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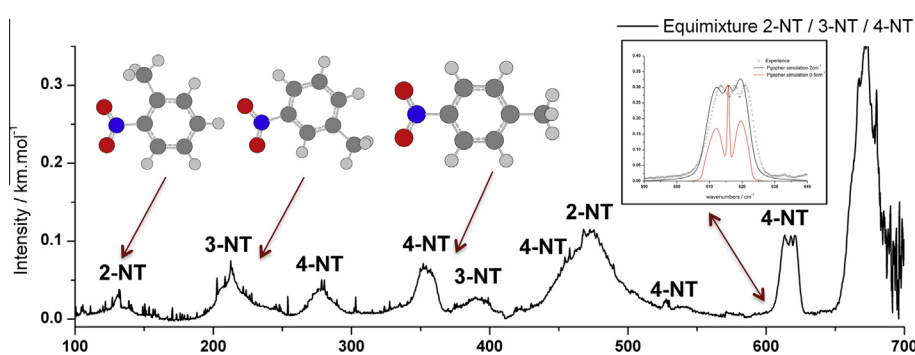
## Synchrotron FT-FIR spectroscopy of nitro-derivatives vapors: New spectroscopic signatures of explosive taggants and degradation products

Arnaud Cuisset<sup>a,\*</sup>, Sébastien Gruet<sup>b</sup>, Olivier Pirali<sup>b,c</sup>, Thierry Chamaillé<sup>c</sup>, Gaël Mouret<sup>a</sup><sup>a</sup> Laboratoire de Physico-Chimie de l'Atmosphère, EA-4493, Université du Littoral – Côte d'Opale, 59140 Dunkerque, France<sup>b</sup> Synchrotron SOLEIL, L'orme des Merisiers, Saint-Aubin – BP48, 91192 Gif-sur-Yvette, France<sup>c</sup> Institut des Sciences Moléculaires d'Orsay, UMR-8214 CNRS, Université Paris-Sud, 91405 Orsay Cedex, France

## HIGHLIGHTS

- We measured room temperature FIR cross-sections of the 3 isomer forms of mononitrotoluene.
- The anharmonic calculations allows to simulate some rotational patterns in the FIR NT spectra.
- DNT FT-FIR spectra were recorded at  $T > 380$  °K in a specially designed heated multi-pass cell.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We report on the first successful rovibrational study of gas phase mononitrotoluene and dinitrotoluene in the TeraHertz/Far-Infrared (THz/FIR) spectral domain. Using the AILES beamline of the synchrotron SOLEIL and a Fourier Transform spectrometer connected to multipass cells, the low-energy vibrational cross-sections of the different isomers of mononitrotoluene have been measured and compared to calculated spectra with the density functional theory including the anharmonic contribution. The active FIR modes of 2,4 and 2,6 dinitrotoluene have been assigned to the vibrational bands measured by Fourier Transform FIR spectroscopy of the gas-phase molecular cloud produced in an evaporating/recondensing system. This study highlights the selectivity of gas phase THz/FIR spectroscopy allowing an unambiguous recognition and discrimination of nitro-aromatic compounds used as explosive taggants.

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## Introduction

The detection, quantification and monitoring of explosive vapors at trace levels with high selectivity and sensitivity devices show an increasing interest since the last decades for its applications in defense, military, forensics and environmental uses [1–4]. Contrary to Improvised Explosive Devices (IED) such as TriAcetone TriPeroxide (TATP) or HexaMethylene Triperoxide

Diamine (HMTD) unstable but relatively volatil, classical explosives such as cyclotrimethylene trinitramine (RDX) or trinitrotoluene (TNT) exhibit a very low vapor pressure at room temperature and their detection in air requires very sensitive techniques with levels usually better than 1 ppb. To overcome this difficulty, it is not the explosive itself which is detected, but another compound more volatil present in the explosive [5]. This volatil compound can exist naturally in the explosive due to the manufacturing process. For example, in the case of DiNitroToluene (DNT), the molecule is a degradation product of TNT [6] and is required for its manufacture. The different isomers of DNT (2,4-DNT, 2,6-DNT...

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can be detected as an environmental contaminant in the soil using standard analytical chemistry technics [7]. Ortho-Mononitrotoluene (2-NT) and para-mononitrotoluene (4-NT) can be also used as detection taggants for explosive detection. Contrary to chemical analytical methods, optical spectroscopy and particularly Terahertz (THz) spectroscopy does not require a sampling method to capture the gas phase species, nor a comparison with a calibration standard, and an adapted detection technique to the molecular system studied [8,9]. Explosives and their derivatives have been extensively studied by various spectroscopic techniques. Only ultra sensitive spectroscopic methods such as photothermal deflection [3], cavity-ringdown [10,11] and photoacoustic [12,13] spectroscopies probing intense vibrational transitions in the 2.5–14.5  $\mu\text{m}$ , 7–8  $\mu\text{m}$  and 9–11  $\mu\text{m}$  spectral regions, respectively, was able to record the gas phase vibrational signatures of TNT and RDX classical explosives at a subppm level. Unfortunately the localized modes (C–H, C–N, N–N stretchings, C–H (ring) and O–N–O bendings and  $\text{CH}_3$  deformation...) excited at those wavelengths, does not allow to unambiguously discriminate compounds of the same family and isomers. Conventional gas phase Fourier Transform InfraRed (FTIR) absorption spectroscopy is limited to the study of those vibrations and required to heat the gas cell in order to increase the vapor pressures [2]. The lower frequency modes active in the Far InfraRed (FIR) are well suited to discriminate compounds with similar functional groups, isomers and conformers [14,15] but their intensities are by one or several order of magnitude weaker than the most intense vibrations in the Mid InfraRed (MIR). Therefore, most of the FIR studies of explosives and their derivatives have been performed in condensed phase allowing to increase drastically the density of probed molecules. Wideband THz Time-Domain Spectroscopy (THz-TDS) and Fourier-Transform FIR (FT-FIR) spectroscopy were prolific in this domain providing the more conclusive results for the low-frequency vibrational fingerprints of explosives (TNT, RDX, ...) and related compounds (2,4-DNT, 2,6-DNT, 4A-DNT, ...) in pure solids [16,17], in polyethylene pellets or liquid solvents [6,18,19]. The Raman FIR active modes have also been studied from explosive vapors resublimated on cooled nanostructures gold substrates [20]. To the best of our knowledge, low-frequency vibrational signatures of explosive vapors have never been observed in the THz/FIR spectral regions. In 2006, Foltynowicz et al., using THz-TDS and a THz path length of 34 cm, measured the gas phase absorption spectrum of 2,4-DNT below 2.7 THz [21]. This study shows effectively the difficulty to measure at THz frequencies in gas phase the absorption spectrum of a derivative explosive compound such as 2,4-DNT. Indeed the best results were obtained with a static pressure lower than 0.005 Pa at 150 °C for 4 h. Only the pure rotational pattern of the 2,4-DNT vapor is observed below 0.5 THz with a small  $S/N$  ratio (<3).

Synchrotron FT-FIR spectroscopy has been used to investigate the THz/FIR gas phase spectra of nitro-derivatives vapors. Room temperature gas phase absorption cross-sections of different isomers of NitroToluene (NT) are determined and compared with Density Functional Theory (DFT) calculated intensities. A specific heated multipass-cell has been designed for the study of much more weakly volatile compound allowing to measure for the first time the low-frequency vibrational fingerprints of 2,4-DNT and 2,6-DNT vapors. Gas phase signatures may be directly compared and assigned from DFT calculations on isolated molecular systems.

## Experimental and computational details

### Experimental method

Nitrotoluene compounds were obtained from Aldrich Chemical Company with a purity better than 97% and were used without

further purification. At room temperature and atmospheric pressure, 2-NT and 3-NT are liquids and 4-NT, 2,4-DNT and 2,6-DNT are solids. Due to the low volatility of those compounds, a high sensitivity was required for these experiments.

The mononitrotoluene vapor pressures have been studied for the different isomers. The vapor pressures of 2-NT, 3-NT and 4-NT have been respectively measured to 12.7 Pa, 8.6 Pa and 3.8 Pa at  $T = 293 \text{ K}$  [22]. For the study of those explosive taggants, the spectrometer was coupled to a multipass cell (in a White type configuration) and adjusted to reach a 150 m optical path length. This cell was isolated from the interferometer by 50  $\mu\text{m}$  thick polypropylene windows and directly filled with the room temperature vapor pressures of the compounds. The details of the experimental set-up have been partially described in [15]. In this article, we demonstrate that, even at middle resolution, we can benefit from the exceptional properties of the AILES beamline for the study of low volatile compounds. Particularly the high flux of and the weak divergence of the Synchrotron Radiation (SR) [23] allow to work with long optical path even at larger wavelengths. The SR was focused onto the entrance aperture of the Bruker IFS125 Fourier Transform interferometer containing a 6- $\mu\text{m}$  mylar-Silicon composite beamsplitter suitable for the THz spectral range. The detector was a He-cooled silicon bolometer equipped with an optical filter, with a  $33\text{--}670 \text{ cm}^{-1}$  (1–20 THz) band pass.

The vapor pressures of dinitrotoluenes are two orders of magnitude smaller than the mononitrotoluenes. At  $T = 293 \text{ K}$ , the vapor pressures of 2,4-DNT and 2,6-DNT are estimated to 0.05 and 0.025 Pa, respectively [24]. For those compounds, we did not succeed to record any representative spectra at room temperature. For these very weakly volatile compounds, a specially designed heated multipass cell presented in Fig. 1 has been used. The cell consists of a classical white-type multipass cell equipped with 50 cm focal length spherical mirrors. The optical set-up has been adjusted to obtain 24 m optical path length. The evaporating and recondensing systems are placed in the center of the cell. The evaporating system consists of a melting-pot containing the samples and a copper tube shield as shown in Fig. 1. The shield is 45 cm long and 15 cm in diameter. Both elements could be heated independently up to 473 K. Note that a higher temperature is applied on the shield to avoid sample recondensation on it. The proper condensing system which is slightly longer than the shield is a copper cylinder placed few centimeters above the melting-pot; it is water cooled down to 10–20 °C. In this configuration, a typical operation requires few grams of samples which are placed in the melting pot and evaporated by adjusting the temperature. The gas phase molecular cloud is probed by the synchrotron beam prior to its final recondensation on the cold trap. This arrangement avoids any recondensation on the mirrors, which would reduce drastically their reflexion. The melting-pot was filled with around 5 g. of DNT. Both to the melting-pot and to the shield we applied a temperature ramp from 293 K to 443 K. The DNT vaporized was directly recondensed on the cooled part of the cell. The interferometer was used in repeated modes up to the complete vaporization/recondensation of DNT. In those conditions, we can repeat around 20 times the co-addition of 50 interferograms recorded at  $0.5 \text{ cm}^{-1}$ . For dinitrotoluene compounds, FIR vibrational bands are observed only after heating of the sample and increasing of the vapor pressure. Up to 400 K, residual water vapor lines appear clearly on the spectra. The optimized experimental conditions to record the FT-FIR spectra of mononitrotoluene and dinitrotoluene compounds are summarized in Table 1.

### Computational details

The full geometry optimization and frequency computation were performed using GAUSSIAN09 package [25] with the

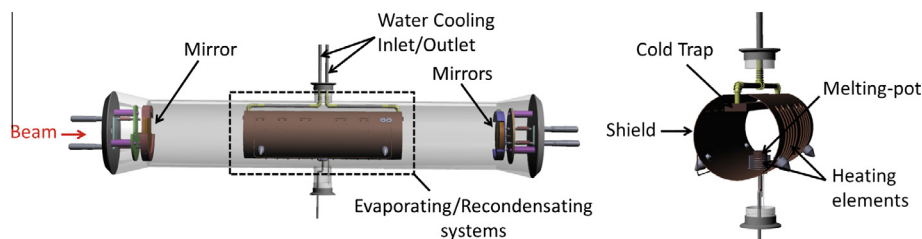


Fig. 1. Schematic view of the heated multipass-cell. To the left a profile view and to the right a front view of the control temperature system.

**Table 1**  
Optimized experimental conditions for the FT-FIR spectroscopy of the 5 studied nitro-derivative vapors.

Molecules	THz pathlength (m)	Temperature (°K)	Pressure (μbar)*	Resolution (cm <sup>-1</sup> )	Number of scans
2-NT	151	298	20	0.5	200
3-NT	151	298	60	0.5	200
4-NT	151	298	20	0.5	200
2,4-DNT	36	425	1200	0.5	50
2,6-DNT	36	385	1000	0.5	50

\* Pressure inside the multipass cell during the scans.

Becke-3-Lee-Yang-Parr (B3LYP) functional [26,27]. Different basis-set have been tested on nitrotoluene derivative compounds and the best compromise between the cost of the calculations and the accuracy of the results was obtained with the 6-311+G(2d,p) basis-set. Frequency calculations are performed with the method and basis set used for the optimization. Minimum energy structures were found, which were confirmed by vibrational analyses. No negative frequencies were found. For the 3 mononitrotoluene isomers, the anharmonic force field has been computed allowing to determine vibrational frequencies with anharmonic corrections and the rotational constants and their vibrational dependencies for each normal mode. The molecular structures optimized at the B3LYP/6-311+G(2d,p) level of theory are presented Fig. 2.

## Results and discussion

### Mononitrotoluene study

2-NT, 3-NT and 4-NT have 45 vibrational normal modes belonging to the irreducible representation A of the symmetry group C<sub>1</sub>. According to the B3LYP/6-311+G(2d,p) calculations, 12 normal modes are located below 700 cm<sup>-1</sup>. In the case of mononitrotoluenes, the gas phase FT-FIR spectra were measured at room temperature with stabilized pressures close to the equilibrium vapor pressures. In those conditions, FIR cross-sections may be straightforwardly determined and compared to the theoretical intensities provided by the quantum chemistry calculations [28]. FIR absorption cross-sections  $\sigma(\nu)$  may be directly calculated from the FIR absorbance  $A(\nu)$ .  $\sigma(\nu)$  is usually calculated in cm<sup>2</sup> molecule<sup>-1</sup> but in this study km mol<sup>-1</sup> unit is used for a direct comparison with the GAUSSIAN09 theoretical infrared intensities. Therefore  $\sigma(\nu)$  in km mol<sup>-1</sup> is obtained with the relation:

$$\sigma(\nu) = 10^{-1} \frac{R\theta}{PL} \ln(A(\nu)) \quad (1)$$

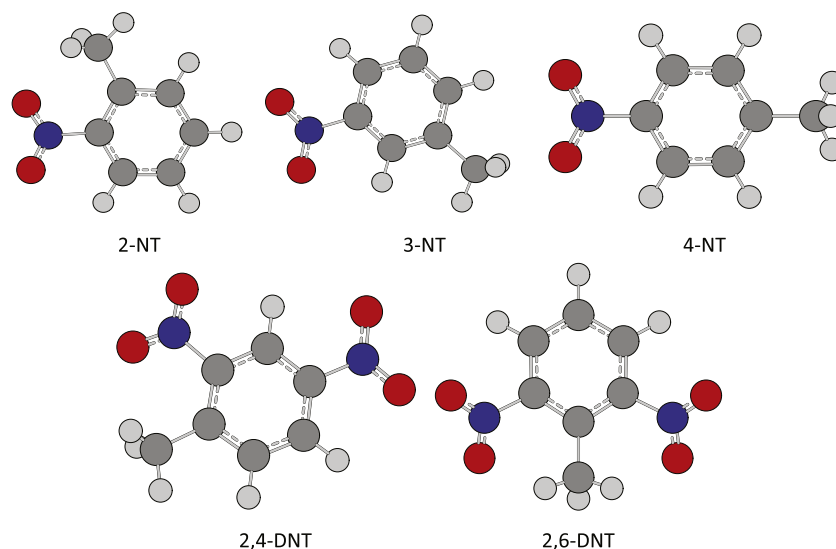
with the gas constant  $R = 8.3144621 \text{ J mol}^{-1} \text{ K}^{-1}$ , the temperature  $\theta$  in K, the Pressure  $P$  in mbar and the length cell  $L$  in cm. In the present work, the broadening contributions due to collisions or Intramolecular Vibrational energy Redistribution (IVR) effects cannot be evidenced and only the vibrational lineshape was considered.

At low pressure and in the gas phase, a gaussian lineshape was chosen in a first approximation to take into account the thermal motion [28] and to model rotationally unresolved vibrational bands. The FIR integrated cross-sections  $I_{\text{exp}}$  are obtained by fitting the observed broad vibrational bands with a gaussian profile:

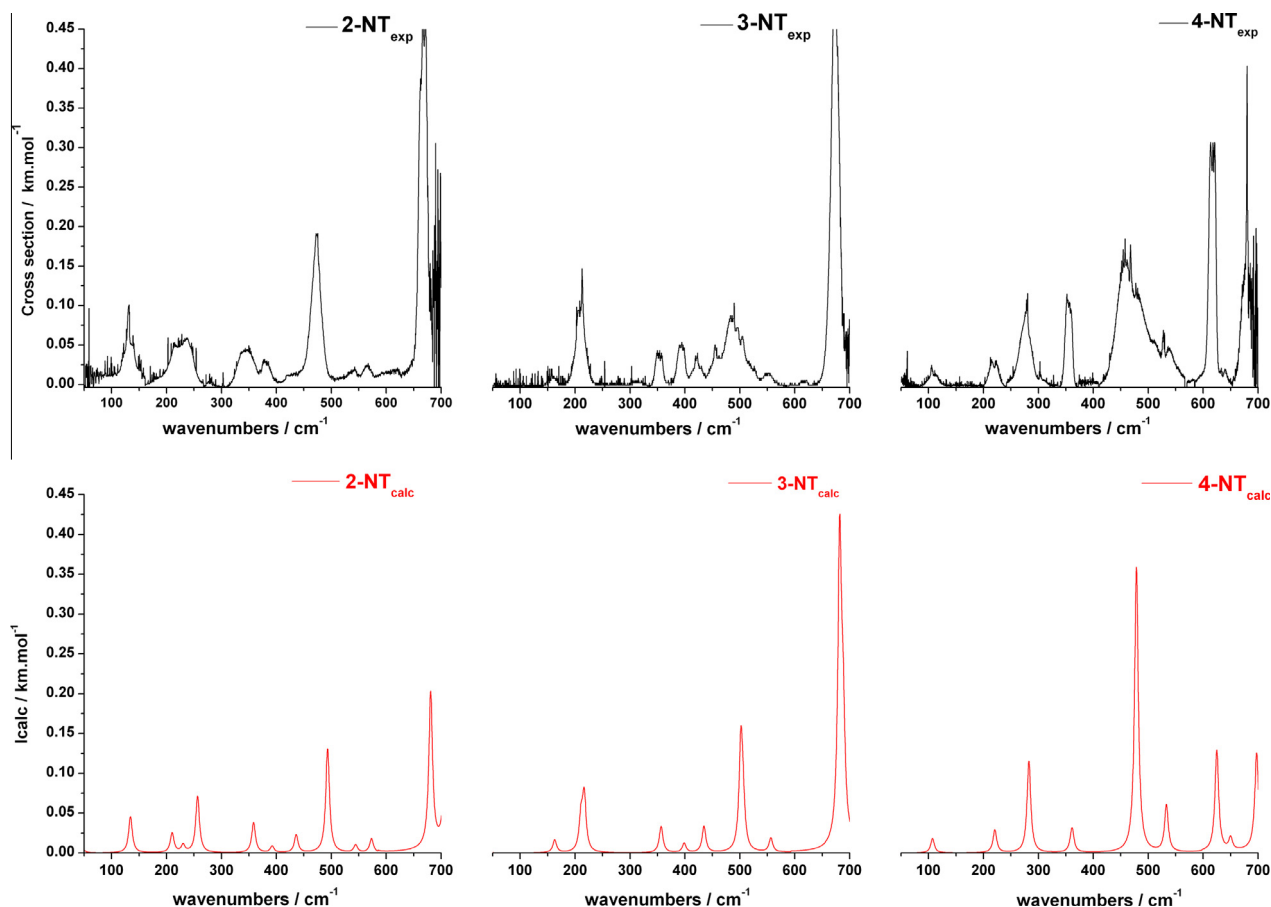
$$I_{\text{exp}} = \int_{-\infty}^{\infty} \frac{2\sqrt{\ln 2}\sigma(\nu)}{\sqrt{\pi}\Delta\nu} \exp\left(-\frac{4\ln 2(\nu - \nu_c)^2}{\Delta\nu^2}\right) d\nu \quad (2)$$

The center frequency  $\nu_c$ , the FWHM (full width half middle)  $\Delta\nu$  and the integrated cross-sections  $I_{\text{exp}}$  in Eq. (1) were fitted. Fig. 3 illustrates the good agreement between the calculated FIR spectra at the B3LYP/6-311+G(2d,p) level of theory and the experimental FIR cross-sections determined from Eq. (1).

In Fig. 4, the FIR cross-sections of 2-NT, 3-NT, and 4-NT are superimposed (lower part) and the averaged spectrum of an equimixture of the 3 isomers has been calculated from the individual experimental spectra (upper part). This figure highlights the capability of FIR gas phase spectroscopy to discriminate different isomers of a targeted compound from the lowest frequency vibrational bands. Indeed, contrary to the localized modes at higher frequencies, the large amplitude motions probed in the FIR allow an unambiguous discrimination between isomers. Several studies demonstrate that FT-FIR spectroscopy based on synchrotron sources is an efficient tool to analyze the conformers [14,15], rotamers [28] and isomers [30] forms of flexible molecules. Considering the spectrum of an equimixture of the 3 mononitrotoluenes shown Fig. 4, some observed bands result from the overlapping of the vibrational fingerprints of the 3 isomeric forms: this is the case for the bands centred at 671.6 cm<sup>-1</sup> and 474.4 cm<sup>-1</sup> associated to the in plane and out of plane ring deformations. However, several bands of the equimixture spectrum correspond to the vibrational fingerprint of an individual isomer. As example, the bands centred at 131.4 cm<sup>-1</sup> (CH<sub>3</sub> and NO<sub>2</sub> out of plane bending mode), 212.3 cm<sup>-1</sup> (CH<sub>3</sub> and NO<sub>2</sub> in plane bending mode) and 276.4 cm<sup>-1</sup> (CH<sub>3</sub> torsion mode) may be used to identify respectively the isomers 2-NT, 3-NT and 4-NT. Typically the lowest frequency vibrational modes active in the THz region allow to discriminate the different isomers. We can remark one exception for 4-NT: the band centred at 617.8 cm<sup>-1</sup> associated with the symmetric stretchings of the CH<sub>3</sub> and NO<sub>2</sub> groups is a specific signature of the para-NT form.



**Fig. 2.** Optimized structures of 2-NT, 3-NT, 4-NT, 2,4-DNT, 2,6-DNT at the B3LYP/6-311+G(2d,p) level of theory. Red, blue, gray and white colors are associated to oxygen, nitrogen, carbon and hydrogen atoms respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

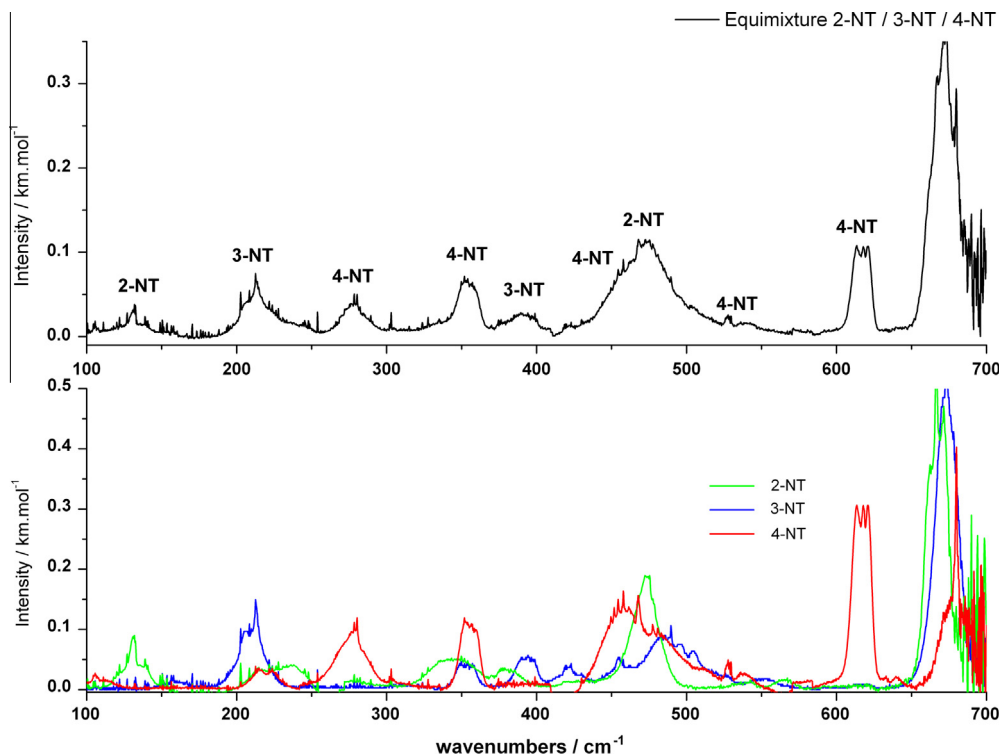


**Fig. 3.** Experimental (upper traces) and theoretical (lower traces) FIR cross-sections of 2-NT, 3-NT, and 4-NT in km/mol. Experimental FT-FIR spectra were measured in the conditions summarized in Table 1. Theoretical spectra were calculated at the B3LYP/6-311+G(2d,p) level of theory.

The assignment of the vibrational bands observed in the FT-FIR gas phase spectra was relatively straightforward using the harmonic and anharmonic DFT frequencies and intensities. A summary of this assignment is presented Table 2. More than 83% of the predicted fundamental vibrations have been observed on the mononitrotoluene spectra. For the 3 isomers, the root mean square

(r.m.s) values associated with the harmonic frequency relative uncertainties are better than 10% for the 3 isomers. The extension to the anharmonic force field does not allow to reduce the r.m.s values. However for 2-NT and 3-NT, with few exceptions, the anharmonic corrections improve the prediction of a majority of vibrational wavenumbers. This is not the case for 4-NT where the





**Fig. 4.** Upper trace: FT-FIR cross-sections of an equimixture of the 3 isomers of mononitrotoluene. Lower trace: superposition of experimental FIR cross-sections of 2-NT (green), 3-NT (blue), and 4-NT (red) in km/mol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

consideration of the anharmonic contribution does not improve the frequency calculation. This observation is relatively current for the calculation of low-frequency modes where a loss of accuracy in the calculated anharmonic force field is expected in the case of large amplitude motion. This is particularly the case when the potential is highly anharmonic, the method used in Gaussian fails to give reasonable results [31]. It will be interested to test advanced DFT methods including anharmonic force field calculations [32] for the lowest frequency modes of nitro-derivatives compounds.

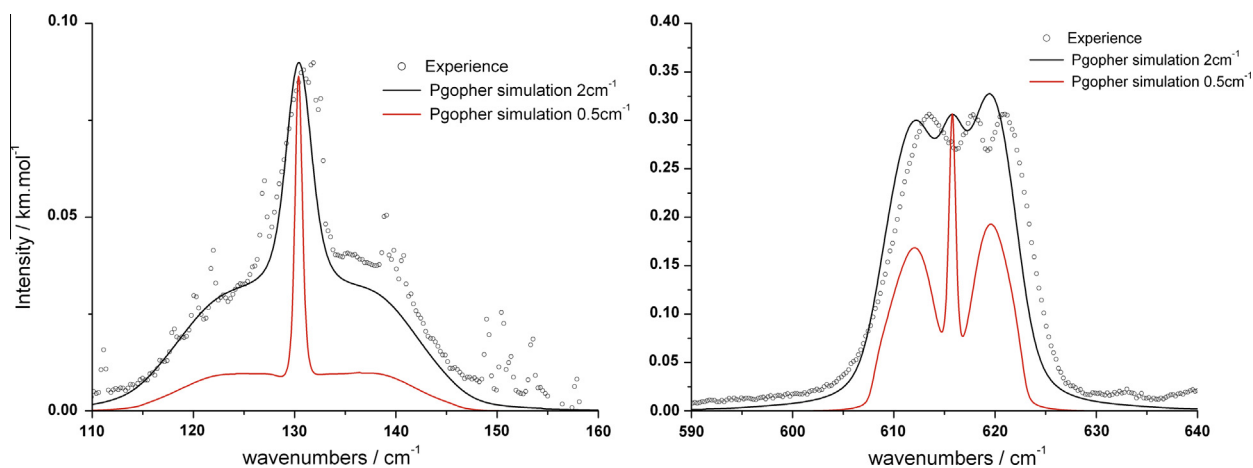
In addition to the frequency analysis, experimental and calculated FIR intensities have been compared. In Table 2, we calculated the relative uncertainty on intensity in percent defined by:

$\frac{\Delta I}{I} = 100 \times \frac{I_{\text{exp}} - I_{\text{calc}}}{I_{\text{exp}}}$  with  $I_{\text{exp}}$  deduced from Eq. (2) and  $I_{\text{calc}}$  calculated at the B3LYP/6-311+G(2d,p) level of theory. Compared to the previous results on frequencies, the r.m.s on the intensity relative uncertainties are larger. Due to the weakness of the FIR bands, the precision of the intensity values are less accurate than the frequency values. Experimental intensities may be overestimated or underestimated depending on several approximations: as example, we used gaussian profiles unable to reproduce the rotational pattern sometimes clearly visible (e.g: mode  $\nu_{44}$  of 2-NT or mode  $\nu_{36}$  of 4-NT, see Fig. 5), we did not take into account the contribution of hot and combination bands present in FIR spectra recorded at room temperature. Nevertheless, most of intensities are determined with a relative uncertainty better than 50%.

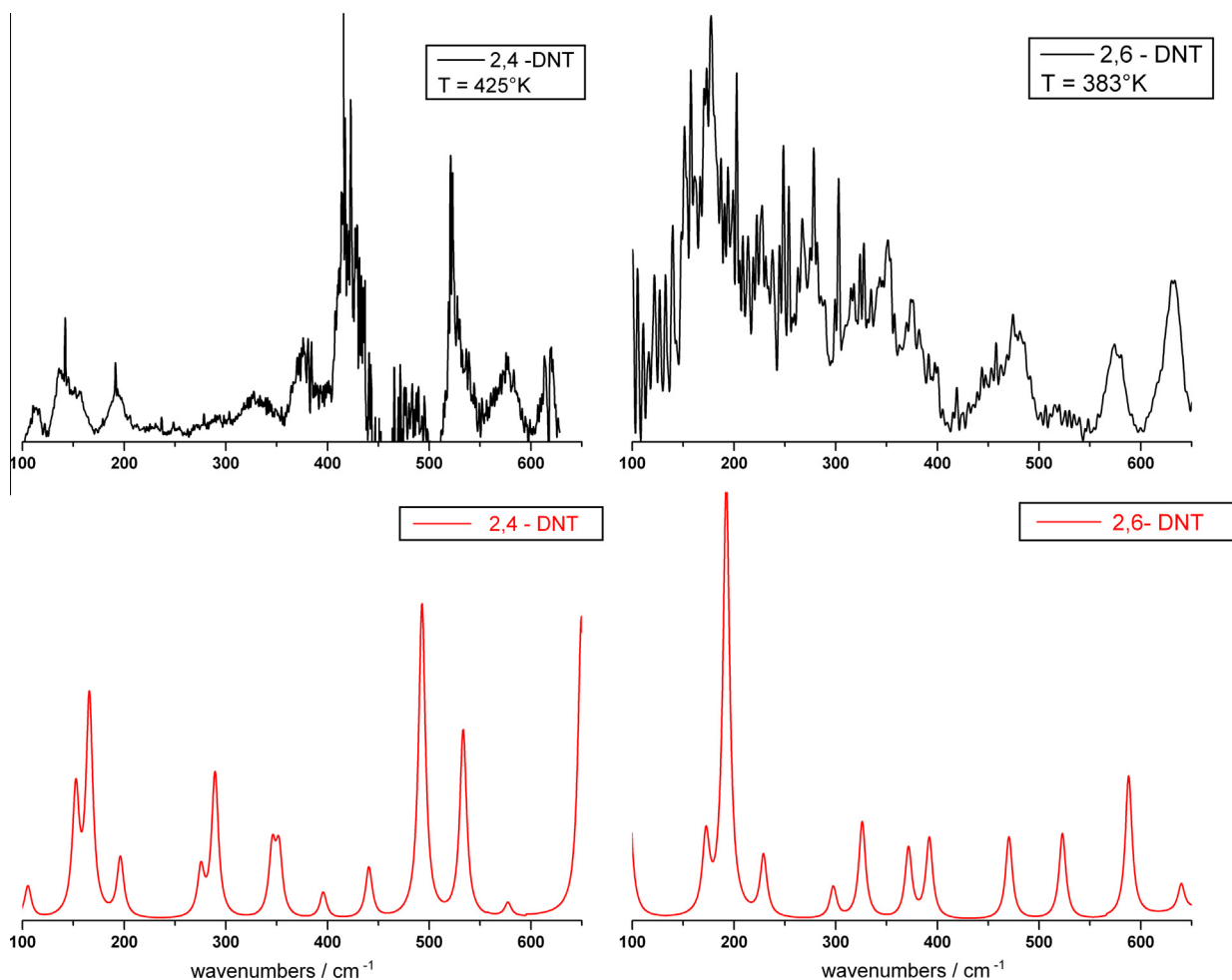
**Table 2**  
Frequencies (in  $\text{cm}^{-1}$ ) and intensities (in  $\text{km mol}^{-1}$ ) of the FIR vibration fundamental bands for the three mononitrotoluene isomers.  $\nu_{\text{exp}}$  and  $I_{\text{exp}}$  are obtained by modeling each fundamental band with a Gaussian lineshape adjusted to the FT-FIR spectrum.  $\nu_{\text{harm}}$ ,  $\nu_{\text{anharm}}$  are the calculated frequencies at the B3LYP/6-311+G(2d,p) level of theory.  $\frac{\Delta I}{I}$  is the relative uncertainty on intensity in percent defined by:  $\frac{\Delta I}{I} = 100 \times \frac{I_{\text{exp}} - I_{\text{calc}}}{I_{\text{exp}}}$  with  $I_{\text{exp}}$  deduced from Eq. (2) and  $I_{\text{calc}}$  calculated at the B3LYP/6-311+G(2d,p) level of theory. Root mean squares (r.m.s.) are given in percent.

	2-NT					3-NT					4-NT				
	$\nu_{\text{exp}}$	$\nu_{\text{harm}}$	$\nu_{\text{anharm}}$	$I_{\text{exp}}$	$\frac{\Delta I}{I}$	$\nu_{\text{exp}}$	$\nu_{\text{harm}}$	$\nu_{\text{anharm}}$	$I_{\text{exp}}$	$\frac{\Delta I}{I}$	$\nu_{\text{exp}}$	$\nu_{\text{harm}}$	$\nu_{\text{anharm}}$	$I_{\text{exp}}$	$\frac{\Delta I}{I}$
$\nu_{45}$		46.3	39.3					47.7	36.8				56.1	56.2	
$\nu_{44}$	131.4	134.4	130.3	1.1	−45.4	161.8	162.8	160.5	0.5	−6.0	108.4	107.3	115.6	0.4	−18.2
$\nu_{43}$	213.0	210.2	141.1	0.9	−5.5	205.5	210.6	205.6	1.2	−26.1	218.8	220.7	221.0	0.8	3.7
$\nu_{42}$	187.9	230.1	203.2	0.5	35.0	212.3	216.5	209.9	2.0	−42.3	276.4	282.7	287.2	2.4	−36.9
$\nu_{41}$	237.3	256.5	245.1	1.9	30.0	353.0	356.6	351.0	1.0	−28.0	360.1	359.5	362.6	0.5	65.4
$\nu_{40}$	344.7	358.4	348.1	1.7	21.4	392.9	398.6	390.0	0.3	65.6	352.5	361.6	356.8	1.1	34.2
$\nu_{39}$	381.9	392.3	384.6	0.6	41.1	422.6	434.6	432.4	1.0	−17.1		421.0	415.0		
$\nu_{38}$		436.0	429.4			470.3	501.8	502.9	1.7	−127.3	465.6	478.5	481.3	8.3	−24.8
$\nu_{37}$	472.2	493.2	483.9	4.9	6.1	499.2	505.7	499.7	1.3	−1.5	529.5	533.0	521.7	1.60	6.2
$\nu_{36}$	538.6	544.2	538.8	0.3	−6.4	550.3	556.3	556.1	0.7	28.8	616.6	624.8	615.8	4.4	15.7
$\nu_{35}$	565.3	573.1	567.1	0.3	−107.9	673.4	681.7	706.4	9.7	−13.2	638.0	649.9	643.8	0.3	−35.3
$\nu_{34}$	667.6	680.8	673.5	8.4	19.0		687.9	678.7			679.4	697.3	714.1	3.9	12.0
r.m.s.*		7.9	11.1		42.9		2.7	2.9		50.1		1.8	3.2		30.7

\* For the frequencies:  $100 \times \sqrt{\sum_{i=1}^n \frac{1}{n} \left( \frac{\nu_{\text{exp},i} - \nu_{\text{calc},i}}{\nu_{\text{exp},i}} \right)^2}$ . For the intensities:  $100 \times \sqrt{\sum_{i=1}^n \frac{1}{n} \left( \frac{\Delta I}{I} \right)^2}$ .



**Fig. 5.** Simulation of the rotational pattern of the  $\nu_{44}$  band of 2-NT (left) and the  $\nu_{36}$  band of 4-NT with the spectroscopic anharmonic parameters calculated at the B3LYP/6-311+G(2d,p) level of theory (right). Black circles correspond to the experimental values. Red and black lines correspond to the simulation performed with the PGOPHER program [29] with a resolution of 0.5 cm<sup>-1</sup> and 2 cm<sup>-1</sup>, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 6.** FIR absorption spectra of 2,4-DNT (left) and 2,6-DNT (right). Black: FT-FIR gas phase synchrotron spectra recorded at 393 and 425 K. Red: Theoretical spectra calculated at the B3LYP/6-311+G(2d,p) level of theory. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Anharmonic calculations provide, in addition to the rotational constants in the ground state, their correction in the vibrationally excited states. Those computed data allow to calculate the rotational pattern of the vibrational bands. Using the PGOPHER

program [29], we simulated the P, Q and R branches of the  $\nu_{44}$  band of 2-NT centred at 131.4 cm<sup>-1</sup> and the  $\nu_{36}$  band of 4-NT centred at 616.6 cm<sup>-1</sup> at room temperature. The simulations are performed with the computed anharmonic DFT/6-311++G(2d,p) rotational

constants A, B and C and their quartic centrifugal distortion corrections. C-type and A-type rovibrational transitions with  $J < 150$  are considered for 2-NT  $\nu_{44}$  and 4-NT  $\nu_{36}$ . The results are shown Fig. 5. Two simulations normalized on the Q branches intensities at two different spectral resolutions are presented. At the experimental resolution ( $0.5 \text{ cm}^{-1}$ ), P and R branch intensities appear significantly underestimated compared to the Q branch intensities. In addition to the limitation of the anharmonic calculations to determine corrections of the spectroscopic constants from the ground to the vibrationally excited states, the simulation does not take into account the contribution of hot bands or the splitting of energy levels due to the internal rotation of the methyl groups. With a 4 times lower resolution ( $2 \text{ cm}^{-1}$ ), Q branches are substantially enlarged compared to the P and R branches and the simulated rotational patterns agree better with the measured vibrational bands.

### Dinitrotoluene study

2,4-DNT and 2,6-DNT have 51 vibrational normal modes belonging to the irreducible representation A of the symmetry group  $C_1$ . According to the B3LYP/6-311+G(2d,p) calculations, 16 normal modes are located below  $650 \text{ cm}^{-1}$ . Compared to the FT-FIR spectra of mononitrotoluene measured at room temperature, the FT-FIR spectra of 2,4-DNT and 2,6-DNT, presented Fig. 6 are recorded at 425 K and 383 K, respectively with a limited signal to noise ratio by means of the specially designed heated multipass-cell shown Fig. 1. In those experimental conditions, the interaction distance is reduced to a non-defined zone in the evaporating–recondensing system and the absorption FIR cross-sections cannot be determined. Nevertheless some vibrational bands are unambiguously observed and may be assigned by a comparison with harmonic DFT calculations. This assignment is summarized in Table 3. As for mononitrotoluene, the two DNT isomers are clearly distinguishable from their low-frequency vibrational fingerprints. For 2,4-DNT strongest absorptions are observed in the higher frequency part of the spectrum with two bands centred at  $422.8 \text{ cm}^{-1}$  and  $520.9 \text{ cm}^{-1}$  and assigned to the  $\nu_{39}$  and  $\nu_{38}$  modes involving ring deformations. For 2,6-DNT strongest absorptions are observed in the lower frequency part of the spectrum with two bands centred at  $177.4 \text{ cm}^{-1}$  and  $202.6 \text{ cm}^{-1}$  and assigned to the

$\nu_{46}$  and  $\nu_{45}$  bending modes of methyl and nitro groups. Both for 2,4-DNT and 2,6-DNT, 9 vibrational modes have been assigned to the observed vibrational bands with a r.m.s. for the frequencies lower than 10%. Finally, we can notice that for the 2 lowest frequency vibrational bands of 2,4-DNT respectively centred at  $142 \text{ cm}^{-1}$  and  $191.4 \text{ cm}^{-1}$ , the P, Q, R rotational branches are visible. Unfortunately anharmonic DFT calculations providing rotational constants in the excited vibrational states may not be performed and the rotational patterns may not be simulated.

### Conclusions

Using the exceptional properties of the SOLEIL synchrotron source and adapted multipass-cells, gas phase FIR rovibrational spectra of different isomers of mononitrotoluene and dinitrotoluene have been investigated. Room temperature FIR cross-sections of the 3 isomer forms of mononitrotoluene have been determined for the lowest frequency vibrational bands located below  $700 \text{ cm}^{-1}$ . Both in frequency and in intensity, the harmonic DFT calculations are in good agreement with the FT-FIR measurements. The extension to anharmonic calculations allows to simulate some rotational patterns observed in the FIR spectra. Compared to the localized modes at higher frequencies, the THz/FIR vibrational bands give an unambiguous discrimination of the different isomers in a mixture. The weaker volatility of dinitrotoluene required to measure the gas phase FT-FIR spectra at higher temperature ( $T > 100^\circ \text{C}$ ) in flux conditions produced by an evaporating/recondensing system. FIR cross-sections may not be determined, but, compared to a previous gas phase THz study [21], an assignment of some active FIR/THz vibrational bands of 2,4-DNT and 2,6-DNT may be performed. The determination of the FIR cross-sections for those compounds require to develop a heated and completely thermalized multipass-cell including mirrors. In addition to providing new spectroscopic signatures of explosive taggants and degradation products, this study demonstrates that the THz/FIR spectral domain is very promising for explosive gas phase sensor in terms of selectivity. Nevertheless, the development of a THz/FIR sensor for explosive vapors requires to focus all efforts to increase the sensitivity of the techniques in order to be competitive with the most sensitive instruments available in the MIR/NIR spectral domains [33]. Rather than a detector sensor of explosive taggants, the selectivity of THz/FIR domain would be very useful to implement analytical tools to identify and discriminate unambiguously different compounds in a complex mixture.

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**Table 3**

Frequencies (in  $\text{cm}^{-1}$ ) and intensities (in  $\text{km mol}^{-1}$ ) of the FIR vibration fundamental bands for the two dinitrotoluene isomers.  $\nu_{\text{exp}}$  is measured on the FT-FIR spectra Fig. 6.  $\nu_{\text{calc}}$ ,  $I_{\text{calc}}$  are the calculated frequencies at the B3LYP/6-311+G(2d,p) level of theory.

	2,4-DNT			2,6-DNT		
	$\nu_{\text{exp}}$	$\nu_{\text{calc}}$	$I_{\text{calc}}$	$\nu_{\text{exp}}$	$\nu_{\text{calc}}$	$I_{\text{calc}}$
$\nu_{49}$	110.4	105.4	0.6		96.0	2.5
$\nu_{48}$	142.0**	152.5	2.1		172.1	1.0
$\nu_{47}$	142.0**	165.8	3.7		173.8	0.3
$\nu_{46}$	191.4	196.3	1.0	177.4	192.4	7.4
$\nu_{45}$		275.5	0.8	202.6	229.0	1.0
$\nu_{44}$	327.6	289.4	2.4	302.9	297.6	0.5
$\nu_{43}$	376.1**	345.7	1.1	351.3	326.0	1.6
$\nu_{42}$	376.1**	352.2	1.1	373.9**	371.6	1.2
$\nu_{41}$		395.7	0.4	373.9**	392.0	1.4
$\nu_{40}$		440.7	0.9		470.3	0.0
$\nu_{39}$	422.8	492.8	5.3	474.4	470.4	1.4
$\nu_{38}$	520.9	533.3	3.2	574.2	522.9	1.5
$\nu_{37}$		577.4	0.2	631.8	588.0	2.4
$\nu_{36}$		649.5	5.0		639.8	0.5
r.m.s*		9.9			7.1	

\* For the frequencies:  $100 \times \sqrt{\sum_{i=1}^n \frac{1}{n} (\frac{\nu_{\text{exp},i} - \nu_{\text{calc},i}}{\nu_{\text{exp},i}})^2}$ .

\*\* Wavenumbers are doubly assigned when an unique observed vibrational band may be assigned to several vibrational modes with close wavenumbers.



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