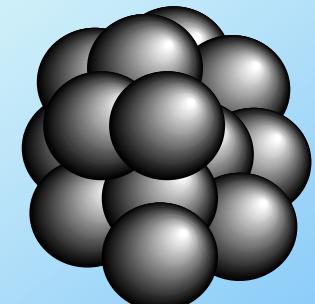
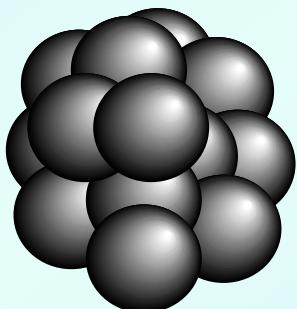


物理化学特論IV

クラスターの科学



横浜市立大学理学部 野々瀬真司

講義内容（予定）

クラスターとは？

1. 金属クラスターの電子構造1；水銀クラスター, 金属－非金属相転移
2. 金属クラスターの電子構造2；アルカリ金属クラスター, 電子殻模型と魔法数, 原子核とクラスターとの類似性と異質性
3. 分子クラスターの反応とダイナミクス； $I_2^-(CO_2)_n$, 光解離と再結合, 微視的な溶媒効果
4. 遷移金属クラスターと気体分子との反応
5. クラスターの衝突反応
6. タンパク質のフォールディング; Levinthalのパラドックス
7. 気相タンパク質イオンの立体構造の変化; イオン移動度の測定
8. 生体分子の質量分析における新技術
9. 孤立状態において生体分子を研究する; Angiotensin Iイオンと気体分子の温度変化によるプロトン移動反応

大学院教育のあるべき姿とは？

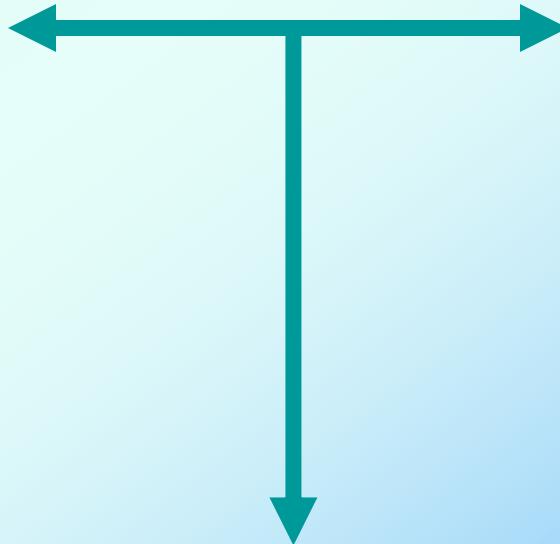
目的・方針：

従来の大学院教育は個別専門教育だけになりがち。自然科学全体を見渡す教育・総括的視点の教育が必要。それは自分野、他分野といった捉え方ではない。自分野と他分野の接点について学び、自然科学全体を見渡す総括的視点を修得することが重要。

講義の中で自分の興味を覚えた部分を掘り下げて理解を深め、将来の自分の専門に役立てよう。生物、無生物を問わず、万物は何れかの化学物質から構成されている。ゆえに、原子・分子とその集合体の構造と機能に関する知識は、必ず諸君に役立つはず。

T型人間になろう

知識・教養は広く



専門は深く



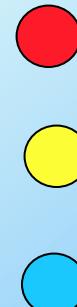
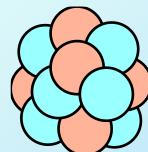
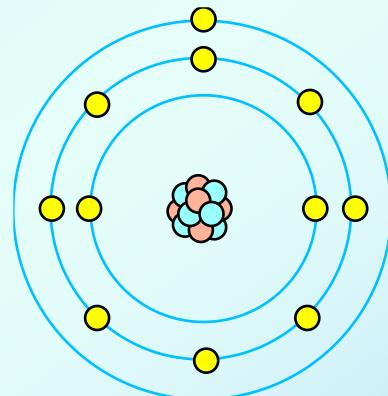
序章

世界の根源をさぐる - 究極の謎

人間
1(m) → 地球
 10^7 (m) → 太陽系
 10^{12} (m) → 銀河系
 10^{21} (m) → 宇宙の果て
 10^{26} ? (m) → ...



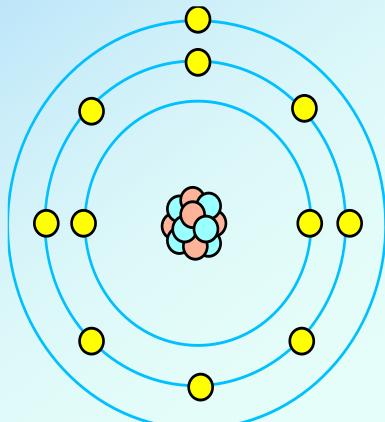
人間
1(m) → 原子
 10^{-10} (m) → 原子核
 10^{-15} (m) → 素粒子
? (m) → ...



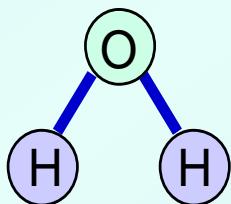
自然科学のもう一つの流れ

分析された要素を組み立て
日常世界を再構築

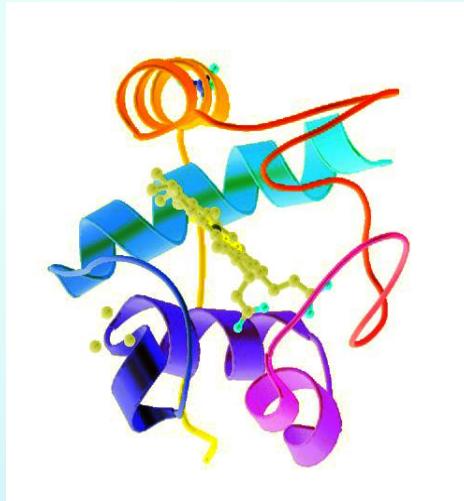
原子
 10^{-10} (m)



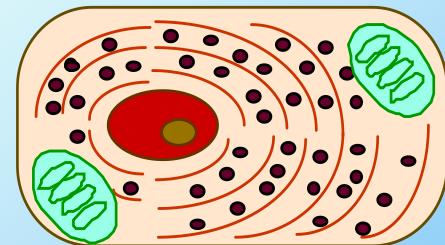
分子
 10^{-9} (m)



生体高分子
(タンパク質・DNA)
 10^{-8} (m)



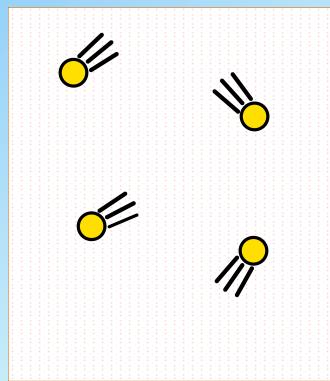
細胞
 10^{-5} (m)



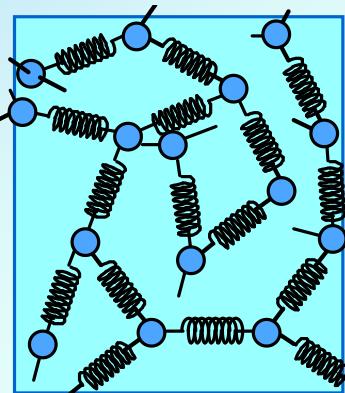
人間
1 (m)

クラスターとは・・・

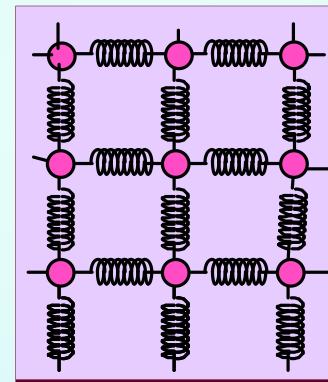
物質の3態



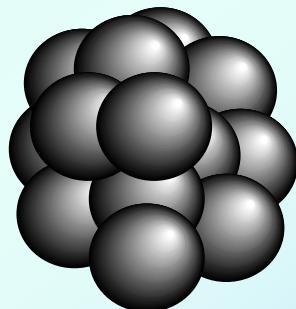
气体



液体

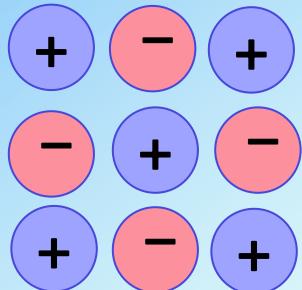


固体

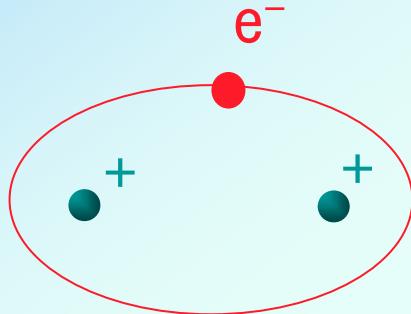


数個から数10個の原子・分子の
“集合体”(クラスター)とは
“第4”の状態

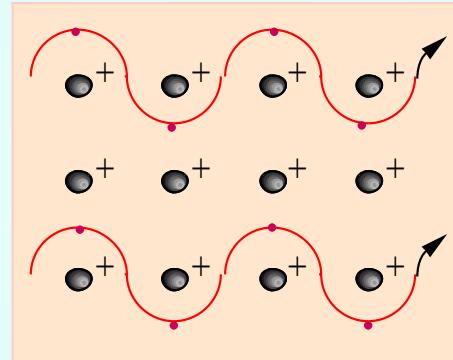
化学結合と分子間力



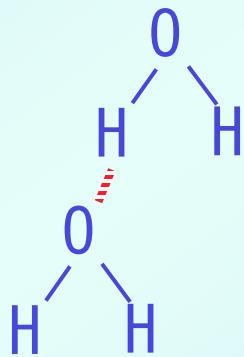
イオン結合



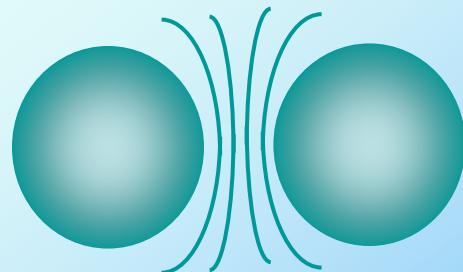
共有結合



金属結合



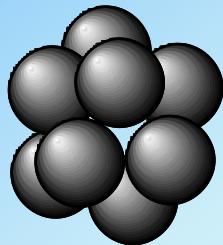
水素結合



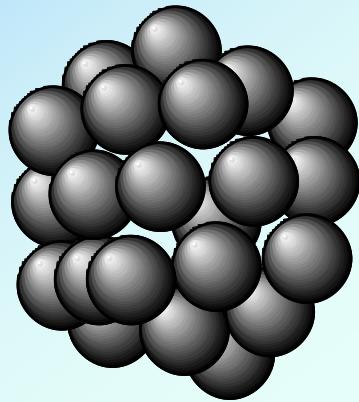
ファンデルワールス力

♣ クラスターの幾何学的な安定性

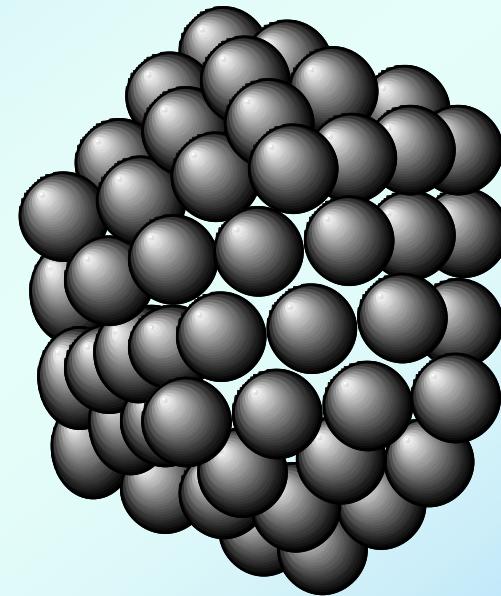
Mackayの正20面体



13個



55個



147個

Mackayの正20面体。各々 13, 55, 147, 309, 561 個の粒子から構成されている。

表面原子の占める割合

$12/13, 42/55, 92/147, 162/309, 252/561$

クラスターは表面原子の占める割合が大きい

希ガスクラスターの質量スペクトル

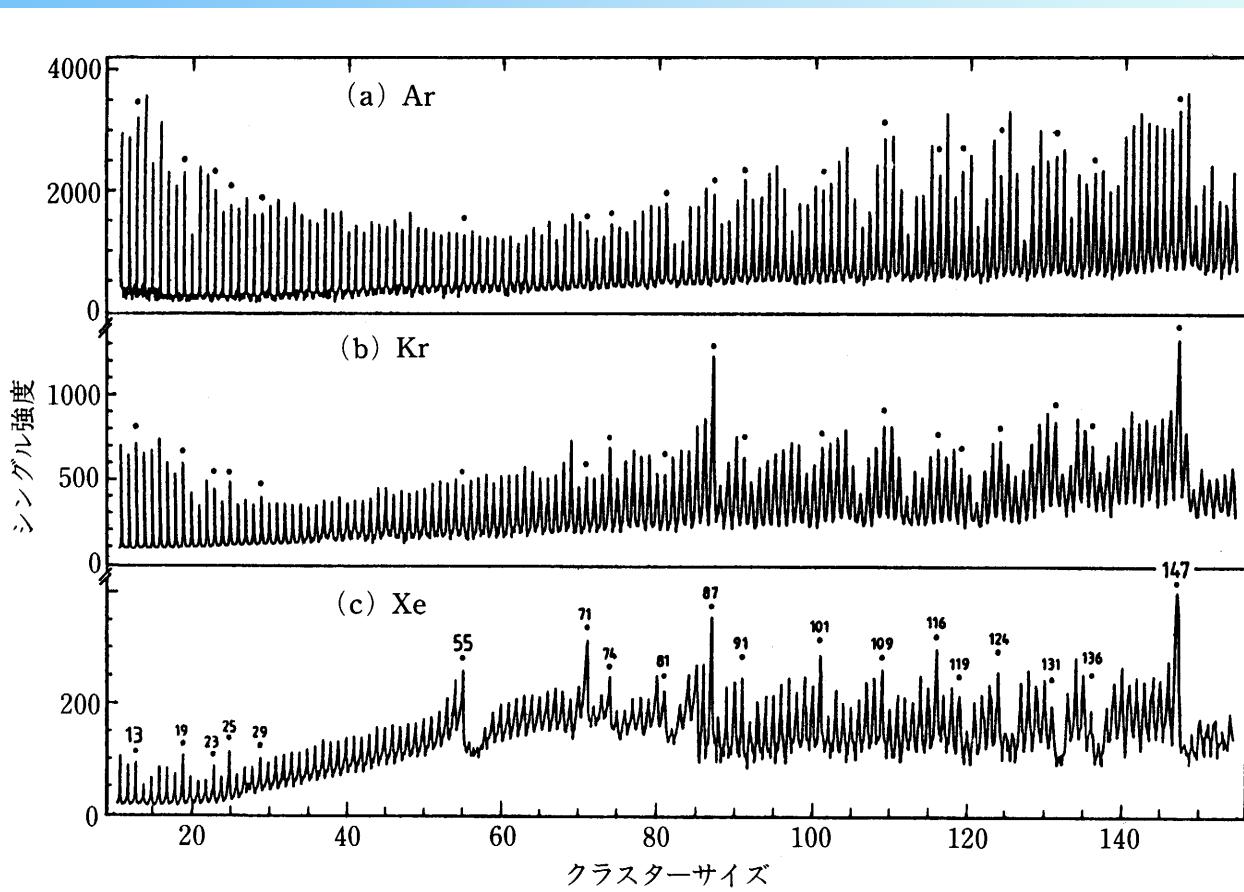


図 5・60 希ガスクラスター、 Ar_n 、 Kr_n および Xe_n の質量スペクトル(クラスター サイズ分布)¹⁰⁵⁾

1~3層正二十面体構造に対応するサイズ領域を示してある。Xeのサイズ分布上で、特に強度の大きなピークに・印がつけられており、その時のサイズ(マジック数)がアラビア数字で示されている。ArおよびKrのスペクトル上にもXeのマジック数に対応するサイズに・印がつけられている。Ar, Kr, Xeに共通なマジック数は $n=147$ であり、これは3層構造(図5・61参照)に対応している。

講義内容（予定）

クラスターとは？

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3. 分子クラスターの反応とダイナミクス； $I_2^-(CO_2)_n$, 光解離と再結合, 微視的な溶媒効果
4. 遷移金属クラスターと気体分子との反応
5. クラスターの衝突反応
6. タンパク質のフォールディング; Levinthalのパラドックス
7. 気相タンパク質イオンの立体構造の変化; イオン移動度の測定
8. 生体分子の質量分析における新技術
9. 孤立状態において生体分子を研究する; Angiotensin Iイオンと気体分子の温度変化によるプロトン移動反応

講義内容（予定）

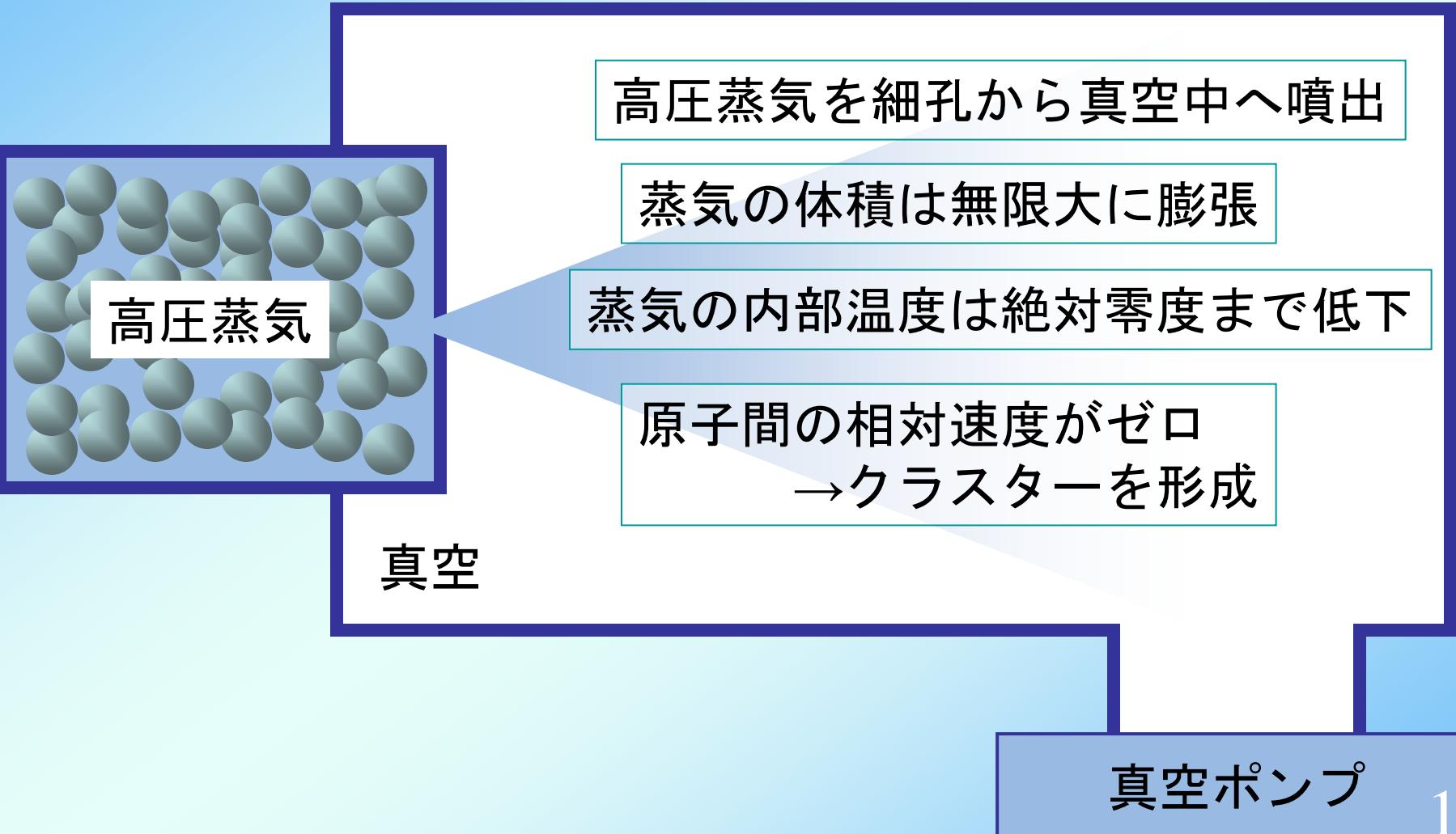
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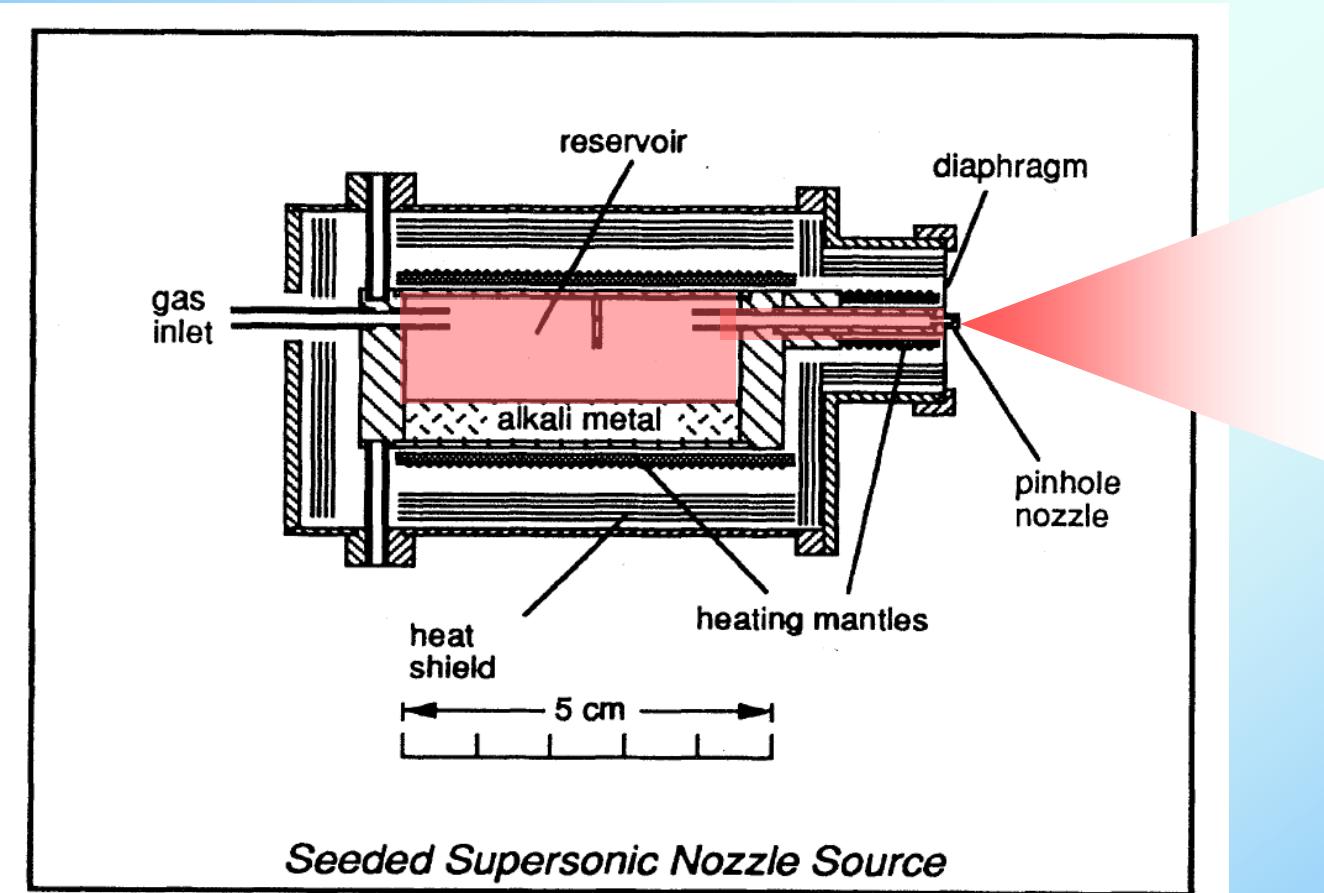


金属クラスターの生成方法

クラスターを生成させるには 断熱膨張を用いる



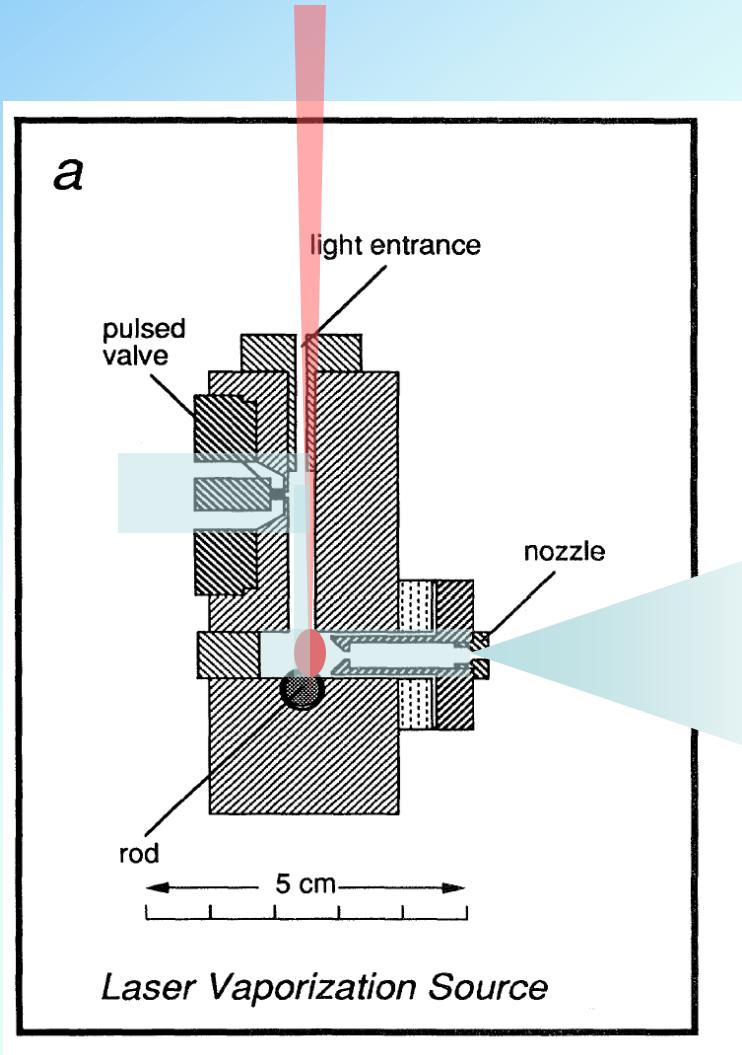
金属クラスターを生成させるには 金属を加熱気化させる



水銀、アルカリ金属ならばクラスターの生成が可能

しかし、遷移金属の沸点は1000°C以上・・・保持できる容器がない

遷移金属クラスターを生成させるには レーザーで金属を加熱気化させる

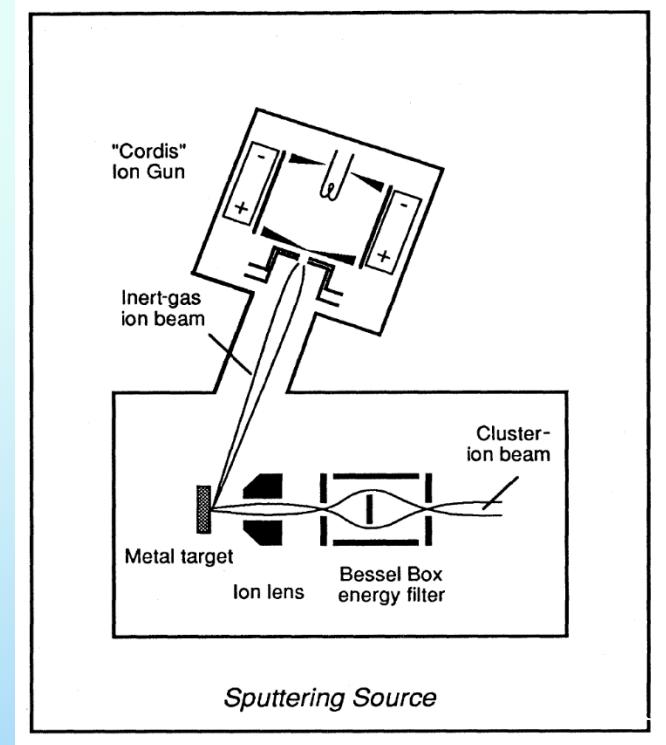
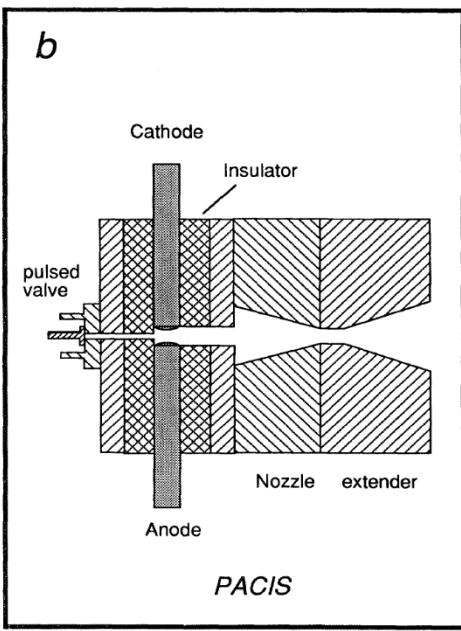
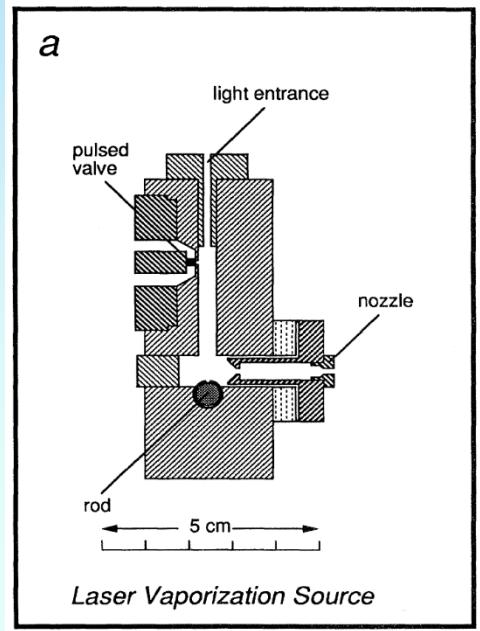
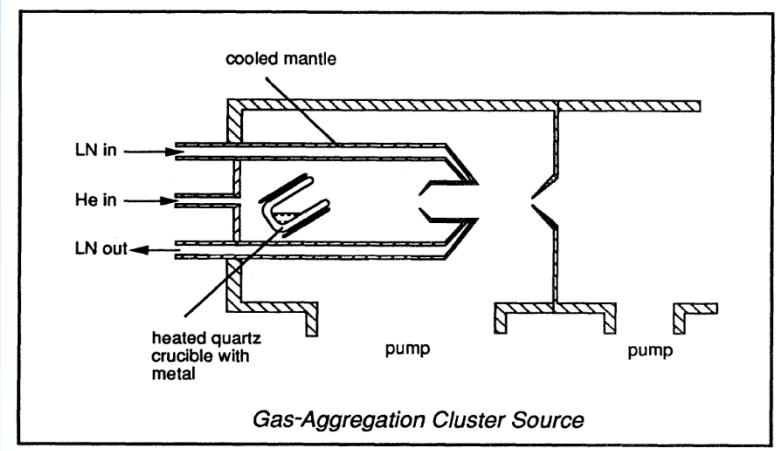
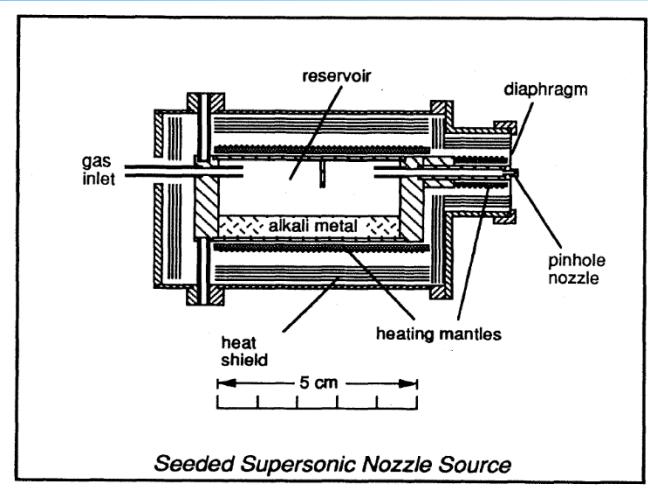


レーザーを試料金属に照射

瞬間的・局所的に超高温

金属蒸気をHeで押し流して
真空中へ噴出

金属クラスター生成装置

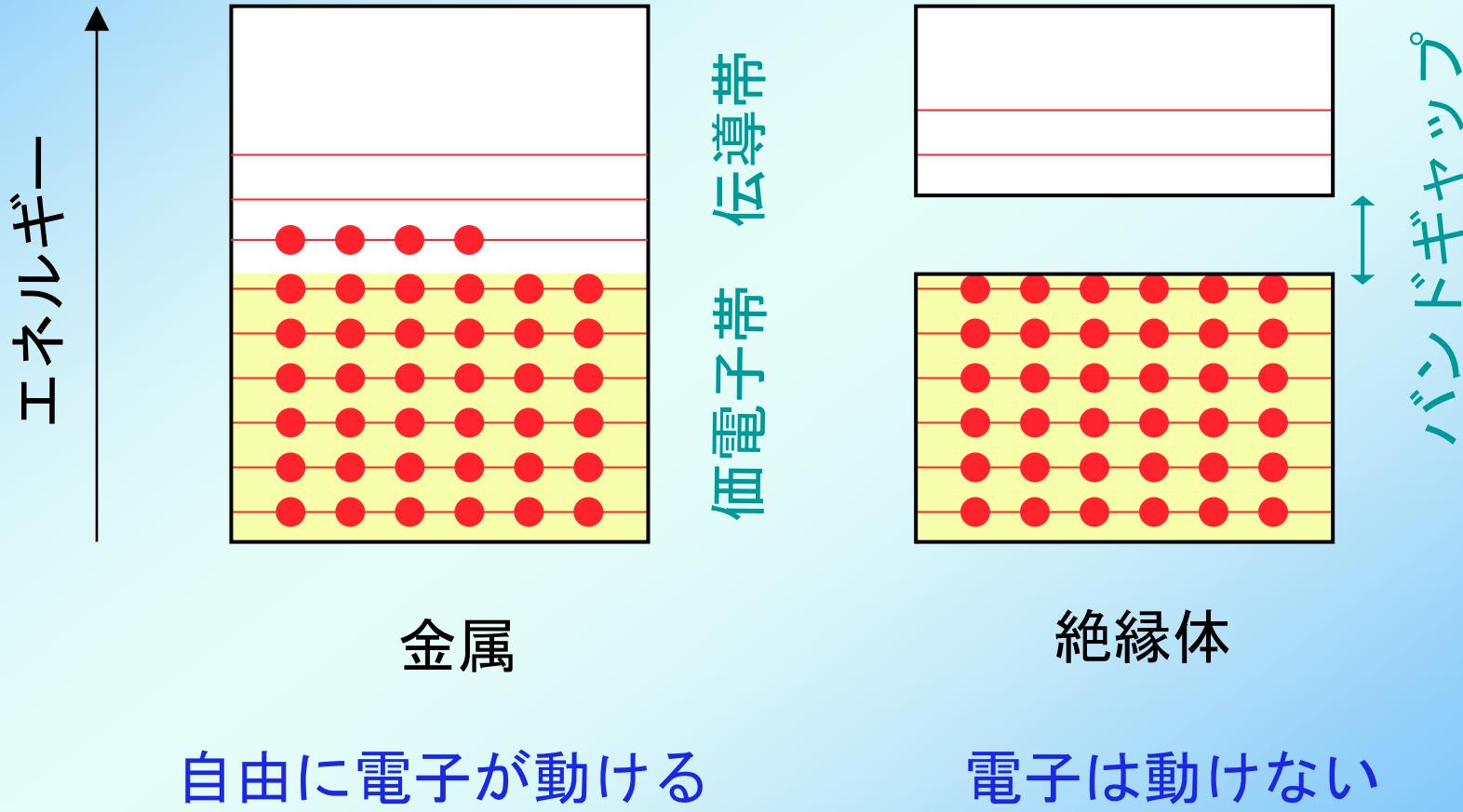




金属クラスターの電子構造

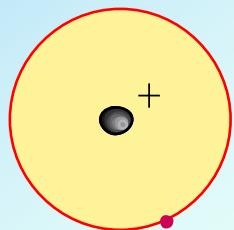
金属の性質

エネルギー・バンド



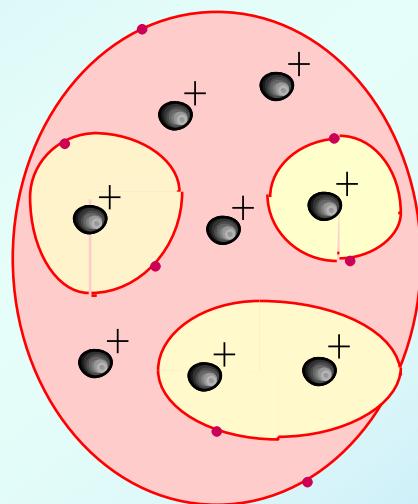
金属原子、クラスター、固体中の電子の挙動

孤立原子

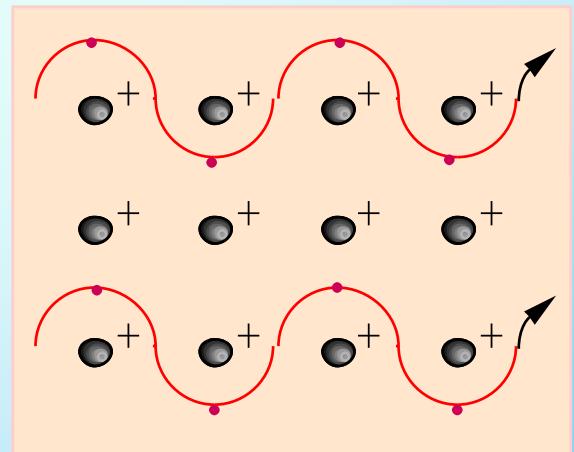


電子 e^-

クラスター

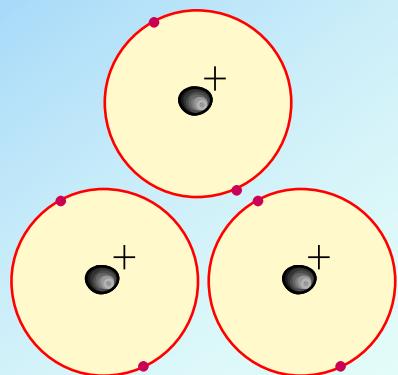


固体



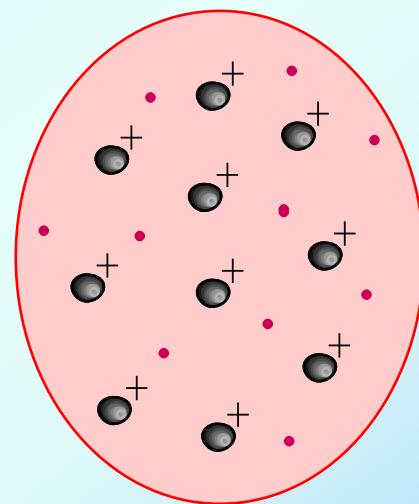
金属クラスター中の電子の結合エネルギー

小さいクラスター

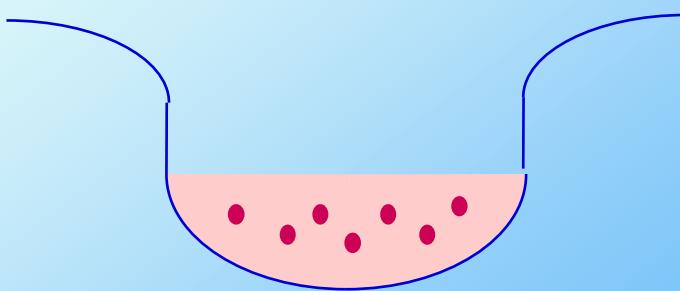
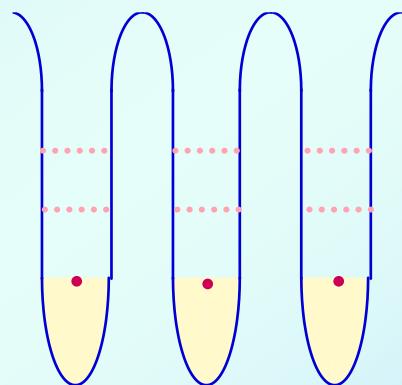


電子は個々の原子に局在

大きいクラスター



電子はクラスター全体に広がっている

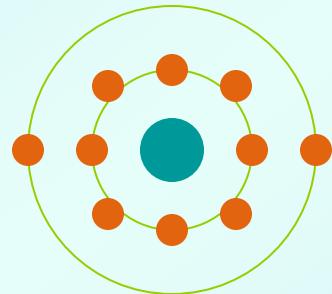


元素の周期表

1A	2A	3A	4A	5A	6A	7A	8	1B	2B	3B	4B	5B	6B	7B	0		
1 H															2 He		
2 Li	Be														10 Ne		
3 Na	Mg														18 Ar		
4 K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5 Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6 Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7 Fr	Ra	A															
		L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

- 典型金属元素
- 半金属元素
- 非金属元素
- 遷移金属元素
- 希ガス

♣ 水銀クラスターの電子構造



水銀原子 - 最外殻軌道 $(6s)^2(6p)^0$ - 準閉殻構造

水銀の液体・固体 - 價電子帯(s帯)と伝導帯(p帯)とは完全に混成

水銀2量体, Hg_2 の原子間の結合エネルギーは7kJ/mol \Rightarrow ファンデルワールス結合

水銀液体の蒸発エンタルピーは58.1kJ/mol \Rightarrow 金属結合

水銀原子が何個集合すると電子構造が非金属から金属へと転移するのか？

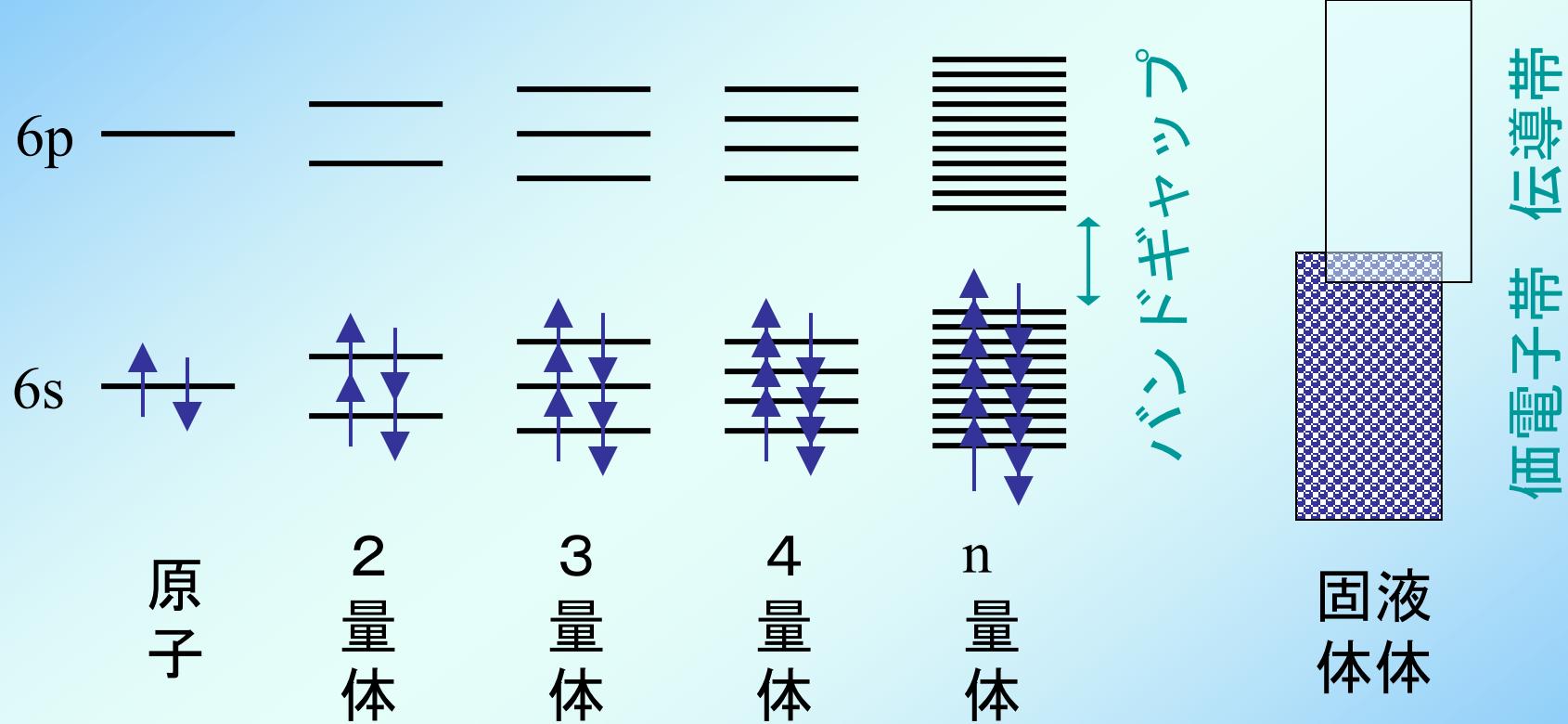
実験

水銀クラスターのイオン化エネルギー

水銀クラスター負イオンの光電子分光

\Rightarrow 價電子帯と伝導帯との間のバンドギャップの測定

水銀クラスターのエネルギーバンド

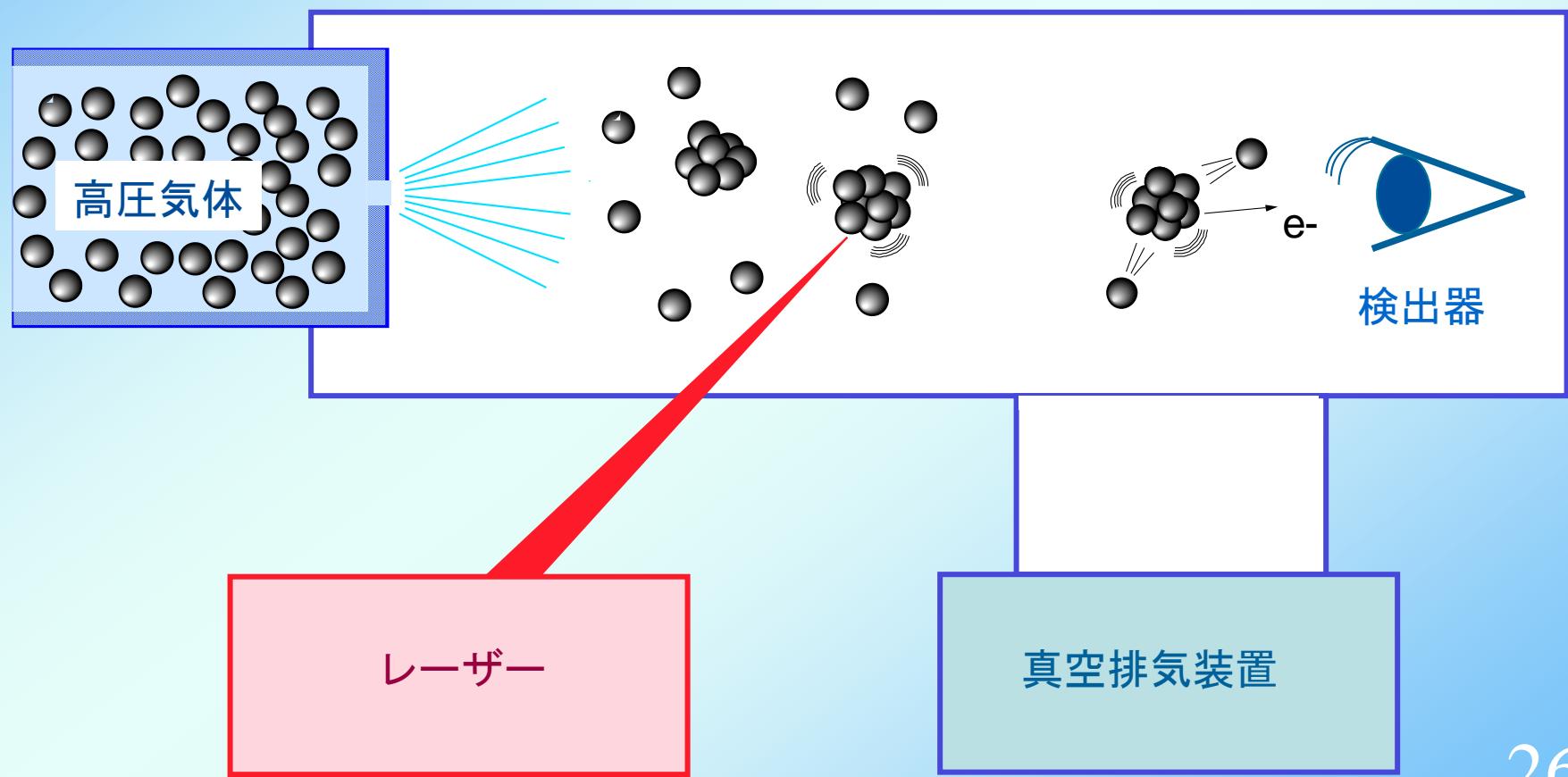


実験方法

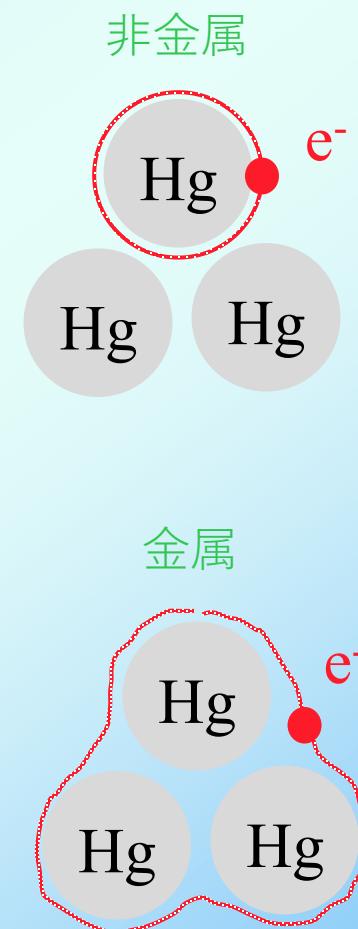
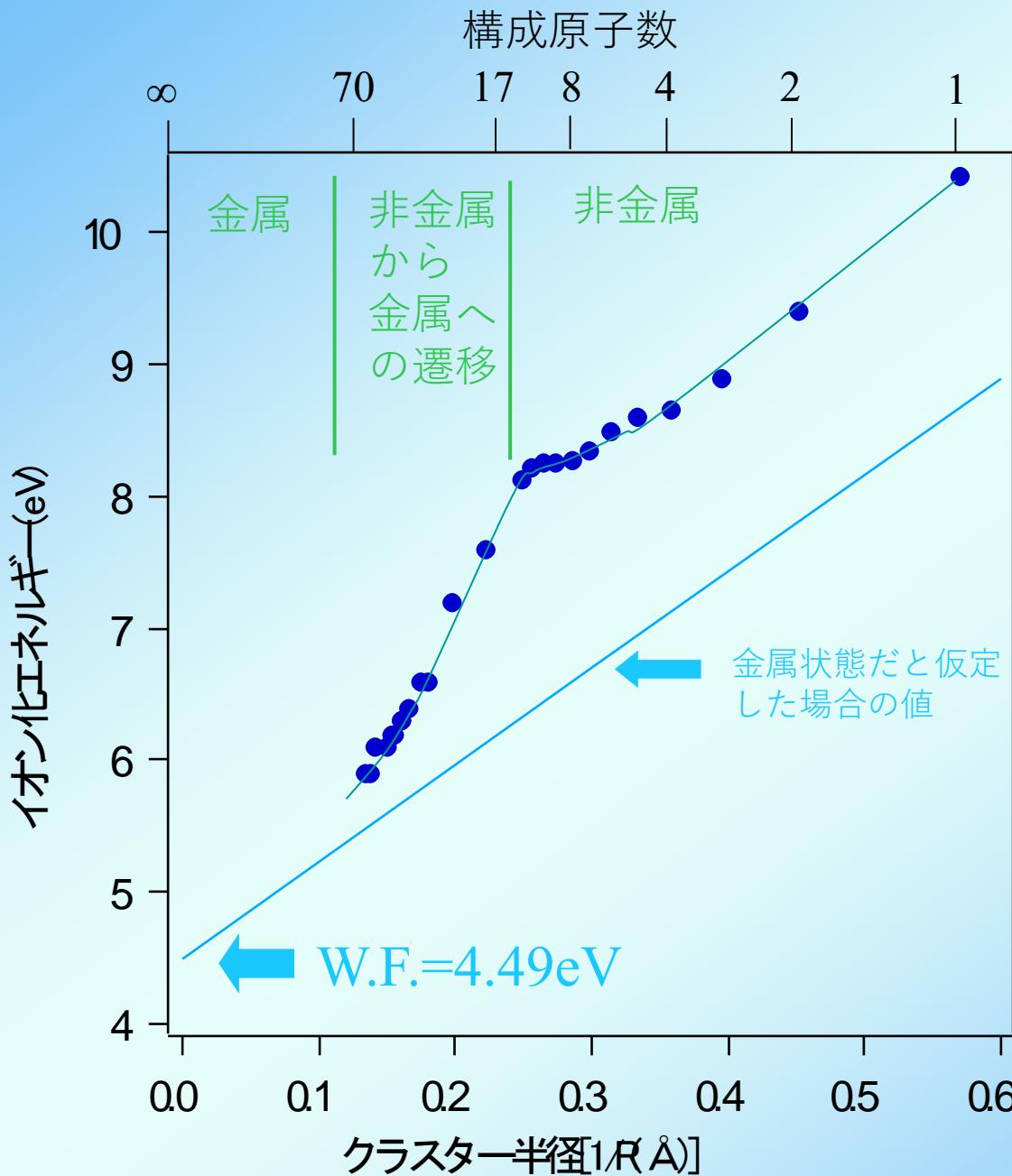
1. 真空中へ噴出させて
クラスターを生成

2. 特定のサイズを
質量選別

3. レーザー照射による
反応を観察

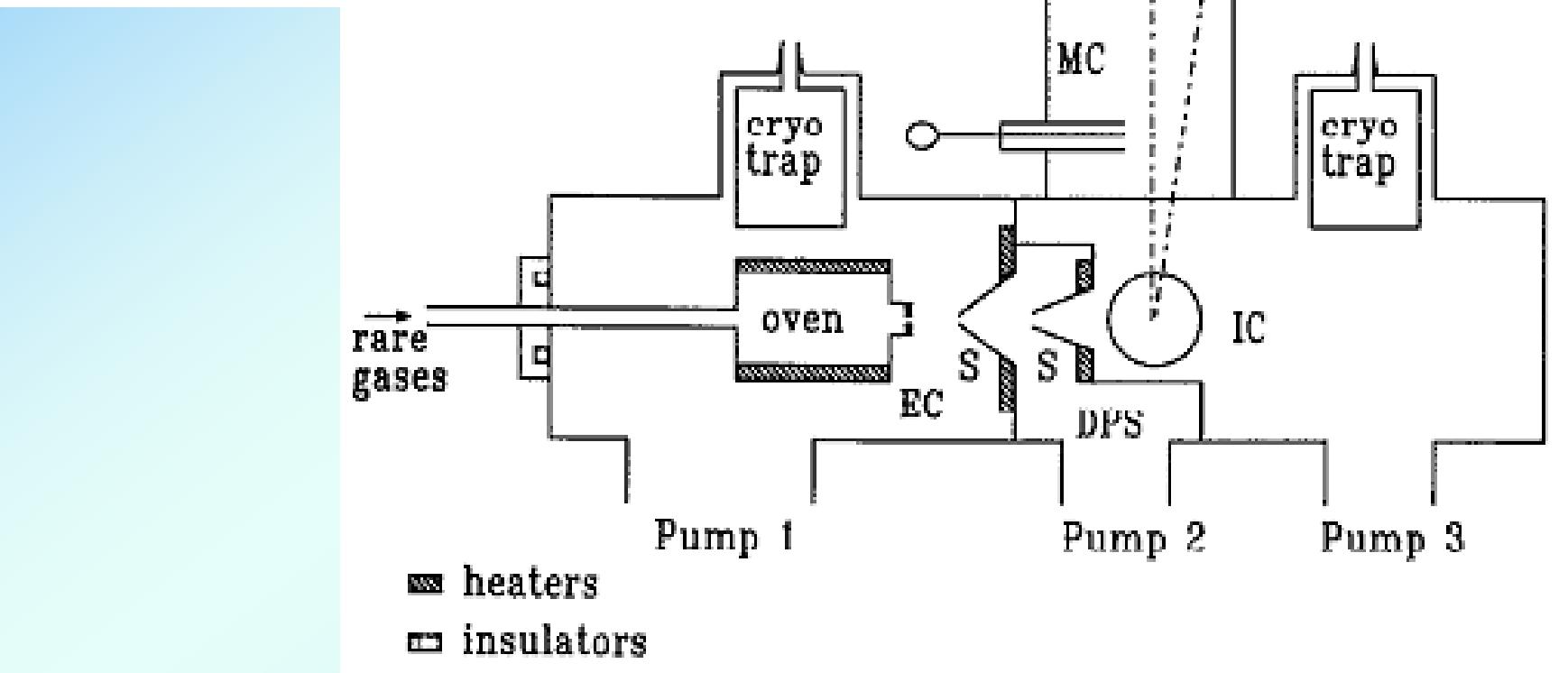


水銀クラスターのイオン化工エネルギー



Coincidence technique for vacuum ultraviolet photoelectron spectroscopy of neutral clusters in a molecular beam

FIG. 1. Schematic drawing (side view cross section) of the molecular beam apparatus and the monochromatized vacuum UV light source. Two conically shaped stainless steel skimmers (*S*) are used to collimate the cluster beam. The skimmer apex orifices are usually between 1 and 2 mm in diameter, the skimmer height 25 mm, and the skimmer exit orifice diameter 15 mm. The oven can be used to vaporize materials at temperatures up to 1200 K. The maximum throughput for noncondensing gases is 20 mbar l s⁻¹. The expansion chamber (EC), the differential pumping stage (DPS), the ionization chamber (IC); the vacuum UV monochromator (VUV-M, ACTON Research VM502), and the mirror chamber (MC) are evacuated by oil diffusion pumps. The working pressure under typical operation conditions is better than 10⁻² mbar (EC), 10⁻⁴ mbar (DPS), and 10⁻⁵ mbar (IC, MC, VUV-M).



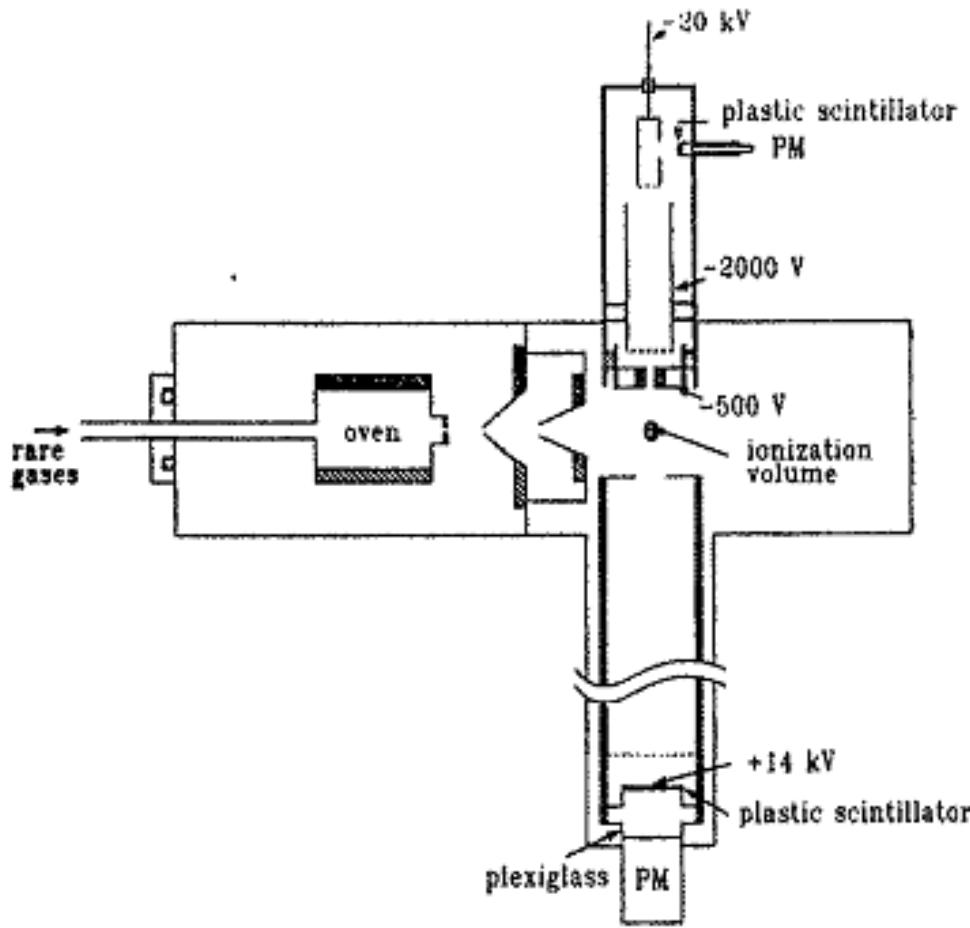


FIG. 2. Schematic drawing (top view cross section) of the electron-cation coincidence spectrometer. The collimated cluster beam is ionized by a short UV-light pulse (start pulse for flight time measurements) on the symmetry axis of both spectrometers. The ionization process occurs in an electrostatic field-free region between both spectrometers. Particle densities in the ionization volume are on the order of 10^{12} cm^{-3} ; the intensity of a single, monochromatized VUV light pulse (bandwidth 2 nm) is typically 10^7 photons. Single photoelectrons are energy analyzed by measuring their flight time in a magnetic mirror electron spectrometer. The electrostatic field free region of this spectrometer is separated from the detector region by a single, high transmission (85%) Ni mesh. A photo-electron passing this mesh is accelerated up to kinetic energies of about 14 keV. If this electron penetrates an aluminum covered plastic scintillator (BICRON 418), a short light pulse will be generated and detected by a photomultiplier (PM: HAMAMATSU R329), which is optically coupled to the scintillator by a plexiglass light guide. The output of this photomultiplier serves as a stop pulse for electron flight time measurements. This stop pulse is also used to activate a high voltage switch (-500 V ; Behlke HTS51) for several μs . Single cluster cations (belonging to the electron that has already been detected) will be drawn out of the ionization region and accelerated up to kinetic energies of about 2 keV. Clusters undergo mass separation in a 180-mm-long field free drift tube. Detection of single ions is accomplished by a modified Daly detector equipped with an aluminum conversion dynode, a plastic scintillator (BICRON 418), and a 800 ps rise time photomultiplier (PM: HAMAMATSU R1635/02 $\frac{3}{8} \text{ in.}$). Mass resolution m/dm can be as high as 350.

光電子分光法の原理

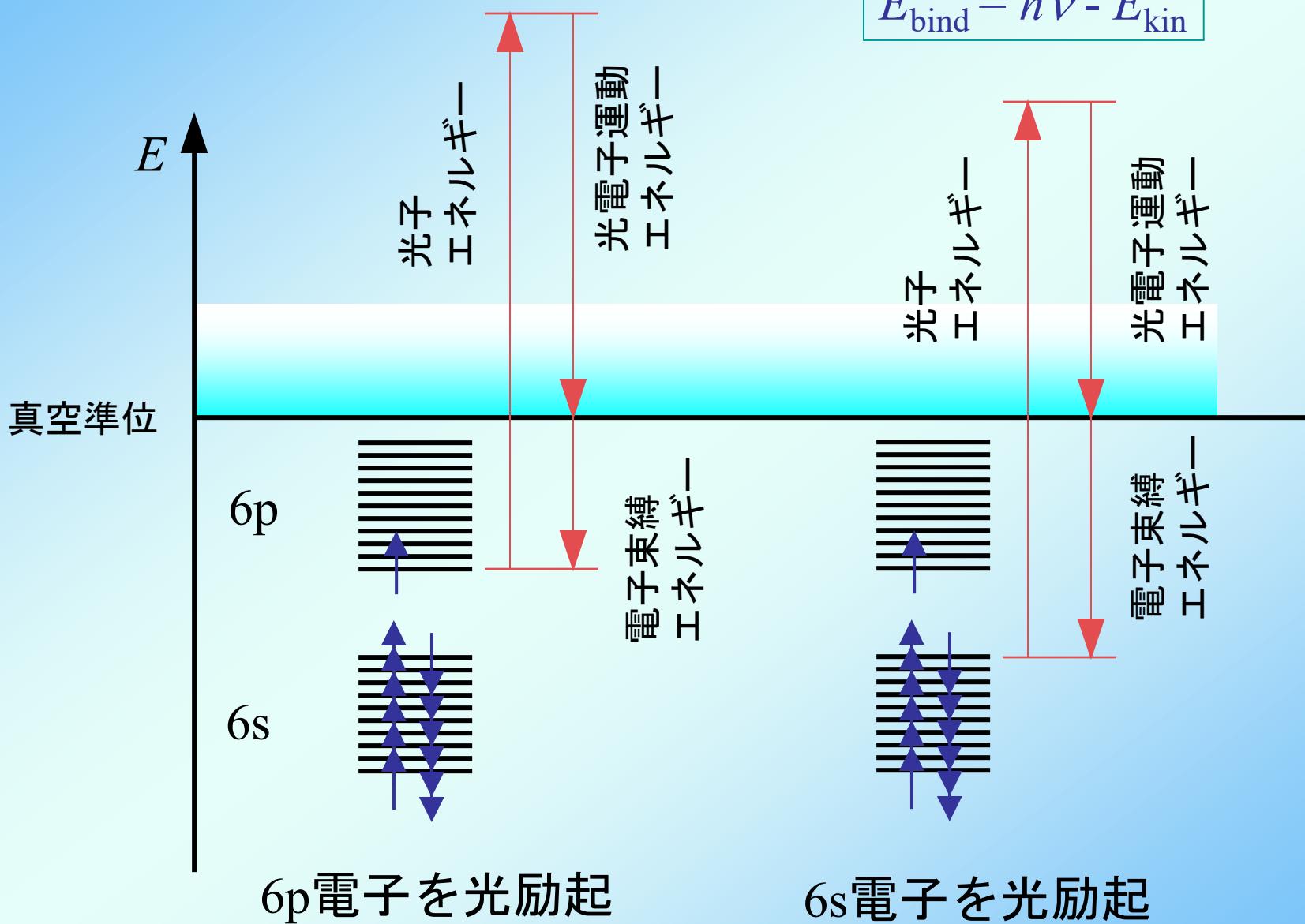
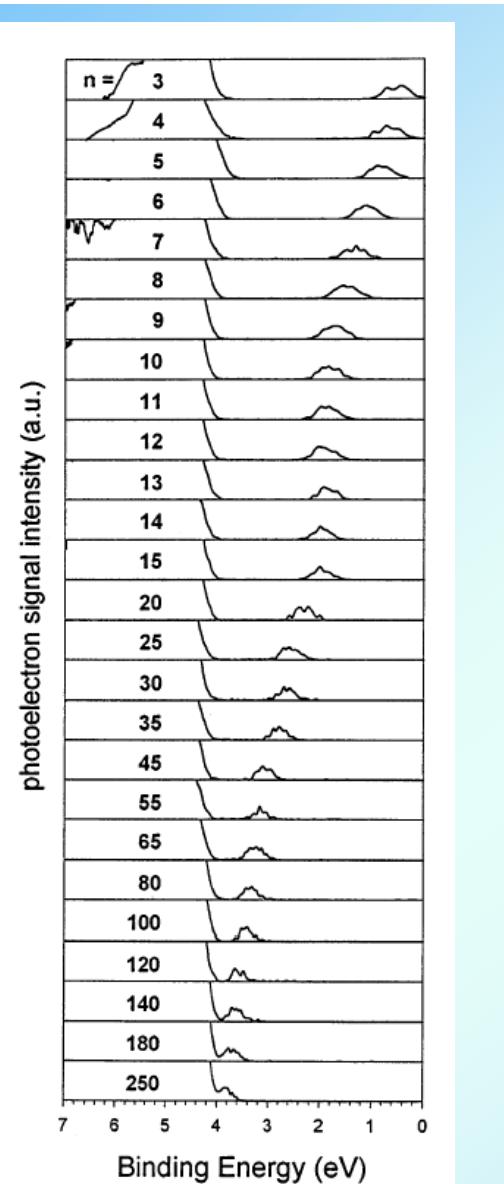


FIG. 2. Photoelectron spectra of Hg^{-n} in the size range of $n = 3$ –250 taken with 7.9 eV laser excitation. The spectra are scaled and truncated to show a constant intensity of the single peak of the detached $6p$ electron. The fine structure of the $6p$ peaks is due to statistical scatter of photoelectron counts.



水銀クラスター負イオンの光電子分光

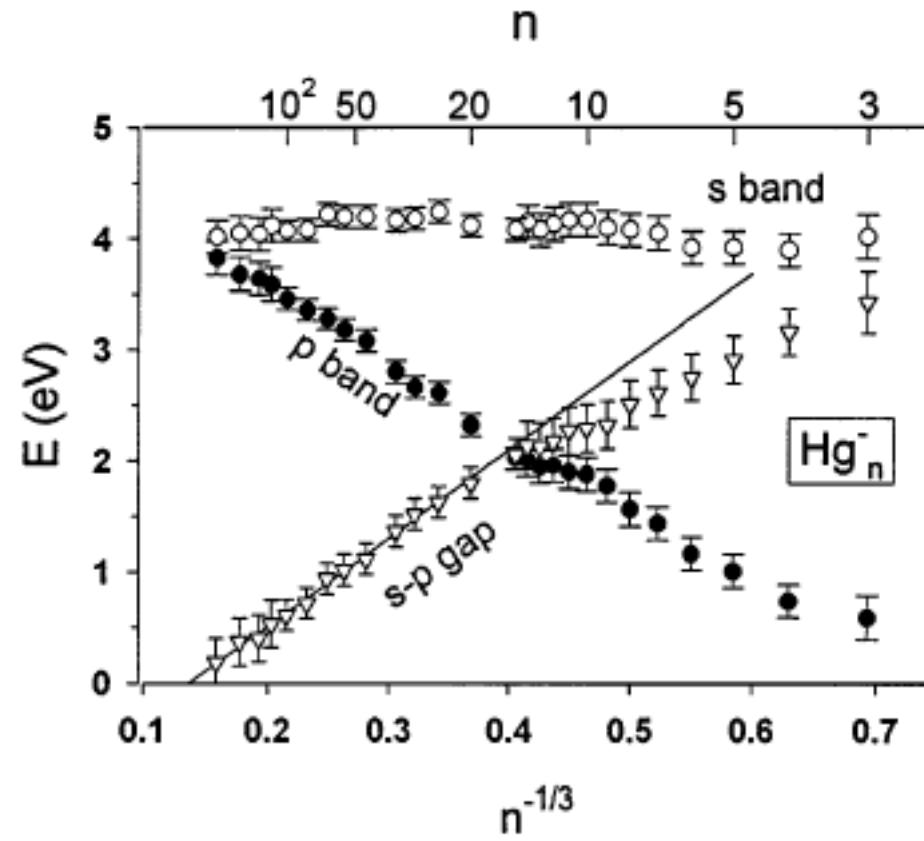


FIG. 3. The size dependence of the BEs of the $6s$ HOMO (open circles) and the $6p$ (full circles) electrons in the PES of Hg^{-n} . The s - p band gap is the difference between these values (open triangles). The linear fitting of the band gap, in the size range $n = 50$ –250, extrapolates to zero at $n = 400 \pm 30$.

Magnetic time-of-flight photoelectron spectrometer for mass-selected negative cluster ions

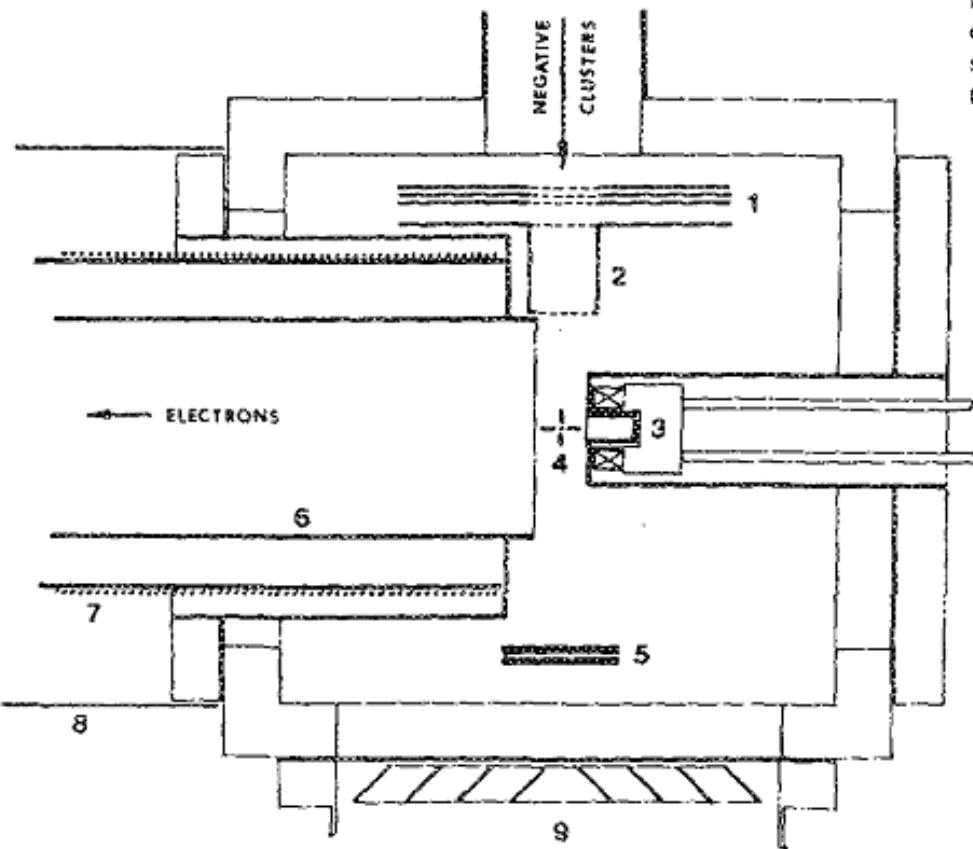
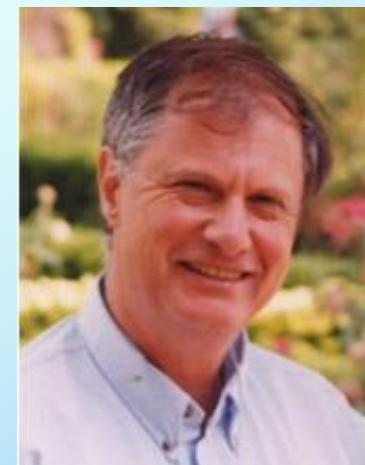


FIG. 1. Horizontal cross section of the photoelectron spectrometer: 1. Pulsed mass gate. 2. Pulsed decelerator. 3. Water-cooled pulsed solenoid. 4. Laser interaction zone. The laser beam and the baffle arms are perpendicular to the page. 5. In-line dual microchannel-plate ion detector. 6. Photo-electron flight tube, 234 cm long. 7. Low field guiding solenoid. 8. mu metal shielding. 9. Cryogenic pump. Note that both of the solenoids are outside of the vacuum chamber.



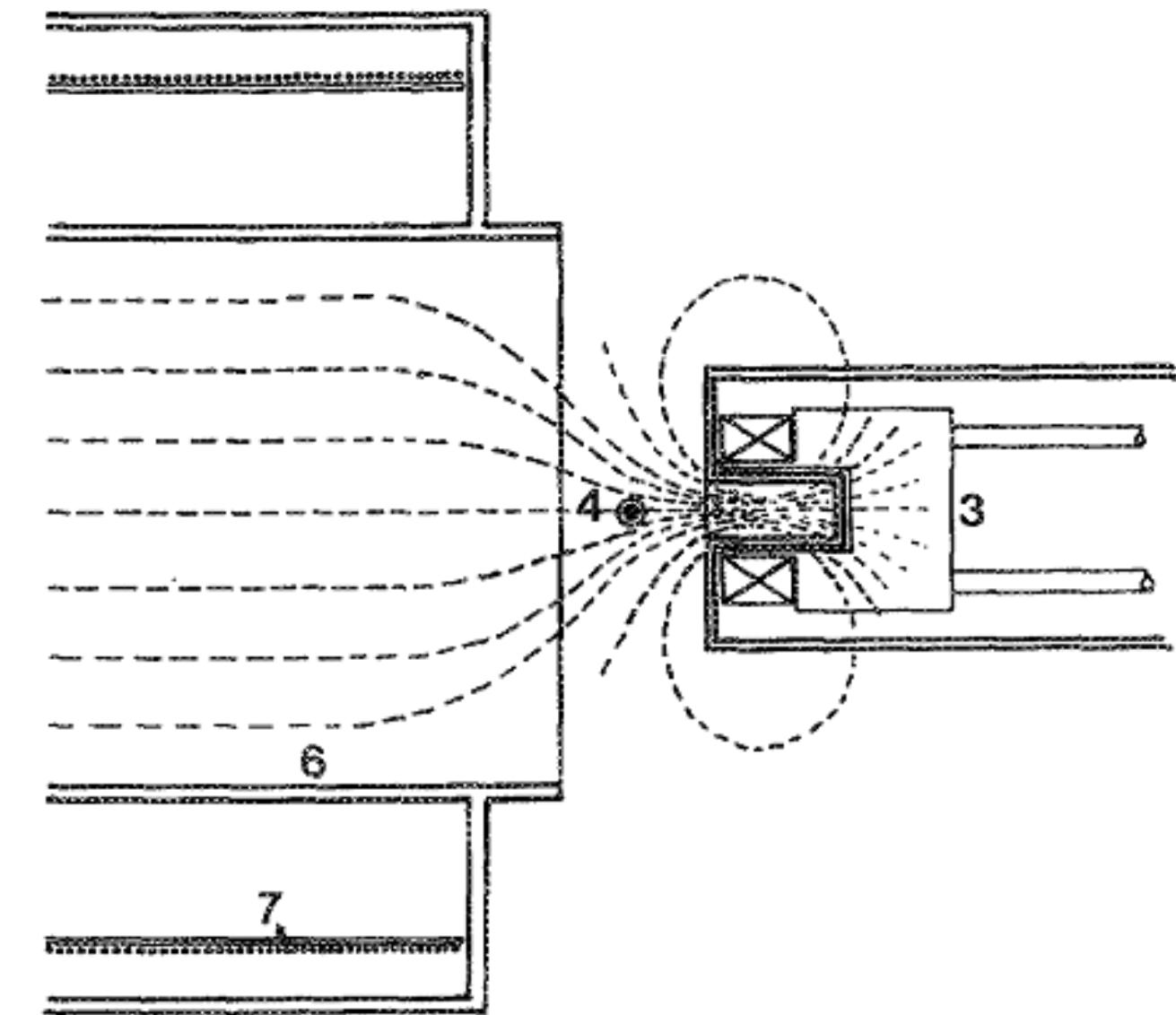


FIG. 2. An expanded view of the main parts of the photoelectron spectrometer. Superimposed are the magnetic field lines generated by the two solenoids. The labels have the same meaning as in Fig. 1.

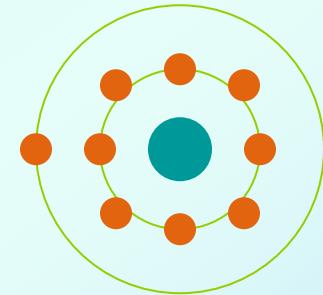
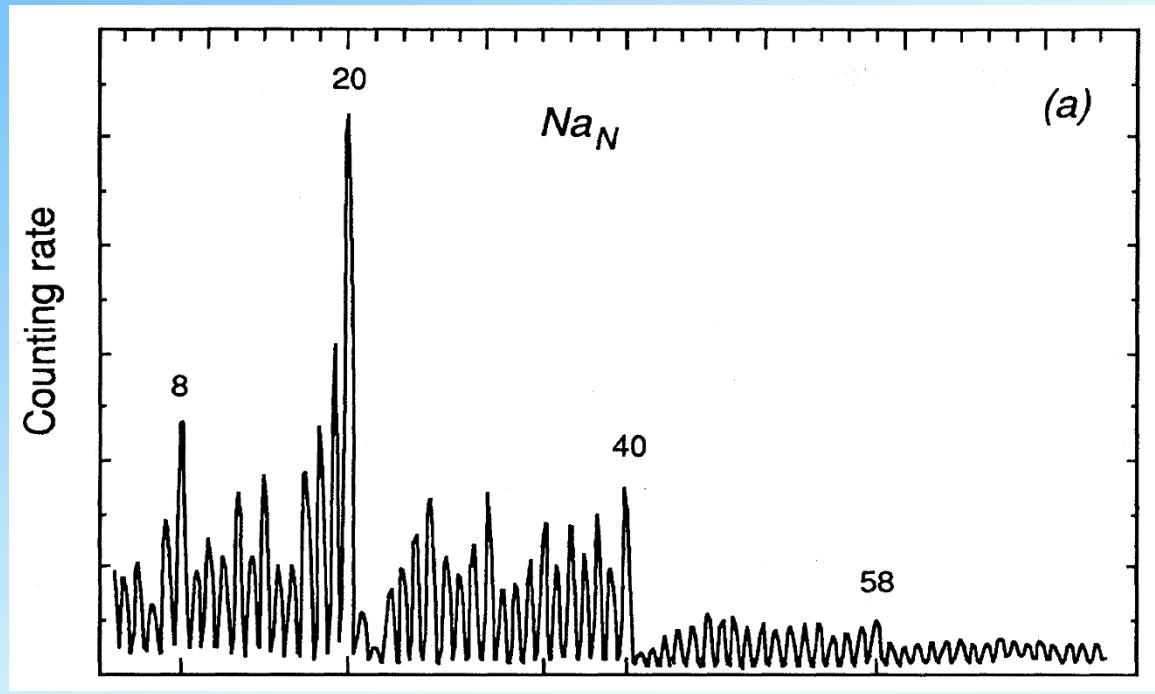
問1. 水銀クラスターの構成原子数が増大するに伴って、クラスターの電子構造が非金属から金属状態へ遷移する。その理由について、簡単に説明しなさい。

問2.

水銀クラスター負イオンについての光電子分光の測定によって、電気的中性の水銀クラスターの電子状態について調べることができる。その理由について、簡単に説明しなさい。



アルカリ金属クラスター



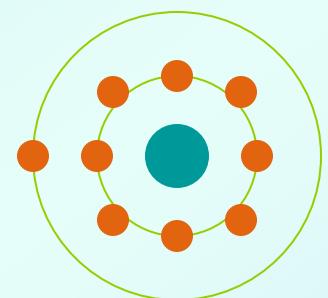
Naクラスターの質量スペクトル。
 $n=8, 20, 40, 58$ の強度が大きい。

電子構造が閉殻なクラスターが安定
(希ガス原子と類似)

W. A. de Heer, Rev. Mod. Phys., 65, 611 (1993).

アルカリ金属原子の電子構造

$$\text{Na}(1s)^2(2s)^2(2p)^6(3s)^1$$



最外殻電子がs軌道に1個

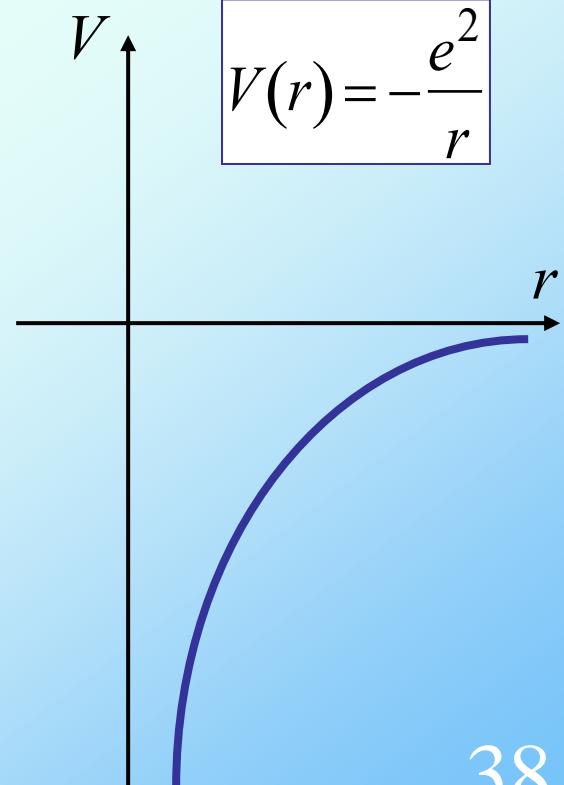
$$\hat{H}\Psi = E\Psi$$

$$\left[-\frac{\hbar^2}{8\pi^2 m_e} \Delta + V(r) \right] \Psi = E\Psi$$

$$V(r) = -\frac{Ze^2}{r}$$

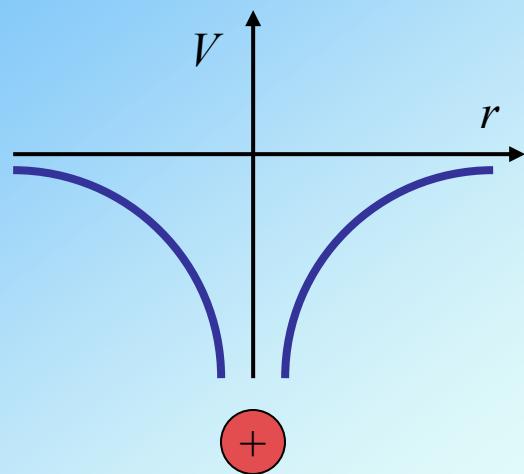
$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{4\pi^2 \hat{l}^2}{h^2 r^2}$$

$$\hat{l}^2 = -\frac{\hbar^2}{4\pi^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$



価電子とイオンとの間のクーロンポテンシャル

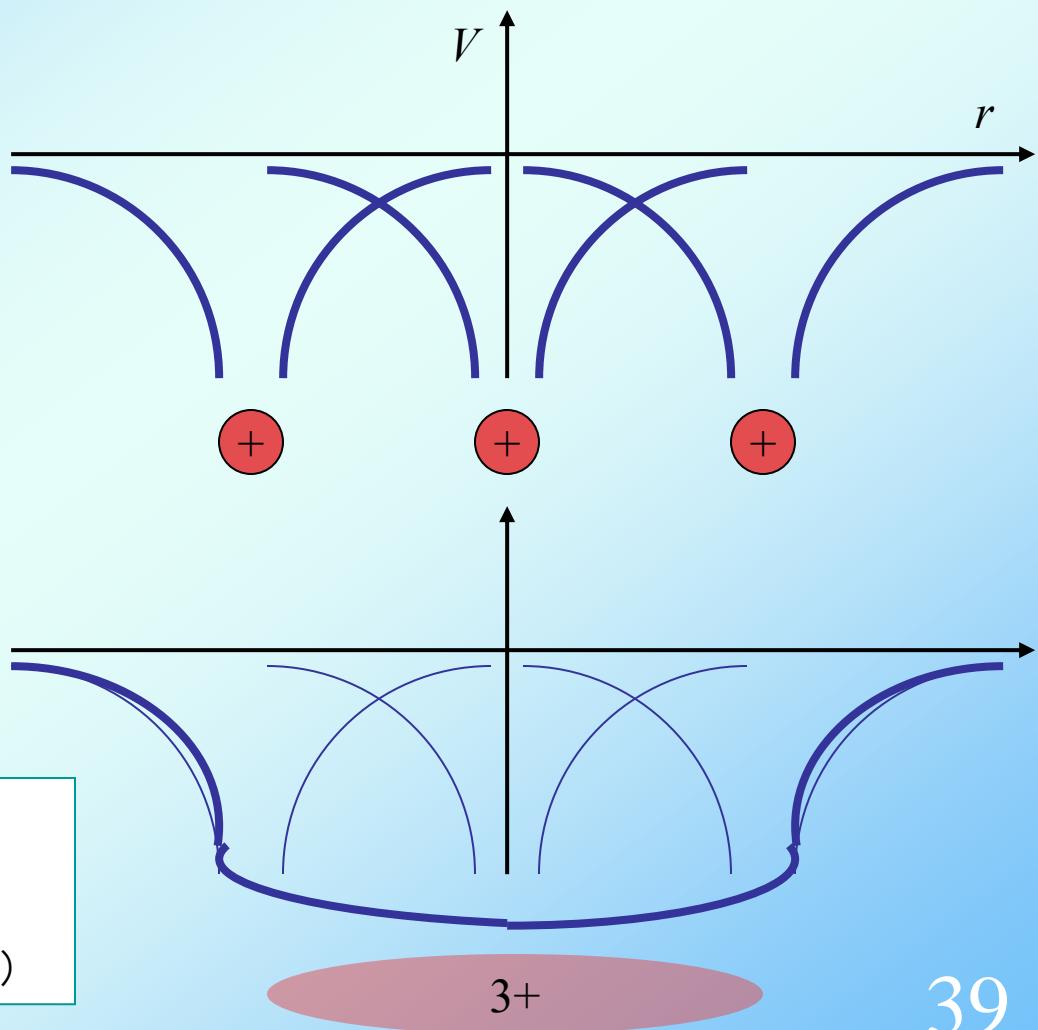
Na原子



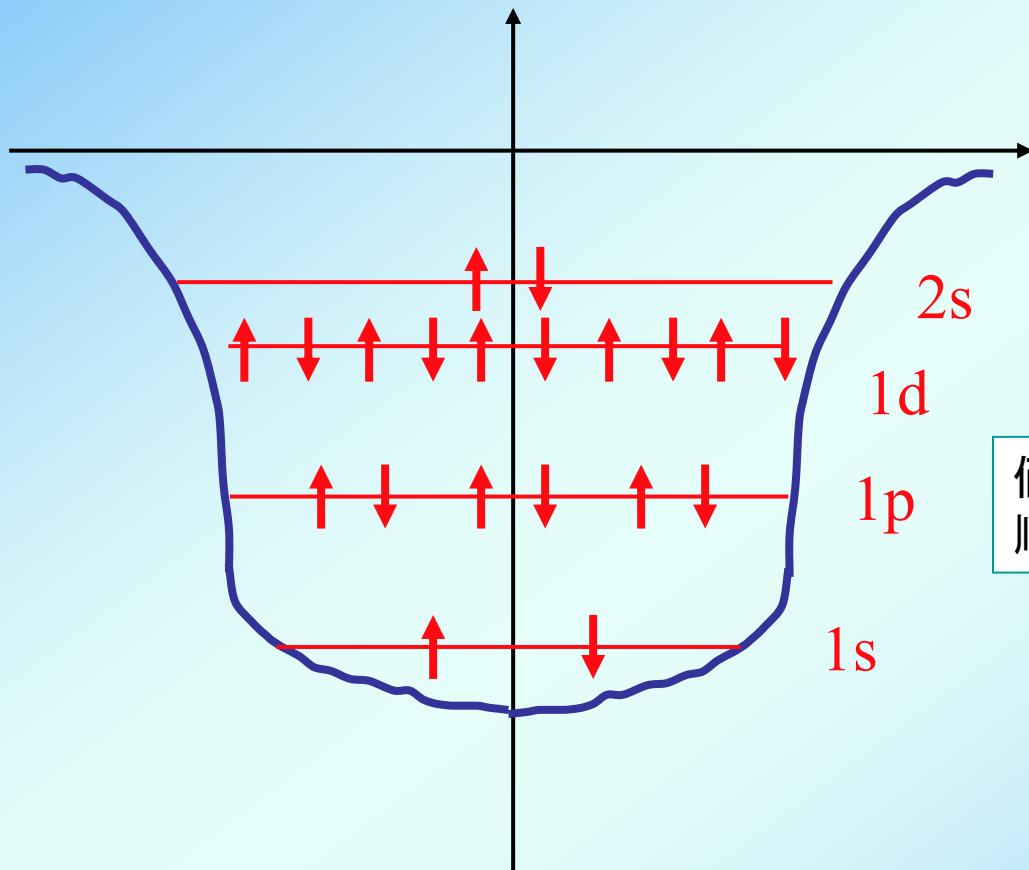
クラスター中の価電子は
クラスター全体に広がり
自由電子のように振る舞う。

クラスター中のクーロンポテンシャルは
他の価電子による遮蔽効果によって
個々のイオン芯を一様に平均した
平均正電荷となる。（ジェリウムモデル）

Naクラスター



Naクラスター中の ジェリウムポテンシャル



ポテンシャル中の量子準位は
エネルギーの低い順に
1s, 1p, 1d, 2s, 1f, 2p, 1g....

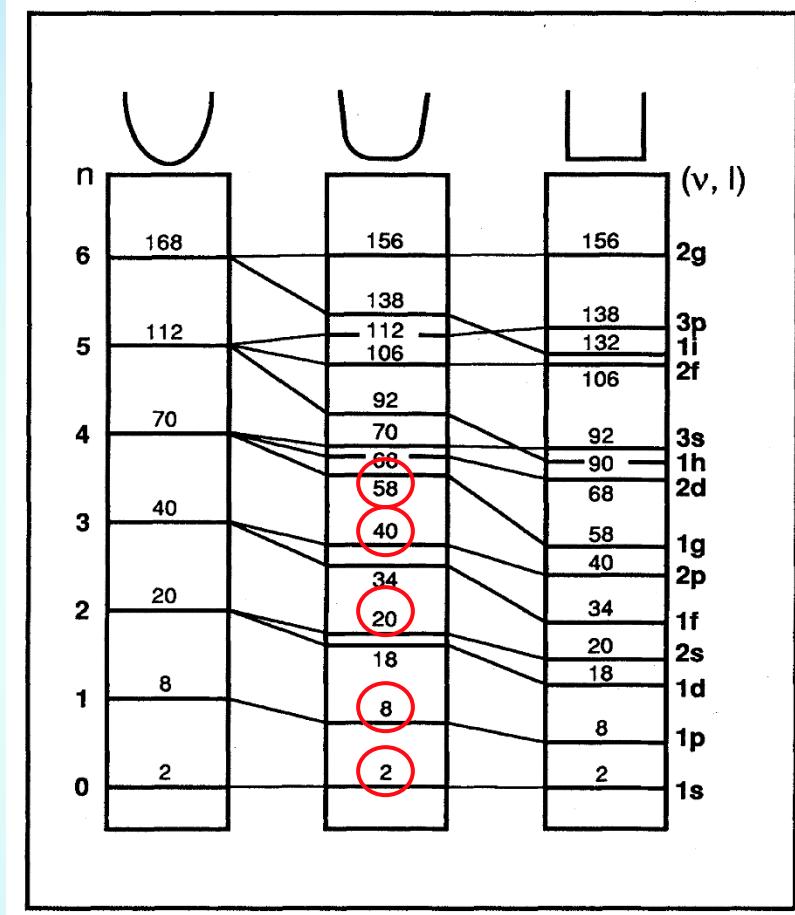
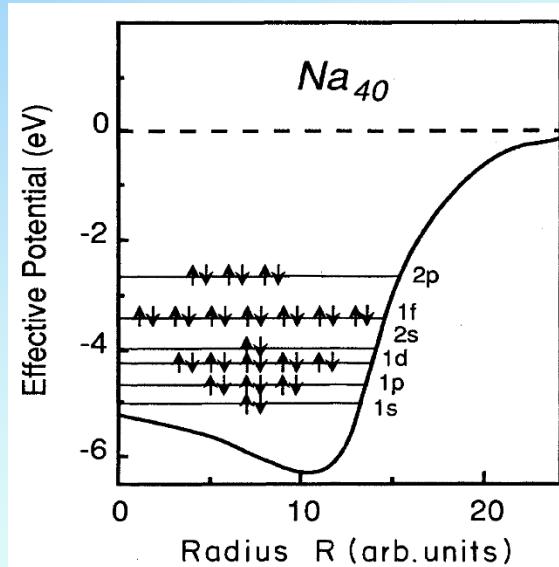
原子軌道の準位に類似しているが、
 $V(r) \propto -1/r$ ではないので
方位量子数の制限がない。

価電子はエネルギーの低い準位から
順番に充填する。

全価電子数が
2, 8, 20, 40...
となったときに
電子配置が閉殻となる。

アルカリ金属クラスターでは
構成原子数 n は価電子数と同じ。

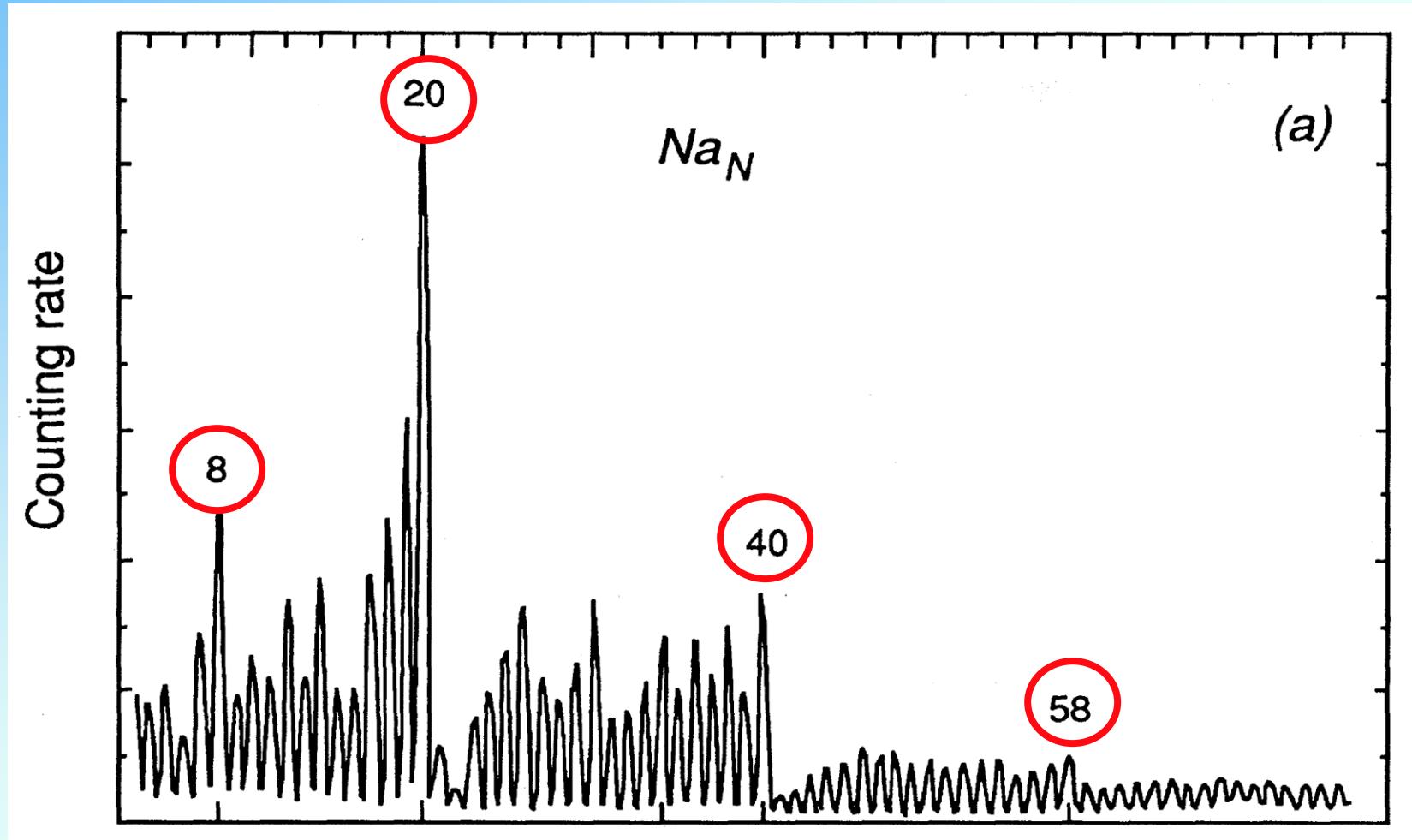
アルカリ金属クラスターの電子殻モデル



Na_{40} 内の
価電子配置。

3次元球対称のエネルギー準位図。
左から調和振動子、中間、四角井戸の
ポテンシャルの場合。

アルカリ金属クラスターの質量スペクトル



電子構造が閉殻なクラスターが安定
(希ガス原子と類似)

Abundance spectra of copper and silver clusters

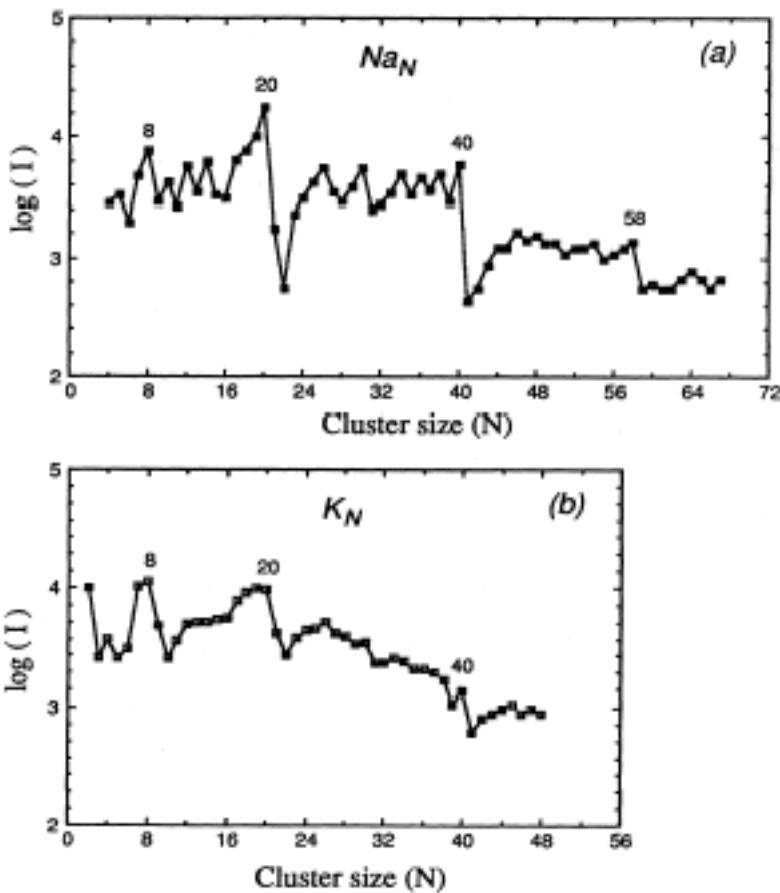


FIG. 15. Alkali abundance spectra: (a) sodium abundance spectrum (from Fig. 1) presented with a logarithmic scale, (b) potassium abundance spectrum (after Knight *et al.*, 1984). Spherical-shell-closing numbers are indicated.

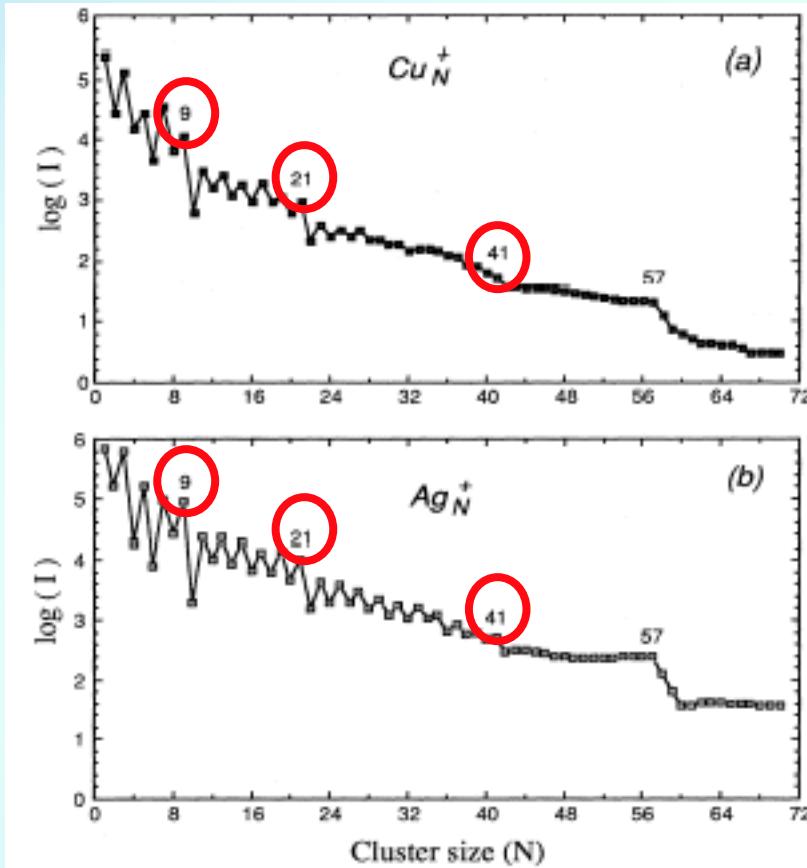
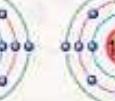


FIG. 17. Logarithmic abundance spectra of (a) copper and (b) silver cluster ions produced in a sputtering source. Numbers correspond to spherical shell closings after Kataeuse *et al.*, 1985.

原子の電子配置の模式図

電子配置									
電子式	H ·								He :
電子配置	       								He :
電子式	Li · · Be · · B · · C · · N · · O · · F · · Ne ·								:Ne:
電子配置	       								:Ar:
価電子数	1	2	3	4	5	6	7	0	
図 4 原子の電子配置の模式図 模式図の同心円は、内側から順に K 裂、L 裂、M 裂を示している。									

原子のイオン化エネルギー

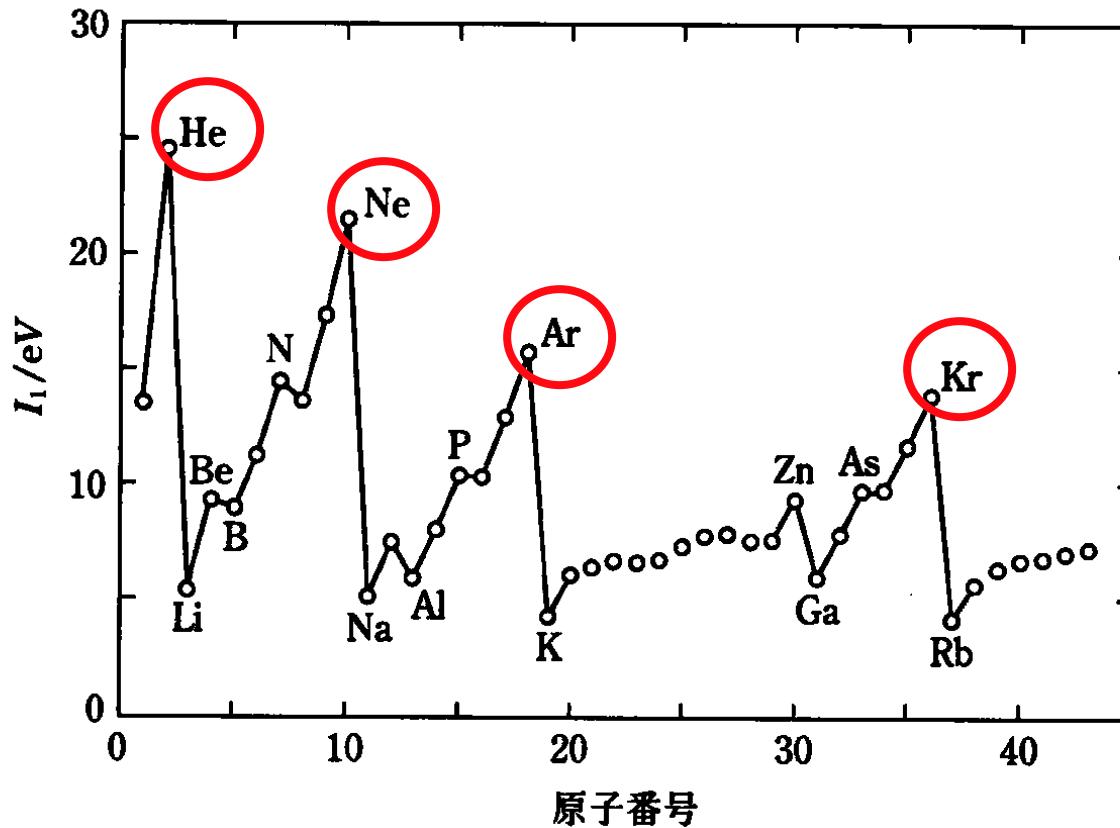


図3.1 原子の第1イオン化エネルギーにみられる周期的変化

Ionization potentials of alkali clusters

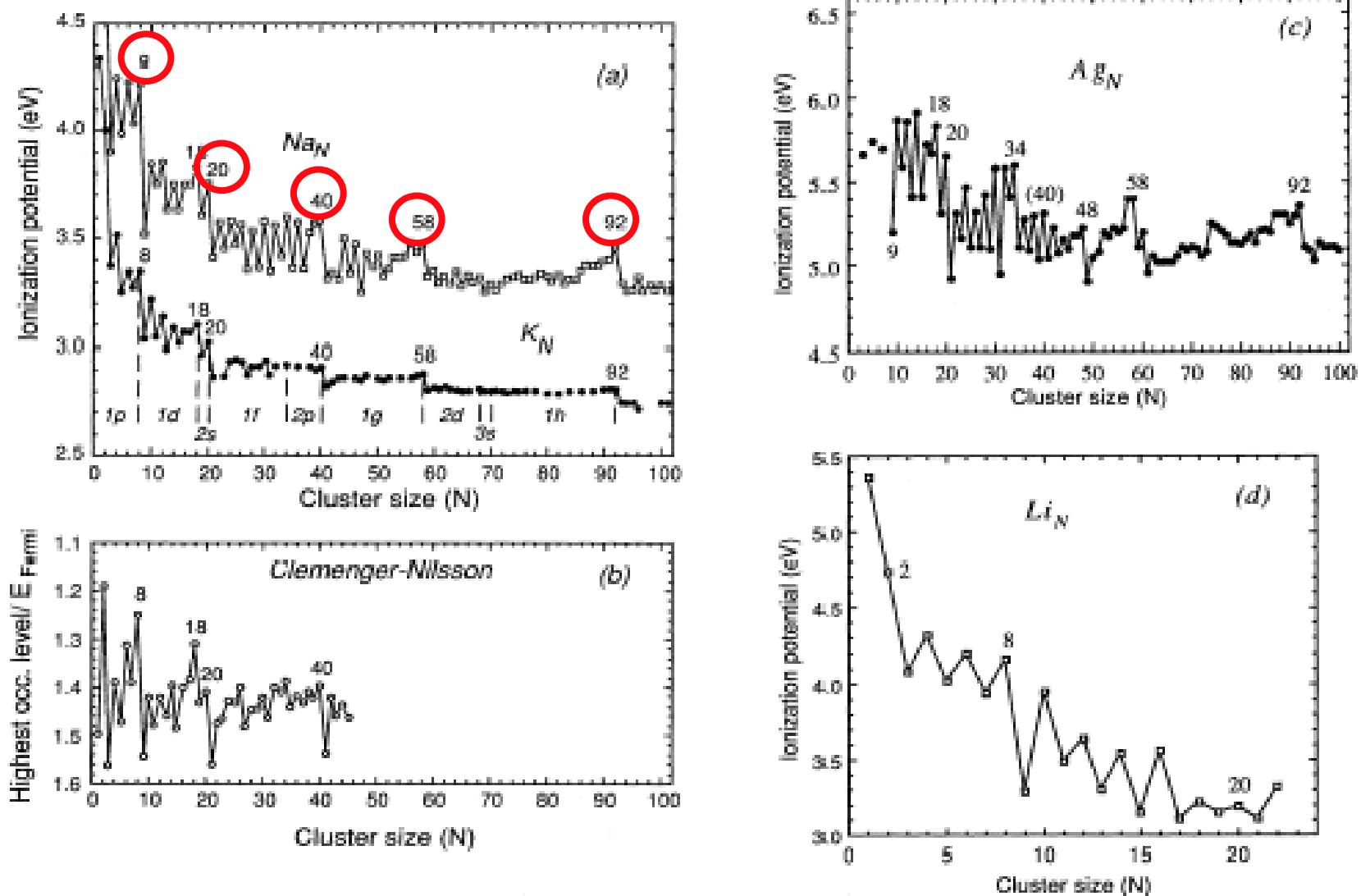
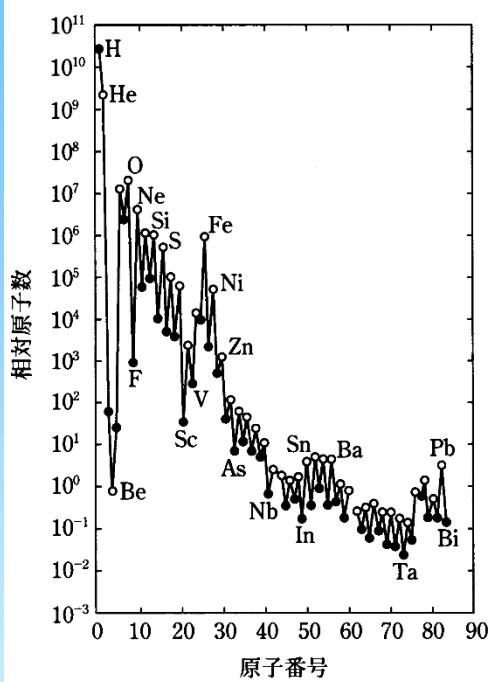


FIG. 26. Ionization potentials of alkali clusters. (a) Ionization potentials of sodium clusters (after Homer *et al.*, 1993, to be published) and of potassium clusters (Saunders *et al.*, 1985; de Heer, Knight, *et al.*, 1987); (b) highest occupied levels in the ellipsoidal shell (Clemenger-Nilsson) model where the electronic kinetic energy is scaled relative to the Fermi energy of the bulk metal; (c) ionization potentials of silver clusters (after Alameddin *et al.*, 1992); (d) ionization potentials of lithium clusters (Dugourd *et al.*, 1992).

太陽系の元素の存在度と原子核の結合エネルギー



元素の太陽系存在度。Si 原子を 10^6 個としたときの相対原子数。○は偶数番元素、●は奇数番元素

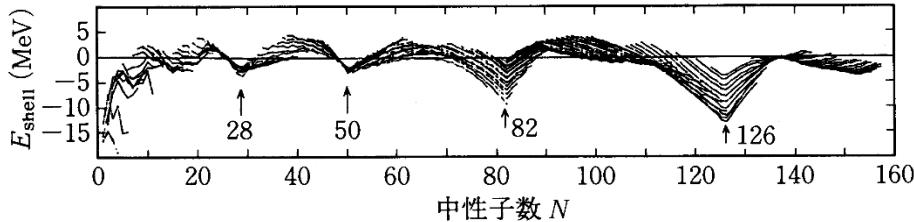


図 1-3 裂構造エネルギー E_{shell} の N 依存性。折れ線は個々のアイソトープを示す。(W. D. Myers and W. J. Swiatecki: Ann. Rev. Nucl. Part. Sci. 32(1982) 309 による。)

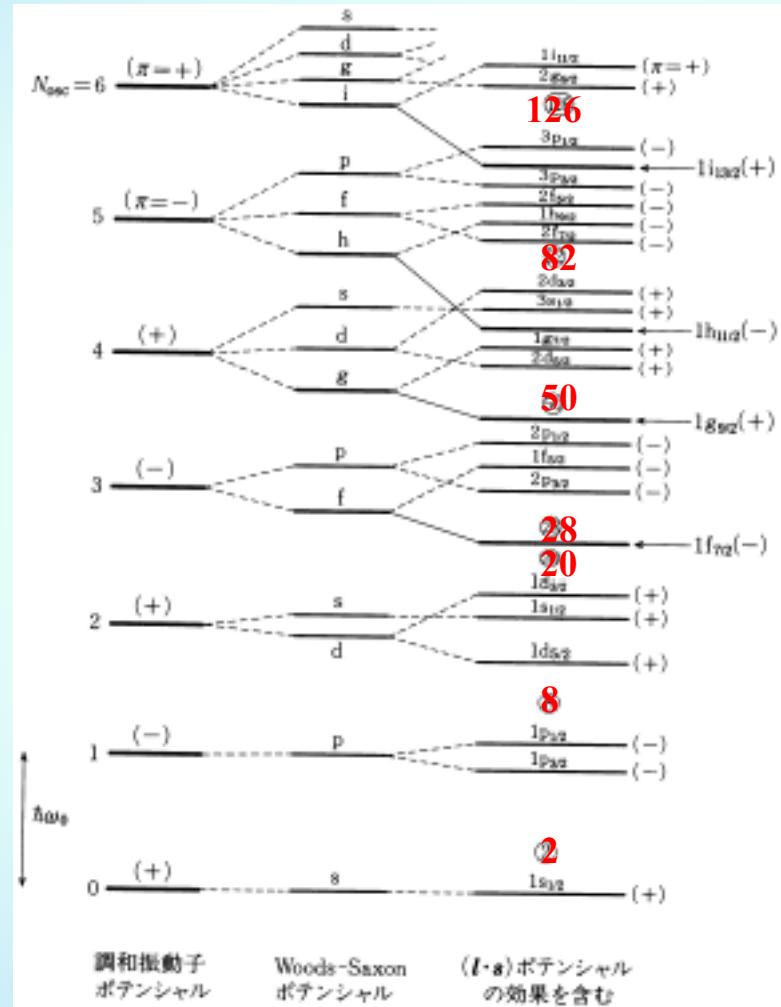
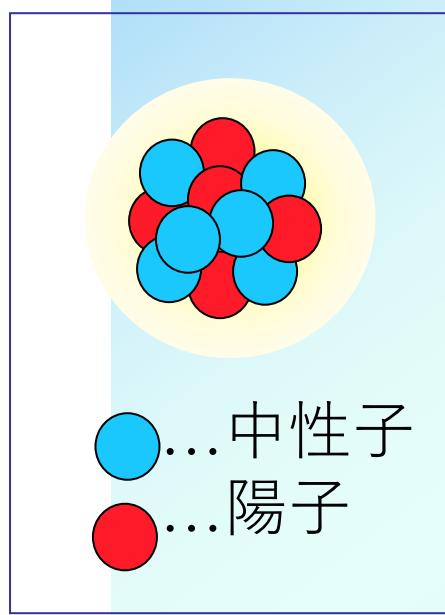
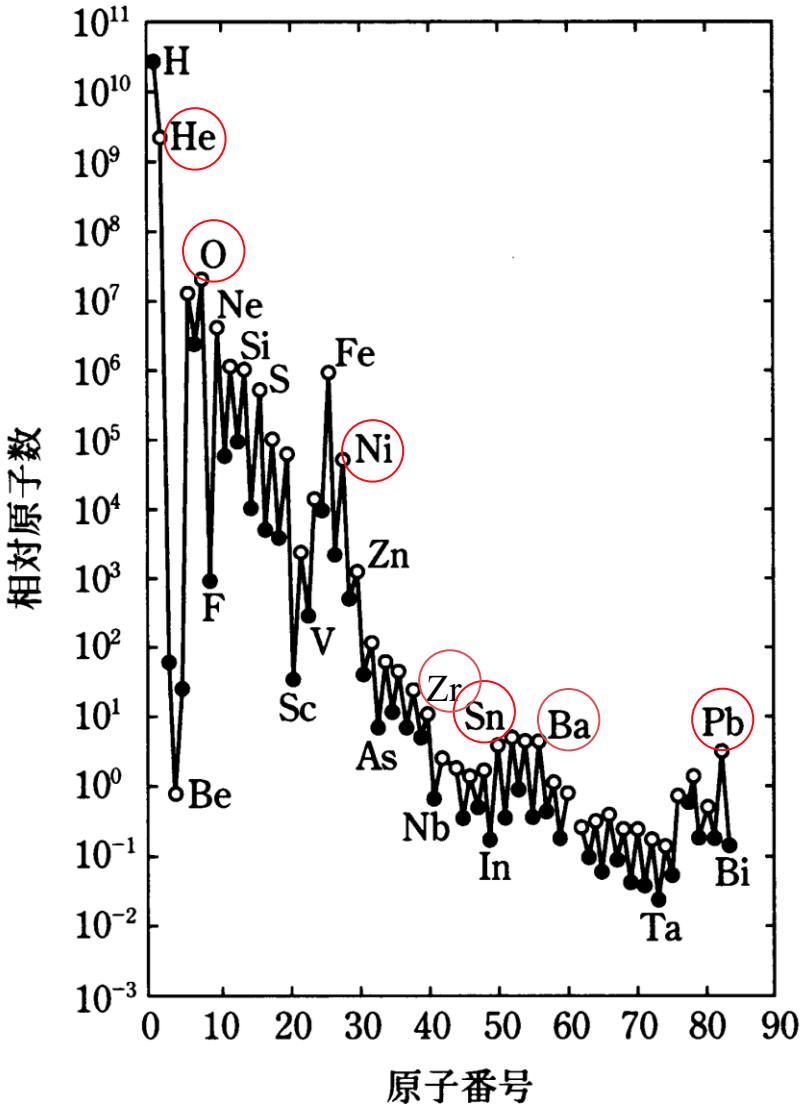


図 2-1 $j-j$ 結合殻モデルの 1 粒子エネルギー単位(概念図)。Woods-Saxon ポテンシャルに $(I-g)$ 項がつけ加わって、魔法数 2, 8, 20, 28, 50, 82, 126 が得られる。記号 s, p, d, f, g, h, i は $l=0, 1, 2, 3, 4, 5, 6$ を示し、例えば $1h_{11/2}$ は $n=1, l=5, j=11/2$ を表わす。これらの単位を下から詰めたときの核子の累計数は、各単位の縮退度 $2j+1$ から計算できる。



元素の太陽系存在度. Si 原子を 10^6 個としたときの相対原子数. ○は偶数番元素, ●は奇数番元素

太陽系の元素の存在度と原子核の結合エネルギー

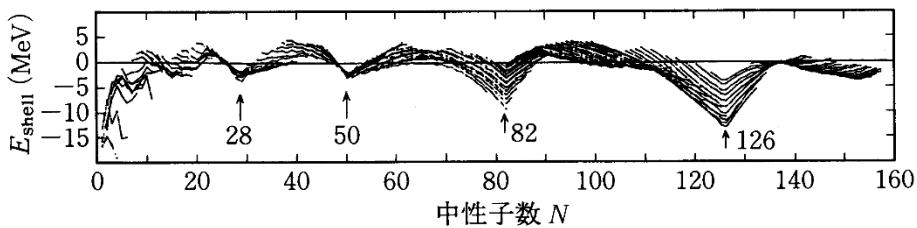


図 1-3 裂構造エネルギー E_{shell} の N 依存性. 折れ線は個々のアイソトープを示す. (W.D. Myers and W.J. Swiatecki: Ann. Rev. Nucl. Part. Sci. 32(1982) 309 による.)

元素と陽子数 Z (原子番号)
He 2個, O 8個, Ni 28個,
Sn 50個, Pb 82個

元素と中性子数 N
He 2個, O 8個,
 ^{90}Zr 50個, ^{138}Ba 82個, ^{208}Pb 126個

太陽系における核種の存在比

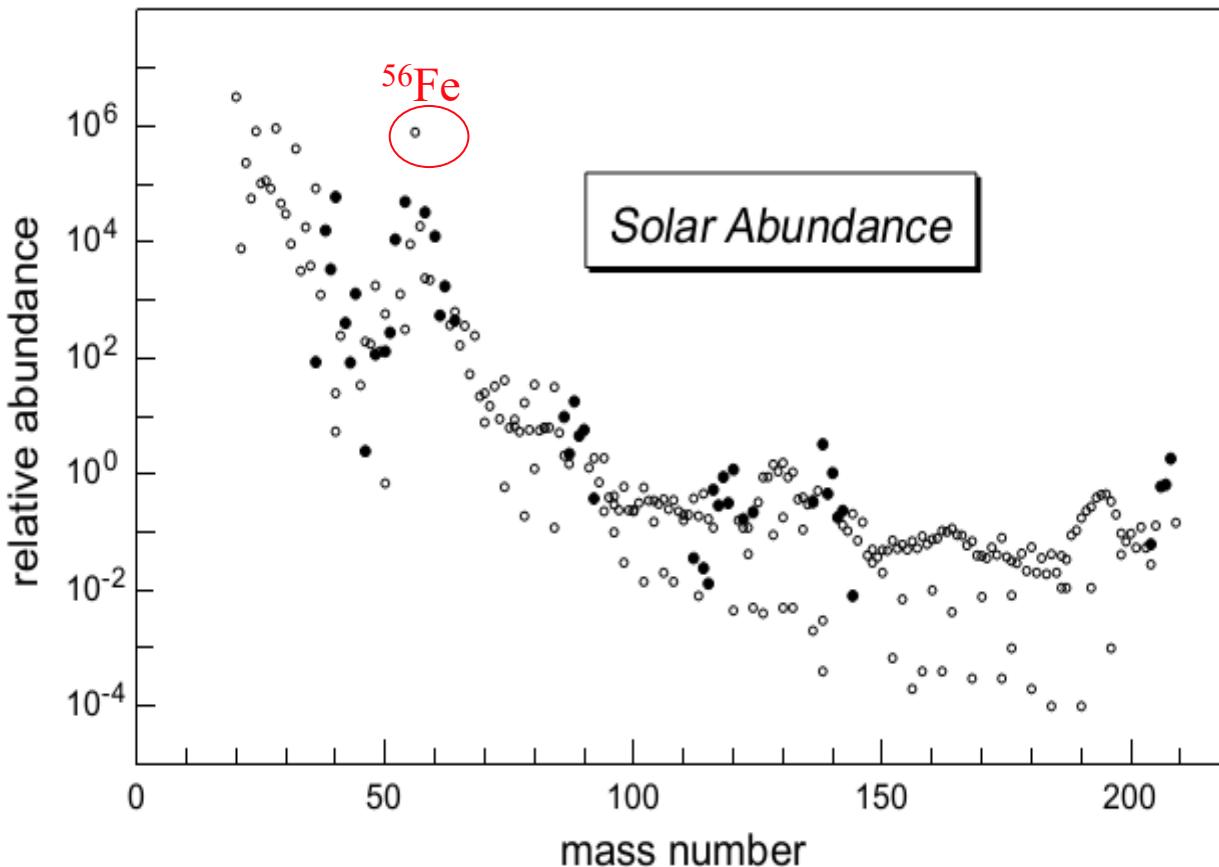


図 5.6: 核種の存在比. 黒丸が魔法数をもつ核種, 白丸がその他の核種を表す.

- 存在量は質量数とともに減少していく.
- 黒丸で示した魔法数をもつ原子核の存在比が大きい.
- きわだって存在量が多いのが ^{56}Fe である. これは, 殻構造のためではなく, 核子あたりの結合エネルギーが最も大きいことが主な原因である.

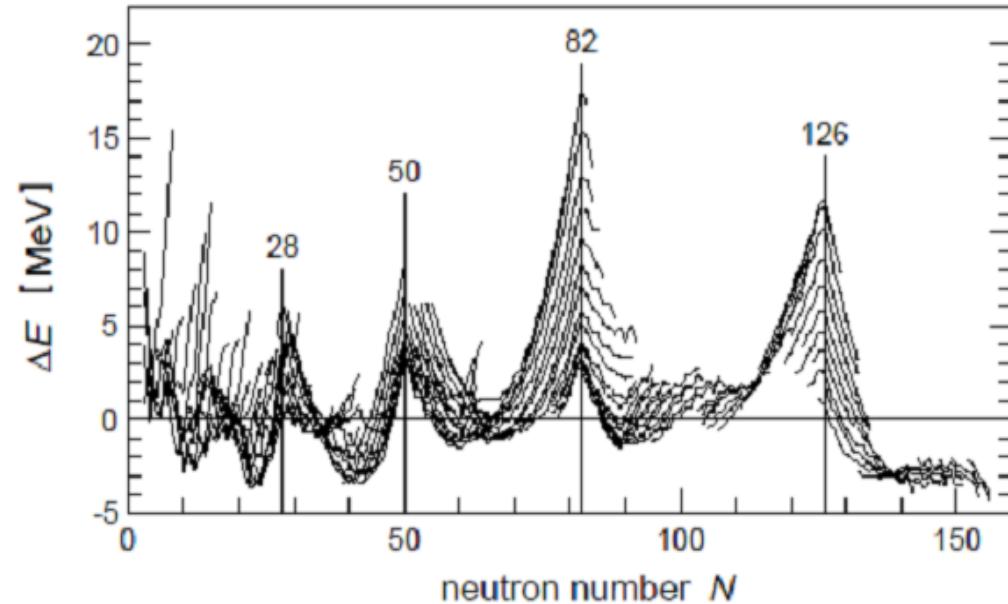
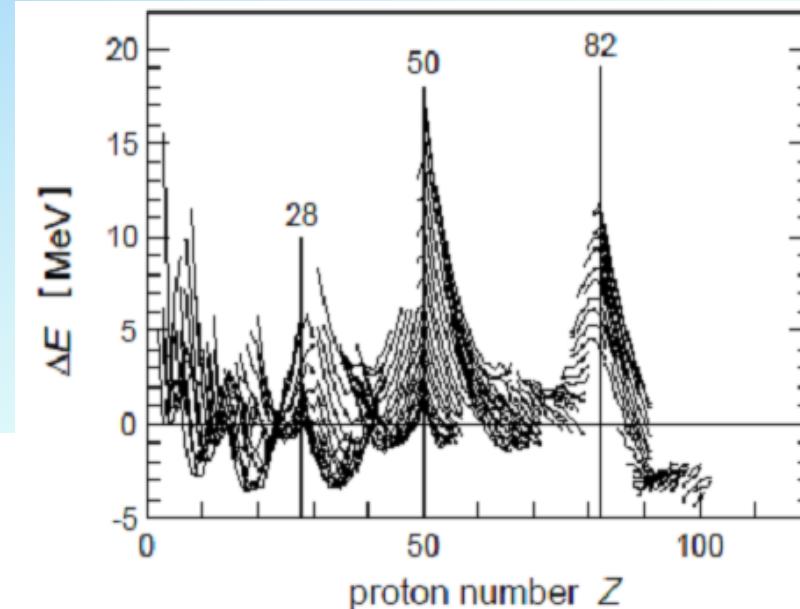
原子核の結合エネルギー

■ 原子核の結合エネルギー 実験値－理論値(質量公式)

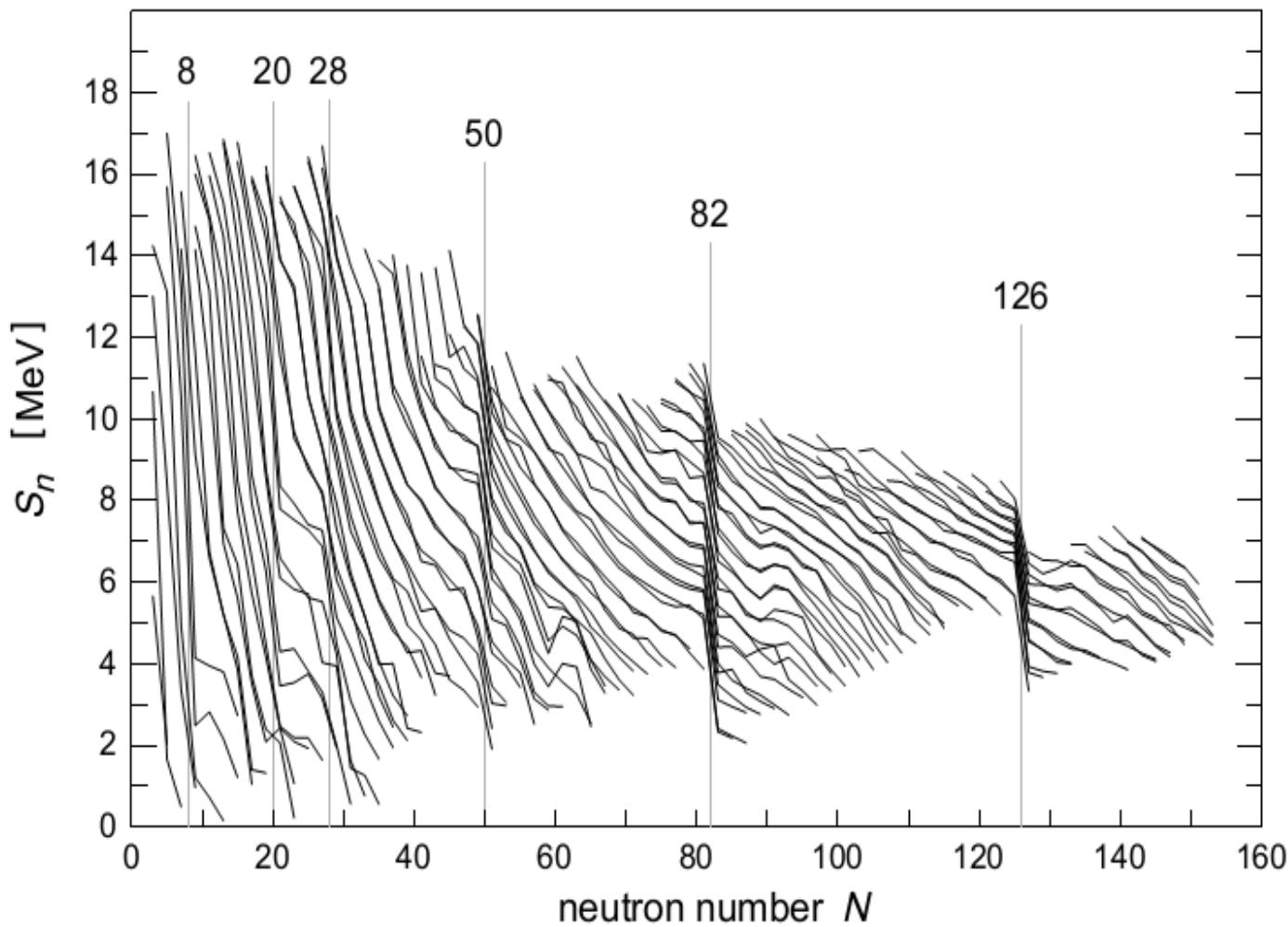
上図 横軸；陽子数 Z
 N が等しい原子核を線で結ぶ

下図 横軸；中性子数 N
 Z が等しい原子核を線で結ぶ

■ 魔法数の近傍で大きな値になる



中性子分離エネルギー



核子放出に対して安定なすべての原子核（ただし、中性子数が奇数の場合）の中性子分離エネルギーを、原子番号が等しい同位体を線で結んで示してある。魔法数 $N = 8, 20, 28, 50, 126$ をはさんで、中性子分離エネルギーが急速に減少している。

実験的原子質量と、B-W質量公式のずれ

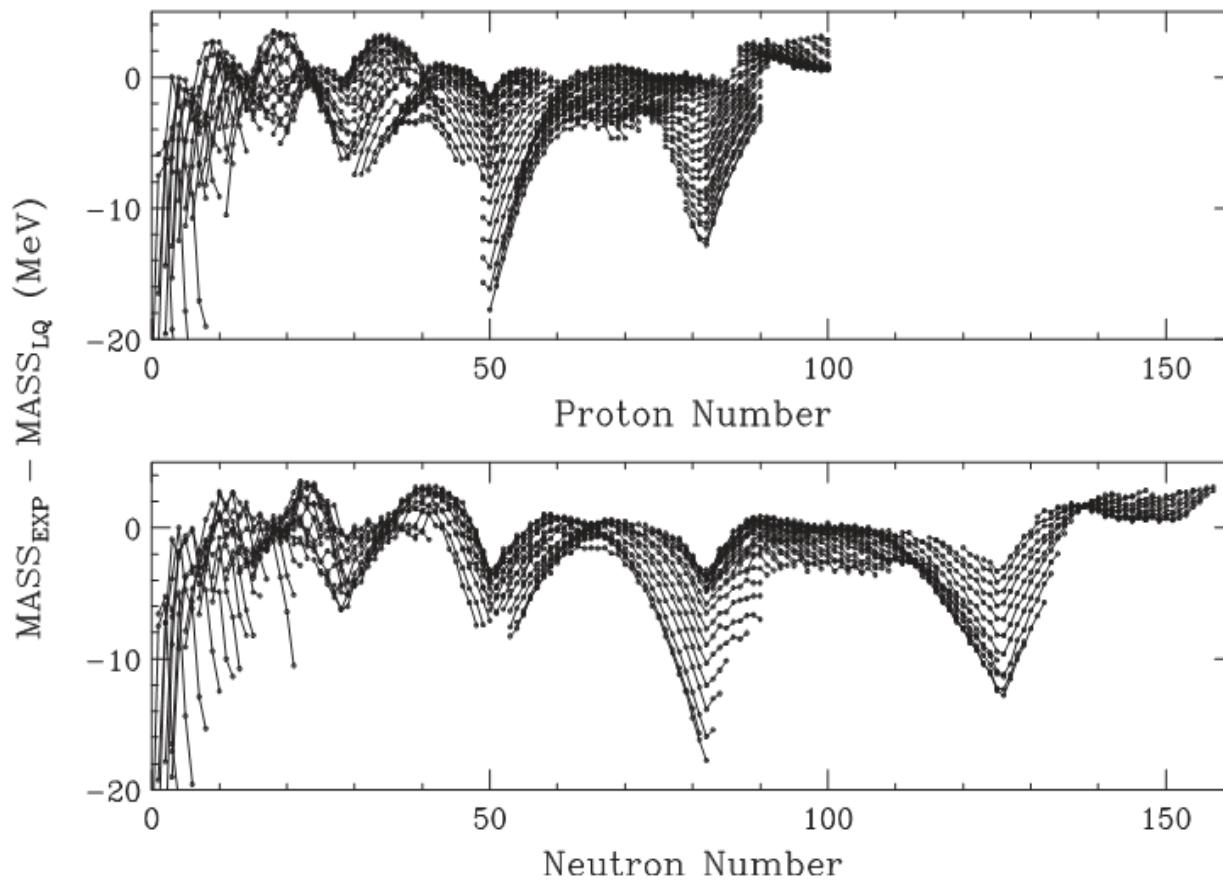


図 3: 実験的原子質量と、B-W 質量公式のずれ。それは魔法数 (2, 8, 20, 28, 50, 82, 126) のところで大きく、これらの原子核がより 安定である (質量が軽い) 事を意味しており、原子核の殻構造を反映している。

ベーテ・ワイゼッカー (Bethe-Weizäcker) の質量公式

$$M^{\text{BW}}(N, Z)c^2 = (Nm_n + Zm_p)c^2 - E_B^{\text{BW}}(N, Z)$$

Sodium cluster abundance spectrum

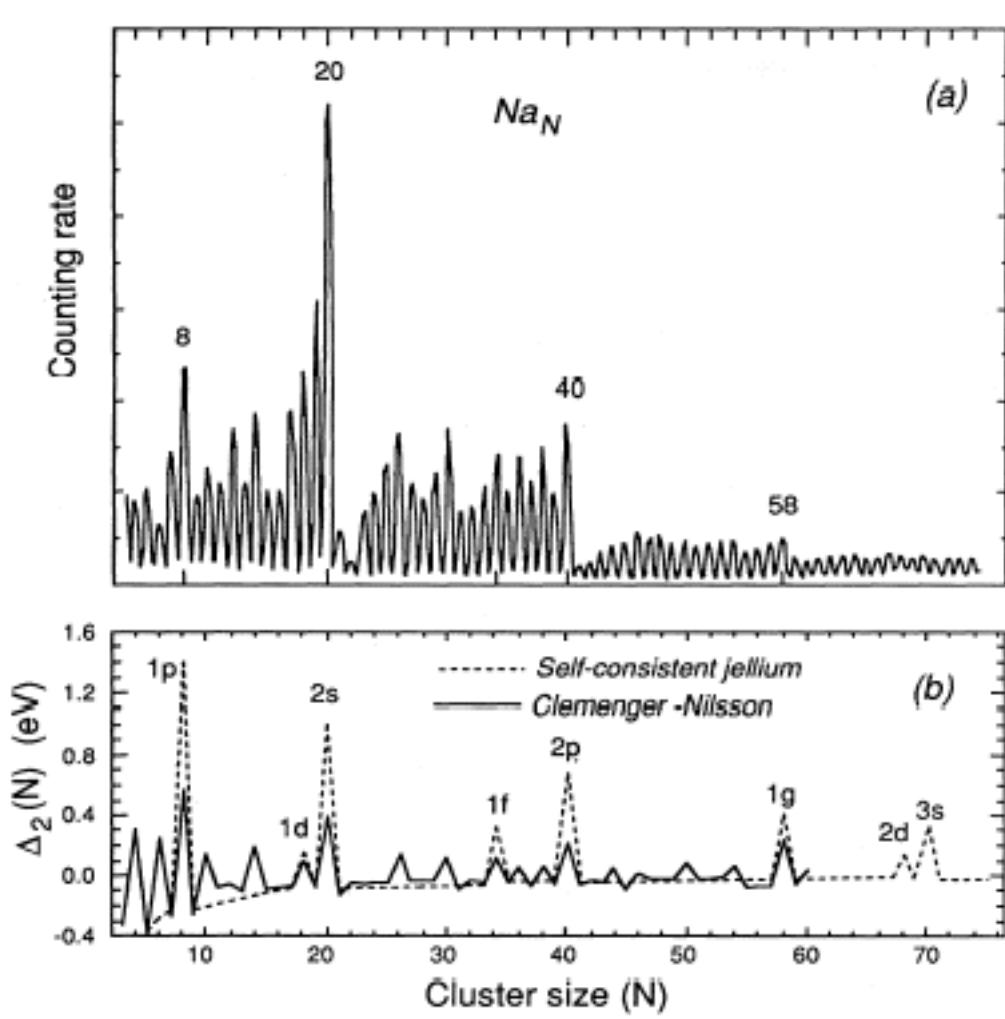


FIG. 1. Sodium cluster abundance spectrum: (a) experimental (after Knight *et al.*, 1984); (b) dashed line, using Woods-Saxon potential (after Knight *et al.*, 1984); solid line, using the ellipsoidal shell (Clemenger-Nilsson) model (after de Heer, Knight, Chou, and Cohen, 1987).

Energy level occupations of spherical jellium model

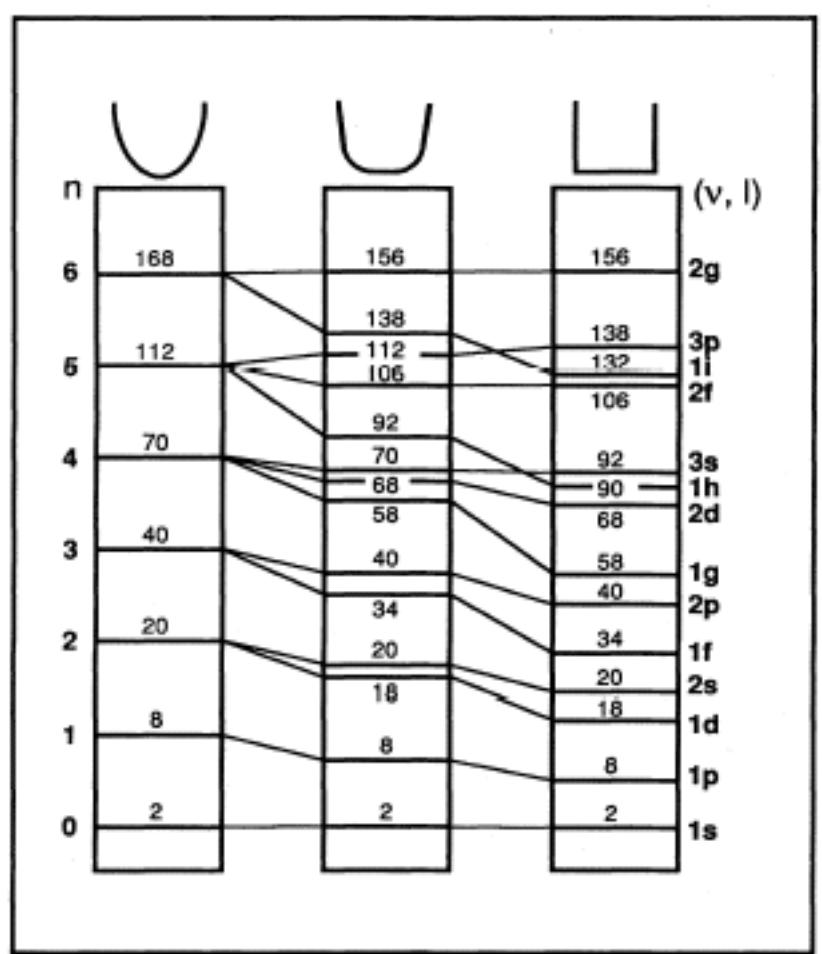


FIG. 2. Energy-level occupations for spherical three-dimensional, harmonic, intermediate, and square-well potentials. After Mayer and Jensen, 1955.

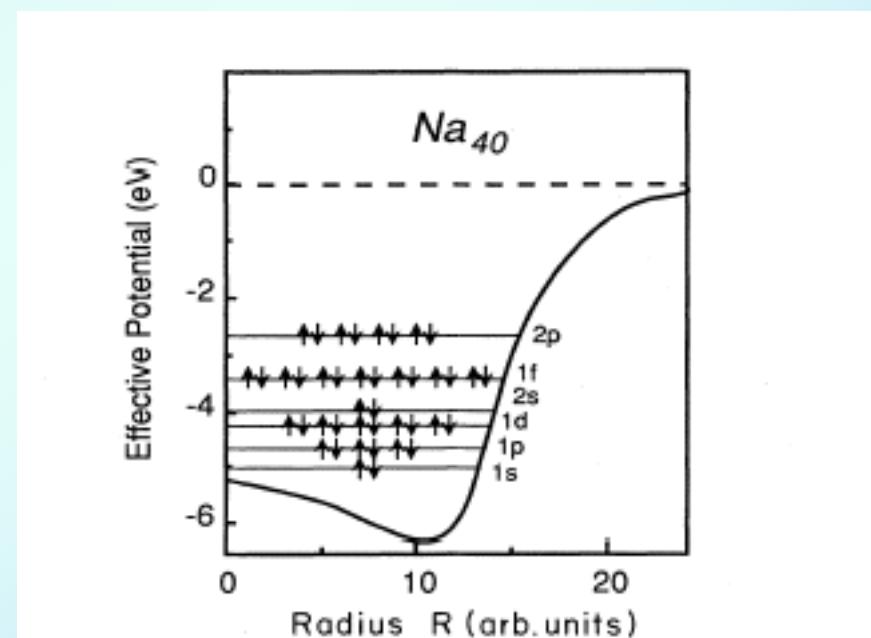


FIG. 3. Self-consistent effective potential of jellium sphere corresponding to Na_{40} with the electron occupation of the energy levels. After Chou *et al.*, 1984.

Cluster shapes according to ellipsoidal shell model

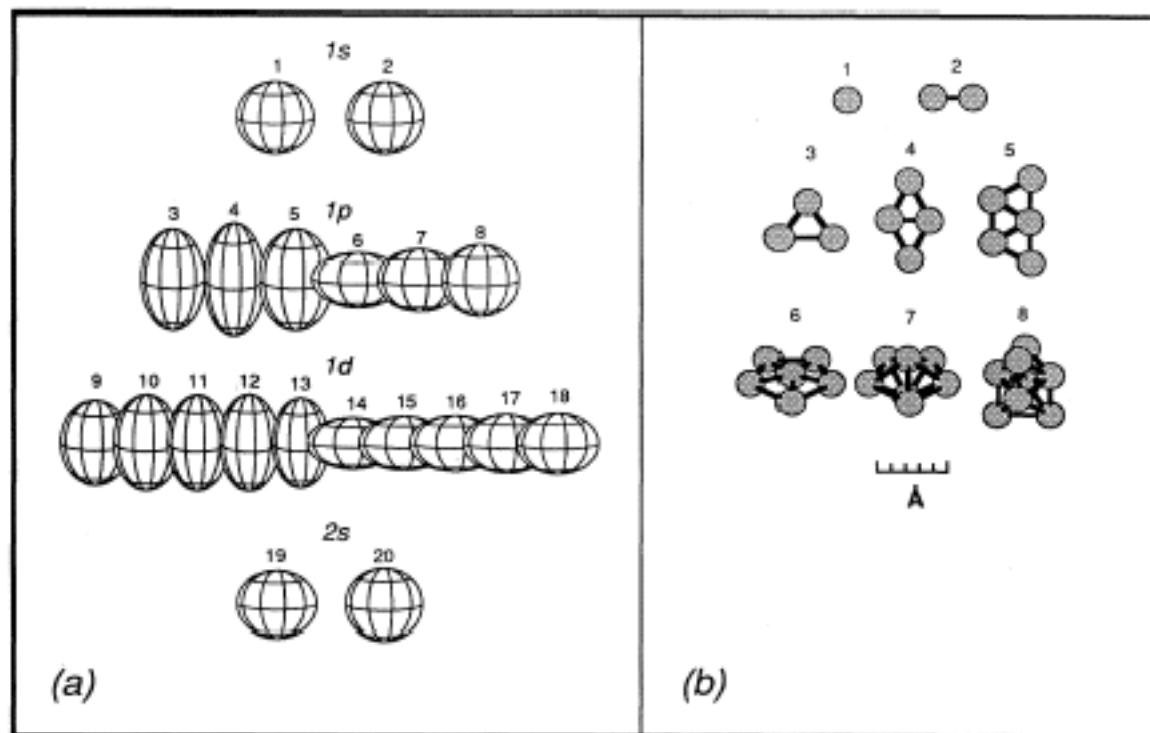


FIG. 4. Cluster shapes (a) according to the ellipsoidal shell model (Clemenger-Nilsson), normalized to the constant volume; (b) from *ab initio* quantum-chemical calculations by Bonacic-Koutecky *et al.* (1988). The midshell change from prolate to oblate predicted in the CN model is also seen in the shapes from *ab initio* calculations.

Single-particle energy levels as a function of anharmonic parameter

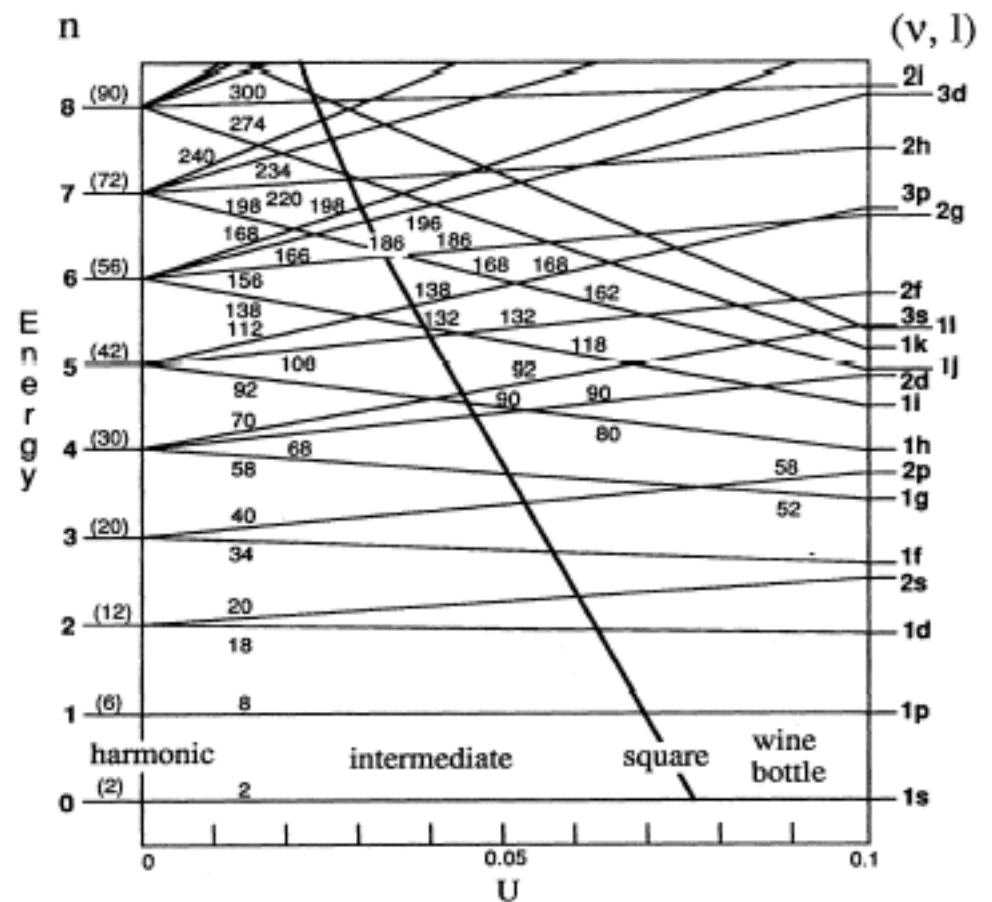


FIG. 52. Single-particle energy levels as a function of the anharmonic distortion parameter U . $U=0$ corresponds to the harmonic oscillator; for positive values of U , the curvature of the bottom of the well is reduced as indicated. The unit of energy is approximately $E_F/N^{1/3}$, as described in the text.

Appendix; Ellipsoidal shell model

Hence the effective single-particle Hamiltonian for electrons with mass m is

$$H = \frac{\mathbf{p}^2}{2m} + \frac{m\omega_0^2 \mathbf{q}^2}{2} - U\hbar\omega_0[l^2 - n(n+3)/6], \quad (\text{A1})$$

The spherical shell model predicts an energy eigenvalue spectrum

$$E_n = \hbar\omega_0\{(n + \frac{3}{2}) - U[l^2 - n(n+3)/6]\}. \quad (\text{A3})$$

The basic assumption of the Clemenger-Nilsson (CN) model (Clemenger, 1985; de Heer, Knight, *et al.*, 1987), as in the Nilsson (1955) model, is that for fixed volume the cluster shape adjusts to minimize the total electronic energy. Ignoring the anharmonic term [i.e., $U=0$, Eq. (A2)] gives the eigenvalues as a function of the shape,

$$E(n_x, n_y, n_z) = \hbar\omega_0 \left[(n_x + \frac{1}{2}) \frac{R_0}{R_x} + (n_y + \frac{1}{2}) \frac{R_0}{R_y} + (n_z + \frac{1}{2}) \frac{R_0}{R_z} \right], \quad (\text{A4})$$

where R_x , R_y , and R_z are the semiaxes of the ellipsoid, and n_x , n_y , and n_z are the harmonic-oscillator quantum

numbers [i.e., for the $1s$ state, $(n_x, n_y, n_z) = (0, 0, 0)$; for the $1p$, they are $(1, 0, 0)$, $(0, 1, 0)$, and $(0, 0, 1)$; for the $n=2$ corresponding to the $1d$, $2s$ levels, they are $(2, 0, 0)$, $(0, 2, 0)$, $(0, 0, 2)$, $(1, 1, 0)$, $(0, 1, 1)$, etc.]. The volume is constrained by $R_x R_y R_z = R_0^3$.

If the shapes are further constrained to spheroids ($R_x = R_y$), then the single-particle energy levels can be expressed in terms of the distortion parameter

$$\eta = 2 \frac{R_z - R_x}{R_z + R_x}. \quad (\text{A5})$$

The total electronic energy can be expressed in terms of the single-particle energies. For the harmonic single-particle potential it can easily be shown that the total electronic energy is related to the sum of the single-particle energies (see, for example, Preston and Bhaduri, 1975, p. 421):

$$E_{\text{tot}}(\eta, N) = \frac{3}{4} \sum E(\eta, n_x, n_y, n_z). \quad (\text{A6})$$

The resulting total electronic energy curve has a minimum at $\eta_0(N)$ and is indicated by a dot at the highest occupied level in the CN diagram. By this procedure we find that the closed-shell clusters, i.e., $2, 8, 20, \dots$, are spherical ($\eta=0$) and that open-shell clusters are either oblate or prolate spheroids. An interesting exception (there are many others) is 34, which in the CN model is ellipsoidal and a subshell closing rather than a spherical shell closing. In addition, 18 is spheroidal when $U=0$, but spherical for $U>0.02$.

Clemenger-Nilsson diagram

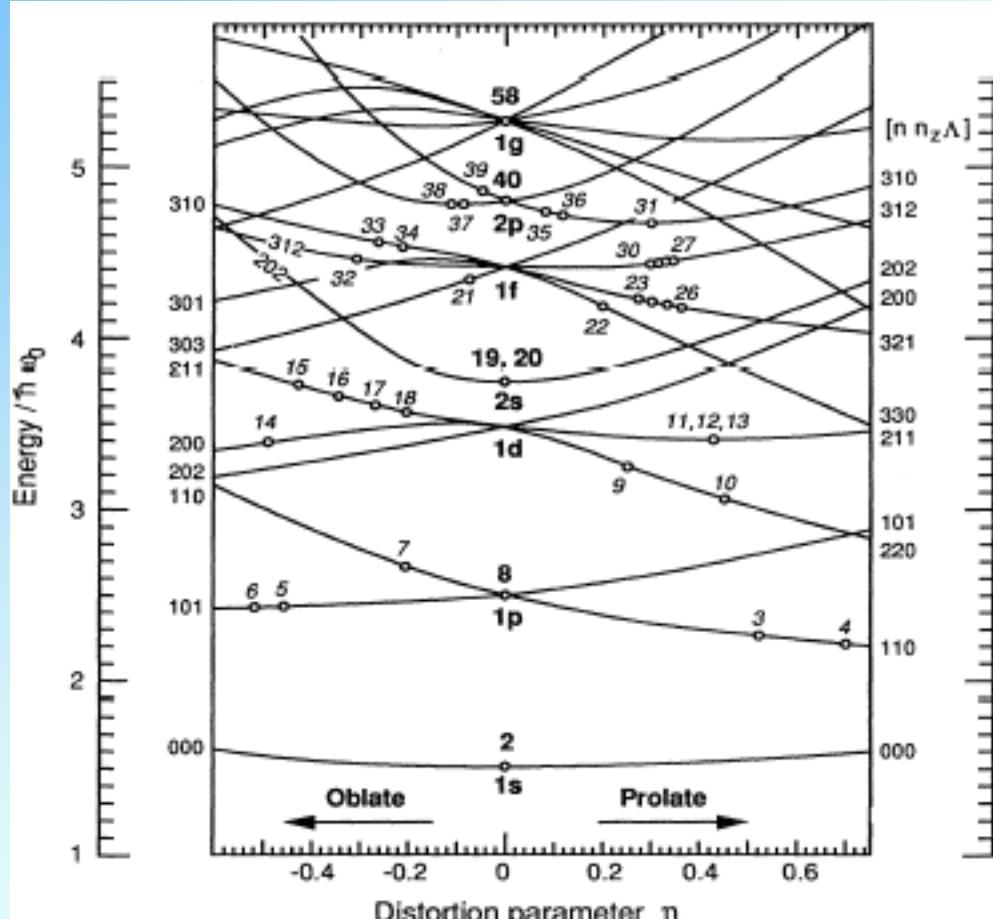
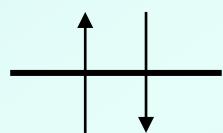
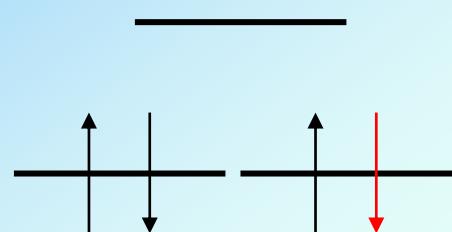
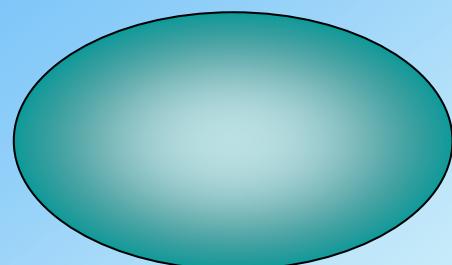
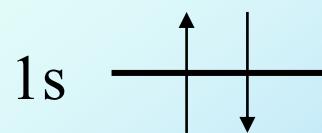
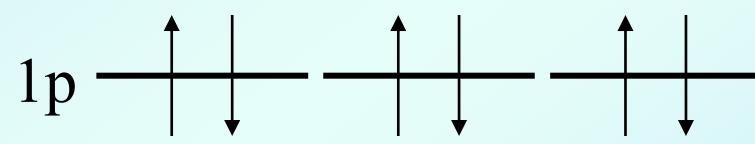
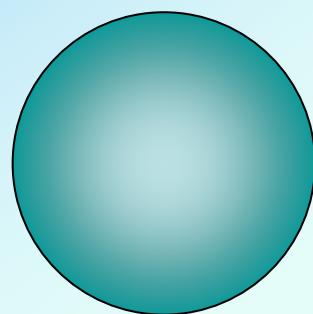


FIG. 53. Clemenger-Nilsson diagram (after Clemenger, 1985). Cluster numbers are positioned at the highest occupied levels and at the equilibrium configuration η . For a detailed description, see the text.

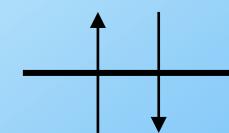
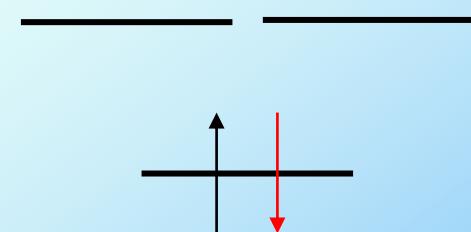
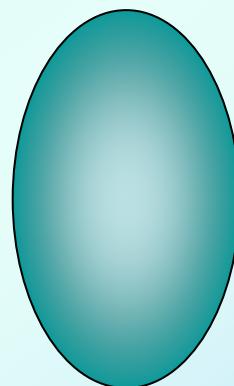
Oblate



Spherical



Prolate



Abundance spectra of copper and silver clusters

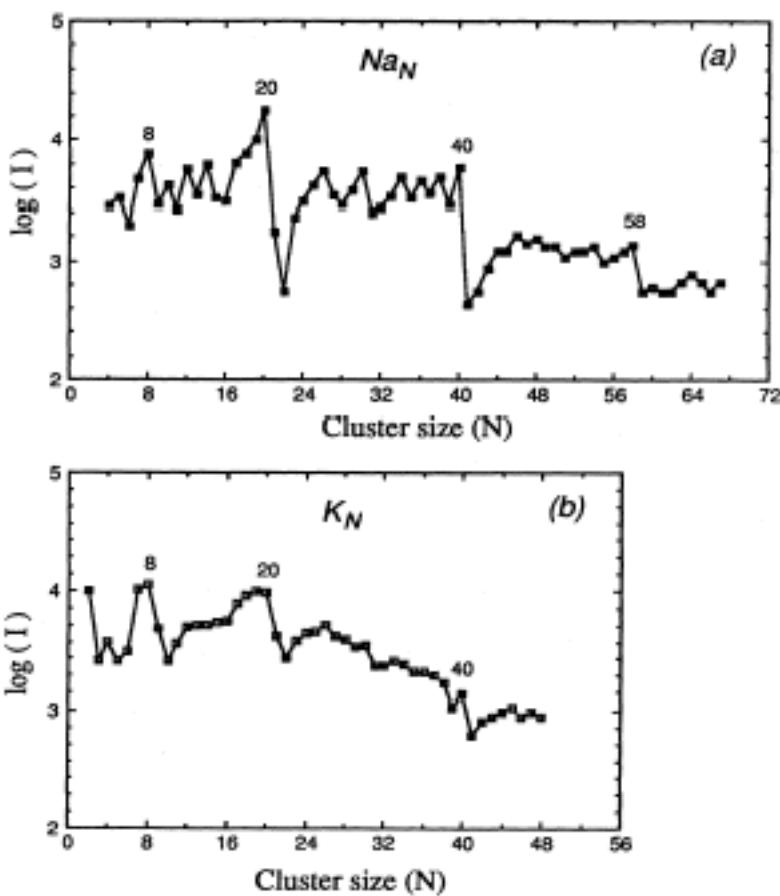


FIG. 15. Alkali abundance spectra: (a) sodium abundance spectrum (from Fig. 1) presented with a logarithmic scale, (b) potassium abundance spectrum (after Knight *et al.*, 1984). Spherical-shell-closing numbers are indicated.

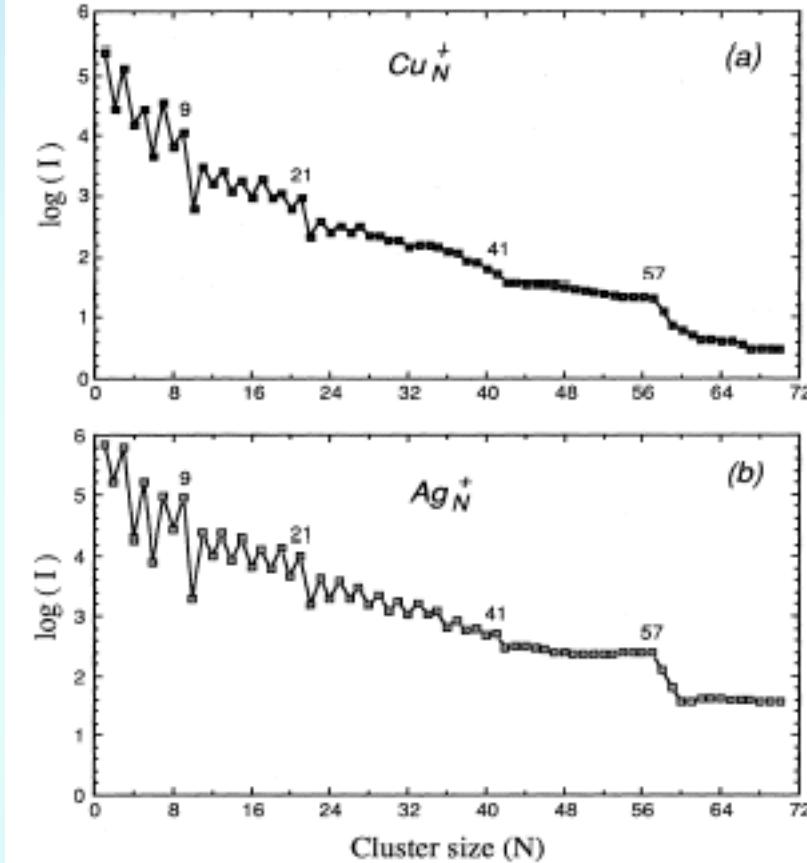


FIG. 17. Logarithmic abundance spectra of (a) copper and (b) silver cluster ions produced in a sputtering source. Numbers correspond to spherical shell closings after Kataeuse *et al.*, 1985.

Evolution to bulk crystal structure

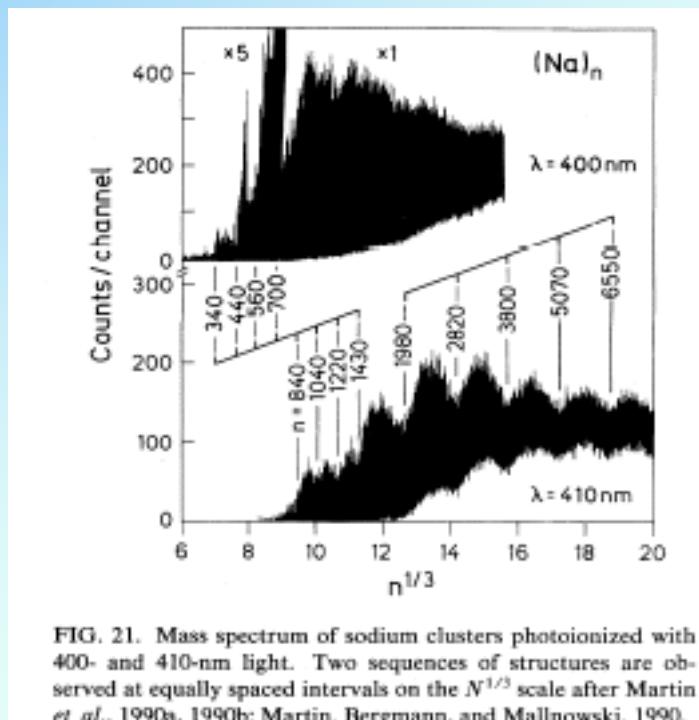


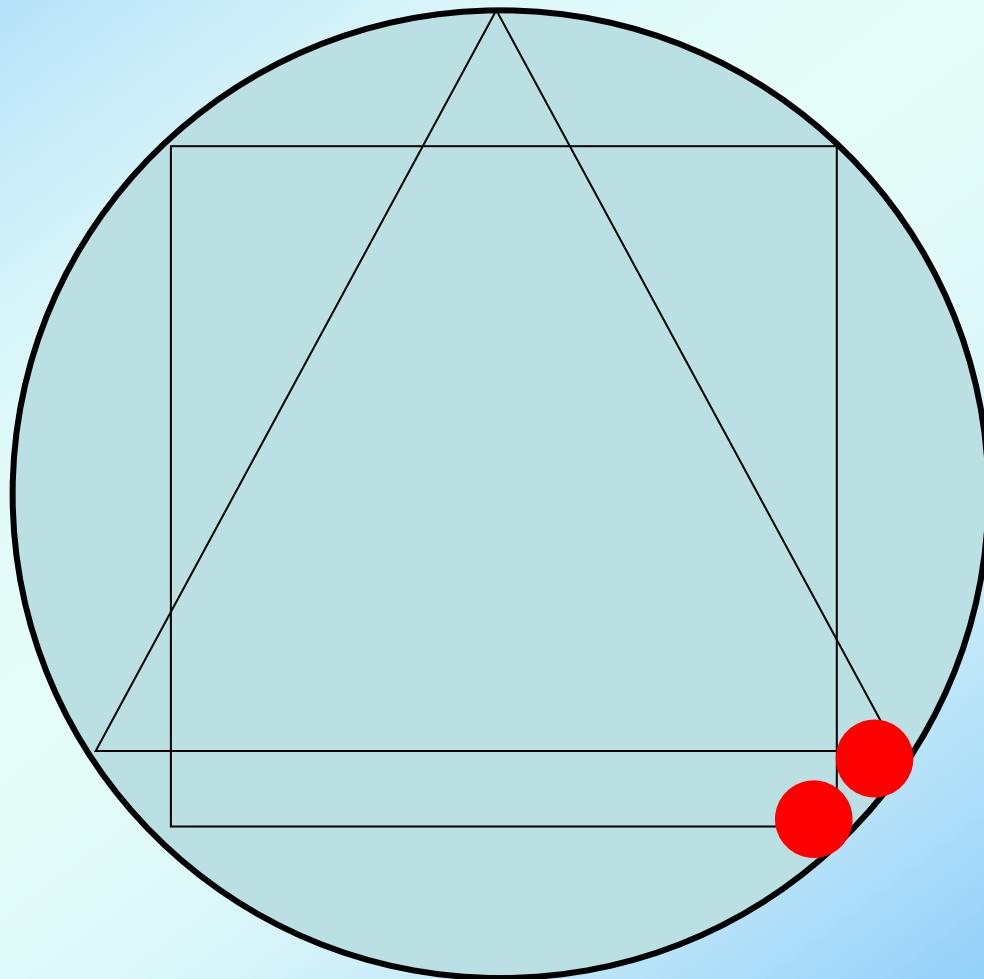
FIG. 21. Mass spectrum of sodium clusters photoionized with 400- and 410-nm light. Two sequences of structures are observed at equally spaced intervals on the $N^{1/3}$ scale after Martin *et al.*, 1990a, 1990b; Martin, Bergmann, and Mallnowski, 1990.

Going much further than this, sodium mass spectra have been recorded up to $N = 25\,000$ by Martin *et al.* (1990a, 1990b; Martin, Bergmann, and Mallnowski, 1990; Martin *et al.*, 1991b) using a gas-aggregation source and laser ionization. Portions of the spectrum, for which two different laser-light wavelengths were used, are shown in Fig. 21. In this case the structure is brought out by using light very close to the ionization threshold, so that the shell structure manifests itself as minima in the mass spectra, since closed-shell clusters have relatively larger ionization potentials. Two series of numbers are identified: 340, 440, 560, 700, 840, 1040, 1220, and 1430, which are spaced as the spherical shell-closing numbers, and a second series for larger clusters, 1980, 2820, 3800, 5070, and 6550, which is continued with 8170, 10200, 12500, 15100, 18000, and 21300, from other spectra, closely following the algorithm

$$N = \frac{1}{3}(10K^3 - 15K^2 + 11K - 3). \quad (4.4)$$

These are not electronic shell-closing numbers, but rather the numbers corresponding to Mackay icosahedra (which are geometrically compact structures analyzed by Mackay, 1962) with K shells of atoms. These results for sodium indicate that at low temperatures the fine structure from electronic shell structure becomes less important compared to geometrical shell structure for sizes near $N = 2000$.

Semi-classical trajectory of electrons



Ionization potentials of alkali clusters

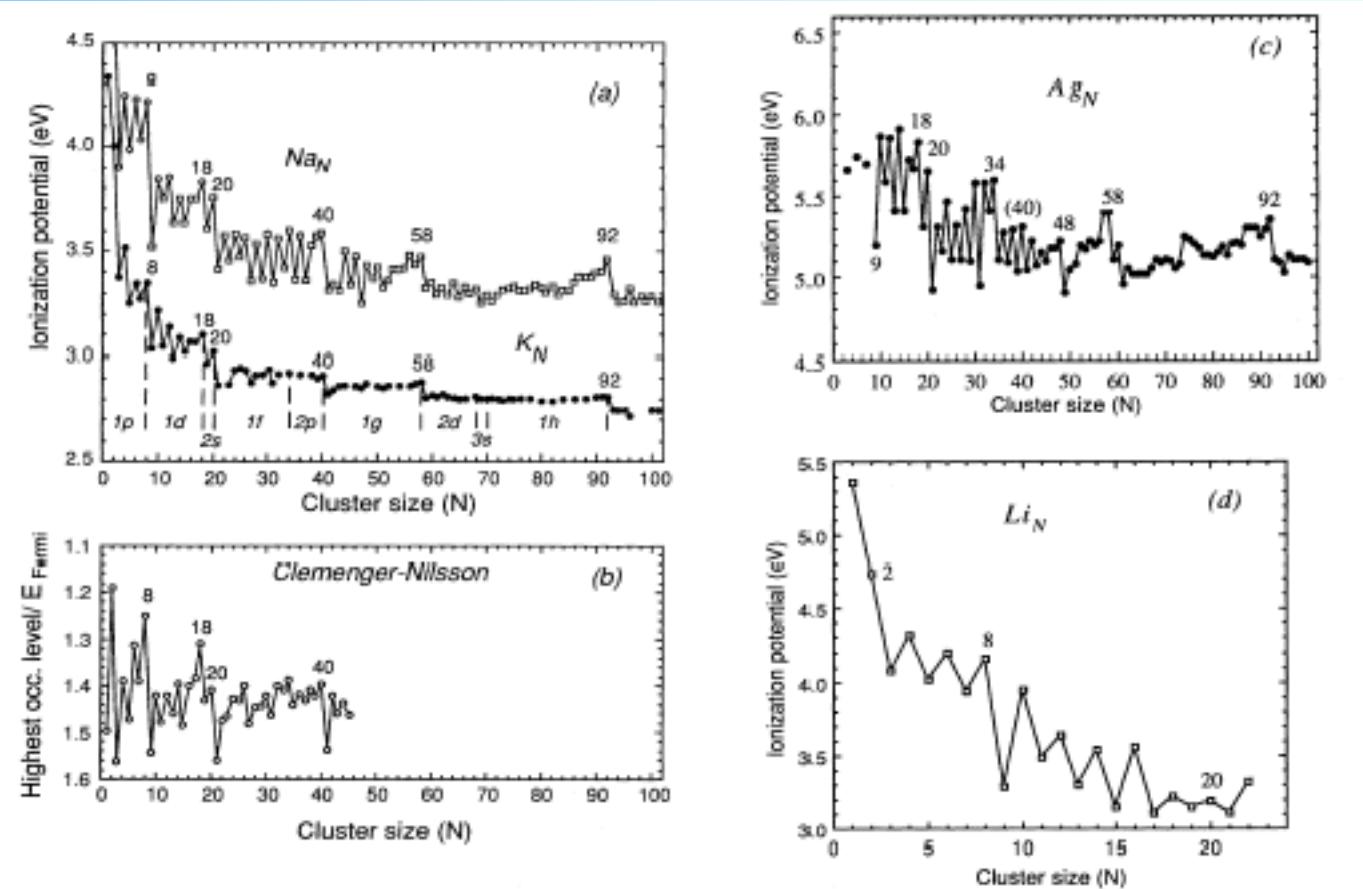


FIG. 26. Ionization potentials of alkali clusters. (a) Ionization potentials of sodium clusters (after Homer *et al.*, 1993, to be published) and of potassium clusters (Saunders *et al.*, 1985; de Heer, Knight, *et al.*, 1987); (b) highest occupied levels in the ellipsoidal shell (Clemenger-Nilsson) model where the electronic kinetic energy is scaled relative to the Fermi energy of the bulk metal; (c) ionization potentials of silver clusters (after Alameddin *et al.*, 1992); (d) ionization potentials of lithium clusters (Dugourd *et al.*, 1992).

Ionization potentials of trivalent clusters

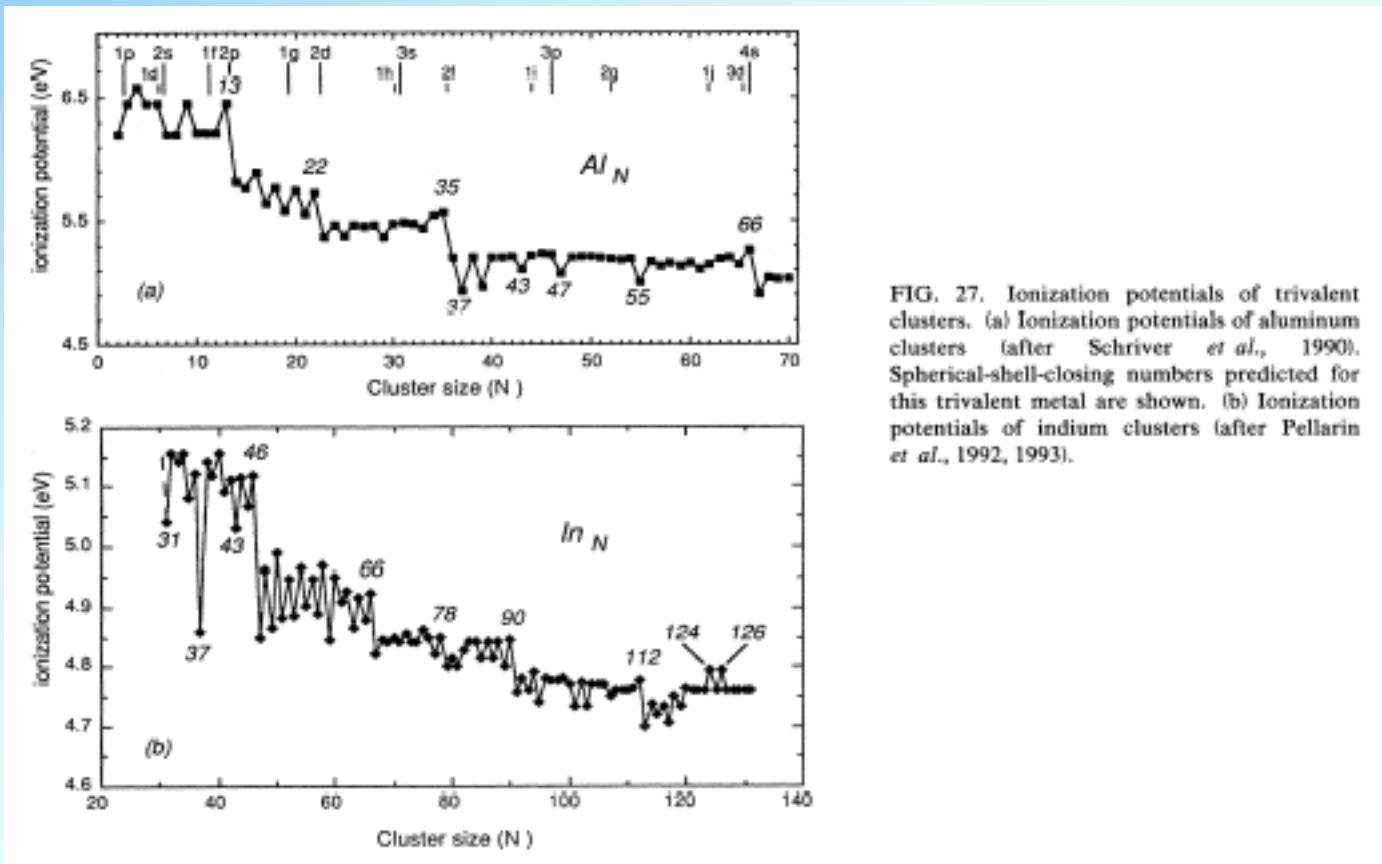


FIG. 27. Ionization potentials of trivalent clusters. (a) Ionization potentials of aluminum clusters (after Schriver *et al.*, 1990). Spherical-shell-closing numbers predicted for this trivalent metal are shown. (b) Ionization potentials of indium clusters (after Pellarin *et al.*, 1992, 1993).

Semiclassical conducting-sphere model

A simple model for the ionization potential is to treat the cluster as a classical conducting sphere. In this model there are two contributions to the energy needed to remove an electron; one is the binding energy of the electron in the metal, i.e., the work function, and the other is the electrostatic contribution, which reflects the electrostatic energy of a small charged system in the ionized state. The electrostatic contribution is found from elementary considerations and is $e^2/2R$, where R is the radius of the sphere; in the infinite limit, the ionization potential approaches the work function. Hence the conducting-sphere model gives for the ionization potential and the electron affinity (EA),

$$\text{IP} = \text{WF} + \alpha e^2/R , \quad (6.1)$$

$$\text{EA} = \text{WF} - \beta e^2/R ,$$

where WF is the polycrystalline bulk work function and $\alpha = \beta = \frac{1}{2}$ in the classical model (Makov *et al.*, 1988; Perdew, 1988; de Heer and Milani, 1990). Note that Eq. (6.1) is most easily derived by assuming a small but nonzero radius for the classical electron and identifying the ionization potential thus derived for infinite R with the work function (de Heer and Milani, 1990).

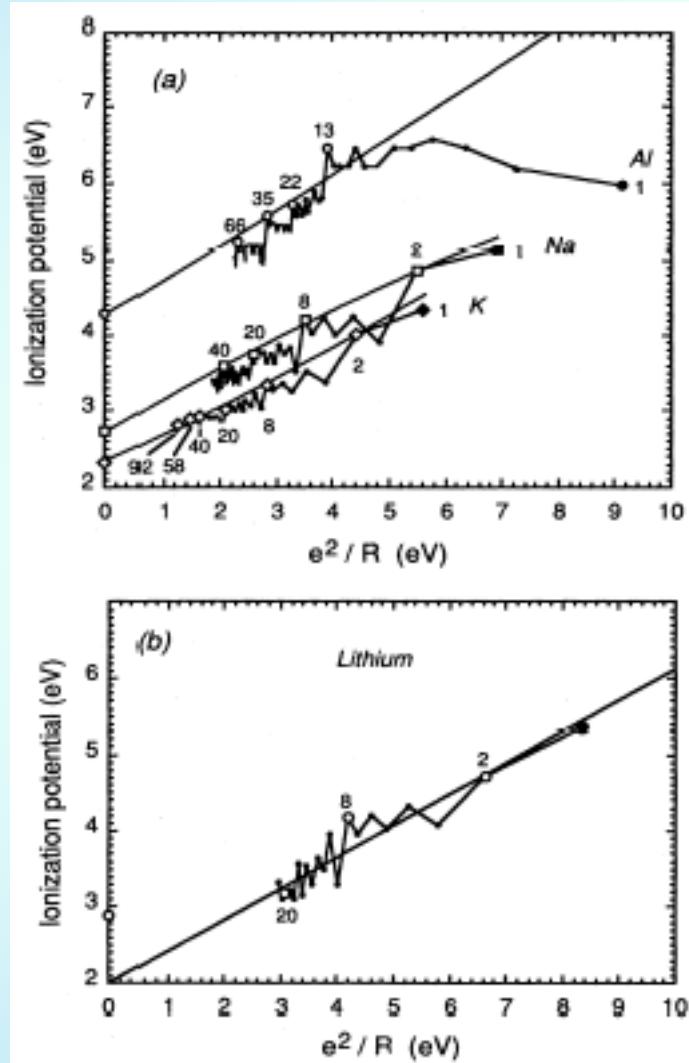
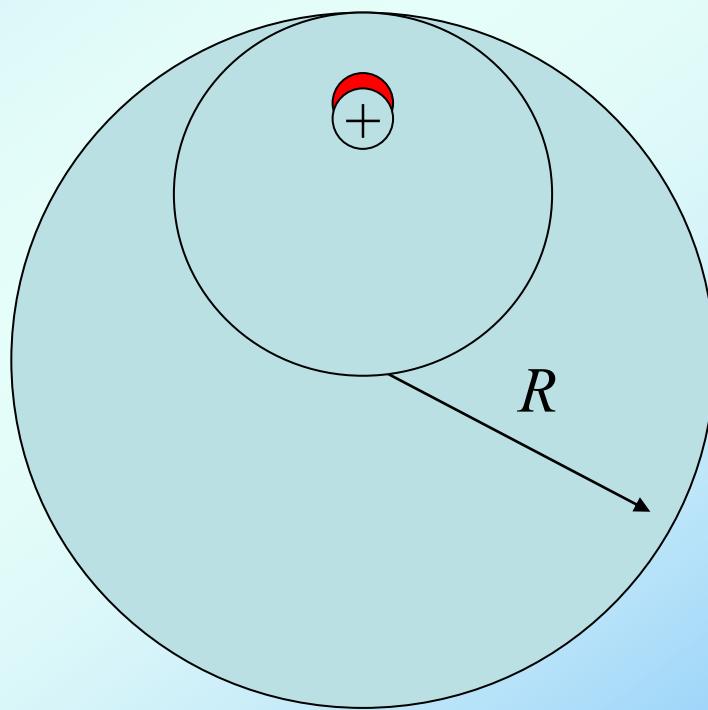
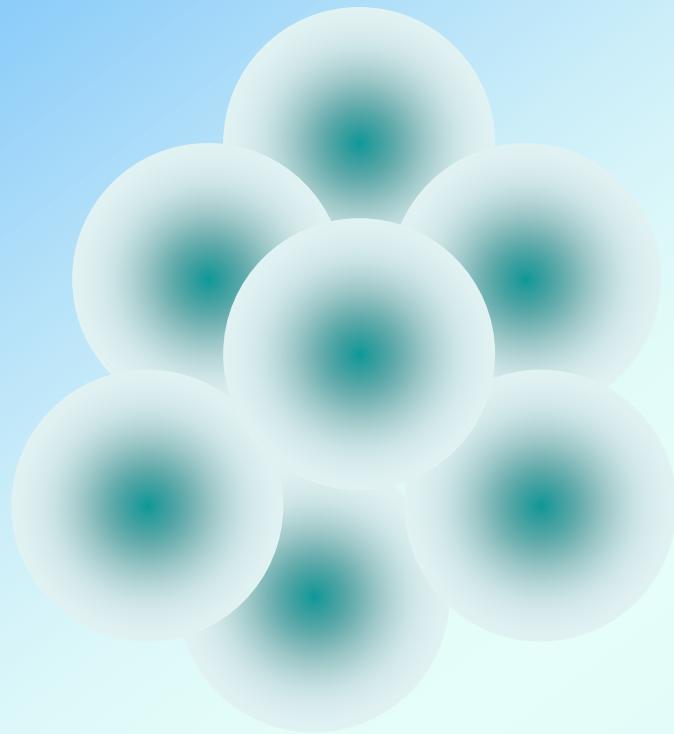


FIG. 28. Experimental ionization potentials (a) for Na, K, and Al clusters plotted against e^2/R , where R is the classical cluster radius. Lines are parabolic fits to the closed-shell clusters and the bulk work function. The fit parameters are given in the text. (b) for lithium clusters, plotted as in (a).

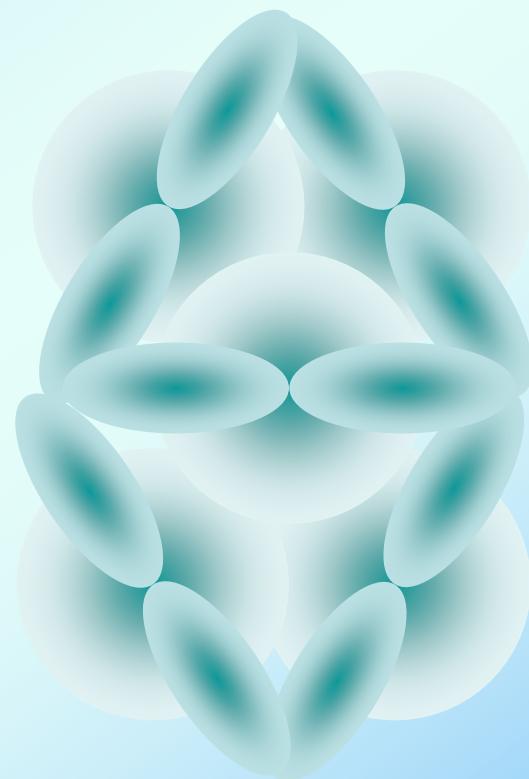
Homogenous electron drop



Alkali metal
s orbital



Alminum
s, p orbital



Metallic bonding

Covalent bonding at
smaller clster size

Photoelectron spectra of potassium cluster anions

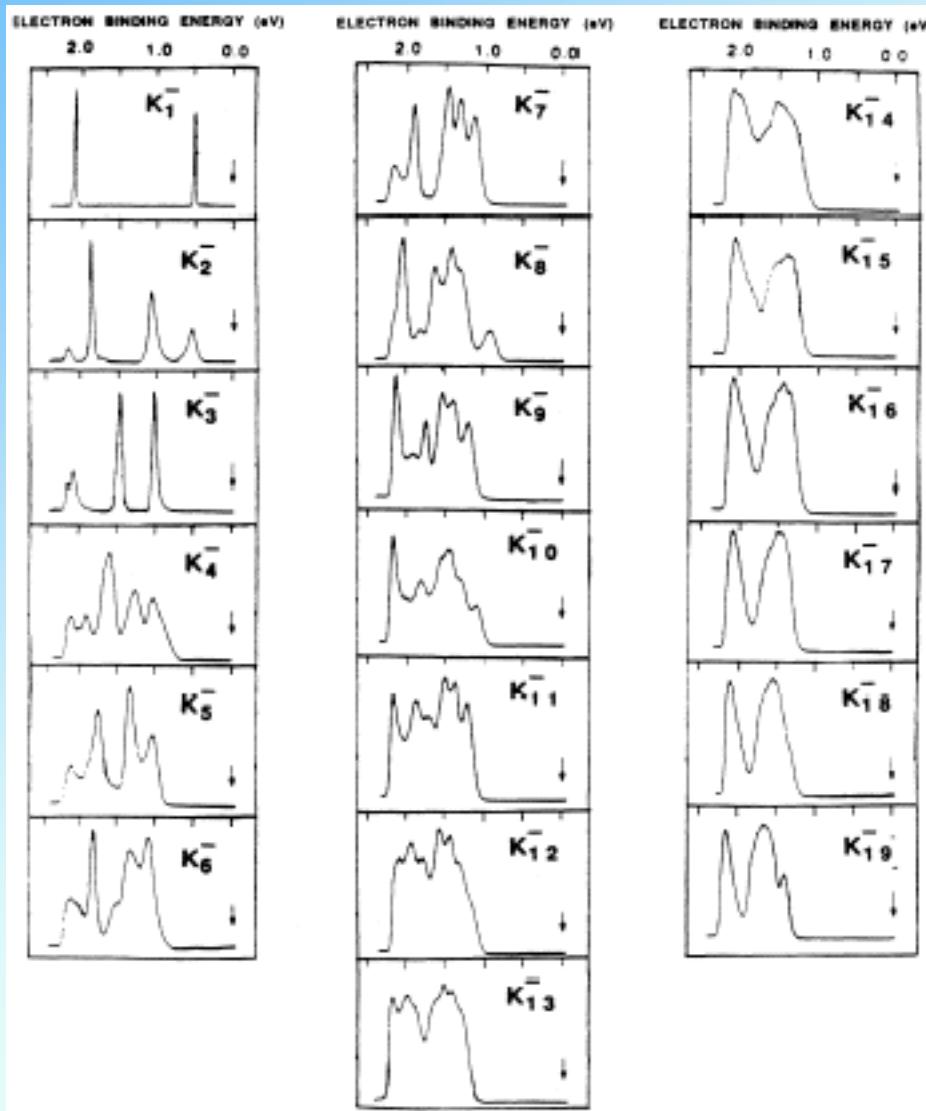


FIG. 32. Photoelectron spectra of potassium cluster anions. After Eaton *et al.*, 1992.

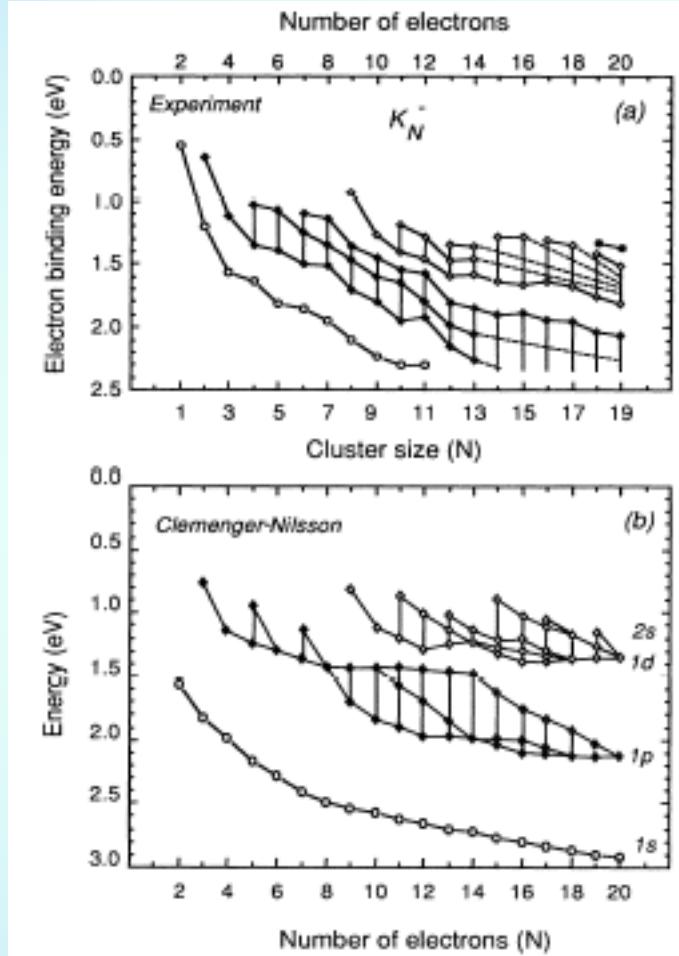


FIG. 33. Systematics of electron binding energies: (a) Experimental photoelectron peaks from Figs. 31 and 32. For $N > 13$ the peaks merge into two bands. Solid lines between clusters follow the measured peaks; vertical lines indicate the bands. (b) Calculated highest occupied orbitals from the ellipsoidal shell (Clemenger-Nilsson) model; note the correspondence to (a) (see also Fig. 5).

Electron affinities

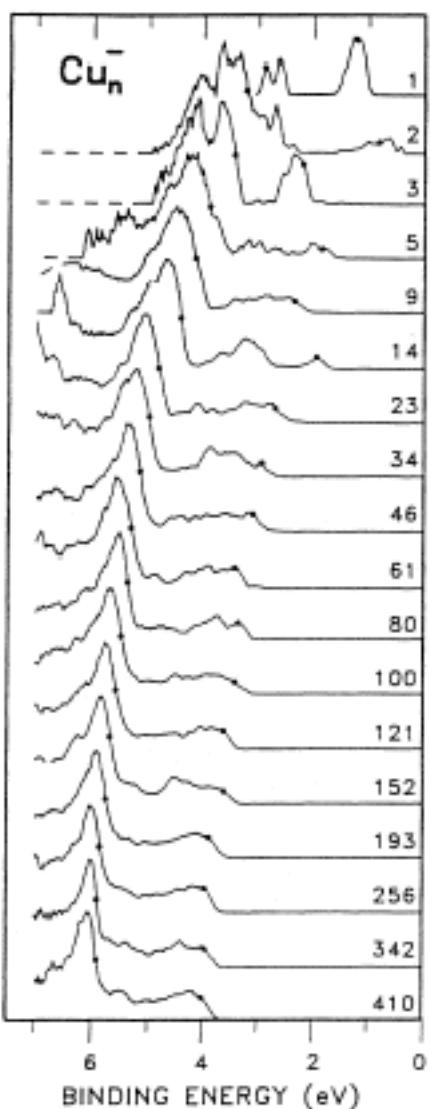


FIG. 34. Photoelectron spectra of copper anionic cluster. Dots indicate the positions of the highest levels correspondin to the two bands. The spectrum of Cu_{410}^- closely resembles the bulk. After Chesnovsky *et al.*, 1990.

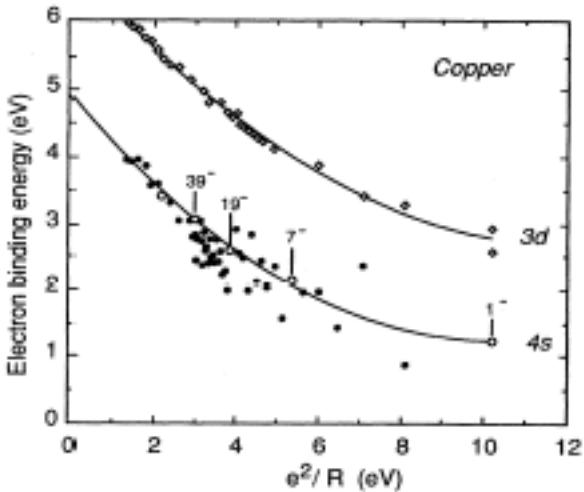


FIG. 38. Electron affinities of Cu_N (i.e., of the 4s electrons) and the binding energies of the top of the 3d band plotted against $1/R$. The 3s electrons show shell structure, whereas the 3d electrons do not. Lines correspond to parabolic fits; the fitting parameters are given in the text. The two points for the 3d electrons of Cu^- correspond to the $2D^{3/2}$ and $2D^{1/2}$ states.

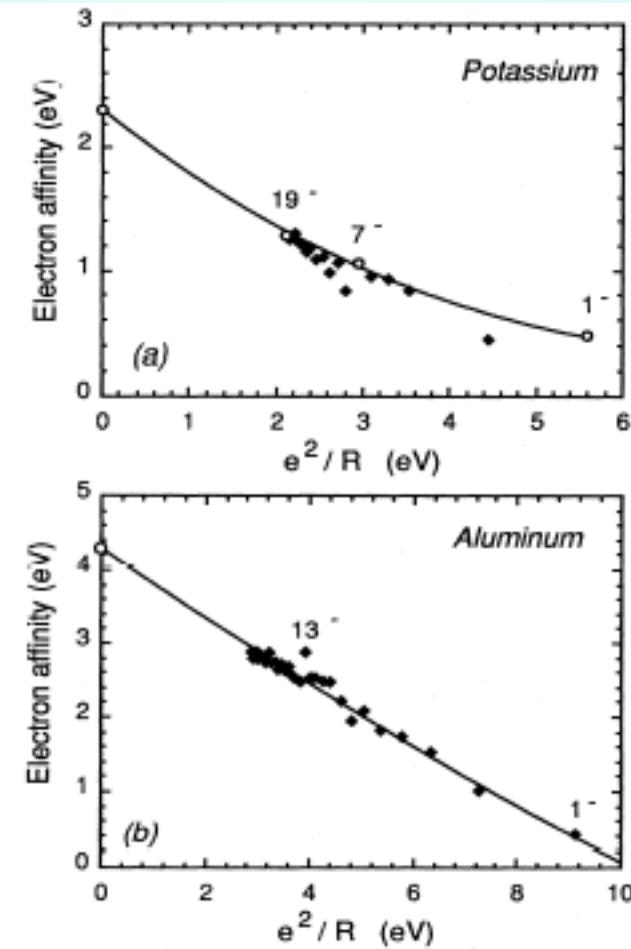
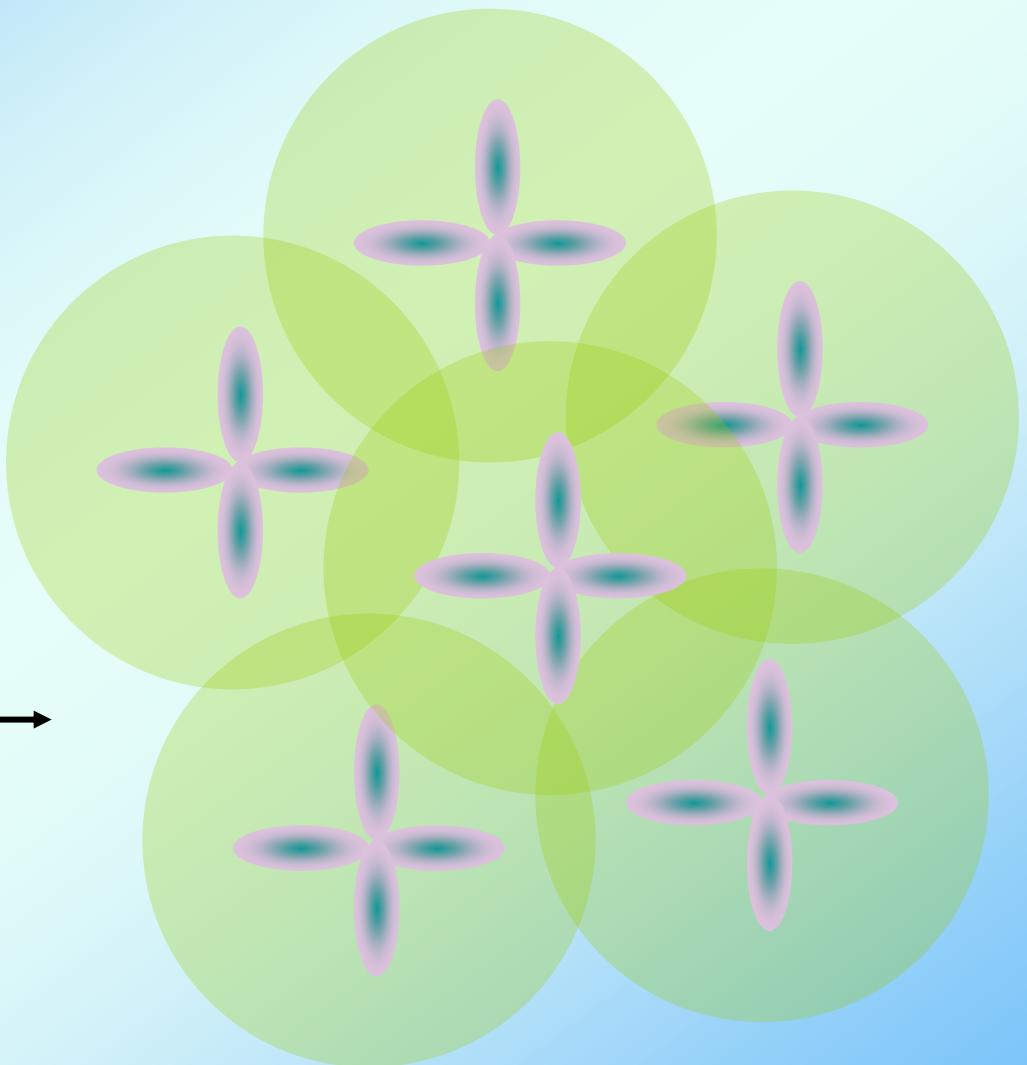
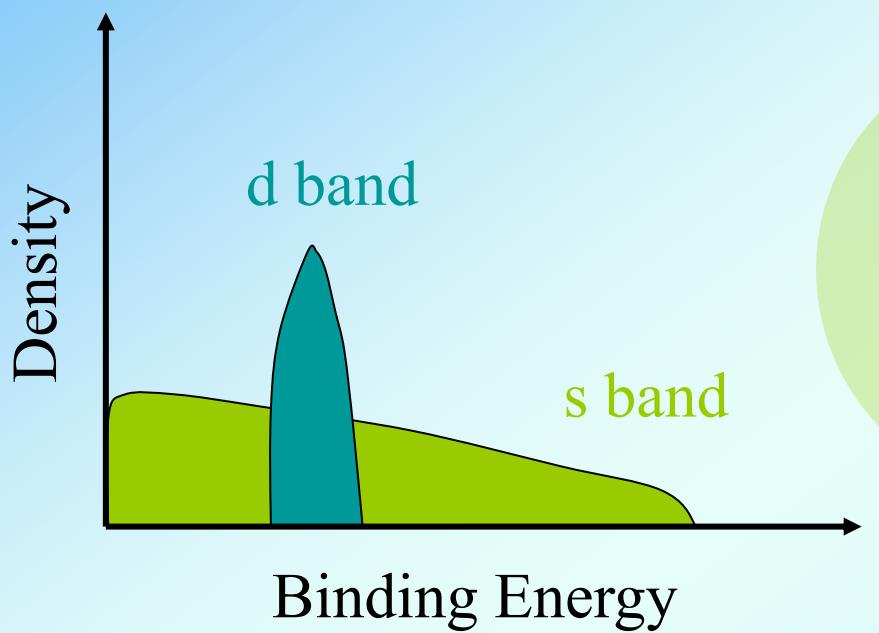


FIG. 37. Electron affinities of (a) K_N and (b) Al_N , plotted against $1/R$. Lines correspond to parabolic fits; the fitting parameters are given in the text.



Jahn-Teller effect in alkali trimers

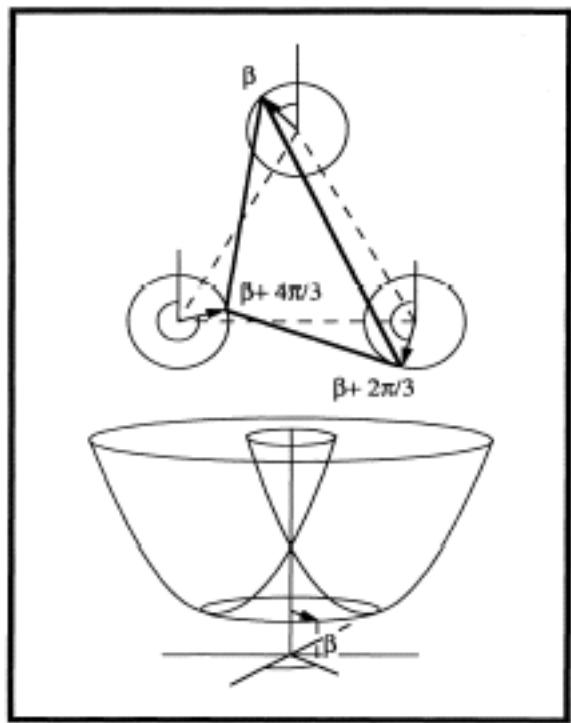
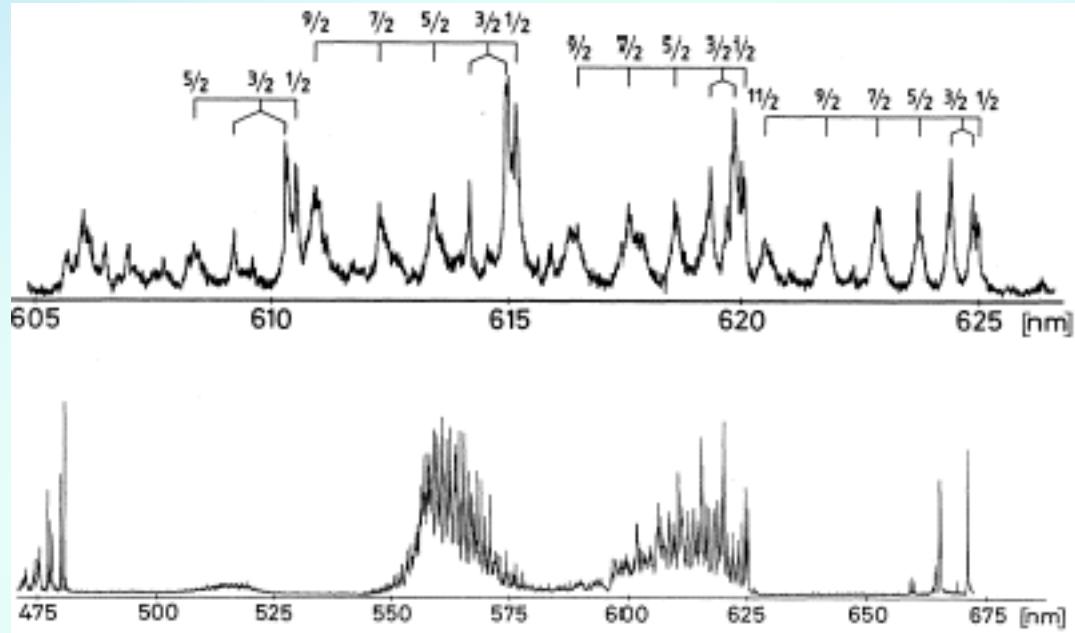
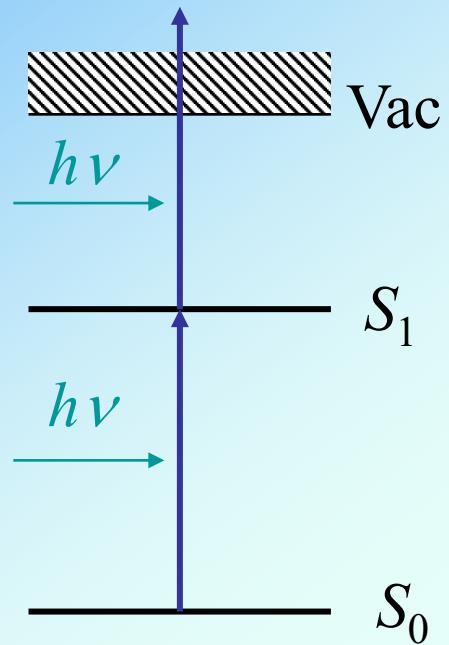


FIG. 39. First-order Born-Oppenheimer surface for alkali trimers, showing the Jahn-Teller effect (lower drawing). Upper drawing shows the trimer configuration in real space, where the circles about the equilateral triangle (dashed line) configuration correspond to the bottom of the "moat" of the Born-Oppenheimer surface. Hence the atoms are free to precess in unison (pseudorotate) about the equilateral configuration. In higher order the Born-Oppenheimer surface develops three symmetrically positioned wells in the moat.

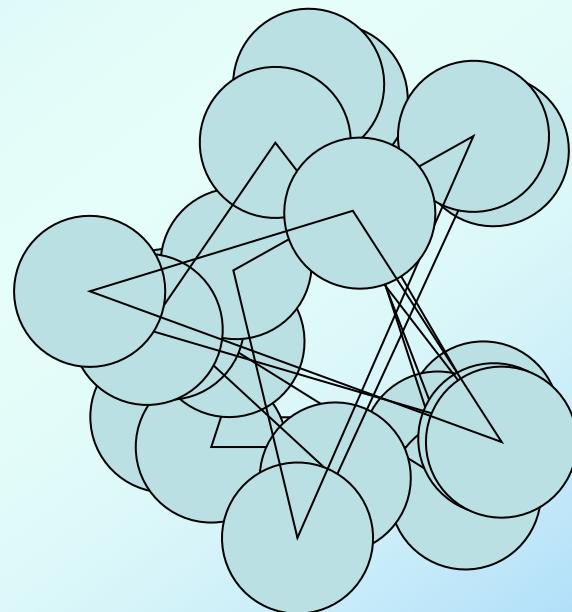


Resonant two-photon ionization spectrum of Na_3 (bottom), and expanded spectrum in 600-625-nm region with pseudorotation-state labels j (top).

Resonant two-photon Ionization



Pseudo rotation



Surface plasma resonance in metal clusters

Following de Heer, Selby, *et al.* (1987), we use the Drude model (Ashcroft and Mermin, 1975) as a starting point for the dynamic polarizabilities of very small metal spheres. Applying a uniform electric field induces a dipole, which in this approximation is described as a small uniform displacement of the electronic cloud to cancel the internal electric fields. In the static limit this displacement is $d = \alpha E$, where α is the polarizability (Sec. IV). The model is easily extended for oscillating fields and, among other things, predicts a resonance at ω_M :

$$\omega_M^2 = \frac{Q^2}{M_N \alpha} = \frac{Ne^2}{M_1 R^3}, \quad (8.3)$$

where Q and M_N are the total charge and mass of the valence electrons, M_1 the atomic mass, R the cluster radius (see below), and α is assumed to be independent of the frequency. The right-hand expression is valid for monovalent metals. For brevity this collective excitation will be called the surface plasmon, conforming with current usage.

If the electronic motion is resistively damped in one way or another, then the surface plasmon energy is dissipated in the cluster, leading to a broadening of the resonance. Assuming that the collective mode accounts for all the dipole oscillator strength of the cluster (in fact, this is already implicit in the derivation of ω above), we can give the photoabsorption cross section by

$$\sigma = \frac{4\pi Ne^2}{3m_e c} \frac{\omega^2 \Gamma}{(\omega^2 - \omega_M^2)^2 + (\omega \Gamma)^2}, \quad (8.4)$$

where N is the number of electrons and m_e the electron mass.

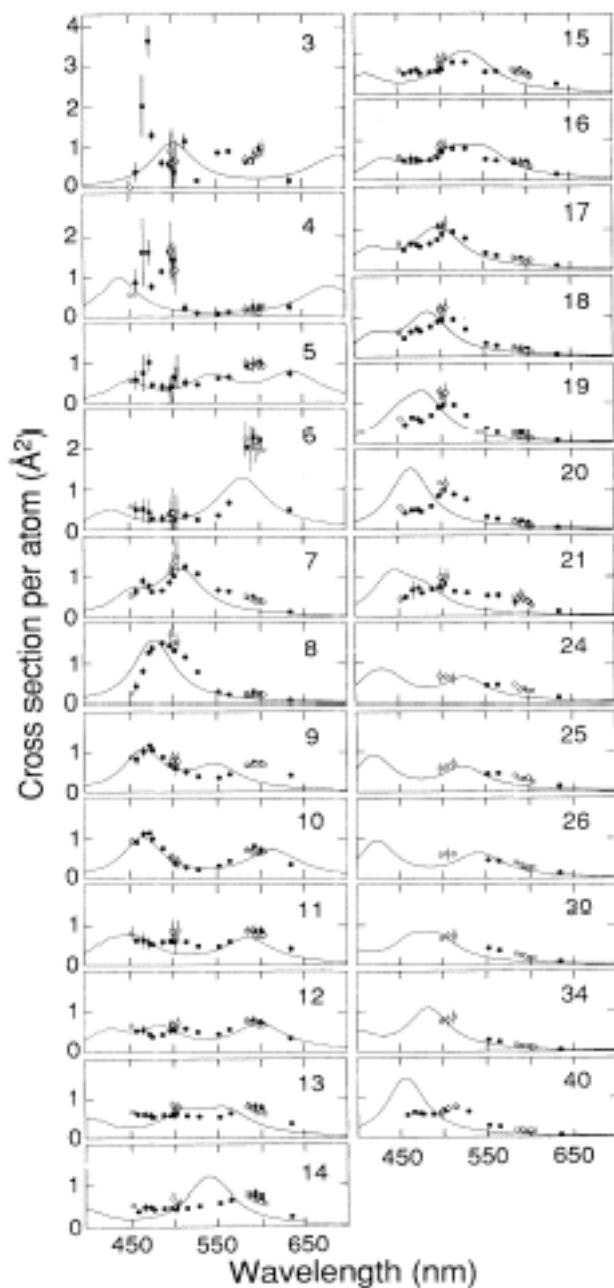


FIG. 43. Photoabsorption cross sections of sodium clusters (after Selby *et al.*, 1991). Continuous curves are calculated using the basic model.

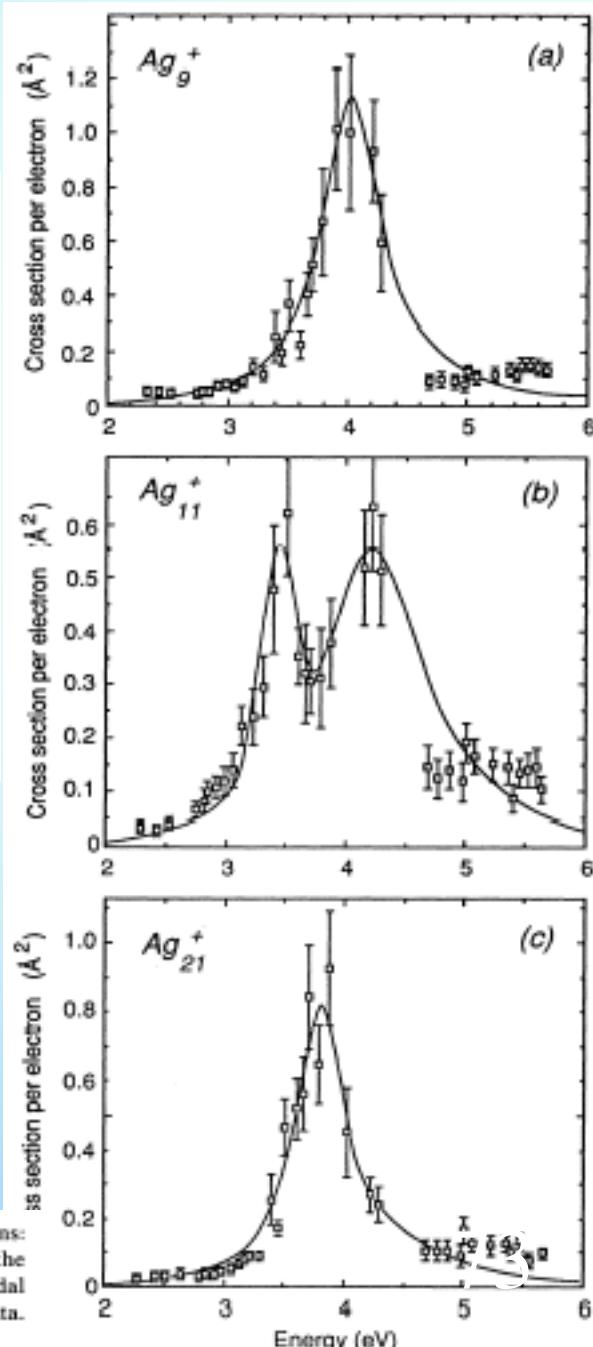
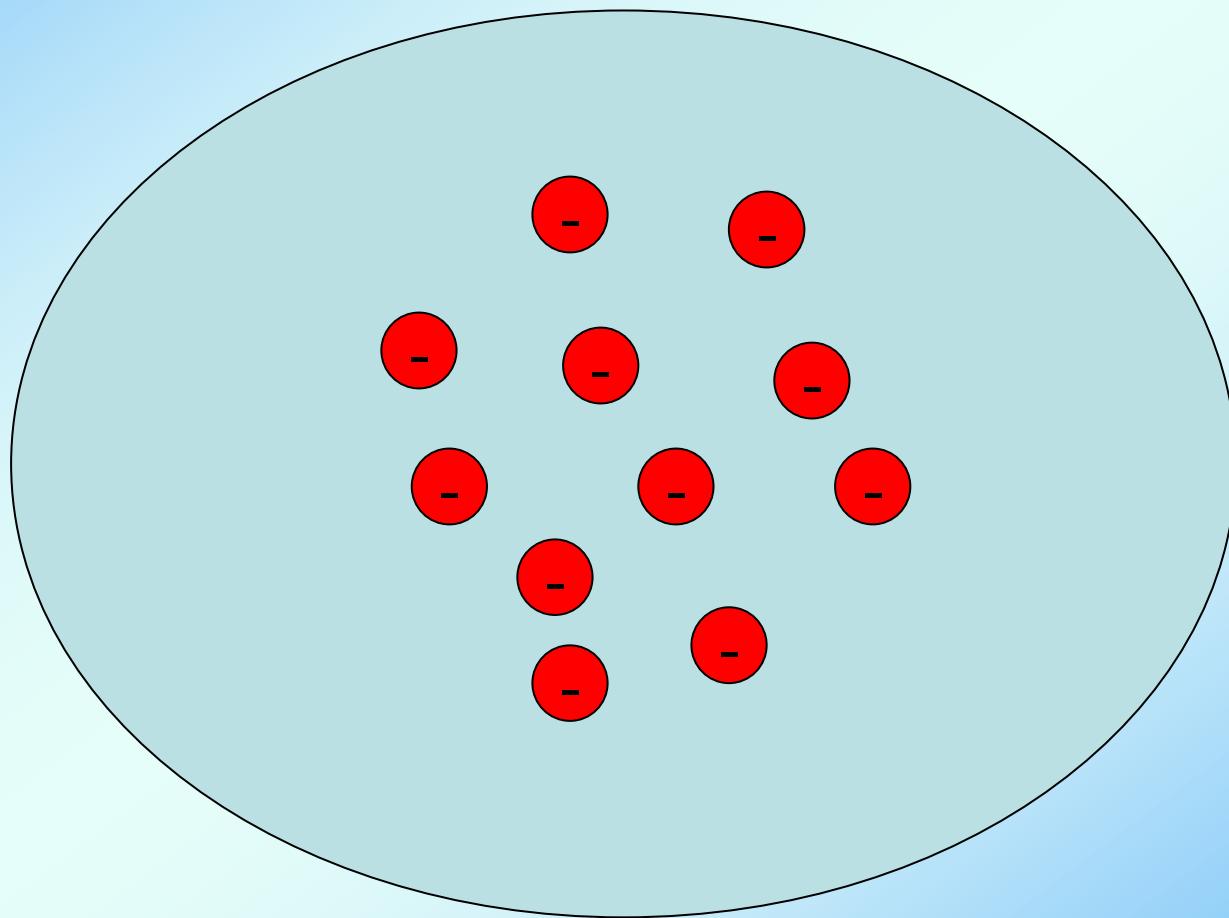


FIG. 48. Photoabsorption cross sections of silver cluster ions: (a) and (c) are closed-shell clusters and have single peaks; (b) the open-shell Ag_{11}^+ has two peaks, as predicted in the ellipsoidal shell (Clemenger-Nilsson) model. Solid lines are fits to the data. After Tiggesbäumer *et al.*, 1992.

Collective motion of electrons induced by electric field



問. アルカリ金属クラスターと原子核との類似性と異質性について、簡単に説明しなさい。

講義内容（予定）

クラスターとは？

1. 金属クラスターの電子構造1；水銀クラスター, 金属－非金属相転移
2. 金属クラスターの電子構造2；アルカリ金属クラスター, 電子殻模型と魔法数, 原子核とクラスターとの類似性と異質性
3. 分子クラスターの反応とダイナミクス； $I_2^-(CO_2)_n$, 光解離と再結合, 微視的な溶媒効果
4. 遷移金属クラスターと気体分子との反応
5. クラスターの衝突反応
6. タンパク質のフォールディング; Levinthalのパラドックス
7. 気相タンパク質イオンの立体構造の変化; イオン移動度の測定
8. 生体分子の質量分析における新技術
9. 孤立状態において生体分子を研究する; Angiotensin Iイオンと気体分子の温度変化によるプロトン移動反応

講義内容（予定）

クラスターとは？

1. 金属クラスターの電子構造1；水銀クラスター, 金属ー非金属相転移
2. 金属クラスターの電子構造2；アルカリ金属クラスター, 電子殻模型と魔法数, 原子核とクラスターとの類似性と異質性
3. 分子クラスターの反応とダイナミクス； $I_2 \cdot (CO_2)_n$, 光解離と再結合, 微視的な溶媒効果
4. 遷移金属クラスターと気体分子との反応
5. クラスターの衝突反応
6. タンパク質のフォールディング; Levingthalのパラドックス
7. 気相タンパク質イオンの立体構造の変化; イオン移動度の測定
8. 生体分子の質量分析における新技術
9. 孤立状態において生体分子を研究する; Angiotensin Iイオンと気体分子の温度変化によるプロトン移動反応

- ♣ 分子クラスターの反応とダイナミクス
光解離と再結合, 微視的な溶媒効果

I_2^- Photodissociation and Recombination Dynamics in Size-Selected $I_2^-(CO_2)_n$ and $I_2^-(OCS)_n$ Cluster Ions

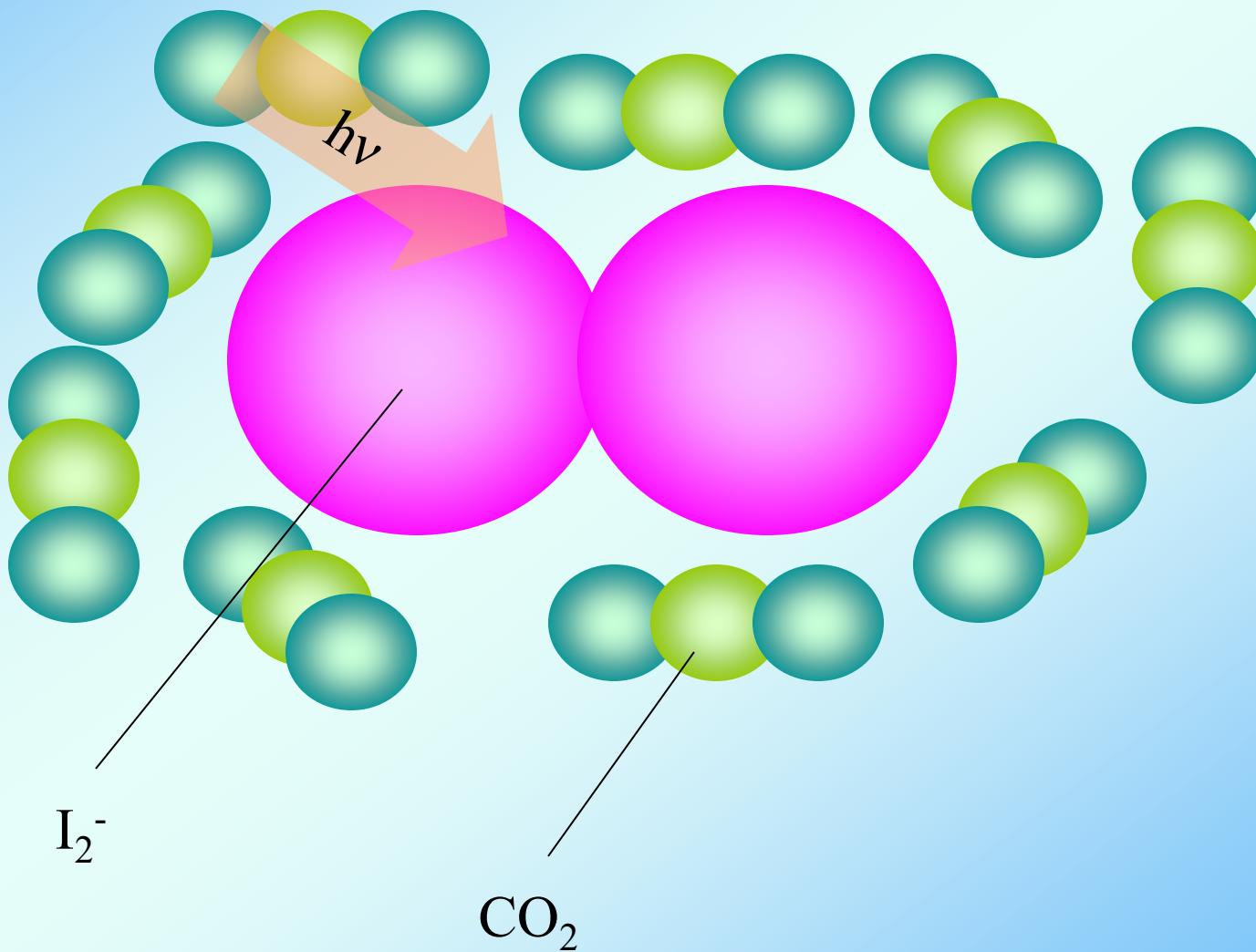
W. C. Lineberger

J. Phys. Chem., 95, 8028 (1991).

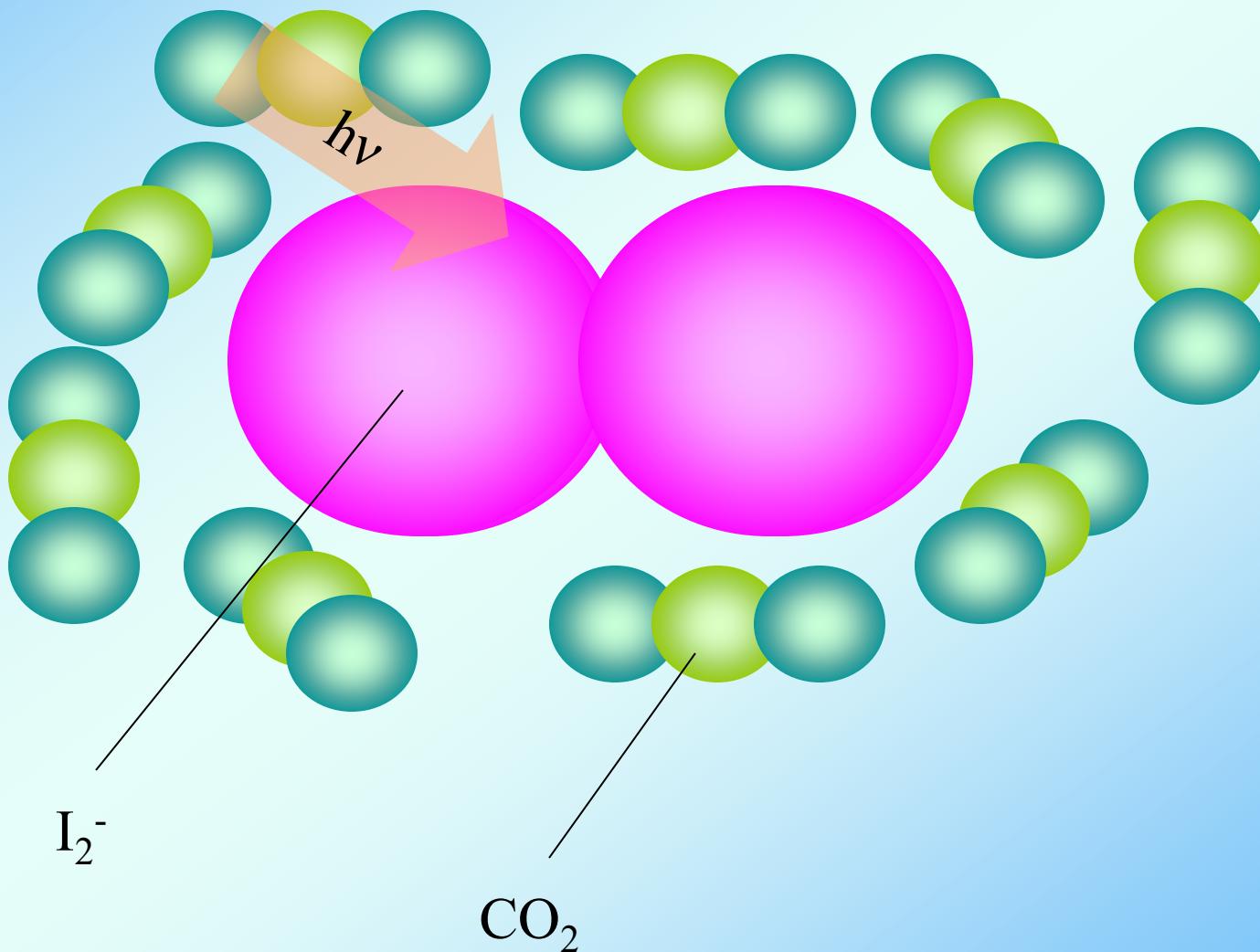
J. Chem. Phys., 99, 8733 (1993).

Phys. Chem. Comm., 5, 165 (2002).

Abstract

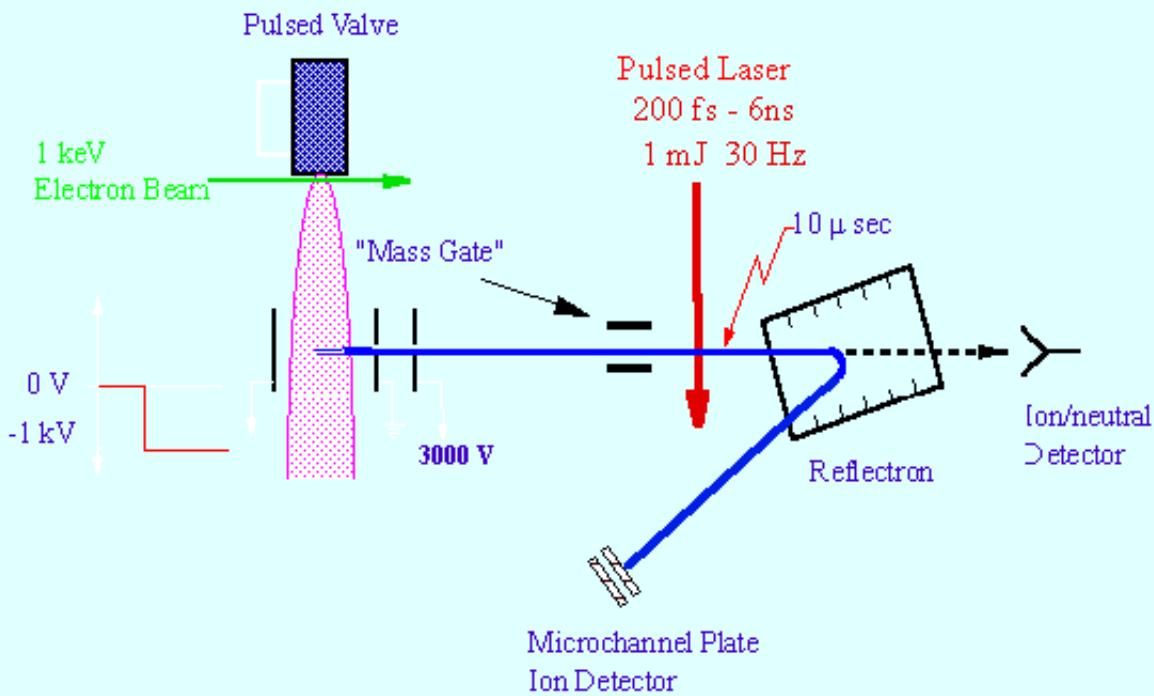


Abstract

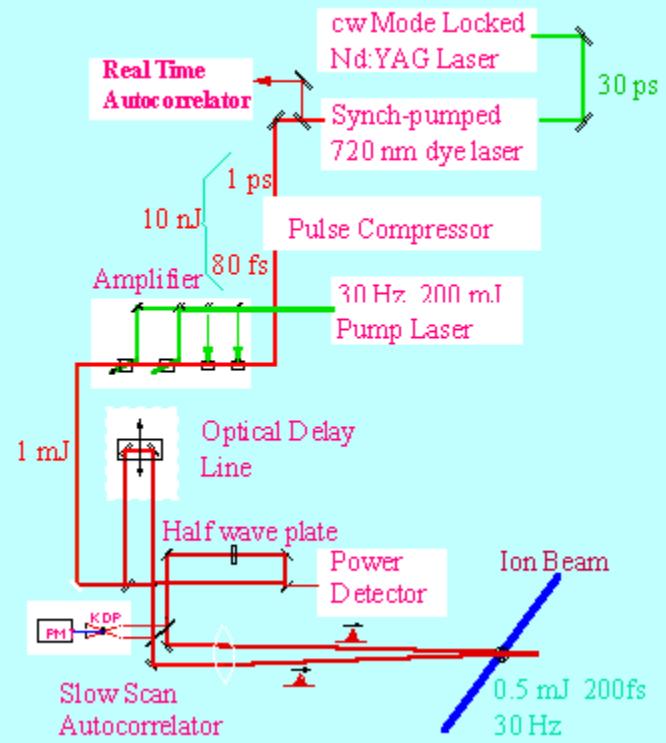


Experimental setup

Cluster Ion Source and Tandem Time of Flight Mass Spectrometer

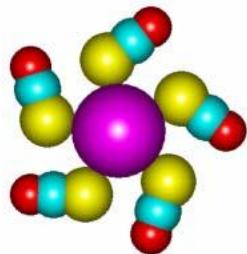
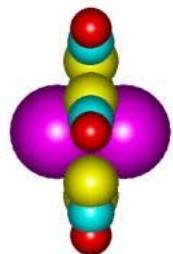


Picosecond Laser System

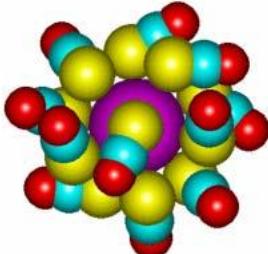
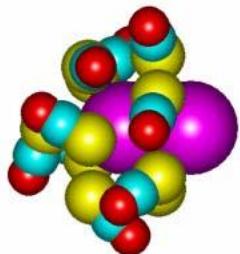


Potential energy curves for I_2^-

(a) $I_2^-(OCS)_5$



(b) $I_2^-(OCS)_{11}$



(c) $I_2^-(OCS)_{17}$

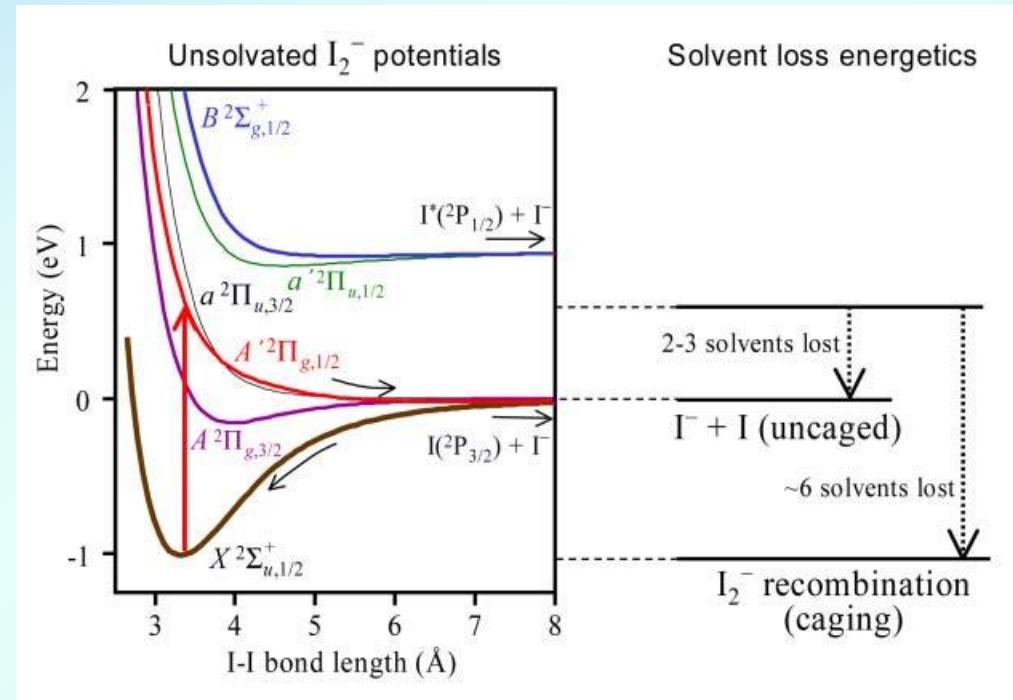
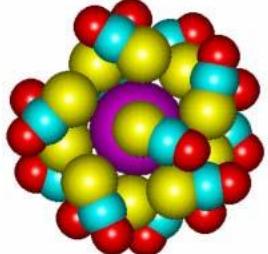
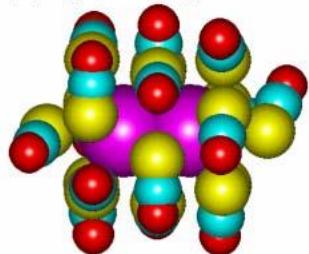


Fig. 3 Potential energy diagram of I_2^- (from ref. 22) and solvent loss energetics in 790 nm experiments on I_2^- (OCS)_n or I_2^- (CO_2)_n.

Fig. 1 Calculated minimum-energy structures of I_2^- (OCS)_n, $n = 5, 11$, and 17 . Each structure is shown from two different angles, viewed perpendicular and along the I_2^- bond (left and right columns, respectively). These structures correspond to the isomers selected out of many nearly isoenergetic solvent configurations. While the general manner of solvent packing around I_2^- is reproduced in all low-energy isomers, local structural details, such as the relative orientation of neighboring OCS molecules, may vary. Adapted from ref. 22.

Photofragmentation Mass Spectra for $I_2^-(CO_2)_n$

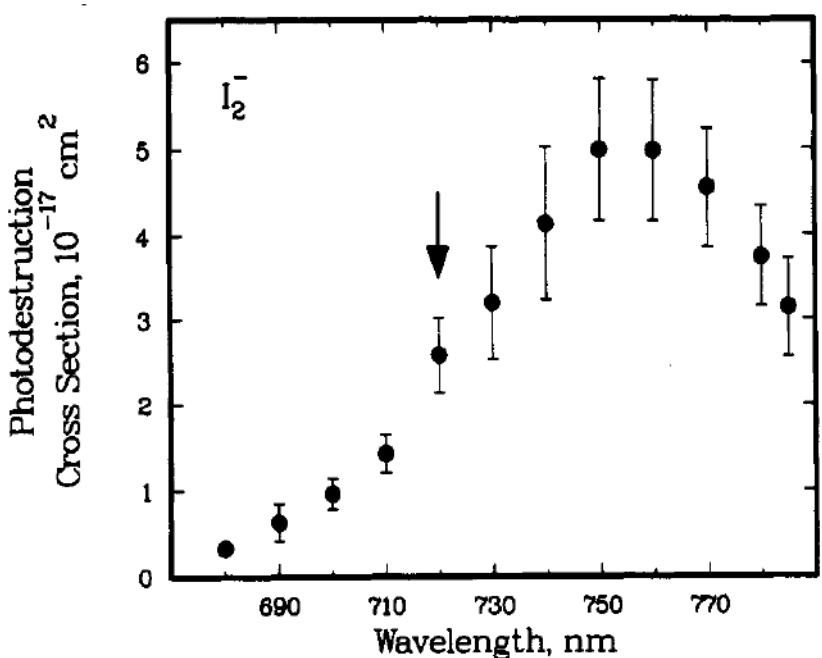


Figure 4. Absolute I_2^- photodestruction cross section. The error limits represent one standard deviation statistical fluctuation on the mean. The uncertainty in the absolute cross section is a factor of 2. The vertical arrow indicates the wavelength (720 nm) at which cross-section measurements for $I_2^-(CO_2)_n$ cluster ions were performed. See text for details.

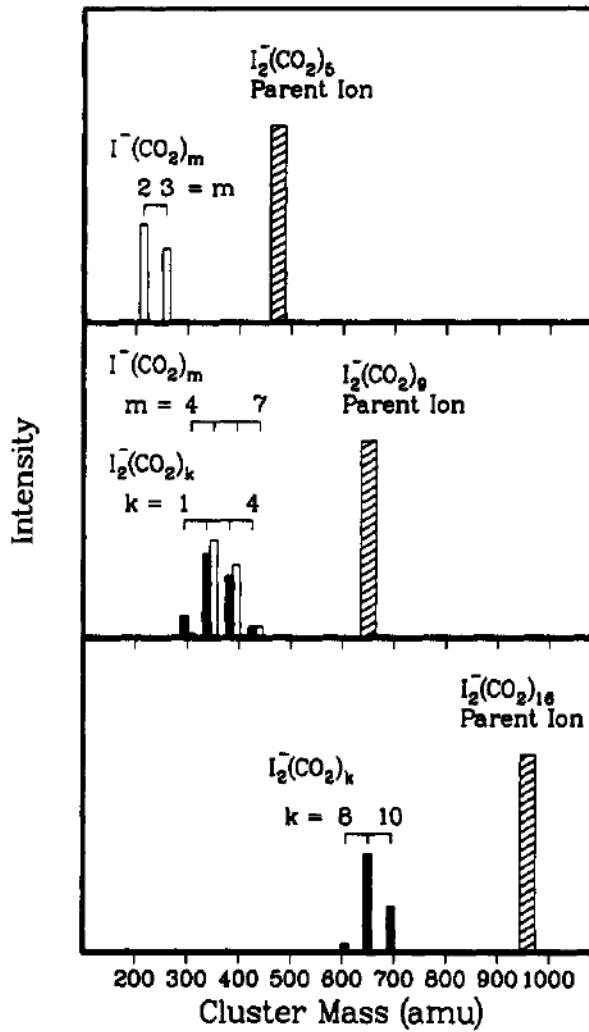


Figure 6. Photofragmentation mass spectra for representative precursor ions: $I_2^-(CO_2)_5$, $I_2^-(CO_2)_9$, and $I_2^-(CO_2)_{16}$. The low mass distribution represents the photofragments observed following the absorption of a 720-nm photon. The relative intensities of the photofragment ions are drawn to scale; however, the intensity of the precursor ion is not. Cross-hatched bars represent parent ions, open bars represent uncaged photofragment ions, and filled bars represent caged photofragment ions.

Schematic of Sequential two-Photon Mechanism

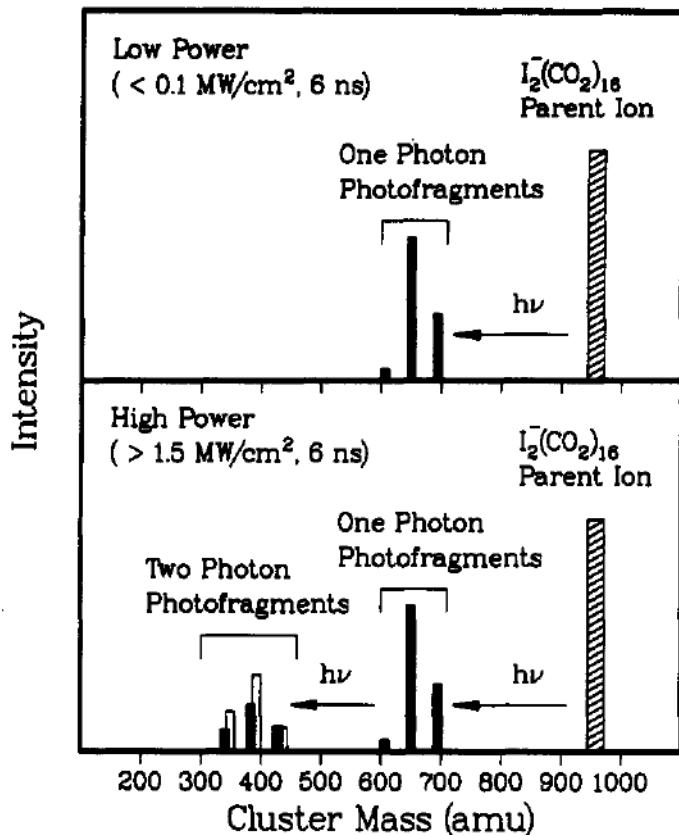


Figure 9. Effects of laser power on the photofragment ion distribution for $I_2^-(CO_2)_{16}$. At low laser powers, only one-photon photofragment ions are observed, while at higher laser powers, both one- and two-photon photofragment ions are observed as shown. Cross-hatched bars represent parent ions, open bars represent uncaged photofragment ions, and filled bars represent caged photofragment ions.

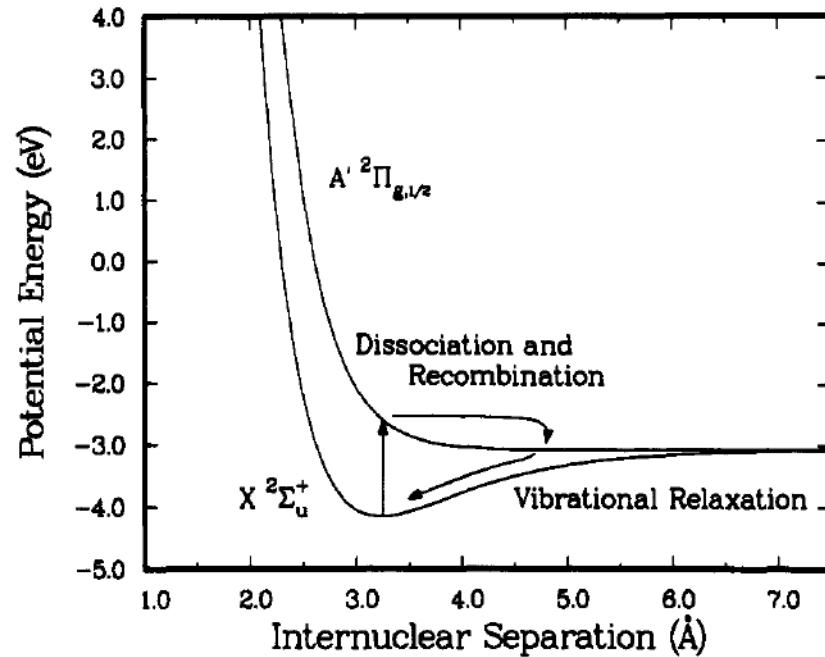


Figure 10. Schematic representation of the sequential two-photon absorption mechanism. After absorption of the first photon, the CO_2 cluster can induce recombination of the dissociating I_2^- onto the ground-state potential energy curves. The resulting highly vibrationally excited I_2^- partially relaxes after which it can absorb a second photon.

Probability of Recombination

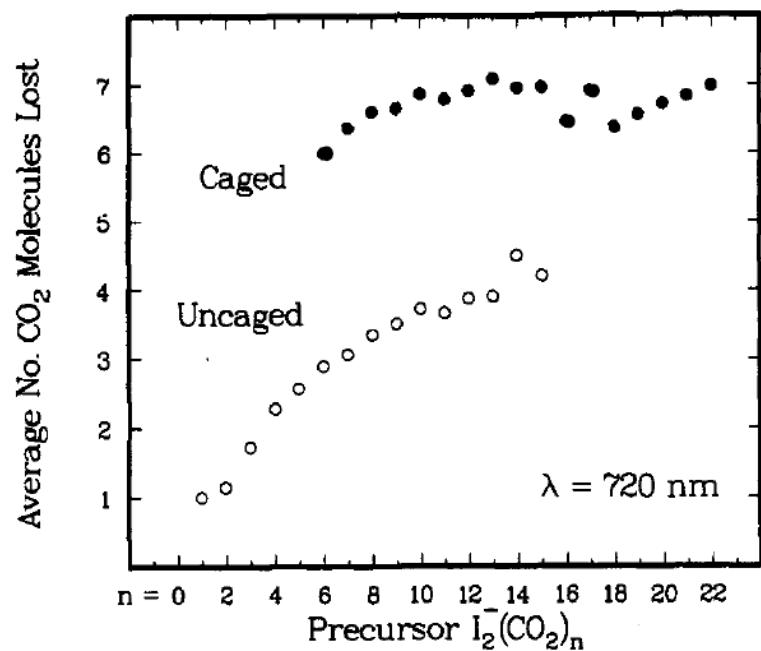


Figure 7. Average number of CO_2 molecules lost to form caged and uncaged photofragment ions following the absorption of a 720-nm photon.

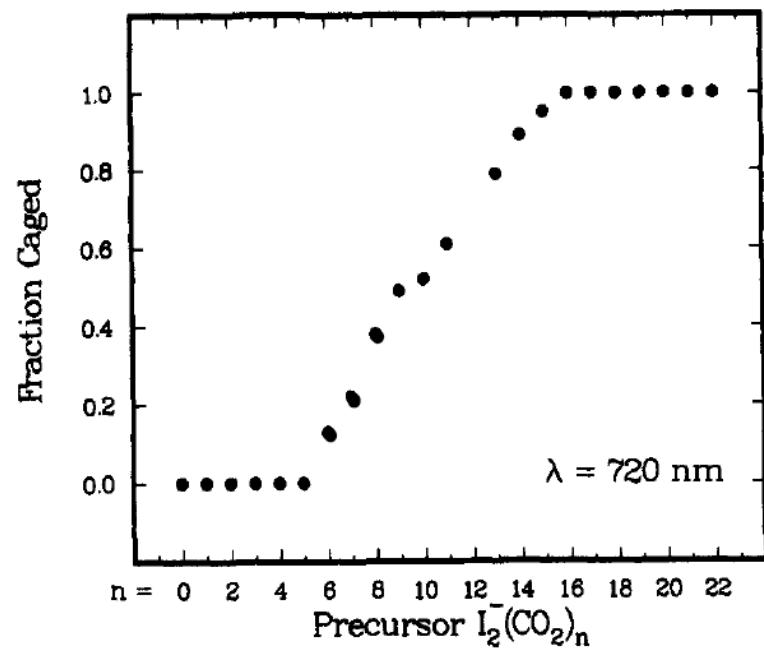
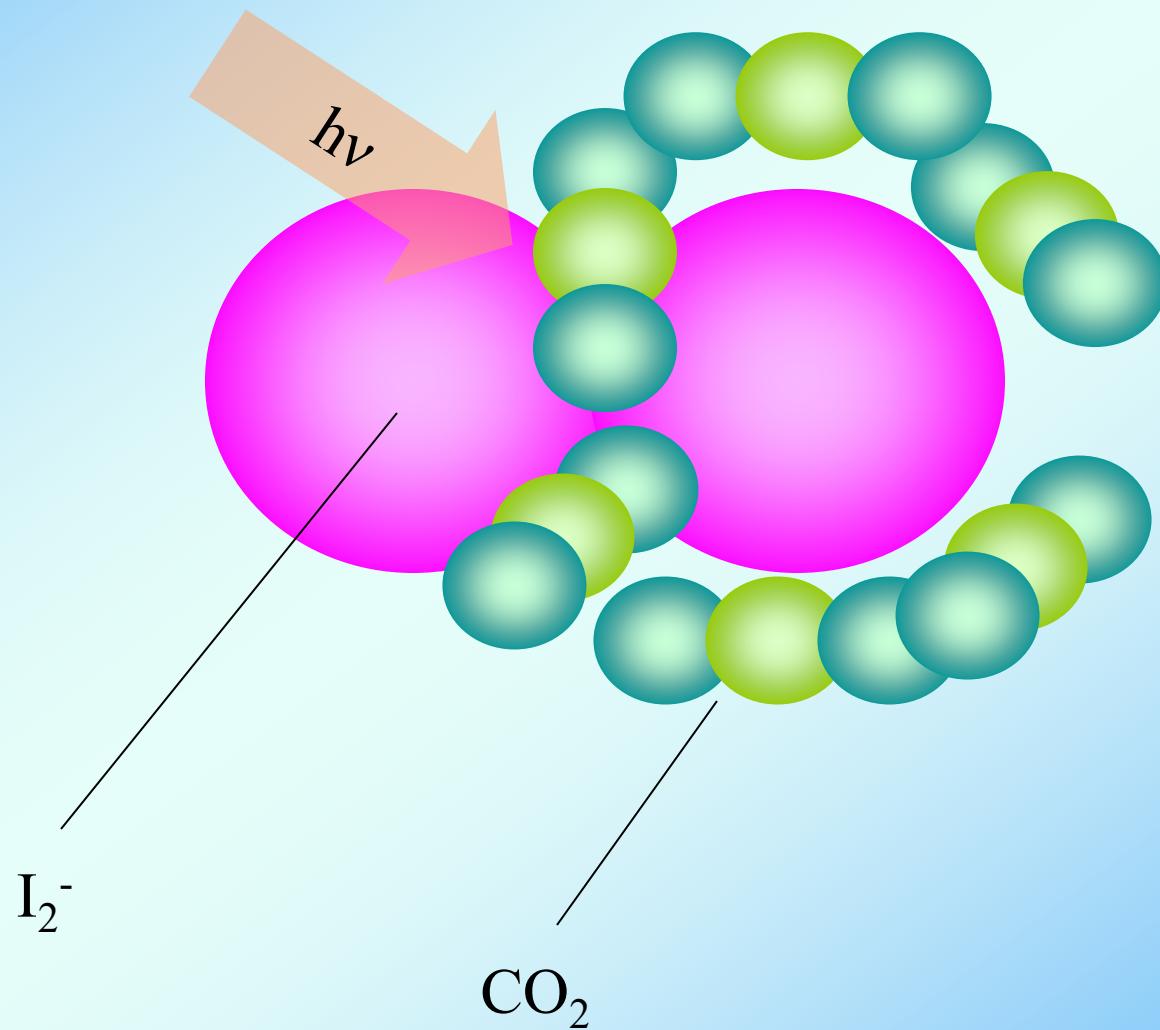
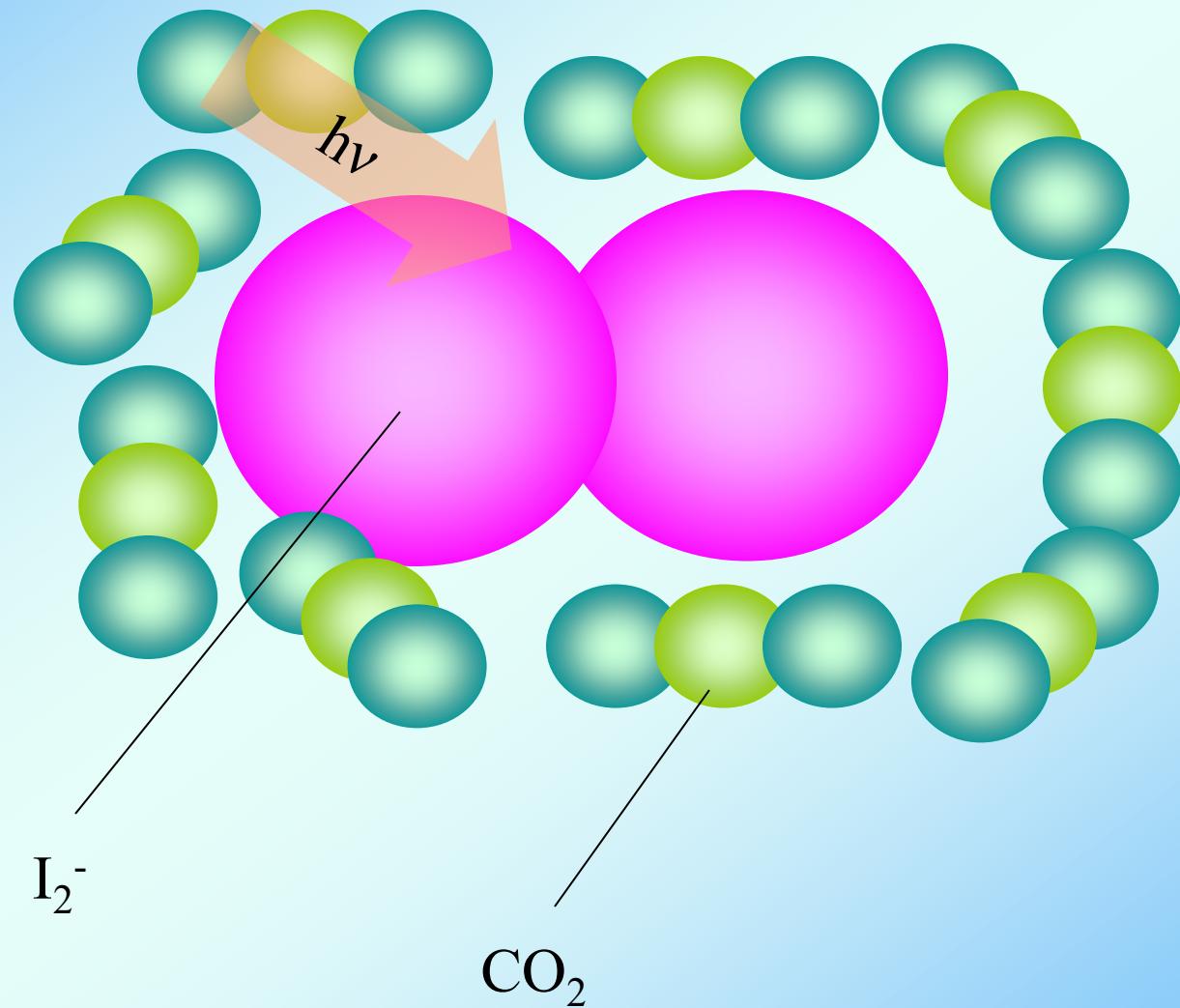


Figure 8. Branching ratio for the production of caged photofragment ions as a function of precursor cluster ion size following absorption of a 720-nm photon.





Absorption Recovery Data Caging and Recombination

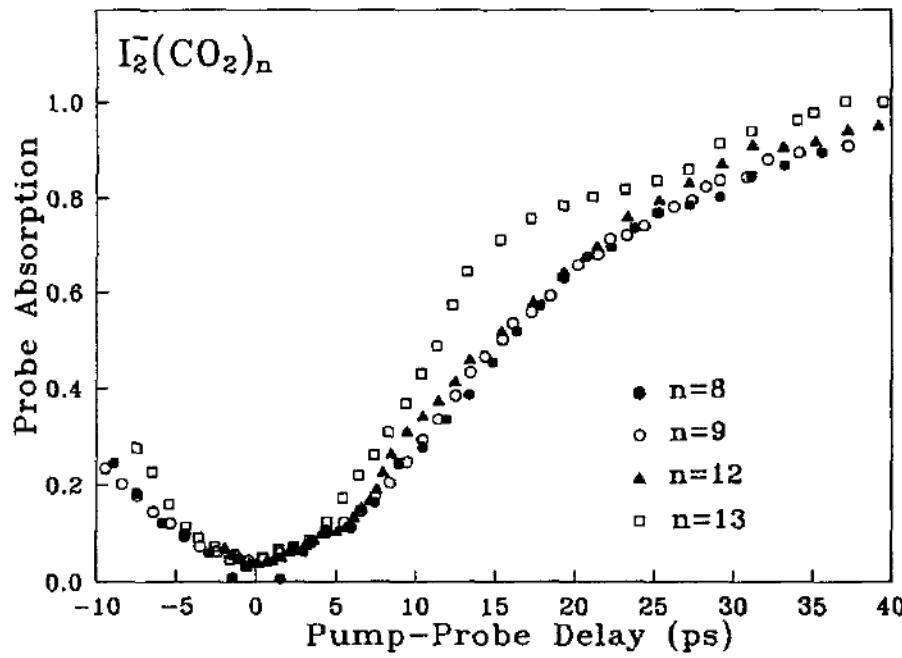


FIG. 5. $I_2(CO_2)_n$ ($n=8, 9, 12$, and 13) absorption recovery data obtained with 720 nm pump and probe pulses with parallel polarization. Since the pump and probe pulses are identical, these curves should be symmetric about zero ps delay. The smoothing algorithm used to remove high frequency noise from the data is described in the text.

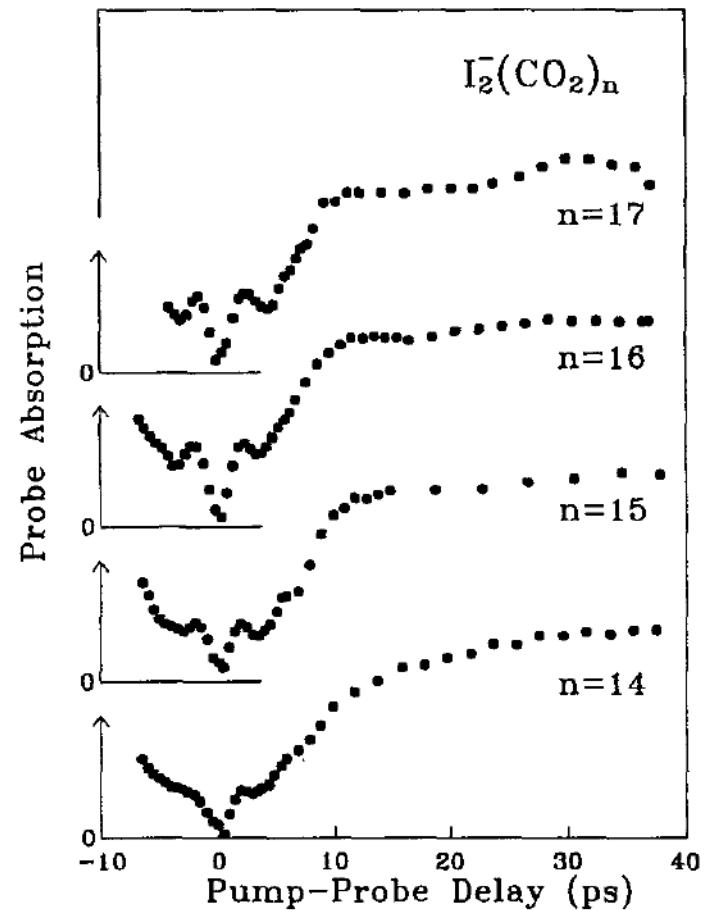


FIG. 6. $I_2(CO_2)_n$ ($n=14-17$) absorption recovery data obtained with 720 nm pump and probe pulses with parallel polarization.

Absorption Recovery Data Polarization of Lasers

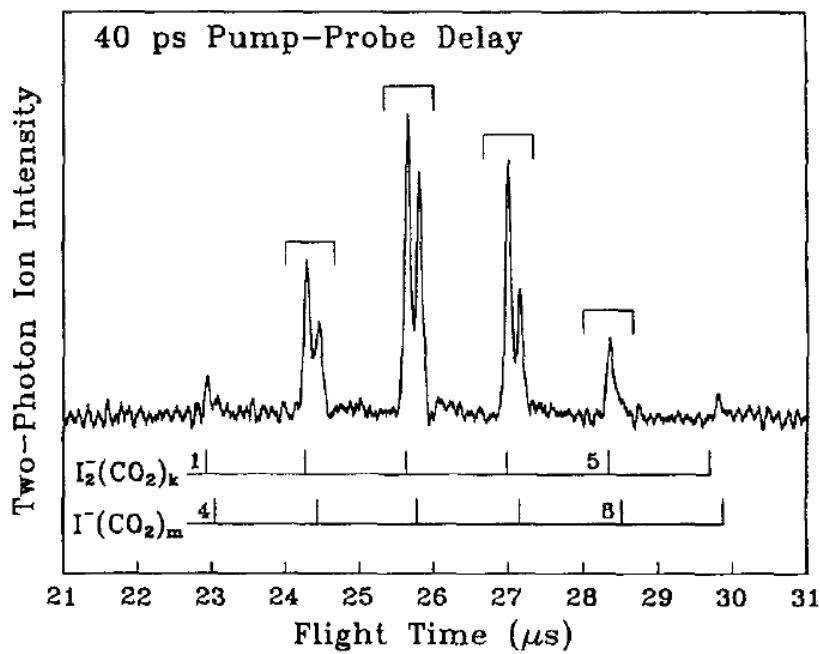


FIG. 7. Two-photon photofragment distribution of $I_2^-(CO_2)_{16}$ observed following the sequential absorption of two 720 nm photons separated by 40 ps. This mass spectrum was obtained by averaging the two-photon signal over 3000 laser shots.

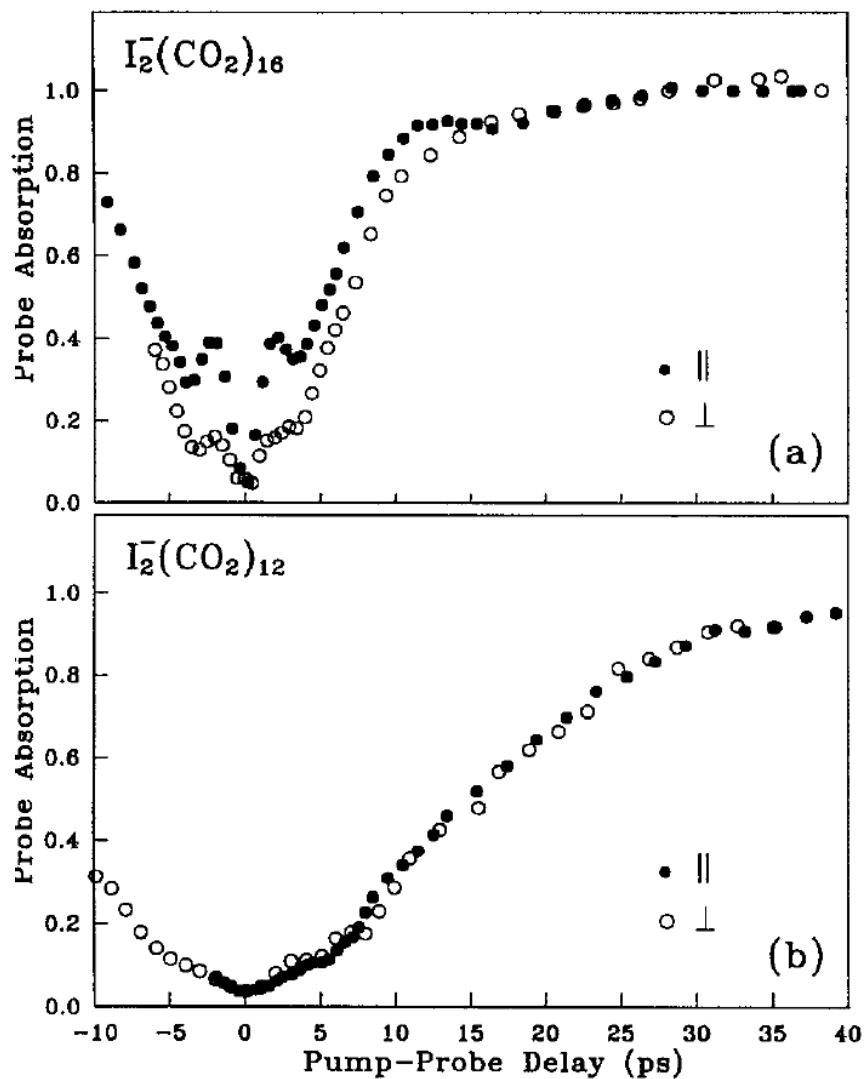
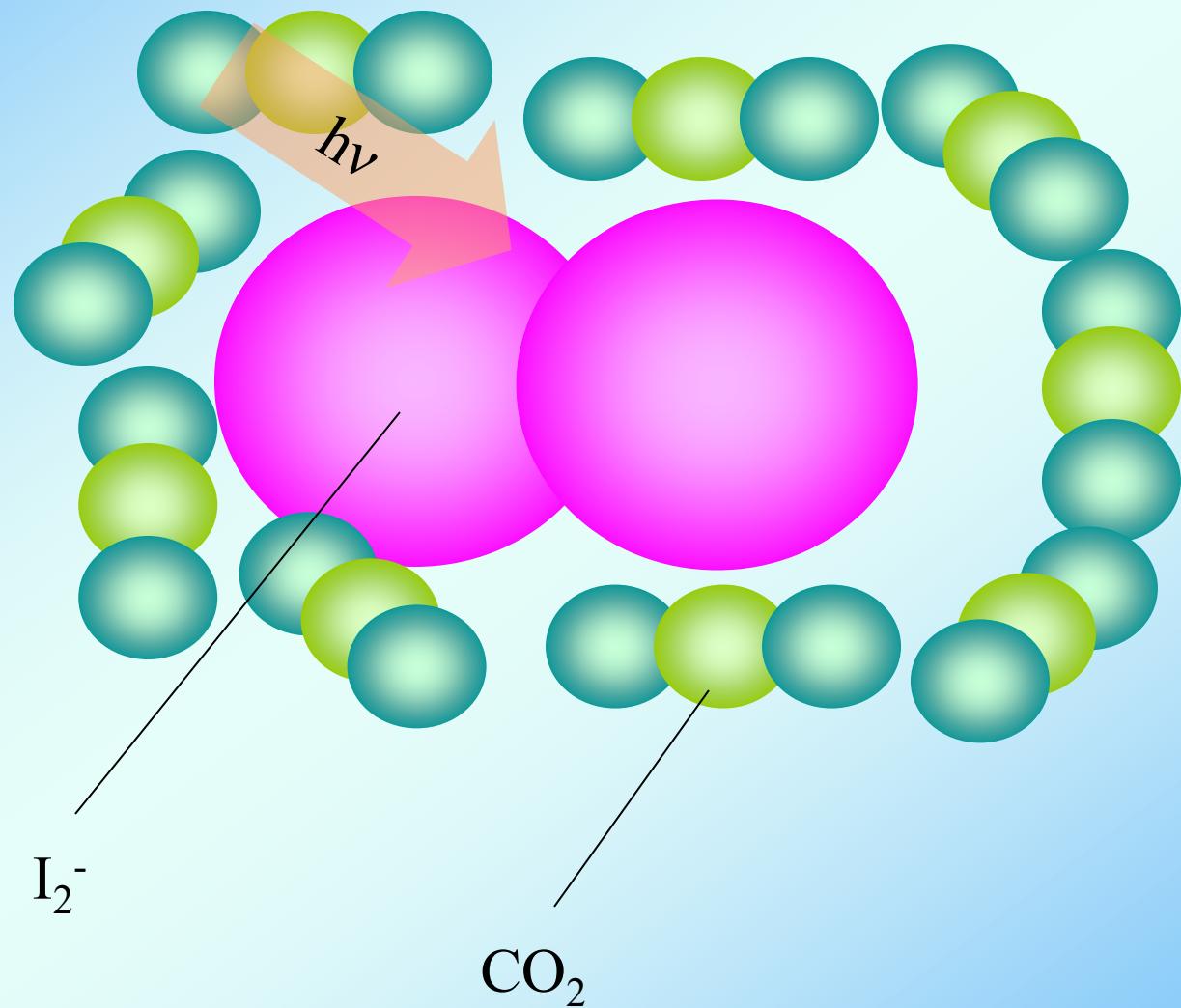


FIG. 8. Absorption recoveries for (a) $I_2^-(CO_2)_{16}$ and (b) $I_2^-(CO_2)_{12}$ obtained with perpendicular polarizations (open circles). These absorption recovery curves are superimposed on the parallel polarization data (solid circles) reproduced from Figs. 5 and 6.



Absorption Recovery Time

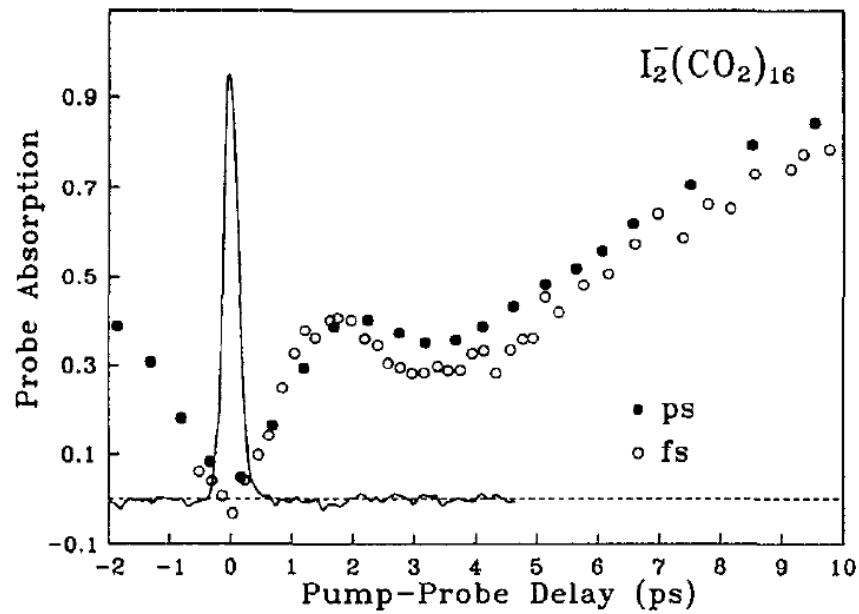


FIG. 10. Expanded view of the $\text{I}_2^-(\text{CO}_2)_{16}$ absorption recovery obtained using the femtosecond laser apparatus. Superimposed on the data is the parallel absorption recovery obtained using the picosecond laser system and a typical autocorrelation trace of the amplified femtosecond laser pulse. Unlike the picosecond data, the femtosecond data have not been smoothed.

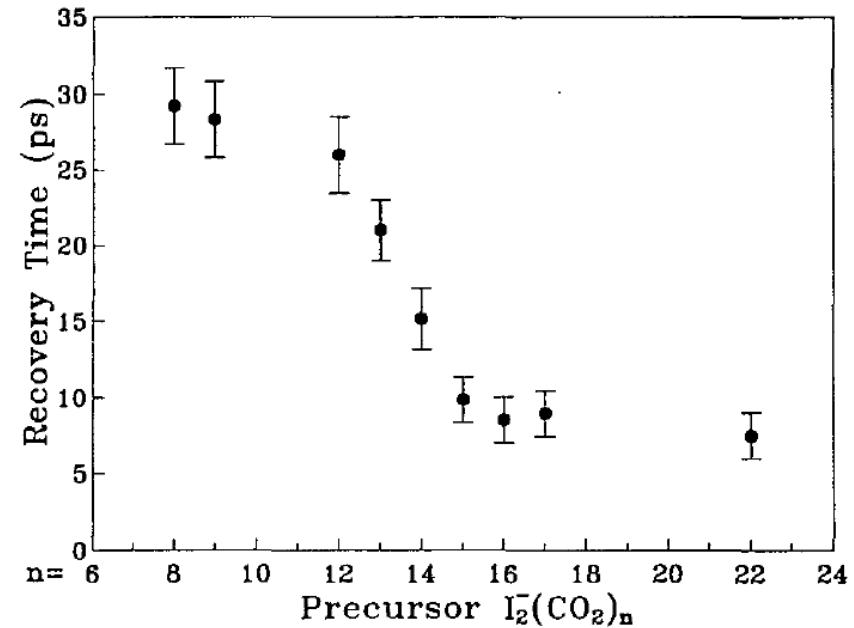
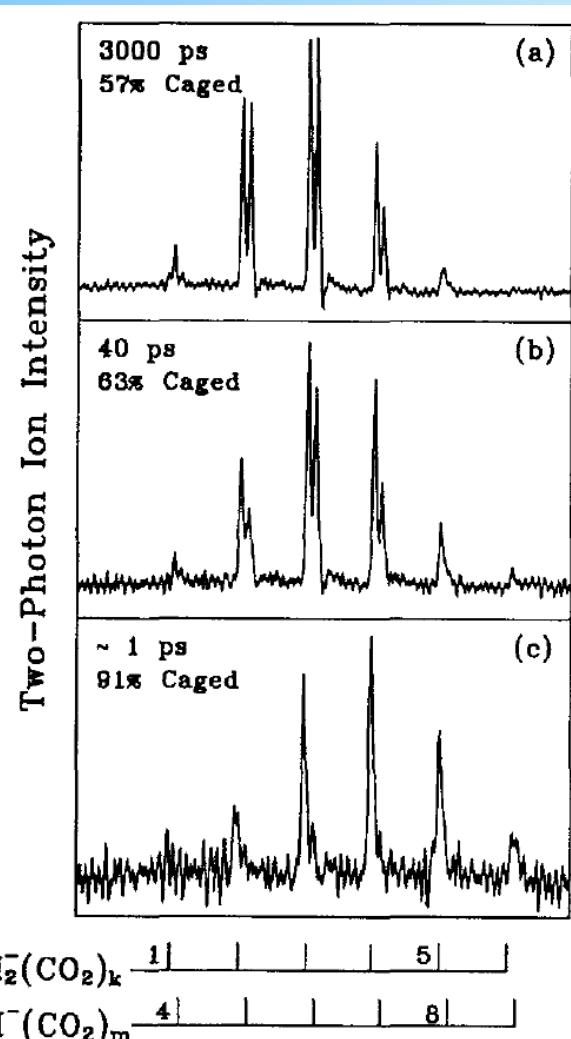


FIG. 12. Absorption recovery time displayed as a function of cluster ion size. The absorption recovery time is defined as the pump-probe delay time at which the parallel absorption recovery (Figs. 5 and 6) reaches 80% of its asymptotic value.

Two-Photon Photofragment Distribution for Various Delay Time



Potential energy curves for I_2^-

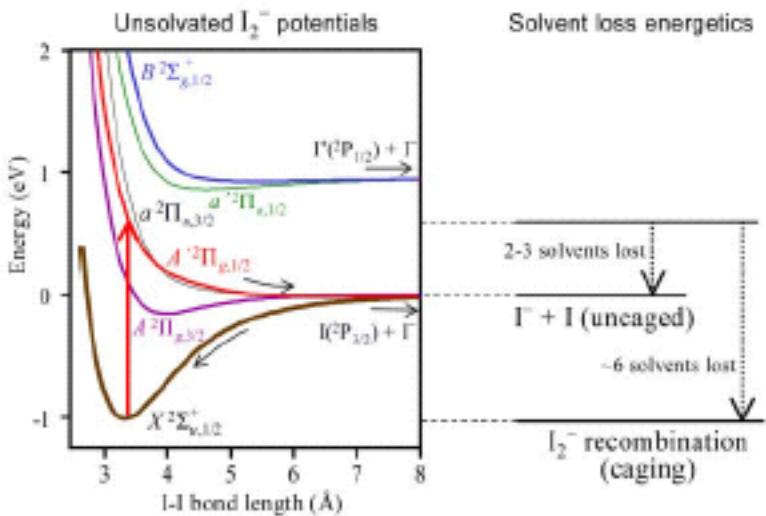


Fig. 3 Potential energy diagram of I_2^- (from ref. 88) and solvent loss energetics in 790 nm experiments on $\text{I}_2^-(\text{OCS})_n$ or $\text{I}_2^-(\text{CO}_2)_n$.

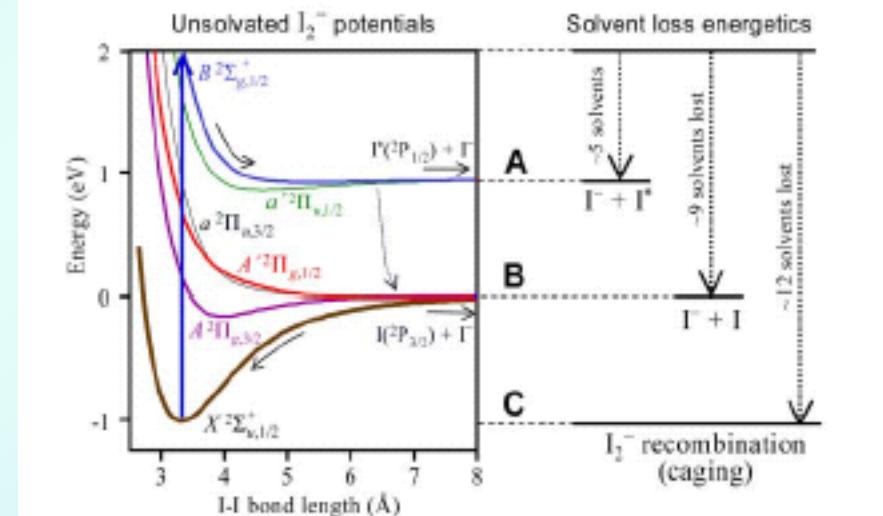


Fig. 4 Potential energy diagram of I_2^- (from ref. 88) and solvent loss energetics in 395 nm experiments on $\text{I}_2^-(\text{OCS})_n$ or $\text{I}_2^-(\text{CO}_2)_n$.

Probability of Recombination

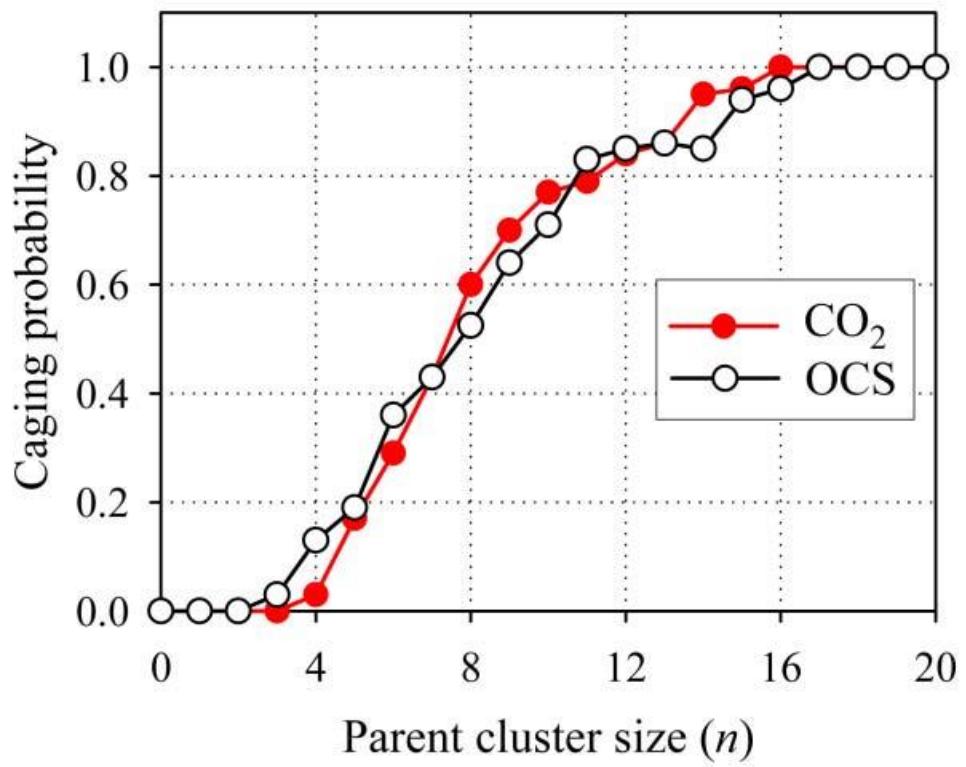


Fig. 5 Probabilities of recombination (caging) of the I_2^- chromophore in $I_2^-(CO_2)_n$ and $I_2^-(OCS)_n$ clusters following photoexcitation at 790 nm, as functions of the parent cluster size. Data from ref. 22 and 24.

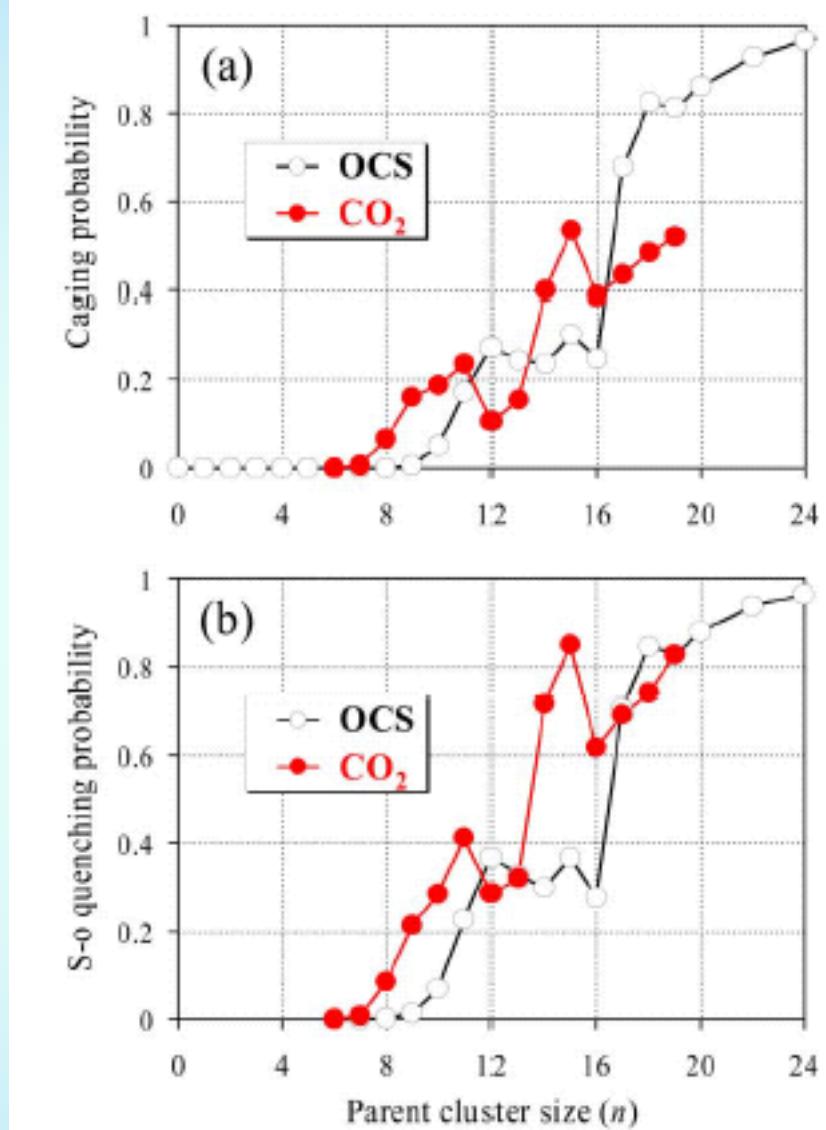


Fig. 6 (a) Probabilities of recombination (caging) of the I_2^- chromophore in $I_2^-(CO_2)_n$ and $I_2^-(OCS)_n$ clusters following photoexcitation at 395 nm, as functions of the parent cluster size. (b) Similar curves for the probability of I^- spin-orbit quenching. Data from ref. 22 and 24.

Absorption recovery of $I_2^-(OCS)_n$.

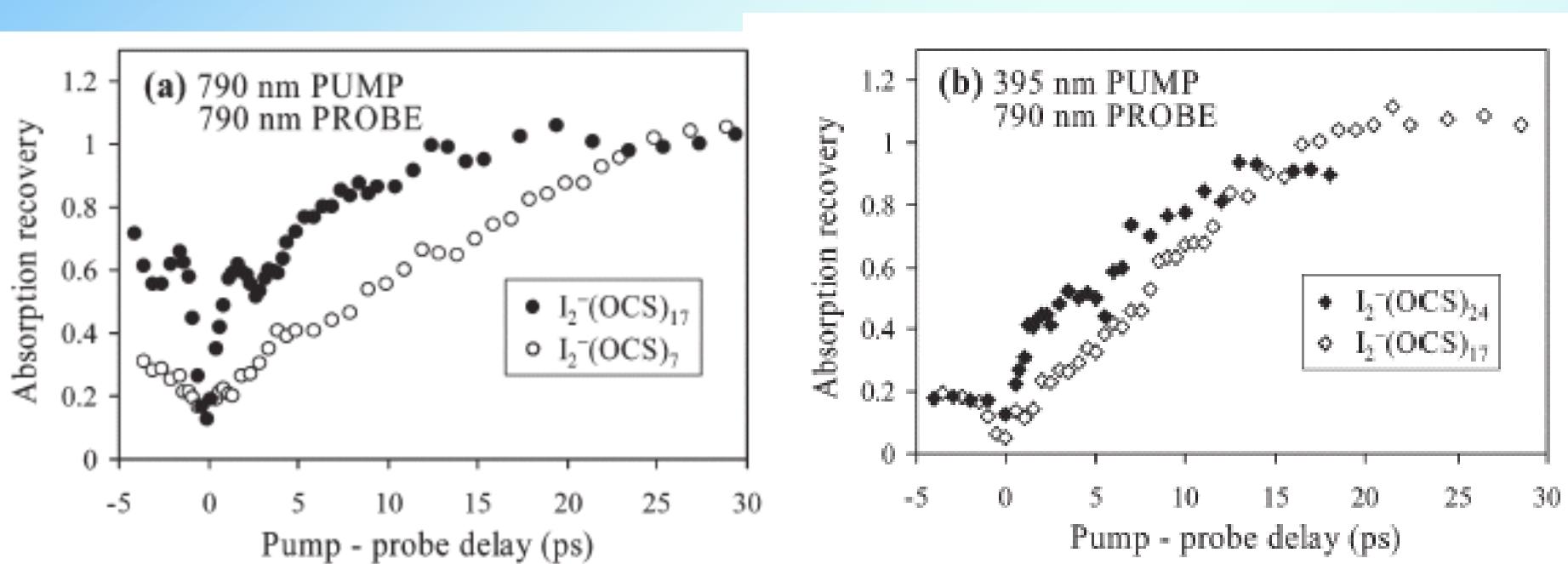
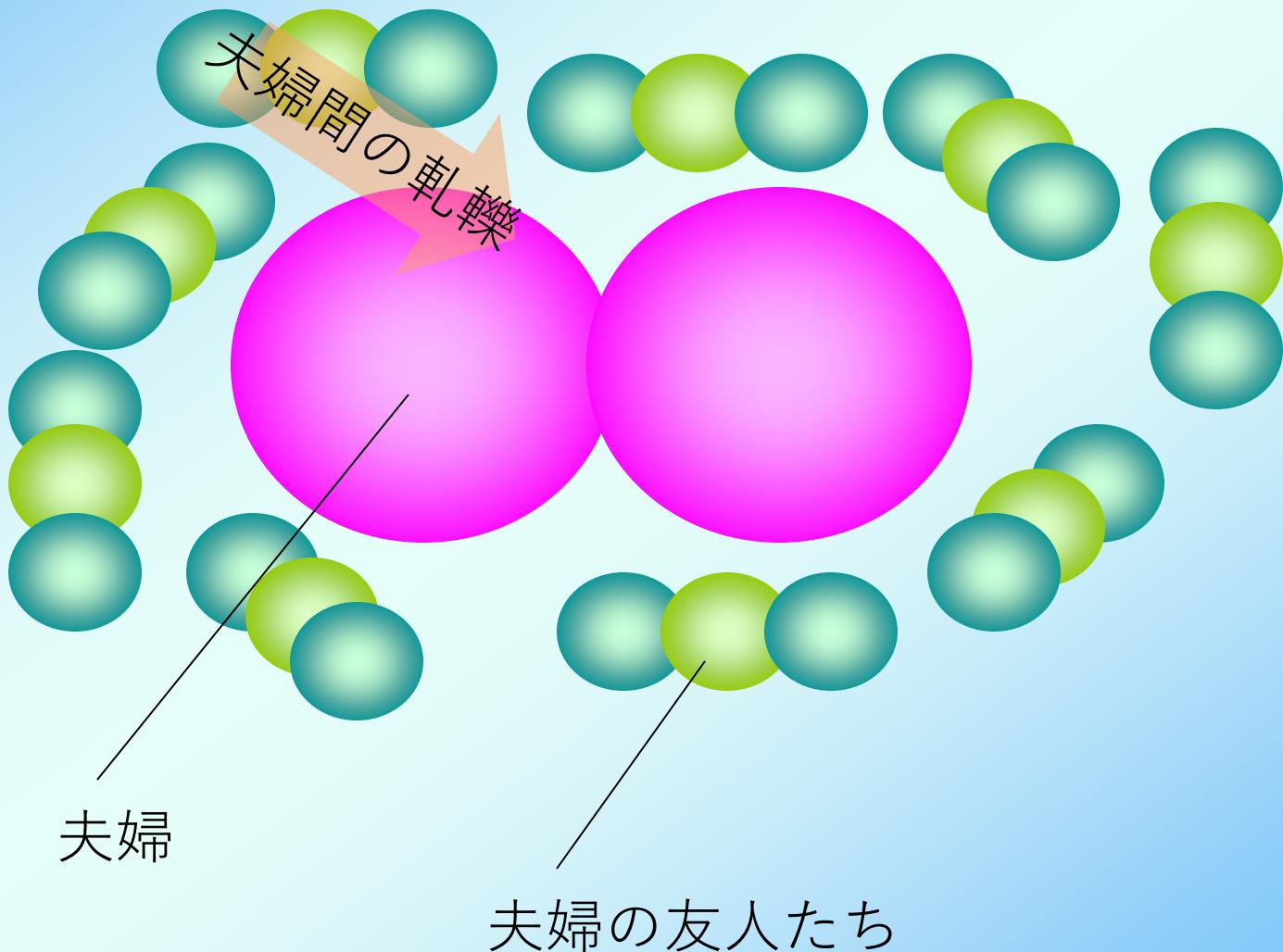
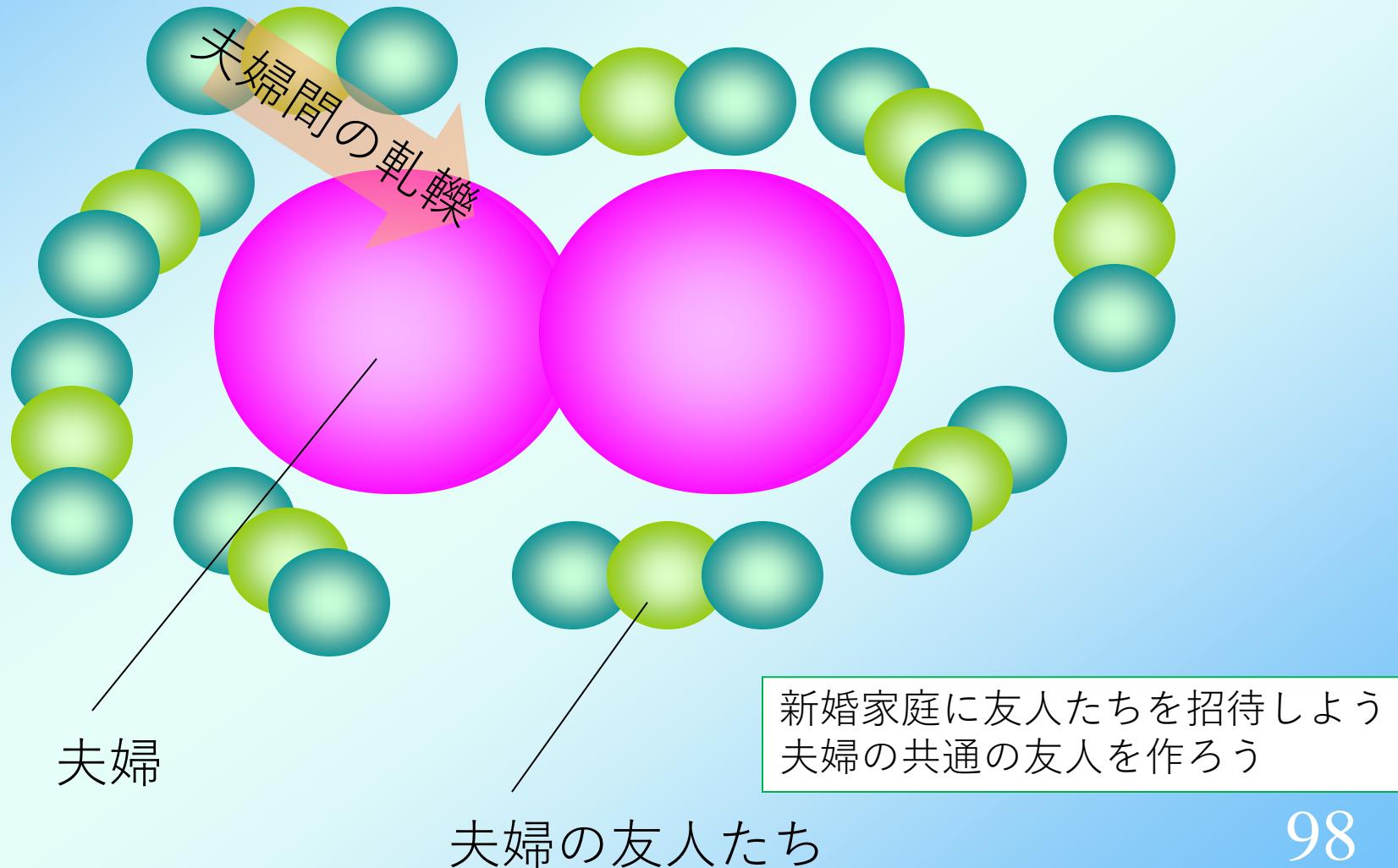


Fig. 7 Delay-dependent absorption recoveries of indicated $I_2^-(OCS)_n$ cluster ions following the excitation at (a) 790 nm and (b) 395 nm. In (b), the relaxation processes leading to I_2^- caging include the spin-orbit relaxation of I^- , while in (b) the spin-orbit relaxation step is not involved. Adapted from ref. 24.

$I_2^-(CO_2)_n$ と人間社会



$I_2\cdot(CO_2)_n$ と人間社会



問.

クラスター中の化学反応と、
バルクの溶液中の化学反応とを比較して、
類似する点と異なる点について、
簡単に説明しなさい。