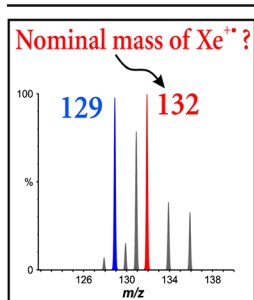


## CORRESPONDENCE

## Nominal Mass?

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**Abstract.** The current IUPAC-recommended definition of the term “nominal mass,” based on the most abundant naturally occurring stable isotope of an element, is flawed. We propose that *Nominal mass* should be defined as the sum of integer masses of protons and neutrons in any chemical species. In this way, all isotopes and isotopologues can be assigned a definitive identifier.

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The technical term “nominal mass” is widely used not only in undergraduate and high-school chemistry textbooks but also in high-level mass spectrometric discussions. According to IUPAC recommendations, the nominal mass is defined as the “mass of a molecular ion or molecule calculated using the isotope mass of the most abundant constituent element isotope of each element rounded to the nearest integer value and multiplied by the number of atoms of each element” (IUPAC RECOMMENDATIONS 2013, K. K. Murray, R. K. Boyd, M. N. Eberlin, G. J. Langley, L. Li, and Y. Naito, *Pure Appl. Chem.* 2013, 85, 1515–1609) [1]. The recommendation for this terminology has been adapted from a statement in a publication by Yergey et al. on isotopic distributions in mass spectra of large molecules [2]. The original statement reads, “NOMINAL MASS of the molecular ion, calculated by using the most abundant isotope, without regard for the mass defect.” The point the authors wanted to stipulate was that in the spectra recorded for large ions, a peak that represents the true “nominal” is not observed. It is most unlikely that the authors expected or intended that their statement should be taken as a universal definition for the nominal mass.

Unfortunately, the statement of Yergey et al. has been adopted widely by the public [3–5]. For example, according to Wikipedia, the nominal mass of an ion or molecule is calculated using the integer mass (ignoring the mass defect) of the most abundant isotope of each element [6]. Sometimes the statement is even misstated as “the mass of an ion with a

given *empirical* formula calculated using the integer mass numbers of the most abundant isotope of each element” [7].

Occasionally, some people even say that the nominal mass is a rounded-up number. Obviously, the use of rounding is inappropriate because mathematically, 149.6 is rounded to 150 whereas 149.4 is rounded to 149. A few others advocate that the nominal mass of an element is the integer mass of the most abundant naturally occurring stable isotope of an element. In general, all these definitions are flawed. If these definitions were to be accepted, one isotope of an element is artificially and discriminately selected to represent all other isotopes of the element. For example, xenon is a mixture of numerous naturally occurring isotopes (Table 1). Its atomic weight is 131.29 g/mol. So what is the nominal mass of Xenon? Looks like  $^{132}\text{Xe}$  wins by a nose over its nearest competitor  $^{129}\text{Xe}$  by the IUPAC definition, while constituting just a little over a quarter of the overall isotopic abundance of the element. Simply because  $^{132}\text{Xe}$  is more abundant by a whisker than its competitor  $^{129}\text{Xe}$  in nature, should  $^{132}\text{Xe}$  be appointed to represent all atoms of xenon? Moreover, the natural abundances of isotopes are variable depending on the geographical origin of the sample. It would not be surprising if a specific sample were found with  $^{129}\text{Xe}$  as the most abundant nuclide. In other words, it is not sensible to assign 131.904154 u as the monoisotopic mass of xenon because it corresponds to the most abundant isotope of the element.

Furthermore, according to the IUPAC recommendations,  $^1\text{H}^+$ ,  $^1\text{H}^\bullet$ , and  $^1\text{H}^-$  do not bear the same exact mass, but they all share the same nominal mass of 1 u. However, if we were to accept the IUPAC definition, then  $^2\text{D}^+$ ,  $^2\text{D}^\bullet$ , and  $^2\text{D}^-$  should

**Table 1.** Nuclides of Xenon

Nuclide	Exact mass (u)	Natural abundance (%)	Proposed nominal mass (u)
<sup>124</sup> Xe	123.905896	0.09	124
<sup>126</sup> Xe	125.904269	0.09	126
<sup>128</sup> Xe	127.903530	1.92	128
<sup>129</sup> Xe	128.904779	26.44	129
<sup>130</sup> Xe	129.903508	4.08	130
<sup>131</sup> Xe	130.905082	21.18	131
<sup>132</sup> Xe	131.904154	26.89	132
<sup>134</sup> Xe	133.905395	10.44	134
<sup>136</sup> Xe	135.907220	8.87	136

not be assigned the nominal mass of 2 u because deuterium is not the most abundant isotope of the element hydrogen.

By the IUPAC definition, molecular deuterium and D<sub>2</sub>O simply cannot be assigned nominal masses because deuterium is not the most abundant isotope of hydrogen. Worse yet, none of the above definitions enable us to assign an unambiguous nominal mass to molecules such as CD<sub>3</sub>OH, CH<sub>3</sub>OD, CD<sub>3</sub>-CH<sub>3</sub>, or any isotopically labeled compound. It can even be argued, tongue-in-cheek, that D<sub>2</sub> is a massless form of the element hydrogen because no nominal mass can be assigned to it, and hence “heavy water,” D<sub>2</sub>O, is by definition lighter than H<sub>2</sub>O! Some people even go to the extreme of saying that deuterium is not an element because it is not the most abundant isotope of hydrogen. What results do we expect then if we subject a compound such as CD<sub>3</sub>-CH<sub>3</sub> to elemental analysis? Must a separate “isotope” analysis be performed since deuterium “is not an element”? Moreover, by the IUPAC definition, all man-made elements should not be assigned nominal masses because their natural abundances are zero.

Clearly, there is a need for an improved definition that is universally applicable to all molecules, charged or not. We propose to define the *nominal mass* of any chemical species as the sum of the unified-mass-scale- based integer masses of its constituent protons and neutrons. By this definition, all nuclides of any element, and each isotopologue of a polyatomic molecule, radical, molecular cluster, or ion can be assigned a specific nominal mass. In other words, <sup>79</sup>Br or <sup>107</sup>Ag are not given preference over their slightly less abundant isotopes, and <sup>1</sup>H<sup>37</sup>Cl, H<sub>2</sub><sup>18</sup>O, D<sub>2</sub>, and D<sub>2</sub>O can each now be assigned a definitive nominal mass. It follows that isobars and isotopomers are species with the same nominal mass. Moreover, with this new definition, we can assign nominal masses to entities such as neutral radicals, fragment ions, nuclides, and individual ions in a cluster of charged isotopologues, some of which were in fact, perhaps inadvertently, excluded from the IUPAC definition.

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