On the Vibrational Interlacing Rule in Deuterated Thiophene: I. Out-of-plane Vibrations*

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Abstract. According to the interlacing rule, if **A** and **B**$_\tau$ are two molecules which differ by a single isotopic substitution at atomic site τ, vibrational frequencies of a molecule **A** are interlaced with the vibrational frequencies of molecule **B**$_\tau$. This rule is valid within the harmonic approximation, and in the case of planar molecules one has two interlacing rules, one for in-plane and another for out-of-plane frequencies. The validity of this rule is verified for theoretical and experimental out-of-plane frequencies of thiophene and deuterated thiophene molecules. This rule can help to analyze vibrational spectra, especially in assignments of experimental frequencies to various vibrational types.

Keywords: vibrational isotope effect, deuterated thiophenes, out-of-plane vibrations, interlacing rule, Low rank perturbation

INTRODUCTION

Vibrational spectra provide a large amount of information about a molecule.[1,2] An efficient study and analysis of experimental frequencies requires correct assignment of those frequencies to various vibrational types and normal modes. Besides vibrational spectra of the original molecule, there are also vibrational spectra of isotopically substituted molecules, which generate a huge amount of additional experimental data. Those data are important as a valuable source of information for the correct assignment and interpretation of experimental spectra. This assignment is highly facilitated by some simple rules which apply to vibrational frequencies of isotopically related molecules. One such rule is well known order rule.[3] If in a mechanical system that exhibits harmonic oscillations one increases the mass of one or few particles without changing the potential energy, the frequencies of normal vibrations do not increase. Those frequencies either decrease or remain the same.[3] In particular, if frequencies v_i of initial molecule **A** are arranged in the increasing order, and if frequencies ω_k of the heavier isotopic molecule **B** are also arranged in the increasing order, then[3]

$$\omega_1 \le v_1, \omega_2 \le v_2, \ldots, \omega_k \le v_k, \ldots \qquad (1)$$

Order rule involves all frequencies of such isotopic molecules **A** and **B** where all substituted isotopes in the molecule **B** are heavier than the corresponding isotopes in the molecule **A**.

Since the order rule is derived within the harmonic approximation, anharmonicity effects may violate this rule in some cases. Several studies beyond the harmonic approximation were done.[4] However, anharmonicity effects are usually small and experimental frequencies almost always satisfy this rule.

Order rule can be generalized to the so-called interlacing rule.[5] This rule is also derived within the harmonic approximation. Order rule limits each frequency ω_k of heavier isotopic molecules from above, while interlacing rule limits this frequency from both sides. Interlacing rule is hence much more restrictive then order rule and it is more efficient in facilitating frequency assignments of various isotopomers. In addition, in the case of planar molecules interlacing rule applies separately to out-of-plane and to in-plane vibrations.[5] Particularly simple is interlacing rule for out-of-plane vibrations of planar molecules.[5]

In this paper we will consider interlacing rule for theoretical and experimental out-of-plane frequencies of thiophene and deuterated thiophenes.

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INTERLACING RULE FOR OUT-OF-PLANE VIBRATIONS OF PLANAR MOLECULES

Rule 1 (Single isotopic substitution)[5]

Consider two *n*-atom planar molecules **A** and **B**$_\tau$ which differ by a single isotopic substitution at the site τ and let molecule **B**$_\tau$ be heavier than the molecule **A**. Let further v_i and ω_k be proper out-of-plane frequencies of molecules **A** and **B**$_\tau$, respectively. Arrange those frequencies in the nondecreasing order. Then, those two sets of frequencies are interlaced according to[5]

$$\omega_1 \le v_1 \le \omega_2 \le v_2 \le \dots \qquad (2)$$

Interlacing rule for single isotopic substitutions can be generalized to the case of multiple isotopic substitutions.[5]

Rule 2 (Multiple isotopic substitutions)

Consider two *n*-atom planar molecules **A** and **B** which differ by ρ isotopic substitutions. Let κ substituted isotopes be heavier in molecule **B** and let remaining $\rho - \kappa$ substituted isotopes be heavier in molecule **A**. Let further v_i be proper out-of-plane frequencies of molecule **A** arranged in nondecreasing order and let ω_k be proper out-of-plane frequencies of molecule **B** arranged in a nondecreasing order. Then these frequencies satisfy[6]

$$v_{i-\kappa} \le \omega_i \le v_{i+\rho-\kappa}, \ i = \kappa+1, \kappa+2, \dots \qquad (3)$$

In the case of single isotopic substitution when molecule **B** is heavier from molecule **A** one has $\rho = 1$ and $\kappa = 1$, and rule 2 reduces to rule 1.

Relations (2) and (3) imply order rule (1) which is thus a special case of interlacing rule. In addition, order rule applies only to such cases when all substituted isotopes in molecule **B** are heavier from the corresponding isotope in molecule **A**, while interlacing rule 2 applies to any possible combination of heavier and lighter isotopes in those two molecules. This is also true for a more general interlacing relations that apply to arbitrary (not necessarily planar) molecules.[5]

OUT-OF-PLANE VIBRATIONS OF THIOPHENE AND DEUTERATED THIOPHENE

Thiophene with the corresponding atom numbering is shown in Figure 1. There are 10 deuteration patterns for thiophene. The interlacing hierarchy of these isotopomers is shown in Figure 2. This hierarchy is an example of *partial ordering*.[7] Such partial orderings are usually investigated in order to see whether various properties are in consonance with those orderings.[7] One can make as many as 16 comparisons between various pairs of deuterated thiophenes that differ by a single isotopic
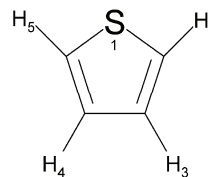

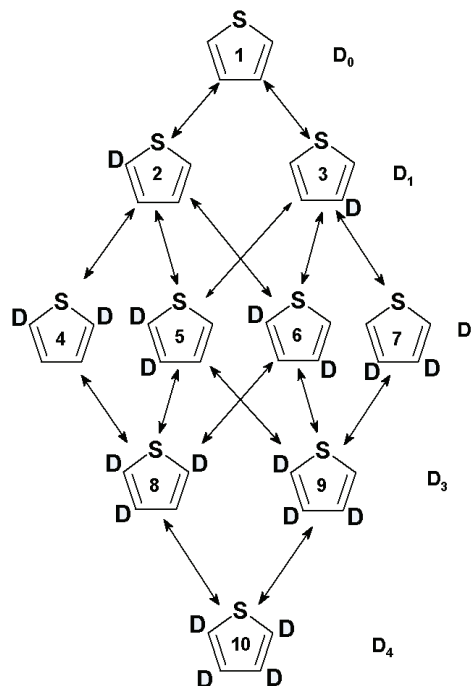**Figure 1.** Thiophene atom numbering.

Figure 2. Interlacing hierarchy of (H,D)-thiophene isotopomers.

substitution. Such pairs are in Figure 2 connected by an arrow. Frequencies of all such pairs should satisfy interlacing rule 1.

Each thiophene isotopomer has 9 atoms and hence 9 out-of-plane (*z*-direction) degrees of freedom. However, one combination of the out-of-plane displacements describes the translation in the *z*-direction and other two combinations describe rotations around in-plane *x*- and *y*-axes, respectively. Hence each thiophene isotopomer has $9 - 3 = 6$ out-of-plane vibrations.

INTERLACING RULE AND EXPERIMENTAL FREQUENCIES OF THIOPHENE (H,D)-ISOTOPOMERS

Experimental out-of-plane frequencies[8] of thiophene (H,D)-isotopomers are shown in Table 1. Using data in this table one finds that thiophene and two **D**$_1$-thiophenes frequencies satisfy (all frequencies are in cm^{-1}).

Table 1. Theoretical[a] and experimental[b] out-of-plane vibrational frequencies of thiophene and deuterated thiophenes (all frequencies in cm^{-1})

	1		2		3		4		5		6		7		8		9		10	
	d_0		2-d_1		3-d_1		2,5-d_2		2,3-d_2		2,4-d_2		3,4-d_2		2,3,5-d_3		2,3,4-d_3		d_4	
	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]	DFT[a]	Exp.[b]
1	447	452	429	433	441	446	415	419	425	427	427	427	438	442	413	416	424	427	411	414
2	569	565	550	533	517	516	522	528	510	511	509	504	489	488	508	504	489	486	489	484
3	674	683	569	567	649	645	569	566	554	553	552	561	588	587	522	531	530	531	522	531
4	716	712	701	701	678	685	584	584	666	668	649	645	667	671	580	579	610	614	534	531
5	866	867	839	839	801	800	820	819	744	744	783	786	774	775	709	711	739	738	680	684
6	906	898	902	896	886	882	893	887	885	882	865	861	810	811	865	860	786	788	753	750

[a] DFT scaled frequencies. B3LYP/6-31G** calculation[9]
[b] Experimental frequencies[8]

$$\begin{pmatrix} 433(2) \\ 446(3) \end{pmatrix}_1 < 452(1)_1 < \begin{pmatrix} 533(2) \\ 516(3) \end{pmatrix}_2 < 565(1)_2 <$$

$$\begin{pmatrix} 567(2) \\ 645(3) \end{pmatrix}_3 < 683(1)_3 < \begin{pmatrix} 701(2) \\ 685(3) \end{pmatrix}_4 < 712(1)_4 < \quad (4)$$

$$\begin{pmatrix} 839(2) \\ 800(3) \end{pmatrix}_5 < 867(1)_5 < \begin{pmatrix} 896(2) \\ 882(3) \end{pmatrix}_6 < 898(1)_6$$

In this expression symbols (1), (2) and (3) denote thiophene and deuterated **D$_1$**-thiophenes 2-C$_4$H$_3$DS and, 3-C$_4$H$_3$DS, respectively (see Figure 2). Subscripts 1 through 6 denote corresponding out-of-plane frequencies *i.e.* normal modes. As shown in this expression, all out-of-plane frequencies of those isotopomers satisfy interlacing rule.

Interlacing rule for isotopomer 2 (**D$_1$**-thiophene 2-C$_4$H$_3$DS) and three **D$_2$**-thiophenes is verified in the following expression

$$\begin{pmatrix} 419(4) \\ 427(5) \\ 427(6) \end{pmatrix}_1 < 433(2)_1 < \begin{pmatrix} 528(4) \\ 511(5) \\ 504(6) \end{pmatrix}_2 < 533(2)_2 <$$

$$\begin{pmatrix} 566(4) \\ 553(5) \\ 561(6) \end{pmatrix}_3 < 567(2)_3 < \begin{pmatrix} 584(4) \\ 668(5) \\ 645(6) \end{pmatrix}_4 < 701(2)_4 < \quad (5)$$

$$\begin{pmatrix} 819(4) \\ 744(5) \\ 786(6) \end{pmatrix}_5 < 839(2)_5 < \begin{pmatrix} 887(4) \\ 882(5) \\ 861(6) \end{pmatrix}_6 < 896(2)_6$$

Compound 4 is 2,5-C$_4$H$_2$D$_2$S, compound 5 is 2,3-C$_4$H$_2$D$_2$S, while compound 6 is 2,4-C$_4$H$_2$D$_2$S (see

Figure 2). Again, the interlacing rule is satisfied for all out-of-plane frequencies considered.

Comparison of the out-of-plane frequencies of the isotopomer 3 (**D$_1$**-thiophene 3-C$_4$H$_3$DS) with out-of-plane frequencies of three **D$_2$**-thiophenes is shown in the following expression

$$\begin{pmatrix} 442(7) \\ 427(5) \\ 427(6) \end{pmatrix}_1 < 446(3)_1 < \begin{pmatrix} 488(7) \\ 511(5) \\ 504(6) \end{pmatrix}_2 < 516(3)_2 <$$

$$\begin{pmatrix} 587(7) \\ 553(5) \\ 561(6) \end{pmatrix}_3 < 645(3)_3 \leq \begin{pmatrix} 671(7) \\ 668(5) \\ 645(6) \end{pmatrix}_4 < 685(3)_4 < \quad (6)$$

$$\begin{pmatrix} 775(7) \\ 744(5) \\ 786(6) \end{pmatrix}_5 < 800(3)_5 < \begin{pmatrix} 811(7) \\ 882(5) \\ 861(6) \end{pmatrix}_6 \leq 882(3)_6$$

Compound 7 is 3,4-C$_4$H$_3$DS, compound 5 is 2,3-C$_4$H$_3$DS and compound 6 is 2,4-C$_4$H$_3$DS.

Comparison of the out-of-plane frequencies of the isotopomer 8 (**D$_3$**-thiophene 2,3,5-C$_4$H$_1$D$_3$S) with out-of-plane frequencies of three **D$_2$**-thiophenes is shown in the expression (7)

$$416(8)_1 < \begin{pmatrix} 419(4) \\ 427(5) \\ 427(6) \end{pmatrix}_1 < 504(8)_2 \leq \begin{pmatrix} 528(4) \\ 511(5) \\ 504(6) \end{pmatrix}_2 <$$

$$531(8)_3 < \begin{pmatrix} 566(4) \\ 553(5) \\ 561(6) \end{pmatrix}_3 < 579(8)_4 < \begin{pmatrix} 584(4) \\ 668(5) \\ 645(6) \end{pmatrix}_4 < \quad (7)$$

$$711(8)_5 < \begin{pmatrix} 819(4) \\ 744(5) \\ 786(6) \end{pmatrix}_5 < 860(8)_6 < \begin{pmatrix} 887(4) \\ 882(5) \\ 861(6) \end{pmatrix}_6$$

Out-of-plane frequencies of the isotopomer 9 (**D₃**-thiophene 2,3,4-$C_4H_1D_3S$) are compared with out-of-plane frequencies of three **D₂**-thiophenes in the following expression

$$427(9)_1 \leq \begin{pmatrix} 442(7) \\ 427(5) \\ 427(6) \end{pmatrix}_1 < 486(9)_2 < \begin{pmatrix} 488(7) \\ 511(5) \\ 504(6) \end{pmatrix}_2 <$$

$$531(9)_3 < \begin{pmatrix} 587(7) \\ 553(5) \\ 561(6) \end{pmatrix}_3 < 614(9)_4 < \begin{pmatrix} 671(7) \\ 668(5) \\ 645(6) \end{pmatrix}_4 < \quad (8)$$

$$738(9)_5 < \begin{pmatrix} 775(7) \\ 744(5) \\ 786(6) \end{pmatrix}_5 < 788(9)_6 < \begin{pmatrix} 811(7) \\ 882(5) \\ 861(6) \end{pmatrix}_6$$

We finally compare out-of-plane frequencies of **D₄**-thiophene and **D₃**-thiophenes 2,3,5-$C_4H_1D_3S$ and 2,3,4-$C_4H_1D_3S$:

$$414(10)_1 < \begin{pmatrix} 427(9) \\ 416(8) \end{pmatrix}_1 < 484(10)_2 < \begin{pmatrix} 486(9) \\ 504(8) \end{pmatrix}_2 <$$

$$531(10)_3 \leq \begin{pmatrix} 531(9) \\ 531(8) \end{pmatrix}_3 \leq 531(10)_4 < \begin{pmatrix} 614(9) \\ 579(8) \end{pmatrix}_4 < \quad (9)$$

$$684(10)_5 < \begin{pmatrix} 738(9) \\ 711(8) \end{pmatrix}_5 < 750(10)_6 < \begin{pmatrix} 788(9) \\ 860(8) \end{pmatrix}_6$$

As shown in expressions (4)–(9), all experimental out-of-plane frequencies of deuterated thiophenes satisfy the basic interlacing rule 1. This automatically guaranties that the generalized interlacing rule 2 is also satisfied.

INTERLACING RULE AND SCALED THEORETICAL FREQUENCIES OF THIOPHENE (H,D)-ISOTOPOMERS

In addition to experimental frequencies, one has also theoretical frequencies. It is important to verify interlacing rule also for those theoretical frequencies. In particular, in the absence of experimental frequencies interlacing rule can be a valuable instrument for judging consistency and reliability of the theoretical model applied. Violation of interlacing rule by theoretically obtained frequencies usually indicates some inconsistency or inadequacy of the applied theoretical method.[6]

Theoretical DFT vibrational frequencies of thiophene isotopomers were calculated by A. A. El-Azhary and R. H. Hilal[9] (see Table 1). Those calculations were done using the Gaussian94 program under the C_{2v} sym-

metry constrain. Cartesian coordinate force fields were calculated at the corresponding optimized geometries at the B3LYP level of theory using 6-31G** basis set.[9] Cartesian coordinate force field was transferred to internal coordinate force field and harmonic vibrational frequencies were calculated using the program of Schachtschneider.[10] The internal coordinate force field was scaled using the equation[11,12]

$$F_{ij}^{scaled} = F_{ij}^{theo}(C_i C_j)^{1/2} \qquad (10)$$

where C_i and C_j are scale factors to internal coordinates q_i and q_j, respectivelly.[9] This scaling was done for the ten thiophene (H,D)-isotopomers with 8 scaling factors. Those factors were chosen in such a way as to minimize standard deviation between calculated and experimental frequencies.[9] Such multi-scaling method is used in order to improve the agreement between theoretical and experimental frequencies.[9,13]

Scaled thiophene and deuterated thiophene frequencies are also shown in Table 1. In the following expression are compared scaled frequencies of thiophene and two **D₁**-thiophenes

$$\begin{pmatrix} 429(2) \\ 441(3) \end{pmatrix}_1 < 447(1)_1 < \begin{pmatrix} 550(2) \\ 517(3) \end{pmatrix}_2 < 569(1)_2 \leq$$

$$\begin{pmatrix} 569(2) \\ 649(3) \end{pmatrix}_3 < 674(1)_3 < \begin{pmatrix} 701(2) \\ 678(3) \end{pmatrix}_4 < 716(1)_4 < \quad (11)$$

$$\begin{pmatrix} 839(2) \\ 801(3) \end{pmatrix}_5 < 866(1)_5 < \begin{pmatrix} 902(2) \\ 886(3) \end{pmatrix}_6 < 906(1)_6$$

There is no violation of the interlacing rule. Scaled out-of-plane frequencies of the isotopomer 2 (**D₁**-thiophene 2-C_4H_3DS) are compared with scaled out-of-plane frequencies of three **D₂**-thiophenes in the expression (12), while scaled out-of-plane frequencies of the isotopomer 3 (**D₁**-thiophene 3-C_4H_3DS) are compared with scaled out-of-plane frequencies of three **D₂**-thiophenes in the expression (13).

$$\begin{pmatrix} 415(4) \\ 425(5) \\ 427(6) \end{pmatrix}_1 < 429(2)_1 < \begin{pmatrix} 522(4) \\ 510(5) \\ 509(6) \end{pmatrix}_2 < 550(2)_2 <$$

$$\begin{pmatrix} 569(4) \\ 554(5) \\ 552(6) \end{pmatrix}_3 \leq 569(2)_3 < \begin{pmatrix} 584(4) \\ 666(5) \\ 649(6) \end{pmatrix}_4 < 701(2)_4 < \quad (12)$$

$$\begin{pmatrix} 820(4) \\ 744(5) \\ 783(6) \end{pmatrix}_5 < 839(2)_5 < \begin{pmatrix} 893(4) \\ 885(5) \\ 865(6) \end{pmatrix}_6 < 902(2)_6$$

$$\begin{pmatrix} 425(5) \\ 427(6) \\ 438(7) \end{pmatrix}_1 < 441(3)_1 < \begin{pmatrix} 510(5) \\ 509(6) \\ 489(7) \end{pmatrix}_2 < 517(3)_2 <$$

$$\begin{pmatrix} 554(5) \\ 552(6) \\ 588(7) \end{pmatrix}_3 < 649(3)_3 \leq \begin{pmatrix} 666(5) \\ 649(6) \\ 667(7) \end{pmatrix}_4 < 678(3)_4 < \quad (13)$$

$$\begin{pmatrix} 744(5) \\ 783(6) \\ 774(7) \end{pmatrix}_5 < 801(3)_5 < \begin{pmatrix} 885(5) \\ 865(6) \\ 810(7) \end{pmatrix}_6 < 886(3)_6$$

Scaled out-of-plane frequencies of the isotopomer 8 (**D$_3$**-thiophene 2,3,5-C$_4$H$_1$D$_3$S) are compared with scaled out-of-plane frequencies of three **D$_2$**-thiophenes in the following expression

$$413(8)_1 < \begin{pmatrix} 415(4) \\ 425(5) \\ 427(6) \end{pmatrix}_1 < 508(8)_2 < \begin{pmatrix} 522(4) \\ 510(5) \\ 509(6) \end{pmatrix}_2 \leq$$

$$522(8)_3 < \begin{pmatrix} 569(4) \\ 554(5) \\ 552(6) \end{pmatrix}_3 < 580(8)_4 < \begin{pmatrix} 584(4) \\ 666(5) \\ 649(6) \end{pmatrix}_4 < \quad (14)$$

$$709(8)_5 < \begin{pmatrix} 820(4) \\ 744(5) \\ 783(6) \end{pmatrix}_5 < 865(8)_6 \leq \begin{pmatrix} 893(4) \\ 885(5) \\ 865(6) \end{pmatrix}_6$$

Comparison of the scaled out-of-plane frequencies of the isotopomer 9 (**D$_3$**-thiophene 2,3,4-C$_4$H$_1$D$_3$S) with scaled out-of-plane frequencies of three **D$_2$**-thiophenes is shown in the expression (15)

$$424(9)_1 < \begin{pmatrix} 425(5) \\ 427(6) \\ 438(7) \end{pmatrix}_1 < 489(9)_2 \leq \begin{pmatrix} 510(5) \\ 509(6) \\ 489(7) \end{pmatrix}_2 <$$

$$530(9)_3 < \begin{pmatrix} 554(5) \\ 552(6) \\ 588(7) \end{pmatrix}_3 < 610(9)_4 < \begin{pmatrix} 666(5) \\ 649(6) \\ 667(7) \end{pmatrix}_4 < \quad (15)$$

$$739(9)_5 < \begin{pmatrix} 744(5) \\ 783(6) \\ 774(7) \end{pmatrix}_5 < 786(9)_6 < \begin{pmatrix} 885(5) \\ 865(6) \\ 810(7) \end{pmatrix}_6$$

Finally, scaled out-of-plane frequencies of **D$_4$**-tiophene are compared with two **D$_3$**-thiophenes (2,3,5-

C$_4$H$_1$D$_3$S) and 2,3,4-C$_4$H$_1$D$_3$S) in the following expression

$$411(10)_1 < \begin{pmatrix} 413(8) \\ 424(9) \end{pmatrix}_1 < 489(10)_2 \leq \begin{pmatrix} 508(8) \\ 489(9) \end{pmatrix}_2 <$$

$$522(10)_3 \leq \begin{pmatrix} 522(8) \\ 530(9) \end{pmatrix}_3 < 534(10)_4 < \begin{pmatrix} 580(8) \\ 610(9) \end{pmatrix}_4 < (16)$$

$$680(10)_5 < \begin{pmatrix} 709(8) \\ 739(9) \end{pmatrix}_5 < 753(10)_6 < \begin{pmatrix} 865(8) \\ 786(9) \end{pmatrix}_6$$

As shown above, all scaled out-of-plane frequencies of thiophene and deuterated thiophenes satisfy interlacing rule. Those scaled frequencies were obtained by scaling force field according to the expression (10). As illustrated above, theoretical frequencies obtained by scaling force field do not violate interlacing rule. Those frequencies are hence in accord with harmonic approximation.

Another scaling technique which is widely used in literature is frequency scaling.[13–15] In this approach scaled frequencies for various isotopomers are obtained using individual mode scaling factors, which optimize agreement between experimental and theoretical vibrational frequencies of the initial nondeuterated molecule.[13] Given sufficient scaling factors, vibrational frequencies of the initial nondeuterated molecule are exactly reproduced.[13] Since those factors accurately (or optimally) predict vibrational frequencies of the initial molecule, it is assumed that the same scaling factors will also improve vibrational frequencies of various isotopomers. This is a reasonable assumption. However, multiple frequency scaling may violate the interlacing rule. Each such violation indicates that those frequencies are not in accord with harmonic approximation and/or with the assumption that force field does not change upon isotopic substitutions. Such violations should be hence examined and considered with extreme care. In particular, scaled frequencies of benzene and deuterated benzenes[13] do not satisfy the interlacing rule.[6] This suggests that force field scaling is inherently more consistent with harmonicity assumption then frequency scaling.

CONCLUSION

According to the interlacing rule 1, out-of-plane vibrational frequencies of planar molecule **A** are interlaced with the corresponding frequencies of molecule **B$_\tau$** that differs from **A** by a single isotopic substitution at atomic site τ. In this paper, we verified the validity of this rule for out-of-plane frequencies of deuterated thiophenes.

Generalized interlacing rule (rule 2) is also satisfied, since it follows by iterative application of a basic interlacing rule 1. Both rules are derived under the assumption of the harmonic approximation and assuming that force field does not change upon isotopic substitutions. Those rules generalize well-known order rule.

There are 10 deuterated isotopomers of thiophene and each of those isotopomers has 6 out-of-plane vibrations. One can make as many as 16 direct "basic" comparisons of vibrational frequencies of these isotopomers. In all cases, experimental frequencies are in complete agreement with the interlacing rule. This is also true for theoretical DFT thiophene and deuterated thiophene frequencies which were obtained by multiple force field scaling. In general, anharmonicity effects may violate interlacing rule. However, those effects are relatively small, and each violation of the interlacing rule usually indicates either erroneous experimental data or erroneous assignment of experimental frequencies to various molecular vibrations. If, instead of force field scaling, one uses frequency scaling, violation of interlacing rule is quite likely. For example, in the case of the DFT scaled frequencies of benzene and deuterated benzene[13] there are several violations of this rule.[6] This suggests that, as far as scaling technique is considered, multiple force field scaling is preferable to multiple frequency scaling.

In general, interlacing rule can highly facilitate analysis of vibrational spectra and it can also help in assignments of experimental frequencies to various vibrational types. The agreement of experimental and theoretical DFT thiophene and deuterated thiophenes frequencies with the interlacing rule shows that those frequencies are consistent with the harmonicity assumption.

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SAŽETAK

O vibracijskom pravilu ispreplitanja kod deuteriranih tiofena: I. izvanravninske vibracije

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Prema pravilu učešljenja, ako su **A** i **B**$_\tau$ dvije molekule koje se razlikuju samo u jednoj izotopnoj substituciji na atomu τ, vibracijske frekvencije molekule **A** su učešljane s vibracijskim frekvencijama molekule **B**$_\tau$. To pravilo vrijedi unutar harmonijske aproksimacije i u slučaju planarnih molekula imamo dva pravila učešljenja, jedno koje vrijedi za unutar-ravninske, a drugo koje vrijedi za izvan-ravninske vibracije. To pravilo je provjereno za teorijske kao i za eksperimentalne izvan-ravninske frekvencije tiofena i deuteriranih tiofena. Pravilo učešljenja može pomoći pri analizi vibracijskih spektara, napose kod asignacije pojedinih eksperimentalnih frekvencija raznim vibracijskim modovima.