

先端計測装置開発のモチベーション

—計測装置の行動への影響と超伝導を使って取得できる新たなデータ—

大久保雅隆

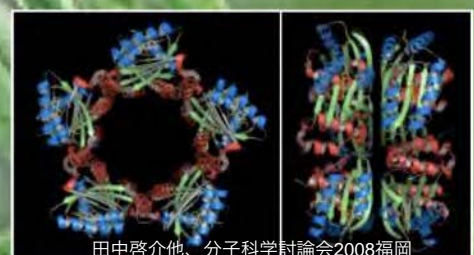
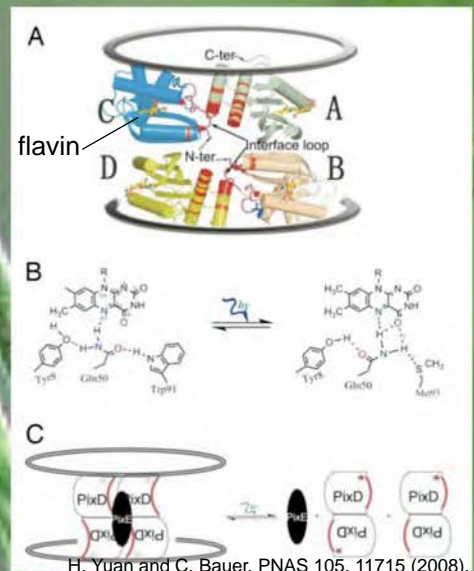
産業技術総合研究所 つくばイノベーション推進本部/ナノエレクトロニクス研究部門
上席イノベーションコーディネータ



筑波山、平沢官衛遺跡

シアノバクテリアの走光性

- | 光合成 → O₂ 20%
- | 光合成に有利な環境 → 走光性
- | 青色光受容体タンパク質
 - PixD(17.6 kDa)が環状に5量体を形成し、それが2つ重なった10量体の高分子。
 - PixE(43.7 kDa)がこのオリゴマー形成を助長。
 - 暗順応でPixD₁₀-PixE₅という395kDaの巨大な複合体を形成。
 - 光子吸収で、10量体 → PixE + PixDの2量体。
- | 光子吸収でダイナミックに変化する光受容体タンパク質を獲得したシアノバクテリアが生き残ってきた。



田中啓介他、分子科学討論会2008福岡

青色光受容体タンパク質

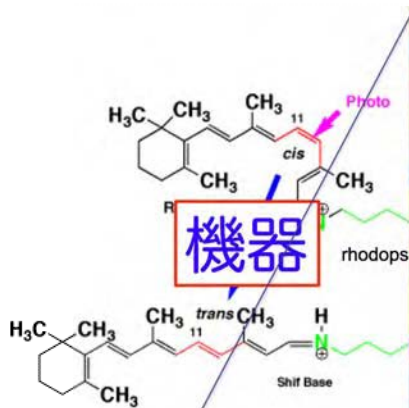
人類の視覚

- 明暗
- 色
- 立体視
- エッジ強調
- ハチ
- 季節
- 自然の息吹



計測分析技術の進化(機器, 手法, 知識)

計測技術 → 分析技術 → 課題解決
(蜂、近い) → 逃げろ!

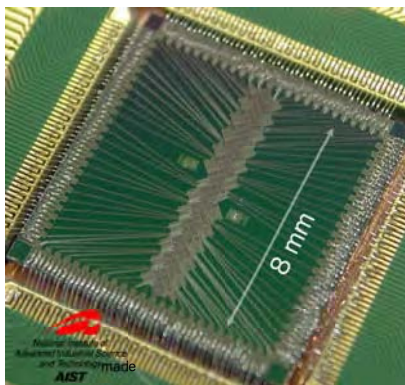
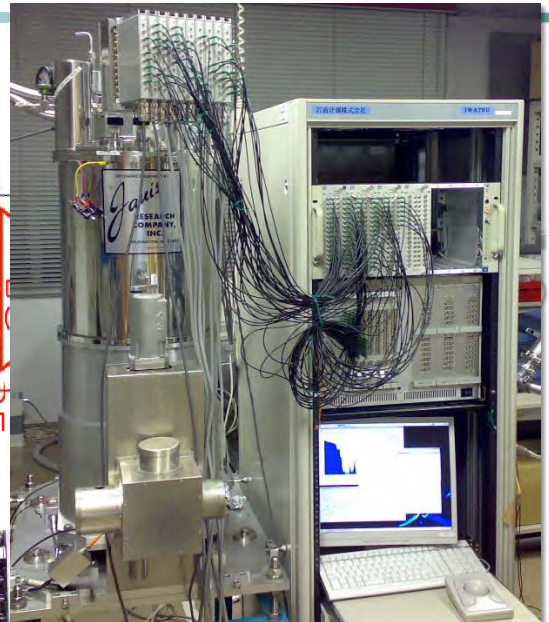
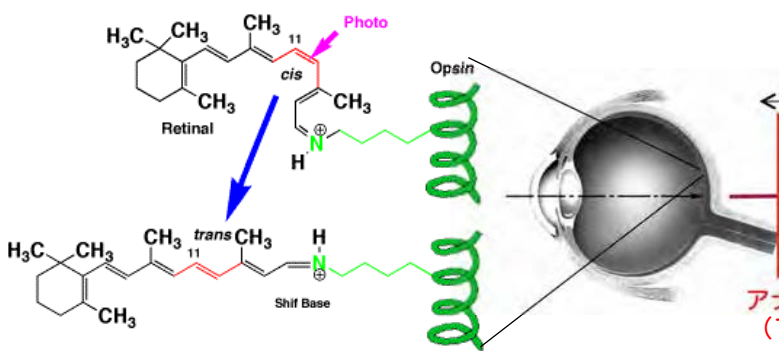


意識は我々の行動を制御していないかもしれない！

センサー感度の重要性

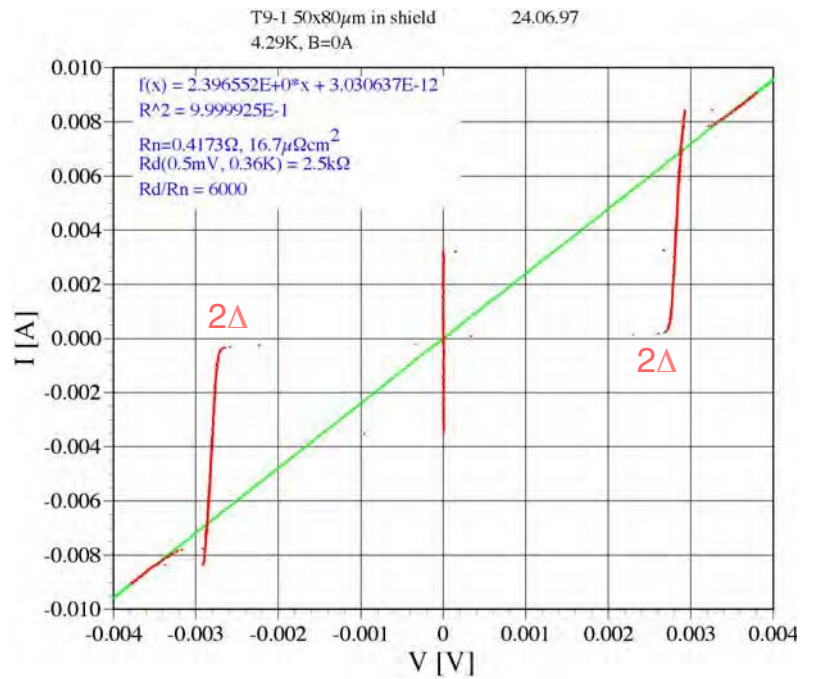
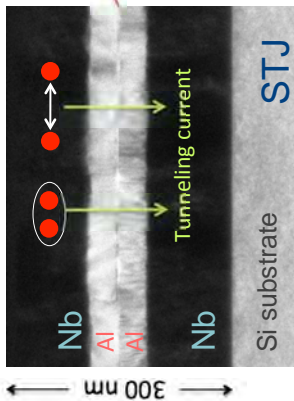
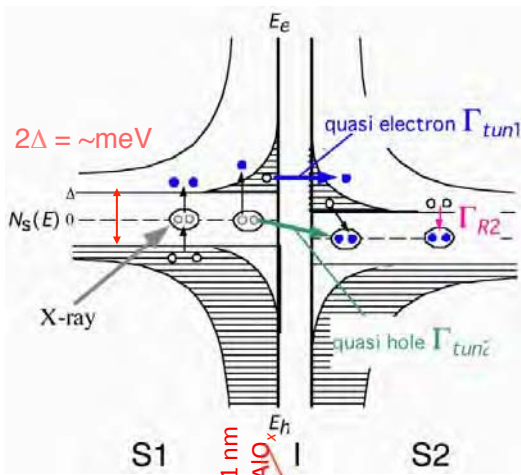


先端計測？

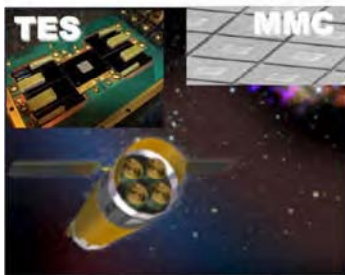


超伝導体

ジョセフソン効果 (トンネル効果) (1962)



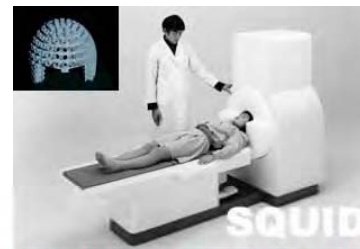
超伝導を応用した計測分析機器



X-ray satellite



Sub-mm astronomy



Magnetoencephalography (MEG)
Magnetocardiography (MCG)

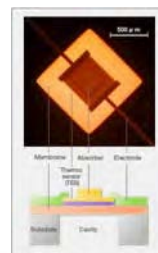


Synchrotron radiation
X-ray absorption spectroscopy



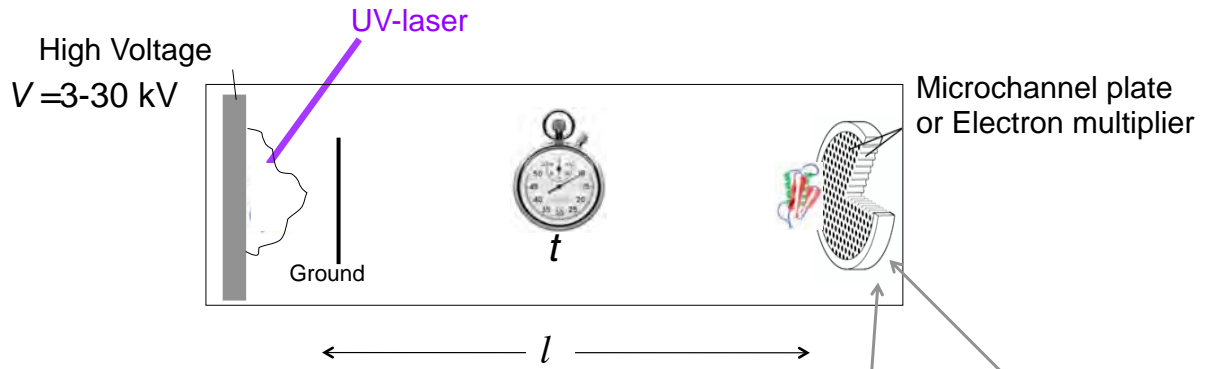
μ calorimeter
X-ray material analysis

Star http://www.starcryo.com/microcal_ed.s.htm
SII <http://www.sii.co.jp/info/eg/mems4.html>



Metal contamination test
AFD <http://www.aftweb.co.jp/index.html>

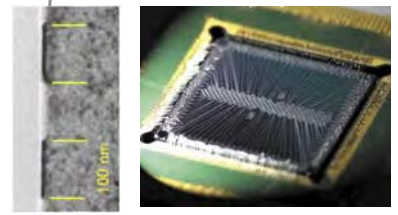
質量分析装置(TOF-MS)



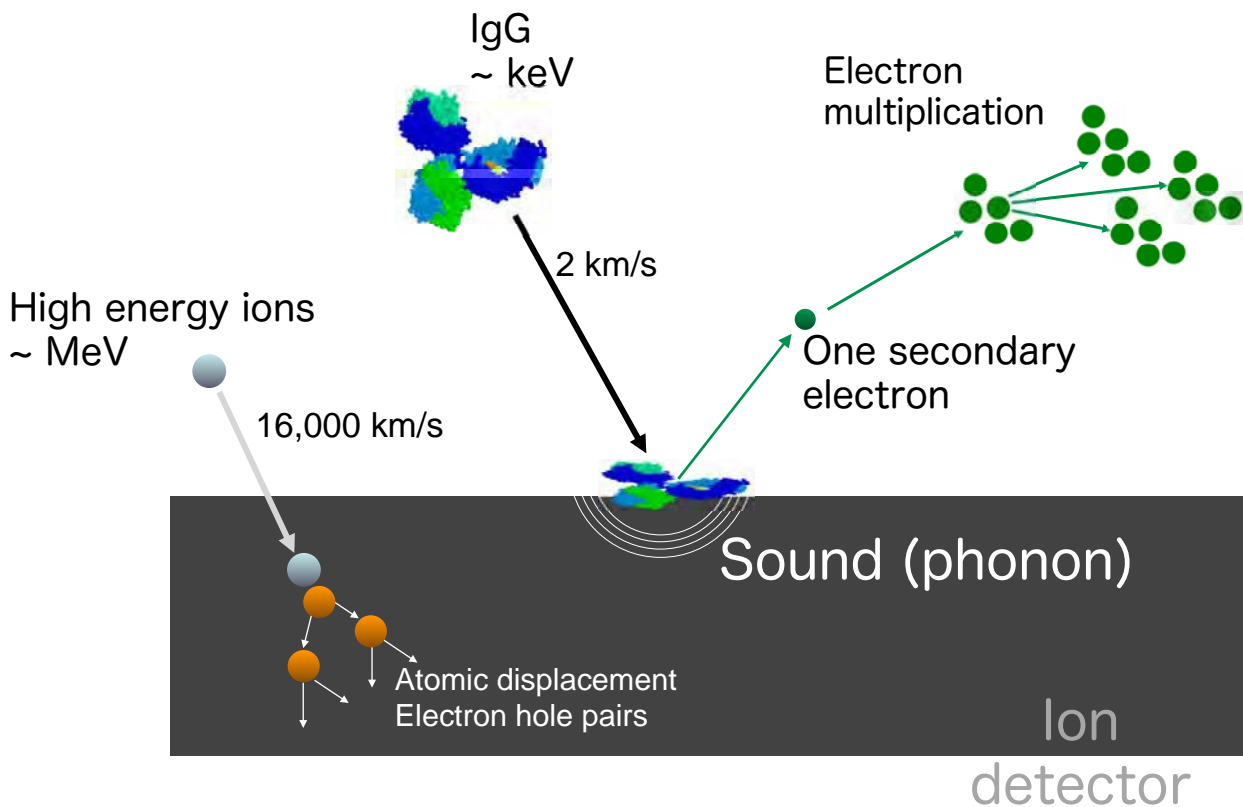
$$t = l/v = l \left(\frac{m}{2zeV} \right)^{1/2} = 71.987e^{-6} l \left(\frac{MW}{zV} \right)^{1/2}$$

$$\frac{m}{\Delta m} = \frac{t}{2\Delta t} \quad m : \text{mass}, z : \text{charge number}$$

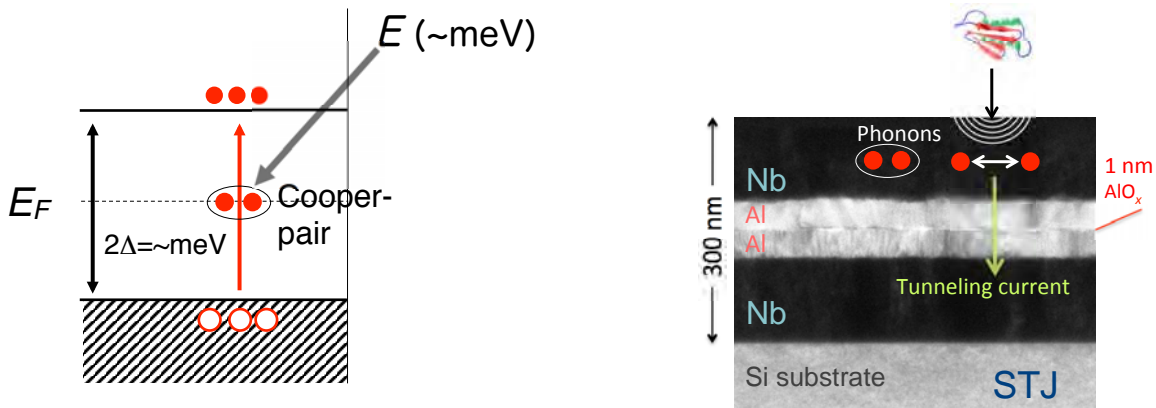
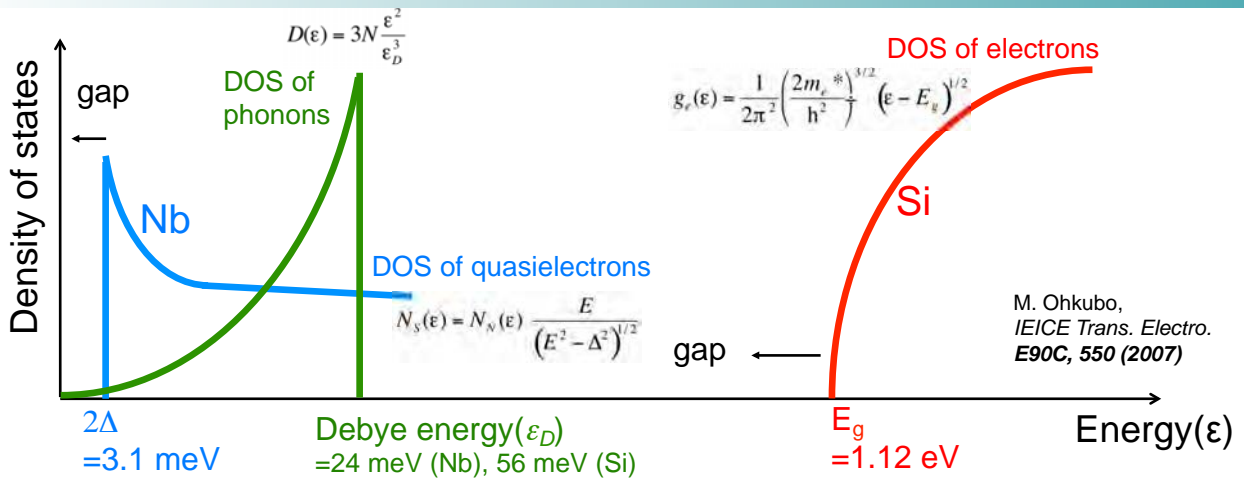
1 ns for $m/\Delta m = 10,000$ (a peptide, Angiotensin I)



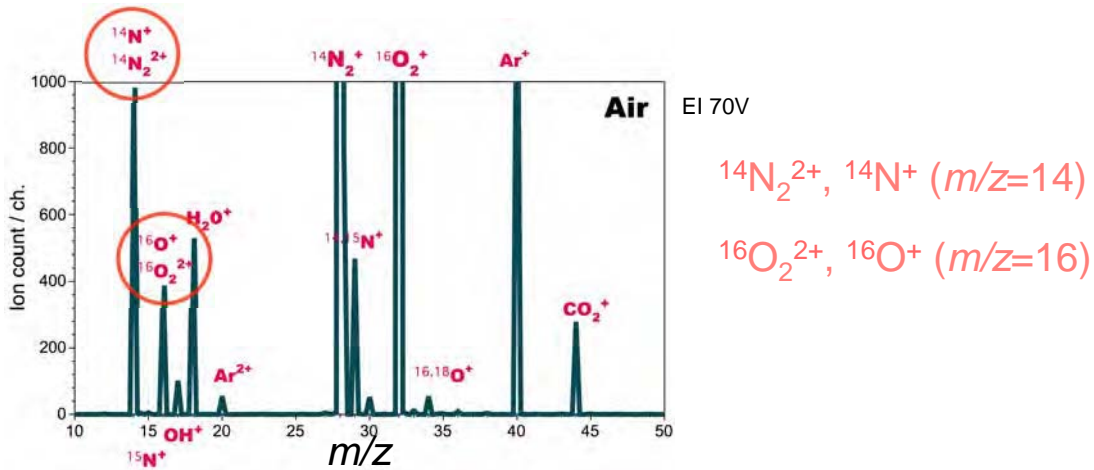
粒子の検出方法



超伝導体と半導体の比較



質量分析の2つの限界



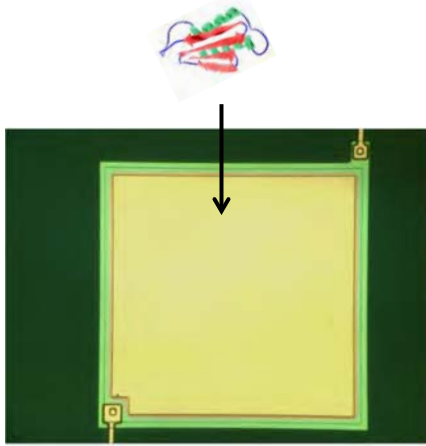
MS is a method to measure mass/charge (m/z) ratios of ions.
(Unified atomic mass / charge number)

- 1st limitation: z is always speculative. m/z spectrometry?
- 2nd limitation: Neutral atoms or molecules cannot be analyze.

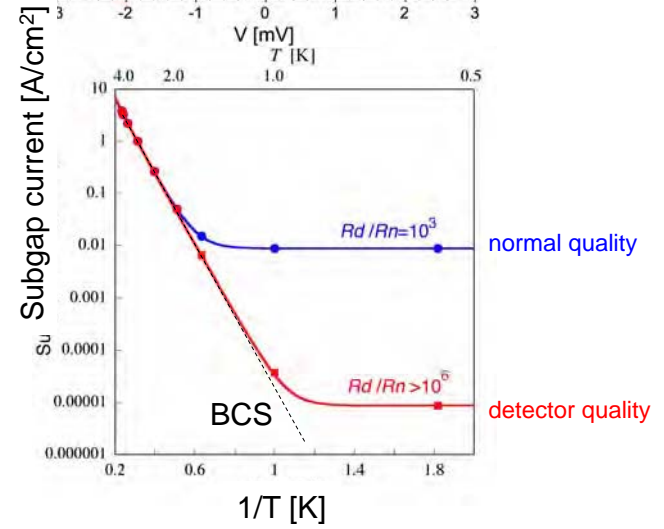
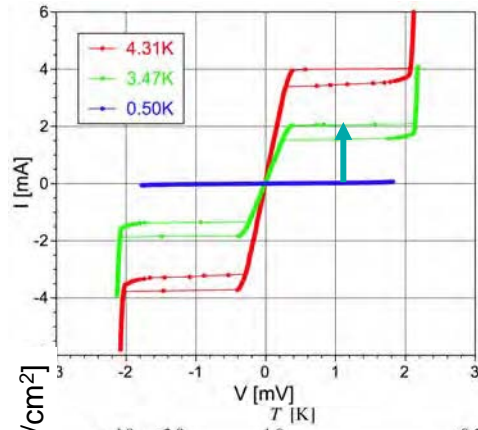
m/z overlap and neutral loss

準粒子トンネリング

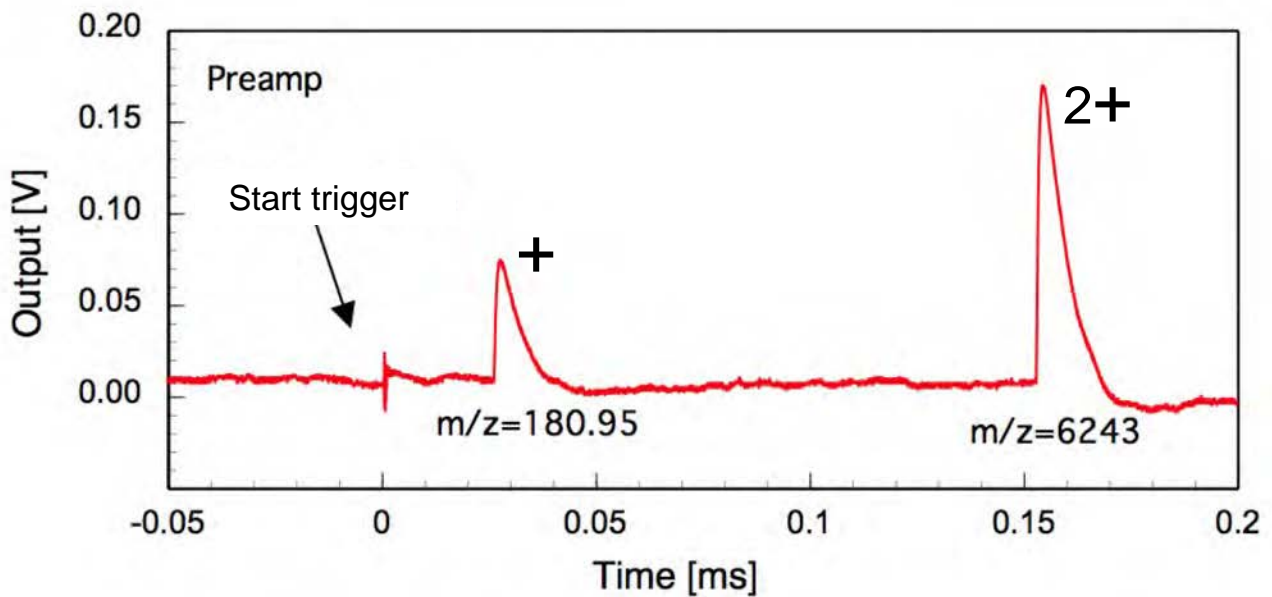
STJ detector physics



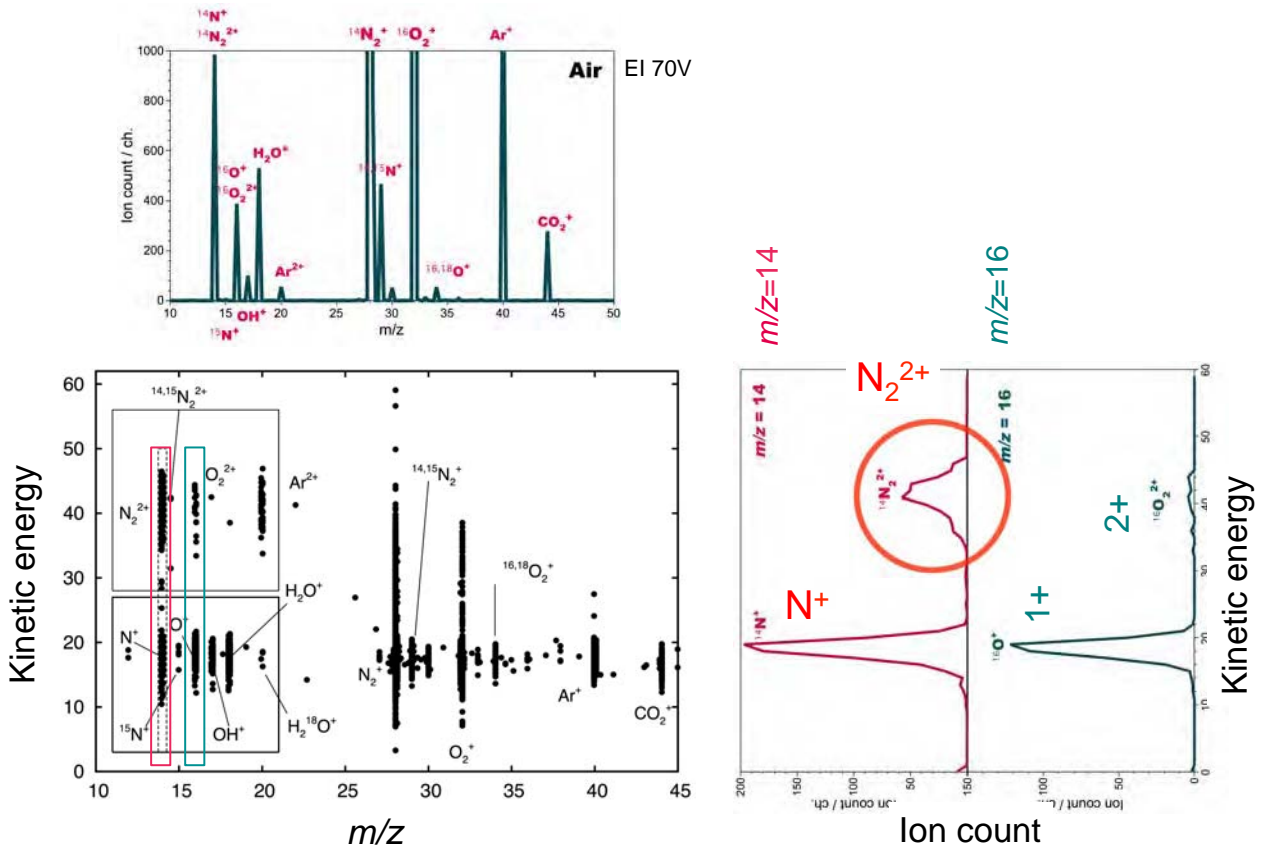
- Uncovered Nb electrode
- Large junction (100 - 200 μm)
- Extremely low leakage current



m/z と運動エネルギー測定

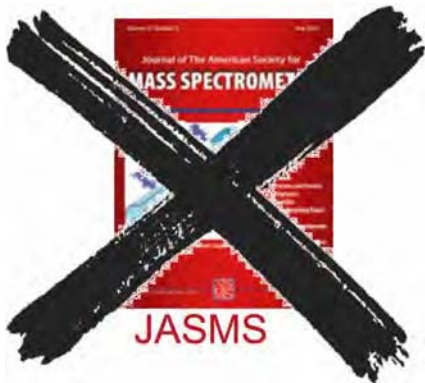


m/z - 運動エネルギープロット



S. Shiki, et al., *J. Mass Spectrom.* **43**, 1686 (2008).

等核2原子分子の2価イオン分離成功への反応



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Kinetic-energy-sensitive MS distinguishes different ions with the same m/z

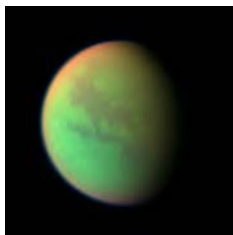
Instrument can measure doubly charged monoisotopic diatomic molecules without using heteroisotopic molecules.

Christine Piggee
Publication Date (Web): November 13, 2008

Because the details are still under debate, the ionization and dissociation processes of diatomic molecules are of great interest to researchers in areas such as astrophysics, plasma physics, and atmospheric science. The ionization cross section has been difficult to measure for these diatomics because the doubly charged diatomic ions such as $^{14}\text{N}_2^{2+}$ could not be separated from the singly charged monoatomic ions such as $^{14}\text{N}^+$. Now, Masataka Ohkubo and colleagues at the National Institute of Advanced Industrial Science and Technology, the University of Tsukuba, and Osaka Prefecture University (all in Japan) have constructed a kinetic-energy-sensitive (KE-sensitive) mass spectrometer that, for the first time, could separate homonuclear diatomic ions (e.g., $^{14}\text{N}_2^{2+}$ and $^{16}\text{O}_2^{2+}$) from monatomic ions with the same m/z values (e.g., $^{14}\text{N}^+$ and $^{16}\text{O}^+$).

S. Shiki, et al., *J. Mass Spectrom.* **43**, 1686 (2008).

惑星からの大気放出



Evolution of planets relates to chemical processes in Earth, Mars, Venus, Titan, and Io

R. Thissen, *et al.*, PCCP 13, 18264 (2011).

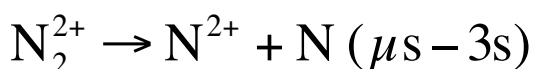
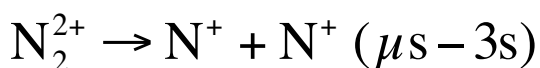
KER in dissociation processes of doubly-charged ions may produce ions with energies over escape threshold values.

Table 13 Typical escape energy (eV) for the C⁺, N⁺ and O⁺ ions in the atmosphere of Venus, Earth, Mars and Titan, at the exobase

Ion/planet	Venus	Earth	Mars	Titan
C ⁺	6.4	7.4	1.5	0.28
N ⁺	7.5	8.6	1.8	0.32
O ⁺	8.6	9.8	2.0	0.37

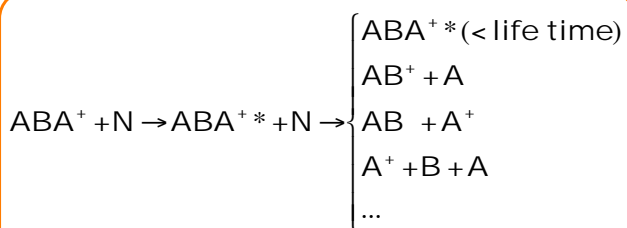
Phys. Chem. Chem. Phys., 2011, 13, 18264–18287 | 18281

ionization energies

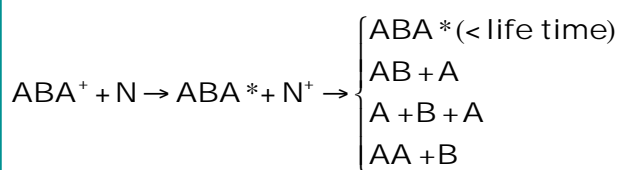


There is no report for N₂²⁺ detection in ionospheres.

生命の起源としての星間有機分子



Collisionally Activated Dissociation (CAD)



Electron Transfer Dissociation (ETD)

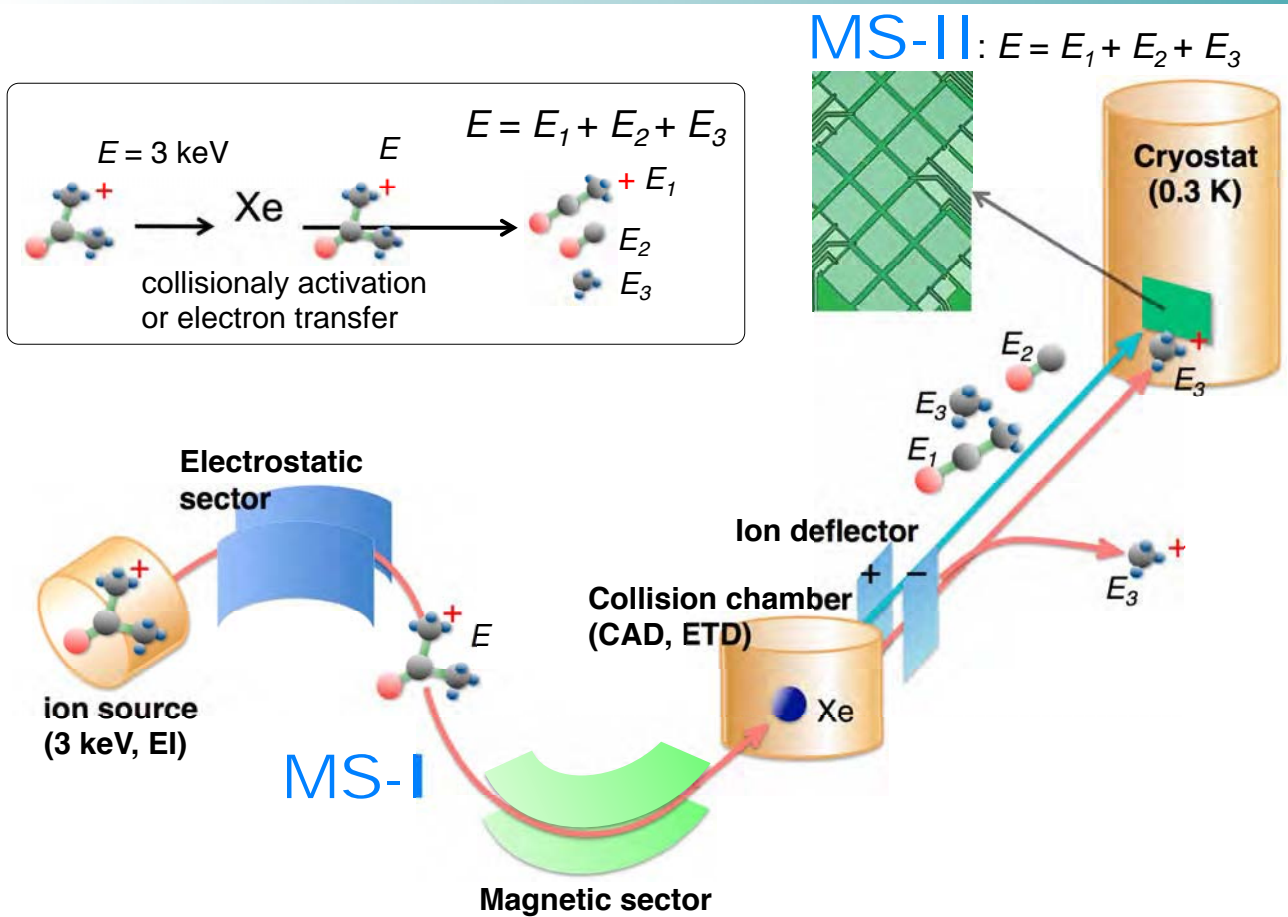
- Neutral fragments are lost, which is called “**neutral loss**.”

Distinctive prebiotic molecules were found in the Sagittarius B2 at the center of our Milky Way.

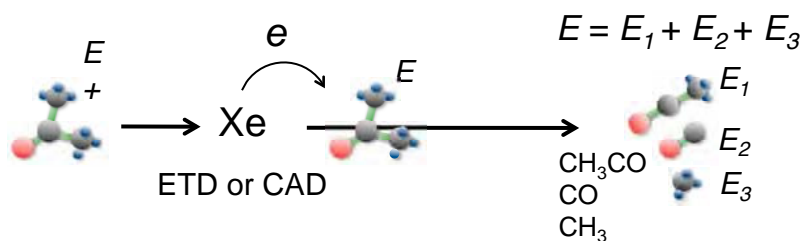
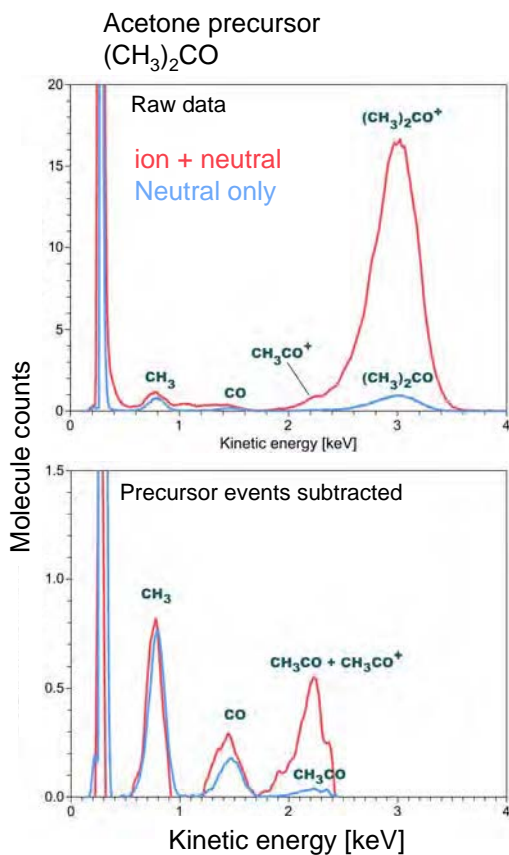


acetic acid, CH₃COOH
 formic acid, HCOOH
 acetone, CH₃COCH₃
 ethyl methyl formate, CH₃CH₂CN

Tandem MS experiment for ionic and neutral fragments



Reaction branching ratios of acetone (CH_3COCH_3)



- $(\text{CH}_3)_2\text{CO}^+ + \text{A} \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3 \cdot$ (CAD) 70%
- $(\text{CH}_3)_2\text{CO} (\text{A}) \rightarrow \text{CH}_3\text{CO} \cdot + \text{CH}_3 \cdot$ (ETD) 10%
- $(\text{CH}_3)_2\text{CO} (\text{A}) \rightarrow \text{CH}_3 \cdot + \text{CH}_3 \cdot + \text{CO}$ (ETD) 20%

まとめ

- 見るということは、ハード、手法、知識を含む。
- 我々が人工で作る機能は、我々の身体の機能を外に出したただけである！
- 科学と技術による急激な進化! 見えないものを見えるようにしましょう。
- 我々の意識は、我々の行動を制御していないかもしれない。
- 検出器の性能が我々の行動を決めている？