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On the Vibrational Interlacing Rule in Linear and Planar Molecules

Tomislav P. Živković

Ruđer Bošković Institute, P. O. Box 180, HR-10002 Zagreb, Croatia
(E-mail: zivkovic@rudjer.irb.hr)

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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. The interlacing rule is particularly simple in the case of stretching and bending vibrations of linear molecules as well as in the case of out-of-plane vibrations of planar molecules. The validity of the interlacing rule for these vibrations is demonstrated with a few examples. Violation of this rule indicates either (very unlikely) strong anharmonicity effects, or (more likely) erroneous vibrational assignments. Hence, this rule can help in the analysis of vibrational spectra, in particular in the assignments of experimental frequencies to various vibrational types.

Key words: interlacing rule, vibrational isotope effect, harmonic approximation, linear molecules, planar molecules.

INTRODUCTION

Vibrational spectra are quite important in the study and analysis of molecular properties.[1,2] Recently, numerical methods were developed that unable calculation of the frequencies and normal modes of molecular systems containing as many as several hundreds of atoms.[3] Besides the vibrational spectra of the original molecule, there are also vibrational spectra of isotopically substituted molecules, which generate a huge number of additional experimental data. These data provide important information for the construction of the force field[1] and they are also important as an additional source of information for the correct assignment and interpretation of experimental spectra. It is, therefore, quite useful to have simple rules relating vibrational frequencies of molecules that differ by a single or multiple isotopic substitutions. Such rules can highly facilitate and improve assignment and interpretation of experimental frequencies.

It is well known that 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 ν_i of the 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:[4]

$$\omega_1 \leq \nu_1,\ \omega_2 \leq \nu_2,\cdots,\omega_k \leq \nu_k,\cdots \tag{1}$$

The above order rule applies to such pairs of isotopic molecules A and B where all substituted isotopes in molecule B are heavier than the corresponding isotopes in molecule A. The order rule is derived within the harmonic approximation.[1] It is hence possible that anharmonicity effects might in some cases invalidate this rule. Several studies beyond the harmonic approximation were done.[5] Those treatments also offer the possibility to study the effect of isotope substitutions. However, anharmonicity effects are usually small. Moreover, as far as the order rule is concerned, these effects partially cancel in the original and in the isotopically substituted molecule. Hence, experimental frequencies almost always satisfy this rule.

Recently, the order rule was generalized to the so-called interlacing rule.[6] This rule is also derived within the harmonic approximation. While the order rule limits each frequency ω_k from above, the interlacing rule limits this frequency from above as well as from below. Particularly simple is the interlacing rule for linear molecules and for out-of-plane vibrations of planar molecules.[6] Slightly more complicated is the interlacing rule for in-plane vibrations of planar molecules.[6] We will state here the interlacing rule for linear and planar molecules in the case when molecules A and B_τ differ by a single isotopic substitution at atomic site τ. Generalization to multiple isotopic substitutions is straightforward.[6] Validity of this rule will be verified with a few examples of linear and planar molecules. All experimental frequencies are from Ref. 4, which contains an extensive selection of these frequencies. For the sake of consistency, gas frequencies, as more reliable, are considered. Only if no gas frequency is reported, we consider the liquid frequency. In the following figures, each liquid frequency is indicated by an asterix (*).

LINEAR MOLECULES

In the case of linear molecules, one has:[6]

Interlacing Rule 1 (Linear Molecules)

Consider two n-atom linear molecules A and B_τ, which differ by a single isotopic substitution at atomic site τ. Let molecule B_τ be heavier than molecule A, and let ν_i and ω_k be proper stretching (bending) frequencies of molecules A and B_τ, respectively. Arrange these frequencies in the nondecreasing order. Then, the frequencies are interlaced according to:

$$0 \le \omega_1 \le \nu_1 \le \omega_2 \le \nu_2 \le \omega_3 \le \nu_3 \le \cdots \tag{2}$$

As an example, ethyne molecule is shown in Figure 1 (Figure 1(a)) together with bending (Figure 1(b), symmetry type Π) and stretching (Figure 1(c), symmetry type Σ) vibrations of this molecule. There are two bending

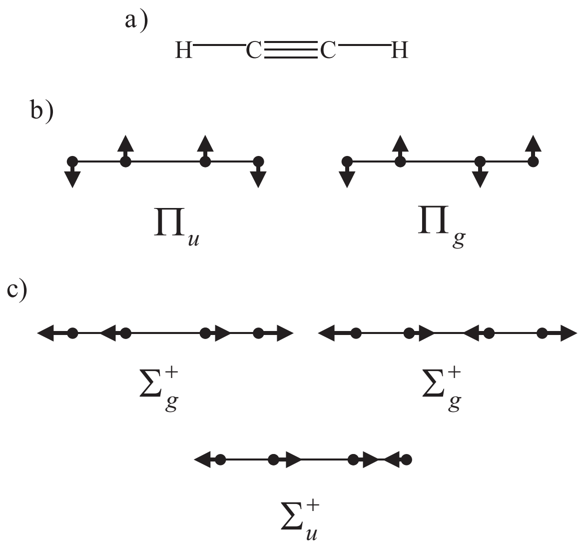

Figure 1. (a) Ethyne molecule; (b) ethyne bending vibrations; (c) ethyne stretching vibrations.

and three stretching vibrations. As shown in Figure 2, stretching (bending) vibrations of C_2H_2 (**D0**) are interlaced with stretching (bending) vibrations of C_2HD (**D1**) according to the interlacing rule, while stretching (bending) vibrations of C_2HD are also interlaced with stretching (bending) vibrations

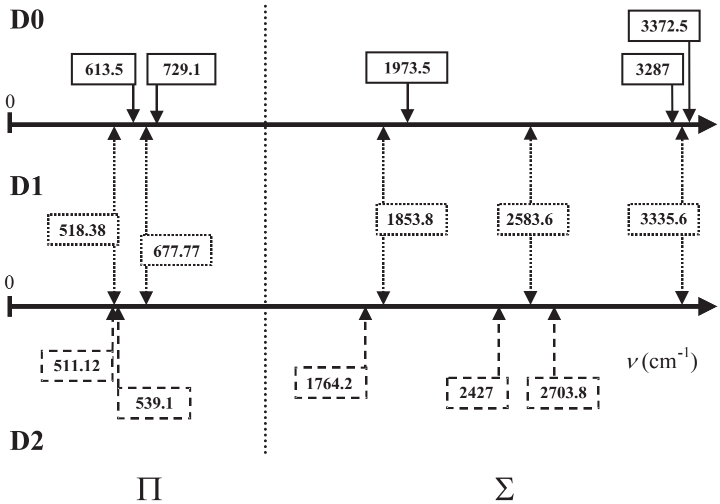

Figure 2. Interlacing of stretching (Σ) and bending (Π) frequencies for C_2H_2 (**D0**) (solid arrows), C_2HD (**D1**) (dotted arrows) and $\mathbf{C_2D_2}$ (**D2**) (dashed arrows) molecules. Experimental data (IR and Raman gas frequencies) are from Ref. 4.

of C_2D_2 (**D2**) according to this rule. For example, stretching vibrations of **D0** and **D1** satisfy:

$$1853.8(\mathbf{D1}) < 1973.5(\mathbf{D0}) < 2583.6(\mathbf{D1}) < 3287(\mathbf{D0}) < 3335.6(\mathbf{D1}) < 3372.5(\mathbf{D0})$$

This is in complete agreement with the interlacing requirement (2). Note that the order rule limits each frequency of **D1** only from above, while the interlacing rule limits this frequency from above as well as from below. For example, concerning the highest frequency ν_3 = 3335.6 cm^{-1} of **D1,** interlacing rule implies $3287(\mathbf{D0}) \le 3335.6(\mathbf{D1}) \le 3372.5(\mathbf{D0})$, while the order rule requires only $3335.6(\mathbf{D1}) \le 3372.5(\mathbf{D0})$. The interlacing rule is thus much more powerful than the order rule. In addition, the interlacing rule applies separately to bending and separately to stretching frequencies, while the order rule does not discriminate between these two symmetry types. This distinction becomes important if bending and stretching frequencies partially overlap. In the case of ethyne and deuterated ethyne molecules, these frequencies do not overlap.

As another example, we consider haloethynes. Figure 3 demonstrates the interlacing rule for stretching (Σ) and bending (Π) frequencies of haloethynes C_2HX and deuterated haloethynes C_2DX. Experimental frequencies are IR gas frequencies.[4] All these frequencies are in accord with the interlacing

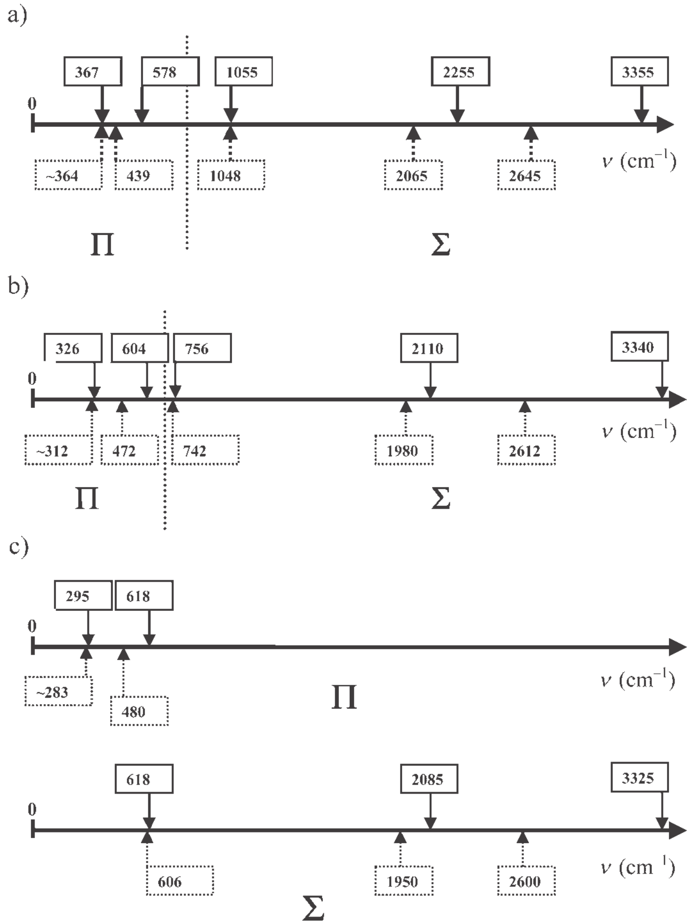

Figure 3. Interlacing of stretching (Σ) and bending (Π) frequencies for haloethynes (solid lines) and deuterated haloethynes (dotted lines). Experimental data (IR gas frequencies) are from Ref. 4. (a) Interlacing of C_2HF and C_2DF frequencies; (b) Interlacing of C_2HCl and C_2DCl frequencies; (c) Interlacing of C_2HBr and C_2DBr frequencies.

rule. In particular and as required, in the case of bromoethynes C_2HBr and C_2DBr (Figure 3(c)), the interlacing rule applies separately to stretching and separately to bending frequencies. In this case stretching and bending frequencies partially overlap, and the interlacing rule does not apply to bromoethyne and deuterated bromoethyne frequencies if the distinction between bending and stretching vibrations is not taken into account. This shows that the requirement that the interlacing rule should apply separately to stretching and separately to bending frequencies is nontrivial.

PLANAR MOLECULES

There are many more planar molecules than linear molecules and therefore the interlacing rule for those molecules is more important. In the case of planar molecules, there are out-of-plane and in-plane vibrations. The interlacing rule for out-of-plane frequencies of planar molecules is identical to the interlacing rule of stretching (bending) frequencies of linear molecules:[6]

Interlacing Rule 2 (Out-of-plane Vibrations of Planar Molecules)

Consider two n-atom planar molecules A and B_τ, which differ by a single isotopic substitution at atomic site τ. Let molecule B_τ be heavier than molecule A, and let ν_i and ω_k be proper out-of-plane frequencies of molecules A and B_τ, respectively. Arrange these frequencies in the nondecreasing order. Then, these frequencies are interlaced according to:

$$0 \leq \omega_1 \leq \nu_1 \leq \omega_2 \leq \nu_2 \leq \omega_3 \leq \nu_3 \leq \ldots \qquad (3)$$

Concerning in-plane frequencies of planar molecules, one obtains a slightly less restrictive interlacing rule:[6]

Interlacing Rule 3 (In-plane Vibrations of Planar Molecules)

Consider two n-atom planar molecules A and B_τ, which differ by a single isotopic substitution at atomic site τ. Let molecule B_τ be heavier than molecule A, and let ν_i and ω_k be proper in-plane frequencies of molecules A and B_τ, respectively. Arrange these frequencies in the nondecreasing order. Then, these frequencies are interlaced according to:

$$\nu_{k-2} \leq \omega_k \leq \nu_k \qquad (4)$$

In the present paper, we consider only out-of-plane frequencies of planar molecules. In-plane frequencies of planar molecules will be considered elsewhere.[7]

As the first example, consider out-of-plane frequencies of deuterated ethenes. There are 7 ethenes and deuterated ethenes. Interlacing hierarchy of these molecules is shown in Figure 4. For example, *cis*-**D2** and **D3** deuterated ethenes differ by a single isotopic substitution and therefore out-of-plane frequencies of these isotopomeres should satisfy the interlacing rule (3), *etc*.

Ethene has three out-of-plane frequencies, usually denoted as ν_4, ν_7 and ν_8.[1] Figure 5 demonstrates the interlacing rule for these frequencies. Experimental frequencies[4] are IR and Raman gas frequencies with three exceptions where gas frequencies were not available and where instead liquid fre-

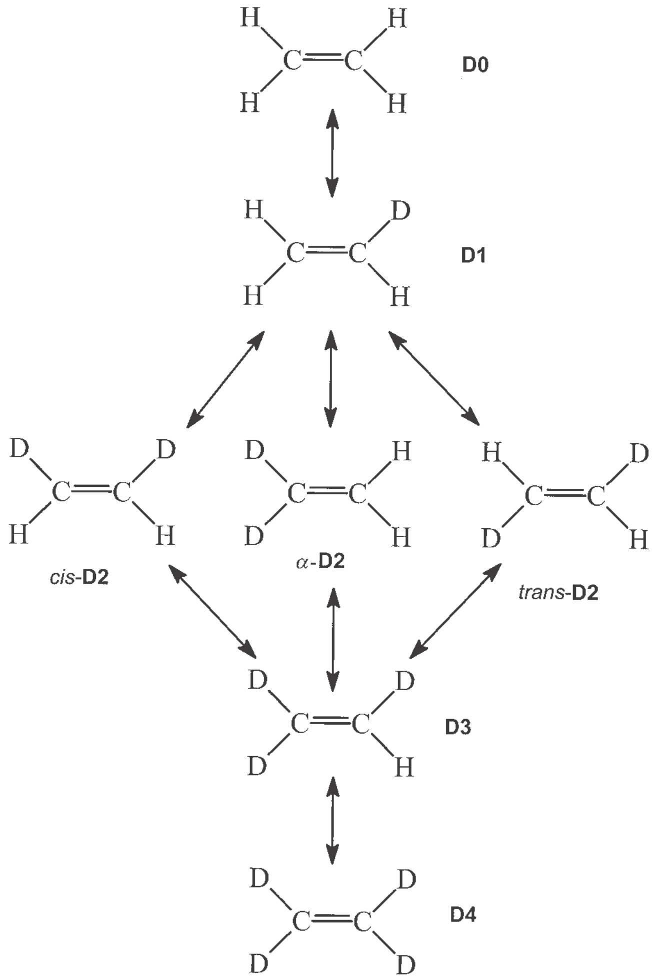

Figure 4. Interlacing hierarchy of deuterated ethenes.

quencies are reported. All these frequencies satisfy the interlacing rule. For example, the largest out-of-plane frequencies of three **D2** deuterated ethenes are interlaced with out-of-plane frequencies of C_2H_3D (**D1**) molecule according to:

$$943(\mathbf{D1}) \leq 943(\alpha\text{-}\mathbf{D2}),\ 978(cis\text{-}\mathbf{D2}),\ 987(trans\text{-}\mathbf{D2}) \leq 1001(\mathbf{D1})$$

As another example, consider haloethenes C_2H_3X (X = F, X = Cl and X = Br) and deuterated haloethenes. For each halogen, there are eight haloethenes and deuterated haloethenes. Interlacing hierarchy of these isoto-

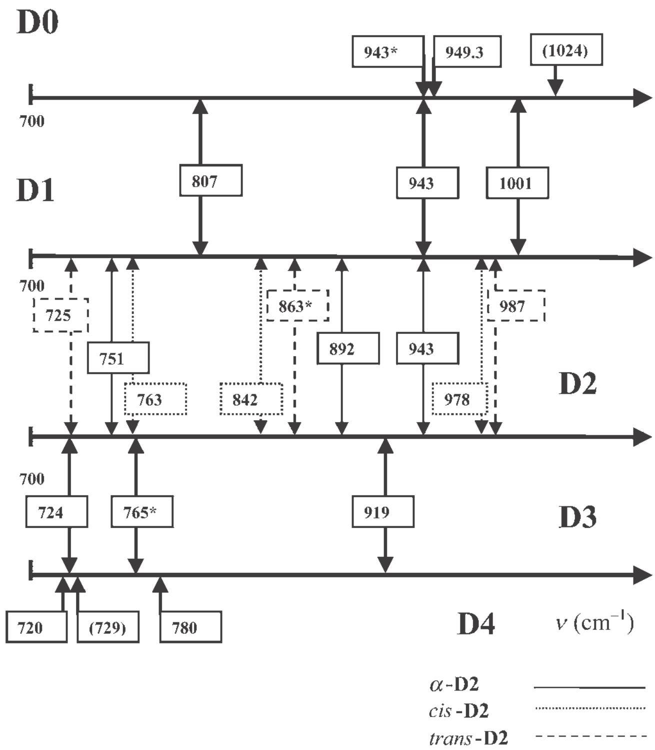

Figure 5. Interlacing of out-of-plane frequencies of deuterated ethenes. Experimental data are from Ref. 4. (*) liquid.

pomers is shown in Figure 6. This hierarchy is more complex than the one shown in Figure 4. For example and as indicated in this figure, a single substitution H → D can transform α-**D1** into *cis*-**D2** and it can also transform α-**D1** into *trans*-**D2**. However, this substitution can not transform α-**D1** into α-**D2**. Therefore, out-of-plane frequencies of α-**D1** and α-**D2** are not required to satisfy the interlacing relation (3), though accidentally this may be the case.

Each haloethene has three out-of-plane frequencies. These frequencies are usually denoted as ν_{10}, ν_{11} and ν_{12}.[4] The interlacing rule for these frequencies is demonstrated in Figures 7, 8 and 9. Experimental frequencies shown in these figures are IR gas frequencies with a single exception in Figure 9 where in the case of *cis*-**D1** molecule gas frequency ν_{11} was not available and hence instead a Raman liquid frequency ν_{11} = 918 cm^{-1} was used.[4] In Figure 7, deuterated fluoroethenes are considered, deuterated chloroethenes are considered in Figure 8, while deuterated bromoethenes are con-

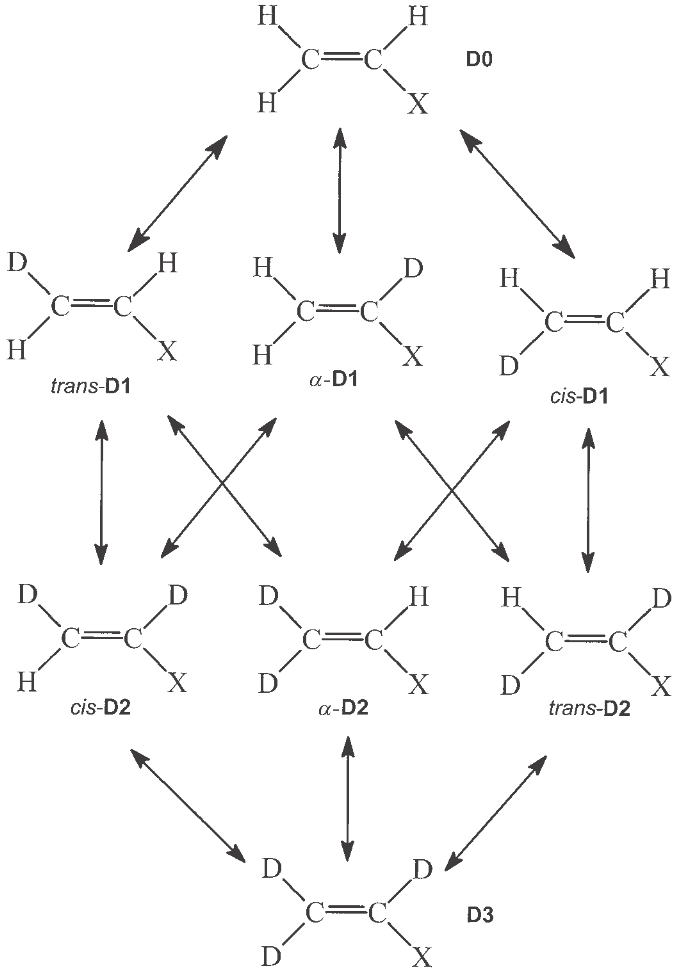

Figure 6. Interlacing hierarchy of deuterated haloethenes.

sidered in Figure 9. In all cases, experimental out-of-plane frequencies are in complete aggreement with the interlacing rule. For example, in the case of fluoroethenes (Figure 7) experimental out-of-plane frequencies of α-**D1**, *cis*-**D1** and *trans*-**D1** are interlaced with out-of-plane frequencies of **D0** according to:

$$\begin{array}{llllll} 678(\alpha\text{-}\mathbf{D1}) & & 830(\alpha\text{-}\mathbf{D1}) & & 867(\alpha\text{-}\mathbf{D1}) & \\ 642(cis\text{-}\mathbf{D1}) & \le 711(\mathbf{D0}) \le & 785(cis\text{-}\mathbf{D1}) & \le 863(\mathbf{D0}) \le & 910(cis\text{-}\mathbf{D1}) & \le 940(\mathbf{D0}) \\ 576(trans\text{-}\mathbf{D1}) & & 815(trans\text{-}\mathbf{D1}) & & 926(trans\text{-}\mathbf{D1}) & \end{array}$$

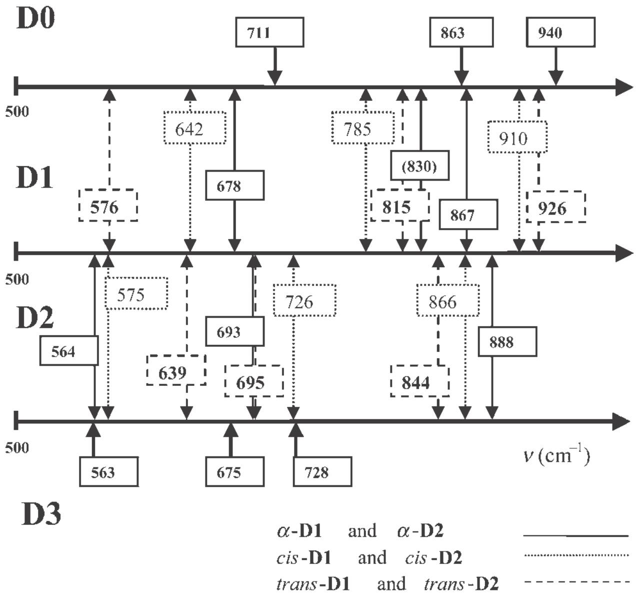

Figure 7. Interlacing of out-of-plane frequencies of deuterated fluoroethenes. Experimental data (IR and Raman gas frequencies) are from Ref. 4.

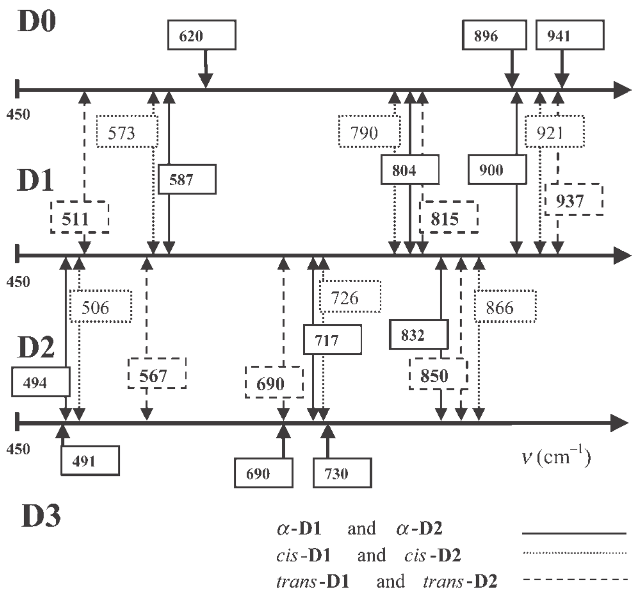

Figure 8. Interlacing of out-of-plane frequencies of deuterated chloroethenes. Experimental data (IR gas frequencies) are from Ref. 4.

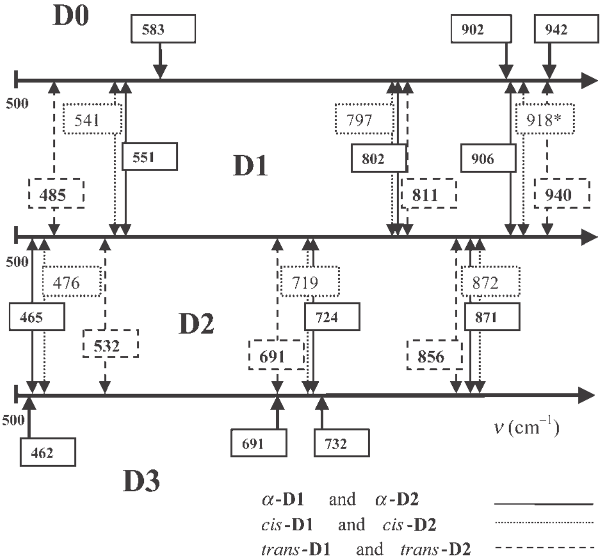

Figure 9. Interlacing of out-of-plane frequencies of deuterated bromoethenes. Experimental data (IR gas frequencies except *cis*-**D1** frequency $\nu_{11} = 918$ cm^{-1}, denoted with an asterix (*), which is a Raman liquid frequency) are from Ref. 4.

However, and as discussed above, out-of-plane frequencies of α-**D1** and α-**D2** are not required to satisfy the interlacing rule. Thus, in the above fluoroethene case one has:

$$564(\alpha\text{-}\mathbf{D2}) \leq 678(\alpha\text{-}\mathbf{D1}) \leq 693(\alpha\text{-}\mathbf{D2}) \leq 830(\alpha\text{-}\mathbf{D1}),\ 867(\alpha\text{-}\mathbf{D1}) \leq 888(\alpha\text{-}\mathbf{D2})$$

in violation of this rule.

CONCLUSION

In this paper, we verify the validity of the interlacing rule in the case of linear and planar molecules. According to this rule, stretching (bending) frequencies of linear molecule A as well as out-of-plane frequencies of planar molecule A are interlaced with the corresponding frequencies of molecule B_τ which differs from molecule A by a single isotopic substitution at atomic site τ.[6] This rule is a generalization of the well-known order rule[4] and it is derived under the assumption of harmonic approximation.[1,6] The validity of the interlacing rule for these vibrations is demonstrated with a few examples. In all cases, the considered experimental frequencies are in complete agreement with this rule. In principle, the interlacing rule could be violated by anharmonicity effects, which were not taken into account in the derivation of this rule. However, anharmonicity effects are usually very small. In addition, one can show that, as far as the interlacing rule is considered, anharmonicity effects for molecules A and B_τ tend to cancel. Therefore, violation of this rule usually indicates either erroneous experimental data or erroneous assignment of vibrational frequencies. Hence, this rule can help in the analysis of vibrational spectra, particularly in the assignments of experimental frequencies to various vibrational types.

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SAŽETAK

Pravilo vibracijskog ispreplitanja za linearne i planarne molekule

Tomislav P. Živković

Ako su A i B_τ dvije molekule koje se razlikuju samo u jednoj izotopnoj supstituciji tada su u harmonijskoj aproksimaciji vibracijske frekvencije molekule A učešljane s vibracijskim frekvencijama molekule B_τ. To pravilo češlja poopćenje je poznatog pravila reda (order rule). Pravilo češlja osobito je jednostavno u slučaju rasteznih i deformacijskih vibracija linearnih molekula kao i u slučaju izvanravninskih vibracija planarnih molekula. Pravilo češlja za te je vibracije ilustrirano s nekoliko primjera. Odstupanje od tog pravila naznačava ili (malo vjerojatne) jake efekte anharmoničnosti, ili (više vjerojatnu) pogrešnu vibracijsku asignaciju. Stoga to pravilo može pomoći u analizi vibracijskih spektara, posebno u asignaciji eksperimentalnih frekvencija raznim tipovima vibracija.