

July 9, 1968

L. FRIEDMAN ET AL
MASS SPECTROMETER UTILIZING AN ION BEAM FOR IONIZING
THE GAS TO BE ANALYZED

3,392,280

Filed Feb. 10, 1967

2 Sheets-Sheet 1

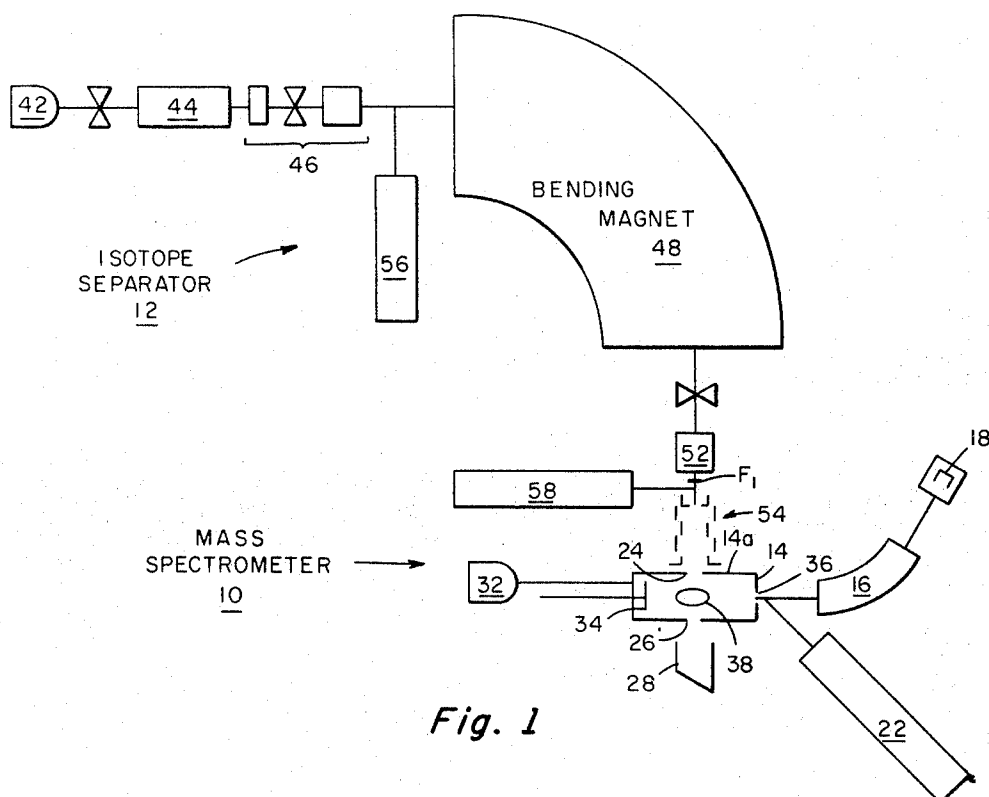


Fig. 1

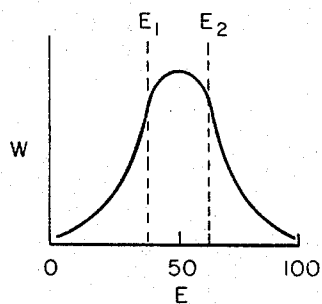


Fig. 1a

INVENTORS.

LEWIS FRIEDMAN

THOMAS F. MORAN

JACOB J. LEVENTHAL

Roland A. Anderson
Attorney

July 9, 1968

L. FRIEDMAN ETAL

3,392,280

MASS SPECTROMETER UTILIZING AN ION BEAM FOR IONIZING
THE GAS TO BE ANALYZED

Filed Feb. 10, 1967

2 Sheets-Sheet 2

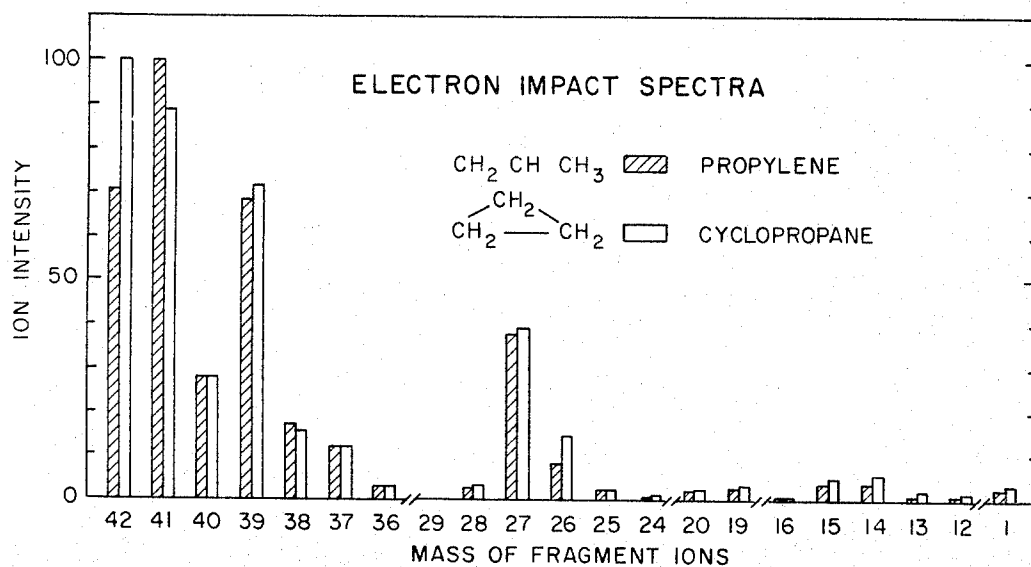


Fig. 2

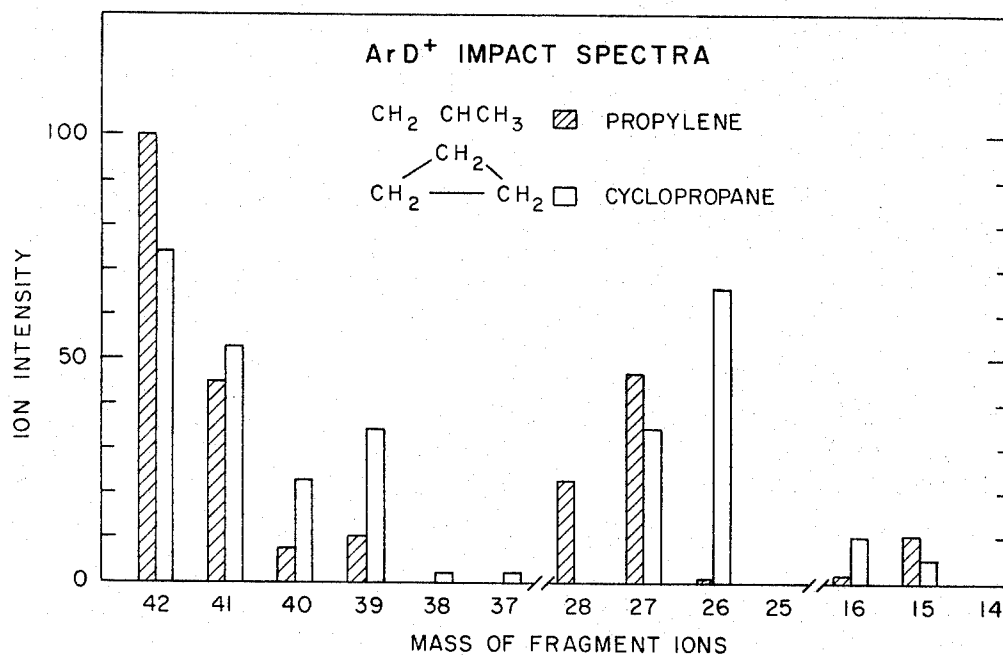


Fig. 3

INVENTORS.

LEWIS FRIEDMAN

THOMAS F. MORAN

JACOB J. LEVENTHAL

Roland A. Anderson
Attorney

1

3,392,280

MASS SPECTROMETER UTILIZING AN ION BEAM FOR IONIZING THE GAS TO BE ANALYZED

Lewis Friedman, Patchogue, N.Y., Thomas F. Moran, Decatur, Ga., and Jacob J. Leventhal, Mount Sinai, N.Y., assignors to the United States of America as represented by the United States Atomic Energy Commission

Filed Feb. 10, 1967, Ser. No. 616,425

7 Claims. (Cl. 250-41.9)

ABSTRACT OF THE DISCLOSURE

A method and apparatus for utilizing ion impactation to identify materials and which is especially useful for distinguishing between isomeric molecules. A mass spectrometer is used in which the material to be investigated is vaporized. The vapor is bombarded by an external beam of ions such as ArD^+ having sufficient energy to ionize the molecules of the material being investigated. The mass spectrogram which is formed for the particular material being investigated is unique and reproducible so that identification, even as between isomers of the same molecule, is possible.

Background of the invention

The invention described herein was made in the course of, or under a contract with, the U.S. Atomic Energy Commission.

Electron impact ionization techniques are used extensively to provide information on molecular structures. By this process ionized species are decomposed unimolecularly to yield mass spectra in mass spectrometers where it is possible to identify the material undergoing examination. This technique has also been extended to the analysis of materials for the purpose of determining molecular structure or configuration. While some success has been attained with the use of electron impactation, less reliable results are obtained where the molecular structures to be investigated have differences which are subtle, as for example, the structural differences between the isomers of an organic molecule. It has been found that the impact energies required for electrons to produce the necessary excitation often is sufficient to obscure these differences by altering the molecular structures being investigated.

Summary of the invention

This invention relates to the use of mass spectra and ion impact techniques in particular for producing mass spectra with improved distinguishability of the differences existing in the molecular structures of complex molecules.

It has been found that ion impact instead of electron impact can be utilized in many cases to ionize the materials under investigation for mass spectra without at the same time effecting changes in molecular structure which would thus obscure the results.

While the theoretical basis for such a result is not yet fully understood, it is thought that this result is due at least in part to the fact that ion impact provides a way of depositing energy by an overall mechanism which is significantly different from that operative in electron impact and permits a more precise control of the magnitude of the excitation in the target molecule. Under this theory, the bulk of the energy deposited in ion impact processes, if relatively low velocity ions are used as projectiles, comes from the recombination energy of the projectile ion and additional energy deposited locally at the point of impact between the colliding molecules by conversion

2

of projectile ion translational energy into target molecule internal energy. Hence, if it is desired to demonstrate differences in decomposition patterns between isomeric molecules, the ideal projectile should have a recombination energy very close to the ionization potential of the target isomers and the additional energy to produce the ion fragments should then come from translational energy of the projectile. The success of such an approach is thought to depend on the validity of the assumption that kinetic energy deposited locally in a molecule ion sets up a forced vibration which favors dissociation prior to redistribution of this excess energy among other internal degrees of freedom in the target molecule ion. If a statistical distribution of energy takes place prior to decomposition, then mass spectra similar to those obtained by electron impact would be expected. The results as herein-after described appear to support this theory.

As will be seen from the discussion and examples presented below, this invention makes it possible to detect small and subtle differences in molecular structures to an extent not heretofore thought to be possible.

It is thus a principal object of this invention to provide a method and apparatus for mass spectral analysis utilizing ion impact.

Other objects and advantages of this invention will hereinafter become evident from the following description of the preferred embodiments of this invention.

Brief description of the drawings

FIG. 1 illustrates schematically apparatus for carrying out the principles of this invention;

FIG. 1a is a graph showing schematically the distribution of ions in a beam having a selected kinetic energy;

FIG. 2 is a graph of the mass spectra obtained in two kinds of organic molecules obtained by electron impact; and

FIG. 3 is a similar graph obtained from ion impact.

Description of the preferred embodiments

Briefly described, the invention comprises the use of a beam of ions to ionize the gaseous species under investigation which is supplied to the ionizing chamber of a mass spectrometer and to produce therefrom a reproducible mass spectrogram representative of this species. The beam of ions is of sufficient intensity to produce measurable interactions with said species. Furthermore, the beam of ions must have a particular kinetic energy not exceeding 100 ev. with an energy distribution that concentrates a major fraction of this beam within 20% of the selected kinetic energy at the lower energy bound of 1 ev. and with much better energy resolution or concentration at higher kinetic energies so as to obtain reproducible results. In the range of 1 to 100 ev. it has been found that the range of intensity of the ion beam is 2×10^{-8} to 2×10^{-12} in units of amperes.

Another requirement of this invention is that the ion projectiles should also have available internal energy which is in excess of but very close to the ionization potential of the target species. The available ion energy consists of recombination and translational energy of the ions. The recombination energy is the energy released when an electron and a singly charged positive ion "neutralize" each other. Ionization potential refers to the energy necessary to remove an electron from a neutral atom or molecule. For a given atom or molecule the recombination energy and ionization potential are generally equal to each other. It will be seen from the discussion below that for certain ions used to carry out the principles of this invention the corresponding neutral molecules are unstable species. For example, the ion ArH^+ consists of an argon atom and a proton "bound" together. The addition of an electron to this argon-hydride ion results in

separate argon and hydrogen atoms (both neutral). As chemically the argon and hydrogen atoms cannot be bound together, it is meaningless to speak of the ionization potential of ArH . Thus, within the context of this invention the recombination energy of ArH^+ or other unstable ions whose neutral molecule is an unstable species is meant simply the amount of energy liberated in the neutralization and production of the separate stable molecules or atoms, in this example, Ar and H.

The requirement that the recombination energy be close to the ionization potential of the neutral gaseous species undergoing investigation ensures that more energy than is actually required to ionize the species will not be left over and be deposited in the ion, i.e., alter the molecular structure. The excess of available internal energy over ionization potential must be relatively small in terms of chemical bond energies which are in the range of 2–10 electron volts. While it is not possible to define in exact terms what is meant by small, it is considered that ordinarily the excess in this energy should be less than 10% of the particular chemical bond energies involved in the particular gaseous species undergoing investigation. In contrast to the use of electron impact to produce the ionized species where the energy deposited is in excess of ionization potential usually by several or more volts, in the present invention the excess is of the order of a few tenths of a volt.

In order to carry out the principles of this invention a unique arrangement of apparatus has been provided to obtain the ionization of the mass to be analyzed by the use of ion beams. Referring to FIG. 1 there is shown somewhat schematically a mass spectrometer 10 arranged to function with an isotope separator 12 in a manner hereinafter to be more particularly described. Mass spectrometer 10 consists of an ionization chamber 14, a bending magnet 16, and a product ion collector 18. A vacuum system 22 maintains spectrometer 10 at a very low pressure as is understood in the art. The impact ions enter chamber 14 by way of a slit or opening 24 in wall 14a and leave by way of an opening 26 and are collected in the primary ion collector 28. The vapor undergoing investigation enters chamber 14 from a source or reservoir 32. The vapor molecules ionized by the beam of ions is caused by a repeller electrode 34 to drift through opening 36 where they are then accelerated by appropriate lenses, not shown, and bent in magnet 16 and directed into collector 18 where the analysis is made as is understood in the art. A description of how this analysis is made as well as a more complete description of mass spectrometer is given in "Mass Spectrometry, Organic Chemical Applications" by Klaus Biemann, published in 1962 by McGraw-Hill Book Company, Inc.

The far wall of chamber 14 shown in FIG. 1 is provided with an opening 38 for a beam of electrons supplied in conventional fashion for electron impact analysis. The conventional mass spectrometer is provided with this opening for the electron beam. In accordance with this invention, rather than merely substitute the ion beam for the electron beam, we have added the ion beam source at right angles to the source of the electron beam to accomplish unique results as to be hereinafter described. Hence, mass spectrometer 10 illustrated in FIG. 1 is conventional in configuration except for the addition of openings 24 and 26, and collector electrode 28.

Isotope separator 12, which is arranged to provide the ion beam for use in ionization chamber 14 of mass spectrometer 10, consists of a reservoir 42 supplying gas to ion source chamber 44 where the gas is ionized in conventional manner, a lens system 46 for collecting the ions produced in chamber 44 and providing a beam of the ions, analyzing magnet 48 for eliminating the unwanted ions, and additional lens 52 and 54 for focusing the ions. The ions are focussed at a focal point F_1 and thereafter spread slightly as they impinge on outer wall 14a of ionization chamber 14. This spread is considered to be

of the order of about 50 volts kinetic energy. As is understood in the art this energy distribution is generated in source chamber 44.

The use of opening 24 located downstream of focal point F_1 makes it possible to select the particular fraction of the ion beam which is at the kinetic energy which has been selected and by this is meant that the major fraction of this beam lies within 20% of the selected value at the lower energy bound and within a smaller deviation as the kinetic energy increases. As illustrated in FIG. 1a showing a typical distribution of the kinetic energy of a beam of ions in the 1 to 100 ev. range, the use of opening 24 permits the ions between E_1 and E_2 to be passed and those outside of this range to be rejected. W represents number of ions, or ion density. From the shape of the curve it will be seen that the major fraction of the ions is covered by this narrow range of energies.

It has been found that when the size of opening 24 into chamber 14 is at 0.5 mm. a suitable spread of about 0.2 volt is obtained. An opening smaller than 0.5 mm. is not considered feasible due to alignment difficulties and reduced beam density, while a large diameter broadens the beam spread of the ions. By this arrangement it is possible to provide a beam of ions into chamber 14 which is remarkably pure or uniform in ion velocity. This leads to improved results in spectrometer 10 due to the narrow energy beam used to ionize the mass undergoing analysis. In addition, the small size of opening 24 has the further advantage of minimizing gas leakage into chamber 14.

Isotope separator 12 is provided with the usual vacuum and inert gas supply systems 56 and 58 as well as other conventional auxiliary apparatus (not shown) to effect the proper operation of the equipment as is understood in the art.

In the operation of the apparatus described, mass spectrometer 10 would be supplied with the vapor of the species to be analyzed from reservoir 32 into ionization chamber 14. Separator 12 would be operated in the usual manner to supply the desired ion beam into chamber 14 through opening 24. Separator 12 can be operated to supply its ion beams in pulses or continuously. Mass spectrometer 10 can be used initially with electron bombardment in conventional manner for the purpose of verifying the mass sample being analyzed and to measure pressure of gas within, i.e., ion production. If desired, the ion and electron beams can be supplied alternately to provide this information continuously. In conventional manner, ions of mass sample are collected at collector 18 where the mass spectra are analyzed in conventional fashion.

By the application of the principles of this invention, determinations have been made of ion impact mass spectra of the isomeric butenes, propylene and cyclopropane, using low velocity ArD^+ , COD^+ , and Ar^+ ions, respectively, as projectiles. The ArD^+ ions are produced in separator 12 by ionizing a mixture of argon and deuterium gases and bringing about the reaction $\text{D}_2^+ + \text{Ar} \rightarrow \text{ArD}^+ + \text{D}$ followed by separation in magnet 48. The COD^+ ions are produced by the electron bombardment of a mixture of CO and D_2 , while Ar^+ is produced from argon alone in separator 12.

As an example of this invention, reference is made to FIG. 2 showing the results obtained with electron impact of propylene and cyclopropane and to FIG. 3 for a similar analysis or mass spectra prepared from impact by 10 ev. ArD^+ ions. In FIG. 2, the unshaded bars represent the mass spectrum obtained for cyclopropane whereas the shaded bars represent the mass spectrum for propylene. It will be seen that the two mass spectra are almost identical and therefore virtually undistinguishable from each other so that on the basis of the mass spectra obtained it is not possible to be certain from a single analysis which of the two isomers is present. On the other hand, referring to FIG. 3, there are shown two sets of mass spectra obtained for these same materials

obtained from the use of ArD⁺ instead of electrons as the impact beam. It will be seen that in this case the mass spectra are clearly different from each other so that these isomers are readily distinguishable from each other. Other sets of mass spectra were obtained for these materials using COD⁺ and Ar⁺ ions as ionizing beams with similar distinguishing results.

Significant differences between the two sets of mass spectra support the conclusion that while extensive dissociation of parent molecule ions takes place in both experiments, fundamentally different energy transfer and dissociation mechanisms must operate.

As a result of this invention, it has been discovered that in producing such ion beams as D₂⁺, D₃⁺, Ar⁺, ArD⁺, and HeH⁺, it is possible to produce such beams with an intensity of about a thousand times greater than they can be produced by any of the other more conventional approaches. Examples of the intensities obtained are given in the following table.

TABLE.—INTENSITY OF MASS ANALYZED PRIMARY IONS IN COLLISION CHAMBER AS A FUNCTION OF KINETIC ENERGY

Ion	Intensity in Units of Amperes		
	2 ev.	10 ev.	100 ev.
D ₂ ⁺	2.6×10 ⁻¹⁰	2.6×10 ⁻¹⁰	1.5×10 ⁻⁹
D ₃ ⁺	3.9×10 ⁻¹¹	3.9×10 ⁻¹¹	2.3×10 ⁻¹⁰
Ar ⁺	7.4×10 ⁻¹⁰	7.4×10 ⁻¹⁰	2.0×10 ⁻⁸
ArD ⁺	1.1×10 ⁻¹⁰	1.1×10 ⁻¹⁰	4.9×10 ⁻⁹
HeH ⁺	2.8×10 ⁻¹²	2.8×10 ⁻¹²	3.2×10 ⁻¹¹

It is thus seen that there has been provided a unique and improved method and apparatus for obtaining and utilizing mass spectra. While the details of the mechanisms operating in producing these spectra are not as yet fully understood, it is clear that the method and apparatus described are capable of producing a degree and type of discrimination not heretofore considered to be possible. While only preferred embodiments of the invention have been described it is understood that the invention is not to be limited thereby but is to be defined only by the scope of the appended claims.

We claim:

1. In the method of mass-spectral analysis, a method of ionizing a gaseous organic species for the purpose of mass structural determination, the improvement comprising bombarding the said gaseous species with a portion of an ion beam said ion beam having sufficient intensity to produce measurable interactions with said species and a well defined kinetic energy selected at a value within the range of about 1 to 100 ev. with said portion of the ion beam having a kinetic energy within 20% of the value of the kinetic energy of said ion beam.

2. The method of claim 1 in which the available ion

energy of the ions in said beam exceeds the chemical bond energy of the molecules of said species by a relatively small amount.

3. The method of claim 2 in which the bombardment of said species is conducted intermittently and the species is bombarded with an electron beam between ion bursts to permit continuous identification of the species and regulation of the gaseous species pressure.

4. Apparatus for the mass-spectral analysis of a gaseous organic species including a mass spectrometer using an isotope separator as a source of an ion beam for the purpose of structural determination, said mass spectrometer having an ionization chamber, means for supplying the species vapor to said chamber, means for accelerating and focusing the species ions, and means for collecting and analyzing spectrally said ions, the improvement comprising:

(a) means for directing the ion beam output of said separator into said ionization chamber of said mass spectrometer, said beam being of sufficient intensity to produce measurable interactions with said species within said chamber and a well defined kinetic energy selected at a value within the range of about 1 to 100 ev., and

(b) means in said mass spectrometer to pass into said ionization chamber only a particular portion of said ion beam having a kinetic energy which is within 20% of said selected value.

5. The apparatus of claim 4 in which said mass spectrometer includes means for permitting delivery of a beam of electrons into said ionization chamber for ionizing said species, thereby permitting sequential ion and electron impaction of said species for indicating conditions within said chamber.

6. The apparatus of claim 5 in which said delivery means comprises an opening in the wall of said spectrometer ionization chamber and a lens system to focus said beam of ions at a point upstream of said opening to permit a slight defocussing of the ions at said opening, the size of said opening being small enough to select for entry a predetermined portion of the spectrum of said ions.

7. The apparatus of claim 6 in which the ion beam consists of ions whose available ion energy exceeds the chemical bond energy of the molecules of said species by a relatively small amount.

No references cited.

50 RALPH G. NILSON, *Primary Examiner.*

S. C. SHEAR, *Assistant Examiner.*