BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 561—563 (1970)

Nuclidic Mass Measurement by Ion Cyclotron Resonance

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(Received August 8, 1969)

Recently Baldeschwieler and his co-workers[1] have applied the double-resonance technique of magnettic resonance to ion cyclotron-resonance spectroscopy (ICRS) and proved it useful for the investigation of the kinetics of organic reactions. Besides the use of ICRS along this line, it is also assumed to be useful for the measurement of the nuclidic masses. This sort of application is important because the atomic masses are, at present, determined by mass spectroscopy[2] as well as by microwave spectroscopy;[3] the effort to build a new and independent method for the determination of nuclidic masses is to be encouraged.[4]

1) L. R. Anders and J. L. Beachamp, R. C. Dunbar and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

2) H. E. Duckworth "Mass Spectroscopy," Cambridge University Press, Cambridge (1960), p. 97.

3) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York (1955), p. 42.

4) A. E. Cameron and E. Wichers, Comprehensive Review, Report of the Commission on Atomic Weights, Comptes rendus of IUPAC XXI (1961), p. 20.

The ICRS is based on the motion of charged particles in magnetic and electric fields. The cyclotron frequency, ω_c, is given by Eq. (1), where e is the charge of the particle; H, the magnetic field strength in Gaussian

$$\omega_c = eH/mc \qquad (1)$$

cgs units; m, the particle mass, and, c, the velocity of light. When an alternating electric field, $E_1(t)$, at a certain frequency ω_1, is applied normaly to H with $\omega_1=\omega_c$, an absorption of energy by the ions occurs; this absorption can easily be observed by a bridge-type detector. With a fixed observing frequency, the mass of the ion can be obtained by measuring the intensity of H by the proton magnetic resonance technique.

With this consideration, an experimental set-up has been built according to the descriptions which have been published in the literature.[5)]

The experimental conditions and some results concerning argon 40 will be described below.

Experimental

Since most of the construction of the apparatus is the same as in the literature,[5)] its details will not be given in this paper. A schematic diagram of the apparatus is shown in Fig. 1, where the observing frequency is calibrated as 99.986 kHz; the magnetic field strength is measured by the proton magnetic resonance technique.

Beauchamp *et al.* have shown the dependence of ω_c on the instrumental factors, especially on the trap voltage, V_T, and have shown a relation of:

$$\Delta H_c = (2\times 10^8/\omega_c d^2)V_T \qquad (2)$$

In Eq. (2), ΔH_c is the deviation of the resonant field from the theoretical value of Eq. (1), and d, the distance between the electrodes. Equation (2) has been derived by the consideration that an additional magnetic field, ΔH_c, is produced by V_T in the probe; it implies that the theoretical resonant field will be obtained by extrapolating V_T to 0. However, we assume this condition is not sufficient to produce the state of $\Delta H_c=0$, and it is assumed to be necessary to take the effect of the drift voltage, V_D, into consideration also. Namely, we assume that this condition is realized in the central region of the probe, when V_T is taken as one half of V_D.[*1] In other words, Eq. (2) is replaced by Eq. (3):

$$\Delta H_c = (K/d^2\omega_c)(V_T - V_D/2) \qquad (3)$$

where K is an experimental constant.

Measurements have been carried out with respect to Ar 40 under the conditions shown in Table 1.

The values of V_D and V_T have been measured with an experimental error of ± 0.001 V. The resonant field has been measured by the proton resonance technique, it is expressed in terms of the frequency scale shown in Fig. 2. Each point of the observed values in Fig. 2 refers to the average of 5 runs and is assumed to be accurate within 1 Hz.

The observed points present a linear relation with V_T as may be seen in Fig. 2. According to the results of the aforementioned consideration, the real resonant field is determined to be 11.081 MHz in frequency units by the point which refers to the condition of $V_T=-0.1$ V on the extrapolated line of Fig. 2. Hence, the atomic weight of Ar 40, M, is calculated either by

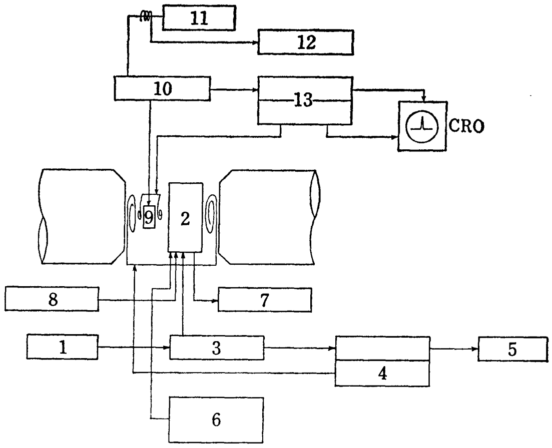

Fig. 1.

ICR part
1. Oscillator
2. Head
3. Detector
4. Amplifier and modulation
5. Recorder
6. Electron regulator (with respect to current and energy)
7. Vacuum control
8. Drift and trapping voltage supplies

NMR part
9. Head
10. Detector
11. Dipmeter
12. Frequency counter
13. Amplifier and modulation source

TABLE 1.

Observing frequency	f_c = 99.986 kHz
Observing electric field	E_1 = 0.02 V/cm
Pressure of sample (Argon)	3×10^{-5} Torr
Voltage of electron collector	+20 V
Energy of electrons	70 eV
Trapping voltage (in the resonance region)	V_T = 0.20—0.00 V
Drift voltage (in the resonance region)	V_D = 0.200 V (plate distance 2.5 cm)
Drift voltage (in the source region)	V_D = 0.205 V (plate distance 2.5 cm)
Electron beam	0.025×10^{-6} A

5) J. L. Beauchamp, L. R. Anders and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

*1 Dr. Beauchamp has written the present author that he also noticed the same phenomenon. The author's thanks are due to Dr. Beauchamp for sending preprint of his work.

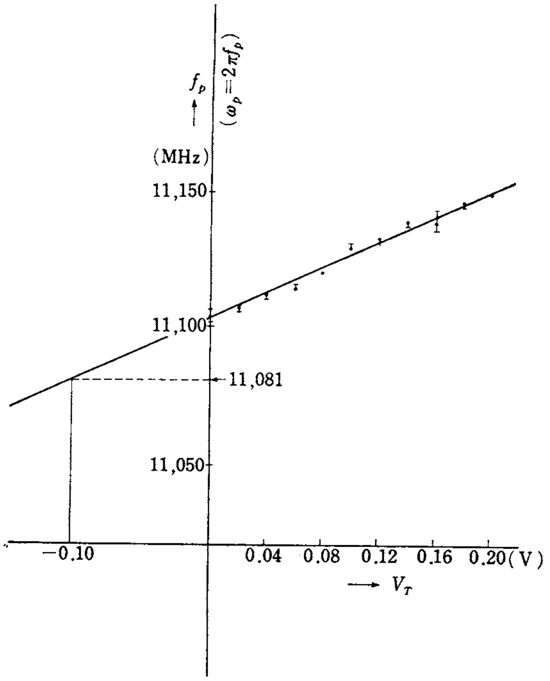

Fig. 2

Eq. (4) or Eq. (5), depending on the choice of the physical constants:

$$M = \frac{e}{c}\frac{N}{\gamma_p}\frac{\omega_p}{\omega_c} \tag{4}$$

$$M = N\frac{m_p}{\mu_p}\frac{\omega_p}{\omega_c} \tag{5}$$

In the sense that the atomic weight thus obtained is still dependent on the mass of the proton, which is determined on the basis of $C=12$ standard, the atomic weight of Ar 40 which has been determined in this experiment still depends on the latter. Calculations after Eqs. (4) and (5) both give a value of 39.970 ± 0.001, which is comparable to that of 39.961324 given in the literature.[6)] Agreement between the two values is fairly good, and this agreement gives a sound basis for the assumption involved in Eq. (3) and also for the experimental techniques adopted in this experiment. The latter statement, in turn, implies that the present technique can be utilized for the precise measurement either of the gyromagnetic ratio or the magnetic dipole moment of the proton with the use of the established data on the mass.[*2] Further investigation along this line is now in progress.

Table 2.*

N	Avogadro's number	6.002216×10^{23}
e	electric charge unit	4.8029×10^{-10}
c	light velocity	2.9979×10^{10}
γ_p	gyromagnetic ratio of proton	2.6751985×10^{4}
m_p	mass of proton	$1.00727663 m_1$ $\left(m_1 = \frac{1}{12} C(C=12)\right)$
μ_p	magnetic dipole moment of proton	2.7928 (Bohr magneton)

* After B. N. Taylor, W. H. Parker and D. N. Langenberg, *Rev. Mod. Phys.*, **41**, 375 (1969).

Hearty thanks of the authors are due to Dr. E. Wichers, the chairman of the International Commission of the Atomic Weights for his keeping interest for us throughout this work and to Dr. T. Farrer of the National Burear of Standards, U.S.A., for supplying the information of the values of physical constants.

6) The Atomic Weights as Computed from Nuclidic Masses and Isotope Abundances, P. J. De Bievre, M. G. Gallet and G. H. Debus, 3rd Preliminary Report 1965, Euratom/Geel, Belgium.

*2 The authors' thanks are due to Dr. S. Peiser of the National Bureau of Standards of U.S.A. and to Professor Roth of the University of Paris, who called the notice of the authors to this application.