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Normal mode and experimental analysis of TNT Raman spectrum

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ABSTRACT

In this study, a Raman spectrum of TNT was characterized through experiments and simulated using 22 hybrid density functional theory (DFT) methods. Among the different hybrid DFT methods, it was found that the most accurate simulation results of the Raman shift frequency were calculated by the O3LYP method. However, the deviations of the calculated Raman frequencies from the experimental value showed no dependency on the abilities of the DFT methods in recovering the correlation energy. The accuracies of the DFT methods in predicting the Raman bands are probably determined by the numerical grid and convergence criteria for optimizations of each DFT method. It was also decided that the prominent Raman shift 1362 cm^{-1} is mainly caused by symmetric stretching of the 4-nitro groups. Findings of this study can facilitate futuristic development of more effective surface enhanced Raman spectroscopy/scattering (SERS) substrates for explosive characterization and detection.

1. Introduction

2,4,6-Trinitrotulune (TNT) represents one of the most widely used energy materials for various military, industry, and security purposes. In practice, Raman spectroscopy serves as the effective approach for detecting and characterizing TNT and its derivatives based on their characteristic vibrational fingerprints ranging from 200 to 1600 cm^{-1} [1]. Recent advances of the detection technology have led to the development of surface enhanced Raman spectroscopy/scattering (SERS) technology [2]. The enhanced Raman shift signals obtained through SERS enabled Sylvia and coworkers to monitor the degradation products of TNT's explosive derivative dinitoluene (DNT) in the gaseous samples [3]. Liu and Chen found that enhanced intensity of Raman shift extends the detection limit to almost 10^{-11} M of TNT [4]. Tao et al. employed monolayers assembled with silver nanowire for SERS detection of DNT and found that such monolayers could yield an electromagnetic field enhancing factor of 200000 for DNT detection [5]. In the study of Carter et al., it was found that a stand-off Raman detector is able to identify explosives 50 m away in the ambient light [6].

Addressing surface enhanced Raman mechanism at atomistic level also helps further advancement of SERS technique for analysis of TNT and its degradation products. The study of detailed mechanism however requires both experimental investigations and supplementary computational simulations. As suggested by Luo and Fang, an electromagnetic interaction model and charge transfer can be possible mechanisms for the enhancement of the Raman signals [7]. Vibrational modes tend to generate considerable increases in Raman signals when subject to Frank-Condon distortion during their excited states. This resonance effect allows the study of Raman shift of chromophores in the context of biomolecules. In general, such vibrations are highly symmetric modes and the excited states are dipole-allowed. Clark and Franks found that the Raman shift at 273 cm^{-1} for $Re_2Cl_6^{2-}$ originates from the resonated ν_{a1g} stretching of quadruple Re–Re bond [8]. Therefore, it is necessary to clarify the specific origin for each Raman band for the targeted Nanostructure design.

Based on the foundation formed by the previous works, the present study aims at (1) addressing the detailed chemical bond origin for experimental Raman bands; and (2) assessing the impact of charge transfer on the enhancement of Raman shift signals in the SERS technology from chemistry point of view. A Raman spectrum of TNT was first measured using a portable Raman spectrometer. Afterwards, popular hybrid density function theory (DFT) methods were employed to conduct the computational simulation. DFT methods were chosen for this study because compared with other

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method such as CCSD-EOM, the DFT methods are much more computational efficient and can save significant computing resources. Even though the simulations of resonance Raman (RR) using CCSD-EOM agreed very well with the experimental results for TNT and RDX isomers [9], the CCSD-EOM method is too computationally expensive comparing with the DFT methods. After DFT computations, the DFT methods that yielded the best results closest to the experimental data would be applied to assign Raman bands to the molecular vibrational normal modes. Contributions of specific vibrations to each of the major Raman vibrational modes were analyzed. In our previous studies, the DFT methods have been successfully applied for investigating crystal structure of TNT metabolite 2-HADNT and determining its chemical shifts and other chemical properties [10,11].

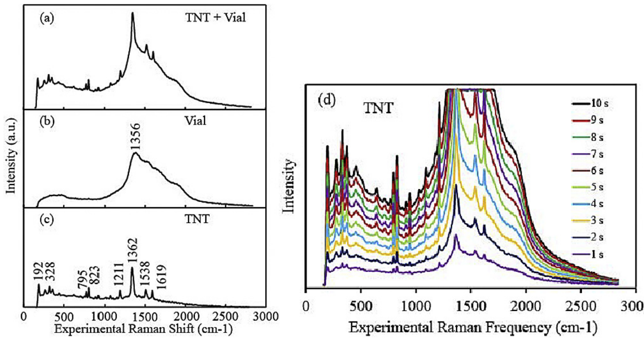

Fig. 1. Experimental Raman spectrum of TNT obtained after subtraction of the background noise of vial. (a) Overall spectrum of TNT sample in a glass vial; (b) Raman spectrum for the empty glass vial; (c) Net Raman spectrum of TNT after deducting the bands caused by the glass vial from the overall spectrum; and (d) Net Raman spectra of TNT under a series of integration time.

2. Research approach

2.1. Experimental method

The TNT sample was obtained and collected following the chemical synthesis approach first proposed by Junk and Catallo [12]. Raman spectra measurement was then performed on this sample using a Ramulaser-785 portable Spectrometer with incident wavelength of 785 nm. The power of the laser generator was maintained at 100 mW, and the integration time was set from 1 to 10 s. The acquisition time was set to four seconds for the present Raman spectrum measurement. To avoid a broad Raman peak, the Raman signals would not be collected until 10 min of “fluorescence burning”.

2.2. Computational method

Structural optimizations of TNT were performed using MP2 and hybrid DFT methods implemented in Gaussian-09 [13]. The crystal structure for TNT was taken from the Cambridge Crystallographic Data Centre (entry ZZZMUC01) [14]. Although two structural forms of TNT had been identified as monoclinic and orthorhombic, isolated molecules would be almost energetically indistinguishable due to their trivial energy differential of approximately 1 kcal/mol. Two basis sets, 6-311 + G** and aug-cc-pVDZ, were applied for quantum mechanics (QM) calculations. The calculated Raman spectra were inspected to ensure that no negative vibrational frequencies were yielded. The normal coordinate analysis (NCA) was then applied for calculating potential energy distribution (PED) for the normal vibrational modes to evaluate their contributions with respect to individual Raman shifts. All of the computations involved in this study were carried out on a quad-core cluster canfire04 at the Center for Advanced Computer Studies (CACS) at the University of Louisiana at Lafayette.

3. Results and discussion

3.1. Major experimental Raman frequencies of TNT

Fig. 1(a–c) display the experimentally measured overall Raman spectrum of the TNT sample in a glass vial, Raman spectrum for the empty glass vial, and the net Raman spectrum of the TNT sample, respectively. Fig. 1(d) plots the net Raman spectra of TNT under a series of integration time. Prominent Raman frequencies distinguished in Fig. 1(c) are listed in Table 1. As suggested in Table 1, seven prominent bands have been extensively studied applying SERS technology for TNT, and they are mainly originated from stretching and bending vibration modes of nitro group, methyl group, and the aromatic ring.

As illustrated in Fig. 1(b), the Raman absorption of the empty glass vial was measured under the same conditions to determine the noisy effect of the TNT sample holder. The Raman spectrum measured for the empty vial is a broad band with a sharp peak, ranging from 180 to 2500 cm^{-1}. That measured band results from a variety of anionic borate entities including di-, ditri-, tri-, tetra-, penta-, pyro-, ortho-, and meta-borate [15]. The sharp peak was measured at 1356 cm^{-1}; except for the strongest absorption, there is no other sharp Raman band observed for the empty glass vial. Therefore, the net Raman signal for the TNT sample can be obtained by subtracting the Raman spectrum for the empty vial from the measured overall spectrum, as shown in Fig. 1(c). Seven major Raman shifts explicitly identified in that figure are listed in Table 1.

Effect of integration time on the Raman spectrum was also assessed under the same power output of CW laser source. As shown in Fig. 1(d), the Raman spectrum measured under the integration time of 4 s was in the optimal condition and should be chosen for further analysis. This is because that when the integration time is beyond 4 s, the detector is saturated by the strongest Raman band of TNT at 1362 cm^{-1} and then the real Raman intensity cannot be correctly recorded. When that time is under 4 s, the ratios of all the Raman bands to background noises are relatively low, which would lead to significant interference from the background on the Raman band intensity.

Our previous experimental study indicated three major Raman bands at 840, 1350, and 1600 cm^{-1} in the Raman spectrum of 2-Hydroxylaminie-dinitrotolune (HADNT) [10,11]. Outcomes of that study motivate us to continue comprehensive investigations of the Raman spectra of TNT and its degradation products. It was measured in our experiments that the seven dominant vibrational nodes for TNT are: 322 cm^{-1} for framework distortion, 792 cm^{-1} for C—H out of plane bend, 824 cm^{-1} for nitro scissoring mode, 1207 cm^{-1} for C_6H_2—C vibration, 1355 cm^{-1} for nitro symmetric stretching, 1542 cm^{-1} for nitro asymmetric stretching, and 1616 cm^{-1} for aromatic stretching. The obtained seven major Raman bands of TNT agreed very well with two previous studies conducted by Wang [19] and Clarkson [20], as displayed in Table 1. Clarkson et al. measured Raman shifts from solid TNT samples and the measured Raman shift for the nitro asymmetric stretching is 1547 cm^{-1}, only five wave numbers higher than our results. All other Raman frequencies measured in the present study are in good agreement with those presented in Clarkson's work, with differences less than five wave numbers.

From the comparison with Wang's work it is found that even though very close, the Raman shifts obtained in the present work are consistently slightly higher than those presented in Wang's study. For example, the vibrational band obtained from this work