# The Inelastic Neutron Scattering spectrum of 2,4-Dinitroimidazole and the Reproduction of Its Solid-State Features by Periodic DFT methods

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## Abstract

The inelastic neutron scattering spectra of 2, 4 –Dinitroimidazole (24DNI) are presented from 25 to 1200 $cm^{-1}$. Direct comparisons were made to the experimental spectra using solid-state calculation methods at the BLYP/dnd, BP/dnd, and PWC/dnd theory levels. Comparison of the observed and calculated INS spectra revealed that the BLYP/dnd calculations provide the best description of the experimental INS spectrum below 1000 $cm^{-1}$. The PWC/dnd calculations were found to give the best vibrational agreement with the experimental frequencies above 1000 $cm^{-1}$. In addition, the six experimental lattice vibrations were assigned. The first overtone of the lattice vibration with the highest vibrational energy is nearly degenerate with one of the fundamental vibrations, suggesting the possibility of a "doorway mode".

## Introduction

The nitro-substituted imidazole family has many practical applications in both chemistry and biology, such as radiosensitizers [1], antibiotics [2], and insensitive energetic materials that are both thermally stable and have low sensitivity to environmental factors such as heat, friction, and impact [3]. Recent characterization of 24DNI, shown in Figure 1, revealed an energy performance similar to RDX but with an impact sensitivity comparable to TATB [4], revealing its potential as an energetic material. An extensive network of hydrogen bonds, consisting of chains of almost linear N-H ··N bonds, is present in the crystal structure of 24DNI [5]. The thermal decomposition of 24DNI has been investigated by mass spectroscopy and is characterized by early sample degradation initiated by impurities remaining from synthesis and water adsorbed from the air. Degradation is quickly followed by NO gas production and then total decomposition occurs, resulting in a complex mixture of gases and molecular residues [6]. While these characterizations of 24DNI provide valuable insight for the energetic materials community, in reality they only scratch the surface of the characterization necessary to

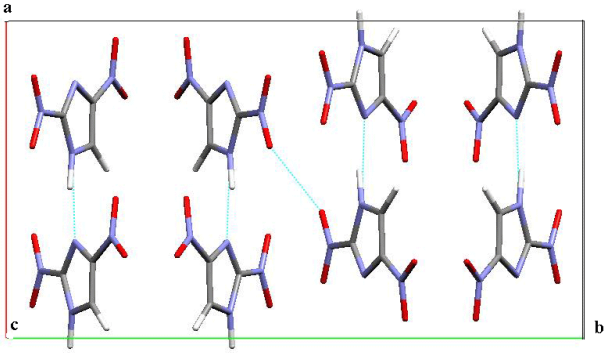


Figure 1. The unit cell structure of 24DNI. Hydrogen bonds are indicated by dashed lines.

understand the chemical and physical processes of this molecule.

Lattice and internal molecular vibrations have been proposed to play a key role in detonation, as is described in Dlott and Fayer's theory of "vibrational up-pumping" [7]. As a shock wave propagates through a molecule, the anharmonic coupling between the phonon modes, where energy is initially stored, and the internal molecular vibrations provides a "doorway" for energy transfer and eventual energy release, leading to molecular dissociation. Investigations into mechanisms such as "vibrational up-pumping" are often complicated because of a lack of fundamental understanding of the complex structure of the vibrational spectra of energetic materials. It is with this in mind that we undertake an examination of the molecular and lattice vibrational properties of 24DNI using inelastic neutron scattering (INS). In addition, INS spectra can be directly correlated to theoretical methods through the vibrational mode energies and eigenvectors given as output of quantum chemical programs. This combined theoretical/experimental approach can then be used to validate the first-principle technique being employed. In this manner, systematic investigations into the accuracy of current functionals being used in quantum chemical programs can be explored in the hope of understanding and predicting various properties of energetic solids and molecules, such as sensitivity, performance, and thermal stability.

**Experimental Details**

Inelastic neutron scattering data was acquired at the NIST Center for Neutron Research (NCNR) using the Filter Analyzer Neutron Spectrometer (FANS) [8] and the Fermi Chopper Time-of-Flight chopper spectrometer (TOF) [9]. The 24DNI sample was obtained from the Armament Research, Development, and Engineering Center of Picatinny Arsenal, NJ, and used without further purification. Approximately one gram of the sample was ground into a fine powder and held at 15K for the duration of the experiments. The experimental spectra were normalized with respect to the background contribution to the spectrum using the Data Analysis and Visualization Environment (DAVE) program [10].

Solid-state quantum chemical calculations of 24DNI were performed with the DMol3 [11] package. Calculations were performed using the DFT functionals BLYP [11], and BP [12], and the LDA functional, PWC [13]. The 'dnd' numerical basis set and 'fine' grid spacing were used in all calculations. Following the geometry optimization, the Hessian matrix was constructed by finite differences of the analytic gradient. The simulated INS spectra were calculated from the normal mode eigenvectors using ACLIMAX v. 5.1.3. [14].

**Results and Discussion**

**Internal Molecular Vibrations.** The experimental INS vibrational frequencies and the calculated vibrational frequencies are shown in Table 1. Table 1 also includes a brief description of the atomic motion associated with the vibrations. The complexity of the vibrational spectrum increases at higher energy due to an enlarging number of multiphonon and multiquanta events. As a result, at higher frequencies broader vibrational peaks are observed and resolving individual vibrational modes is difficult. Therefore, we present and discuss the experimental INS data only to 1200 $cm^{-1}$. From the data presented in Table 1, it can be seen that, in general, there is good frequency

agreement between experiment and all calculated frequencies. The RMS deviation between the INS observed fundamental frequencies and calculated fundamental frequencies calculated using the BLYP/dnd method is 4.56 $cm^{-1}$. The BP/dnd method produces a slightly larger RMS deviation of 8.00 $cm^{-1}$. The PWC/dnd method produces an RMS deviation of 6.92 $cm^{-1}$ between the experimental and calculated frequencies.

| | INS ($cm^{-1}$) | BLYP/ dnd | BP/ dnd | PWC/ dnd | Molecular Motion |
|---|---|---|---|---|---|
| 1 | 85 | 85 | 80 | 72 | skeletal def. |
| 2 | 93 | 94 | 82 | 90 | NO torsion, skeletal def. |
| 3 | 101 | 102 | 86 | 109 | NO torsion |
| 4 | 129 | 126 | 127 | 128 | skeletal deformation, NO torsion |
| 5 | 165 | 171 | 163 | 171 | $NO_2$ OP wag, skeletal def. OP |
| 6 | 186 | 190 | 176 | 186 | $NO_2$ IP wag, C-N def. |
| 7 | 274 | 274 | 285 | 279 | $NO_2$ wag IP, C-N def., skeletal def. |
| 8 | 286 | 288 | 296 | 288 | skeletal def., N-H bend OP |
| 9 | 338 | 336 | 346 | 341 | skeletal def., N-H bend IP, C-H bend IP |
| 10 | 492 | 487 | 500 | 484 | C-N def. IP, N-H wag IP, C-H wag IP |
| 11 | 510 | 512 | 519 | 515 | $NO_2$ torsion OP, C-H IP wag, N-H IP wag |
| 12 | 582 | 585 | 575 | 590 | C-N def, N-H bend IP, C-H bend IP |
| 13 | 613 | 607 | 606 | 603 | skeletal def. IP , $NO_2$ rock |
| 14 | 645 | 636 | 656 | 646 | N-H bend OP, C-H bend OP, C-N OP ring def. |
| 15 | 743 | 739 | 746 | 753 | N-H bend OP, C-H bend OP, $NO_2$ bend OP |
| 16 | 758 | 764 | 752 | 758 | $NO_2$ umbrella, N-H wag, C-H wag |
| 17 | 782 | 791 | 785 | 785 | N-H wag, C-H wag, N-O scissor |
| 18 | 831 | 831 | 825 | 825 | C= C stretch, N-H wag, C-H wag |
| 19 | 891 | 895 | 885 | 890 | N-H bend, C-H bend |
| 20 | 928 | 925 | 910 | 915 | ring deformation, C-H bend, N-H bend |
| 21 | 952 | 955 | 946 | 939 | C-H torsion, ring deformation |
| 22 | 992 | 1000 | 985 | 992 | ring deformation, C-H bend, N-H bend |
| 23 | 1081-1200 | 1127 | 1115 | 1138 | C-N stretch, N-H bend, C-H bend |

Table 1. The experimental and calculated fundamental normal modes of vibration of 24DNI in the vibrational range of 25 – 1200 $cm^{-1}$.

The simulated INS vibrational spectra are plotted against the experimental INS spectrum in Figure 2 in the range of 200 – 1200 $cm^{-1}$. The computer-generated spectra were constructed by combining the contribution of both the fundamental vibrations and combination and overtone modes to the INS spectrum. While the fundamental frequencies compare favorably with the experimental INS fundamental vibrations, including the combinations and overtone vibrations increases the accuracy of the spectral agreement. Evaluation of the three calculation methods shows that the BLYP/dnd method gives the best representation of the vibrational dynamics of 24DNI below 1000 $cm^{-1}$. Above 1000 $cm^{-1}$, the PWC/dnd calculations show the best agreement with experiment. In general, both the BP/dnd and PWC/dnd methods had good agreement of the fundamental frequencies with the experimental data, and a slight shift to lower energy was noted in the combinations and overtones. This is in contrast to reports that the BP functional gives similar or better results than the BLYP functional for hydrogen bonded molecules [15]. In one of our combined DFT/INS studies on the energetic material, 2, 6-

Diamino-3, 5-dinitropyrazine (ANPZ) [16], we have found that the BP/dnd method gives better results than the BLYP/dnd methods.

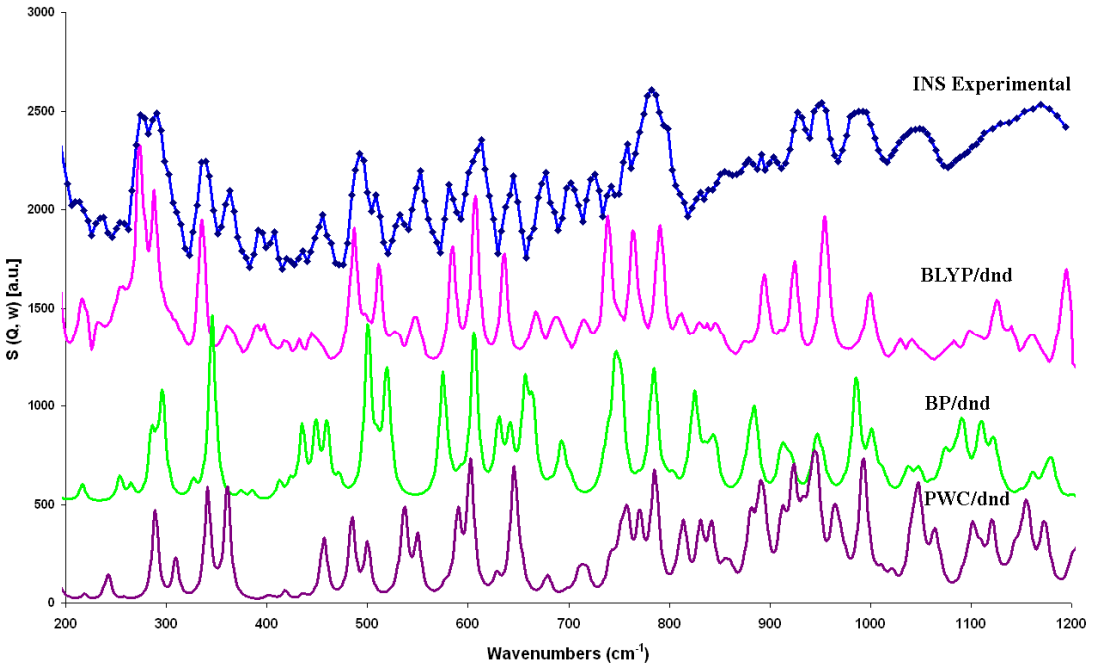


Figure 2. Comparison of the experimental INS spectrum and the simulated spectra using the BLYP/dnd, BP/dnd and PWC/dnd methods. The calculated spectra include contributions from fundamental, combination and overtone vibrations and are offset for ease of comparison.

**Lattice vibrations.** The lattice vibrational modes are of particular interest to the energetic materials community. Figure 3 shows the experimental INS phonon spectrum of 24DNI in the range of approximately 20 – 200 $cm^{-1}$ obtained using the TOF instrument. The spectra are offset for ease of comparison. Table 2 presents a comparison of the vibrational frequencies, obtained using the different methods, and the experimental frequencies.

Six strong lattice vibrational peaks are observed in this region. Three torsional modes are found at 44, 52 and 60 $cm^{-1}$ that split along the three non-equivalent crystal axes. The two lower frequency phonons experimentally observed at 24 $cm^{-1}$ and 36 $cm^{-1}$ are due to stretching motions. The vibration observed experimentally at 64 $cm^{-1}$ is due to sliding-like motion. The BLYP/dnd calculations provide the best agreement with the experimental data, qualitatively reproducing both intensity and frequency. Both the PWC/dnd and BP/dnd methods predict the experimentally observed vibration at 24 $cm^{-1}$ at a lower of frequency. Several intermolecular vibrations also occur in this region and their vibrational assignments may be found in Table 1.

The assignment of the phonon modes of 24DNI brings up several interesting points concerning the possibility of “doorway modes” in this molecule. First, phonon modes which can couple to the internal molecular vibrations to form “doorway modes”

are located in a frequency region defined by twice that of the energy of highest energy lattice vibration [7]. In 24DNI, the first "doorway mode" should be at approximately 128 $cm^{-1}$. Our experimental data shows a fundamental vibration at 129 $cm^{-1}$, which is nearly degenerate with the first overtone of 64 $cm^{-1}$ lattice vibration. The primary molecular motion assigned to the fundamental vibration at 129 $cm^{-1}$ is the torsional motion of the NO group. Combined with the decomposition data, which shows that NO gas is one first products of decomposition, this suggests the high probability that this is indeed a "doorway" mode. However, further experimental characterization is necessary before any definite conclusions can be made as to the validity of the discussion above.

| INS ($cm^{-1}$) | BLYP/dnd | BP/dnd | PWC/dnd |
|---|---|---|---|
| 24 | 23 | 16 | 21 |
| 36 | 32 | 30 | 35 |
| 44 | 45 | 36 | 42 |
| 52 | 50 | 52 | 53 |
| 60 | 59 | 56 | 62 |
| 64 | 72 | 63 | 71 |

Table 2. The phonon modes of the 24DNI molecule.

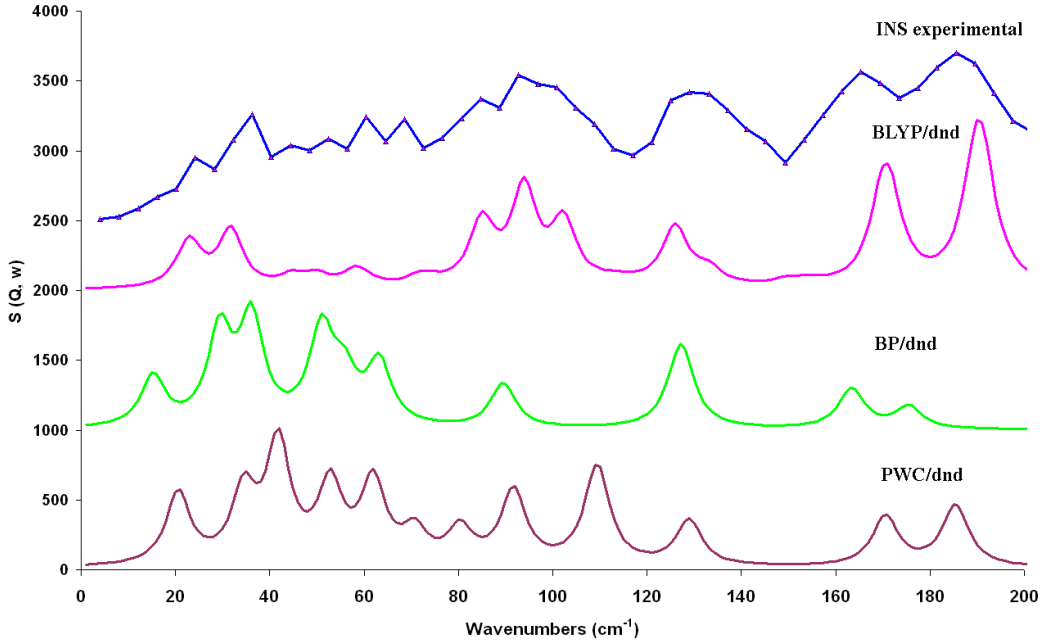


Figure 3. Comparison of the experimental INS phonon spectrum collected on the TOF instrument and the simulated phonon spectra using the three calculation methods. Spectra are offset for ease of comparison.

**Conclusions.**

The normal mode analysis of the 24DNI molecule in the crystalline solid state has been performed using functionals based in density functional theory (BLYP and BP) and the local density approximation (PWC). The numerical basis set 'dnd' was used for all

calculations. Inelastic neutron scattering spectra of crystalline 24DNI have been measured and compared with the simulated spectra. In general, all spectra have good frequency agreement, with the best agreement being observed with the BLYP/dnd calculations (RMS deviation of 4.56 $cm^{-1}$) and the worst in the BP/dnd calculations (RMS deviation of 8.00 $cm^{-1}$). The intensity agreement is best for the BLYP/dnd calculated spectrum. On the basis of the calculations and analysis it was possible to assign molecular motions to the vibrations. In addition, an analysis was presented of the phonon region of the INS spectrum of 24DNI. The BLYP/dnd calculations gave the best frequency agreement for the phonon region. Six phonon modes were observed. The highest energy phonon mode at 64 $cm^{-1}$ was found to have to a nearly degenerate overtone vibration with the fundamental 129 $cm^{-1}$, suggesting the possibility that this mode is a "doorway mode", but further evidence is needed before this can be concluded.

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