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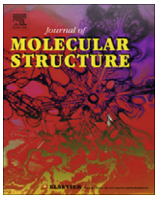

Experimental and theoretical study of vibrational spectra of 3-nitrofluoranthene

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ABSTRACT

The comparative studies of the infrared and Raman spectra of fluoranthene and 3-nitrofluoranthene (3-NF) were made via both FT-IR and density functional theory calculation with a triple ζ Gaussian basis set (B3LYP/6-311 + G(d,p)). The scaled theoretical vibrational frequencies show good agreement to experiment to within $\sim$5 cm^{-1} for frequencies <1800 cm^{-1}. In addition, predictions of the DFT frequencies below 1800 cm^{-1} yielded an overall root mean square (RMS) of ±4.3 and ±27.4 cm^{-1} for fluoranthene and 3-NF, respectively. The vibrational assignments are proposed, with particular emphasis on the nitro group vibrations. This study shows the influence the geometrical distortions of the fluoranthene structure have upon nitro group substitution and provides vibrational spectral data useful for the development of spectroscopy-mutagenicity relationships in nitrated polycyclic aromatic hydrocarbons.

1. Introduction

Nitro-substituted polycyclic aromatic hydrocarbons (NPAHs) are members of a class of environmental contaminants found in airborne particulate matter, fossil fuel combustion products, coal fly ash, cigarette smoke and vehicular emissions and are formed by reactions of polycyclic aromatic hydrocarbons (PAHs) with nitrogen oxides [1–4]. Investigations have shown many NPAHs to be formed by OH-radical-initiated reactions of NO_3^-, NO_2 and N_2O_5 with gas-phase PAHs adsorbed onto particulate matter surfaces [5,6]. As environmental pollutants, their mutagenic, carcinogenic, tumorigenic, teratogenic activities pose significant health threats to humans and animals [2,7–10].

Fluoranthene is one of the most abundant PAHs found in soils and sediments. It is closely associated with coal tars, and may be degraded in some instances by bacteria [11]. The existence of mononitrated fluoranthene isomers: 1-, 2-, 3-, 7-, and 8-nitrofluoranthenes (1-, 2-, 3-, 7-, 8-NF) [12–14] is well known. Since Dewar et al.'s early syntheses of nitro-PAHs [15–17], nitrated fluoranthene isomers have been characterized and quantified in the environment via separation techniques, $^{1}H/^{13}C$ NMR, and UV–vis techniques [12,18]. Biological investigations have further shown mononitrofluoranthenes to exhibit differential mutagenic potencies on cells [12,19,20]. To explain the varied mutagenic/carcinogenic effects, proposals that correlate the nitro group orientation relative to the aromatic moiety and carcinogenic/mutagenic effects have been made [21].

Whereas gas-phase, matrix-assisted isolation and theoretical methods provide infrared (IR) spectroscopic and structural signatures of PAHs, detailed IR spectroscopic data is scarce for many nitro-PAHs. Such data is necessary for developing trace analysis of nitrated PAHs by sensitive vibrational spectroscopic techniques, such as surface enhanced spectroscopies. In the case of mono nitrated fluoranthenes isomers, the significant differences in their mutagenic properties (2-, 3- and 8-, are more toxic than the 1- and 7- isomer) are related to their structure [22]. Thus, correlations between vibrational spectra and biological activities can have predictive powers for toxicity of nitro-PAHs.

While the Raman and IR spectrum of fluoranthene have been made [23], the present study utilizes the B3LYP/6-311 + G(d,p) method. For nitro-PAHs, recent investigations employing both experimental and theoretical methods were utilized to study the IR/Raman spectra of 2-nitrofluorene, 1-nitropyrene, 1-, 3-, and 6-nitrobenzo[a]pyrenes, 1-, and 2-nitronaphthalenes, 6-nitrochrysene, 1- and 2-nitrotriphenylenes, and in some cases normal mode assignments made [10,24–29]. For nitrated fluoranthenes however, only few studies have assigned normal modes, and have largely used group frequency tables. Early studies [30–33] provided the bands of nitrated fluoranthenes, without detailed spectral assignments. Because of the paucity of detailed experimental and theoretical studies of mono nitrated fluoranthenes, the present study was focused on the comprehensive vibrational analysis of the spectra of 3-nitrofluoranthene. The interest in 3-NF in this paper is of particular interest because of its ease of synthesis vis-à-vis other mono nitrated fluoranthenes that require tedious chromatographic separations. The vibrational analysis is based on the experimental FT-IR spectrum, and predicted Raman data. Through

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B3LYP/6-311 + G(d,p)) calculations on fluoranthene and 3-NF, corresponding vibrational frequencies were obtained, and assignments made via normal mode analysis. This information provides insight into the geometrical changes that occur in the fluoranthene structural motif upon substitution of the nitro group, and possible relationships between the structure of 3-NF and its biological activity. The implications and possible correlations between the infrared spectra of 3-NF and its biological activity are also described.

2. Experimental and computational details

Caution: Fluoranthene and 3-nitrofluoranthene are known carcinogens and mutagens. Therefore all necessary safety precautions must be taken in handling them.

2.1. Materials and instrumentation

Fluoranthene (99.8%) and 3-nitrofluoranthene (⩾98%) were purchased from Sigma–Aldrich (Milwaukee, WI, USA) and used without any modification. UV–vis spectra was recorded with a Shimadzu 2501PC spectrophotometer from 200 to 550 nm and confirmed to be in agreement with reported literature [18]. The solid state, mid-infrared spectrum on KBr pellet (99% FT-IR grade, Sigma–Aldrich, 4 cm^{-1} resolution) spectra were acquired from 4000 to 220 cm^{-1} on a Perkin–Elmer model 200 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. 100 scans or more were collected in the transmission mode.

2.2. Theoretical calculations

The density functional theory (DFT) calculations were performed using the Gaussian 03 package [34]. The B3LYP hybrid density functional theory [35,36] was used. The geometries were initially optimized with the 6-31G(d) [37] basis set before re-optimization with the 6-311 + G(d,p) basis set. The B3LYP/6-311 + G(d,p) level of theory has been shown to yield frequencies in better agreement to experimental data. Clarkson and Smith [38] showed the B3LYP/6-311 + G(d,p) level reliable for predicting the fundamental frequencies of nitrobenzene and isopotomers without the need to scale force constants. Further, Andersson and Uvdal showed that the scale factors did not change significantly for basis sets larger than 6-311 + G(d,p) [39]. As a result of including electron correlation DFT methods reliably reproduce geometries [22,28,40–43] and reduce computational costs [44] compared to the more demanding second-order Moller–Plesset (MP2) perturbation methods. Optimized geometries of the molecules were calculated without any geometrical restriction, except those enforced by symmetry**.** Harmonic vibrational frequencies, calculated at the same level of approximation using optimized parameters, were found to be minima on its respective potential energy surfaces as revealed by the lack of imaginary frequencies. The calculated IR and Raman spectra were created from scaled frequencies by applying 1 cm^{-1} step sizes using Gaussian functions. Vibrational assignments of the experimental frequencies in this study are based upon (i) the description of the motions and comparisons of calculated and observed FTIR and FT-Raman, and (ii) visual inspection of the eigenvectors for each mode. GaussView 4 program was used for visual animation and also for the inspection of the normal modes description. While complete optimized structural parameters are available in Ref. [22] for fluoranthene, the present study emphasizes the vibrational modes, and their assignments discussed in Section 3. To complement the infrared frequencies, simulated Raman spectra were performed.

Pulay and co-workers very successfully developed the scaled quantum mechanical (SQM) method for which sets of transferable scaling factors to different types of harmonic force constants in natural internal coordinates can be derived. The SQM method gave significant improvement of the normal modes and improvement on the calculated intensities. However, one should be aware of the possible source of ambiguity introduced by this approach [45]. It has also been demonstrated [45] that the application of two scaling factors, one for vibrations below 1800 cm^{-1} and one above 1800 cm^{-1}, lead to very good results. This procedure was, therefore, applied in this paper. The simple scaling procedure without the need for the use of SQM was demonstrated to give excellent results without the use of internal coordinates [46].

3. Results and discussion

3.1. Molecular and structural properties

In a previous report the structural geometry of fluoranthene [47–51] and its nitrated derivatives (1-, 2-, 3-, 7-, and 8-NF) [22] were calculated using the B3LYP method with the 6-31G* and 6-311 + G(d,p) basis sets. The labeling of atoms in fluoranthene and 3-NF (along with the IUPAC numbering scheme) is shown in Fig. 1. Fluoranthene and nitrobenzene have previously been used to calibrate calculations at both levels of theory. For fluoranthene, the structural parameters were in good agreement with neutron, X-ray and neutron diffraction data [52–55]. In agreement with neutron diffraction data, the shortest bonds in fluoranthene were predicted at C6–C6a, C1–C1a and C6a–C7a, C1a–C10a. In nitrobenzene, the N–O bond distance is 1.2272/1.2234 Å and the calculated value is 1.2245 Å. The selected geometric parameters (bond lengths (C–C, C–N, N–O), bond angles (C–C–C, O–N–O, C–C–N), and C–C–C–C, C–C–N–O dihedral angles) of fluoranthene and 3-NF are presented in Ref. [22].

Calculations predict 3-NF to be non-planar with C–C–N–O dihedral angles of 18.3° and 18.9° [22]. The non-planarity of 3-NF stems from the O12···H15, O13···H16 steric interactions. Because 6-311 + G(d,p) basis set yields structural data in better agreement to available experimental data, all of the subsequent sections are focused on vibrational data derived at the B3LYP/6-311 + G(d,p) level of theory.

3.2. Infrared and Raman spectra

Fluoranthene and 3-NF have 26 and 28 atoms, and display 72 and 78 normal vibrational modes, respectively. With C_{2v} and C_1 point groups, for fluoranthene and 3-NF, respectively, all the normal modes are infrared and Raman active. For a detailed discussion, detailed vibrational frequencies, measured band positions, relative intensities, and spectra are compared in each subsection and comprehensive assignments of fluoranthene and 3-NF are presented in Supplementary Tables S1–2. Although experimental bands for fluoranthene have been reported previously [23,50], we report all bands including new bands and provide detailed assignments of the fundamental absorptions. This also calibrates the B3LYP/6-311 + G(d,p) level of theory.

3.2.1. CH Stretching frequencies (ν(C–H), 3200–2800 cm^{-1} region)

3.2.1.1. Fluoranthene (FL). Fig. 2A depicts the experimental and simulated spectral data compared on the same scale. The scaled frequencies overestimate experimental bands by ~50–80 cm^{-1}. Prominent modes observed at 3076, 3060, 3049 and 3037 cm^{-1} are comparable to peaks obtained via KBr pellet and matrix isolation methods [23,50]. Other bands occurring at 3141, 3097, 3003, 2991, 2968, 2942, 2908, 2890, 2877, and 2832 cm^{-1}, are in agree-