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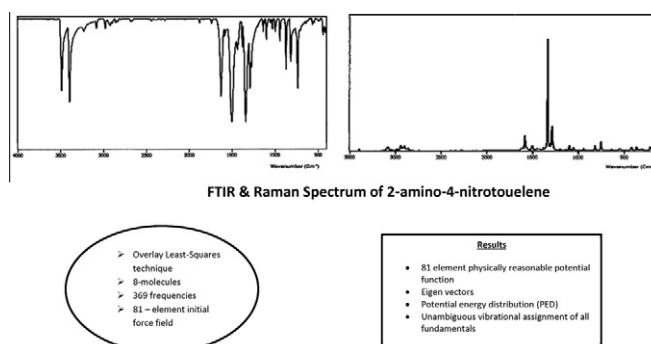
Vibrational analysis and valence force field for nitrotoluenes, dimethylanilines and some substituted methylbenzenes

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HIGHLIGHTS

- ▶ Four hundred and forty-four valence force constants for eight molecules are reduced to 81 using 369 frequencies.
- ▶ Vibrational assignment is made for all the fundamentals using eigen vectors and PED.
- ▶ The average error between observed and calculated frequencies is 13 cm^{-1} .
- ▶ Transferability of 81-element valence force field has been demonstrated for related molecules.
- ▶ The dispersions of force constants are small in these molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

The Fourier transform infrared (FTIR) and Raman spectra of 2-amino-4-nitrotoluene; 2-amino-5-nitrotoluene; 2,4-dimethylaniline; 2,5-dimethylaniline; 2,6-dimethylaniline; 1,2,4-trimethylbenzene; 1,3,5-trimethylbenzene and pentamethylbenzene have been recorded in the range $4000\text{--}400\text{ cm}^{-1}$ and $4000\text{--}30\text{ cm}^{-1}$, respectively. A normal coordinate analysis was carried out for both in-plane and out-of-plane vibrations of these molecules using an 81-parameter modified valence force field. The force constants were refined using 369 frequencies of eight molecules in the overlay least-squares technique. The reliability of the force constants was tested by making a zero-order calculation for both in-plane and out-of-plane vibrations for five related molecules. The potential energy distributions and eigen vectors calculated in the process were used to make unambiguous vibrational assignments of all the fundamentals.

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Introduction

Investigators in the field of molecular spectroscopy have been struggling hard to develop ‘a priori’ method of predicting vibra-

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tional frequencies of a given molecule. To this end two different and distinct approaches, namely theoretical and experimental, have been in the process of development. The theoretical approach comprises of ab initio computations refined to include density functional theory (DFT) [1–5]. However, the vibrational frequencies computed in this way are higher than the Corresponding observed frequencies, especially in the case of relatively large molecules. This overestimation is due to the use of finite basis set, incomplete implementation of the electronic correlation and

the neglect of anharmonicity effects in quantum mechanical methods used [6]. Because of this, ab initio force fields generally have to be scaled using spectroscopic data for getting better agreement between the observed and calculated frequencies. Pulay's method, which is the basis of scaled quantum mechanical (SQM) force field, that yields scale factors which are transferable between similar molecules, became very popular [7]. Yoshida et al. [8] introduced a method that is an improvement over the method of determining global scale factors for different levels of theory by a least squares fit of the calculated frequencies to the experimental frequencies. They found a linear relationship between the scale factor and the calculated frequencies. Sundius [9] modified his MOLVIB program that is capable of performing scale factor calculations according to several methods. The quantum chemistry community using DFT calculations incorporated into ab initio method, has shown that the computed vibrational spectra and their intensities (both infrared and Raman in some cases) of many organic molecules, agree reasonably well with experimental results on scaling [10–19].

The experimental approach uses the overlay technique wherein a set of related molecules are treated together to reduce the number of force constants [20]. The goal is to find a few hundred force constants capable of reproducing the spectra of a few thousand molecules [21]. Such a scheme was applied with success to *n*-paraffins [20], trans-decalin [22], *n*-alkyl chlorides [23], secondary chlorides [24,25], amides [26], nitriles [27], aliphatic ethers [28], aliphatic amines [29], a series of molecules containing C=O group [21], alkyl benzenes [30], benzene derivatives having unsaturated substituents [31,32], pyruvic acid [33], biomolecules and related systems [34–38], cyclohexane and related oxanes [39] and polymeric materials [40]. The modified (or selective) valence force field (MVFF or SVFF) used in the above investigations consists of all the diagonal (or principal) force constants and some near-neighbor interaction constants chosen by a judicious use of chemical intuition that can reasonably be expected to have chemical significance. The diagonal constants comprise the core of the valence force field. Attempts were made to gain insight into the physical meaning of these constants by making force constant–structure correlation plots. But such investigations are limited to a very few bonds. These are N–O [41,42], C–O [43,44], C–H, C–C, C–N, N–H, C–F, C–Cl, C–Br and C–I [42,44] bonds. These studies clearly demonstrate that the bond-stretching force constant is closely related to bond length. The interaction constants are unquestionably helpful in obtaining a better fit with experimental frequencies, which is similar to the role of scale factors used in quantum chemical methods. In simple molecules they have been discussed in terms of bond hybridization during the vibration by Thompson and Linnett [45]. Further, in linear triatomic molecules, an expression for bond–bond interaction constant was derived by the application of second order perturbation theory by Ken Ohwada [46]. Bond hybridization obviously is a relevant factor. But in large molecules other influences such as Van der Waals and electrostatic forces between nonbonded atoms must also be considered. Further, in complex molecules the number of interaction constants is artificially constrained by the imposition of a modified valence force field. In view of the above considerations Jones et al. [47] suggested to regard the interaction constants as semi-empirical parameters similar to those used in quantum chemistry calculations to improve the fit between calculated and observed electronic energy levels of molecules (e.g. Huckel and self-consistent field calculations).

However, it is very important to realize that the experimental approach is not a substitute for theoretical approach and vice versa. Because, the experimental approach aims at determining the barest possible minimum number of force constants of a common modified (or selective) valence force field for a set of related molecules, whereas the theoretical method determines the general

valence force field (GVFF) consisting of $n(n + 1)/2$ force constants (where *n* is the number of basis coordinates), which differs from molecule to molecule. A comparative study of philosophies of the two methods namely scaling the quantum mechanical molecular force field and philosophy of solving the inverse vibrational problem has been made [48]. As a result of these considerations, we have been engaged in the task of finding physically reasonable set of force constants for some representative molecules, employing overlay technique, that are transferable to related systems. We have already reported this type of work for aliphatic amides [49–51], monohalogenated nitrobenzenes [52], polyhalogenated anisoles [53], chlorinated nitrobenzenes [54], nitrosubstituted anilines, anisoles and anisidines [55–57], monohalogenated anisoles [58], monohalogenated benzonitriles [59], monohalogenated benzaldehydes [60], substituted phenols [61] and mononitro substituted benzamides, benzaldehydes and toluenes [62]. As a continuation of this general program of work, we have now investigated some substituted methylbenzenes. In this paper we report the results of our study on:

1. 2-amino-4-nitrotoluene (4NT),
2. 2-amino-5-nitrotoluene (5NT),
3. 2,4-dimethylaniline (4DMA),
4. 2,5-dimethylaniline (5DMA),
5. 2,6-dimethylaniline (6DMA),
6. 1,2,4-trimethylbenzene (4TMB),
7. 1,3,5-trimethylbenzene (5TMB) and
8. Pentamethylbenzene (PMB).

Vibrational frequencies of some of the above molecules were reported by several workers [63–66]. However, to the best of our knowledge, a systematic vibrational spectroscopic investigation of these molecules supported by normal coordinate analysis is yet to appear in literature.

Experimental

The compounds were purchased from Aldrich Chemical Company (USA). They have stated purity of about 97% and were used without further purification. At room temperature, all the samples except 4NT, 5NT and PMB are liquids. The FTIR spectra of these compounds were measured in the range 4000–400 cm^{-1} using Bruker IFS 66 V spectrometer with a scanning speed of 30 $\text{cm}^{-1} \text{min}^{-1}$ of spectral width 2.0 cm^{-1} . The FTIR spectra of solid samples were measured using KBr Pellet technique, whereas those of liquid samples were recorded as micro films of unknown thickness between two plates of KBr. The Raman spectra were recorded in the range 4000–30 cm^{-1} using FRA 106 Raman module equipped with Nd:YAG laser source operating at 200 mw power with spectral resolution of 2 cm^{-1} .

Normal coordinate analysis

Wilson's GF matrix method was used for the normal coordinate analysis [67]. A representative structure of the molecules is shown in Fig. 1. The amino group is assumed to be planar and coplanar with the plane of the aromatic nucleus. This is also the case with the nitro group. In the case of the methyl group, one of the hydrogen atoms is assumed to be in the plane of the benzene ring and the other two atoms are situated symmetrically about this plane, one above and the other below the plane. Thus, the symmetry of all molecules under investigation is C_s point group. C_s symmetry leads to two types of vibrations, namely a' (in-plane) and a'' (out-of-plane). It is seen that 51 fundamentals of each of aminonitrotoluenes fall into 34 in-plane fundamentals of a' species and 17 out-of-plane

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