

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

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If **A** and **B**_τ are two molecules that differ by a single isotopic substitution then in the harmonic approximation vibrational frequencies of molecule **A** are interlaced with vibrational frequencies of molecule **B**_τ. This interlacing rule is a generalization of the well-known order rule. In the case of planar molecules, the interlacing rule applies separately to in-plane and to out-of-plane vibrations. This rule is particularly simple in the case of out-of-plane vibrations. The validity of the interlacing rule is verified for benzene and deuterated benzene molecules. Violation of this rule indicates (very unlikely) strong anharmonicity effects, or (more likely) erroneous vibrational assignments and/or erroneous experimental data. Hence this rule can help to analyze vibrational spectra, in particular in the assignments of experimental frequencies to various vibrational types.

INTRODUCTION

Vibrational spectra are quite important in the study and analysis of molecular properties.^{1,2} These spectra contain a large amount of information on molecular electronic structure, geometry, charge distribution, *etc.*^{1,2} Numerical methods were developed that enable calculation of frequencies and normal modes of molecular systems containing as many as several hundred atoms.³ Besides vibrational spectra of the original molecule, there are also vibrational spectra of isotopically substituted molecules that generate extensive additional experimental data. Those data provide important information for the construction of the associated force field.¹ They are also important as an additional source of information for the correct assignment and interpretation of experimental data. Without the correct assignment of experimental frequencies to various vibrational types and normal mo-

des, an efficient study and analysis of experimental frequencies is not possible. Therefore it is quite useful to have simple rules relating vibrational frequencies of molecules that differ by single or multiple isotopic substitutions. Such rules can highly facilitate and improve assignment and interpretation of experimental data.

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.⁴ These frequencies either decrease or remain the same. In particular, if frequencies ω_i of the initial molecule **A** are arranged in increasing order, and if frequencies ω'_k of the heavier isotopic molecule **B** are also arranged in the increasing order, then⁴

$$\omega'_1 \leq \omega_1, \omega'_2 \leq \omega_2, \dots, \omega'_k \leq \omega_k, \dots \quad (1a)$$

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

In addition, those frequencies satisfy⁴

$$\frac{\omega_i}{\omega'_i} \leq \sqrt{\frac{m'}{m}} \quad (1b)$$

where m and m' are the masses of the lighter and heavier isotopes, respectively. In particular, in the case when hydrogen is substituted with deuterium one has

$$\frac{\omega_i}{\omega'_i} \leq \sqrt{\frac{m_D}{m_H}} = 1.414 \quad (1c)$$

Relations (1) are known as order rule.⁴ This rule applies to such pairs of isotopic molecules **A** and **B** where all substituted isotopes in the molecule **B** are heavier than the corresponding isotopes in the molecule **A**. The order rule is derived within the harmonic approximation.¹ Hence it is possible that anharmonicity effects might in some cases invalidate this rule. Several studies beyond the harmonic approximation have been done.⁵ However, anharmonicity effects are usually small. Hence experimental frequencies almost always satisfy this rule.

Besides the order rule, there are some additional rules that relate vibrational frequencies of molecules **A** and **B**. Best known are Teller-Redlich product rules and various sum rules.⁴ There are also some rules which apply only to restricted molecular types such as molecules of a type XY_n ($n = 2, 3, 4$) etc.⁴ All those additional rules are also derived within the harmonic approximation.⁴ From a practical point of view the order rule is the most important, especially in the case when the number of atoms in a molecule is relatively large. Thus if a nonlinear molecule contains n atoms, it has as many as $3n - 5$ vibrations. Accordingly, expression (1a) contains as many as $3n - 5$ inequalities while each additional rule (such as the product rule, sum rule, etc.) contains only one or at best only a few such inequalities. Therefore as n increases relative importance of order rule increases.

Expression (1a) limits each frequency ω'_k of the heavier isotopomer from above, while expression (1b) limits this frequency from below. Thus the order rule limits each frequency ω'_k from above as well as from below. However expression (1b) is in practical applications not so useful. This is especially true for deuterium substitutions when (1b) reduces to (1c) with a rather large factor 1.414. In almost all cases the isotopic shift $\omega_k \rightarrow \omega'_k$ is rather small, certainly much smaller than the shift limited by the factor 1.414. In addition, as n increases frequencies ω'_k as well as frequencies ω_k tend to be closer to each other, which further decreases the utility of the expression (1b). Therefore, the practical significance of the order rule is essentially contained in the expression (1a).

The order rule can be generalized to the so-called interlacing rule.⁶ This rule is also derived within the harmonic approximation and it also limits each frequency

ω'_k from above as well as from below. However, lower limits imposed by the interlacing rule are much stronger than lower limits imposed by the expression (1b) of the order rule. This significantly increases utility of the interlacing rule. In addition and unlike the order rule, the interlacing rule is not restricted to those cases when all isotopes substituted in molecule **B** are heavier from the corresponding isotopes in the original molecule **A**. In particular, this rule allows for any combination of heavier and lighter isotopic substitutions. Further, in the case of linear molecules the interlacing rule applies separately to stretching and bending vibrations, while in the case of planar molecules it applies separately to out-of-plane and to in-plane vibrations.⁶ Particularly simple is interlacing rule for linear molecules and for out-of-plane vibrations of planar molecules.⁶ We will first consider the interlacing rule for out-of-plane vibrations of planar molecules in the case when molecules **A** and **B_τ** differ by a single isotopic substitution at atomic site τ . This basic interlacing rule can be easily generalized to the interlacing rule valid in the case of arbitrary multiple isotopic substitutions. Similar rules apply to in-plane vibrations of planar molecules.⁶ Interlacing rules for those in-plane vibrations will be considered elsewhere.⁷

The validity of the interlacing rule will be verified with benzene and deuterated benzene molecules. Since experimental frequencies are not available for all benzene isotopomers, we will first apply the interlacing rule to theoretical frequencies. In particular, theoretical frequencies obtained within the B3LYP/6-31G(d,p) calculations⁸ will be considered. We will also apply the interlacing rule to some available experimental frequencies.⁴

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

In the case of planar molecules there are two basic interlacing rules.⁶ One rule applies to out-of-plane vibrations and another to in-plane vibrations of such molecules. In both cases one compares corresponding frequencies of two n -atom planar molecules **A** and **B_τ** which differ by a single isotopic substitution at atomic site τ . Without loss of generality one can assume that the molecule **B_τ** is heavier than molecule **A**. In this case one has:

Interlacing Rule for Out-of-plane Vibrations of Planar Molecules (Single Isotopic Substitution)

Let ω_i and ω'_k be proper out-of-plane frequencies of molecules **A** and **B_τ**, respectively. Arrange frequencies ω_i as well as frequencies ω'_k in nondecreasing order. Then, those two sets of frequencies are interlaced according to⁶

$$\omega'_1 \leq \omega_1 \leq \omega'_2 \leq \omega_2 \leq \omega'_3 \leq \omega_3 \leq \dots \quad (2a)$$

This rule is identical to the basic interlacing rule of stretching (bending) frequencies of linear molecules.⁶

Rule (2a) applies to molecules **A** and **B_τ** that differ by a single isotopic substitution. By iterative application of this rule one can derive a more general rule that applies to molecules **A** and **B** which differ by multiple isotopic substitutions. One thus finds:

Generalized Interlacing Rule for Out-of-plane Vibrations of Planar Molecule, Multiple Isotopic Substitutions

Consider planar molecules **A** and **B** that differ by *k* isotopic substitutions. Let *k_a* substituted isotopes be heavier in molecule **B** and let *k_b* substituted isotopes be heavier in molecule **A** (*k* = *k_a* + *k_b*). Let further ω_i be proper out-of-plane frequencies of molecule **A** arranged in a nondecreasing order and let ω'_k be proper out-of-plane frequencies of molecule **B** arranged in a nondecreasing order. Then these frequencies satisfy

$$\omega_{i-k_a} \leq \omega'_i \leq \omega_{i-k_b} \quad i = 1, 2, \dots \quad (2b)$$

In the case *k_a* = *k* = 1 this rule reduces to the basic interlacing rule (2a) for a single isotopic substitution.

Note that order rule (1) applies only to those cases when all isotopes in one isotopomer are heavier from the corresponding isotopes in another isotopomer. Generalized interlacing rule (2b) has no such limitation since each isotope in a molecule **B** can be either heavier or lighter from the corresponding isotope in molecule **A**.

OUT-OF-PLANE VIBRATIONS OF BENZENE AND DEUTERATED BENZENES

There are 13 deuteration patterns for benzene. The interlacing hierarchy of these isotopomers is shown in Figure 1. For example, **D1** deuterated benzene (compound 2 in Figure 1) differs by a single isotopic substitution from ortho-, meta-, and para-**D2** deuterated benzenes (compounds 3, 4 and 5 in Figure 1, respectively). One can make as many as 20 comparisons between various pairs of deuterated benzenes that differ by a single isotopic substitution. Interlacing hierarchy shown in Figure 1. is an example of *partial ordering*.^{9,10} Such partial orderings are usually investigated in order to see whether various properties are in consonance with those orderings.^{9,10}

Since benzene has 12 atoms there are 12 out-of-plane (*z*-direction) degrees of freedom. One combination of the out-of-plane displacements describes the translation in the *z*-direction, while two other combinations describe rotations around *x*- and *y*-axes, respectively. Hence each benzene isotopomer has 12 – 3 = 9 out-of-plane vibrations.

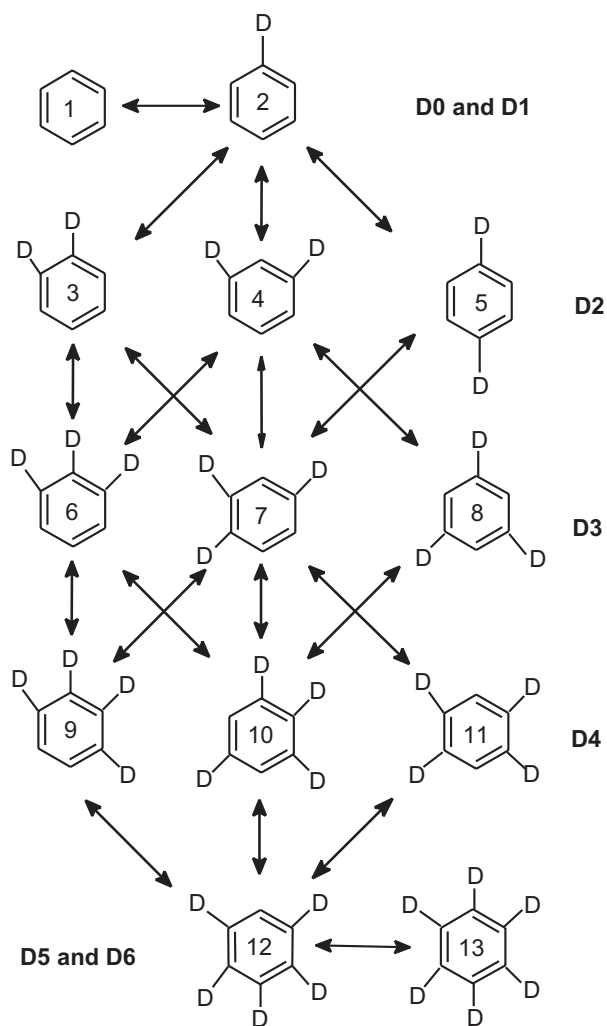


Figure 1. Interlacing hierarchy of 13 benzene isotopomers.

INTERLACING RULE AND B3LYP/6-31G(d,p) THEORETICAL OUT-OF-PLANE FREQUENCIES OF BENZENE ISOTOPOMERS⁸

In order to verify the interlacing rule for out-of-plane vibrations of benzene isotopomers we first consider the theoretical calculation done by Wu and Cremer.⁸ Those authors derived out-of-plane as well as in-plane vibrational frequencies for all benzene isotopomers using the program package COLOGNE 2002.¹¹ This is a rather sophisticated calculation that utilizes density functional theory (DFT) with the hybrid functional B3LYP and with Pople's 6-31G(d,p) basis set.^{8,11} Out-of-plane frequencies for benzene and deuterated benzenes obtained in this way are shown in Table I. Using this table one can verify the validity of the interlacing rule (2a) for those frequencies.

The comparison of benzene and **D1** deuterated benzene is shown in the expression (3) (All frequencies are in cm⁻¹).

Table I. Frequencies of the out-of-plane vibrations of 13 benzene isotopomers (a)

1	2	3	4	5	6	7	8	9	10	11	12	13
C_6H_6 D_{6h}	C_6DH_5 C_{2v}	$1,2-C_6D_2H_4$ C_{2v}	$1,3-C_6D_2H_4$ C_{2v}	$1,4-C_6D_2H_4$ D_{2h}	$1,2,3-C_6D_3H_3$ C_{2v}	$1,2,4-C_6D_3H_3$ C_s	$C_6(DH)_3$ D_{3h}	$1,2,3,4-C_6D_4H_2$ C_{2v}	$1,2,3,5-C_6D_4H_2$ C_{2v}	$1,2,4,5-C_6D_4H_2$ D_{2h}	C_6D_5H C_{2v}	C_6D_6 D_{6h}
1	414 e_{2u} 393 b_2	384 a_2 403 b_2	386 a_2 402 b_2	374 b_{1u} 414 a_u	383 b_2 386 a_2	370 a'' 400 a''	386 e'' 386 e''	368 b_2 384 a_2	368 b_2 386 a_2	361 a_u 390 b_{1u}	361 a_2 376 b_2	361 e_{2u} 361 e_{2u}
2	414 e_{2u}	403 b_2	402 b_2	414 a_u	386 a_2	400 a''	386 e''	384 a_2	386 a_2	390 b_{1u}	376 b_2	361 e_{2u}
3	694 a_{2u}	622 b_2	591 b_2	582 b_2	558 b_2	573 a''	545 a_2''	544 b_2	537 b_2	560 b_{1u}	526 b_2	509 a_{2u}
4	718 b_{2g}	714 b_2	676 a_2	648 b_{3g}	670 b_2	647 a'	714 a_2''	640 a_2	646 b_2	631 b_{3g}	628 b_2	615 b_{2g}
5	865 e_{1g}	792 b_2	782 a_2	750 b_{3g}	719 a_2	718 a''	719 e''	698 a_2	718 b_2	673 b_{2g}	673 a_2	673 e_{1g}
6	865 e_{1g}	865 a_2	797 b_2	865 b_{2g}	790 b_2	782 a''	719 e''	746 b_2	719 a_2	779 b_{3g}	719 b_2	673 e_{1g}
7	974 e_{2u}	934 b_2	900 a_2	879 b_{1u}	840 b_2	873 a''	934 e''	822 a_2	810 b_2	791 a_u	791 a_2	791 e_{2u}
8	974 e_{2u}	974 a_2	960 b_2	974 a_u	934 a_2	934 a''	934 e''	873 b_2	934 a_2	931 b_{1u}	825 b_2	791 e_{2u}
9	1013 b_{2g}	1003 b_2	998 a_2	978 b_{3g}	991 b_2	976 a'	934 a_2''	976 a_2	934 b_2	936 b_{3g}	934 b_2	837 b_{2g}

(a) Unscaled frequencies in cm^{-1} . B3LYP/6-31G(d,p) calculations.⁸Table II. Scaled frequencies of the out-of-plane vibrations of 13 benzene isotopomers⁸

1	2	3	4	5	6	7	8	9	10	11	12	13
C_6H_6 D_{6h}	C_6DH_5 C_{2v}	$1,2-C_6D_2H_4$ C_{2v}	$1,3-C_6D_2H_4$ C_{2v}	$1,4-C_6D_2H_4$ D_{2h}	$1,2,3-C_6D_3H_3$ C_{2v}	$1,2,4-C_6D_3H_3$ C_s	$C_6(DH)_3$ D_{3h}	$1,2,3,4-C_6D_4H_2$ C_{2v}	$1,2,3,5-C_6D_4H_2$ C_{2v}	$1,2,4,5-C_6D_4H_2$ D_{2h}	C_6D_5H C_{2v}	C_6D_6 D_{6h}
1	398 e_{2u} 378 b_2	369 a_2 387 b_2	371 a_2 386 b_2	360 b_{1u} 398 a_u	379 b_2 382 a_2	356 a'' 385 a''	371 e'' 371 e''	354 b_2 369 a_2	354 b_2 371 a_2	347 a_u 375 b_{1u}	347 a_2 363 b_2	347 e_{2u} 347 e_{2u}
2	398 e_{2u}	387 b_2	386 b_2	398 a_u	382 a_2	385 a''	371 e''	369 a_2	371 a_2	375 b_{1u}	363 b_2	347 e_{2u}
3	673 a_{2u}	603 b_2	573 b_2	592 b_{1u}	541 b_2	556 a''	528 a_2''	528 b_2	521 b_2	582 b_{1u}	510 b_2	494 a_{2u}
4	707 b_{2g}	703 b_2	666 a_2	638 b_{3g}	656 b_2	637 a'	703 a_2''	630 a_2	636 b_2	621 b_{3g}	618 b_2	606 b_{2g}
5	846 e_{1g}	775 b_2	765 a_2	734 b_{3g}	706 a_2	702 a''	703 e''	683 a_2	702 b_2	658 b_{2g}	658 a_2	658 e_{1g}
6	846 e_{1g}	846 a_2	812 b_2	846 b_{2g}	775 b_2	765 a''	703 e''	730 b_2	703 a_2	762 b_{3g}	703 b_2	658 e_{1g}
7	967 e_{2u}	927 b_2	894 a_2	873 b_{1u}	841 b_2	867 a''	913 a_2''	816 a_2	804 b_2	785 a_u	785 a_2	785 e_{2u}
8	967 e_{2u}	967 a_2	927 b_2	956 b_{3g}	935 a_2	927 a''	927 e''	867 b_2	913 b_2	915 b_{3g}	819 b_2	785 e_{2u}
9	990 b_{2g}	980 b_2	975 a_2	967 a_u	973 b_2	954 a'	927 e''	954 a_2	927 a_2	924 b_{1u}	913 b_2	818 b_{2g}

$$\begin{aligned}
 &393(2)_1 < 414(1)_1 \leq 414(2)_2 \leq 414(1)_2 < 622(2)_3 < 694(1)_3 < \\
 &714(2)_4 < 718(1)_4 < 792(2)_5 < 865(1)_5 \leq 865(2)_6 \leq 865(1)_6 < \quad (3) \\
 &934(2)_7 < 974(1)_7 \leq 974(2)_8 \leq 974(1)_8 < 1003(2)_9 < 1013(1)_9
 \end{aligned}$$

In this expression symbols (1) and (2) denotes benzene (C_6H_6) and deuterated **D1**-benzene (C_6H_5D), respectively (see Figure 1). Subscripts 1 through 9 denote corresponding out-of-plane frequencies. Due to high symmetry, benzene has several pairs of degenerate frequencies. There is double degenerate e_{2u} vibration with frequency 414 cm^{-1} , double degenerate e_{1g} vibration with frequency 865 cm^{-1} and double degenerate e_{2u} vibration with frequency 974 cm^{-1} .^{4,8} As shown above, all out-of-plane frequencies, including those degenerate frequencies satisfy interlacing rule.

Interlacing rule for **D1** deuterated benzene and three **D2** deuterated benzenes is verified in the expression (4)

$$\begin{aligned}
 &\begin{pmatrix} 384(3) \\ 386(4) \\ 374(5) \end{pmatrix}_1 < 393(2)_1 < \begin{pmatrix} 403(3) \\ 402(4) \\ 414(5) \end{pmatrix}_2 \leq 414(2)_2 < \begin{pmatrix} 591(3) \\ 582(4) \\ 611(5) \end{pmatrix}_3 < 622(2)_3 < \\
 &\begin{pmatrix} 676(3) \\ 714(4) \\ 648(5) \end{pmatrix}_4 \leq 714(2)_4 < \begin{pmatrix} 782(3) \\ 719(4) \\ 750(5) \end{pmatrix}_5 < 792(2)_5 < \begin{pmatrix} 797(3) \\ 830(4) \\ 865(5) \end{pmatrix}_6 \leq 865(2)_6 < \quad (4) \\
 &\begin{pmatrix} 900(3) \\ 934(4) \\ 879(5) \end{pmatrix}_7 \leq 934(2)_7 \leq \begin{pmatrix} 960(3) \\ 934(4) \\ 974(5) \end{pmatrix}_8 \leq 974(2)_8 < \begin{pmatrix} 998(3) \\ 991(4) \\ 978(5) \end{pmatrix}_9 < 1003(2)_9
 \end{aligned}$$

Compound 3 is 1,2- $C_6D_2H_4$, compound 4 is 1,3- $C_6D_2H_4$, while compound 5 is 1,4- $C_6D_2H_4$ (see Figure 1). Again, the interlacing rule is satisfied for all out-of-plane frequencies and in the case of all those isotopomers.

Comparison of the out-of-plane frequencies of the isotopomer 7 (**D3**-deuterated benzene 1,2,4- $C_6D_3H_3$) with out-of-plane frequencies of three **D4**-deuterated benzenes is shown in the expression (5), while comparison of out-of-plane frequencies of isotopomer 7 with three **D2**-deuterated benzenes is shown in the expression (6)

$$\begin{aligned}
 &\begin{pmatrix} 368(9) \\ 368(10) \\ 361(11) \end{pmatrix}_1 < 370(7)_1 < \begin{pmatrix} 384(9) \\ 386(10) \\ 390(11) \end{pmatrix}_2 < 400(7)_2 < \begin{pmatrix} 544(9) \\ 537(10) \\ 560(11) \end{pmatrix}_3 < 573(7)_3 < \\
 &\begin{pmatrix} 640(9) \\ 646(10) \\ 631(11) \end{pmatrix}_4 < 647(7)_4 < \begin{pmatrix} 698(9) \\ 718(10) \\ 673(11) \end{pmatrix}_5 \leq 718(7)_5 < \begin{pmatrix} 746(9) \\ 719(10) \\ 779(11) \end{pmatrix}_6 < 782(7)_6 < \quad (5) \\
 &\begin{pmatrix} 822(9) \\ 810(10) \\ 791(11) \end{pmatrix}_7 < 873(7)_7 \leq \begin{pmatrix} 873(9) \\ 934(10) \\ 931(11) \end{pmatrix}_8 \leq 934(7)_8 \leq \begin{pmatrix} 976(9) \\ 934(10) \\ 936(11) \end{pmatrix}_9 \leq 976(7)_9
 \end{aligned}$$

$$\begin{aligned}
 &370(7)_1 < \begin{pmatrix} 384(3) \\ 386(4) \\ 374(5) \end{pmatrix}_1 < 400(7)_2 < \begin{pmatrix} 403(3) \\ 402(4) \\ 414(5) \end{pmatrix}_2 < 573(7)_3 < \begin{pmatrix} 591(3) \\ 582(4) \\ 611(5) \end{pmatrix}_3 < \\
 &647(7)_4 < \begin{pmatrix} 676(3) \\ 714(4) \\ 648(5) \end{pmatrix}_4 < 718(7)_5 < \begin{pmatrix} 782(3) \\ 719(4) \\ 750(5) \end{pmatrix}_5 \leq 782(7)_6 < \begin{pmatrix} 797(3) \\ 830(4) \\ 865(5) \end{pmatrix}_6 < \quad (6) \\
 &873(7)_7 < \begin{pmatrix} 900(3) \\ 934(4) \\ 879(5) \end{pmatrix}_7 \leq 934(7)_8 \leq \begin{pmatrix} 960(3) \\ 934(4) \\ 974(5) \end{pmatrix}_8 < 976(7)_9 < \begin{pmatrix} 998(3) \\ 991(4) \\ 978(5) \end{pmatrix}_9
 \end{aligned}$$

Comparison of the out-of-plane frequencies of three **D4**-deuterated benzenes 9, 10 and 11 with **D5**-deuterated benzene 12 is shown in the expression (7), while the comparison of the out-of-plane frequencies of **D5**-deuterated benzene 12 with the out-of-plane frequencies of **D6**-deuterated benzene (13) is shown in the expression (8).

$$\begin{aligned}
 &361(12)_1 \leq \begin{pmatrix} 368(9) \\ 368(10) \\ 361(11) \end{pmatrix}_1 < 376(12)_2 < \begin{pmatrix} 384(9) \\ 386(10) \\ 390(11) \end{pmatrix}_2 < 526(12)_3 < \begin{pmatrix} 544(9) \\ 537(10) \\ 660(11) \end{pmatrix}_3 < \\
 &628(12)_4 < \begin{pmatrix} 640(9) \\ 646(10) \\ 631(11) \end{pmatrix}_4 < 673(12)_5 \leq \begin{pmatrix} 698(9) \\ 718(10) \\ 673(11) \end{pmatrix}_5 < 719(12)_6 \leq \begin{pmatrix} 746(9) \\ 719(10) \\ 779(11) \end{pmatrix}_6 < (7) \\
 &791(12)_7 \leq \begin{pmatrix} 822(9) \\ 810(10) \\ 791(11) \end{pmatrix}_7 < 825(12)_8 < \begin{pmatrix} 873(9) \\ 934(10) \\ 931(11) \end{pmatrix}_8 \leq 934(12)_9 \leq \begin{pmatrix} 976(9) \\ 934(10) \\ 936(11) \end{pmatrix}_9
 \end{aligned}$$

$$\begin{aligned}
 &361(13)_1 \leq 361(12)_1 \leq 361(13)_2 < 376(12)_2 < 509(13)_3 < 526(12)_3 < \\
 &615(13)_4 < 628(12)_4 < 673(13)_5 \leq 673(12)_5 \leq 673(13)_6 < 719(12)_6 < (8) \\
 &791(13)_7 \leq 791(12)_7 \leq 791(13)_8 < 825(12)_8 < 837(13)_9 < 934(12)_9
 \end{aligned}$$

This completes the comparison of out-of-plane frequencies of 14 pairs of deuterated benzenes. It remains to make 6 additional comparisons.

In the expression (9) comparison is made of the out-of-plane frequencies of **D2**-deuterated benzene 4, with two **D3**-deuterated benzenes 6 and 8:

$$\begin{aligned}
 &\begin{pmatrix} 383(6) \\ 386(8) \end{pmatrix}_1 \leq 386(4)_1 \leq \begin{pmatrix} 386(6) \\ 386(8) \end{pmatrix}_2 < 402(4)_2 < \begin{pmatrix} 558(6) \\ 545(8) \end{pmatrix}_3 < 582(4)_3 < \\
 &\begin{pmatrix} 670(6) \\ 714(8) \end{pmatrix}_4 \leq 714(4)_4 < \begin{pmatrix} 719(6) \\ 719(8) \end{pmatrix}_5 \leq 719(4)_5 \leq \begin{pmatrix} 790(6) \\ 719(8) \end{pmatrix}_6 < 830(4)_6 < \quad (9) \\
 &\begin{pmatrix} 840(6) \\ 934(8) \end{pmatrix}_7 \leq 934(4)_7 \leq \begin{pmatrix} 934(6) \\ 934(8) \end{pmatrix}_8 \leq 934(4)_8 \leq \begin{pmatrix} 991(6) \\ 934(9) \end{pmatrix}_9 \leq 991(4)_9
 \end{aligned}$$

while in the expression (10) comparison is made of the out-of-plane frequencies of **D4**-deuterated benzene 10 with two **D3**-deuterated benzenes 6 and 8:

$$368(10)_1 < \left(\begin{matrix} 383(6) \\ 386(8) \end{matrix} \right)_1 \leq 386(10)_2 \leq \left(\begin{matrix} 386(6) \\ 386(8) \end{matrix} \right)_2 < 537(10)_3 < \left(\begin{matrix} 558(6) \\ 545(8) \end{matrix} \right)_3 < \\ 646(10)_4 < \left(\begin{matrix} 670(6) \\ 714(8) \end{matrix} \right)_4 < 718(10)_5 < \left(\begin{matrix} 719(6) \\ 719(6) \end{matrix} \right)_5 \leq 719(10)_6 \leq \left(\begin{matrix} 790(6) \\ 719(8) \end{matrix} \right)_6 < \quad (10) \\ 810(10)_7 < \left(\begin{matrix} 840(6) \\ 934(8) \end{matrix} \right)_7 \leq 934(10)_8 \leq \left(\begin{matrix} 934(6) \\ 934(8) \end{matrix} \right)_8 \leq 934(10)_9 \leq \left(\begin{matrix} 991(6) \\ 934(8) \end{matrix} \right)_9$$

In the next expression are given two remaining comparisons, **D2**-compound 3 versus **D3**-compound 6 (expression (11a)) and **D3** compound 6 versus **D4** compound 9 (expression (11b)):

$$383(6)_1 < 384(3)_1 < 386(6)_2 < 403(3)_2 < 558(6)_3 < 591(3)_3 < \\ 670(6)_4 < 676(3)_4 < 719(6)_5 < 782(3)_5 < 790(6)_6 < 797(3)_6 < \quad (11a) \\ 840(6)_7 < 900(3)_7 < 934(6)_8 < 960(3)_8 < 991(6)_9 < 998(3)_9$$

$$368(9)_1 < 383(6)_1 < 384(9)_2 < 386(6)_2 < 544(9)_3 < 558(6)_3 < \\ 640(9)_4 < 670(6)_4 < 698(9)_5 < 719(6)_5 < 748(9)_6 < 790(6)_6 < \quad (11b) \\ 822(9)_7 < 840(6)_7 < 873(9)_8 < 934(6)_8 < 976(9)_9 < 991(6)_9$$

As shown in expressions (3)–(11), all theoretical frequencies from Table I satisfy the basic interlacing rule (2a). This automatically guarantees that the generalized interlacing rule (2b) is also satisfied.

INTERLACING RULE AND SCALED THEORETICAL FREQUENCIES OF BENZENE ISOTOPOMERS

Besides the frequencies given in Table I, Wu and Cremer report also scaled frequencies for benzene isotopomers.⁸ Those frequencies are obtained using individual mode scaling factors, which accurately reproduce experimental vibrational frequencies of benzene. It is assumed that, since those scaling factors exactly reproduce vibrational frequencies of benzene, the same scaling factors should also more accurately predict vibrational frequencies of benzene isotopomers. This is a reasonable assumption. However, this scaling technique may in some cases violate the interlacing rule. A violation of this rule may occur only if the anharmonicity effects are significant. Therefore this scaling procedure should be applied with extreme caution.

Scaled out-of-plane frequencies of benzene isotopomers are shown in Table II. Most of those frequencies satisfy interlacing rule. We will consider here only those cases when scaled frequencies violate the interlacing rule.

If one compares scaled frequencies of isotopomer 7 with scaled frequencies of isotopomer 4, one finds

$$356(7)_1 < 371(4)_1 < 385(7)_2 < 386(4)_2 < 556(7)_3 < 564(4)_3 < \\ 637(7)_4 < 703(4)_4 ? 702(7)_5 < 703(4)_5 < 765(7)_6 < 812(4)_6 < \quad (12) \\ 867(7)_7 < 927(4)_7 \leq 927(7)_8 \leq 927(4)_8 < 954(7)_9 < 968(4)_9$$

Scaled frequency 703(4) cm⁻¹ of isotopomer 4 and scaled frequency 702(7) cm⁻¹ of isotopomer 7 violate the scaled interlacing rule. Though this violation is very mild (only 1 cm⁻¹), it nevertheless suggests that (at least) one of these two frequencies is in error. Note that the scaled frequency 703(4) cm⁻¹ of isotopomer 4 is doubly degenerate. This degeneracy is accidental and not due to symmetry. The corresponding unscaled frequencies are not degenerate (see Table I and expressions (4), (6) and (9)).

In a similar way comparing isotopomers 7 and 11 one finds two additional violations of the interlacing rule:

$$347(11)_1 < 356(7)_1 < 375(11)_2 < 385(7)_2 < 582(11)_3 ? 556(7)_3 < \\ 621(11)_4 < 637(7)_4 < 658(11)_5 < 702(7)_5 < 762(11)_6 < 765(7)_6 < \quad (13) \\ 785(11)_7 < 867(7)_7 < 915(11)_8 < 927(7)_8 ? 924(11)_9 < 954(7)_9$$

According to the above comparison, the scaled frequency 582(11) cm⁻¹ of isotopomer 11 is either too high and/or the scaled frequency 556(7) cm⁻¹ of isotopomer 7 is too low. The violation of the interlacing rule (26 cm⁻¹) is rather large, which almost certainly excludes the possibility that this violation might be due to anharmonicity effects. Similarly, the scaled frequency 927(7) cm⁻¹ of isotopomer 7 is either too high and/or the scaled frequency 924(11) cm⁻¹ of isotopomer 11 is too low. In this case however the violation of the interlacing rule (3 cm⁻¹) is much smaller. Assuming the scaled frequency 556(7) cm⁻¹ to be as large as 582 cm⁻¹ (in order to satisfy the interlacing rule), this value would produce new violation of the interlacing rule in the comparison of related frequencies of isotopomers 4 and 7 (see expression (12)). Concerning scaled frequency 927(7) cm⁻¹, any change of this frequency would also produce new violations of the interlacing rule in the comparison of isotopomers 4 and 7. This suggests that scaled frequencies 582(11) cm⁻¹ and 924(11) cm⁻¹ are most likely in error. Accordingly, the scaling procedure as applied to the isotopomer 11 is not very reliable.

The comparison of scaled frequencies of isotopomer 12 with scaled frequencies of isotopomer 13 produces one more violation of the interlacing rule

$$347(13)_1 \leq 347(12)_1 \leq 347(13)_2 < 363(12)_2 < 494(13)_3 < 510(12)_3 < \\ 606(13)_4 < 618(12)_4 < 658(13)_5 \leq 658(12)_5 \leq 658(13)_6 < 703(12)_6 < \quad (14) \\ 785(13)_7 \leq 785(12)_7 \leq 785(13)_8 < 819(12)_8 ? 818(13)_9 < 913(7)_9$$

This violation is very mild and it amounts only to 1 cm⁻¹.

There are finally three violations of the interlacing rule in the comparison of scaled out-of-plane frequencies of isotopomer 4 with isotopomers 6 and 8:

$$\left(\begin{array}{c} 379(6)? \\ 371(8) \end{array} \right)_1 371(4)_1 \leq \left(\begin{array}{c} 382(6) \\ 371(8) \end{array} \right)_2 < 386(4)_2 < \left(\begin{array}{c} 541(6) \\ 528(8) \end{array} \right)_3 < 564(4)_3 < \\ \left(\begin{array}{c} 656(6) \\ 703(8) \end{array} \right)_4 \leq 703(4)_4 \leq \left(\begin{array}{c} 706(6)? \\ 703(8) \end{array} \right)_5 703(4)_5 \leq \left(\begin{array}{c} 775(6) \\ 703(8) \end{array} \right)_6 < 812(4)_6 < (15) \\ \left(\begin{array}{c} 841(6) \\ 913(8) \end{array} \right)_7 < 927(4)_7 \leq \left(\begin{array}{c} 935(6)? \\ 927(8) \end{array} \right)_8 927(4)_8 \leq \left(\begin{array}{c} 973(6) \\ 927(8) \end{array} \right)_9 < 968(4)_9$$

All three violations involve comparisons of isotopomers 6 and 4 while there is no violation of the interlacing rule in the comparison of isotopomers 8 and 4. This suggests that the corresponding scaled frequencies of isotopomer 6 are in error. Some additional considerations also support this conclusion. For example, frequency 935(6) cm⁻¹ of isotopomer 6 should be interlaced with two degenerate frequencies 927(4) cm⁻¹ of isotopomer 4. This frequency is hence very likely in error and instead of 935(6) cm⁻¹ it should read 927(6) cm⁻¹.

The above examples exhaust all those cases when scaled frequencies violate the scaled interlacing rule. The existence of such violations shows that this scaling technique should be applied with extreme care. The interlacing rule is based on the harmonic approximation and the anharmonicity effects are usually very small. In addition, these effects partially cancel in the original and in the isotopically substituted molecule. Each violation of the interlacing rule should hence be separately analyzed and either rejected or properly justified.

INTERLACING RULE AND EXPERIMENTAL FREQUENCIES OF BENZENE ISOTOPOMERS

Let us finally verify the interlacing rule for benzene isotopomer out-of-plane frequencies with available experimental data. Those frequencies are not known for all isotopomers shown in Figure 1. Here we use frequencies reported by L. M. Sverdlov, M. A. Kovner, and E. P. Krainov.⁴ They report experimental frequencies of isotopomers 1, 2, 5, 8, 11 and 13 in Figure 1. Experimental out-of-plane frequencies for those isotopomers are shown in Table III. The basic interlacing rule (2a) can be applied only to isotopomer pairs (1,2) and (2,5). For example, isotopomer 8 can not be derived from isotopomer 5 by a single isotopic substitution, and hence this basic interlacing rule does not apply to the isotopomer pair (5,8).

Concerning isotopomers 1 and 2 one finds:

$$380(2)_1 < 405(1)_1 \leq 405(2)_2 \leq 405(1)_2 < 608(2)_3 < 671(1)_3 < 698(2)_4 < 703(1)_4 < 775(2)_5 < 849(1)_5 \leq 849(2)_6 \leq 849(1)_6 < 922(2)_7 < 970(1)_7 \leq 970(2)_8 \leq 970(1)_8 < 995(2)_9 ? 985(1)_9 \quad (16)$$

The interlacing rule is violated only in the case of frequencies 995(2)₉ and 985(1)₉. The vibrational mode 985(1) has symmetry b_{2g} with all hydrogen atoms involved in a vibration. Replacement of a hydrogen with a heavier deuterium should decrease this frequency, contrary to 995(2)₉ > 985(1)₉. Moreover, the corresponding scaled frequencies satisfy 980(2)₉ < 990(1)₉, as required (see Table II). This suggests that (at least) one of these two frequencies is in error. One possibility is erroneous experimental measurement. However, there is another possibility. The experimental frequency 995(2)₉ as well as the experimental frequency 985(1)₉ is assigned to out-of-plane vibration. It is possible that this assignment is in error and that either of those two frequencies corre-

Table III. Experimental out-of-plane frequencies of some benzene isotopomers⁴

	1		2		5		8		11		13	
	C ₆ H ₆ D _{6h}		C ₆ DH ₅ C _{2v}		1,4-C ₆ D ₂ H ₄ D _{2h}		C ₆ (DH) ₃ D _{3h}		1,2,4,5-C ₆ D ₄ H ₂ D _{3h}		C ₆ D ₆ D _{6h}	
1	405	e _{2u}	380	b ₂	367	b _{1u}	373	e''	352	a _u	352	e _{2u}
2	405	e _{2u}	405	a ₂	405	a _u	373	e''	383	b _{1u}	352	e _{2u}
3	671	a _{2u}	608	b ₂	597	b _{1u}	533	a ₂ ''	548	b _{1u}	496	a _{2u}
4	703	b _{2g}	698	b ₂	634	b _{3g}	691	a ₂ ''	615	b _{3g}	601	b _{2g}
5	849	e _{1g}	775	b ₂	736	b _{3g}	710	e''	664	b _{2g}	662	e _{1g}
6	849	e _{1g}	849	a ₂	849	b _{2g}	710	e''	767	b _{3g}	662	e _{1g}
7	970	e _{2u}	922	b ₂	876	b _{1u}	920	a ₂ ''	793	a _u	793	e _{2u}
8	970	e _{2u}	970	a ₂	967	b _{3g}	947	e''	925	b _{1u}	793	e _{2u}
9	985	b _{2g}	995	b ₂	970	a _u	947	e''	930	b _{3g}	827	b _{2g}

sponds to some in-plane vibration. For example, there is an experimental frequency 980 cm^{-1} of isotopomer 2 that is in reference 4 attributed to an in-plane vibration of symmetry type a_1 . If this frequency were to replace experimental frequency $995(2)_9$, this frequency would be in agreement with the interlacing rule.

Concerning the comparison of out-of-plane frequencies of isotopomer 2 with isotopomer 5 one finds:

$$\begin{aligned} 367(5)_1 < 380(2)_1 < 405(5)_2 \leq 405(2)_2 < 597(5)_3 < 608(2)_3 < \\ 634(5)_4 < 698(2)_4 < 736(5)_5 < 775(2)_5 < 849(5)_6 \leq 849(2)_6 < & (17) \\ 876(5)_7 < 922(2)_7 < 967(5)_8 < 970(2)_8 \leq 970(5)_9 < 995(2)_9 \end{aligned}$$

These experimental frequencies are in complete agreement with interlacing rule (2a).

The basic interlacing rule (2a) cannot be applied to any other pair of isotopomers reported in Table III. However, one can apply the generalized interlacing rule (2b) to isotopomer pairs (2,8), (5,11) and (11,13). In all three cases the heavier isotopomer **B** differs from lighter isotopomer **A** by two isotopic substitutions, *i.e.* one has $k = k_a = 2$. Hence expression (2b) reduces to

$$\omega_{i-2} \leq \omega_i' \leq \omega_i \quad (18)$$

Comparison of the out-of-plane frequencies of these pairs of isotopomers is shown in Figure 2. Figure 2a concerns isotopomer pair (2,8), Figure 2b concerns isotopomer pair (5,11), while Figure 2c concerns isotopomer pair (11,13). In all three cases, out-of-plane frequencies of these isotopomers satisfy the generalized inter-

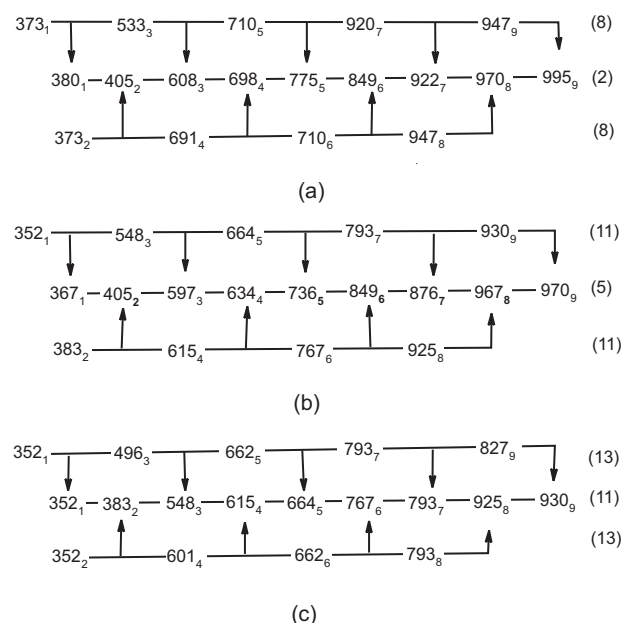


Figure 2. Verification of generalized interlacing rule (2b). In all three cases one has $k = k_a = 2$ and expression (2b) reduces to the expression (18): (a) isotopomer pair (2,8), (b) isotopomer pair (5,11), (c) isotopomer pair (11,13).

lacing rule. For example, frequency 533_3 of isotopomer 8 is interlaced with frequencies 380_1 and 608_3 of isotopomer 2 according to $380(2)_1 < 533(8)_3 < 608(2)_3$. In a similar way frequency 691_4 of isotopomer 8 is interlaced with frequencies 405_2 and 698_4 of isotopomer 2 according to $405(2)_2 < 691(8)_4 < 698(2)_4$, *etc.* (see Figure 2a). This is in complete agreement with the expression (18).

CONCLUSION

The interlacing rule⁶ applies to vibrational spectra of molecules **A** and **B** that differ by single or multiple isotopic substitutions. This rule is a generalization of the well-known order rule⁴ and it is derived under the assumption of the harmonic approximation.⁶ Therefore it should be as reliable as the order rule which is derived under the same assumption.

In the case of planar molecules there are two interlacing rules, one that applies to out-of-plane-vibrations and another that applies to in-plane vibrations.⁶ In the former case out-of-plane frequencies of isotopomer **A** are interlaced with out-of-plane frequencies of isotopomer **B**_τ that differs from **A** by a single isotopic substitution at atomic site τ according to the expression (2a). In the case of multiple isotopic substitutions one has the generalized interlaced rule (2b).

In this paper we analyze the interlacing rule in the case of out-of-plane vibrations of benzene and deuterated benzenes. There are 13 such isotopomers and each of those isotopomers has 9 out-of-plane vibrations. One can make as many as 20 direct »basic« comparisons of vibrational frequencies of these isotopomers. In all cases considered theoretical frequencies⁸ derived within the rather sophisticated B3LYP/6-31G(d,p) calculation are in complete agreement with the interlacing rule.

We have also considered scaled frequencies.⁸ These frequencies are obtained by scaling theoretical frequencies with individual mode factors that accurately reproduce experimental benzene frequencies. It is argued that such a scaling technique should improve the accuracy of theoretical frequencies.⁸ However, in some cases such a scaling technique results in the violation of the interlacing rule, though initial nonscaled frequencies satisfy this rule. Since violation of the basic interlacing rule is to be expected only in some rare and exceptional cases when anharmonicity effects are quite significant, this suggests that this scaling technique should be applied with extreme care. In particular one should always analyze the agreement of scaled frequencies with the interlacing rule and one should be very suspicious to any violation of this rule.

Finally some available experimental frequencies are also analyzed in terms of the interlacing rule. Experimental frequencies reported by Sverdlov, Kovner, and Krainov⁴ are considered. Those authors report experi-

mental frequencies for just 6 of the benzene isotopomers. One finds that all those frequencies satisfy the interlacing rule, except for the experimental frequencies 985 cm^{-1} and 995 cm^{-1} of benzene and monodeuterated benzene C_6DH_5 , respectively. The violation of the interlacing rule (10 cm^{-1}) is rather large, which very likely excludes the possibility that this violation might be due to the anharmonicity effects. Hence either the frequency 995 cm^{-1} is too high and/or the frequency 985 cm^{-1} is too low. There is a possibility that the experimental measurement of those frequencies is in error. Another possibility is an erroneous assignment of those frequencies. Both frequencies are assigned to out-of-plane vibrations. However, it is possible that this assignment is in error and that either frequency 995 cm^{-1} or frequency 985 cm^{-1} corresponds in fact to an in-plane vibration. If this is the case there must exist another experimental frequency that corresponds to an out-of-plane vibration but which is erroneously assigned to an in-plane vibration. For example, reference 4 reports an experimental frequency 980 cm^{-1} of monodeuterated benzene, which is assigned to in-plane vibration of symmetry type a_1 . If one permutes this frequency with above frequency 995 cm^{-1} , one would avoid the violation of the interlacing rule for out-of-plane vibrations.

In conclusion, the interlacing rule could be violated by anharmonicity effects that are not taken into account in the derivation of this rule. However, anharmonicity effects are usually very small. In addition, as far as the interlacing rule is concerned, anharmonicity effects for the molecules **A** and **B_r** should tend to cancel. Therefore, violation of this rule usually indicates either erroneous experimental data or erroneous assignment of vibrational frequencies. This is especially true if the violation of the interlacing rule is rather large, in which case this violation cannot be attributed to anharmonicity effects. The interlacing rule thus provides a simple and quite power-

ful tool that may help to analyze vibrational spectra in order to obtain correct assignments of experimental frequencies to various vibrational types.

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SAŽETAK

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

Tomislav P. Živković

Ako su **A** i **B_r** dvije molecule koje se razlikuju samo u jednoj izotopnoj supstituciji tada su u harmonijskoj aproksimaciji vibracijske frekvencije molecule **A** učešljane s vibracijskim frekvencijama molecule **B_r**. To pravilo češlja, poopćenje je dobro poznatog pravila reda (order rule). U slučaju planarnih molekula, pravilo češlja se posebno odnosi na unutarravninske i na izvanravninske vibracije. To pravilo je posebno jednostavno u slučaju izvanravninskih vibracija. Valjanost pravila češlja je provjerena kod benzena i deuteriranih benzena. Kršenje tog pravila naznačava (malo vjerojatne) jake efekte neharmoničnosti, ili (više vjerojatno) pogrešnu vibracijsku asignaciju i/ili pogrešne eksperimentalne podatke. Stoga to pravilo može pomoći pri analizi vibracijskih spektara, nadalje u asignaciji eksperimentalnih frekvencija raznim tipovima vibracija.