A Computational Study of the Vibrational Spectra of Mono-nitrated Fluoranthenes

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Abstract

(i) Raman and infrared (IR) spectra of mononitrated fluoroanthene (1, 2, 3, 7, and 8-nitrofluoranthene), are important environmental pollutants that induce mutagenic/carcinogenic effects upon mammalian and bacterial cells.

(ii) Their spectra were studied via density functional theory using optimized geometries at the B3LYP/6-311+G(d,p) level of theory.

(iii) The harmonic frequencies below 2000 cm⁻¹ are in good agreement to experiment to < 5 cm⁻¹.

(iv) The ν(υ)(NO₂) frequency shifts are correlated to the observed mutagenic potencies, thus shedding light on their relative reactivity.

(v) The observed differential mutagenic-vibrational correlations, implicate of the ν(NO₂) shifts/biological mutagenic potencies between nitrofluoranthene isomers.

2. Materials and Methods of Study

Methods

1. FT-Raman Spectroscopy
2. FT-Infrared Spectroscopy
3. Density functional theory
   - B3LYP/6-311+G(d,p)

Materials

1. Fluoranthene (99.8%) and 3-nitrofluoranthene (≥ 99%) were purchased from Sigma-Aldrich (Milwaukee, WI, USA).

2. Diffuse reflectance spectra were acquired on a Perkin Elmer Spectrum 100 FTIR spectrometer with a Cal beam splitter.

3. Raman spectra was acquired with a Perkin Elmer Raman Station 400, 785 nm line @50 mW.

3. Results (Fluoranthene: FTIR, Raman and Calc’d)

Results (3-NitroFL)

Results (IR/Raman: 1, 2, 3, 7, and 8-NitroFL)

1. Reason for Study

1. Mono-nitrated PAHs are known carcinogens and mutagens.

2. To predict the harmonic frequencies using the DFT functional B3LYP, and 6-311+G(d,p) basis set.

3. Assign the bands using potential energy distributions (PEDs).

PAHs Studied

Figures A-D: Experimental IR spectrum (black). Figure B: Raman spectrum (red) for Fluoranthene. Figure C: Theoretical IR spectrum of fluoranthene using B3LYP/6-311+G(d,p).

4. Conclusions

1. Vibrational studies show IR/Raman spectroscopy as a powerful analytical technique useful for distinguishing closely related nitrated polyaromatic isomers.

2. These studies are important for future quantitative structure-activity relationships (QSAR) and for predictive assessments of mutagenic potentials of nitro-PAHs.

References


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