

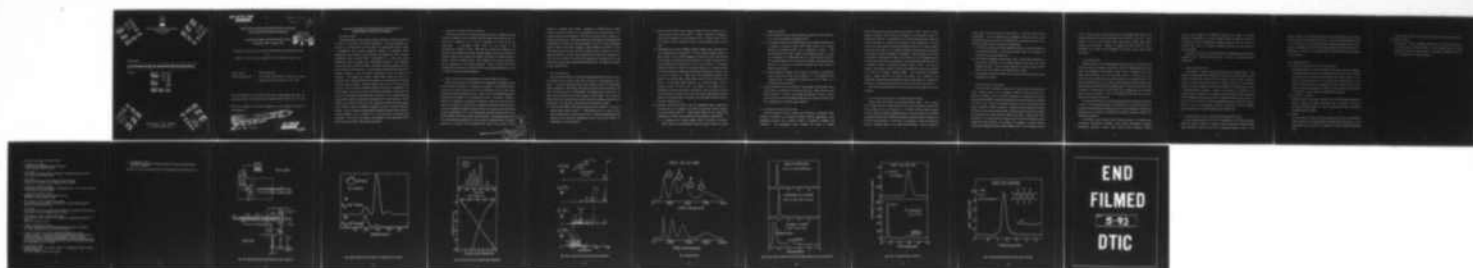
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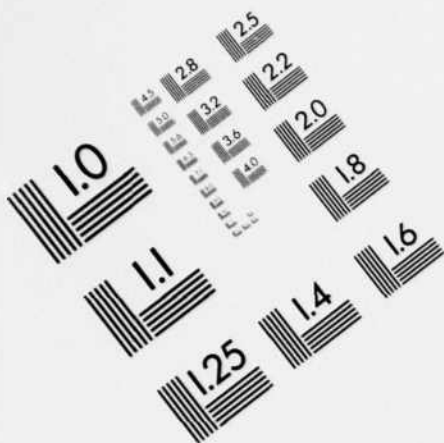
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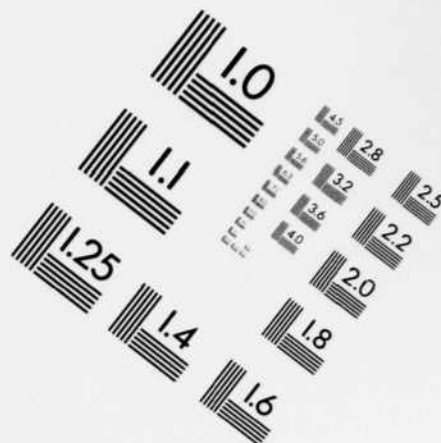




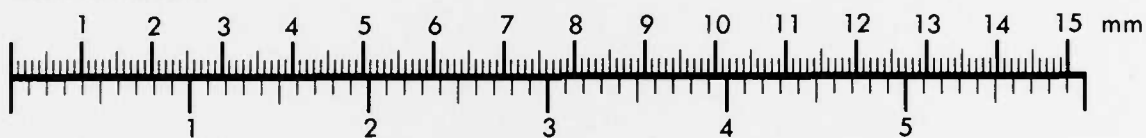
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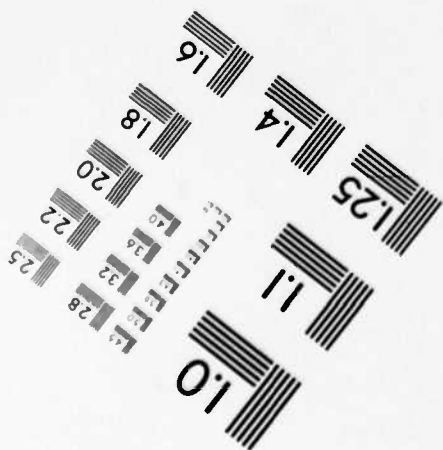
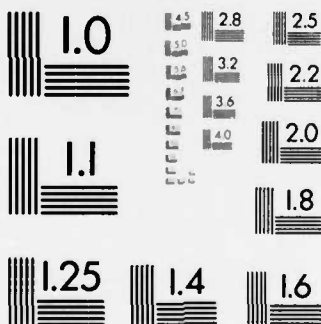
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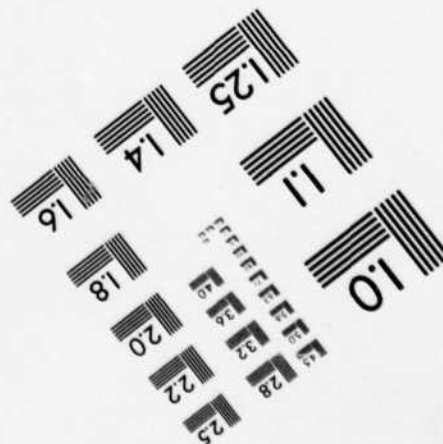
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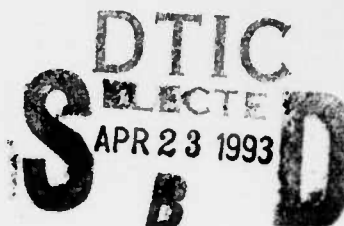
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Molecular Ionization and Dissociative Ionization at Hyperthermal Surface Scattering

Final Research Report Covering the Research Period

25 September 1989 - 24 March 1993



Submitted to the United States Army Research, Development and Standardization Group

by

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Contract number:

DAJA 45-89-C-0033

Contracting Representative:

Mr. R. Elishav, Head, Section of Contracts and Grants

Applications, Tel Aviv University, Tel Aviv, Israel

The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army.

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MOLECULAR IONIZATION AND DISSOCIATIVE IONIZATION AT HYPERTHERMAL SURFACE SCATTERING

Final Report Abstract

Hyperthermal surface scattering induced molecular ionization was studied in depth both in terms of its mechanism and analytical applications. Five main mechanisms were illuminated, (a) molecule-surface electron transfer, (b) surface-molecule electron transfer, (c) hyperthermal surface induced dissociative ionization, (d) chemically induced hyperthermal surface ionization, and (e) local hot spot hyperthermal surface ionization. Hyperthermal surface ionization (HSI) is characterized by a unique mass spectral fragmentation which can originate from non-statistical dissociation. The collisionally activated dissociation in HSI was studied in alkyl halide molecules, piperidine and in the large poliatomic molecule cholesterol. A new supersonic molecular beam-mass spectrometry apparatus, optimized to study the analytical applications of HSI was designed and constructed. The apparatus also included a unique electron impact ion source for a comparative study. Oxidized rhenium foil was found to be an ideal surface for analytical HSI with long term stability, very high ionization yields even over 10% and tunable selectivity. Over 10^{+4} selective anthracene ionization over decane was demonstrated. We have developed a unique fast GC inlet to the HSI mass spectrometer. This fast GC inlet proved to be a powerful inlet system which allows an ultrafast (< 1 sec) GC-MS measurements and improved the GC-MS of thermolabile and relatively non volatile compounds. The fast GC-MS was also tested in the analysis of target compounds in complex "real world" samples such as caffeine in coffee or tetraethyllead in gasoline, and clean two seconds GC-MS were obtained. We have succeeded in demonstrating 400 attogram minimum detected amount of deuterated anthracene. This is considered to be a record sensitivity in quadrupole mass spectrometry. The results of this research were published in twelve publications and Dr. Danon was awarded his Ph.D. degree Summa Cum Laude.

1. *Introduction and General Scope of the Research*

The research was focused on molecular ionization phenomena at hyperthermal surface scattering. Hyperthermal surface ionization (HSI) was studied in depth both in terms of its various active mechanisms, and in terms of elucidating its various features and characteristics. A considerable research effort was also devoted to the practical-analytical applications of HSI. While the basic research was performed in an ultra high vacuum molecular beam-surface scattering apparatus, a new mass spectrometry in supersonic molecular beam apparatus was designed, constructed and optimized during this research. This newer apparatus allowed a close evaluation of the analytical potential of HSI in confronting real world analytical applications. Thus we find that this research comprised both of basic fundamental research of the newly discovered HSI phenomena, as well as its analytical mass spectrometric applications.

2. *The New Supersonic Molecular Beam-Mass Spectrometry (SMB-MS) Apparatus*

While the basic research on the establishment of the mechanisms of hyperthermal surface ionization (HSI) was performed, a new apparatus was designed. The philosophy behind its construction was both to speed up the rate of data collection and to test several ideas concerning the analytical applications of HSI. In figure 1 this fast GC-SMB-MS apparatus is described with an expanded view of the unique fast GC inlet. The sample is inserted, or injected from a syringe into the vaporizing oven (3) and is swept by the carrier gas, whose flow rate is controlled by V_1 needle valve to a megabore (0.53 mm ID) capillary column (4). The flow rate through this separately heated GC column is also regulated by the make up gas introduced through needle valve V_2 . The sample-carrier gas mixture expands into the vacuum chamber through a home-made all ceramic supersonic nozzle (5). The emerging supersonic free jet is doubly differentially pumped by a 4" and a second 63 mm diffusion pumps. The sample molecules can be ionized by the fly-through electron impact (EI) ion source and 90°

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deflected to a quadrupole mass analyzer. Alternatively, a suitable surface is inserted instead of the 90° ion deflector for the hyperthermal surface ionization (HSI) of the supersonic molecular beam constituents. The ions are extracted and mass analyzed by a quadrupole mass analyzer (8). The molecular beam can also be square wave modulated by the beam chopper (9). The data is processed and presented on a PC (10). The fast GC-SMB-MS apparatus contains several unique components, carefully designed and optimized. Several such central components are the fast GC, the sample injection device, the fast GC flow regulation system, the all ceramic channel supersonic nozzle source, the fly-through EI ion source, the 90° ion deflector, the HSI surface preparation and mounting device, the ion transfer optics and the vacuum system-perpendicular QMS design. This apparatus is described in detail in publication 12.

3. *HSI - The Mechanisms*

Since the surface ionization of molecules having hyperthermal kinetic energy was new and surprising, we have devoted a major effort to the study of its mechanisms and various features. In HSI, the hyperthermal kinetic energy effectively bridges the thermodynamic energetic requirements of the difference between the molecular ionization potential and the surface work function (positive ion HSI (PHSI)) or the difference between the surface work function and the molecular electron affinity (negative ion HSI (NHSI)). Thus, virtually all organic molecules can undergo efficient ionization following a hyperthermal collision with a suitable surface. Five main types of HSI processes were observed and studied;

- (a) Positive ion HSI (PHSI), where positive molecular ions were produced as a result of a molecule-surface electron transfer^[3,7,11]. PHSI benefits the use of a surface with a high work function such as rhenium oxide or Pt(111). PHSI results predominantly with molecular ions but consecutive fragmentation can also occur near the surface^[11] or unimolecularly far from the surface^[8].

- (b) Negative ion HSI (NHSI), where negative molecular ions were produced due to a surface-molecule electron transfer process^[3,7]. NHSI is optimized on semiconductor surfaces such as diamond(111), silicon Si(100) or Si(111). Probably surfaces with low work function can also be effective, but they are more chemically reactive and less stable.
- (c) Hyperthermal surface induced dissociative ionization (HSIDI), where both negative and positive fragment ions were produced^[3,7,11]. We have studied the HSIDI mechanism in detail recently^[11] and our proposed mechanism is based on an initial surface-molecule electron transfer to molecules such as R-X where R is an organic radical and X is a group with high electron affinity such as Cl, Br, I, NO₂, CN, PO₂, etc. The negative molecular ion formed is unstable since the electron affinity of X is much larger than that of R-X and thus RX⁻ spontaneously dissociates near the surface to R and X⁻. This X⁻ species are scattered as a negative ions with *reneutralization* probability that depends on its electron affinity, kinetic energy, surface reactivity and surface work function. R, the organic radical possesses a low ionization potential. Thus, it effectively transfers an electron back to the surface (to the single hole in a semiconductor) and may scatter away as a positive ion. The overall result is a surface catalyzed dissociative ionization, with a much lower kinetic energy threshold than that required for gas phase dissociative ionization, and with different ionization yield for the positive and negative ions.
- (d) Chemically induced HSI (CIHSI), where the hyperthermal kinetic energy-surface scattering results in the creation of new species with favorable electronic properties that promote efficient HSI^[1,4,6-8,11]. CIHSI presents perhaps the most surprising and intriguing aspect of HSI. Several examples that were extensively studied include:
- d1. Cl₄ scattering from a thoriated tungsten surface was involved with collision induced chlorine atom chemisorption followed by thermal negative ion surface

desorption ionization^[1].

- d2. Xenon scattering from Pt(111) surface resulted in the formation of NaXe^+ and KXe^+ due to surface-atom impurity ion transfer process^[4].
- d3. The scattering of amines such as DABCO ($\text{C}_6\text{H}_{12}\text{N}_2$) with a high proton affinity from a hydrogen (or deuterium) covered Pt(111) surface resulted in the effective generation of protonated molecular ions as demonstrated in figure 2. This surface-molecule proton transfer reaction was experimentally proven to be the first demonstration of an Eley-Rideal type of a catalytic chemical reaction^[6,8]. The proposed mechanism involves a first step of molecule-surface electron transfer followed by a second step of surface-ion hydrogen atom transfer during the impulsive scattering event.
- d4. Simple hydrocarbon molecules such as octane or cyclohexane are hyperthermal surface ionized to give $(M-1)^+$ quasi molecular ion. The hyperthermal surface scattering induces a molecule-surface hydrogen atom transfer followed by a radical-surface electron transfer^[7].
- (e) Local hot spot HSI was observed in Hg-Pt(111) scattering where the atom-surface energy transfer induced a transient local hot spot which facilitates a high efficiency thermal surface ionization^[5]. In figure 3 the resulting mass spectrum of mercury is shown. Note that mercury possesses the highest ionization potential among all the metal atoms and is unamenable for conventional surface ionization.

4. *Collisionally-activated Dissociation in HSI*

Upon the formation of positive molecular ions following the hyperthermal surface scattering, the molecular ion can undergo an efficient consecutive fragmentation. These fragmentation processes were extensively studied in cholesterol^[9], alkylhalide and piperidine^[11]. The hyperthermal surface scattering also mediate an efficient

kinetic-vibrational molecular energy transfer in the range of 15-20%. Thus as the kinetic energy is increased, a gradual increase in the degree of ion dissociation is observed, as demonstrated in figure 4. In cholesterol at 5.3 eV incident molecular kinetic energy, the HSI mass spectrum was dominated by the undissociated parent molecular ion. Upon the increase of the kinetic energy, lower mass ions appeared while at 22 eV incident cholesterol kinetic energy, the parent ion was completely dissociated and the mass spectrum exhibited only extensive consecutive fragmentation. Cholesterol is a large polyatomic molecule thus its dissociation is unimolecular far away from the surface, and all the fragments observed also appear in electron impact mass spectrometry. On the other hand, smaller molecules such as piperidine^[11] exhibit a non-statistical dissociation unique to HSI. The HSI mass spectra of small polyatomic molecules reveal only few fragment ions, usually heavy fragments with relatively low fragment ionization potential. This non-statistical fragmentation pattern is largely affected by the surface work function and is attributed to fast intramolecular vibrational energy redistribution near the surface followed by subpicosecond dissociation. The fragments can then transfer an electron to the surface and be ionized.

Note that the non-statistical HSI mass spectra contain extensive isomer and structural information.

5. *Electron Impact Mass Spectrometry in Supersonic Molecular Beams*

Electron impact (EI) ionization is the standard ionization method. We have realized that it is highly desirable to couple HSI and EI. Thus, the new apparatus contains EI and HSI ion sources in line on the beam axis. EI provides relatively uniform ionization efficiency with known statistical fragmentation pattern. Thus, the comparison of EI and HSI mass spectra provides useful information concerning non-statistical dissociation pathways in HSI and isomer information. It also allows easy assessment of relative sensitivities and provides a calibration method for the relative HSI efficiencies. We have studied the

various features of electron impact mass spectrometry in supersonic molecular beams (EI-MS-SMB)^[2]. We have demonstrated that hyperthermal supersonic molecular beam, considerably enhances the performance of EI provided that a fly-through ion source is used. The following unique features were studied and demonstrated;

- (a) The internal vibrational supercooling considerably enhances the relative abundance of the undissociated molecular ion and allows a gradual control of the molecular ion dissociation via the electron energy used.
- (b) The directional hyperthermal kinetic energy allows vacuum related background ion filtration due to differences in the ion kinetic energies of beam species and vacuum background molecules. Thus the detection sensitivity is increased and the ion source response is ultra fast regardless of the sample molecules volatility.
- (c) EI complements and supplements HSI in the same mass spectrometry apparatus and inlet including the fast GC-MS.

6. *The Search for the Ideal HSI Surface*

We have devoted a considerable amount of time to the search of an ideal practical surface. While this search is not yet completed for negative ion HSI, we believe that a simple foil of rhenium is close to be ideal for the purpose of analytical positive ion HSI. We used a 20 μm thick Re foil (Goodfellow 99.99%) which is a technical inexpensive metal and not a single crystal. The surface was cleaned outside the vacuum by acids and heated with oxygen in vacuum^[12] to enhance its efficiency. Temperature control and heating were simply performed by a direct current heating (2-8 Amp). Oxygen was leaked into the vacuum chamber near the surface for the surface oxidation, probably to form ReO_2 . Oxygen serves for both the creation of a very high surface work function (6.4 eV) and for the continuous catalytic combustion of organic impurities. Thus, rhenium oxide exhibited a very good long term stability under contaminated medium vacuum conditions (10^{-6} - 10^{-5} torr). Rhenium oxide can

serve as a universal organic molecules HSI surface with the highest yields observed. We estimate the HSI yield of large aromatic molecules, drugs or amines to be over 10%. A small drawback is that due to the very high surface work function a slight vacuum thermal background is also observed. Tungsten is a slightly less efficient surface, but with a considerable lower thermal vacuum background and smaller oxygen partial pressure requirements.

7. *Fast GC-MS with HSI*

Referring to figure 1, a 50 cm long megabore column serves for a fast GC separation and connects the injector and supersonic nozzle source. The fast GC-MS sampling is based on a septum free atmospheric pressure heatable injector with a conventional syringe based splitless sample injection. The carrier gas linear velocity is controlled by a by-pass (make up) gas flow introduced after the column and prior to the supersonic nozzle. The supersonic expansion serves as a jet separator and the skimmed supersonic molecular beam (SMB) is highly enriched with the heavier organic molecules. The supersonic molecular beam constituents are ionized either by electron impact (EI) or hyperthermal surface ionization (HSI) and then mass analyzed. The use of hyperthermal SMB facilitates an ultra fast response time of both these ion sources.

A one second fast GC-MS of four aromatic molecules solvated in methanol is demonstrated in figure 5 and the fundamental aspects of fast GC-MS with a time limit constraint were calculated and studied both experimentally and on a PC. Flow programming was developed and implemented and the analysis of thermolabile and relatively non-volatile molecules was demonstrated and studied.

Fast GC-MS of several mixtures with the following molecules was studied; benzene, chlorobenzene, bromobenzene, iodobenzene, nicotine, caffeine, methylstearate, testosterone, progesterone, cholesterol, L-proline, purine, atrazine, decane, anthracene, perylene,

coronene, ovalene, phthalocynine, tetraethyllead, paracetamol and codeine. The GC-MS separation and quantification of "real world" complex mixture was studied (see figure 6) in the detection of lead (as tetraethyllead) in gasoline, caffeine in coffee and codeine in a commercial drug. Only a few seconds were required in all these and other fast GC-MS analysis performed.

We consider our work on fast GC-MS with HSI to be a breakthrough in analytical mass spectrometry with a considerable future potential. This work is described in detail in publication 12.

8. *Selective Ionization with HSI*

In the analysis of complex mixtures, selective ionization is highly desirable. Since HSI yield strongly depends on the molecular ionization potential and other features, we have studied the possible selective HSI, with ways to control or tune the degree of selectivity achieved. We have found that HSI can serve as a selective ion source that can minimize the ionization of aliphatic compounds without largely affecting the ionization yield of aromatic or nitrogen heterocyclic compounds. In figure 7 this selectivity is demonstrated in the selective detection of anthracene in a solution with 100 times higher decane concentration. The fast GC-MS traces show that the selective anthracene ionization can be tuned in the range 10^{+1} - 10^{+4} . Note that 10^{+4} selectivity (anthracene/decane) can be achieved with only a factor of 3.8 loss in the anthracene ionization and practically no loss in anthracene detection limits due to a substantial reduction of the chemical noise.

9. *Sensitivity and the Search for Attogram Range Minimum Detected Level*

One of the primary goals of our work was to demonstrate record detection sensitivities. Indeed very recently we achieved a "milestone" record of subfemtogram minimum detected amount with HSI. In figure 8 a fast GC trace of deuterated anthracene is shown. 0.1 μ L

methanol solution of 1 ppb deuterated anthracene was injected and single ion monitoring at 188 amu was performed with HSI on rhenium oxide. Since the deuterated anthracene contains only ~ 80% anthracene-D₁₀, the injected amount was actually 80 femtogram and the extracted signal to two RMS noise was 220. Thus the linear extrapolated minimum detected level is ~ 400 attogram. To the best of our knowledge this is the record detection limit in quadrupole mass spectrometry.

10. *Administrative Actions*

10a. *A collaboration with Dr. Brad E. Forch of the U.S. Army*

During this research I have visited Dr. Brad E. Forch several times at his laboratory in the Ballistic Research Laboratory at Aberdeen Proving Ground. We have discussed several aspects of this work that were presented in several seminars there. We also initiated a collaboration on the use of a pulsed flame ionization detector for the study of laser-flame ignition that was studied by Dr. Forch. While this effort was not continued, I enjoyed very much my visits and the warm and friendly research atmosphere at his laboratory. I hope to enhance our collaboration in the future.

10b. *Participation in conferences*

During the period of this research I attended, every year, the Pittsburgh conference on analytical chemistry and applied spectroscopy and the American Society Mass Spectrometry meetings (ASMS). Our work was presented and I believe it initiated a considerable interest and impact.

10c. *Students*

Dr. Albert Danon was working on this research and wrote his thesis on Hyperthermal Surface Ionization. He was awarded his Ph.D. with Summa Cum Laude which is a very rare achievement in Tel Aviv University. Dr. Danon is now working at the Dimona Research Center.

Mr. Shai Dagan is currently working on this research as part of his graduate research.

10d. *Continued research*

We thank the U.S. Army for funding this research. Since we evaluate this research as a very successful one, we intend to continue it in order to initiate a new area of "Mass Spectrometry in Supersonic Molecular Beam". The research is continued at a low rate and a new funding source is being searched for.

11. *Publications Describing this Research's Results*

1. A. Danon and A. Amirav
Chemically Induced Hyperthermal Surface Ionization.
J. Chem. Phys. 92, 6968-6970 (1990).
2. Aviv Amirav
Electron Impact Mass Spectrometry of Cholesterol in Supersonic Molecular Beams.
J. Phys. Chem. 94, 5200-5202 (1990).
3. Aviv Amirav
Processes in Hyperthermal Atom and Molecule Surface Scattering.
Invited review - Comments. At. Mol. Phys. 24, 187-211 (1990).
4. A. Danon, A. Vardi and A. Amirav
NaXe and KXe Positive Ion Formation in Hyperthermal Xenon - Pt(111) Surface Scattering.
J. Chem. Phys. 93, 7506-7507 (1990).
5. A. Danon, A. Vardi and A. Amirav
Hyperthermal Surface Ionization of Mercury on Pt(111).
Phys. Rev. Lett., 65, 2038-2041 (1990).
6. E.W. Kuipers, A. Vardi, A. Danon and A. Amirav
Surface Molecule Proton Transfer - A Demonstration of the Eley-Rideal Mechanism.
Phys. Rev. Lett., 66, 116-119 (1991).
7. Aviv Amirav
Electron Impact and Surface Ionization Mass Spectrometry in Supersonic Molecular Beams.
Invited review - Org. Mass. Spectrom. 26, 1-17 (1991).
8. E.W. Kuipers, A. Vardi, A. Danon and A. Amirav
Surface-Molecule Proton Transfer in the Scattering of Hyperthermal DABCO from H/Pt(111).
Surf. Sci., 261, 299-312 (1992).
9. S. Dagan, A. Danon and A. Amirav
Collision-Activated Dissociation in Hyperthermal Surface Ionization of Cholesterol.
Int. J. Mass. Spectrom. & Ion. Proc., 113, 157-165 (1992).
10. A. Penner, A. Danon, E.W. Kuipers, S. Dagan, R. Bersohn and A. Amirav
"Selective Reactions of Metal Activated Molecules-Predissociation Spectroscopy of Cadmium Dimethyl and Hyperthermal Surface Induced Dissociative Ionization".
"Stereoselective Reactions of Metal-Activated Molecules" - Symposium Book Ed. by H. Werner, A.G. Griesbeck, W. Adam, G. Bringmann and W. Kiefer, Vieweg-Braunschweig. ISBN No. 3-528-06450-1, pp 105-117 (1992).
11. A. Danon and A. Amirav
Isotope, Molecular Tail and Surface Effects on Hyperthermal Surface Induced Dissociative Ionization.
Int. J. Mass. Spectrom. & Ion. Proc. (in press).

12. S. Dagan and A. Amirav
Fast, High Temperature and Thermolabile GC-MS in Supersonic Molecular Beams.
Anal. Chem. (submitted).

Publications 11 and 12 are enclosed while 1-10 where already sent with interim reports 1-7.

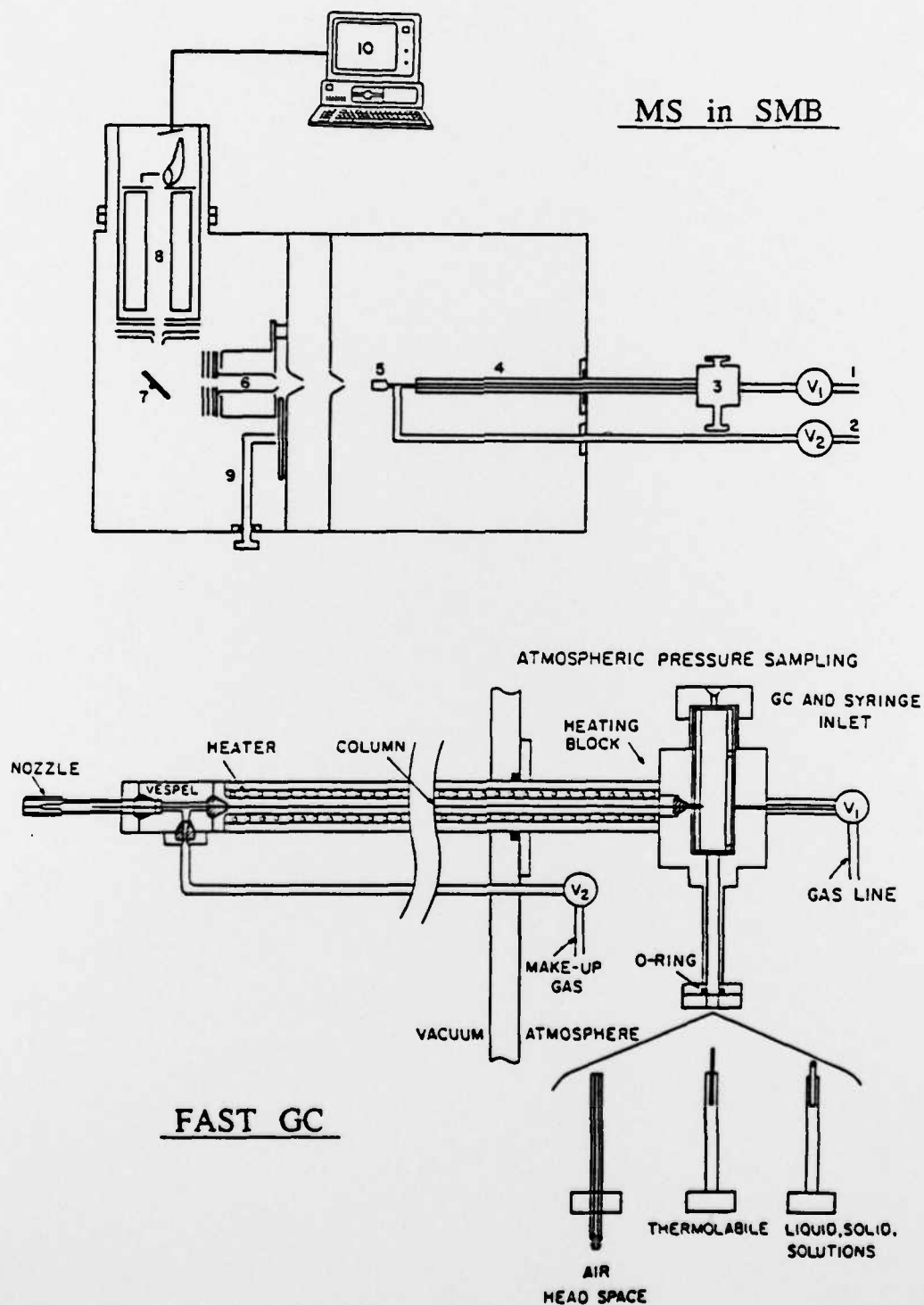


Fig.1. The Supersonic Molecular Beam-Mass Spectrometry Apparatus

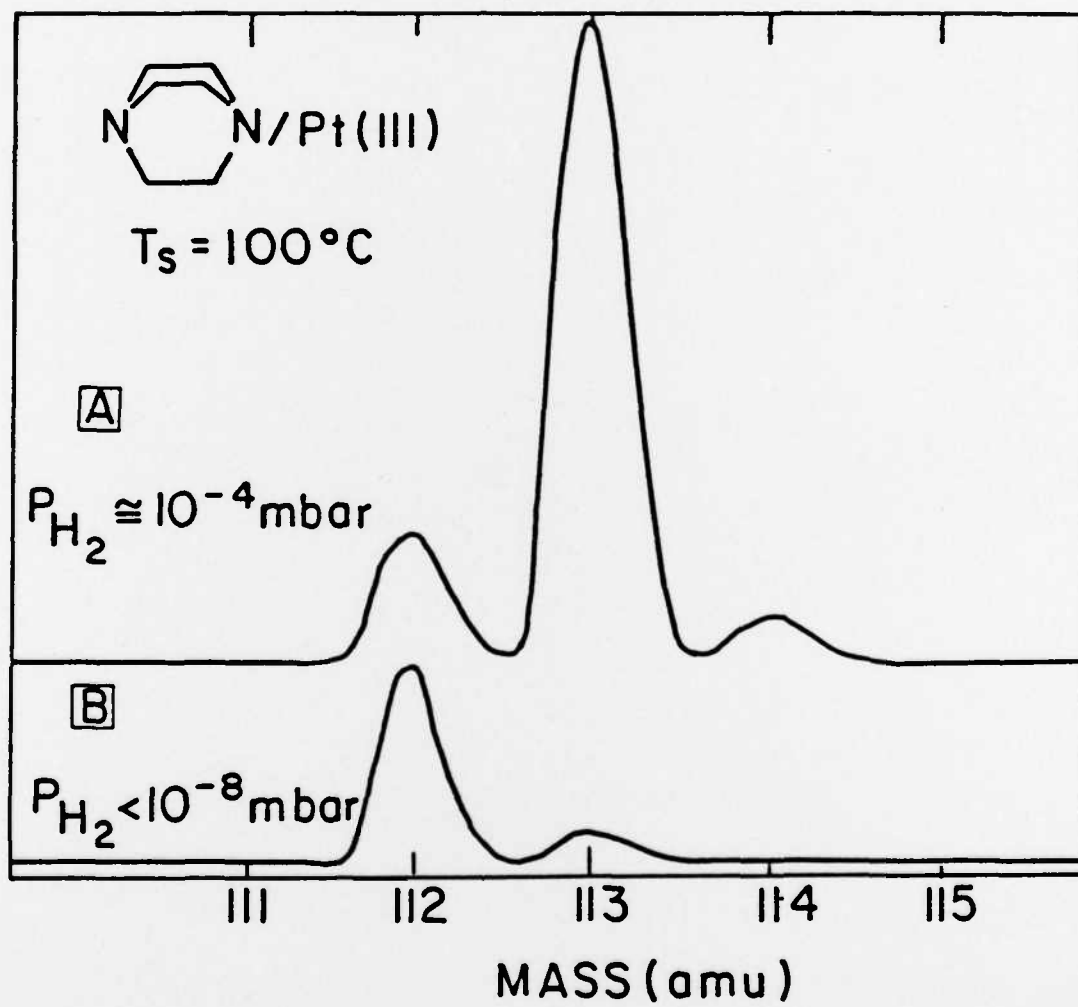


Fig.2. Surface Molecule Proton Transfer in the DABCO-Pt(III)-H System

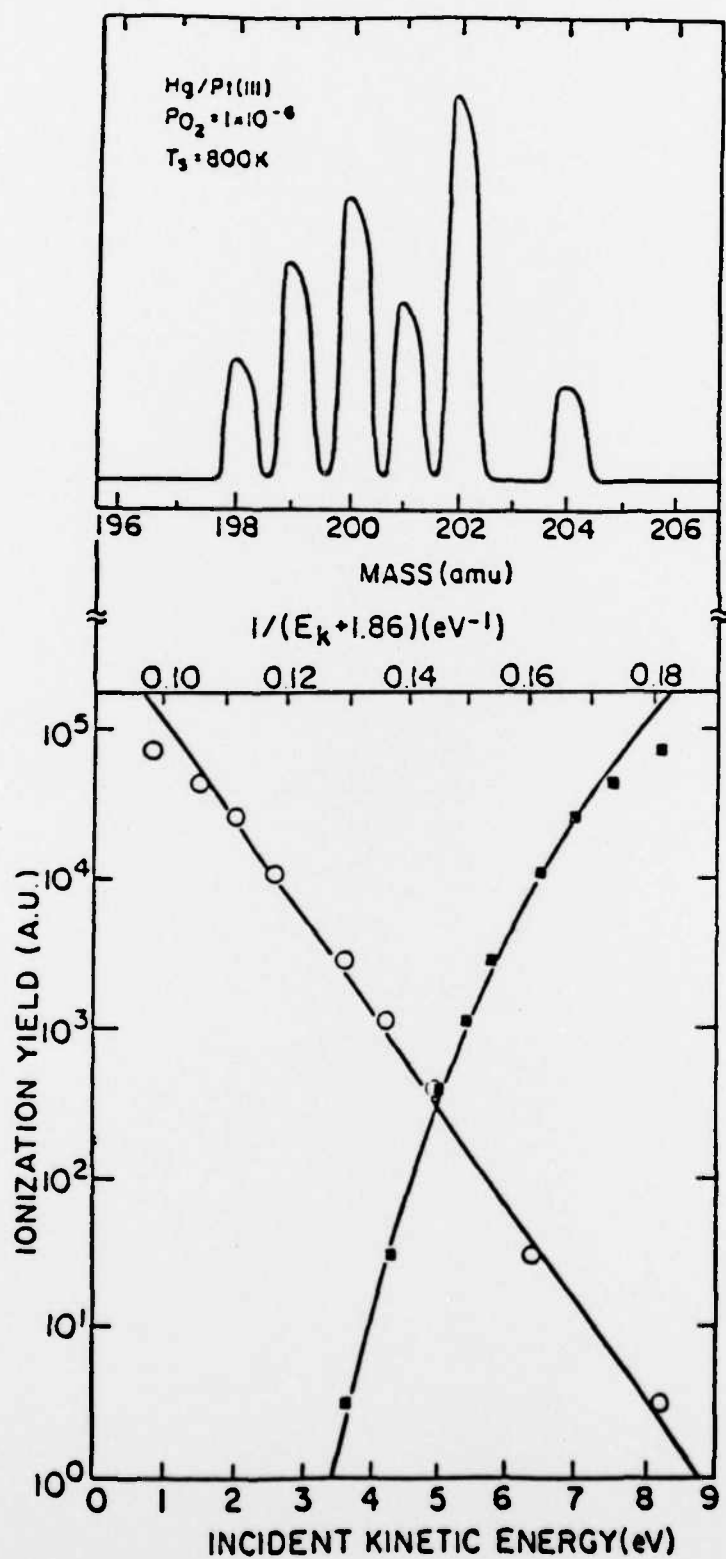


Fig.3. HSI of Mercury and its Kinetic Energy Dependence

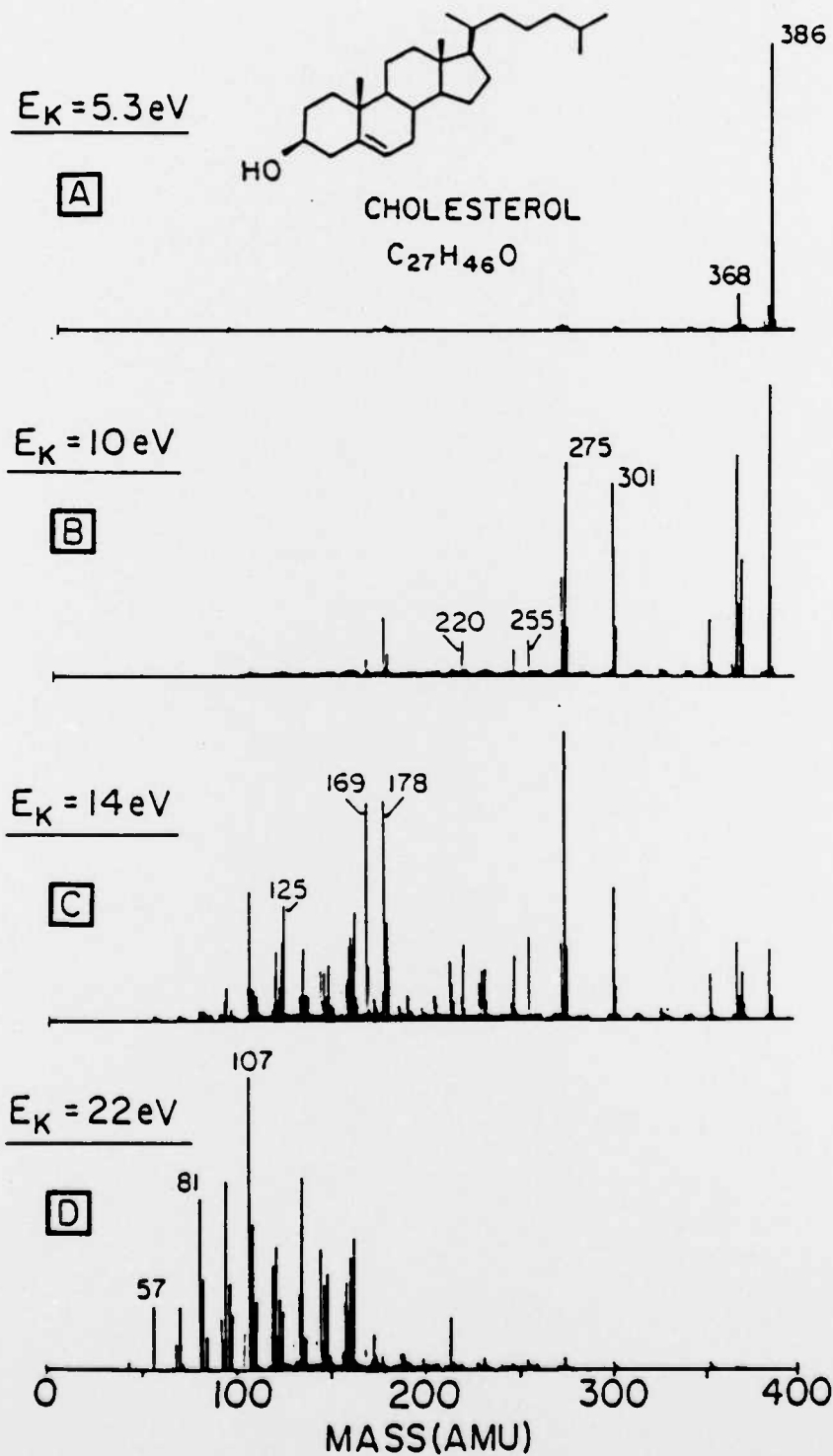


Fig.4. HSI of Cholesterol and its Kinetic Energy Dependence

FAST GC-EI-MS

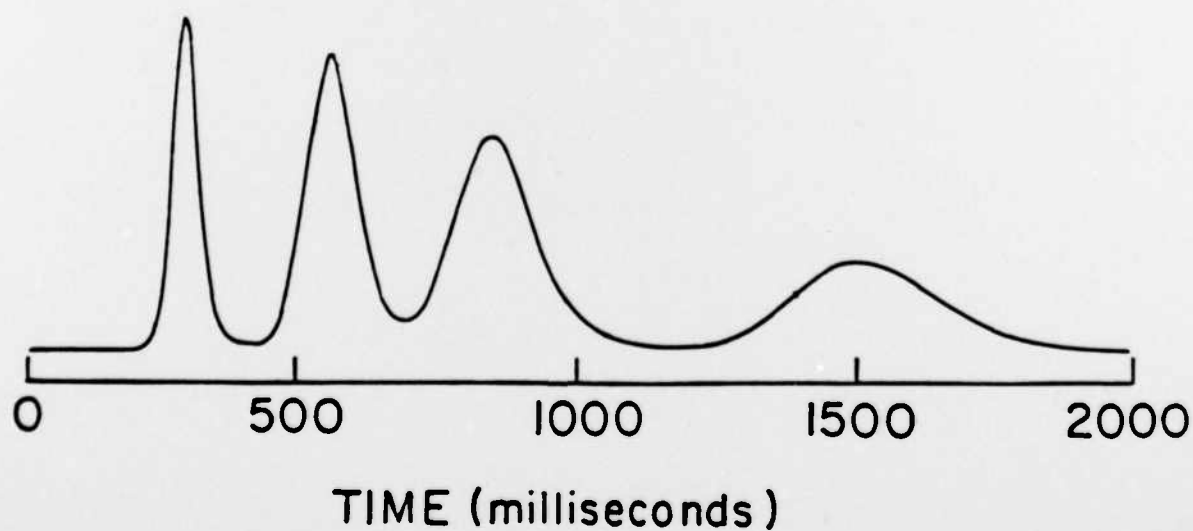
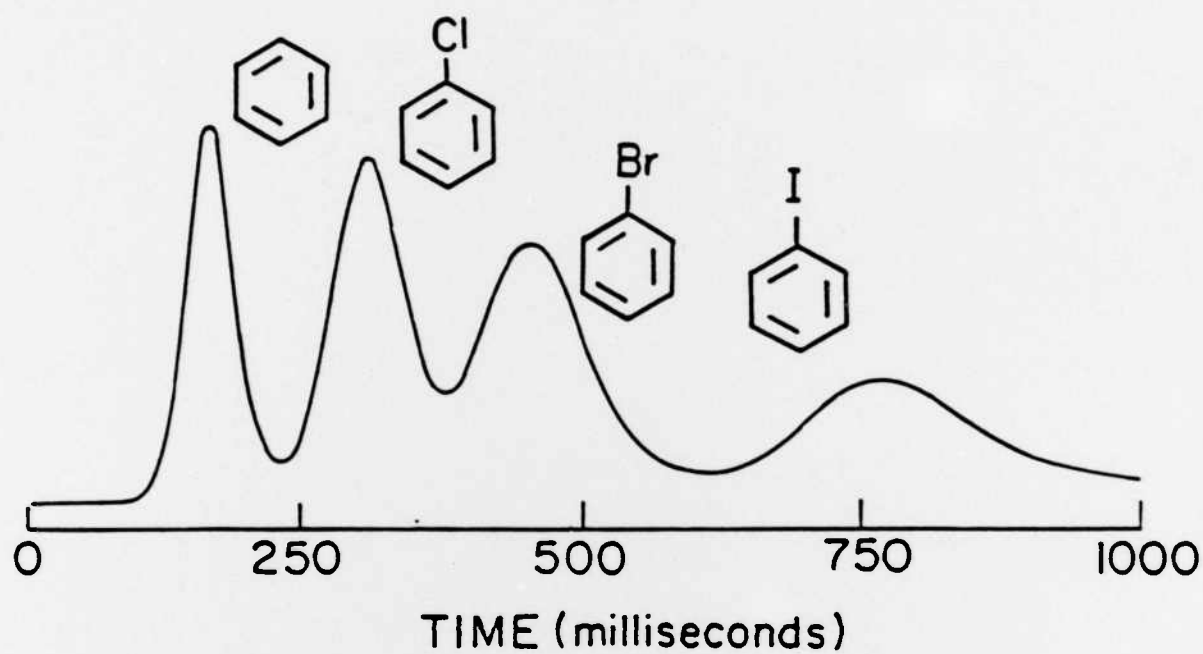


Fig.5. Ultrafast GC-MS

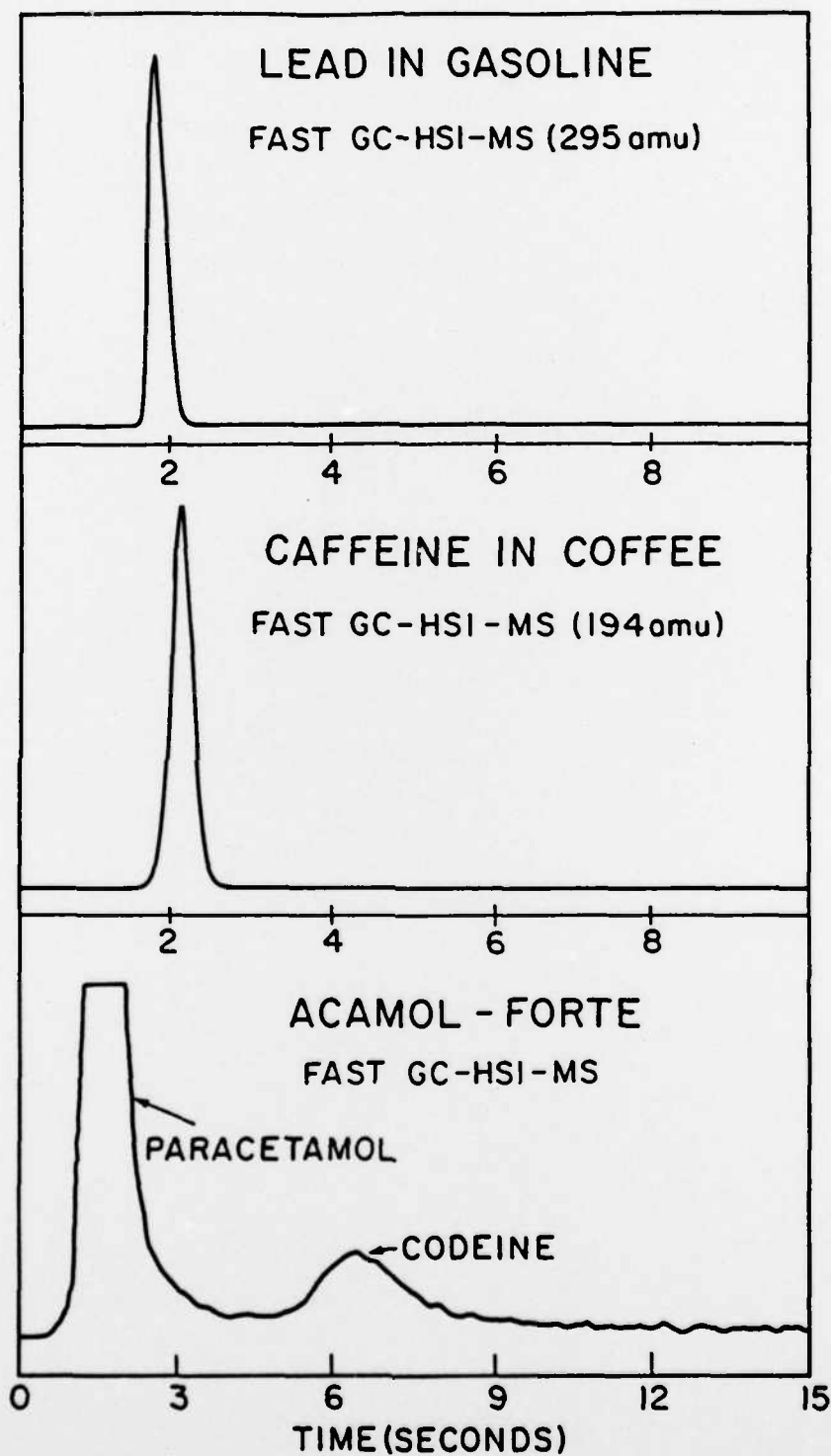


Fig.6. Target Compound Analysis in Real World Complex Mixtures with Fast GC-HSI-MS

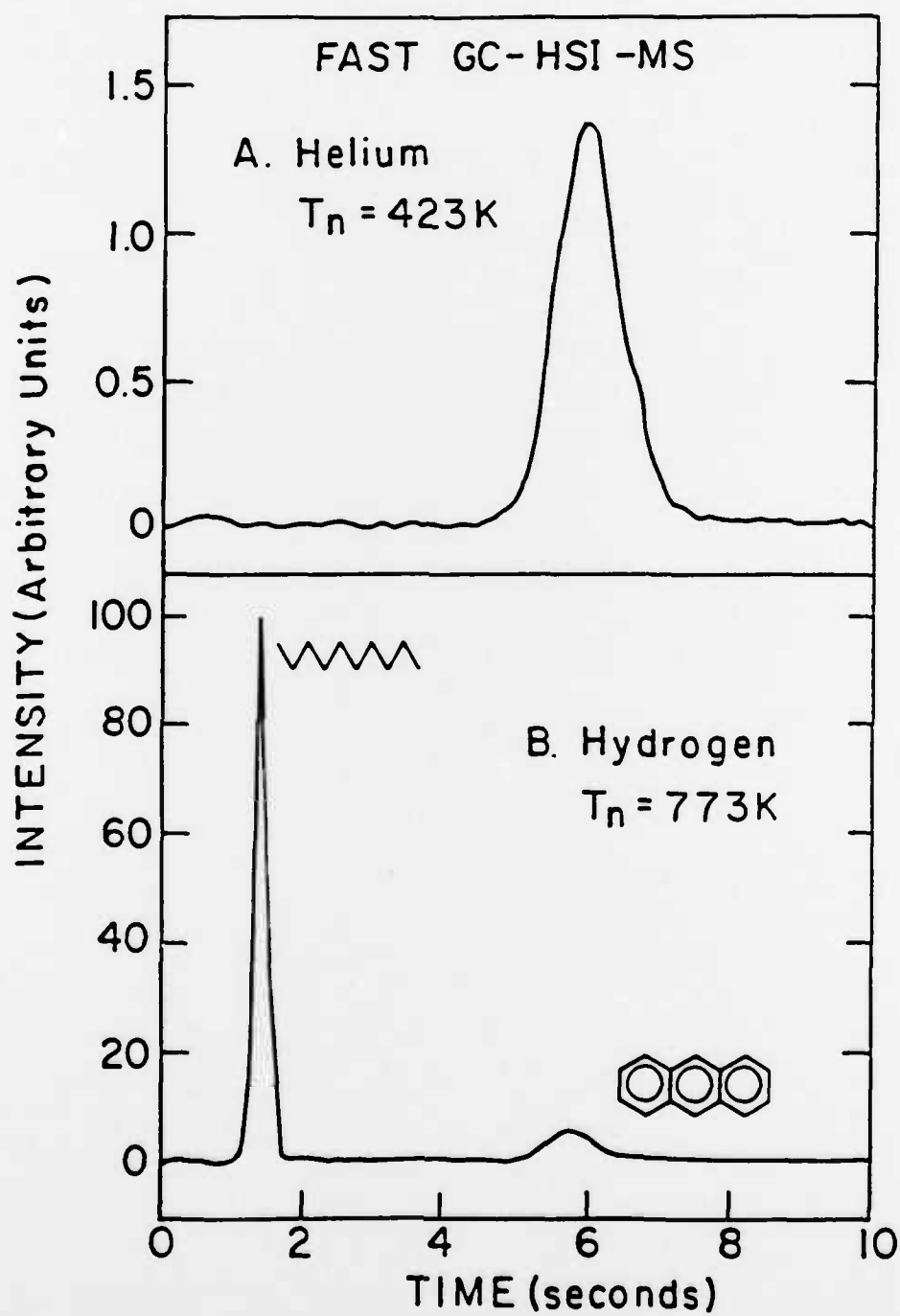


Fig.7. HSI as a Tunable Selective Ion Source

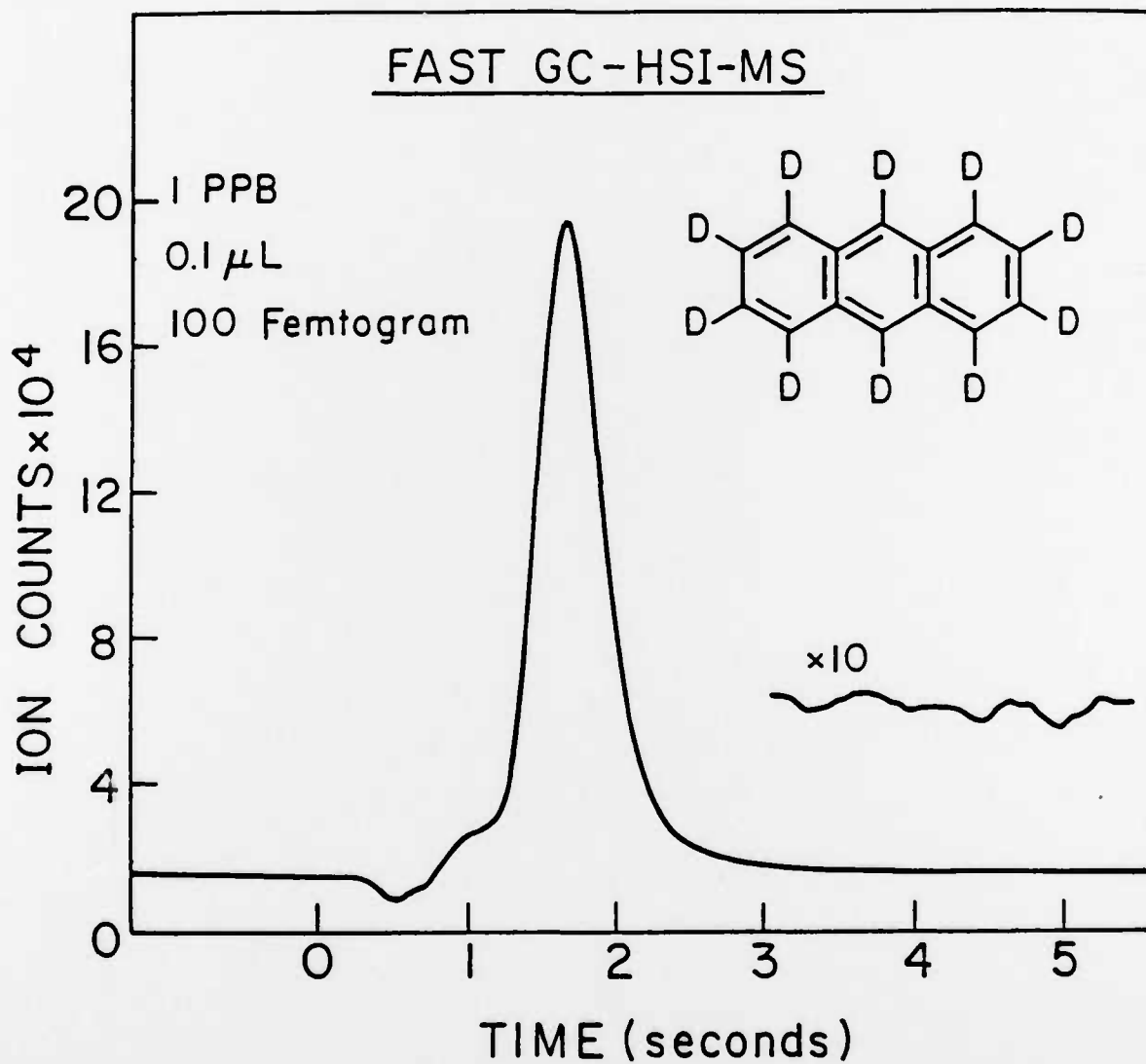


Fig.8. Attogram Range Minimum Detected Amounts with HSI

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Indeed very recently we achieved a "milestone" record of subfemtogram minimum detected amount with HSI. In figure 8 a fast GC trace of deuterated anthracene is shown. 0.1 μ L

