Fragment isotope distribution as a signature of molecular fluxionality

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A formula is presented that gives the distribution of isotopes in the fragments of a molecule in which the isotopes are distributed statistically. This serves as a test for molecular fluxionality, provided that the parent molecule has been labeled in some nonstatistical manner.

1. Fluxional molecules

Fluxional molecular systems have a curious fascination for chemists. These systems are interesting and important in understanding structure and reactivity relationships. Particularly interesting examples are the degenerate Cope rearrangements in bullvalene [1],

all atoms become equivalent (1)
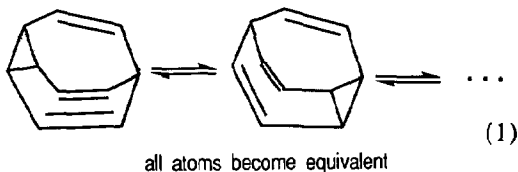
pseudorotation in PF_5 [2],

(2)

and organometallic ring whizzers [3]

$M = Re(CO)_5$
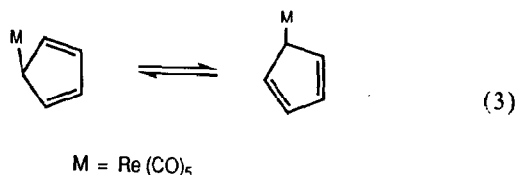
Most often, fluxionality is revealed through spectroscopic analysis, especially NMR. Sometimes ambiguity remains. For example, isomerization between two unsymmetrical structures is often difficult to distinguish from a static, symmetric structure, as occurs with the dynamic Jahn–Teller effect [4].

Another class of important fluxional systems involves the transition from solids to liquids. Berry [5] among others [6,7] has dealt with the spectroscopy of this kind of system and its applications in finite (small) systems. In some cases, NMR is too "slow" a method to reveal what is happening, and vibrational spectroscopy is a more appropriate tool.

It is especially interesting to examine the issue of fluxionality in the important developing area of cluster chemistry [8]. Will clusters exhibit the kind of symmetry associated with statistical randomness as

would be the case for a fluxional or liquid system, or do they maintain a more rigid structure? Especially in the case of ionic clusters, both the excess energy involved in the formation at low pressures and the relatively long lifetimes that are a consequence of the deep well depths that are associated with ionic potential surfaces may give rise to energy-rich activated systems that may exhibit fluxional or liquid-like behavior. Fluxionality or partially fluxional behavior can also arise in reactions that have potential surfaces such that exchange reactions can occur without any net reaction being visible. These reactions can be made apparent, however, by use of isotopic labeling. Mass spectroscopy is usually the method of choice for following such scrambling reactions, because the m/z of the fragmentation products provides a direct measure of the process. Its time scale is generally in between that of vibrational spectroscopy and NMR. Thus, gas-phase ions and ion–molecule reactions are a particularly attractive area for study, because the reaction and the analysis can be conducted simultaneously. In such studies, clusters or complexes must be formed with an initially nonstatistical distribution of isotopes, or fluxionality cannot be revealed in this way.

In this paper we present an expression for the distribution of isotopes in the fragments of a decomposing fluxional molecule. In simple cases the analysis can be done by inspection, but for more complex problems a closed mathematical expression may prove useful. The present treatment is an extension and generalization of one reported previously by Levine [9], who considered only a restricted set of this general problem.

2. Fragment isotope patterns

Consider a molecular complex containing $p+q$ nuclei of the same element E, p of isotope E_1, q of isotope E_2. Let this complex decompose into fragments. We determine the probability of finding that the fragment containing $i+j$ nuclei of element E that has i of isotope E_1 and j of isotope E_2, provided that the molecular complex is fluxional. (Here $0 < i+j < p+q$; otherwise no fragmentation occurs.)

This problem has a simple solution using combinatorials: The number of ways to choose i nuclei of

isotope E_1 in the fragment given p nuclei of isotope E_1 in the parent is p things taken i at a time, i.e.

$$\binom{p}{i} = \frac{p!}{i!(p-i)!}.\tag{4}$$

Similarly, the number of ways to choose j nuclei of isotope E_2 in the fragment when there are q nuclei of isotope E_2 in the parent is

$$\binom{q}{j} = \frac{q!}{j!(q-j)!}.\tag{5}$$

Thus, together there are $\binom{p}{i}\binom{q}{j}$ different ways of making up the fragment from the parent with this specific isotopic composition.

To find the fractional probability $P(p, q \to i, j)$ for the occurrence of this particular combination, we must divide by the number of ways you can choose $i+j$ nuclei of element E in the fragment out of $p+q$ nuclei of element E in the parent:

$$\binom{p+q}{i+j} = \frac{(p+q)!}{(i+j)![(p+q)-(i+j)]!}.\tag{6}$$

Hence

$$P(p, q \to i, j) = \binom{p}{i}\binom{q}{j} \Big/ \binom{p+q}{i+j}$$

$$= \frac{p!q!}{(p+q)!} \frac{(i+j)!}{i!j!} \frac{(p-i+q-j)!}{(p-i)!(q-j)!}.\tag{7}$$

Note that this probability is normalized to unity, i.e.

$$\sum_{i=0}^{p} \sum_{j=0}^{q} P(p, q \to i, j) = 1.\tag{8}$$

To illustrate this result, consider the process $CH_3^+ + D_2 \to HD_2^+ + CH_2$ or $CH_3 + D_2^+ \to HD_2^+ + CH_2$ or the reverse reactions. In any case we have a complex $[CH_5^+]$ containing five nuclei of the element hydrogen in which three are H and two are D, i.e. $p=3$ and $q=2$. Suppose that all the hydrogens are equivalent in the complex and we want to know the expected isotope ratios in the product containing two hydrogen nuclei, i.e. $i+j=2$. We must evaluate

$$P(3, 2 \to 2, 0) = \binom{3}{2}\binom{2}{0} \Big/ \binom{5}{2} = 0.3,$$

$$P(3,2\rightarrow1,1)=\binom{3}{1}\binom{2}{1}\Big/\binom{5}{2}=0.6,$$
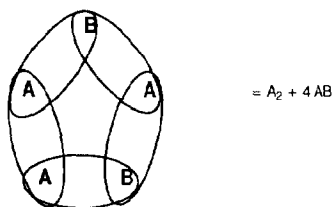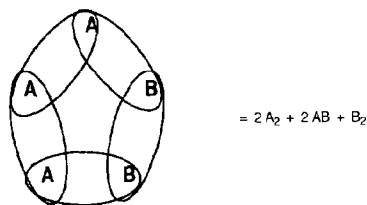
$$P(3,2\rightarrow0,2)=\binom{3}{0}\binom{2}{2}\Big/\binom{5}{2}=0.1,$$

and as expected the probabilities sum to unity.

Alternatively, this result can also be readily derived from examining graphs. Thus $P(3, 2\rightarrow i, j)$ where $i+j=2$ is obtained by considering the two rings

that occur with equal probability, and working out the pairwise cuts:

$$= 2A_2 + 2AB + B_2$$

$$= A_2 + 4AB$$

from which its is concluded that A_3B_2, if fluxional, may be decomposed into $3A_2+6AB+B_2$.

Of course, this is a fairly simple example. The expression for $P(p, q\rightarrow i, j)$ given by eq. (7) is general. Clearly, few would want to enumerate graphs when p, q, i, j become sizable integers, as might be encountered in many large cluster ions.

A more complex example is the recent study of isomerization reactions in Ar clusters, which provides a possible application of our approach. Wales [10] has calculated energies for five transition states for the Mackay icosahedral Ar_{55} cluster. These tran-

sition states allow exchange between the inner and outer icosahedral shells and result, eventually, in statistical scrambling of the atoms in the cluster. If it were possible to synthesize such a cluster by addition of labeled Ar atoms to a small Ar cluster, one could then ascertain from subsequent fragmentation into large fragments whether (and how much) exchange had occurred. This problem is an unusually interesting one, because it deals with transitions between liquid-like and solid-like freezing/melting in finite systems. Moreover, if the smaller fragment is detected, the dynamic range of the ratio of labeled to unlabeled fragment spans nearly a decade. Carbon atom clusters (e.g. ref. [11]) offer a different type of system where the forces are stronger and much more directional in character. The cations of such clusters, however, will be generally more fluxional than are the neutrals.

Obviously, when the parent molecule is synthesized or created, the distribution of isotopic labels must differ from that arising from a purely random distribution. Isotopic randomness can also be accomplished by selective excitation. Because a fluxional system always gives an isotopic distribution equivalent to a random distribution, the isotopic analysis of the fragments from a parent with a random distribution of isotopes cannot record any change. Thus, the degree of fluxionality or rigidity remains hidden.

In addition, this treatment neglects the familiar small isotope effect that is related to zero-point energy differences resulting from the different masses of the isotopes [12]. Indeed, these small energy differences can generate nonrandom distributions of isotopomers at very low temperatures, which are characteristic of supersonic expansions.

The opening up of additional phase space due to permutation of nuclei via skeletal rearrangement increases the number of available states of the activated molecule. Note however that there is also a corresponding increase in the number of decay modes, which exactly compensates, by eq. (8), the increase in the number of states. The rate of dissociation is thus unaffected. The rate of formation of a particular isotopomer (i, j) is the fraction $P(p, q\rightarrow i, j)$ of the total rate.

The proposed signature of fluxionality can be verified only for energy-rich molecules above the

threshold for dissociation, activated by photons, collisions or chemical reactions. There is both theoretical [5,13,14] and computational [15–17] evidence that some ordinary molecules, which are rigid at lower levels of excitation, will become fluxional even below the onset of fragmentation. The observation of isotopic scrambling shows that, prior to dissociation, the energy-rich molecule has indeed sampled all (or much) of the available phase space.

Acknowledgement

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