transmission geometry in the energy range 15.74-40.93 keV. The mass attenuation coefficients, effective atomic numbers and electron densities for Cd, Se, Te in elemental state and semiconductor CdSe, CdTe were estimated using an Ultra-LEGe detector at different energies from 9.7 to 87.3 keV by Cevik et al. [2]. Kaewkhao et al. [3] obtained the mass attenuation coefficients, total interaction cross sections, effective atomic numbers, effective electron

densities and photon mean free paths of the Cu/Zn alloy at 356, 511, 662, 835 and 1275 keV energies using a NaI(Tl) scintillation detector. The effective atomic numbers and electron densities were determined from the experimental values of mass attenuation coefficients for some natural minerals at 22.1, 25.0, 59.5 and 88.0 keV energies using a Si(Li) detector system by Han et al [4]. Sharma et al. [5] calculated the effective atomic numbers by two different methods such as ratio of atomic to electron cross section and logarithmic interpolation of molecular cross section for different chemical compositions of calcium-strontium-borate glasses in the energy range from 1 keV to 100 GeV. Sidhu et al. [6] obtained the total mass attenuation coefficients, total photon interaction cross sections, effective atomic numbers and electron densities for some dosimetric compounds using transmission geometry at 59.54 keV photon energy. To understand of interaction of Xray photons with bacteriorhodopsin, the mass attenuation coefficients, effective atomic numbers and electron densities of bacteriorhodopsin and its comprising amino acids for photon energies 1 keV to 100 GeV were calculated by Ahmadi et al. [7]. Akça and Erzeneoğlu [8] estimated the mass attenuation coefficients, molecular, atomic, and electronic cross sections, effective atomic numbers and electron densities for compounds of biomedically important some elements such as Na, Mg, Al, Ca and Fe at 59.5 keV energy using a Si(Li) detector and a ^{241}Am radioactive source. Akman et al. [9] determined the effective atomic numbers and electron densities from the total mass attenuation coefficients for some selected samarium compounds in the energy range from 36.847 up to 57.142 keV using the transmission geometry. Akman et al. [2016] determined the K shell absorption jump ratios, jump factors, effective atomic numbers and electron densities for some selected gadolinium compounds and the results were interpreted according to some chemical parameters.

In this work, the mass attenuation coefficients, molecular, atomic and electronic cross sections, effective atomic numbers and electron densities of some selected indium complexes such as $C_5H_{10}InNO_9$, $C_3H_6InNO_9$ and $C_9H_{10}InNO_9$, were estimated with experimentally and theoretically using transmission geometry at 59.54 keV photon energy. The results were compared with the theoretical calculations which obtained from the WinXCOM program. Also, the results were interpreted based on some chemical parameters such as energy gap, ionization energy, electron affinity, hardness, chemical potential, electronegativity and global electrophilicity values of malonate, 2,2 dimethylmalonate and phenylmalonate which were calculated using the density functional theory (DFT/B3LYP).

2. Experimental process and data analysis

The experimental set-up used for determining the mass attenuation coefficients, atomic, and molecular cross sections effective atomic numbers and electron densities is shown in Fig. 1.
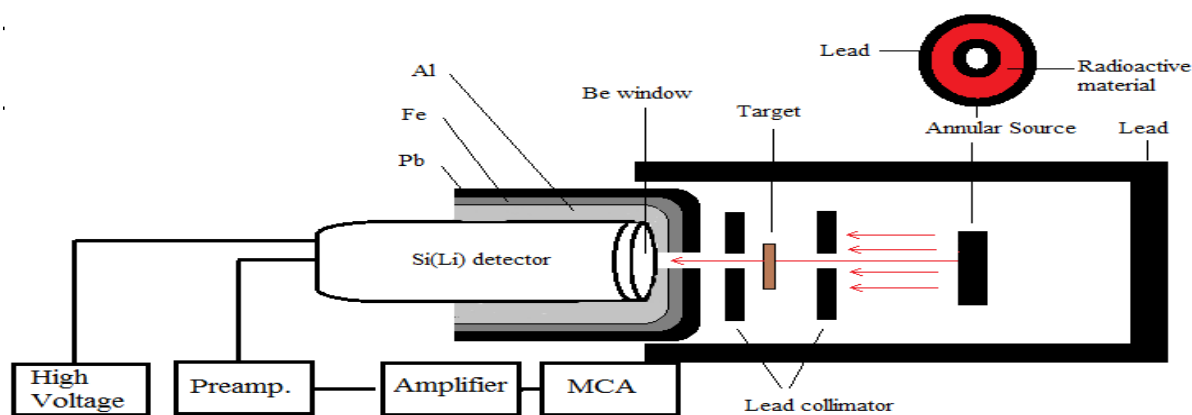
Figure 1. The experimental set-up

The samples were irradiated by 59.54 keV photon energy which emitted from 100 mCi annular [241]Am radioactive source. The unattenuated (I_0) and attenuated (I) intensities counted with a Si(Li) detector having 160 eV resolution at 5.9 keV, active area 12.5 mm^2, sensitive depth 5 mm and Be window thickness 8 μm with coupled to 2048 multi-channel analyzer. The detector placed within the graded shield made from Pb, Fe and Al to filter of 26.4 keV energy coming from [241]Am source and Np characteristic L X-rays. The detector energy calibration was done in the range 0 to 88 keV using standard test sources. The selected indium complexes such as $C_5H_{10}InNO_9$, $C_3H_6InNO_9$ and $C_9H_{10}InNO_9$ and pure In element were used as samples. The details of the preparation of samples were given in our earlier report [10]. The live time was selected as 1800 s for each sample. The areas under the attenuated and unattenuated photo-peak were estimated using Microcal Origin 7.5 demo software program. The net peak areas of each sample were determined after the background subtraction. The least square fit method with a Multi-Gaussian function was used to obtain the net peak area. A typical spectrum of $C_5H_{10}InNO_9$ sample is given in Fig. 2.
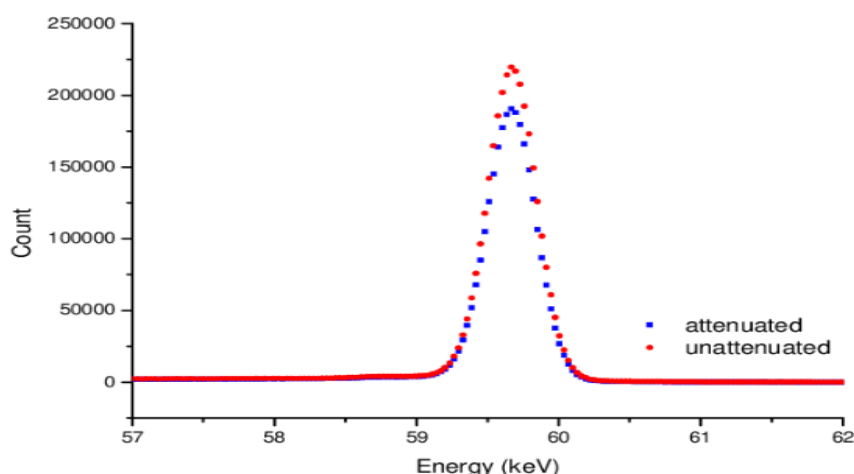

Figure 2. A typical spectrum of $C_5H_{10}InNO_9$

The energy gap, ionization energy, electron affinity, hardness, chemical potential, electronegativity and global electrophilicity parameters for malonate, 2,2 dimethylmalonate and phenylmalonate ions were calculated with DFT/B3LYP method using 631G+(d, p) basis set with the aid of Windows version of the GAUSSIAN 09 package program [11] and Gaussview molecular visualization program [12]. The calculated parameters for the present ions are listed in Table 1.

**Table 1.** Some parameters for ions obtained with DFT/B3LYP method using 631G+(d, p) basis set

DFT/B3LYP/631G+(d, p)			
Parameters (eV)	Malonate	2,2 dimethylmalonate	Phenylmalonate
Energy Gap (ΔE)	4.67	3.88	2.89
Ionization energy (I)	-2.66	-2.39	-1.94
Electron affinity (A)	-7.34	-6.28	-4.83
Hardness(η)	2.34	1.94	1.44
Chemical potential (μ)	5.00	4.33	3.38
Electronegativity (χ)	-5.00	-4.33	-3.38
Global electrophilicity (ω)	5.34	4.83	3.95

The frontier molecular orbitals and electrostatic potential surfaces (ESP) for malonate, 2,2 dimethylmalonate and phenylmalonate ions are given in Figs. 3-4, respectively.
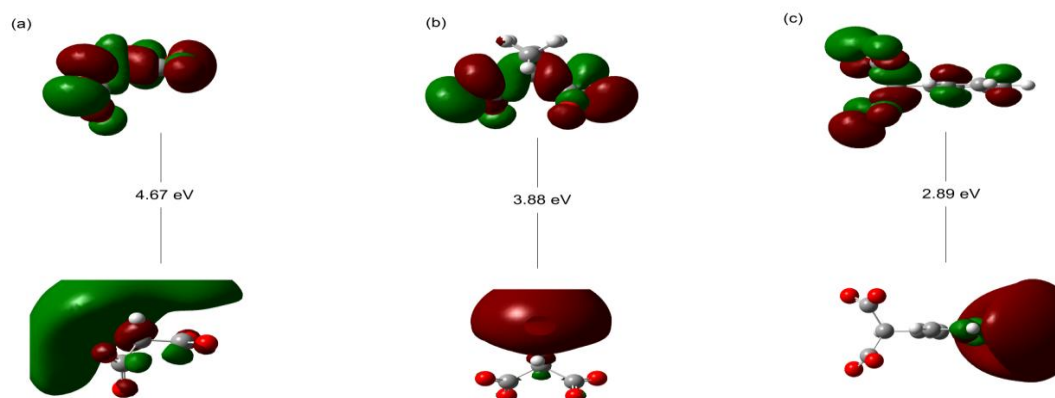
Figure 3. Frontier molecular orbitals for (a) malonate (b) 2,2 dimethylmalonate (c) phenylmalonate ions

The ESP was computed at B3LYP/631G+(d, p) by means of the optimized geometry for prediction of electron poor region (nucleophilic) and electron rich region (electrophilic). As seen from Fig. 4, the negative electrostatic potential is around the oxygen atoms which is seen as reddish blob, namely, the ion can be connected to the central atom from this points. The energy values of HOMO and LUMO and their energy gap reflect the chemical activity of the molecules. A small energy gap between HOMO and LUMO means low kinetic stability, more polarizable and high chemical reactivity of the molecule. The ionization energy and electron affinity can be expressed using HOMO and LUMO orbital energies (I=-EHOMO and A=-ELUMO). The global electrophilicity is the power of a ligand (w=μ2/2η), where η is the stability (η=(-EHOMO+ELUMO)/2)) and μ is the chemical potential (μ=1/2(EHOMO+ELUMO).
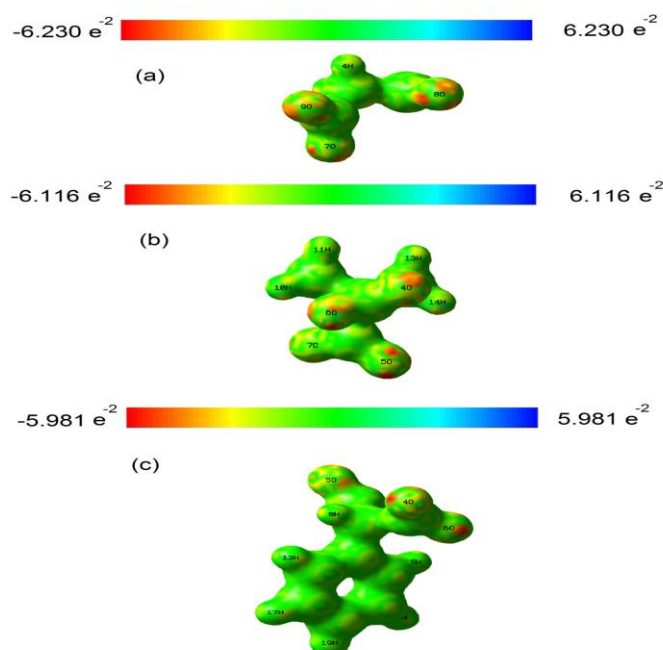
Figure 4. Electrostatic Potential (ESP) for (a) malonate (b) 2,2 dimethylmalonate (c) phenylmalonate ions

To obtain the mass attenuation coefficient for the present complexes, the following equation is used,

$$\mu/\rho = -\frac{1}{\rho x} ln\left(\frac{I}{I_0}\right) \tag{1}$$

where, μ/ρ is the mass attenuation coefficient, I_0 and I are the unattenuated and attenuated intensities and ρx is the mass per unit area of the complex and determined by,

$$\rho x = \frac{m}{\pi r^2} \tag{2}$$

here, r is the radius and m is the mass of the complex. For any compound, alloy, mixture or complex, the mass attenuation coefficient is determined by,

$$\left(\mu/\rho\right)_{complex} = \sum W_i(\mu/\rho)_i \tag{3}$$

in the equation, $(\mu/\rho)_{complex}$ is the mass attenuation coefficient of complex, $(\mu/\rho)_i$ is the mass attenuation coefficient of i.th constituent element in a complex and W_i is the weight fraction and given by,

$$W_i = \frac{a_i A_i}{\sum_j a_j A_j} \tag{4}$$

where, a_i is the number of atoms of i.th constituent element and A_i is the atomic weight of i.th element in the complex. The total molecular cross section (cm^2/molecule) can be estimated using the following equation,

$$\sigma_{t,m} = \frac{1}{N}\left(\mu/\rho\right)_{complex} \sum_i (n_i A_i) \tag{5}$$

here, n_i and A_i are the number of the atoms and the atomic weight of the i.th element in a complex and N is the Avogadro number. The total atomic cross section (cm^2/atom) can be obtained simply using the molecular cross section,

$$\sigma_{t,a} = \sigma_{t,m} \frac{1}{\sum_i n_i} \tag{6}$$

The total electronic cross section (cm^2/electron) is calculated theoretically for elements from the following equation,

$$\sigma_{t,e} = \frac{1}{N} \sum_i \frac{f_i A_i}{Z_i}\left(\mu/\rho\right)_i \tag{7}$$

in the equation, f_i is the fractional abundance of the i.th constituent element with respect to total number of atoms and Z_i is the atomic number.

From the values of atomic and electronic cross sections, the effective atomic number can be obtained semi-empirically using the following equation,

$$Z_{eff} = \frac{\sigma_{t,a}}{\sigma_{t,e}} \tag{8}$$

namely, the effective atomic number can be determined from the ratio of the atomic to electronic cross section. Lastly, the effective electron density (electrons/g) is estimated with the help of the effective atomic numbers,

$$N_E = \frac{Z_{eff}}{A_{tot}}(Nn_{tot}) \tag{9}$$

here, n_{tot} is the total number of atoms and A_{tot} is the total atomic weight of complex.

3. Results and discussion

The mass attenuation coefficients (μ/ρ), molecular ($\sigma_{t,m}$), atomic ($\sigma_{t,a}$) and electronic ($\sigma_{t,e}$) cross sections, effective atomic numbers (Z_{eff}) and electron densities (N_E) for some selected indium complexes at 59.54 keV are listed in Table 2 along with the theoretical calculated which is used WinXCOM program [13]. This program presents the attenuation coefficients of any substance as the

sum of appropriately weighted contributions from the individual atoms. It is clearly seen from Table 2 that the μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, $\sigma_{t,e}$, Z_{eff} and N_E values depend on the number of elements within complex. The maximum uncertainty in the determination of μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, Z_{eff} and N_E values is estimated as %1.61. this uncertainty is attributed to systematic uncertainties, I_0 and I intensities uncertainties and mass per unit area measurements.

Table 2. The μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, $\sigma_{t,e}$, Z_{eff} and N_E values at 59.54 keV

Sample	μ/ρ		$\sigma_{t,m} \times 10^{23}$	
	Experimental	Theoretical	Experimental	Theoretical
In	6.222±0.063	6.439	118.626±1.196	122.76
$C_5H_{10}InNO_9$	2.366±0.032	2.284	134.741±1.821	130.06
$C_3H_6InNO_9$	2.431±0.039	2.470	127.093±2.041	129.14
$C_9H_{10}InNO_9$	1.948±0.021	2.025	126.482±1.369	131.46

Table 2. continued.

$\sigma_{t,a} \times 10^{24}$		$\sigma_{t,e} \times 10^{25}$	Z_{eff}		$N_E \times 10^{-23}$	
Experimental	Theoretical	Theoretical	Experimental	Theoretical	Experimental	Theoretical
1186.264±11.959	1227.59	250.53	47.350±0.477	49.00	5.819±0.059	6.02
51.824±0.701	50.02	15.30	33.882±0.458	32.71	74.720±1.010	72.13
63.546±1.020	64.57	18.21	34.903±0.560	35.47	59.208±0.951	60.16
42.161±0.456	43.82	14.03	30.040±0.325	31.22	76.439±0.827	79.45

According to the Table 2, the μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, Z_{eff} and N_E values depend on the total atomic weight. The maximum differences between the measured and theoretical values of of μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, Z_{eff} and N_E are found to be 3.80%. From these differences, we can sat taht the measured parameters are in good agreement with the theoretically calculated ones within the experimental uncertainties.

As seen from Table 1 and 2, the μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, Z_{eff} and N_E values changed with energy gap, ionization energy, electron affinity, hardness, chemical potential, electronegativity and global electrophilicity. According to the Table 1 and 2, it is possible to say that the μ/ρ, $\sigma_{t,a}$, and Z_{eff} values increase with increasing energy gap, hardness, chemical potential and global electrophilicity values and decreasing ionization energy, electron affinity and electronegativity values. Also, the N_E values increase with decreasing energy gap, hardness, chemical potential and global electrophilicity values and increasing ionization energy, electron affinity and electronegativity values. The same effects are shown in the theoretical values. To the best of the authors, the μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, Z_{eff} and N_E values have been discussed based on these chemical parameters for the first time in the present work.

It can be concluded that the μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, Z_{eff} and N_E values depend on the chemical environment of complex and these values depend on the total atomic weight and numbers of elements within complex. The measured values change with chemical parameters such as energy gap, ionization energy, electron affinity, hardness, chemical potential, electronegativity and global electrophilicity. It is believed that the measured μ/ρ, $\sigma_{t,m}$, $\sigma_{t,a}$, Z_{eff} and N_E values are sufficiently reliable for In complexes. This method should be used for the other complexes or compounds at different energies.

Acknowledgements

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