

Raman spectroscopy of 'Bisphenol A'

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ABSTRACT

Raman spectra (95–3000 cm^{-1}) of 'Bisphenol A' are presented. Absorption peaks have been assigned by Density Functional Theory (DFT) with B3LYP 6–311++G (3df, 3pd) and wB97XD 6–311++G (3df, 3pd). B3LYP 6–311++G (3df, 3pd) gives frequencies which are nearer to experimental frequencies than wB97XD 6–311++G (3df, 3pd) which involves empirical dispersion. Scale factor for wB97XD 6–311++G (3df, 3pd) is found out to be 0.95008 by least squares fit.

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1. Introduction

'Bisphenol A' (BPA) is extensively used agent in plastic industry. Epoxy resins from BPA are being used as coating for the interior walls of many food and beverage cans as well as in making thermal paper which is used in sales receipts. BPA has been associated to a number of highly dangerous and terrible adverse health effects and may be a possible genotoxic, carcinogen, endocrine disruptor and neurotoxin according to World Health Organization [1]. It's being banned in using baby bottles and food packaging which is arising a hot debate on this chemical. BPA molecule is shown in Fig. 1. BPA has been investigated by Terahertz and Fourier Transform Infrared spectroscopy, however, the main discussion was focused on C–H and O–H stretching interactions in the region above 2500 cm^{-1} [2]. BPA has also been widely studied by different spectroscopic techniques like ultraviolet (UV), Raman difference and Spectrofluorimetry but major emphasis was either on the detection of BPA or shifts in the Raman frequency when BPA undergo structural changes [3–5]. Similarly, a nanoprobe based on surface-enhanced Raman scattering has been presented to measure the quantity of BPA in human blood [6]. Couples of highly sensitive sensors to

detect BPA have been reported out of which some are based on surface enhanced Raman scattering [7–10]. Spectroscopy of some other probable carcinogens has also been done [11].

2. Methods

BPA, CAS No (80–5–7) is bought from "Sinopharm Chemical Reagent Co. Ltd" [12] and is ground to very fine powder. Our Raman spectroscope RamanStation 400F [13], from PerkinElmer is used to take the measurements at excitation source of near infrared 785 nm laser and the same frequency is used in DFT Raman calculations. Experimental Raman spectra are measured under atmospheric conditions because water and CO_2 vapors have weak scattering and hence purging is not needed. DFT calculations are carried out in Gaussian 09 package [14] optimized to minimum and two Ground State methods B3LYP and wB97XD along with 6-311G basis set [15] together with (3df, 3pd) and ++ diffuse functions [16]. Two different configurations (DFT) B3LYP 6–311++G (3df, 3pd) and (DFT) wB97XD 6–311++G (3df, 3pd) have been used. The experimental Raman spectra are then compared with the calculated vibrational spectra and absorption peaks are assigned to relevant molecular vibrations. Potential energy distributions (PEDs) analysis is done by MOLVIB [17,18].

3. Results and discussion

B3LYP is reasonably in good agreement with the experimental values especially after scaling with the scale factor 0.9679

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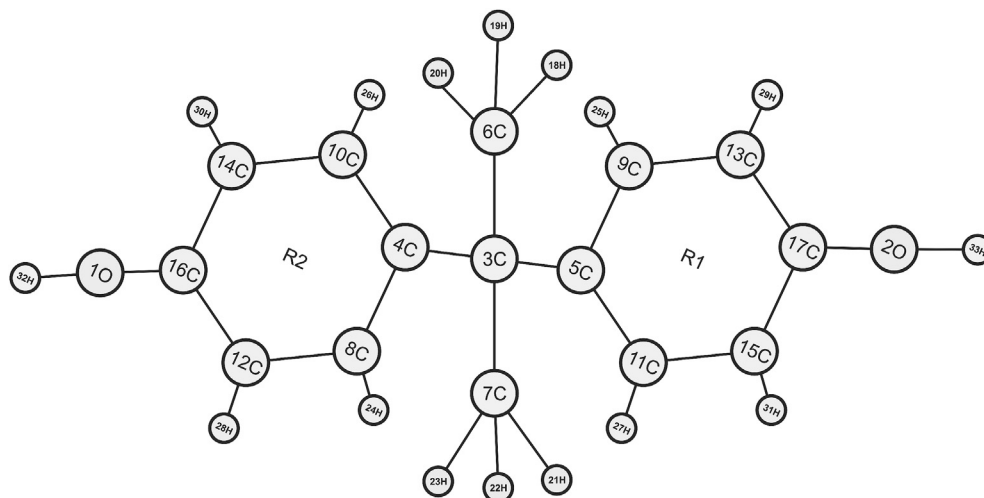


Fig. 1. 'Bisphenol A' (BPA) molecule.

calculated by Andersson and Uvdal [19] for high frequency vibrations. wB97XD [20] even with the inclusion of empirical dispersion, is deviating larger from experimental values than B3LYP. The scale factor for wB97XD is calculated by least squares fit with a value of 0.95008 which brings most of the calculated values nearer to the experimental as shown in Table 1 but B3LYP is still in better agreement for majority. Scale factors are calculated to correct calculated vibrational frequencies which differ systematically from experimental frequencies. A database of such scale factors is maintained for such purpose however, not all scale factors for particular methods are available [21].

Fig. 2 shows the spectra of 'Bisphenol A' from 200 to 600 cm^{-1} . It's clear from Table 1 that motions in this region are bit complex and dominated by torsional and out of plane bending movements. Experimental peak at 345 cm^{-1} is assigned to the torsion of CO bond which is resulted mainly because of the large motion of hydrogen atom connected to oxygen. There are only two oxygen atoms in 'Bisphenol A' molecule which are connected individually to both the rings and to the other side with hydrogen atoms as shown in the Fig. 1. This produces torsion in both CO bonds whose frequencies are in close proximity to each other and thus hard to distinguish. So, the experimental peak 245 cm^{-1} is assigned to two simulated frequencies because none of the other peak is visible in the experimental spectra. It is also noticeable that at these frequencies, the simulated B3LYP values fairly match with experimental values without any scaling and those of wB97XD are bit higher than experimental values and well distinguishable. We can observe from Table 1 that at low frequencies, raw DFT values are close to experimental values but scaled values are deviating larger. It is because at low frequencies, scale factors are calculated by least square fit of inverse of vibrational frequencies [2]. However, we don't need to calculate scale factors for low frequencies in our case because DFT values are already near to the experimental values. Alternatively, we can also use here a scale factor of 1.0100 for low frequency vibrations as reported by Andersson and Uvdal [19] which can only be applied to B3LYP values.

Fig. 3 shows spectra of 'Bisphenol A' in the range 600–1400 cm^{-1} . Experimental peak 641 cm^{-1} is once again assigned to two molecular vibrations, 658 and 659 cm^{-1} of B3LYP which are resulting from the change of bond angle of CCC in ring 2 and ring 1 respectively. It can also be seen here that the assignments are based purely on the relative intensities and hence 648 cm^{-1} is assigned to 646 cm^{-1} (raw) of B3LYP. 735 cm^{-1}

(experimental) is mainly due to torsions in both the rings together and partially by CO and CC out of plane bending. It is therefore assigned to 747 cm^{-1} (B3LYP) and corresponding wB97XD value of 762 cm^{-1} . 819 cm^{-1} is predominantly due to CH out of plane bending (95% PED) and thus assigned to both 825 and 826 cm^{-1} (B3LYP) values because of their close proximity. It must be noted that this isn't the vibration of a single CH out of plane bending. It's the result of cumulative motion (out of plane bending) of Carbon atoms in both the rings connected directly to hydrogen atoms. As 'Bisphenol A' is slightly larger molecule with 33 atoms, it has 93 (3N-6) modes where 'N' is the number of atoms in the molecule. It causes dense vibrational peaks and makes the assignment difficult. This is the case with 834 cm^{-1} experimental value which is assigned to four DFT values out of which 3 are mainly because of CH out of plane bending and 1 from CO stretching. However, in Fig. 3, only 844 cm^{-1} (B3LYP) and 856 cm^{-1} (wB97XD) are clearly visible and other peaks are hidden under the same curve. 920 and 939 cm^{-1} can be assigned easily to 929 and 943 cm^{-1} (B3LYP) which are dominated by complex CC stretching. In Fig. 3, There seem two peaks around 1000 cm^{-1} in the experimental spectra but their amplitude is too low and thus we skip their assignments. In the next, B3LYP and wB97XD are deviating in the range 1100–1210 cm^{-1} not only in the values but also in the curve shaping. Here, wB97XD presents a clearer picture than B3LYP. So the peaks in this range are assigned on the basis of relative intensities of wB97XD and corresponding B3LYP are also shown. As can be seen clearly in Table 1, the assignment of 1083 and 1112 cm^{-1} to 1102 and 1139 cm^{-1} (B3LYP) respectively and corresponding Potential Energy Distribution (PED) analysis reveals that these modes are largely due to wagging of H atoms which are attached to C atoms. 1181 cm^{-1} is assigned to two DFT vibrational modes which are 1204 and 1206 cm^{-1} (B3LYP) where wB97XD shows almost a single peak but B3LYP shows two clearly distinct peaks as shown in Fig. 2.

Experimental peak of 1234 cm^{-1} is assigned to two DFT peaks (B3LYP) of 1281.7 cm^{-1} and 1281.91 cm^{-1} which are caused mainly by CO stretching and CC stretching in both the rings simultaneously. Similarly, 1259 cm^{-1} experimental peak is also assigned to two B3LYP peaks of 1326 cm^{-1} and 1328 cm^{-1} and main contributions in these vibrational modes come from CC stretching in both the rings whose detail is given in Table 1.

Fig. 4 shows spectra of 'Bisphenol A' in the range 1400–1800 cm^{-1} . Experimental peak of 1441 cm^{-1} in Fig. 4 is

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