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Mass of ^{17}O from Penning-trap mass spectrometry and molecular spectroscopy: A precision test of the Dunham-Watson model in carbon monoxide

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By fitting the Dunham-Watson model to extensive rotational and vibrational spectroscopic data of isotopic variants of CO, and by using existing precise masses of ^{13}C, ^{16}O, and ^{18}O from Penning-trap mass spectrometry, we determine the atomic mass of ^{17}O to be $M[^{17}\text{O}] = 16.999\,131\,644(30)$ u, where the uncertainty is purely statistical. Using Penning-trap mass spectrometry, we have also directly determined the atomic mass of ^{17}O with the more precise result $M[^{17}\text{O}] = 16.999\,131\,756\,6(9)$ u. The Dunham-Watson model applied to the molecular spectroscopic data hence predicts the mass of ^{17}O to better than 1 part in 10^8.

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I. INTRODUCTION

The most precise measurements of atomic masses, with fractional uncertainties of 0.1 parts per billion (ppb) or better, are currently made by comparing cyclotron frequencies of single ions trapped in a cryogenic Penning trap [1–11]. As specific examples, by using such techniques, the atomic masses of ^{13}C [4,8], ^{16}O [7], and ^{18}O [9] (relative to ^{12}C, which is 12 u by definition) have been determined with reported fractional one-standard-deviation uncertainties of 0.02, 0.01, and 0.07 ppb, respectively. Nevertheless, for chains of isotopes, it is still interesting to consider the method, of historical importance, in which isotopic masses are determined from the mass dependence of rotational and vibrational transitions of isotopic variants of simple molecules [12]. Here, we investigate the use of the Dunham-Watson model for the rovibrational energies of a closed-shell diatomic molecule, together with an extensive set of precision spectroscopic data for rotational and vibrational transitions of CO in all its stable isotopologs, i.e. containing ^{12,13}C and ^{16,17,18}O [13–20], for predicting masses of oxygen isotopes. If an expression with only first-order Born-Oppenheimer breakdown parameters is used, and the masses of ^{13}C and two of the three oxygen isotopes are used as input, the fit can be used to predict the mass of the third oxygen isotope. Although analogous studies can be carried out with other diatomics with several isotopologs, CO has the advantage of the largest quantity of high-accuracy data.

Previously, by making use of these high-precision atomic masses for ^{13}C and ^{16}O and a mass value for ^{17}O with quoted uncertainty of 7 ppb as given in the 2003 Atomic Mass Evaluation (AME2003) [21], we used the spectroscopic fit to derive a value for the (then) least-well-known mass of the three oxygen isotopes, that of ^{18}O. The result was $M[^{18}\text{O}] = 17.999\,159\,74(5)(25)$ u, where the first number in parentheses is a statistical uncertainty derived from the χ^2 of the fit and the second is the uncertainty due to propagating the uncertainty in the AME2003 value for the mass of ^{17}O. This result for $M[^{18}\text{O}]$, which disagreed somewhat with the accepted AME2003 value of 17.999 161 0(7) u by 1.3(0.7) μu, was subsequently confirmed by Penning-trap mass spectrometry, which gave 17.999 159 613 0(13) u [9] [i.e., only 0.13(0.25) μu or 7(14) ppb lower than the molecular spectroscopy result]. Here, the uncertainty in the comparison is limited by the uncertainty due to the propagated uncertainty in the mass of ^{17}O. This already indicated, at least in favorable cases, the ability of molecular spectroscopy and the Dunham-Watson model to predict isotopic masses at the part-in-10^8 level of precision.

Here, we report an extension of the precision of such comparisons to below the part-in-10^8 level. To provide a direct test of the predictive power of the Dunham-Watson model applied to the molecular data, we chose the following simple protocol: First, we used a new fit to the CO spectroscopic data, together with the previous Penning-trap masses of ^{13}C [4,8] and ^{16}O [7] and the new Penning-trap mass of ^{18}O given in Ref. [9], to predict the (now) least-well-known mass, that of ^{17}O. Subsequently, we directly measured the atomic mass of ^{17}O using precision cryogenic mass spectrometry.

II. MASS OF ^{17}O FROM SPECTROSCOPY OF ISOTOPOLOGS OF CO

The lower vibrational and rotational energies of the $^1\Sigma$ ground state of the diatomic molecule CO, whose lowest excited electronic state ($^3\Pi$) lies 48 000 cm^{-1} higher [22], are expected to be well described by the Dunham expression [23]:

$$E(\upsilon,J) = \sum_{ij} Y_{ij}\left(\upsilon + \frac{1}{2}\right)^i J^j (J+1)^j. \qquad (1)$$

Following Watson [24–26], the Dunham coefficients Y_{ij} can be expressed in terms of *isotope-independent* parameters U_{ij} and first-order Born-Oppenheimer breakdown corrections $\Delta^{C,O}$, using

$$Y_{ij} = U_{ij}\left(1 + \frac{m_e \Delta^C_{ij}}{M_C} + \frac{m_e \Delta^O_{ij}}{M_O}\right)\mu^{\frac{-(i+2j)}{2}}, \qquad (2)$$

where $M_{C,O}$ are the atomic masses of the isotopes and μ is the reduced molecular mass.

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TABLE I. Average cyclotron frequency ratios (i.e., inverse mass ratios) and systematic corrections for each ion pair. N is the number of runs. Δ_{trap} is the estimated systematic correction in ppt, with uncertainty in parentheses, for trap field imperfections; Δ_{i-i} for ion-ion interaction; Δ_{fz} for shifts in f_z due to ion-detector interaction and differential voltage drift; and Δ_{mol} for polarizability shifts (for $^{16}OH^+$) and vibrational excitation (for $^{17}O_2^+$), respectively. σ_{sys} is the total systematic uncertainty and σ_{stat} is the statistical uncertainty (in ppt) for each average ratio. $\langle R\rangle$ is the average ratio after applying systematic corrections, with statistical and systematic uncertainties combined in quadrature.

Ion pair	N	Δ_{trap}	Δ_{i-i}	Δ_{fz}	Δ_{mol}	σ_{sys}	σ_{stat}	⟨R⟩
$^{16}OH^+/^{17}O^+$	4	0(25)	0(5)	−1(28)	−161(9)	39	82	0.999 787 798 486(91)
$^{28}SiD_3^+/^{17}O_2^+$	8	−1(16)	0(3)	−1(3)	−13(7)	18	33	0.999 383 622 618(38)

In the general context of producing line lists for the Cologne Database for Molecular Spectroscopy (CDMS) [27], these expressions were used in a global fit of rotational and rovibrational data of isotopic species of CO. The data set included very accurate ground-state rotational data, summarized in Klapper *et al.* [13] and in Cazzoli *et al.* [14], with relative accuracies reaching between 0.55×10^{-9} and 4.7×10^{-9} for each isotopic species, rotational transitions in excited states up to $v = 3$ for $^{12}C^{16}O$ [15], and to-be-published data for $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ [16]. Also included were very accurate $v = 1$–0 and 2–1 frequencies from Wappelhorst *et al.* [17], as well as additional accurate rovibrational data up to $v = 9$–8 [18–20]. Initial Dunham parameters were taken from George *et al.* [28].

To predict the mass of ^{17}O, the masses of ^{13}C [4,8], ^{16}O [7], and ^{18}O [9] were fixed at their respective precise Penning-trap values, and the χ^2 of the fit as a function of the mass of ^{17}O was minimized. The result was $M[^{17}O] = 16.999\ 131\ 644(30)$ u, where the uncertainty is purely statistical. The uncertainty due to the propagated uncertainties in the Penning-trap masses is negligible. However, there are additional contributions to the uncertainty that are difficult to evaluate. These include possible systematic errors, as well as effects of possible underestimation of uncertainties, in the original spectroscopic data.

III. MASS OF ^{17}O FROM PENNING-TRAP MASS SPECTROMETRY

The mass of ^{17}O was accurately determined from measurements of the cyclotron frequency ratios $^{17}O^+/^{16}OH^+$ and $^{17}O_2^+/^{28}SiD_3^+$ using the Florida State University precision Penning-trap mass spectrometer. The techniques were similar to those described in Refs. [8,9] and so are only very briefly described here. This mass spectrometer measures ratios of cyclotron frequencies of single ions, trapped for periods of days, in cryogenic ultrahigh vacuum, in an 8.5-T magnetic field. The cyclotron frequency was obtained by measurement of the accumulated cyclotron phase, with phase-evolution times up to 60 s, with cyclotron frequencies of several megahertz. The two ions to be compared were simultaneously trapped but alternated between the trap center, where the cyclotron frequency was measured, and a large cyclotron orbit, where the ion was temporarily "parked" [3].

TABLE II. Mass difference equations corresponding to the ratios given in Table I. The statistical, systematic, and total uncertainties are shown in parentheses.

Ion pair	Mass difference	Result (u)
$^{16}OH^+/^{17}O^+$	$^{16}O + H - {}^{17}O$	0.003 607 896 1 (14)(7)(16)
$^{28}SiD_3^+/^{17}O_2^+$	$^{28}Si + 3D - 2(^{17}O)$	0.020 968 355 7 (12)(7)(14)

By measuring cyclotron frequency ratios of ions of the same total mass number, we suppress systematic errors due to imperfections in the Penning-trap magnetic and electrostatic fields and also due to the main ion-ion interaction effects [8,9]. The measurement of two ratios, at different mass-to-charge ratios, provides a strong check of systematic errors. The results for the measured ratios are presented in Table I. A detailed discussion of the various systematic corrections applied, and their estimated uncertainties, is given in Ref. [9]. Table I, under Δ_{mol}, includes a correction to the observed $^{16}OH^+/^{17}O^+$ cyclotron frequency ratio to allow for the shift in the cyclotron frequency of $^{16}OH^+$ due to its polarizability in its rotational ground state [29]. For $^{28}SiD_3^+$, assuming a planar equilateral triangular structure, this correction should be negligible. However, for $^{28}SiD_3^+/^{17}O_2^+$, under Δ_{mol}, there is a small (13 ppt) correction to allow for long-lived vibrational excitation of $^{17}O_2^+$ [30].

By allowing for electronic and molecular binding energies [31,32], the mass ratios in Table I can be converted into linear equations, giving the mass differences between neutral atoms. These mass-difference equations, which are intended for use in future global atomic mass evaluations, are presented in Table II.

Finally, using the mass difference equations given in Table II and $M(H) = 1.007\ 825\ 032\ 07(10)$ u [21], $M(D) = 2.014\ 101\ 778\ 16(14)$ u [7], $M(^{16}O) = 15.994\ 914\ 619\ 56(16)$ [21], and $M(^{28}Si) = 27.976\ 926\ 534\ 96(62)$ u [8], we obtained two values for $M(^{17}O)$. In Table III, these results and their weighted averages are compared to previous values in the AME2003 [21]. In obtaining the averages, we have combined the systematic uncertainties and uncertainties in the reference masses linearly, and the statistical uncertainties in quadrature.

TABLE III. Atomic masses for ^{17}O obtained from the different ratios, and their weighted averages, compared with the result of the AME2003.

Source	Mass (u)
$^{16}OH^+/^{17}O^+$	16.999 131 755 5(16)
$^{28}SiD_3^+/^{17}O_2^+$	16.999 131 756 9(9)
Weighted average	16.999 131 756 6(9)
AME 2003	16.999 131 70 (12)

IV. DISCUSSION AND CONCLUSIONS

Since our Penning-trap measurements follow tested procedures and because of the agreement between the masses obtained using $^{17}O^{+}$ and $^{17}O_2^{+}$, we report $M[^{17}O] = 16.999\,131\,756\,6(9)$ (with a relative precision of 0.05 ppb) as our final result for the atomic mass of ^{17}O. This result agrees with but improves upon the precision of the result in the AME2003 by a factor of 130.

The mass of ^{17}O obtained by interpolating between Penning-trap masses for ^{16}O and ^{18}O using the rotational and vibrational spectroscopy data for CO and the Dunham-Watson expression is $M[^{17}O] = 16.999\,131\,644(30)$ u, which is 6.6(1.8) ppb smaller than our new Penning-trap result. Concerning the remaining difference, if the mass of ^{17}O is fixed at the Penning-trap value, inclusion of a second-order breakdown term ${\Delta'_{01}}^{O}\ (m_e/M_O)^2$ in the fit leads to ${\Delta'_{01}}^{O}$ two orders of magnitude larger than the first-order parameter ${\Delta_{01}}^{O}$. Nevertheless, because of the many parameters that are determined by the fit and because it is possible that items of data may have uncertainties that have been underestimated, it is not clear that inclusion of such a term is justified. We also note that the effects of finite nuclear size are negligible for such light nuclei as C and O [33]. In any case, we conclude that the spectroscopic data for CO and the Dunham-Watson model, with first-order Born-Oppenheimer breakdown parameters, has predicted the mass of ^{17}O to better than 1 part in 10^8.

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[1] E. A. Cornell, R. M. Weisskoff, K. R. Boyce, R. W. Flanagan Jr., G. P. Lafyatis, and D. E. Pritchard, Phys. Rev. Lett. **63**, 1674 (1989).
[2] F. DiFilippo, V. Natarajan, K. R. Boyce, and D. E. Pritchard, Phys. Rev. Lett. **73**, 1481 (1994).
[3] G. Gabrielse, A. Khabbaz, D. S. Hall, C. Heimann, H. Kalinowsky, and W. Jhe, Phys. Rev. Lett. **82**, 3198 (1999).
[4] S. Rainville, J. K. Thompson, and D. E. Pritchard, Science **303**, 334 (2004).
[5] J. K. Thompson, S. Rainville, and D. E. Pritchard, Nature **430**, 58 (2004).
[6] M. Redshaw, J. McDaniel, W. Shi, and E. G. Myers, Int. J. Mass Spectrom. **251**, 125 (2006).
[7] D. B. Pinegar, S. L. Zafonte, and R. S. Van Dyck Jr., Hyperfine Interact. **174**, 47 (2007).
[8] M. Redshaw, J. McDaniel, and E. G. Myers, Phys. Rev. Lett. **100**, 093002 (2008).
[9] M. Redshaw, B. J. Mount, and E. G. Myers, Phys. Rev. A **79**, 012507 (2009).
[10] A. Solders, I. Bergström, S. Nagy, M. Suhonen, and R. Schuch, Phys. Rev. A **78**, 012514 (2008).
[11] L. S. Brown and G. Gabrielse, Rev. Mod. Phys. **58**, 233 (1986); Phys. Rev. A **25**, 2423 (1982).
[12] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw Hill, New York, 1955).
[13] G. Klapper, L. Surin, F. Lewen, H. S. P. Müller, I. Pak, and G. Winnewisser, Astrophys. J. **582**, 262 (2003), and references therein.
[14] G. Cazzoli, C. Puzzarini, and A. V. Lapinov, Astrophys. J. **611**, 615 (2004), and references therein.
[15] R. Gendriesch, F. Lewen, G. Klapper, K. M. Menten, G. Winnewisser, J. A. Coxon, and H. S. P. Müller, Astron. Astrophys. **497**, 927 (2009).
[16] R. Gendriesch, F. Lewen, G. Klapper, and H. S. P. Müller (unpublished).
[17] M. H. Wappelhorst, S. Saupe, B. Meyer, T. George, W. Urban, and A. Le Floch, J. Mol. Spectrosc. **181**, 357 (1997).
[18] C. R. Pollock, F. R. Petersen, D. A. Jennings, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. **99**, 357 (1983).
[19] M. Schneider, K. M. Evenson, M. D. Vanek, D. A. Jennings, J. S. Wells, A. Stahn, and W. Urban, J. Mol. Spectrosc. **135**, 197 (1989).
[20] M. Schneider, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. **139**, 432 (1990).
[21] G. Audi, A. H. Wapstra, and C. Thibault, Nucl. Phys. A **729**, 337 (2003).
[22] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Toronto, 1950).
[23] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
[24] J. K. G. Watson, J. Mol. Spectrosc. **45**, 99 (1973).
[25] J. K. G. Watson, J. Mol. Spectrosc. **80**, 411 (1980).
[26] J. K. G. Watson, J. Mol. Spectrosc. **217**, 157 (2003).
[27] H. S. P. Müller, F. Schlöder, J. Stutzki, and G. Winnewisser, J. Mol. Struct. **742**, 215 (2005).
[28] T. George, W. Urban, and A. Le Floch, J. Mol. Spectrosc. **165**, 500 (1994).
[29] M. Cheng, J. M. Brown, P. Rosmus, R. Linguerri, N. Komiha, and E. G. Myers, Phys. Rev. A **75**, 012502 (2007).
[30] C. W. Walter, P. C. Cosby, and J. R. Peterson, J. Chem. Phys. **98**, 2860 (1993).
[31] M. W. Chase, J. Phys. Chem. Ref. Data, Monograph No. **9** (1998).
[32] Y. H. Le Teuff, T. J. Millar, and A. J. Markwick, Astron. Astrophys. Suppl. Ser. **146**, 157 (2000).
[33] S. A. Cooke, M. C. L. Gerry, and D. P. Chong, Chem. Phys. **298**, 205 (2004).