SHORT COMMUNICATION

Unsuitability of $^{12}C_{60}$ as a Standard of Atomic Weight

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A critical discussion is given of the suggestion by Dougherty et al. (*J. Am. Soc. Mass Spectrom.* **1994**, *5*, 120) that the $^{12}C_{60}$ molecule replace the ^{12}C atom as the primary standard of atomic mass. Adoption of the proposed standard would require that the unified atomic weight/mass scale, finally achieved with much difficulty in 1960, be abandoned without demonstrable benefit. Furthermore, the proposed standard has a molecular mass that is inherently ambiguous at a level that makes it unacceptable for that purpose. (*J Am Soc Mass Spectrom 1995, 6, 1243–1246*)

In a recent article, Dougherty et al. [1] commented on the definitions of the current atomic weight/mass standard, the unit of atomic mass, u (defined as 1/12 the mass of a gas-phase ^{12}C atom), and the mole (defined to contain as many elementary entities as the number of atoms in 0.012 kg of carbon 12). They pointed out that, in each case, if the definition does not include a statement about the physical state of the ^{12}C, for example, by failing to distinguish between gas-phase carbon atoms and graphite or diamond, the definition is ambiguous. Because the heat of atomization of graphite is 7.4245 eV/atom, and this energy is lost when carbon is condensed and carries with it relativistic mass, 0.012 kg of ^{12}C graphite contains $\sim 4.0 \times 10^{14}$ more ^{12}C atoms than the same mass of gas-phase carbon atoms. Similarly, 0.012 kg of ^{12}C diamond, at 298 K, contains $\sim 1 \times 10^{12}$ fewer atoms than the same mass of ^{12}C graphite. Correspondingly, the authors noted that the $^{12}C^+$ ion is lighter than the ^{12}C atom by the mass of the electron, but heavier by 11.256 eV (the ionization potential of the carbon atom). With this in mind, Dougherty et al. suggested that the unit of atomic mass be redefined as 1/720 the mass of the $^{12}C_{60}$ buckminsterfullerene molecule, and that the mole correspondingly be defined as the number of $^{12}C_{60}$ molecules in 0.720 kg of solid $^{12}C_{60}$. Their justification for this definition is that ignoring the heat of vaporization of the solid-phase standard or the ionization potential of the gas-phase species causes a much smaller error ($\sim 3 \times 10^{-12}$) than would result if the heat of vaporization of graphite were ignored ($\sim 7 \times 10^{-10}$) in the present definition. Additionally they point

out that the uncertainties in these quantities, per carbon atom, are at least an order of magnitude smaller for the $^{12}C_{60}$ molecule compared to the ^{12}C atom, so that the definitions should be correspondingly more precise.

The reason given for advancement of this proposal at this time is that mass measurement precision of ~ 100 ppb is now obtainable in 3-T Fourier transform ion cyclotron resonance (FTICR) mass spectrometers and that "there is a reasonable basis for the expectation that the precision in mass measurement accuracy will be capable of reaching the levels below ~ 1 ppb with the new generation of instruments" (i.e., with high field FTICR instruments).

Comments on the Proposal

Status of the Present Definition

We note first that the effect of the chemical state of carbon on the definition of the mole has not been "neglected," as suggested in ref 1. The formal definition of the mole as a base unit of the Système International d'Unités (SI) was adopted by the 14th Conférence Général des Poids et Mesures [CGPM (1971), resolution 3]. Beginning with the fourth edition of *Le Système International d'Unités* published by the Bureau International des Poids et Mesures (BIPM) in 1982 and continuing in the most recent (6th) edition [2], the definition is followed immediately by the statement: "In the definition of the mole, it is understood that *unbound atoms of* ^{12}C, *at rest and in their ground state* are referred to" (emphasis added). A similar sentence also appears in the most recent IUPAP (the International Union of Pure and Applied Physics) statement of the definition of the mole [3]; although such a statement

was omitted in the current IUPAC (the International Union of Pure and Applied Chemistry) statement, it will be included in the forthcoming revision (E. Richard Cohen, private communication). Thus the potential errors that arise from confusion over the physical state of carbon have been recognized clearly and addressed precisely.

A direct experimental connection between the mole and the unit of atomic mass (u) is not readily available, that is, it is not feasible to assemble 0.012 kg of gas-phase carbon atoms and determine the number of atoms present (Avogadro's number). Although these quantities can be linked by accurate measurements of the heat of atomization of graphite or diamond, where the error in the definition of the mole associated with such a determination is currently less than $\sim 1 \times 10^{-13}$, it is quite unlikely that a determination of the mole would use either graphite or diamond (or buckminsterfullerene). The material required must be an extremely pure element of known isotopic composition that can be grown into a large, nearly perfect single crystal, and in which the number of atoms can be determined by precise x-ray diffraction techniques. At present silicon is by far the best candidate for such measurements [4, 5], and the link between the unit of atomic mass and the mole relies on accurate measurement of the atomic masses and isotopic abundances of the silicon isotopes. The proposed change in the atomic mass standard would not improve the accuracy of such measurements.

Status of Experimental Precision

The proposal made in ref 1 is to alter a fundamental definition, on the basis of determinations with a particular type of apparatus (FTICR), assuming a precision not yet realized with that apparatus.

Mass measurement with a precision that approaches ~ 1 ppb has, in fact, been attained for well over 20 years, both with the radiofrequency mass spectrometer of Smith [6] for the light elements and with magnetic deflection instruments [7] in the upper mass region. Thus, in the 1983 Atomic Mass Evaluation of Wapstra and Audi [8] the masses of light nuclides already were known to a few nanounits (where 1 nu = 0.93 eV). Mass differences of heavier nuclides, such as ^{37}Cl- ^{35}Cl, similarly were determined with < 2-ppb accuracy, although the corresponding energy uncertainty at this mass is some 50 eV [9]. Measurements of ^{67}Zn- ^{68}Zn and of ^{57}Fe- ^{56}Fe mass differences were made to $\sim$ 2.5-ppb precision on an instrument originally constructed in the 1950s [10].

Recent developments with Penning ion trap mass spectrometers have improved the level of precision to well below the 1-ppb level, notably in the work of Van Dyck et al. [11], Natarajan et al. [12], and DiFilippo et al. [13], where single multiply charged ions are studied (and appropriate corrections are made for the ionization potentials of these ions). Results from these

instruments [11, 12] have been incorporated into the 1993 Atomic Mass Evaluation of Audi and Wapstra [14]. Although FTICR instruments also have been used for mass determinations [15], the results to date have been 2 or 3 orders of magnitude less precise. Moreover, these results indicate that the coupling of the motions of ions that have masses that differ by small amounts introduces systematic effects that are not corrected readily at this level of precision [16].

The relativistic effects of chemical potential and electron binding energies on atomic masses were recognized clearly many years ago. For example, the possibility was considered that electronically excited metastable ions could have influenced the mass determination of ^3He [17], and a 2.5-nu correction was made in measurements of the ^1H mass to account for the chemical binding energy difference between two doublet components $C_9H_{20}^+$ and $C_{10}H_8^+$ [18]. More recently, the direct measurement of the mass of an isotope in an excited nuclear state has been made [19].

Criteria for a Primary Standard

The most important criteria that govern the choice of a primary atomic (and molecular) mass standard are that its mass be defined precisely and that it be experimentally accessible, that is, the standard must allow the most convenient and accurate comparisons possible for the masses to be determined.

The latter criterion was a principal factor that governed the choice, in a coordinated action by the IUPAP and IUPAC in 1960, of ^{12}C to replace the previous ^{16}O standard [20]. By this time mass spectrometry had become the principal means to obtain atomic masses for individual isotopes. Precise atomic masses are determined, with deflection mass spectrometers, by making the most accurate possible measurements of the smallest possible mass difference between the mass to be determined and a secondary standard, typically a molecular hydrocarbon ion. The almost unlimited variety of hydrocarbon ions allows relatively narrow mass doublets to be constructed for almost all the stable isotopes, where the reference mass usually contains only ^{12}C and ^1H, whereas only a limited number of such doublets are possible with oxygen-containing ions. The ^1H mass has been determined accurately (with hydrocarbon ions as in [18] or with a Penning trap as in [11]) for use as a secondary standard. (We note that doublet measurements involve a comparison of two ion species, so that the electron is removed from both and the ionization potential affects the mass difference only as the *difference* in ionization potentials of the two species involved; typically this would be a correction of no more than 1-2 eV at mass $\sim$ 100-150, that is, $\sim$ 1 part in 10^{11} with an uncertainty 2-3 orders of magnitude smaller. The difference in chemical binding energies of the two ion species is typically a larger correction [18].)

Experimental Accessibility

The requirement for narrow mass doublets for accurate mass measurement highlights an important deficiency of $^{12}C_{60}$ as a primary mass standard. This choice offers no direct narrow mass doublet comparisons with any of the stable isotopes. It could be argued that these measurements could be done as before, with the ^{12}C atom as a secondary standard whose mass is determinable from the $^{12}C_{60}$ standard with some thermochemical information. However, the thermochemical information required is the heat of atomization of $^{12}C_{60}$, which is almost identical to that of graphite and carries similar errors, so that nothing is gained in this approach. Even if there were no other problem with the definition of the proposed standard, we question the utility of redefinition of the mass standard in a way that makes atomic mass measurements more indirect, but no more accurate. It also might be argued that $^{12}C_{60}$ has benefits as a *molecular* mass standard, but the number of molecules whose masses are sufficiently close to that of $^{12}C_{60}$ to allow accurate determination in narrow mass doublets is so limited as not to be a factor.

It is granted that the development of accurate mass measurement techniques by using cyclotron resonance instruments may eventually make it unnecessary to rely on narrow doublets; measurement of large frequency differences of factors of 2 or more is possible today with a precision that is far better than 1 ppb. However, it is noted that precise mass determination, in common with other precise measurement problems, is frequently limited by systematic errors that scale with the size of the primary measurement attempted (i.e., in this case with the mass separation of the target doublet). Cyclotron resonance techniques may not be immune to such errors.

The most precise ion trap measurements to date have been obtained with single ion cyclotron resonance (SICR) instruments operated for masses far below that of the proposed standard. For example, in the work of DiFilippo et al. [13], a precision better than 1 part in 10^{10} was attained for ions that have $m/z \sim 40$. The ion traps that have been used to study the higher masses [15, 19] have achieved a much lower level of precision, especially in the case of FTICR [15, 16]. Thus, with $m/z = 720$, the proposed standard would be remote—virtually inaccessible for the most precise (SICR) measurements, while contributing no improvement to measurements at masses of interest in molecular studies (e.g., FTICR). We argue that a mass standard whose usefulness is related primarily to making measurements that are less accurate than those based on the existing standard has little to recommend it.

Precise Definition of a Standard

A final deficiency of $^{12}C_{60}$ as a mass standard lies in the fact that $^{12}C_{60}$ is a molecule that has 174 vibra-

tional modes, each of which has mass associated with it when excited. In fact the zero-point energy of the molecule is calculated to be 10.2 eV. The mass associated with this vibrational energy would be an additional correction factor to the atomic mass scale and ignoring it, as in ref 1, introduces an error of ~ 0.014 ppb. However, this correction can be made without difficulty. (Note, however, that operationally the zero-point energies of the $^{12}C_{60}^{+}$ and $^{12}C_{60}^{-}$ ions and of the neutral molecule are needed, and these will differ slightly.) A more intractable problem is the fact that the $^{12}C_{60}$ molecule can be excited vibrationally at any temperature above absolute zero and thus the molecule has a *temperature-dependent* mass. From the vibrational frequency spectrum (J. Menendez, Arizona State University, 1994, private communication) it may .be estimated that the molecule is ~ 2.5–3 eV heavier at a sublimation temperature of ~ 700 K than at 0 K. Although even this quantity is, in principle, calculable because the vibrational properties of the molecule are so well studied and we might hope to know the average temperature of a properly equilibrated $^{12}C_{60}$ vapor, a more severe difficulty arises because measurements necessarily must be performed with ions, which typically will be excited additionally through Franck–Condon transitions in the process of ionization. It appears at present that it would be extremely difficult to determine or to specify the vibrational temperature of a positive or negative $^{12}C_{60}$ ion in the same measurement in which it would be used as a mass standard. Although the uncertainties involved are small (a few electronvolts per $^{12}C_{60}$ molecule), they are significantly larger than the uncertainty in the ground state $^{12}C_{60}$ mass calculated by using the present standard, which result from the uncertainty in the heat of atomization of $^{12}C_{60}$ (~ 10 meV per $^{12}C_{60}$ molecule if the accuracy is similar to that for graphite) and the uncertainty in the ground-state energy (perhaps 100 meV).

Conclusion and Recommendation

We agree with Dougherty et al. that the definition of the mole is ambiguous (but not uncertain) if the physical state of the carbon reference material is not specified. However, neither the CGPM nor the IUPAP definitions are ambiguous when the full statements are considered because both specify that the carbon atoms in the definition are unbound, at rest, and in their ground states [2, 3]. Ambiguity in the IUPAC statement will be removed in the forthcoming revision with a similar statement. With these definitions, the unit of atomic mass can be connected to the mass of a carbon atom in graphite, at 298 K, with an uncertainty of only ~ 1 part in 10^{14} that arises from the heat of atomization. If gas-phase $^{12}C_{60}$ ions were to be used to define the unit of atomic mass, the uncertainty in the connection to the mole that arises from the combination of a temperature-dependent molecular mass and an inde-

terminate molecular temperature would increase to ~ 1 part in 10^{12}. Although this is well below any projected measurement precision for atomic or molecular masses, or the mole, it seems unproductive to sacrifice 2 orders of magnitude in precision in the definition of a fundamental constant in the absence of other benefits, such as dramatically improved accuracy and convenience in measurement.

Following the CGPM and IUPAP statements, and the forthcoming IUPAC revision, and maintaining the principle of unified definitions, we recommend that the primary standard of atomic mass remain 1/12 the mass of an isolated ^{12}C atom, at rest, in its atomic and nuclear ground state.

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