2 光子励起によるX 線散乱

手塚泰久
弘前大
（X線発光UG）

内殻分光

- 共鳴過程
  物理現象が強調されて観測される
  通常観測されない現象が観測される
  多体効果などが観測される

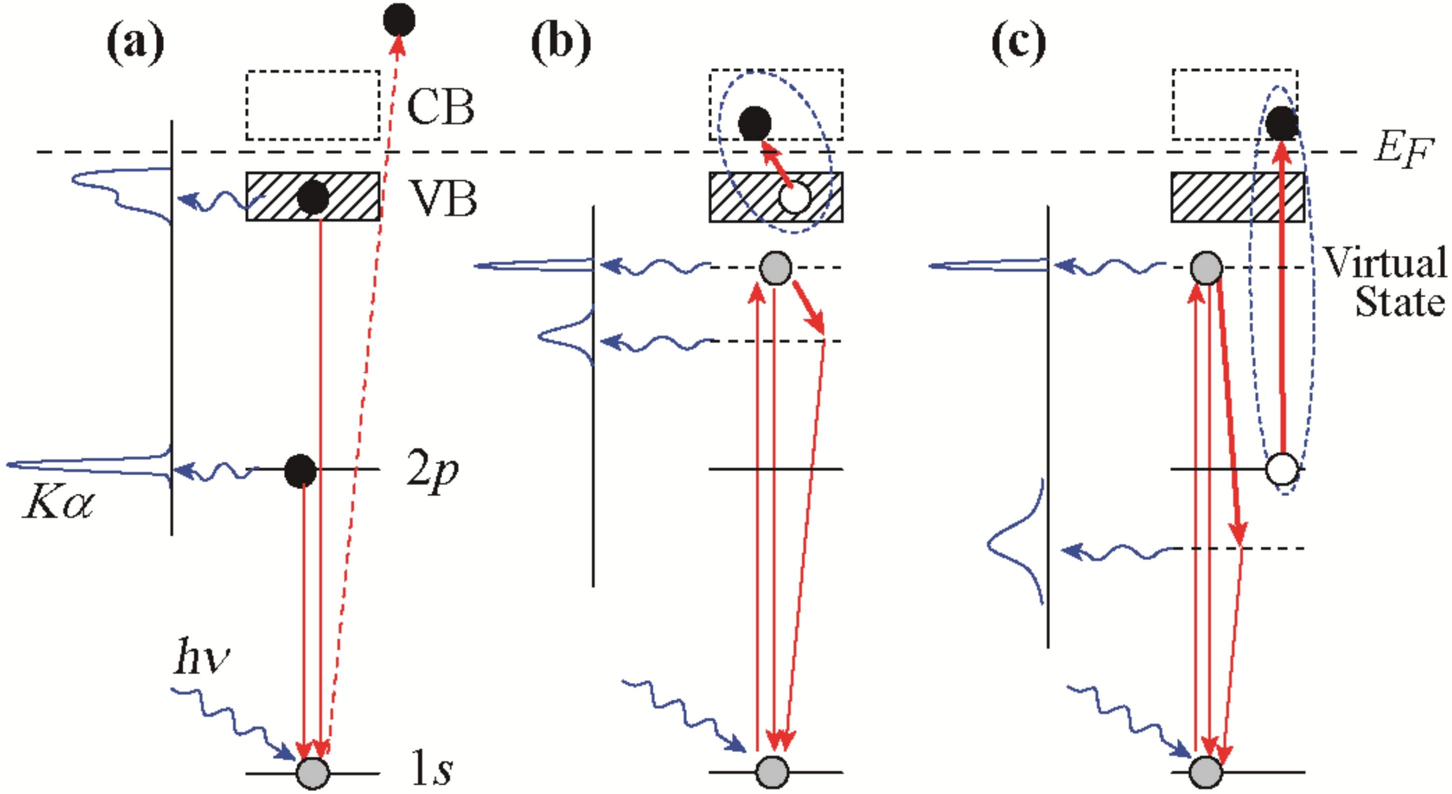
- 軟X線
  高輝度必須（要Undulator）
  → 新リング

- 硬X線
  Bending可
  → 開発研究多機能ビームライン

- 内殻エネルギー
  遷移金属 *K*端: 4500~9000 eV
  遷移金属 *L*端: 400~1000 eV
  軽元素*K*端: 50~ 700 eV

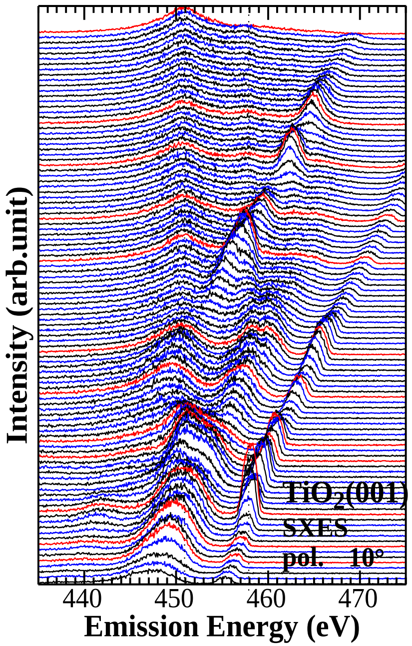
X線発光・散乱

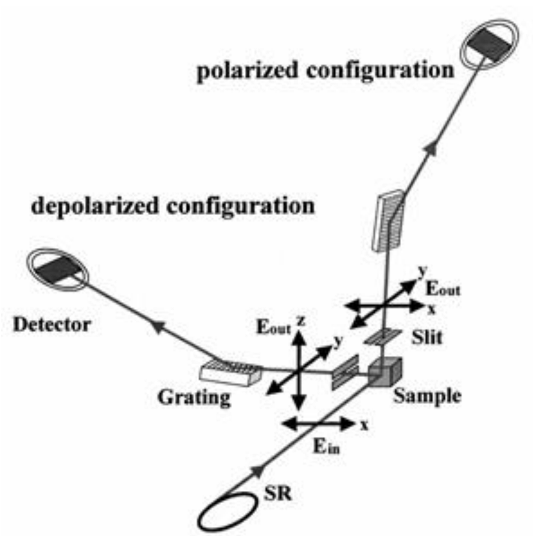
X-ray Emission Spectroscopy



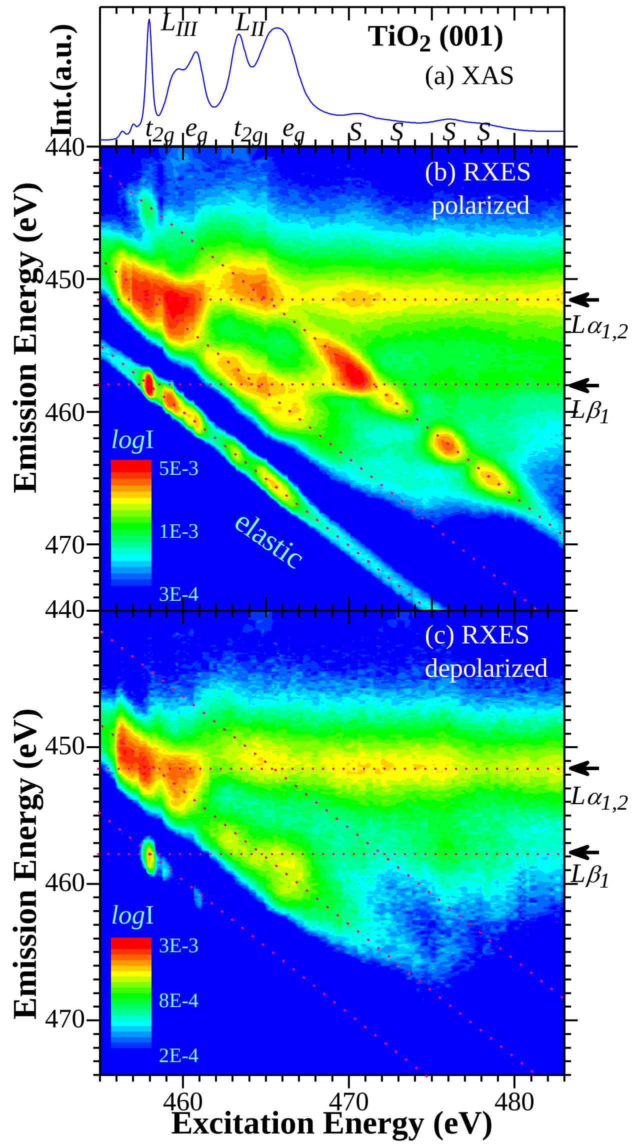
Fluorescence	X-ray Raman Scattering	
	Exciton, Phonon, etc	Core Excitation
Partial DOS (occupied)	Elementary Excitation (Charge Transfer)	Partial DOS (unoccupied)

軟X線ラマン散乱



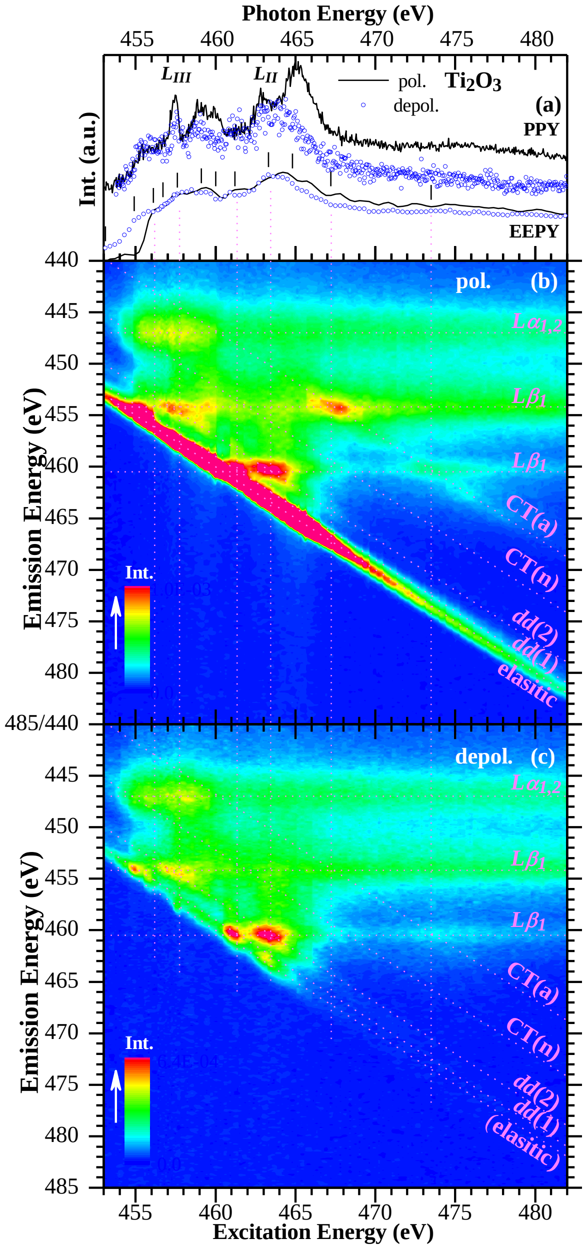


TiO_2 ($3d^0$)



電荷移動励起（O 2p→Ti 3d）

Ti_2O_3 ($3d^1$)

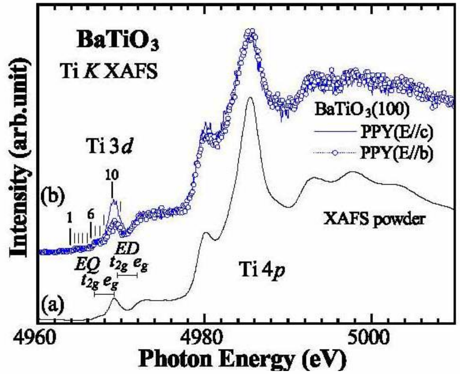


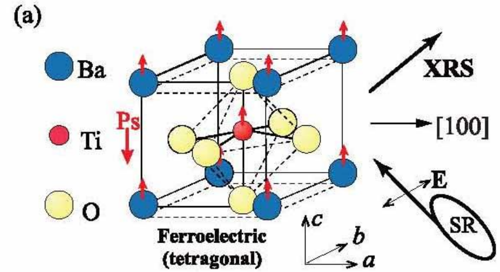
配位子場励起（Ti 3d →Ti 3d）

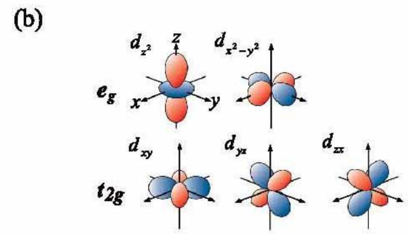
硬X線ラマン散乱

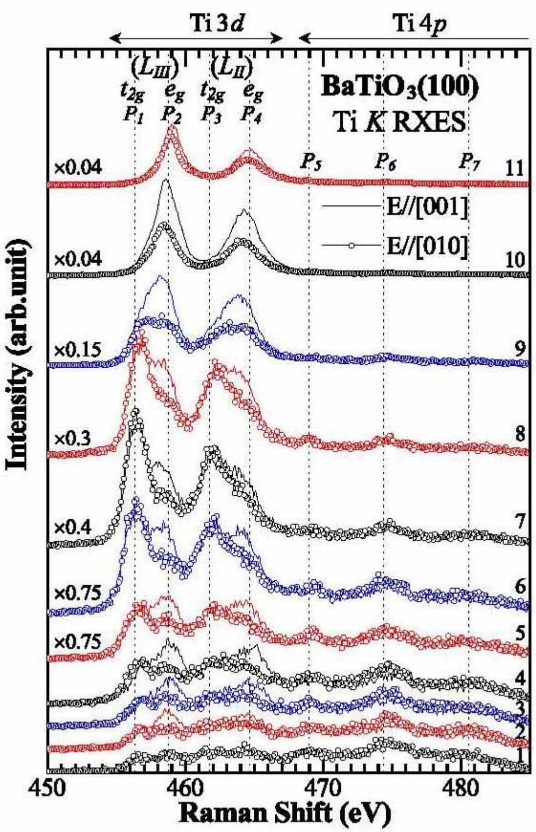
$BaTiO_3$ 強誘電相転移

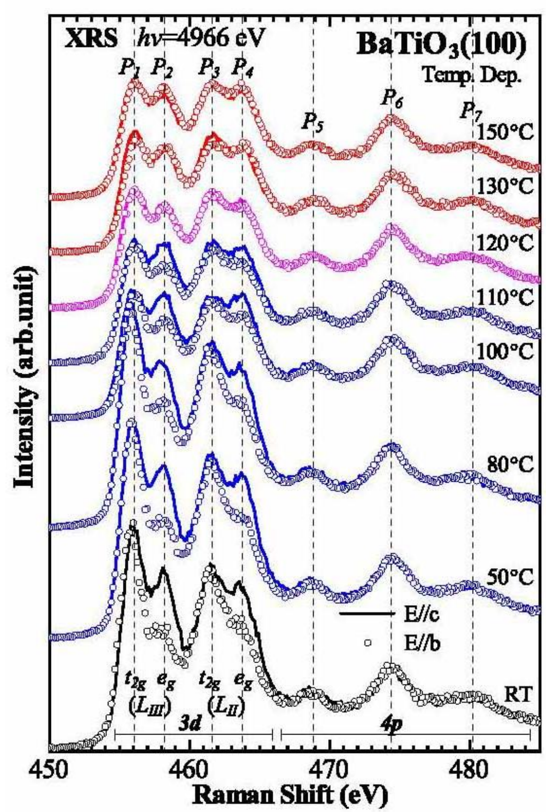
Y. Tezuka, et al., Phys. Rev B104, 235148 (2022)

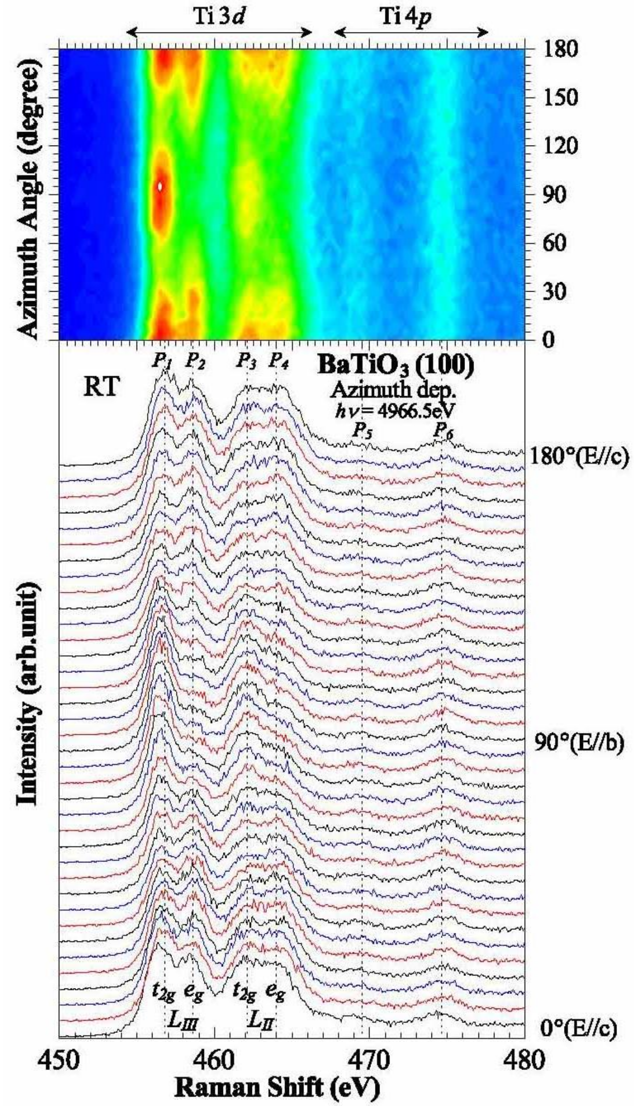












共鳴XRS

温度依存性

方位角依存性

2光子励起

- 1内殻同時励起
  非線形ラマン散乱

- 2内殻励起
  電子相関
  原子間相関

- 誘導輻射
  素励起の強調
  ポンププローブ

2光子励起（非線形ラマン散乱）

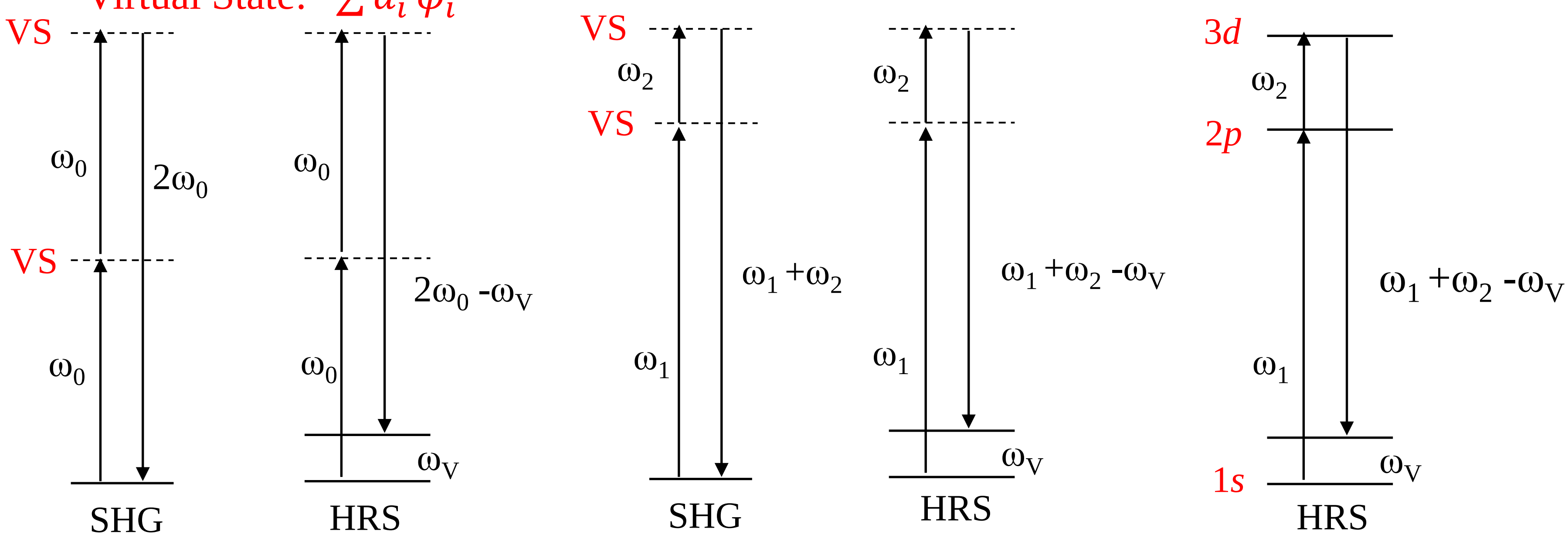
Hyper-Raman Scattering

レーザー：可能
放射光：　かなり難しい

Virtual State: $\sum a_i \phi_i$

２ビーム

内殻共鳴



夢物語？

現実？

Δℓ=1,3：双極子、**８重極子**
通常のラマン散乱で観測できない素励起の観測

cf. Raman Scattering
Δℓ=0,2：単極子、４重極子

要
- 光子密度
- 時間コヒーレンス

***cf.* KEK 放射光 Conceptual Design Report (2016)**
非線形非弾性X線散乱
（２光子吸収による非弾性散乱）

エキゾティック相転移

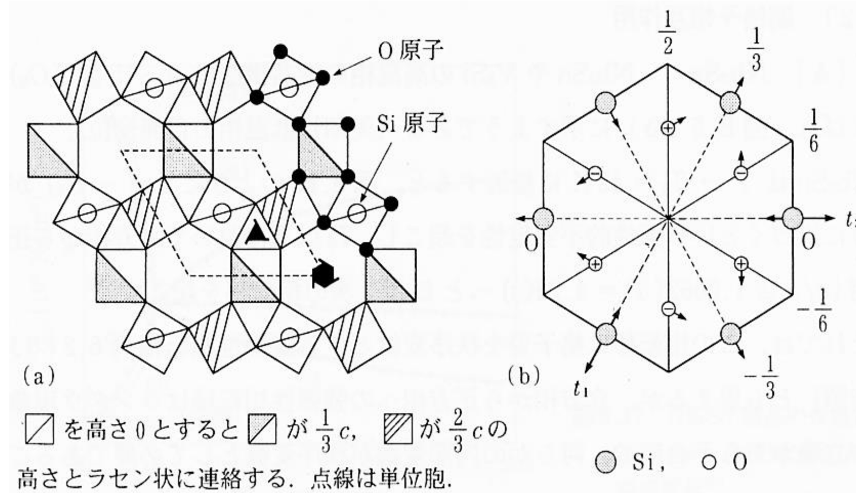
水晶：　α-β 相転移（573°C）

α 水晶 ：三方晶系(trigonal System)

D_3	E	$2C_3$	$3C_2$	基底 変位、回転	基底 分極率
A_1	1	1	1		$\alpha_{xx}+\alpha_{yy}$, α_{zz} β_{xxx}, β_{yyx}
A_2	1	1	-1	T_z, R_z	β_{xxy}, β_{xxz}, β_{yyy}, β_{yyz}, β_{zzz}
E	2	-1	0	(T_x,T_y), (R_x,R_y)	$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$, $(\alpha_{yz}, \alpha_{zx})$ β_{xxx}, β_{xxy}, β_{xxz}, β_{yyx}, β_{yyy}, β_{yyz}, β_{zzx}, β_{zzy}, β_{zzz}, β_{xyz}

β水晶 ：六方晶系(hexagonal System)　SHG禁制

D_6	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	基底 変位、回転	基底 分極率
A_1	1	1	1	1	1	1		$\alpha_{xx}+\alpha_{yy}$, α_{zz}
A_2	1	1	1	1	-1	-1	T_z, R_z	β_{xxz}, β_{yyz}, β_{zzz}
B_1	1	-1	1	-1	1	-1		β_{xxx}, β_{yyx}
B_2	1	-1	1	-1	-1	1		β_{xxy}, β_{yyy}
E_1	2	1	-1	-2	0	0	(T_x,T_y), (R_x,R_y)	$(\alpha_{yz}, \alpha_{zx})$ β_{xxx}, β_{xxy}, β_{yyx}, β_{yyy}, β_{zzx}, β_{zzy}, β_{zzz}
E_2	2	-1	-1	-2	0	0		$(\alpha_{xx}-\alpha_{yy}, \alpha_{zy})$ β_{xxz}, β_{yyz}, β_{xyz}



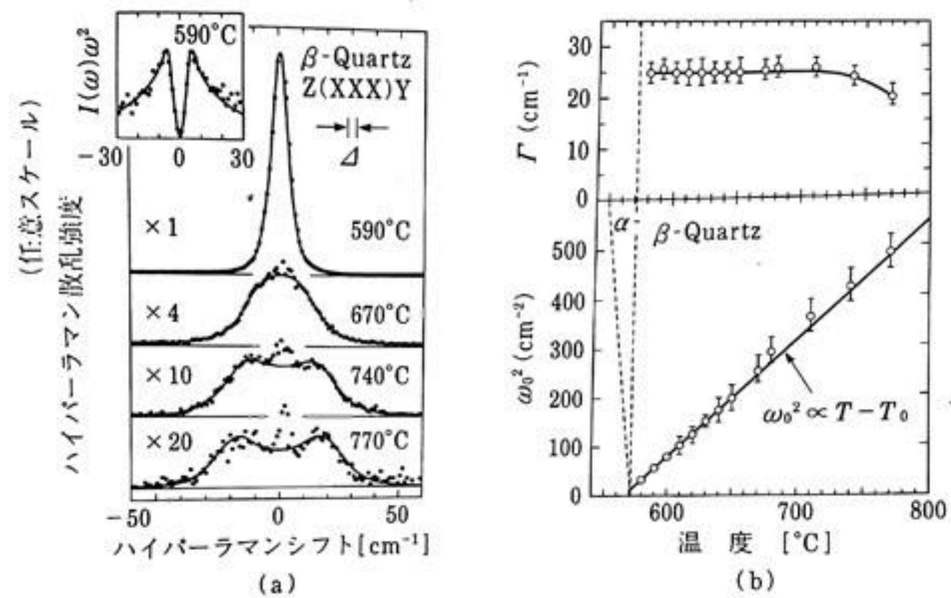
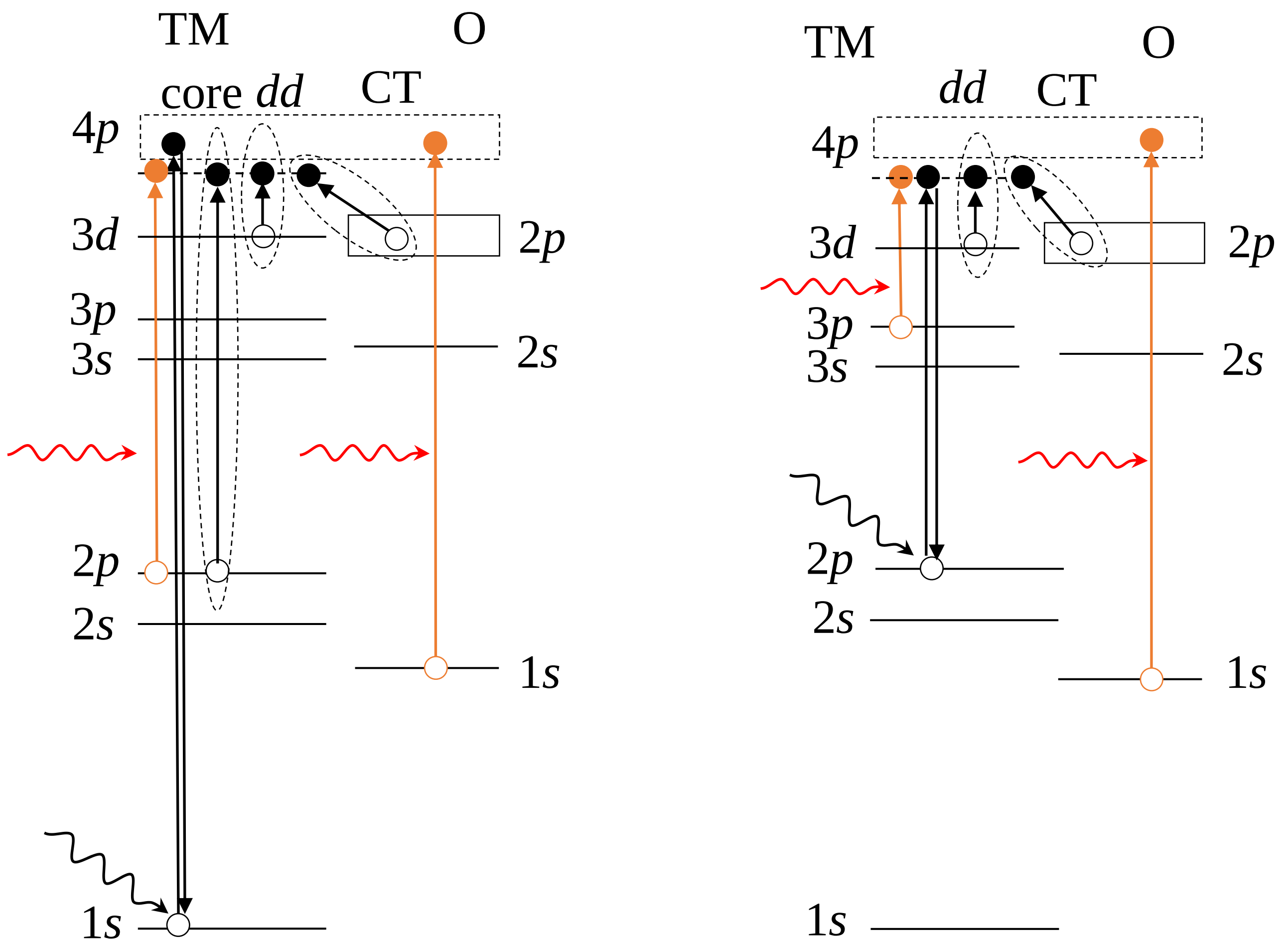


図8.16　(a) 高温相におけるハイパーラマン散乱スペクトル
(b) 減衰調和振動子でフィットしたソフトフォノンの ω_0^2 と Γ の温度変化[20]

20) Y. Tezuka, S. Shin and M. Ishigame: Phys. Rev. Lett. 66 (1991) 2356.

X線ラマン散乱（2内殻励起）



Kα RXRS

HX & SX

TM 2*p* RXRS

SX & SX

より高次の多体効果

Ni, Cu *etc* : $3d^9$

Coherent X-ray Raman Spectroscopy

S.Tanaka and S. Mukamel, PRL 89, 043001(2002)

Coherent X-Ray Raman Spectroscopy: A Nonlinear Local Probe for Electronic Excitations

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(Received 27 November 2001; published 9 July 2002)

Nonlinear x-ray four-wave mixing experiments are becoming feasible due to rapid advances in high harmonic generation and synchrotron radiation coherent x-ray sources. By tuning the difference of two x-ray frequencies across the valence excitations, it is possible to probe the entire manifold of molecular electronic excitations. We show that the wave vector and frequency profiles of this x-ray analogue of coherent Raman spectroscopy provide an excellent real-space probe that carries most valuable structural and dynamical information, not available from spontaneous Raman techniques.

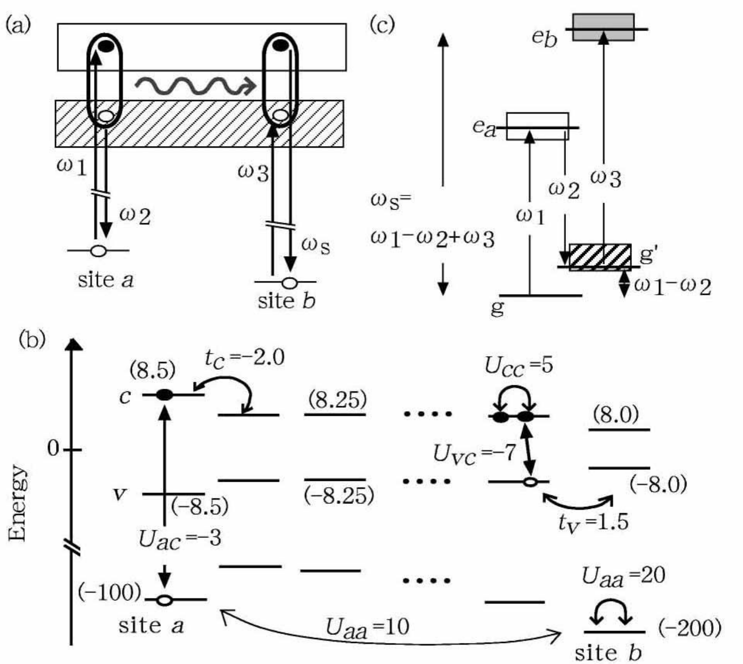


FIG. 1. (a) One-body picture of CXRS. The open and hatched blocks are unoccupied conduction and unoccupied valence states, respectively. (b) One-dimensional molecular chain model system. The strengths of the interactions are written (in eV) and the site energies are given in parentheses. (c) Level scheme for CXRS.

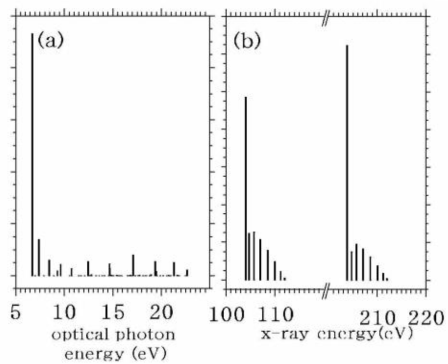


FIG. 2. The calculated optical absorption (a) and x-ray absorption spectra (b).

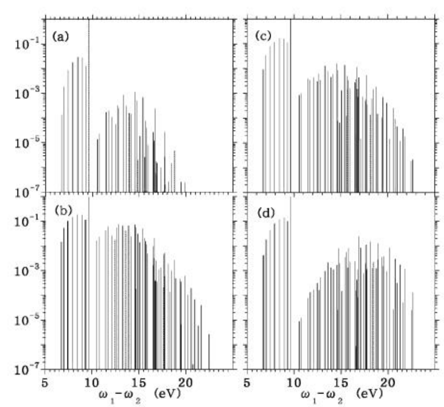


FIG. 3. (a) CXRS, (b) SXRS, (c) the ratio of CXRS to SXRS, and (d) the local component of the optical absorption $|j_{g,g'}(a)|^2$ (log scale).

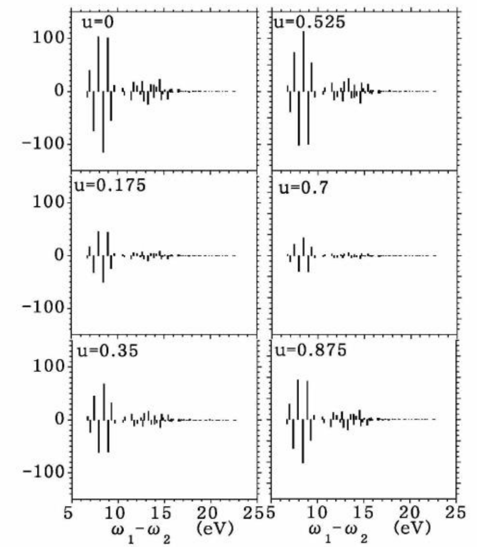


FIG. 4. Wave vector dependence of CXRS when $\omega_1 = 104.05$ eV and $\omega_s = 203.77$ eV. The grating wave vectors are $q = 2\pi u/|\mathbf{R}_a - \mathbf{R}_b|$, for various values of u as indicated.

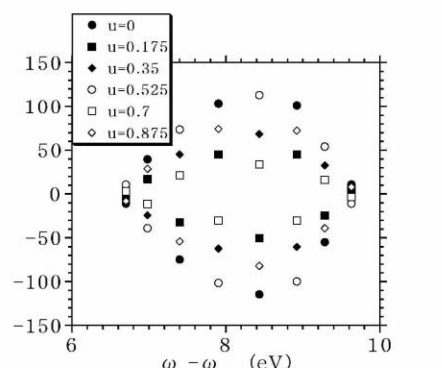
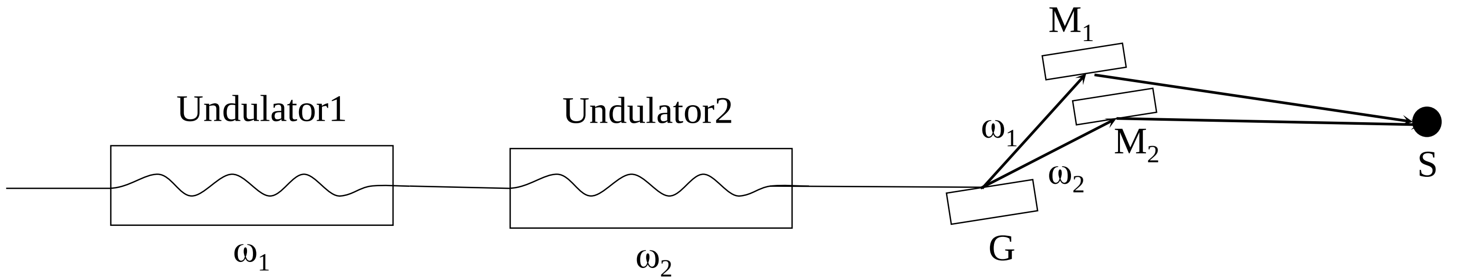


FIG. 5. Wave vector dependence of CXRS for the exciton peaks of Fig. 4.

軟X線における2ビーム利用

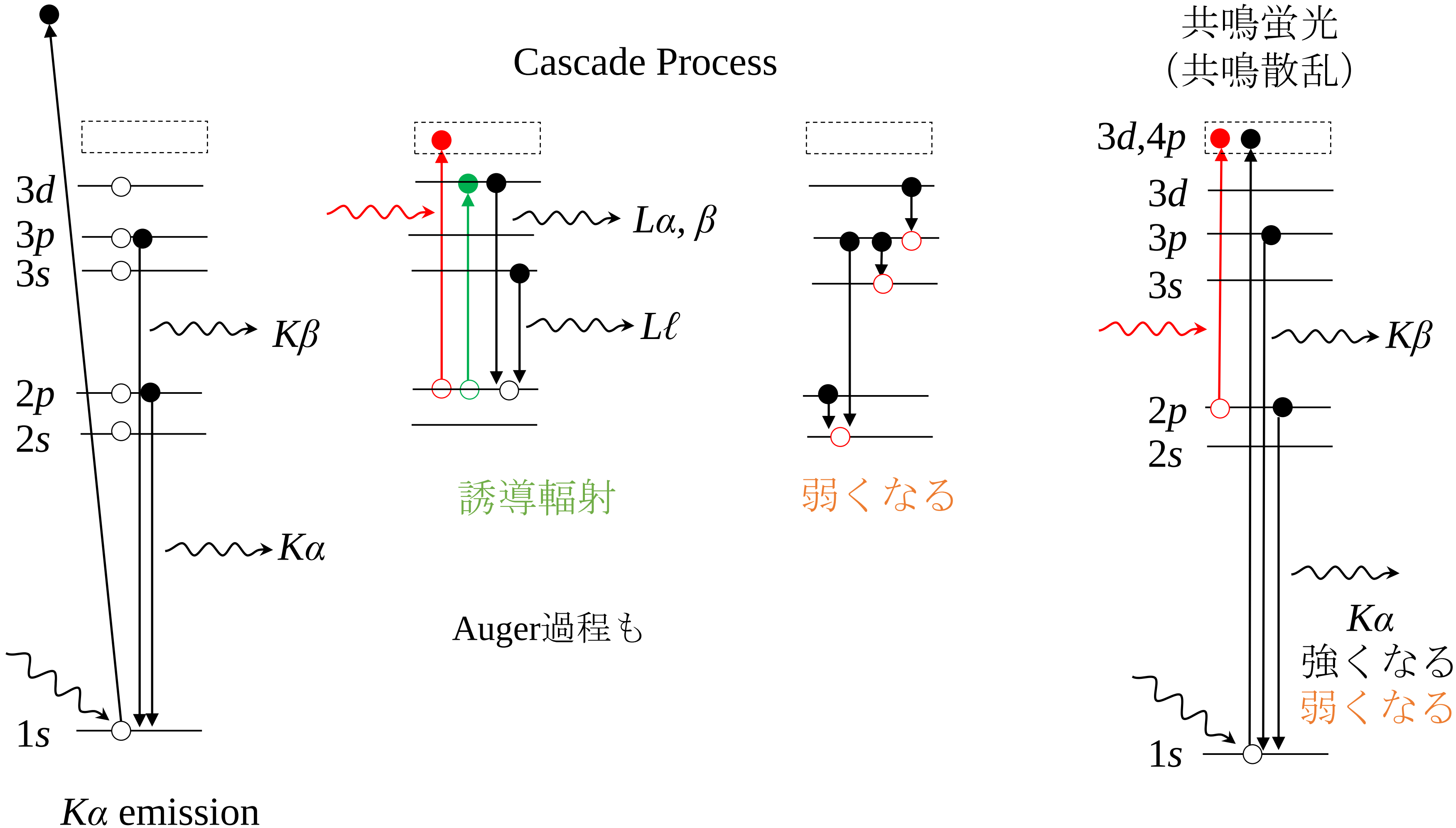
- 高輝度な2-ビーム
- Coherence



ビームラインの提案

Undulator　×2

蛍光X線



- 蛍光X線の選択的強度変調
- 軟X線の増幅

内殻吸収