

NMR Line-Shape Analysis and Modes of Rearrangements

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We classify the possible permutational isomerizations of a given molecular skeleton in NMR-modes. Such a mode is the set of permutations which are indistinguishable from the point of view of NMR-line shape analysis. The present classification is compared to earlier ones and its advantages are underlined.

Key words: NMR-line shape analysis – Permutational isomerism

Considerable interest has been devoted to the application of group-theoretical concepts to the classification of intramolecular rearrangements. Several classifications and theories have been extensively discussed and developed in the literature [1–7]. More recently attention has been polarized on the problem of classification of permutational isomerization reactions with respect to NMR line-shape theory [2, 5–7] since this method has been proved up to here to be the most powerful tool for studying experimentally such rearrangements [7–9]. Different authors have discussed this problem [3–7] but essentially in two papers group theoretical concepts have led to a classification of permutational isomerization reactions with respect to the detection method used to observe them, namely NMR line shape analysis [5, 6]. The aim of this paper is to propose an alternative classification to those developed by Jesson and Meakin [6] and by Klein and Cowley [5].

Let us consider a set of N magnetically equivalent nuclei. By definition [10–12]

- a) all their chemical shifts are identical: $\sigma_1 = \sigma_2 = \sigma_3 = \dots = \sigma_N$
- b) the coupling constants between each of these nuclei and any other nucleus X in the molecule are identical $J_{1X} = J_{2X} = \dots = J_{NX}$ for all nuclei X of the molecule.

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It can then be shown that all the line splittings on the NMR spectrum due to couplings within the set of N nuclei are unobservable. This means that the spin Hamiltonian reduces to an effective NMR Hamiltonian [11] where all the J_{ij} coupling constants ($i \neq j$; $i=1, 2, \dots, N$; $j=1, 2, \dots, N$) have been put equal to zero. According to Jesson and Meakin [6] we represent the group leaving this effective NMR hamiltonian invariant by H (R_{eq} in Ref. [5]). Thus any permutation of nuclei belonging to H leaves the line-shape of the NMR spectrum unaffected. For simplicity, we restrict ourselves to the classification of permutational rearrangements [4].

In conformity with Ruch *et al.* [15], we call ordered molecule (OM) any distribution of numbered ligands on numbered skeletal positions. All the possible rearrangements are then representable by a group of allowed permutations [4] acting on an ordered molecule in which the numbers of the ligands and the sites coincide (reference ordered molecule: ROM [15]). We symbolize this group by the letter S^1 . As discussed by Jesson and Meakin [6] and by Klemperer the group S is a direct product of groups of permutation of ligands of identical chemical nature. Thus, if there are n_1 ligands of type 1, n_2 ligands of type 2, ..., n_j ligands of type j , such that $n_1 + n_2 + \dots + n_j = n$ the ligands of type 1 can be permuted on the sites numbered 1 to n_1 , the ligands of type 2 on the sites numbered $n_1 + 1$ to $n_1 + n_2$, ..., the ligands of type j on the sites numbered $n_1 + n_2 + \dots + n_j - 1 + 1$ to n . In this way, all the possible ordered molecules of the considered chemical system are represented by the permutation group S which is merely a direct product of symmetric groups:

$$S = S_{n_1} \otimes S_{n_2} \otimes \dots \otimes S_{n_j}. \quad (1)$$

Finally, in order to achieve the partition of the group S of all allowed permutations in sets of NMR-equivalent permutations [5]² we need to define the subgroup G , a permutation group isomorphic with the symmetry group of the rigid molecule.³ From the preceding it is clear that the G group is a subgroup of the H group, which in turn is a subgroup of the S group. In addition we call A the permutation group which is isomorphic with the rotational subgroup of the molecular skeleton.

For simplicity, we will discuss here the concept of NMR-mode in achiral environment [4]. The discussion presented here could be extended to the chiral environment problem although it is certainly more delicate to be handled [4].

1. Several authors have shown [3–7] that two permutations x and y such that

$$y = gxg^{-1} \quad \text{for any } g \in G \quad (2)$$

are symmetry equivalent [3] permutations. If there exists a mechanism consistent with x , there exists also a mechanism consistent with y occurring at the same rate constant. For that reason they are NMR-equivalent permutations. The set of all

¹ Throughout this work we adopt the permutation convention in which for instance the permutation (143)(2) means: ligand on place 1 replaces ligand on place 4, ligand on place 4 replaces ligand on place 3, ligand on place 3 replaces ligand on place 1, ligand on place 2 stays on place 2; see Refs. [3–7, 14].

² The concept of NMR-mode is called observable process by Musher, J.I. (Ref. [2]) and equivalent basic permutational sets by Jesson, J.P. and Meakin, P. (Ref. [6]).

³ We exclude linear or planar molecules.

symmetry equivalent permutational rearrangements has been called basic permutational set by Jesson and Meakin [6, 7] and set of indistinguishable permutational isomerization reactions in achiral environment by Klemperer [4].

2. When two equi-energetic configurations k and l (respectively represented by right cosets Ax^k and Ax^l) are separated by an energy barrier, it is clear that the rearrangements relating configuration k to configuration l and reverse rearrangements leading from l to k , have to be characterized by the same rate constant, as a consequence of the principle of detailed balance [4, 5, 13, 17, 18]. This implies that any permutation x and its inverse x^{-1} are mode-equivalent and as a consequence NMR-mode equivalent, even if they are not symmetry equivalent.

3. It has been shown previously [3, 4, 16] that a right coset of the type Ax , where $x \in S$, contains all the permutations relating the ROM to all the OM's corresponding to the same configuration of the molecule, since they only differ by a rotational permutation a belonging to A . Moreover [3, 4], all the elements belonging to a right coset Gx transform the ROM into OM's which altogether correspond to a pair of enantiomeric configurations. Similarly, all the permutations contained in a right coset Hx transform $H_{\text{eff.}}^{\text{spin}}$ (ROM), the effective NMR-spin hamiltonian of the ROM into another effective NMR-spin hamiltonian $H_{\text{eff.}}^{\text{spin}}(x)$.

On the other hand, Hx also transforms the ROM into a set of OM's which possess all the same effective NMR-spin hamiltonian $H_{\text{eff.}}^{\text{spin}}(x)$. For this reason these OM's have to be considered together in a coset Hx that we call NMR configuration. This means that the isomerization into the various configurations Ax_i belonging to the same NMR-configuration Hx are indistinguishable. In the same way, two mechanisms consistent with permutations x and y related neither by 1. nor by 2. and occurring for this reason with different rate constants should be put together if y belongs to Hx . Of course, two different NMR configurations have the same NMR spectrum in the absence of isomerizations between them: indeed their effective NMR spin hamiltonians, although different, are isomorphic [10, 11, 16].

Summarizing these three features, we may assert that a permutation y is NMR-equivalent to x if and only if:

$$1. \quad y = gxg^{-1} \quad \text{for any } g \in G \quad (3)$$

or

$$2. \quad y = x^{-1} \quad (4)$$

or

$$3. \quad y = hx \quad \text{for any } h \in H \quad (5)$$

or if y is related to x by any combination of the three preceding relations.

We now want to show that the set of all NMR-equivalent permutations related by one or more of the three preceding relations is a union of double cosets (D.C.)

$$M_{(x)}^{\text{NMR}} = HxH \cup Hx^{-1}H. \quad (6)$$

We call such a complex an NMR-mode.

Proof. A) Any permutation belonging to $M_{(x)}^{\text{NMR}}$ is NMR-equivalent to x .

Any permutation y belonging to the double coset HxH is related to x in the following way: $y = h_\alpha x h_\beta$ where h_α and h_β belong to H .

Four cases may arise.

- a) h_α and h_β both belong to G or
- b) h_β belongs to G , h_α does not belong to G .

In both cases, y may be written as

$$y = h_\alpha x g_\nu. \quad (7)$$

On the other hand, it is always possible to find an element $h_\gamma \in H$ such that

$$h_\alpha = h_\gamma g_\nu^{-1} \quad (8)$$

so that

$$y = h_\gamma (g_\nu^{-1} x g_\nu). \quad (9)$$

Therefore, x and y are NMR-equivalent by combination of relations (3) and (5).

- c) h_α belongs to G ; h_β does not belong to G .

Consequently, y may be written as

$$y = g_\mu x h_\beta. \quad (10)$$

From (10), it follows that

$$y^{-1} = h_\beta^{-1} x^{-1} g_\mu^{-1}. \quad (11)$$

In analogy with relation (7), it can be deduced that y^{-1} and x^{-1} are NMR-equivalent. Now, x^{-1} is NMR-equivalent to x and y^{-1} is NMR-equivalent to y . So y and x are also NMR-equivalent.

- d) h_α and h_β do not belong to G ; then, these elements may always be written as

$$h_\alpha = g_\mu h_\gamma \quad g_\mu \in G; h_\alpha, h_\gamma \notin G \quad (12)$$

and

$$h_\beta = g_\nu h_\delta \quad g_\nu \in G; h_\beta, h_\delta \notin G \quad (13)$$

since G is a subgroup of H . Then,

$$y = h_\alpha x h_\beta = g_\mu h_\gamma x g_\nu h_\delta = g_\mu z h_\delta$$

where $z = h_\gamma x g_\nu$.

In analogy with relation (10), z is NMR-equivalent to y ; in analogy with relation (7), x is NMR-equivalent to z . So x is NMR-equivalent to y .

So far we have proved that any permutation of the D.C. HxH is NMR-equivalent to x . Since the D.C. $Hx^{-1}H$ contains merely all the inverses of the permutations contained in the D.C. HxH , all the elements of the D.C. $Hx^{-1}H$ are NMR-equivalent to the elements of the D.C. HxH in virtue of relation (4).

- B) Conversely, any permutation y which is NMR-equivalent to x belongs to $M_{(x)}^{\text{NMR}}$. This is evident from inspection of relations (2–5).

We have thus proved that all the NMR-equivalent rearrangements, i.e. all the permutations which have to be carried together in a line-shape analysis in achiral environment are contained in a union of double cosets. The set of all the union of

D.C.'s is a partition of the group S of allowed permutations [3–7]. So, theoretically, there are as many qualitatively distinguishable line-shape patterns as there are different $M_{(x)}^{\text{NMR}}$ sets in the group S . This does not warrant however that NMR-line shapes corresponding to different NMR-modes are qualitatively distinguishable (see for instance Ref. [6]), but such a situation can only be due to some unfavourable combination of experimental parameters. The number of sets defined by relation (7) is merely the maximal number of distinguishable NMR-modes in achiral environment [4]. Note moreover that one of these sets (when x is an element of H) corresponds to the NMR-mode for which the line-shape remains unaffected (the trivial identity NMR-mode, $M_{(x_0)}^{\text{NMR}} = H$).

The theoretical treatment proposed here is more general than the proposal of Jesson and Meakin [6] since these authors did not anticipate the possibility that the D.C. HxH is not self-inverse. This fact was already outlined by Klein and Cowley [5]. It should be mentioned that if 2. (relation (4)) is not assumed, our theorem would lead to an HxG NMR-mode and *not* to the HxH NMR-mode predicted by Jesson and Meakin [6]. This comes from the different argumentation used by us and these authors. Indeed relation (1) of Ref. [6]

$$p_i = g_k p_j g_k^{-1} \quad (14)$$

coincides with our requirement (1), (relation (3)). However, our requirement (3), (relation (5)) does not correspond to relation (2) of Ref. [6]

$$p_i = h_z p_j h_i \quad (15)$$

which is suggested without justification by Jesson and Meakin and which has been replaced by the requirement

$$p_i = h_r p_j \quad (16)$$

in our theorem. It is then clear that combination of (14) and (16) leads to an HxG NMR-mode.

On the other hand, the set of NMR-equivalent permutations defined here does not correspond conceptually and mathematically to the one proposed by Klein and Cowley. In the formalism of Klein and Cowley [5], the argumentation is divided into two main steps: construction on an idealized skeleton of the modes of rearrangements followed by an adjustment of the set obtained in this way to the actual symmetry of the molecular species under consideration. Such a reasoning does unfortunately not lead to a NMR-mode as being the set of all those permutations which are indistinguishable by line shape analysis, since Klein and Cowley need a supplementary step, namely the construction of the site exchange matrix to find out whether their modes are distinguishable or not [5]; therefore the permutations contained in the set (29) or (25) of Ref. [5] do not correspond to the set of permutation $M_{(x)}^{\text{NMR}}$ of relation (7). The difference between our formulation and that of Klein and Cowley relies on the fact that these authors start from the Kubo-Sack formula and from their expressions Ref. [5], Eqs. (25, 27, 29). It is possible that some stochastic assumption contained in the Kubo-Sack formula through Ref. [5], Eq. (27) leads to indistinguishable line-shapes for different complexes of type Ref. [5], Eq. (29). However, these stochastic assumptions are accounted for by the use of the effective NMR hamiltonian.

The main advantage of the NMR-mode concept discussed here is that it defines immediately the full set of permutations which have to be considered together in a line-shape analysis both on the basis of symmetry and kinetics. We now want to illustrate these facts on two simple examples.

Let us consider a six-coordinate octahedral molecular skeleton with six identical monoatomic ligands. In this case, the group S and the group H are the symmetric group of permutations of six objects, S_6 . So, all the possible permutations will belong to only one NMR-mode which is trivially the group S_6 itself in this case, so that line-shape analysis is not of any use in this problem. This result can also be obtained by the formalism of Jesson and Meakin [6] since in this case the only existing double coset is self-inverse. The use of relation (25) of Ref. [5], however, will lead in a first step to five sets of permutations (the five modes of the octahedron [1, 3, 4]). In a second step, by calculating the site exchange matrix, they however will appear indistinguishable because the symmetry of the effective NMR hamiltonian has not been expressed in the first step. The second example we want to discuss briefly is the very elegant study by Whitesides, Eisenhut and Bunting [8a, 8d]. In that particular case, the groups G and H reduce to the trivial identity group. So double cosets HxH all contain one element. As is seen from table 1 of Ref. [8d], all couples of mutually inverse permutations have to be considered together because of the principle of detailed balance (see relation (5) and Refs. [4, 5, 8d, 13, 18]). This type of constraints cannot be deduced from the formalism of Jesson and Meakin [6], whereas they are automatically included by the mode concept discussed by Klein and Cowley and by the NMR-mode definition given here. We think that with the NMR-mode concept defined here it is possible to pass round some difficulties encountered when constructing NMR-modes by use of the preceding formalisms. These difficulties have led us to propose an alternative approach to the problem of defining NMR-modes in achiral environment which could be used by searchers interested in experimental distinguishability of rearrangements by NMR line shape analysis.

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