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

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Abstract

(i) Raman and infrared (IR) spectra of mononitrated fluoranthenes (1-, 2-, 3-, 7-, and 8-nitrofluoranthenes), 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/P-6-311+G(d,p) level of theory. The harmonic frequencies below 2000 cm⁻¹ are in good agreement to experiment to < 5 cm⁻¹.

(iii) The ν(NO) frequency shifts are correlated to the observed mutagenic potencies, thus shedding light on their relative reactivity. The observed differential mutagenic- vibrational correlations implicate the ν(NO) shifts/biological mutagenic potencies between nitrofluoranthenes isomers.

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

Fluoranthenes

3-nitrofluoranthenes

2. Materials and Methods of Study

Methods
1. FT-Raman Spectroscopy
2. FT-Infrared Spectroscopy
3. Density functional theory - B3LYP/P-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 acquired on a Perkin Elmer Spectrum 100 FTIR spectrometer with a CaF beam splitter.
3. Raman spectra was acquired with a Perkin Elmer Raman Station 400, 785 nm line @850 mW.

3. Results (Fluoranthenes: FTIR, Raman and Calc'd)

Figure A: Experimental IR spectrum (black).
Figure B: Raman spectrum (red) for Fluoranthenes. Figure C: Theoretical IR spectrum of 3-NF using B3LYP/P-6-311+G(d,p).

Comparison of symmetric stretches

<table>
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<th>Nitro</th>
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<th>d310 cm⁻¹</th>
<th>d310 Exp</th>
<th>d310 Raman</th>
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4. Conclusions

1. Vibrational studies show IR/Raman spectroscopy as a powerful analytical technique useful for distinguishing closely related nitro polycondensed aromatics.
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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