

[54] **METHOD AND APPARATUS FOR PULSED ION CYCLOTRON RESONANCE SPECTROSCOPY**[75] Inventor: **Robert T. McIver, Jr.**, Stanford, Calif.[73] Assignee: **The Board of Trustees of the Leland Stanford Junior University**, Stanford, Calif.[22] Filed: **Feb. 16, 1971**[21] Appl. No.: **115,216**

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 [51] Int. Cl. B01d 59/44
 [58] Field of Search. 250/41.9 S, 41.9 G,
 250/41.9 SB, 41.9 DS

[56] **References Cited****UNITED STATES PATENTS**

3,390,265	6/1968	Llewellyn.....	250/41.9 DS
3,527,939	9/1970	Dawson	250/41.9 DS
3,152,280	10/1964	Bloom.....	250/41.9 DS
3,502,867	3/1970	Beauchamp	250/41.9 DS
3,475,605	10/1969	Llewellyn.....	250/41.9 DS
3,535,512	10/1970	Baldeschwieler	250/41.9 DS

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[57] **ABSTRACT**

A method and apparatus for pulsed ion cyclotron resonance spectroscopy is disclosed in which a gas sample within an analyzer cell is ionized by means such as a pulse of an electron beam. The ions are subjected to a combined action of a plurality of static electric fields and a magnetic field thereby trapping the ions and causing them to move orbitally within the cell. Following ionization by said pulse of an electron beam and after a reaction time delay period, ions of a given charge-to-mass ratio are brought into resonance with an oscillating electric field applied transversely to the lines of force of the magnetic field. During such detec-

tion period those ions in resonance with the oscillating electric field absorb energy therefrom, which absorbed energy is detected as a measure of the resonant ions. The ions are then swept from the cell. By use of oscillating electric fields of different frequencies for resonance with ions of different charge-to-mass ratio the arrangement serves a mass spectrometer function. For ion-molecule reaction studies the above described cycle is repeated but with different reaction time delay periods whereby the concentration of the resonant ions at different times during the course of reaction is determined. From this, the thermal rate constant for such ion-molecule reaction is readily determined.

The method and apparatus of this invention are readily adapted for double resonance mass spectroscopy. By irradiating the ions with a pulsed radio frequency electric field at a second frequency, ions of a given charge-to-mass ratio may be accelerated to high velocity, yet still remain trapped within the analyzer cell. As above, after a reaction time delay period following said radio frequency pulse, ions of a given charge-to-mass ratio are brought into resonance with the first mentioned oscillating electric field to obtain a measure of such ions. Also as above, this double resonance cycle may be repeated with different reaction time delay periods. By this means the thermal rate constant for the reaction as a function of the kinetic energy of the ions accelerated by the pulsed radio frequency electric field at the second frequency is readily determined.

The spectrometer includes a novel analyzer cell within which ions may be trapped for long periods of time on the order of 100 milliseconds, or greater. The cell includes a hollow electrode array comprising first, second and third pairs of opposite plates. A trapping potential of one polarity is applied to the one pair of opposite plates, and an opposite polarity trapping potential is applied the other two pair of opposite plates to provide an electrostatic potential well within the cell for trapping the ions for extended periods. Various experiments requiring extended ion trapping periods are possible utilizing the novel ion trap.

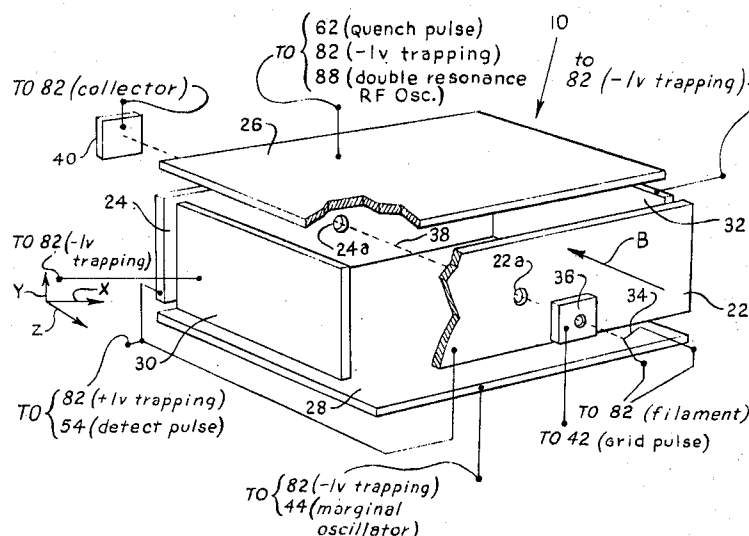
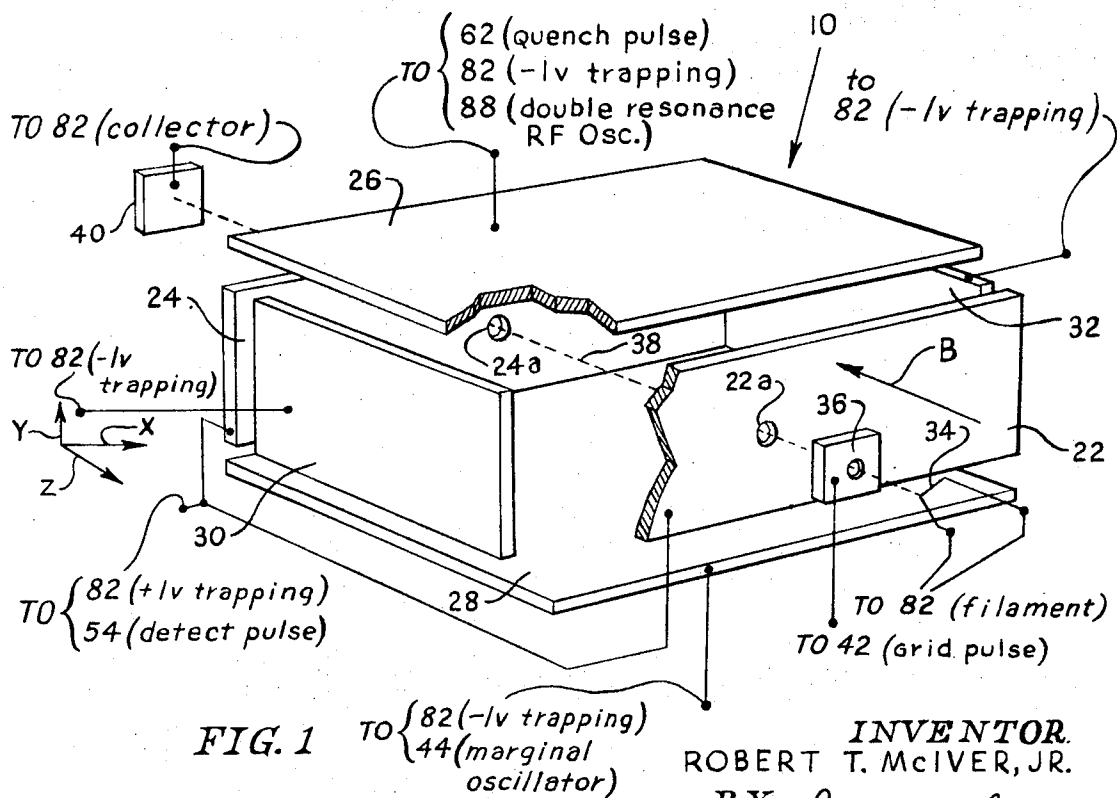
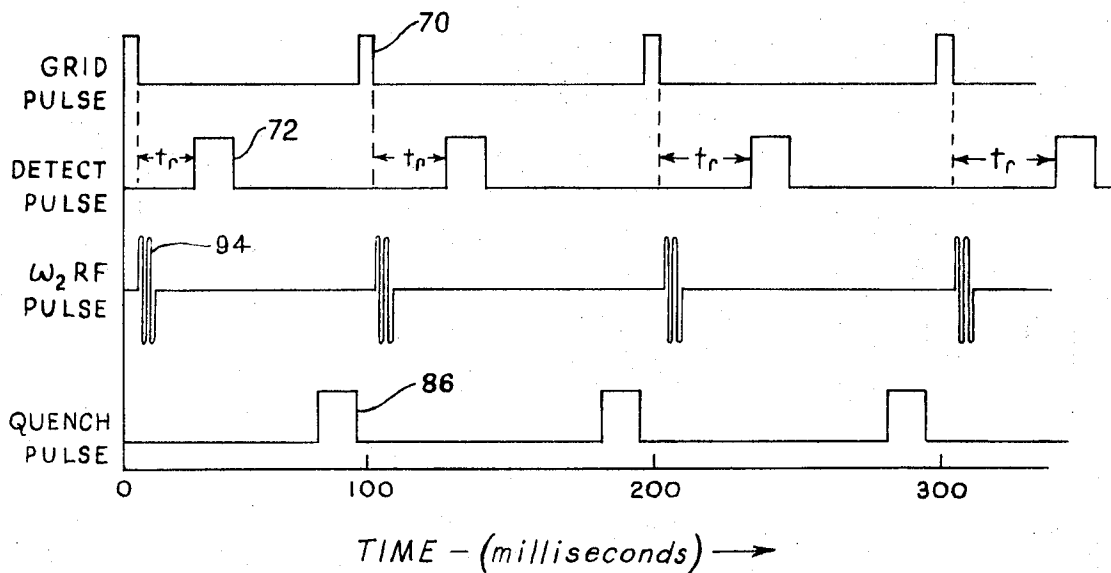
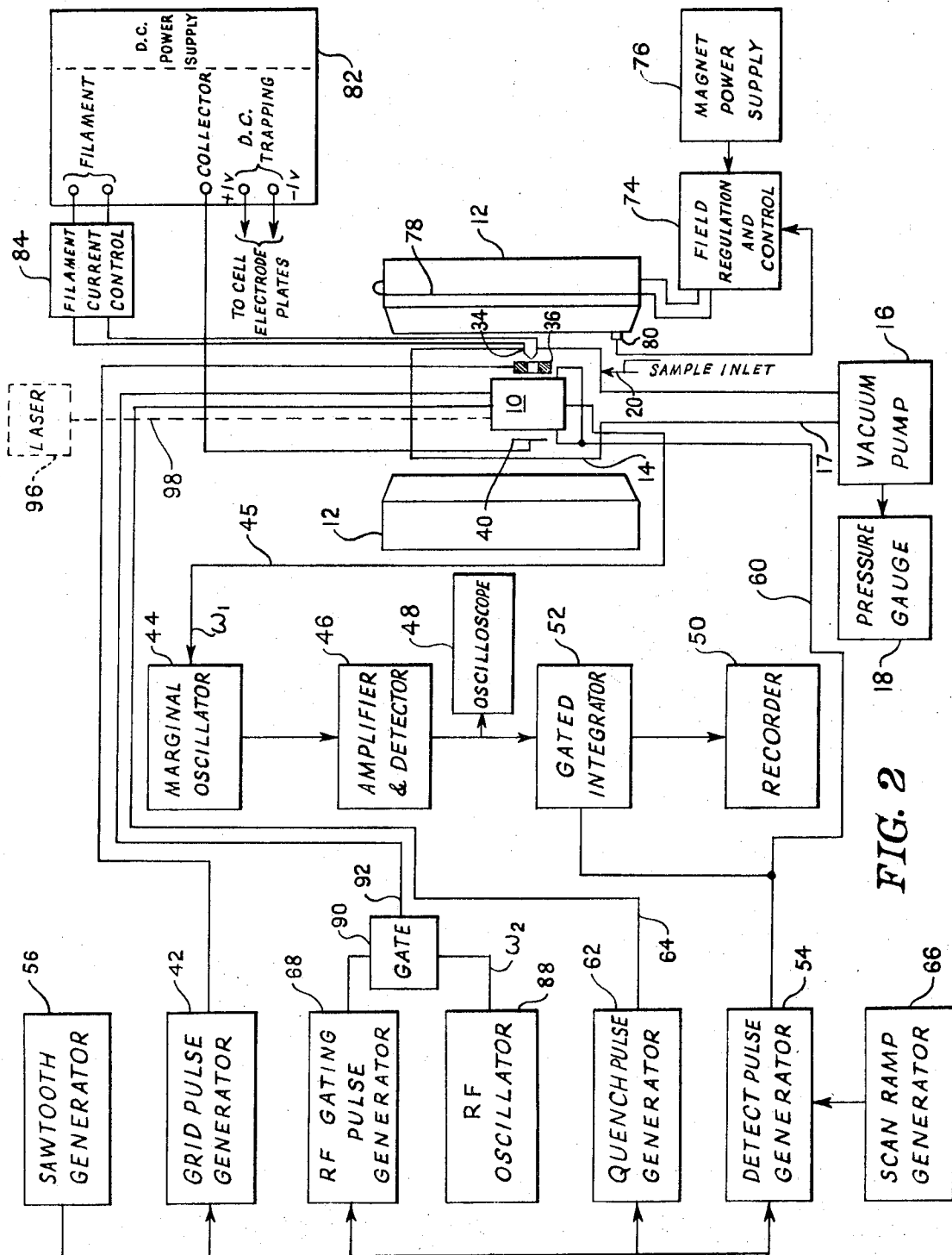
24 Claims, 5 Drawing Figures

FIG. 3



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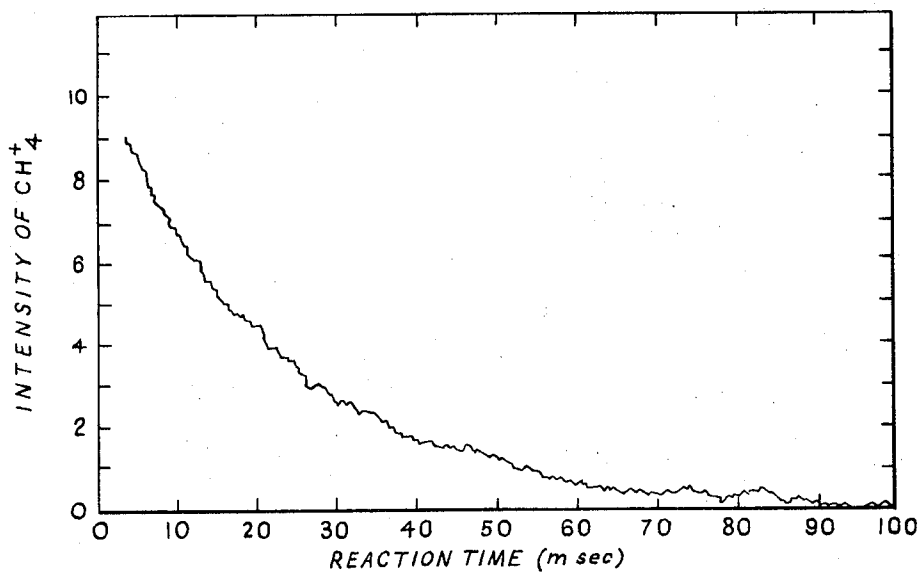


FIG. 4

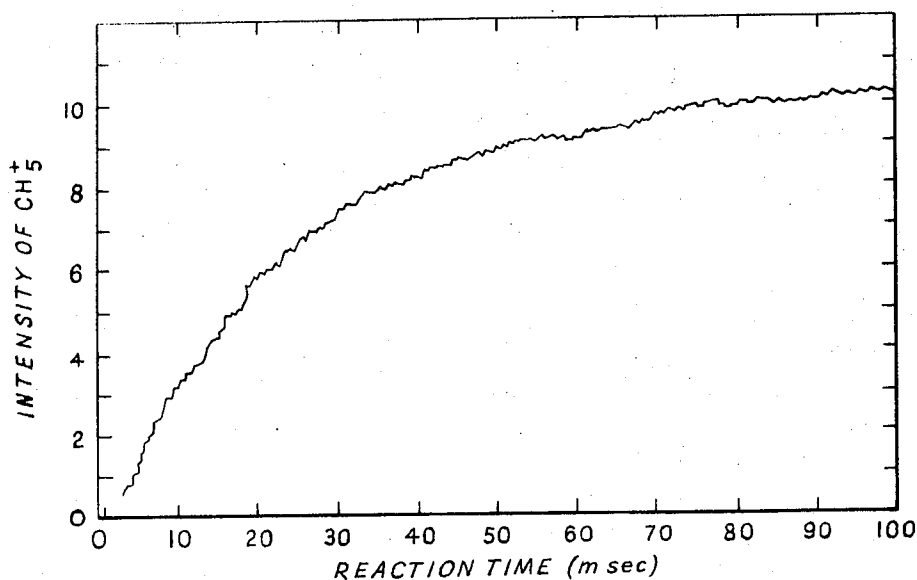


FIG. 5

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METHOD AND APPARATUS FOR PULSED ION CYCLOTRON RESONANCE SPECTROSCOPY

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of work under a grant or award from the United States National Science Foundation.

This invention relates to spectroscopy and more particularly to ion cyclotron resonance spectroscopy.

Ion cyclotron resonance is well known and has been employed in numerous devices and studies. The ion cyclotron resonance technique provides a sensitive and versatile method for detecting gaseous ions. It is well known that a gaseous ion in the presence of a magnetic field is constrained to move in circular orbits in the plane perpendicular to the field and is unrestrained in its motion parallel to the field. The frequency of the circular motion is directly dependent upon the charge-to-mass ratio of the ion and the strength of the magnetic field. By subjecting the orbiting ions to an oscillating electric field disposed at right angles to the magnetic field, those ions having a cyclotron frequency equal to the frequency of the oscillating electric field are accelerated to larger orbital radii and higher kinetic energy. The ions in resonance with the oscillating electric field absorb energy therefrom and separate from the non-resonant ions upon which the oscillating electric field has substantially a negligible effect.

One basic type instrument utilizing the ion cyclotron resonance phenomenon is the omegatron mass spectrometer. With this instrument a gas sample is bombarded by moving electrons to produce ions of various substances present in the sample. The ions are subjected to perpendicular magnetic and oscillating electric fields and, as described above, those ions which are in resonance with the frequency of the oscillating electric field are accelerated to larger velocities and orbital radii. Such resonant ions ultimately impinge upon a collector plate or electrode whereas other ions not in resonance do not impinge thereon. The mass spectrum of a sample to be analyzed may be scanned by varying the frequency of the oscillating electric field or the strength of the magnetic field, or both, so as to bring ions of differing charge-to-mass ratio into resonance with the oscillating electric field.

Such prior art omegatrons have not been widely accepted because of a number of limitations and deficiencies. Such limitations include the fact that some non-resonant ions which have a high initial kinetic energy are collected thereby adversely affecting accuracy of the measurement. Also, the space charge of the electron beam employed to ionize the gas sample produces changes in the resonant condition which contributes to the instrument's inaccuracy. In addition, the mass resolution of the omegatron varies inversely with the ion mass thereby limiting its use to measurements on small molecules.

As noted above, ions in resonance with the oscillating electric field absorb energy therefrom, and this absorption of power from the oscillator producing the electric field may be detected and thereby provide a measure of the resonant ions. An ion cyclotron resonance mass spectrometer utilizing such a magnetic resonance absorption detecting means is disclosed in U.S. Pat. No. 3,390,265 by Peter M. Llewellyn issued June 25, 1968. With this arrangement an attempt to avoid adverse space charge effects of the omegatron is made by con-

tinuously ionizing the gas sample within a first region of the cell, and subjecting the ions to transverse magnetic and static electric fields to move them along a cycloidal path in a direction transverse to both the static electric and magnetic fields in a well known manner, to a second region of the cell removed from the first region. At this second, or analyzing region, the ions also are subjected to the combined action of the magnetic field and a perpendicular oscillating electric field whereby ions of a given charge-to-mass ratio in resonance with the oscillating electric field absorb energy from the electric field, which energy absorption is detected to provide a measure of such resonant ions. By drifting the ions from the first region where they are produced to a second analyzing region spaced therefrom, the effect of space charge in the analysis is reduced. However, other limitations and shortcomings are present in such an arrangement. For example, some of the ions which are created within the cell reach the cell electrode plates creating a surface charge thereon. Since ions are continually formed the concentration of surface charge on the cell electrode plates builds up and alters the motion of the ions through the cell. In addition, since the ions are continually drifting through the analyzing region of the cell, knowledge of the rate of ion drift therethrough is required for mass analysis purposes. It is, however, difficult to accurately determine the drift time through the cell (which may be between say 1 to 5 milliseconds) or even establish reproducible conditions thereby making accurate analysis difficult. Because of the above and other difficulties, only short duration readings can be made with accuracy, and because operation is limited to such short periods, the mass resolution of the device is limited such that only masses of less than about 200 may be examined with any degree of accuracy.

Recently, much interest has been generated in the study of chemical reactions between gaseous ions and neutral molecules, so called ion-molecule reactions, by means of which basic, fundamental, factors which control all chemical reactions may be investigated. The above mentioned prior art spectroscopy techniques are not well suited for such studies. As mentioned above the omegatron mass spectrometer functions poorly for mass spectrometer analysis, much less for analysis of ion-molecule reactions. A double resonance ion cyclotron mass spectrometer for studying ion-molecule reactions, which spectrometer utilizes a cell formed with separate ionizing and analyzing regions, of the type mentioned above, is shown in U.S. Pat. No. 3,535,512 to John D. Baldeschwieler, issued Oct. 20, 1970. Such a spectrometer suffers all of the same deficiencies as when the cell is used for mass spectroscopy. Furthermore, since the drift time is limited to between approximately 1 to 5 milliseconds, slow ion-molecule reactions taking a much longer time (e.g. 100 milliseconds) can not be readily observed. The spectrometer disclosed in U.S. Pat. No. 3,535,512 employs a modulated radio frequency electric field for the double resonance excitation. However, a quantitative knowledge of the kinetic energy imparted to the ions by such electric field is not possible because the ions are continually entering and leaving such field. Consequently, an accurate study of ion-molecule reactions as a function of the kinetic energy of ions is precluded by such prior art arrangement. In addition, the continuous ionizing electron beam included in the above-mentioned prior art arrangement

scatters the ions such that some are directed toward a cell plate. Even at low levels of radio frequency irradiation some of the ions are lost to the cell plate. With the present invention, a short period ionizing pulse leaves the ions at the center of the cell whereby the ions may be accelerated to a high velocity before striking a cell electrode.

SUMMARY OF THE INVENTION

An object of this invention is the provision of a method of and apparatus for ion cyclotron resonance spectroscopy which overcome the above-mentioned shortcomings and difficulties of the prior art and have many advantages over such prior art.

An object of this invention is the provision of a trapped ion analyzer cell and method of utilizing the same whereby ions may be trapped for relatively long time periods during which mass spectrometry, ion-molecule reaction, and other studies involving ions may be performed.

An object of this invention is the provision of an ion cyclotron resonance spectrometer having higher resolution and greater sensitivity than any prior art instrument.

An object of this invention is the provision of an ion analyzer cell formed with at least six closely spaced plates each of which is supplied with small d-c trapping voltages for trapping ions within the cell.

An object of this invention is the provision of an ion cyclotron resonance spectrometer in which primary ions are formed within a short time interval by an energy beam which then is removed so as not to interfere with the subsequent detection of ions.

An object of this invention is the provision of an ion cyclotron resonance spectrometer and method of spectroscopy of the pulsed type whereby ions are formed during a short pulse period and after a reaction time delay period ions are detected during a subsequent pulse period of known duration, the reaction time delay period being variable for accurate measurement of the rate of ion-molecule reactions.

An object of this invention is the provision of a method and apparatus for double resonance ion cyclotron mass spectroscopy for the study of ion-molecule reactions whereby all ions formed during a short pulse period and trapped within a cell by means of an electrostatic potential well are subjected to a short pulsed radio frequency electric field for accelerating ions of a given charge-to-mass ratio to a high velocity with a known acceleration dependent upon the magnitude and duration of the radio frequency electric field pulse.

An object of this invention is the provision of a cyclically operated pulsed ion cyclotron resonance spectrometer wherein each cycle of operation is terminated by a quench pulse applied to the cell for neutralization of all ions within the cell in preparation for the following cycle of operation.

The above and other objects and advantages, in accordance with one teaching of the present invention, are achieved by means of an evacuable envelope to which a gas sample may be admitted. A trapped ion analyzer cell is disposed within the envelope which cell includes four electrode side plates in a generally rectangular arrangement, and a pair of electrode end plates at opposite ends thereof. The gas sample is ionized within a short time period by a pulse of an electron beam through the cell. Ions are trapped within the cell

by application of a low d-c trapping potential of one polarity applied to the pair of electrode end plates and to a pair of opposite electrode side plates, and a substantially equal but opposite polarity d-c trapping potential applied to the other pair of opposite electrode side plates. The ions within the cell are subjected to an unidirectional magnetic field for movement of ions in circular orbits in the plane perpendicular to the magnetic field. An oscillating electric field transverse to the magnetic field is provided and, after a reaction time delay period following formation of ions, the oscillating electric field and ions of a given charge-to-mass ratio are brought into resonance for a predetermined detection period during which power absorbed by said ions is measured. Following the detection period the ions are neutralized and the cycle is repeated. The mass spectrum for a mixture of ions of various masses present after a certain delay time is obtained by sweeping the frequency of the oscillating electric field or the strength of the magnetic field. With a fixed value of the magnetic field and oscillating electric field, the concentration of a given mass ion is obtained as a function of reaction time by sweeping the time delay period. This latter function is a unique capability of the novel spectrometer of this invention. For ion cyclotron double resonance spectroscopy the ions may be irradiated by a pulsed oscillating electric field at a second frequency.

The invention and other objects and advantages thereof will be better understood from the following description taken in connection with the following drawings. In the drawings wherein like reference characters refer to the same parts in the several views:

FIG. 1 is a diagrammatic perspective view partially broken away showing the novel trapped ion analyzer cell structure of this invention,

FIG. 2 is a block diagram of a novel ion cyclotron resonance spectrometer employing the cell shown in FIG. 1,

FIG. 3 is a set of waveforms for use in explaining the operation of the spectrometer shown in FIG. 2, and

FIGS. 4 and 5 are graphs of intensity of ions versus reaction time for two different mass ions undergoing an ion-molecule reaction.

Reference is now made to FIG. 1 wherein there is shown a novel trapped ion analyzer cell construction embodying this invention. The illustrated electrode structure comprises a hollow cell 10 which is immersed in a uniform unidirectional magnetic field B in the $-Z$ direction. The magnetic field may be of a magnitude on the order of 10,000 gauss and is provided as by a magnet which includes magnetic poles 12 shown in FIG. 2.

The cell 10, as seen in FIG. 2, is contained in an evacuable envelope 14 which is evacuated to a very low pressure of say 10^{-8} to 10^{-9} torr prior to introduction of the gas sample. A vacuum pump 16 connected through a tube 17 to the envelope 14 is used to evacuate the envelope. The vacuum pump may be of the well known sputter-ion type which is energized by a suitable power supply not shown. A forepump of the refrigerated sorption type for example may be used for initial evacuation of the envelope prior to energization of the pump 16, and means for baking out the pump and envelope also may be included to aid in evacuation. Vacuum producing means are well known and require no detailed description. A suitable vacuum system which may be employed is disclosed in the above-mentioned U.S. Pat. No. 3,390,265. Obviously, other known

means may be employed for evacuation of the envelope.

Once pump-down to 10^{-8} to 10^{-9} torr is obtained as indicated by a pressure gauge 18 a gaseous sample to be analyzed may be introduced to the envelope through an inlet 20 until a pressure in the range of 10^{-4} to 10^{-7} torr is achieved. A dynamic balance may be maintained by continuous pumping and leaking of gas into the envelope.

As seen in FIG. 1, the illustrated six-sided cell 10 within which ionization and analysis occur is of generally rectangular cross-section and comprises a plurality of spaced electrodes including first and second opposite side plates 22 and 24, third and fourth opposite side plates 26 and 28, and a pair of opposite side plates 30 and 32 at the opposite ends of plates 22, 24, 26 and 28. The elongated side plates 22, 24, 26 and 28 are arranged about the longitudinal X-axis which extends through the plates 30 and 32. The plates are formed of non-magnetic metal such as molybdenum or rhodium plated beryllium copper, or the like, and are held in fixed relative position within the envelope by means of insulating supporting members, not shown.

An ionizing beam source such as an electron gun comprising a filamentary emitter 34 is mounted within the envelope 14 for discharge of electrons in the $-Z$ direction parallel to the magnetic field B . Electrons leaving the emitter pass through an aperture in a control grid 36 which grid normally is biased to cut off the electron beam therethrough. In operation the grid bias is pulsed in a manner described below to provide a burst of electrons therethrough, which electrons then pass through aligned apertures 22a and 24a along the beam axis 38 and are collected at a collector electrode 40. Ionization of the gas sample is effected by collision of the electrons with the gas, with all primary ions being formed within the cell during passage of the burst of electrons through the interior of the cell between plates 22 and 24. For purposes of illustration only, the filamentary emitter 34 normally may be maintained at -15 volts and the control grid at -20 volts to cut off the flow of electrons along the beam axis 38. Periodically, say every 200 milliseconds, a voltage pulse of say -10 volts and having a duration of from 1 to 6 milliseconds may be applied to the control grid from a grid pulse generator 42 for passage of the ionizing beam through the cell during the ionizing period. The collector plate is maintained at say between $+10$ and $+20$ volts to recapture secondary electrons emitted upon primary electron impact. Obviously, other means for ionization of the gas molecules may be employed including the use of ionizing beams of particles other than electrons and electromagnetic radiation.

In accordance with this invention ions which are produced within the cell are trapped therewithin by the combined effect of the magnetic field and the small static trapping voltages applied to the plates of the cell. In order to trap ions of positive charge a static potential of $+1$ volt typically is applied to the opposite side plates 22 and 24, and an equal but opposite polarity static voltage of -1 volt is applied to the other side plates 26 and 28 and to the opposite end plates 30 and 32, to establish a potential well within the cell. The polarity of the voltages thus mentioned is reversed to trap ions of negative charge. The resultant electrostatic fields between the plate 22 and the plates 26, 28, 30 and 32, and between the plate 24, and plates 26, 28, 30 and 32

within the cell are quite complex, but it will be apparent that they approximate a three dimensional quadrupole trap.

The ions formed by electron impact and trapped within the cell are constrained by the unidirectional magnetic field B to circular orbits in a plane normal to the direction of the magnetic field. The angular or cyclotron frequency of this motion is,

$$\omega_c = (q/m) B$$

(1)

where

(q/m) = the charge-to-mass ratio of the ion, and
 B = the magnetic field strength.

It will be understood that the presence of the static trapping fields also affects the motion of the ions, and the cyclotron frequency. Equation (1) is for cyclotron frequency in the absence of trapping electric fields. That is, the ion cyclotron frequency ω_c does not depend solely upon q , m and B , but also is dependent upon the static electric fields used to trap the ions, and use of this fact may be made in the operation of the device as described below. From the above, it will be seen that all ions of a given charge sign (in the illustrated arrangement all positive ions) are trapped regardless of their charge-to-mass ratio.

In ion cyclotron resonance experiments a low level alternating RF electric field perpendicular to the unidirectional magnetic field B is imposed within the cell. To this end, a marginal oscillator 44 is connected to apply an RF electrical potential between the opposite electrode plates 26 and 28 of the cell by way of lead 45 for incorporation of the electrode plates 26 and 28 in the resonant circuit of the marginal oscillator. When the marginal oscillator frequency is equal to the cyclotron frequency of an orbiting ion, the ion is accelerated to larger orbital radii and higher kinetic energy. As a result absorption of marginal oscillator power takes place within the cell thereby reducing the oscillating level. The marginal oscillator output is detected and amplified at amplifier and detector 46. The amplifier output may be monitored by use of an oscilloscope 48, or fed to a recorder 50 through a gated integrator 52. A gating signal for the integrator 52 is obtained from a detect pulse generator 54 which, in turn, is triggered by a sawtooth generator 56. In the illustrated arrangement the detect pulse generator 54 also is connected to the side plates 22 and 24 through lead 60 for shifting the cyclotron frequency to bring ions of a given charge-to-mass ratio into resonance with the marginal oscillator 44 during a detect time period.

In accordance with this invention, after ionization by the electron beam pulse, the primary ions are allowed to react with the neutral gas of the sample for a reaction time delay period, following which the mixture is probed by use of the marginal oscillator 44 for determination of the concentration of any mass ion. In the illustrated arrangement the detect pulse from the detect pulse generator gates open the integrator 52 and simultaneously changes the voltage on the side plates 22 and 24 to shift the cyclotron frequency of an ion having a given charge-to-mass ratio into resonance with that of the marginal oscillator. During this detect period there is a pulsed response from the marginal oscillator 44 which is proportional to the number of such ions.

After the detect pulse period all of the ions within the cell are rapidly neutralized by application of a quench pulse to a wall of the analyzer cell. In the illustrated arrangement the quench pulse from a quench pulse generator 62 is fed through lead 64 to the upper electrode plate 26 of the cell. With application of say a +10 volt quench pulse to the electrode 26 the trapping action of the cell is destroyed and all of the ions, regardless of mass, are neutralized at the cell plates thereby terminating the ion-molecule reaction and preventing ions from one pulse sequence from overlapping into a following sequence.

The entire cycle then is automatically repeated. A pulse from the grid pulse generator 42 to the grid 30 provides a pulse of the electron beam to produce the ions within the cell; after a known period of reaction, the concentration of any mass ion is detected by a pulse from the detect pulse generator 54; and then all of the ions are eliminated from the cell by a pulse from the quench pulse generator 62. By sweeping the delay of the detect pulse, the concentration of a given mass ion can be obtained as a function of reaction time.

For purpose of illustration only, timing for the pulse sequence may be provided by means of the sawtooth generator 56 operating at a frequency of say 2 to 100 cycles per second. The generator output is used to trigger the grid pulse generator 42, an RF gating pulse generator 68, the detect pulse generator 54, and the quench pulse generator 62 in sequence, with triggering action being effected at predetermined levels of output from the sawtooth generator as by means of Schmitt trigger circuits included therein. The RF gating pulse generator is employed in ion cyclotron double resonance spectroscopy studies in a manner described in detail below. As mentioned above, the grid pulse which is identified by reference numeral 70 in FIG. 3, is applied to the grid 36 to pulse the electron beam whereby ions are formed within the cell and timing of the reaction period is initiated. After a time delay period following receipt of the grid pulse signal input, the detect pulse generator 54 is triggered by the sawtooth wave output from the sawtooth generator 56. The scan ramp generator 66 slowly varies the level at which the detect pulse generator 54 is triggered to slowly sweep the delay of the detect pulse from the detect pulse generator. Scanning by the detect pulse, shown as waveform 72 in FIG. 3, is illustrated by the increasing reaction times, designated t_r , for successive pulses.

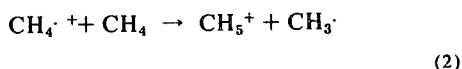
The detect pulse 72 gates open the integrator 52 and, in the illustrated arrangement, is applied to the side electrode plates 22 and 24 of the cell to increase the trapping voltage thereby shifting the cyclotron frequency of the orbiting ions. In the illustrated arrangement the magnetic field B is maintained at a predetermined strength by use of a field regulator and control unit 74 through which the output from the magnet power supply 76 is fed to the field coil 78. A Hall-effect generator 80 for sensing the field strength is included in the regulator circuit. Field regulator and control circuits for the magnet are well known and require no detailed description. Typically, a magnetic field strength of about 10,000 gauss is employed. Also shown in FIG. 2 is a d-c power supply 82 for supply of the necessary filament, collector and d-c trapping potentials. Filament current may be regulated by filament current control unit 84 for control of the pulsed electron beam strength.

In the illustrated arrangement the marginal oscillator 44 is tuned to a frequency ω_1 , removed from the cyclotron resonance frequency of every ion present in the sample, but only slightly removed from the cyclotron resonance frequency of the mass ion to be measured. Consequently, the low level alternating RF electric field has a negligible effect upon the orbiting ions during the reaction time period t_r . Upon application of the detect pulse to the side electrode plates 22 and 24 of the cell the cyclotron frequency is shifted, the cyclotron frequency being inversely related to the trapping potential. The cyclotron frequency of the ions to be measured is thereby shifted to be equal to the marginal oscillator frequency. The gated integrator is simultaneously gated open whereby a record of the pulsed response from the marginal oscillator is provided which is proportional to the number of ions having a given charge-to-mass ratio present during the detect period. Subsequently the quench pulse generator 62 is triggered for application of a positive quench pulse 86 shown in FIG. 3 to the upper electrode 26 to terminate the cycle in preparation for the next cycle. The scan ramp generator 66 slowly varies the reaction time period t_r to provide a sweep of the detection pulse to provide a measure of the concentration of the resonant ions as a function of time. The arrangement provides a straightforward and accurate method of measuring thermal rate constants for ion-molecule reactions.

This invention is well suited for ion cyclotron double resonance spectroscopy. As is well understood in addition to a marginal oscillator, ion cyclotron double resonance spectrometers include means for irradiating orbiting ions with a relatively strong radio frequency electric field at a second frequency to produce cyclotron resonance of a second species of ions. The arrangement illustrated in FIG. 2 includes an RF oscillator 88 operating at a frequency ω_2 and connected to apply a RF electrical potential between the electrode plates 26 and 28 by way of a gate 90 and lead 92. With the generator 68 and oscillator 88 enabled for double resonance operation a radio frequency electric field at frequency ω_2 is applied at right angles to the magnetic field B when the gate 90 is open. The gate 90 is opened and closed under control of the RF gating pulse generator 68, which in turn is triggered by sawtooth generator 56. The gate 90 may be pulsed open immediately following the grid pulse for short irradiating periods on the order of 1 to 6 milliseconds. In the waveforms in FIG. 3 the RF pulse is identified by reference numeral 94. The irradiating frequency ω_2 is in resonance with the cyclotron frequency of ions having a certain charge-to-mass ratio whereby the kinetic energy and orbital radii of such ions are increased. After a reaction time period t_r the reaction mixture is probed by the marginal oscillator upon application of detect pulse 72 in the manner described above. Again, as above, the reaction time delay period may be swept to provide an indication of the concentration of ions with a frequency ω_1 as a function of reaction time. By use of the ω_2 RF pulse to accelerate primary ions to higher kinetic energy, studies of kinetic energy dependence of the reaction rate constant, and the partitioning of the reaction products as a function of reactant ion kinetic energy are made possible.

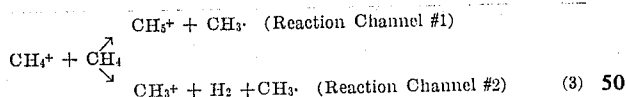
For purposes of explanation, assume that that envelope 14 is supplied with methane gas, CH_4 . The electron beam pulse ionizes the gas to form CH_4^+ which is

trapped within the analyzer cell in the presence of remaining neutral CH_4 gas. The CH_4^+ ions react with the neutral CH_4 via ion-molecule reaction to yield CH_5^+ and CH_3^+ as follows:



After a reaction time delay period t_r , a detect pulse 72 is applied to the cell electrodes 22 and 24 to bring the CH_5^+ ions into resonance with the marginal oscillator 44 for detection of the resonant CH_5^+ ions. Simultaneously, the integrator 52 is gated open for integrating and recording the amplifier output during the detection period. Following the detection period, the ions are neutralized by application of the quench pulse and the entire cycle is repeated but with different reaction time delay periods t_r to provide an indication of the concentration of the CH_5^+ ions as a function of reaction time. As will be understood the concentration of CH_4^+ ions may be detected by use of a marginal oscillator tuned to resonance with the CH_4^+ ions during the detect period. A plot of the concentration of CH_4^+ ions and CH_5^+ ions versus reaction time for the above-described experiments is shown in FIGS. 4 and 5, respectively.

The above described reaction may be studied as a function of the kinetic energy of the CH_4^+ by use of the pulsed double resonance technique. To this end the CH_4^+ ions are constrained to move in circular orbits in a plane perpendicular to the unidirectional magnetic field B at a cyclotron frequency of ω_2 , and the RF oscillator which is tuned to the frequency ω_2 , provides an RF energy pulse to excite resonance of the CH_4^+ ions. By setting the duration of the RF pulse short compared to the mean free time between collisions, an accurate calculation of the average kinetic energy of the CH_4^+ ions can be made by knowing the duration of the pulse and the pulse amplitude. It will be apparent that the novel spectroscopy method and apparatus of this invention offers the unique capability of studying the reactions of translationally excited ions of known energy (in the present example the reactions of the excited CH_4^+ ions.). It is found that the excited CH_4^+ ions can yield either CH_5^+ and CH_3^+ or CH_3^+ , H_2 and CH_3^+ as follows:



The partitioning of the reaction among the various reaction channels is dependent upon the energy imparted to the CH_4^+ by the radio frequency electric field at ω_2 . The present technique enables one to measure rate constants for each reaction channel as a function of the kinetic energy of the CH_4^+ .

The invention having been described in detail in accordance with the requirements of the Patent Statutes, various changes and modifications may suggest themselves to those skilled in this art. For example, ions may be brought into resonance with the marginal oscillator by pulsing the strength of the magnetic field B rather than the trapping voltage during the detection period. To this end, the detect pulse generator 54 output may be connected to the field regulator and control unit 74, instead of to the cell electrodes as shown, for pulsing

the magnetic field strength to bring ions of a given species into resonance with the marginal oscillator during the detection period. Alternatively, a marginal oscillator tuned to the resonant frequency of ions having a given charge-to-mass ratio may be gated on only during the detection period thereby eliminating the need to pulse the trapping potential or magnetic field strength to bring said oscillator and ions into resonance. Also, other means such as a balanced bridge circuit may be used for detecting the power absorbed by resonant ions rather than the illustrated marginal oscillator.

Other changes include the use of a computer in place of the gated integrator 52 and recorder 50 for processing the output from the marginal oscillator. Also, other well known timing circuits, which may include the use of a clock oscillator, may be used for timing the various grid, RF, detect and quench pulses. In addition, the quench pulse may be initiated simultaneously with termination of the detect pulse, and/or may be used to terminate the detection period.

In the illustrated arrangement positive ion trapping is shown. It will be understood that trapping of negative ions for analysis also is possible simply by reversing the polarity of the trapping potential at each plate electrode of the cell. Also, the cell plate electrodes may be of different shape and configuration and are not limited to the illustrated rectangular shape, configuration, or number. For example, three oppositely disposed pairs of generally dish-shaped plates arranged in the form of a hollow sphere may be employed. Also, to form the electrostatic potential well for trapping the ions, it will be apparent that a grid construction may be employed in place of at least some of the illustrated solid plates.

Because the analyzer cell of this invention is capable of extended trapping periods, the cell is well adapted to various other experiments. For example, as shown in phantom line in FIG. 2, a laser 96 may be included for beaming a coherent light pulse of high intensity along beam axis 98 into the cell for reaction with the gas sample therewithin. Such a pulse may be used, for example, in lieu of the ω_2 RF pulse. In addition, where transverse, perpendicular, normal, etc. electric and magnetic fields, or the like, are mentioned or claimed, it will be understood that one field having a substantial component normal to another also is contemplated. It is intended that the above and other such changes and modifications shall fall within the spirit and scope of the invention as defined in the appended claims.

I claim:

1. In a pulsed ion cyclotron resonance spectrometer, an analyzer cell,

means for forming ions within said cell from a sample during an ionizing period,

means including a unidirectional magnetic field and static electric fields for trapping substantially all ions of a given charge sign formed in said cell including ions formed therewithin during the ionizing period, causing them to move orbitally at angular frequencies dependent upon the charge-to-mass ratio thereof,

alternating electric field producing means for supplying an alternating electric field to said trapped ions normal to said unidirectional magnetic field, and

means including the alternating electric field supplied by said alternating electric field producing means for producing ion cyclotron resonance of trapped ions having a given charge-to-mass ratio

while ions of different charge-to-mass ratio remain non-resonant therewith during a detection time period after a reaction time delay period following the ionizing period, said alternating electric field being non-resonant with all trapped ions at all times outside the detection time period.

2. The pulsed ion cyclotron resonance spectrometer as defined in claim 1 wherein,
said analyzer cell comprises at least six spaced electrodes including, (1) first and second electrodes forming first opposite sides, (2) third and fourth electrodes forming second opposite sides, and (3) fifth and sixth electrodes forming third opposite sides,
the lines of force of said unidirectional magnetic field extending across the cell in a direction generally parallel with the third, fourth, fifth and sixth electrodes, and
said static electric fields being produced by means for applying a trapping potential of one polarity to the first and second electrodes, and a trapping potential of opposite polarity to the third, fourth, fifth and sixth electrodes.

3. The pulsed ion cyclotron resonance spectrometer as defined in claim 1 including,
means for detecting the ion cyclotron resonance of said resonant ions having said given charge-to-mass ratio during the detection time period.

4. The pulsed ion cyclotron resonance spectrometer as defined in claim 3 wherein said means for detecting the ion cyclotron resonance of said resonant ions having said given charge-to-mass ratio during the detection time period comprises,
a gated integrator which is responsive to the alternating electric field producing means only during the detection time period.

5. The pulsed ion cyclotron resonance spectrometer as defined in claim 1 including,
means for irradiating the trapped ions with an alternating electric field at the ion cyclotron resonance frequency of a group of the trapped ions during an irradiating period occurring during a portion of the reaction time period prior to the detection time period to accelerate all ions of said group in an amount dependent upon the strength of the irradiating alternating electric field and length of the irradiating period.

6. The pulsed ion cyclotron resonance spectrometer as defined in claim 1 wherein,
said means for producing ion cyclotron resonance of trapped ions having a given charge-to-mass ratio during a detection time period includes means for bringing the alternating electric field and angular frequency of the orbiting ions of said given charge-to-mass ratio into resonance only during the detection time period.

7. The pulsed ion cyclotron resonance spectrometer as defined in claim 6 wherein said means for bringing the alternating electric field and angular frequency of the orbiting ions of said given charge-to-mass ratio into resonance comprises means for changing the magnitude of the static electric fields during the detection time period.

8. The pulsed ion cyclotron resonance spectrometer as defined in claim 1 including,
means for neutralizing the ions after the detection time period.

9. The pulsed ion cyclotron resonance spectrometer as defined in claim 8 including,
means for sequentially operating said ion forming means, ion cyclotron resonance producing means, and said ion neutralizing means.

10. The pulsed ion cyclotron resonance spectrometer as defined in claim 9 including,
means for cyclically operating the spectrometer for repeated sequential operation of said ion forming means, ion cyclotron resonance producing means, and ion neutralizing means, and
means for scanning the reaction time delay period during succeeding cycles of operation for determination of the concentration of the excited trapped ions having said given charge-to-mass ratio as a function of reaction time.

11. A spectroscopy method of analyzing a sample comprising,
ionizing a sample within an analyzer cell during an ionizing period,
trapping substantially all ions of a given charge sign formed within the analyzer cell, causing them to move orbitally at an angular frequency by subjecting the ions to the combined action of static electric fields and a magnetic field,
after a reaction time delay period following the ionizing period, bringing ions of a given charge-to-mass ratio and an oscillating electric field applied transversely to the lines of force of the magnetic field into resonance for resonance detection of said ions during a detection time period, said oscillating electric field being non-resonant with all trapped ions at all times outside the detection time period, neutralizing the trapped ions after the detection time period, and
repeating the cycle of steps defined above.

12. The spectroscopy method as defined in claim 11, which includes,
exciting a group of trapped ions at their resonant frequency by subjecting them to an irradiating pulse comprising a pulsed oscillating electric field applied transversely to the lines of force of the magnetic field during an irradiating pulse period occurring during a portion of the reaction time delay period prior to the detection time period to impart high kinetic energy to said group of trapped ions, which ions remain trapped within the analyzer cell.

13. The spectroscopy method as defined in claim 9 wherein,
ion species of different charge-to-mass ratio are formed by ion-molecule reaction during the irradiating pulse period dependent upon the magnitude and duration of the irradiating pulse and are trapped in the analyzer cell, ions of one said species of different charge-to-mass ratio being detected during the detection time period, the method also including,
scanning the reaction time delay period during succeeding cycles of operation for determination of the concentration of detected resonant ions of said one species as a function of reaction time.

14. The spectroscopy method as defined in claim 12 wherein the group of ions irradiated at their resonant frequency during the irradiating pulse period comprise the ions of a given charge-to-mass ratio which are detected during the detection time period.

15. The spectroscopy method as defined in claim 12 wherein the group of ion irradiated at their resonant frequency comprise ions having a charge-to-mass ratio different from the charge-to-mass ratio of ions detected during the detection time period.

16. The spectroscopy method as defined in claim 11 which includes,

increasing during the initial portion of the reaction time delay period the kinetic energy of a group of the trapped ions by a known amount by exciting said group of ions at their resonant frequency with an oscillating electric field pulse of known duration and magnitude applied transversely to the lines of force of the magnetic field, which ions of increased kinetic energy remain trapped in the analyzer cell through the detection time period.

17. The spectroscopy method as defined in claim 11 including,

scanning the reaction time delay period during succeeding cycles of operation for determination of the concentration of resonant ions as a function of reaction time.

18. The spectroscopy method as defined in claim 11 wherein the method is performed within a single region of an analyzer cell.

19. A spectroscopy method comprising, ionizing a sample within one region of an analyzer cell,

trapping substantially all ions of a given charge sign within said one region of the cell, causing them to move orbitally at angular frequencies dependent upon the charge-to-mass ratio of said ions by subjecting them to a unidirectional magnetic field and a plurality of static electric fields,

during a reaction time period, subjecting the trapped ionized sample to an oscillating electric field applied transversely to the lines of force of the magnetic field at a frequency removed from the angular frequency of all orbiting ions,

by step operation, following the reaction time period, bringing ions having a given charge-to-mass ratio and said oscillating electric field into resonance during a detection time period for determination of the concentration of the resonant ions, and neutralizing all of the ions within the analyzer cell after the detection time period.

20. A spectrometer comprising, a closed chamber to which a gas sample may be admitted,

an analyzer cell within the chamber, means for ionizing a gas sample admitted to the chamber during an ionizing period,

means for producing a magnetic field across the analyzer cell for causing substantially all ions of a given charge sign within the cell to move orbitally at angular frequencies dependent upon their charge-to-mass ratio,

trapping potential means applied to the analyzer cell for trapping the orbitally moving ions therewithin, means for producing a first oscillating electric field across the analyzer cell transverse to the magnetic field, which oscillating electric field is non-

resonant with any trapped ions, pulsed frequency shift means for bringing certain trapped ions having a given charge-to-mass ratio and said oscillating field into resonance only during a detection pulse period following a reaction time delay period whereby said resonant ions absorb energy from the oscillating field during said detection pulse period,

means for sensing such energy absorption only during said detection pulse period, and means for neutralizing all of the ions within the cell after the detection pulse period.

21. The spectrometer as defined in claim 20 wherein said pulsed frequency shift means for bringing certain of said trapped ions and said oscillating field into resonance comprises means for pulse changing the trapping potential means during the detection pulse period to change the angular frequency of said certain ions to the frequency of the oscillating electric field.

22. The spectrometer as defined in claim 20 including,

means for producing a second oscillating electric field across the analyzer cell transverse to the magnetic field for exciting ion cyclotron resonance of an ion species within the cell during an irradiating period during the initial portion of the reaction time period following the ionizing period and preceding the detection period to produce by ion-molecule reaction another species of ions which also are trapped within the analyzer cell.

23. An ion trap for use in a spectrometer or the like comprising,

an evacuable chamber to which a gas sample can be admitted,

an analyzer cell having at least 6 spaced electrodes disposed within said chamber including, (1) first and second electrodes forming first opposite sides, (2) third and fourth electrodes forming second opposite sides, and (3) fifth and sixth electrodes forming third opposite sides,

means for ionizing a gas sample admitted to the chamber within the cell,

means for producing a magnetic field across the cell for causing the ions within the cell to move orbitally, the magnetic lines of force extending through said first and second electrodes and generally parallel with said third, fourth, fifth, and sixth electrodes, and

a d-c potential source of one polarity connected to said first and second electrodes and a d-c potential source of opposite polarity connected to said third, fourth, fifth and sixth electrodes for producing static electric fields between the electrodes whereby orbiting ions having a charge sign of the polarity of said first and second electrodes are trapped within the cell.

24. The ion trap as defined in claim 23 including, means for applying a radio frequency potential across said third and fourth electrodes for the excitation and detection of cyclotron resonance of trapped ions of a given species.

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