Fourier transform infrared and Raman spectra, vibrational assignment and density functional theory calculations of naphthazarin

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Abstract

FT Raman and FTIR spectra of Naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) and its deuterated analogue are recorded. Comparison between the spectra obtained by two techniques, a series of density functional theory (DFT) calculations and the spectral behavior upon deuteration were used for the assignment of the vibrational spectra of this compound. The calculated vibrational frequencies by the B3LYP, B3PW91, G96LYP, G96P86, and MPWLYP density functionals are generally consistent with the observed spectra. Infrared and Raman vibrational transitions predicted by B3LYP/6-311++G** are reported for the titled compound and its deuterated analogous and the assignments are discussed. All experimental and theoretical results support a relatively weak hydrogen bond in naphthazarin (NZ), compared with that in the enol form of normal \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \). The observed \( \nu\text{OH} / \nu\text{OD} \) and \( \gamma\text{OH} / \gamma\text{OD} \) appear at about 3060/2220 and 790/560 cm\(^{-1}\), respectively, which are consistent with the calculated hydrogen bond geometry and proton chemical shift results. Two bands at about 350 and 290 cm\(^{-1}\) are assigned to the \( \text{O} \cdot \cdot \cdot \text{O} \) stretching modes belong to A1 and B2 species, respectively.

Keywords: Naphthazarin; 5,8-Dihydroxy-1,4-naphthoquinone; FTIR; Raman; Vibrational assignment; DFT

1. Introduction

5,8-Dihydroxy-1,4-naphthoquinone, commonly known as naphthazarin (hereafter NZ), is a simple model for an important group of compounds, perylenequinones, alkannin and shikonin. These are biologically active pigments obtainable from natural sources. The biological importance (e.g. antitumor and antiviral activity, wound healing, antimicrobial and antithrombotic properties) of this group of compounds is the main reason for extensive study on the structure and properties of NZ [1–3].

NZ crystallizes in three polymorphic forms, designated A, B, and C. This compound has been extensively studied theoretically [4–6] and experimentally by X-ray and neutron diffraction [7–13], mass spectrometry [14], \( ^{13}\text{C} \) [15–17], \( ^{17}\text{O} \) [18] and proton [19] NMR spectroscopy. The IR and Raman spectra of this compound have been the subject of several