Isotopologue single-molecule mixture

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Date: 2026-05-07T09:44:48+00:00

Abstract

Abstract: This paper explores the concept of isotopomeric single-molecule mixtures in detail and poses an intriguing question: for an aggregate of organic molecules with a single structural formula and a natural isotopic distribution of carbon (or chlorine, bromine) at 1 mol, what is the minimum number of non-equivalent carbon (or chlorine, bromine) atoms required in the molecular structure for the aggregate to exist as an isotopomeric single-molecule mixture with a probability of 99.999%? Corresponding results are provided through a detailed estimation process.

Full Text

Preamble

Isotopologue Unimolecular Mixtures

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摘要

This paper provides a detailed exploration of the concept of isotopomer-based single-molecule mixtures. It poses an intriguing question: for an aggregate of organic molecules with a single structural formula and a natural isotopic distribution of carbon (or chlorine, bromine), what is the minimum number of non-equivalent carbon (or chlorine, bromine) atoms required in the molecular structure to ensure, with a probability of 99.999%, that the aggregate exists as a single-molecule mixture of isotopomers?

Through a detailed estimation process, the corresponding results are presented.

关键词

Single-Molecule Mixtures, Isotopomers, and Isotopologic Single-Molecule Mixtures

A single-molecule mixture refers to a mixture composed of individual molecules, each characterized by a distinct structural formula.

Isotopomers and Isotopologic Single-Molecule Mixtures

In the context of molecular sciences, isotopomers (isotopic isomers) are molecules that have the same number of each isotopic atom but differ in their positions. When a mixture is composed of such unique individual molecules, it can be classified as an isotopologic single-molecule mixture. This concept is particularly relevant when considering the statistical distribution of isotopes within complex molecular frameworks, where the probability of two identical molecules existing in a small-scale sample becomes infinitesimally low.

For a molecule with a single structural formula, different isotopologues are formed due to the variations in isotopic distribution at each site within the structure.

Isomers of this type are referred to as isotopomers. Taking n-propane as an example, all of its carbon isotopomers are illustrated in [Figure 1: see original paper]. A mixture composed of these various isotopomers is defined as an isotopomeric mixture. Furthermore, when the isotopic distribution state of every individual molecule within such a mixture is unique, the mixture is specifically classified as a single-molecule isotopomeric mixture.

Based on the concepts discussed above, an intriguing question arises: for an aggregate of organic molecules with a single structural formula and a natural carbon isotope distribution (^{12}C, 98.9%; ^{13}C, 1.1%), what is the minimum number of non-equivalent carbon atoms required in the molecular structure for the aggregate to exist as a mixture of carbon-isotopomer single molecules with a probability of 99.999%? (As illustrated in [Figure 2: see original paper]). The detailed estimation process is presented below.

First, let us analyze a realistic structural space composed of all possible carbon isotopomers. This structural space contains 2^n possible configurations. For any given structure, its probability of formation is equal to the product of the probabilities of each specific site being substituted by a particular carbon isotope. Consequently, the formation probabilities of individual structures can vary significantly.

They may not be equal; in fact, the actual structural space is highly complex.

Next, we seek to identify the structure with the highest probability of occurrence among all possible isomers. It is evident that the most probable isomer is the one in which all carbon atoms are ^{12}C, with an occurrence probability of 0.989^n.

Real-world systems are extremely complex, necessitating the individual calculation of formation probabilities for every possible isomer. To simplify this system, we have constructed a simplified virtual framework and designated the isomer with the highest formation probability as the reference state. This virtual space contains $p-1$ different types of structures, which are randomly distributed with equal probability such that the probability of selecting any specific structure is p.

Let us discuss the concept of the virtual structure space in greater detail. The virtual structure space is established based on the structure with the maximum generation probability (p) within the real structure space. This space contains $p-1$ structures, where each structure is assigned a generation probability of p.

When compared to the real structure space, the virtual structure space possesses a total number of structures that is less than or equal to the former. Furthermore, the generation probability of any structure within this virtual space is greater than or equal to the generation probability of any structure found in the real structure space.

According to the single-molecule mixture computational model previously constructed in Section 2, if a structure is randomly sampled from this space m times, the probability that all obtained structures are distinct is less than or equal to the probability of obtaining distinct structures when sampling m times from the actual structural space. Consequently, utilizing a simplified virtual structural space as a substitute for the complex real structural space to estimate the generation probability of single-molecule mixed states is both reasonable and feasible.

Based on the relevant computational formulas derived from the aforementioned single-molecule mixture model, if 1 mol of molecules is randomly selected from this space, the number of available molecular structures in that space must be at least 3.63×10^{52} to ensure that the probability of forming a single-molecule mixed state exceeds 0.99999.

Therefore, the following estimation formula is obtained:

$$p - n > 3.63 \times 10^{52}$$

By substituting $p = 0.989$, the calculation yields $n > 10944$. Thus, the minimum value for n is 10945.

Based on the aforementioned computational principles, we can further estimate the scenario in which 1 mol of a single-structure molecule contains n atoms.

When a molecular aggregate contains chlorine atoms with their natural isotopic distribution (^{35}Cl, 75.8%; ^{37}Cl, 24.3%) or bromine atoms (^{79}Br, 50.7%; ^{81}Br, 49.3%), the minimum value of n is determined such that the aggregate exists as a mixture of single-molecule isotopologues with a probability of 99.999%.

For Cl, the condition $n > 437$ implies that the minimum value of n is 438; for Br, the condition $n > 178$ implies that the minimum value of n is 179.

These intriguing computational results reveal that for an organic molecule with a single structural formula and a natural isotopic distribution, the sample has a probability greater than 99.999% of existing as a mixture of isotopomeric single molecules (provided the aggregate quantity is less than or equal to 1 mol) under the following conditions: the molecule contains more than 10,945 chemically non-equivalent carbon atoms, more than 438 chemically non-equivalent chlorine atoms, or more than 179 chemically non-equivalent bromine atoms.

参考文献

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Note: Figure translations are in progress. See original paper for figures.