FOURIER TRANSFORM ION CYCLOTRON RESONANCE SPECTROSCOPY *

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An ion cyclotron resonance (ICR) absorption spectrum has been obtained by exciting an ICR spectral segment with a fixed-frequency electric field pulse, followed by broad-band detection, digitization of the (time-domain) transient response, and digital Fourier transformation to produce the (frequency-domain) absorption spectrum. For a given signal-to-noise ratio and resolution, the FT-ICR method generates a spectrum in a time which is two orders of magnitude shorter than that required in conventional slow-sweep ICR detection. In the present example, a signal-to-noise ratio of 8:1 and a mass resolution of about 0.005 amu for CH_4^+ (from CH_4 at a pressure of 8×10^{-7} torr) have been achieved, using a single data acquisition period of 25.6 msec.

Nuclear magnetic resonance, infrared, and ion cyclotron resonance (ICR) spectroscopy all share a common feature: because of the broad frequency bandwidth of the spectrum, it has been conventional to scan slowly across the spectrum with a detector having a narrow frequency "window" and a detector circuit of long time constant to reduce rapid noise fluctations in the response. Fourier data reduction methods can reduce by orders of magnitude the time required to obtain an absorption spectrum for such a situation [1], and this note constitutes a preliminary report on the construction and testing of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Such an instrument offers the broad-band detection essential to observation of a wide mass range, without the long observation period inherent to conventional slow-sweep operation.

CH_4^+ ions were created by application of an electron beam pulse of 0.5 μA for a period of 10 msec, to a sample of methane at a pressure of 8×10^{-7} torr. Ion cyclotron motion was excited by a 2.8 msec, 20 mV (p–p) rf electric field pulse at a frequency of 307.126 kHz, which corresponds to an applied magnetic field of 0.32 tesla. The excited ion cyclotron motion is converted to an alternating voltage at the resonance frequency by the ICR cell; this voltage was then amplified by a broad-band (10 kHz to 2 MHz) rf amplifier and mixed with the output of a second rf oscillator (see below). The difference frequency was extracted using a 1.5 kHz low-pass filter, and the resultant signal was then digitized at a rate of

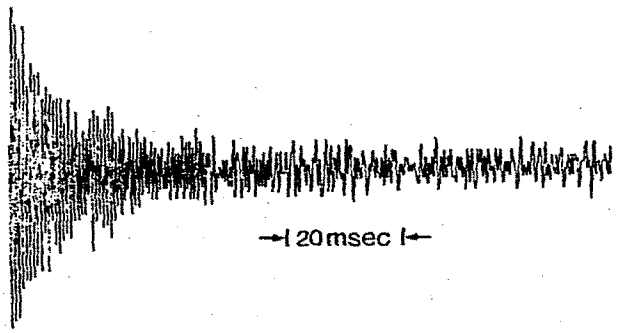

Fig. 1. Digitized ion cyclotron resonance transient response following excitation with a fixed-frequency rf pulse at the ICR frequency. This response represents a single transient of 102 msec duration, and has been subjected to prior frequency-mixing and filtering as explained in the text.

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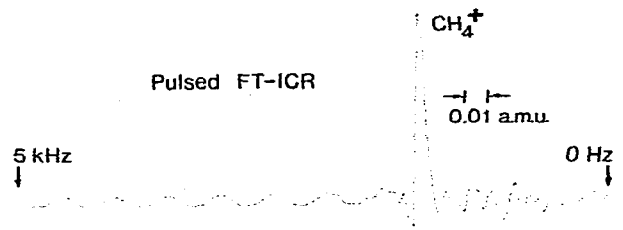

Fig. 2. Ion cyclotron resonance spectrum, obtained by Fourrier transformation of the first 256 of the 1024 digitized data points from the single ICR transient of fig. 1. The filter bandwidth is evident from the suppression of noise at the high-frequency portion of the spectrum. Experimental conditions are described in the text. [The pattern at frequencies higher than the filter cut-off (about 1.5 kHz) is an artifact of the filter response and is irrelevant to the present discussion.]

of 10 kHz using a 1024-channel signal averager to give the digitized (time-domain) response shown in fig. 1.

The first 256 data points in fig. 1 were then recorded on magnetic tape and a discrete Fourier transformation of that array was carried out by a digital computer [1] to yield the ICR absorption spectrum shown in fig. 2. The prior frequency-mixing process simply positions the center of ion cyclotron resonance near the center of the bandwidth of the digitizer; the low-pass filter acts to suppress noise "folded" in from frequencies higher than the digitizer bandwidth (5 kHz).

It is to be emphasized that a signal-to-noise ratio of 8:1 and a mass resolution of about 0.005 amu have been achieved using a single data acquisition period of only 25.6 msec.

Other, more widely applicable means are available for exciting the ion cyclotron resonance, and the FT-ICR technique can readily be extended to such applications as automated signal averaging, enhancement of either mass resolution or signal-to-noise ratio, ion cyclotron double resonance, and ion–molecule reaction kinetics and equilibria [2].

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References

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