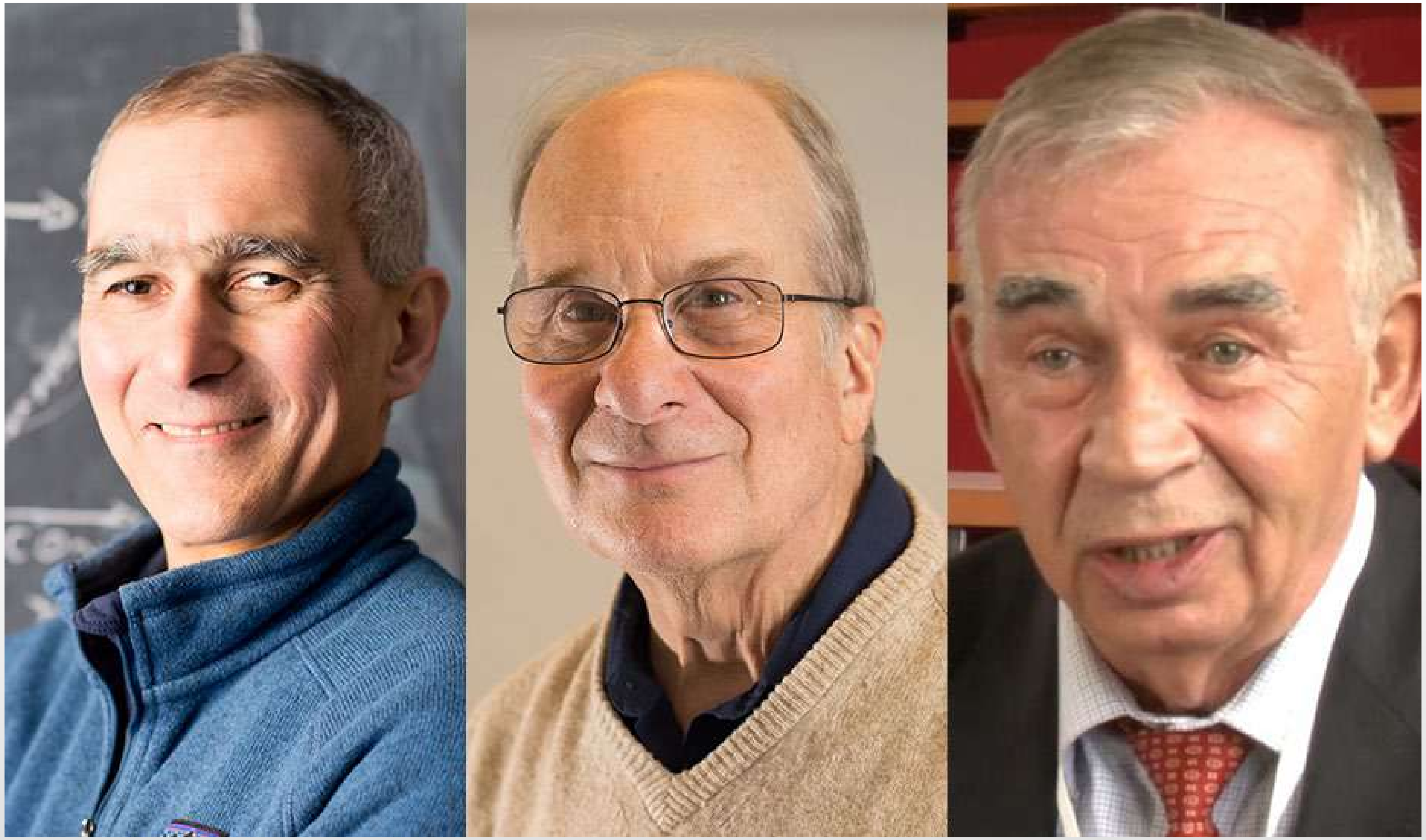
Ученый совет ФИЦ ХФ РАН. 26 октября 2023 г.

Квантовые точки в фотонике, фотокатализе и биофотонике: фемтосекундная динамика экситонов и носителей заряда в системах, проявляющих эффект квантового ограничения.

Надточенко В.А.

Нобелевская премия по химии 2023



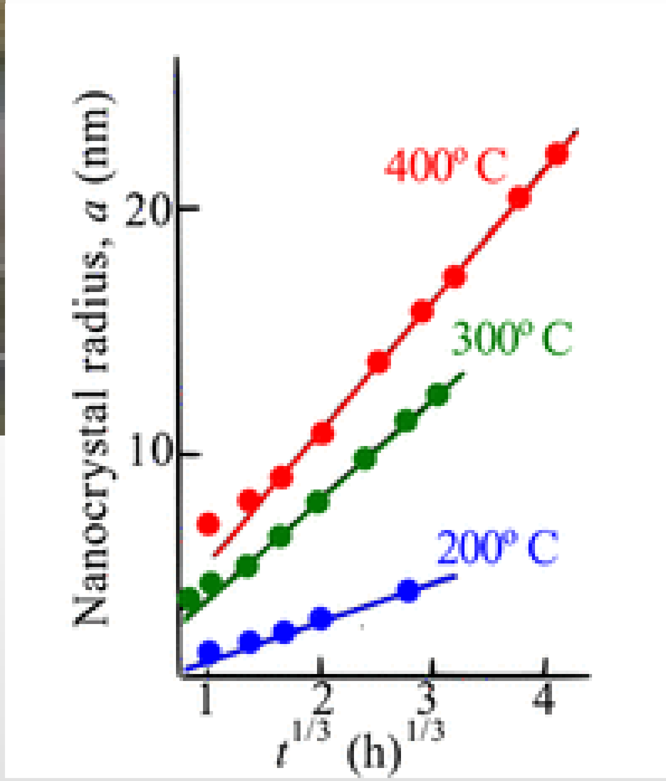
Left to right: Moungi Bawendi, Louis Brus, and Alexei Ekimov.

КВАНТОВЫЕ ТОЧКИ

Cadmium yellow

Cadmium red

Cadmium yellow



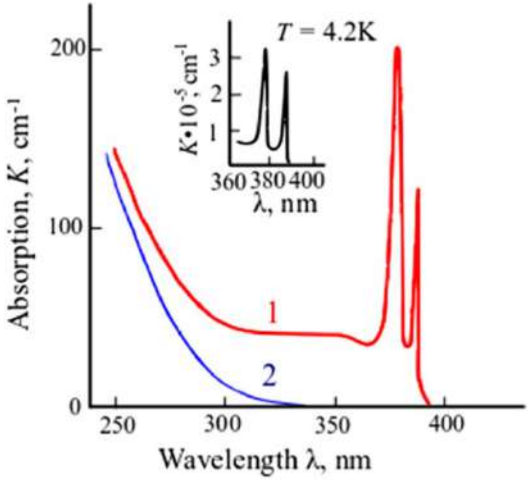
ОНУЩЕНКО Алексей Аркадьевич

В 1975 окончил кафедру молекулярной физики ЛГУ им. А.А. Жданова. Сотрудник ГОИ им. С.И. Вавилова. Канд. физ.-мат. наук (1989, «Спектроскопические свойства микрокристаллической фазы гетерогенных стекол»).

Письма в ЖЭТФ, том 34, вып. 6, стр. 363 – 366 20 сентября 1981 г.

КВАНТОВЫЙ РАЗМЕРНЫЙ ЭФФЕКТ В ТРЕХМЕРНЫХ МИКРОКРИСТАЛЛАХ ПОЛУПРОВОДНИКОВ

А.И.Екимов, А.А.Онущенко



CuCl

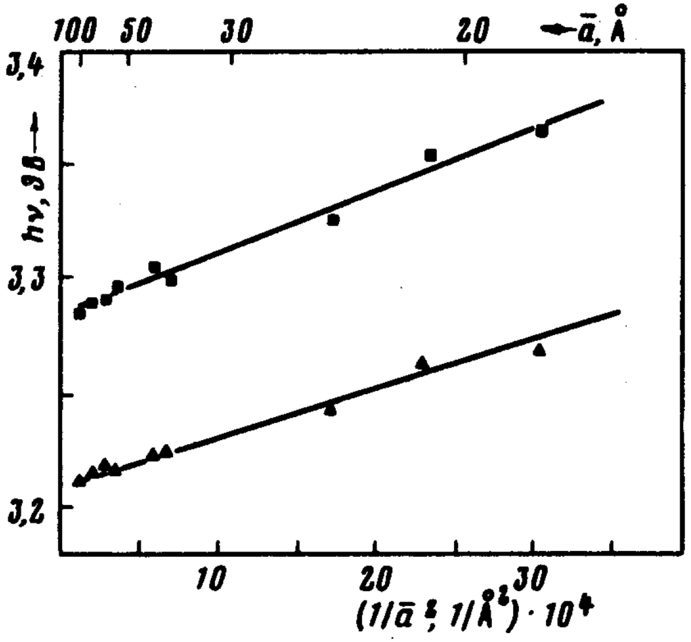


Рис. 3. Зависимость положения линий экситонного поглощения при $T = 4{,}2$ К от величины среднего радиуса микрокристаллов.

В предположении сферически симметричной потенциальной ямы бесконечной глубины, а также пренебрегая дисперсией частиц по размерам, коротковолновый сдвиг, обусловленный размерным квантованием частицы с массой m, может быть описан следующим выражением [7]

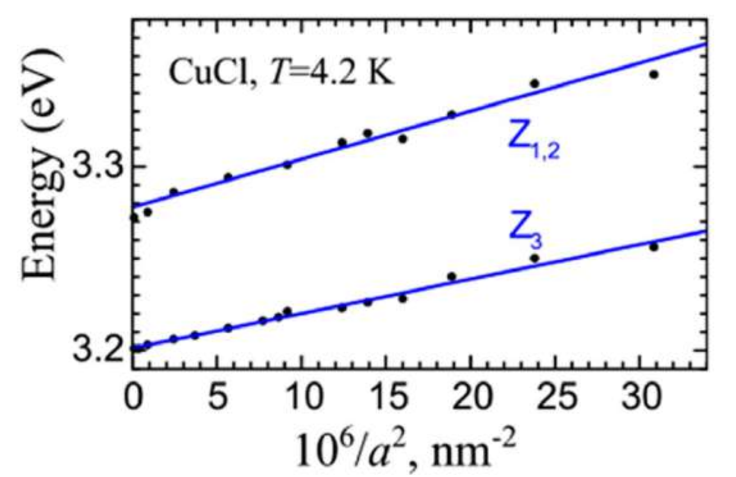
$$\Delta E = \hbar^2 \pi^2 / 2 m \bar{a}^2. \qquad (2)$$

Эфрос А. Л., Эфрос А. Л.
Межзонное поглощение света в полупроводниковом шаре.
ФТП. 1982;16(7)

р. 25.09.1950

ЭФРОС Александр Львович

ЛФТИ им. А.Ф. Иоффе



$$\hbar\omega = E_g - E_{ex} + \frac{\hbar^2\pi^2}{2Ma^2}$$

р. 11.08.1938

ЭФРОС Алексей Львович

С 1961 работал в ЛФТИ им. А.Ф. Иоффе (с 1987 – главн. науч. сотр.).

Канд. физ.-мат. наук (1962, «Квантовая теория проводимости в сильных магнитных полях»).
Д-р физ.-мат. наук (1972, «Теория сильно легированных полупроводников»).

Quantum size effects in the redox potentials, resonance Raman spectra, and electronic spectra of CdS crystallites in aqueous solution

R. Rossetti, S. Nakahara, and L. E. Brus

J. Chem. Phys. 79(2), 15 July 1983

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 31 March 1983; accepted 5 May 1983)

In small crystallites there should be two major effects: (1) increased e^- and h^+ localization kinetic energies and (2) increased attractive electrostatic interaction $\langle e^2/\epsilon r \rangle$ between e^- and h^+. The first term tends to blue shift, and the second term tends to red shift the exciton.

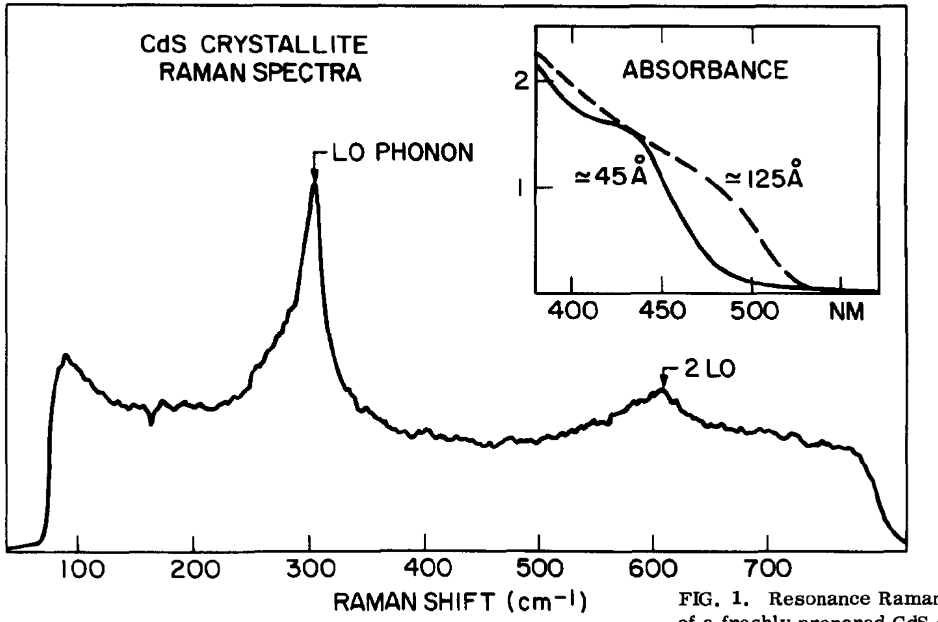
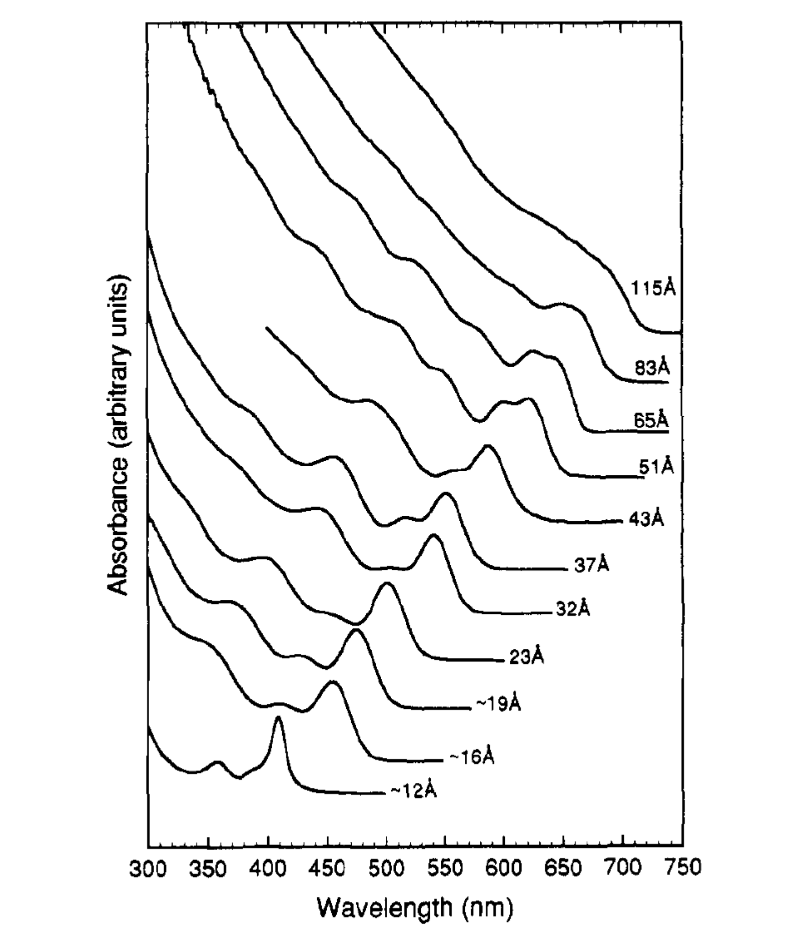


FIG. 1. Resonance Raman spectrum of a freshly prepared CdS colloid at *p*H7. The CdS monomer concentration is 1.55×10^{-3} M. The colloid is stabilized with 1 mgm/cc of styrene/maleic anhydride copolymer. The experimental resolution is 5 cm^{-1}; the CdS peak has a 22 cm^{-1} (FWHM) width. An increase in Raman scattering near 100 cm^{-1} is due to water and not CdS. The insert shows the optical absorbance spectra for both a fresh colloid, and for the same colloid after aging, as described in the text.

J. Am. Chem. Soc. **1993,** *115*, 8706–8715

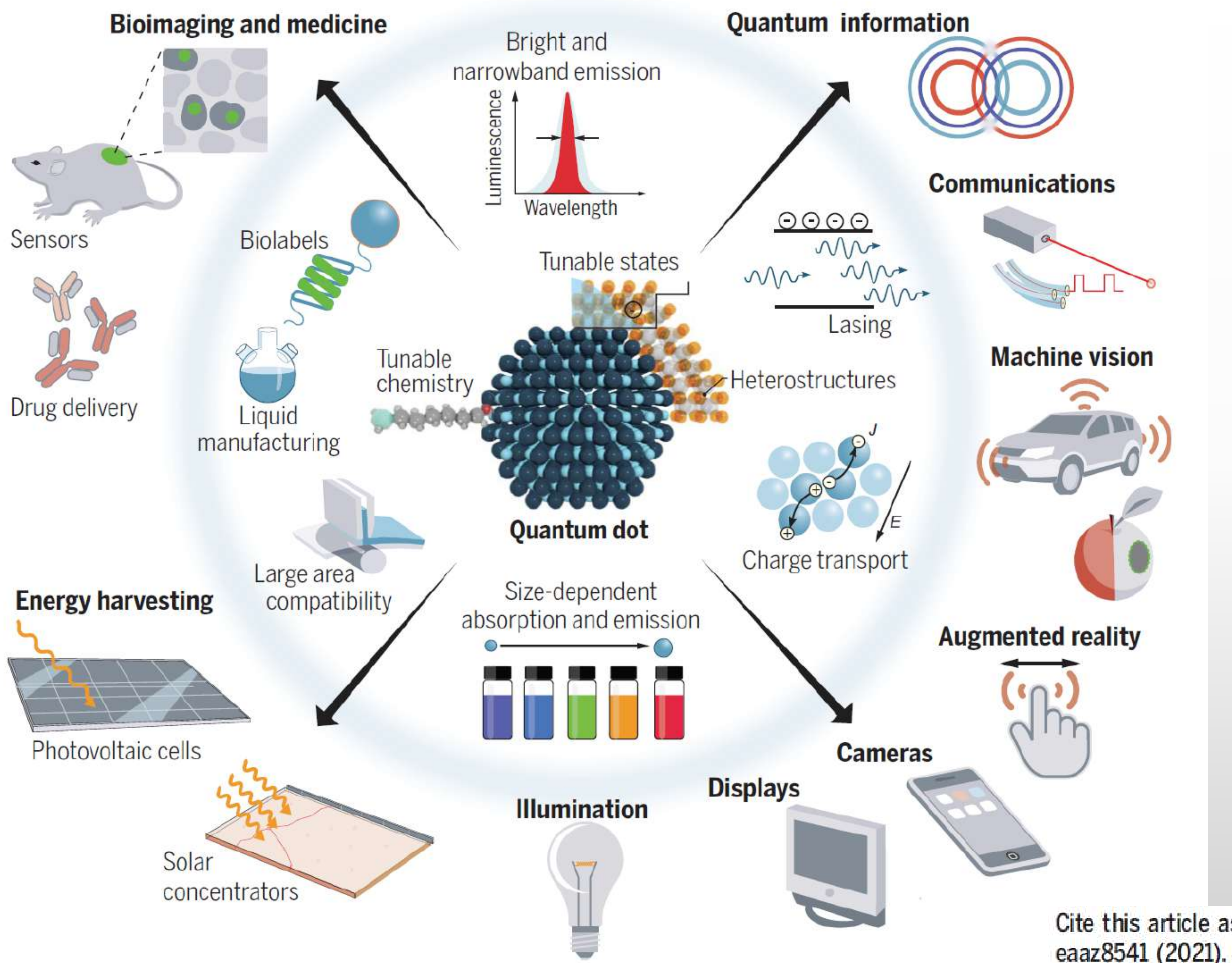
Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites

C. B. Murray, D. J. Norris, and M. G. Bawendi*



tributylphosphine oxide (TBPO)

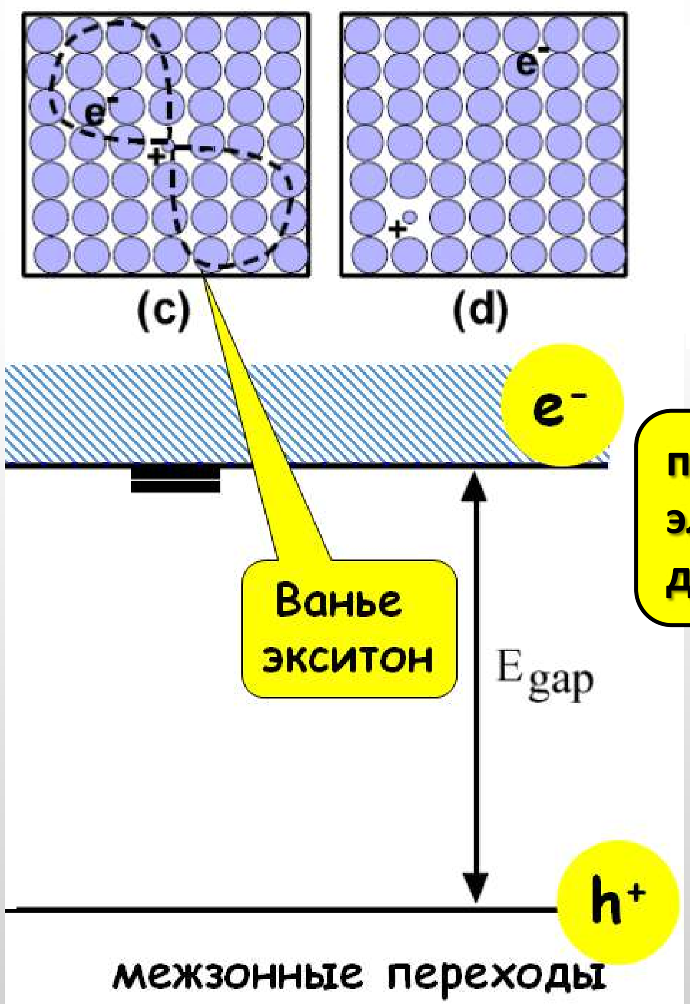
tributylphospine TBP



Cite this article as F. P. García de Arquer *et al.*,[9] *Science* **373**, eaaz8541 (2021). DOI: 10.1126/science.aaz8541

Квантовые точки.

$$\hat{H} = \frac{-\hbar^2}{2m_e^*}\nabla_e^2 + \frac{-\hbar^2}{2m_h^*}\nabla_h^2 - \frac{e^2}{\varepsilon|r_e - r_h|}$$



$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon r},\;;$$

приведенная масса электрона m_e* и дырки m_h*

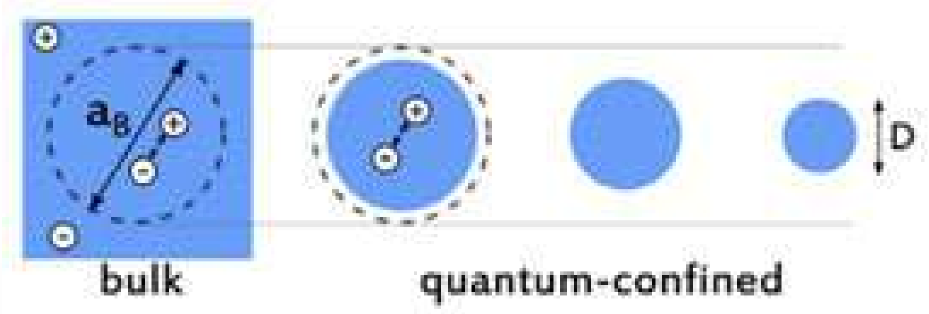
Диэлектрическая проницаемость

$$a_B = a_0\varepsilon\left(\frac{m_0}{\mu}\right)$$

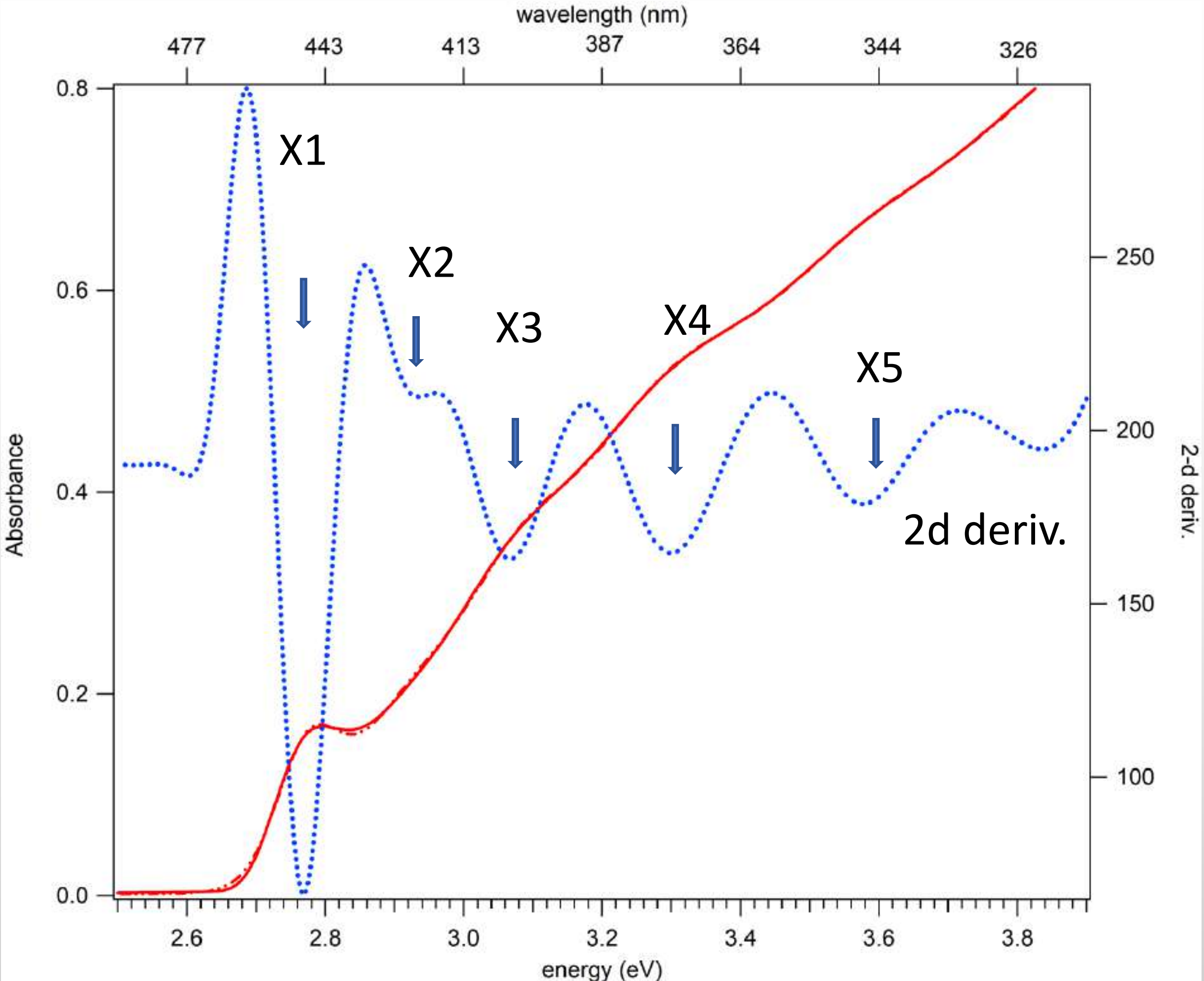
$$\mu = m_e^* \cdot m_h^* / (m_e^* + m_h^*)$$

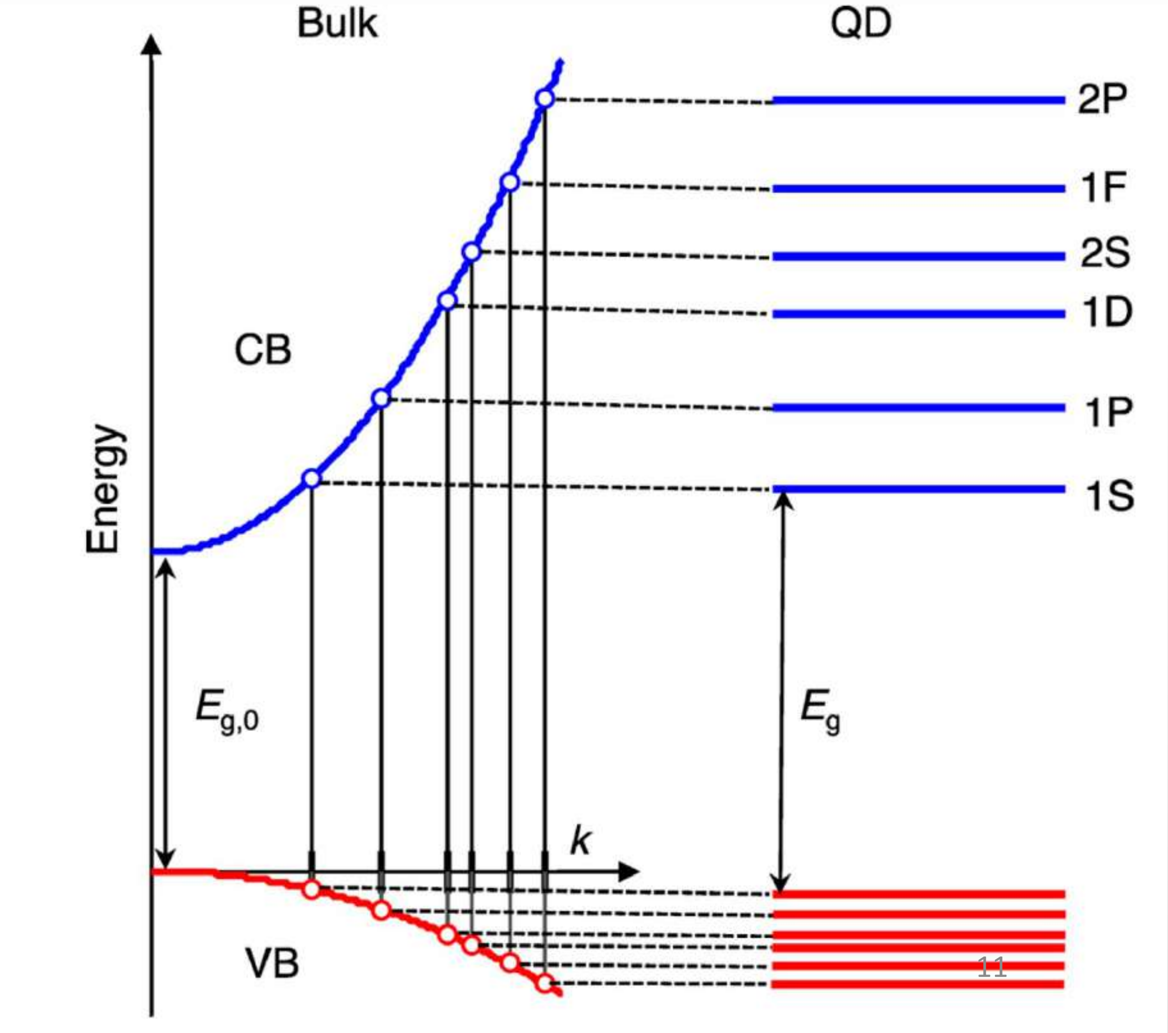
$$Ry^* = 13.6\,\mathrm{eV}\,\frac{\mu}{\epsilon^2}$$

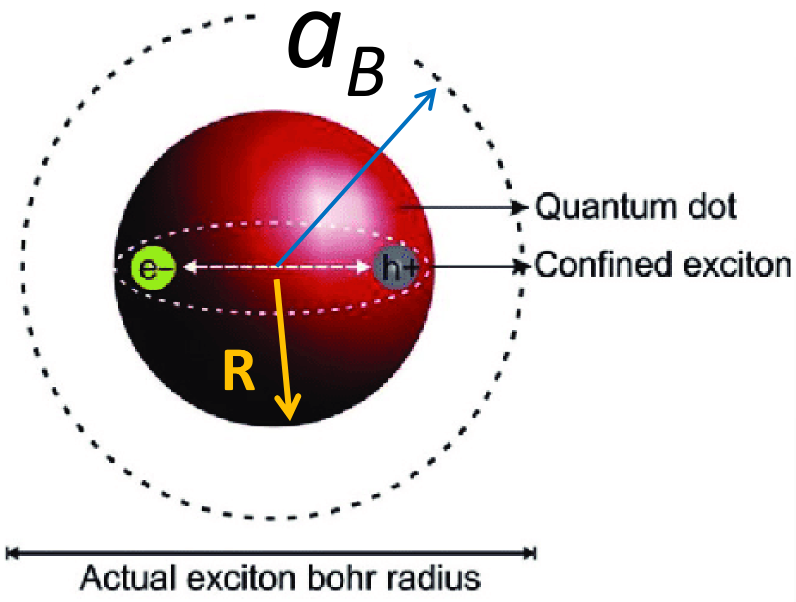
$$E_g = E_{g,bulk} + \frac{\hbar^2 \pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{\varepsilon R}$$



ZnCdS







$$a_B = a_0 \varepsilon \left(\frac{m_0}{\mu} \right)$$

Compound	Band gap (eV)	r_B (nm)
InP	1.35	15
InAs	0.354	34
InSb	0.17	65.6
CdS	2.43	5.8
CdSe	2.87	5.3
CdTe	1.5	7.3
ZnSe	2.67	4.5
TiO_2	**~3.2 eV**	**3.2 nm**

Crystal	m_e^*/m_e	m_h^*/m_e
GaN	0.13	0.8
ZnSe	0.13	0.65
CdS	0.19	0.8
ZnTe	0.12	0.5
CdSe	0.06	0.62
CdTe	0.05	0.46
GaAs	0.07	0.2
InP	0.08	0.3
GaSb	0.04	0.1
InSb	0.01	0.25
Sb_2S_3	1.035	1.843

Квантовые точки.

II - VI

CdTe, CdSe, CdS, ZnS, ZnSe, ZnTe

III - V

InP, InAs

I–III–VI_2

$CuInS_2$, $AgInS_2$

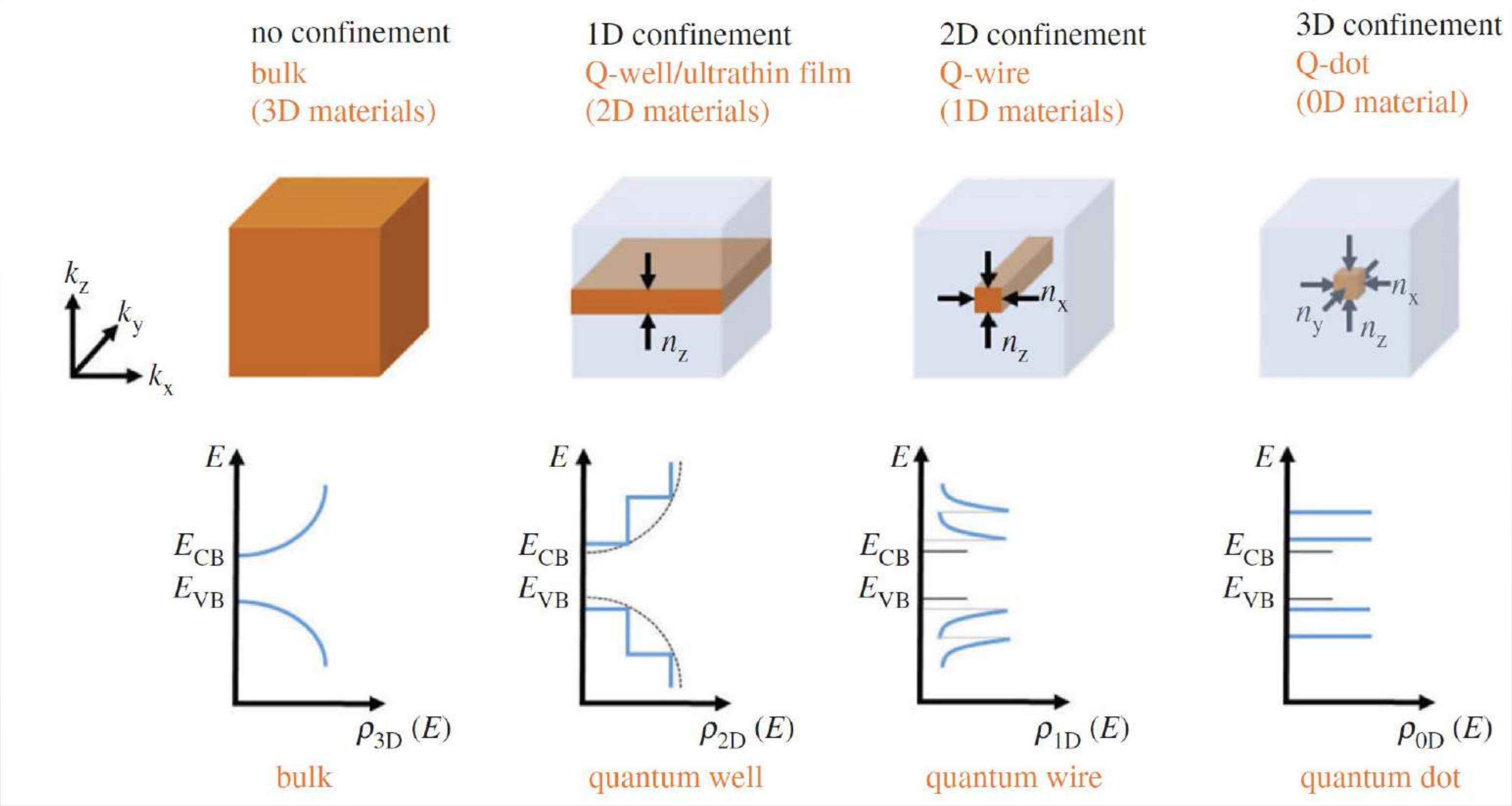
IV–VI

PbSe, PbS, PbTe

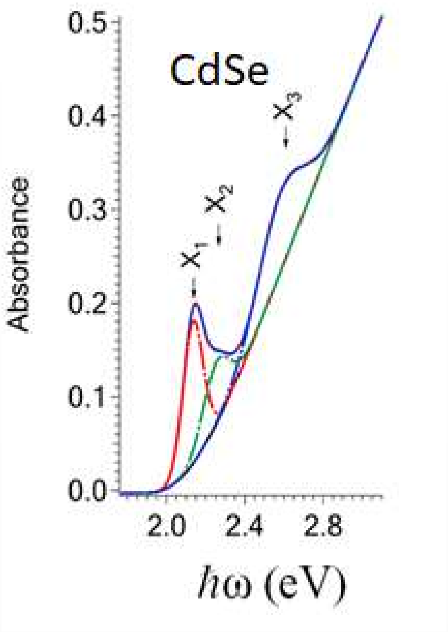
IV

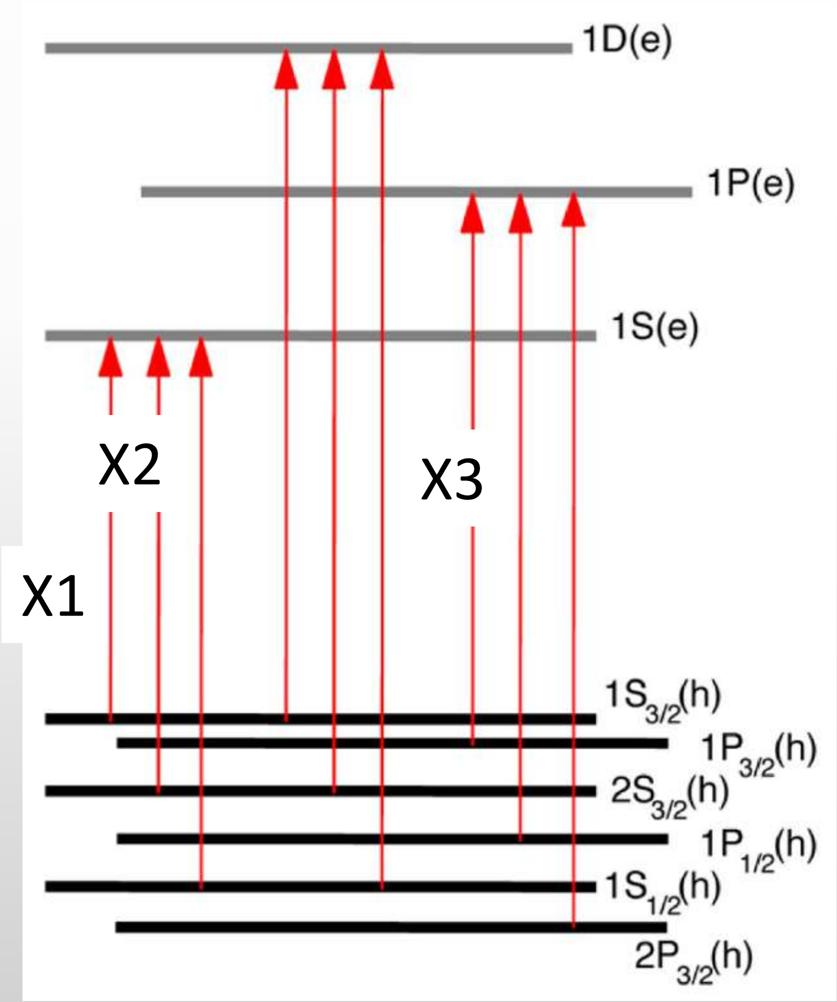
Si, C, Ge

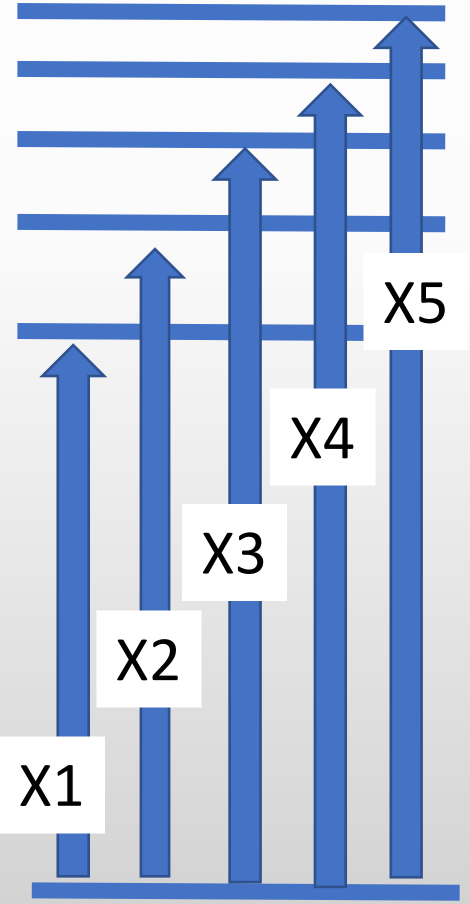
Квантово-размерные эффекты: плотность состояний *ρ(E) = dN/dE*

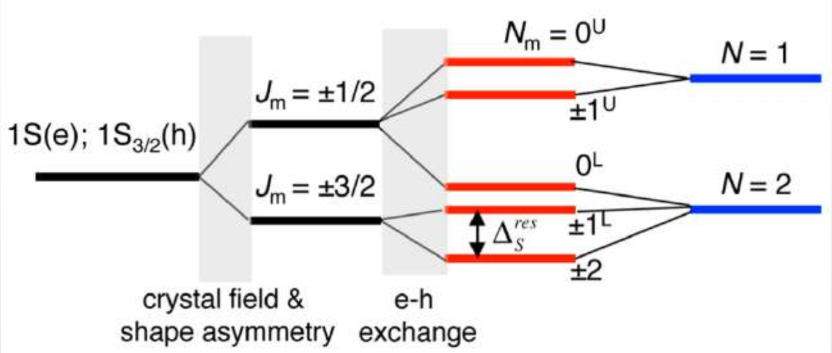


Представление энергетических уровней в квантовых точках: оптические переходы.









Теоретические модели КТ

particle-in-a-sphere (PIS)

Brus, L. E. J. Chem. Phys. 1983.
Brus, L. E. J. Chem. Phys. 1984

multiband effective mass approximation approach (EMA)

Norris, D. J.; Bawendi, M. G. Phys. Rev. B 1996
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Efros, A. L.; Rosen, M. Annu. Rev. Mater. Sci. 2000, 30, 475–521.
Efros, A. L.; et al. M. Phys. Rev. B 1996,
Ekimov, A. I.; et al. Opt. Soc. Am. B 1993,.

empirical pseudopotential method (EPM)

Franceschetti, A.; Zunger, A. Phys. Rev. Lett. 1997,
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Shumway, J.; et al. A. Los Alamos National Laboratory, Preprint Archive, Condensed Matter; 2000; pp 115, arXiv: cond-mat/0012050.
Califano, M.; et al. Nano Lett. 2003, .
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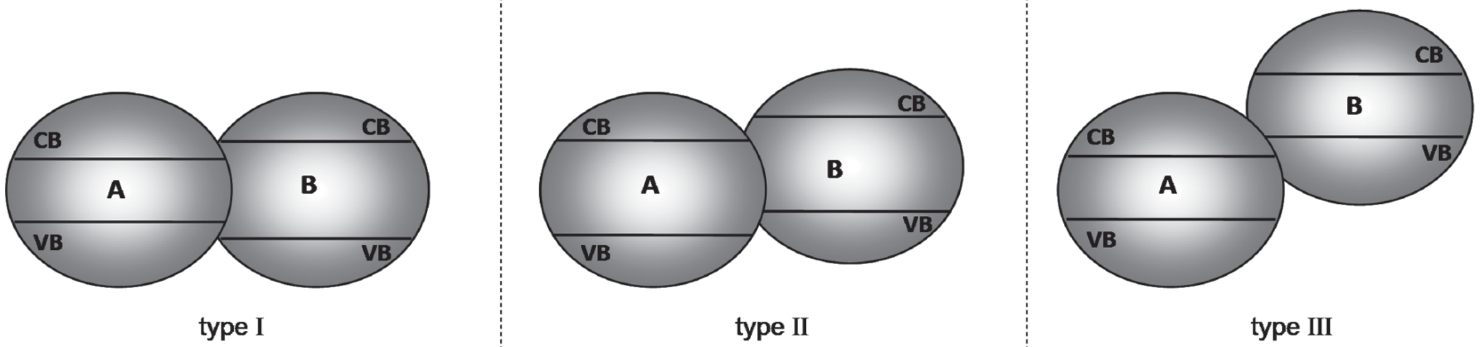
Califano, M.; et al. A. Nano Lett. 2005,
An, J. M.; et al. J. Chem. Phys. 2008
Wang, L.-W.; Zunger, A. J. Phys. Chem. B 1998

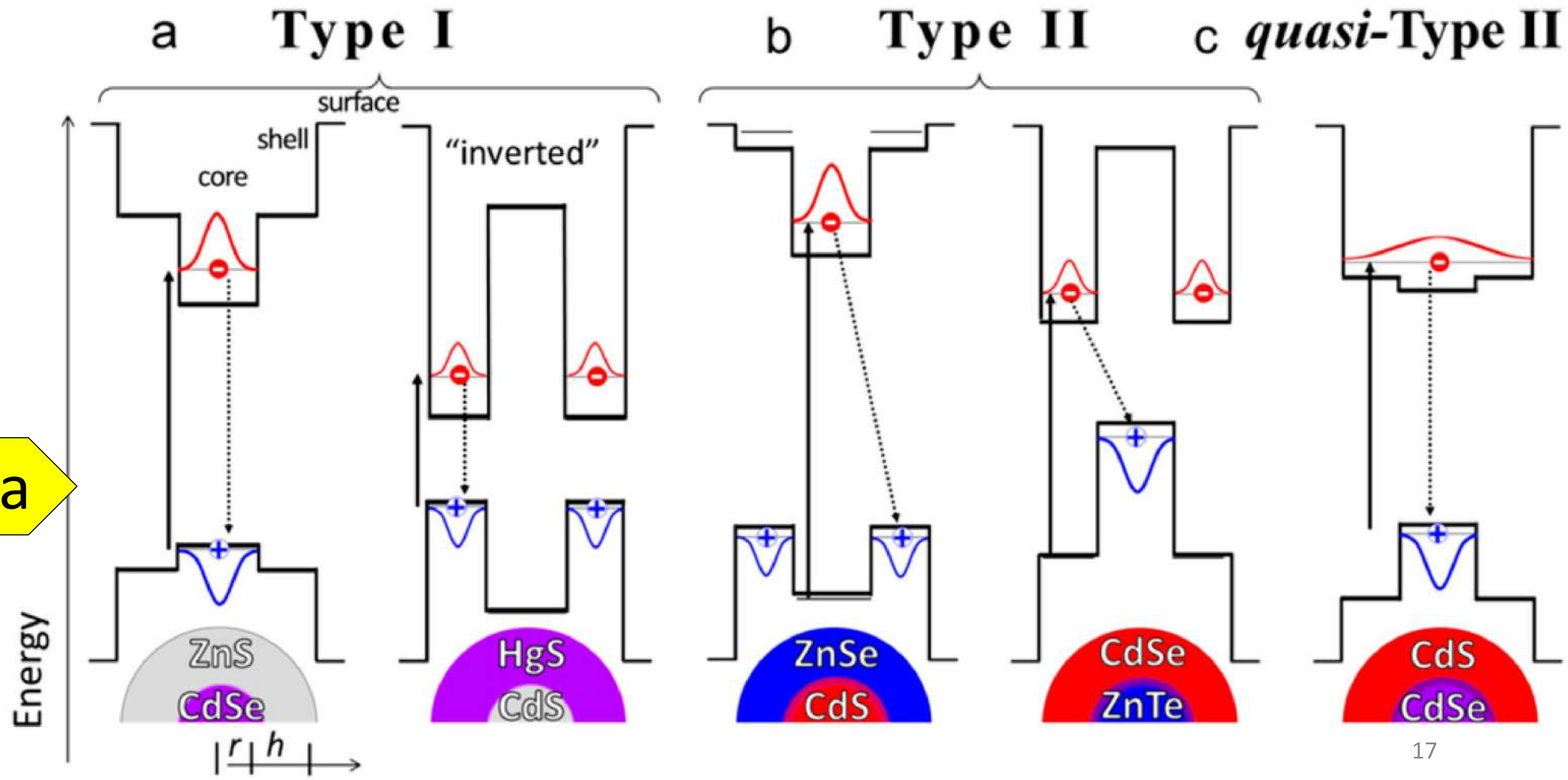
ab initio

Prezhdo, O. V. Acc. Chem. Res. 2009
Madrid, A. B.; et al. ACS Nano 2009
Kilina, S. V.; et al. ACS Nano 2009
Bao, H.; et al. Phys. Rev.B 2009
Prezhdo, O. V. Chem. Phys. Lett. 2008.
Kilina, S. V. J. Phys. Chem. C 2007.

Янус точки



Ядро/Оболочка



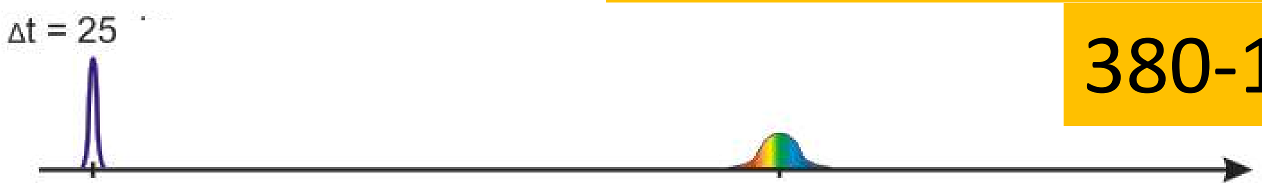
Фемтосекундная спектроскопия:

pump-probe spectroscopy

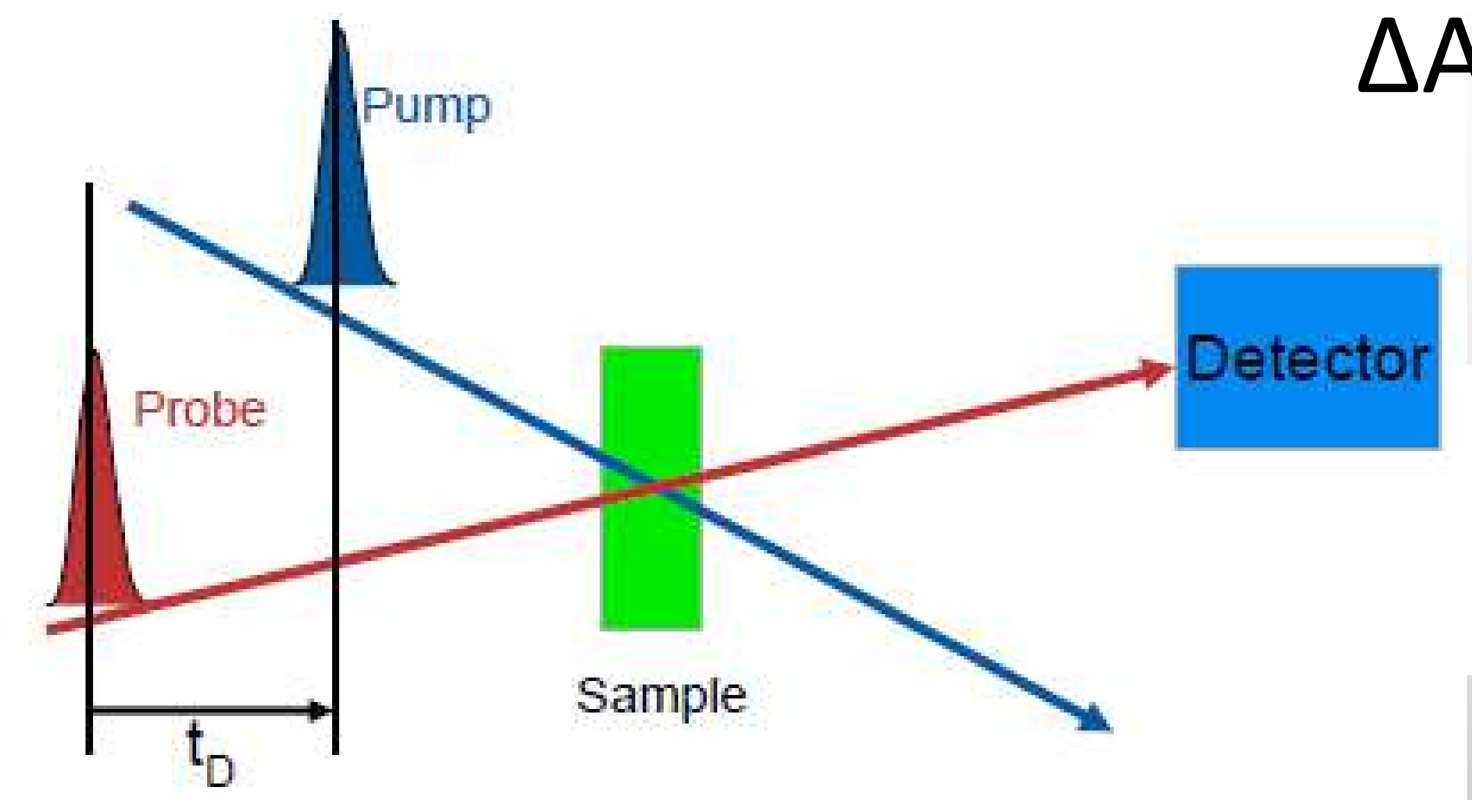
Pump pulse ~ 10-30 fs

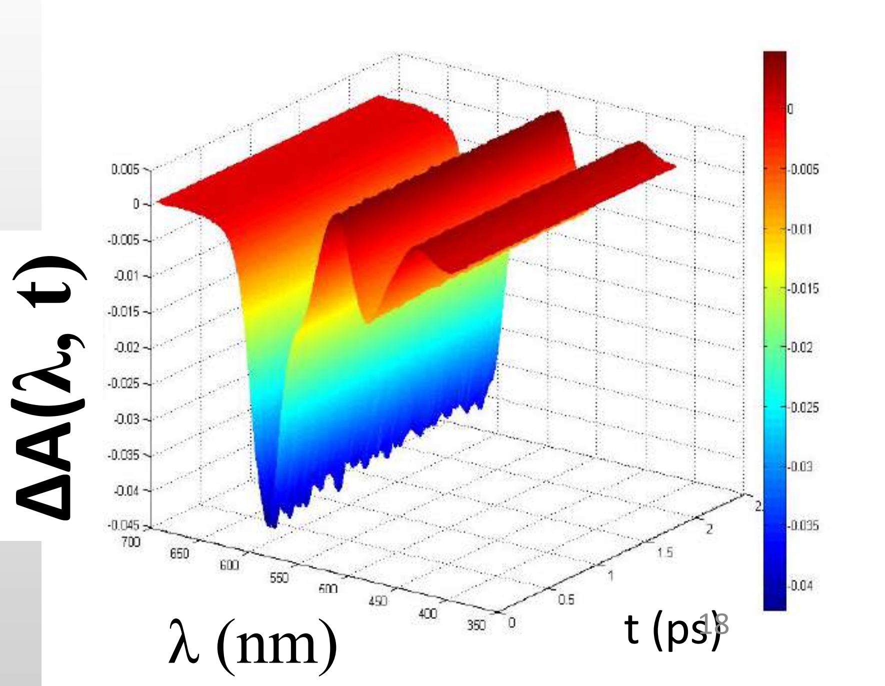
Probe pulse is white supercontinuum

380-1000 nm



$$\Delta A(\lambda,t) = A\,(\lambda,t) - A_0$$

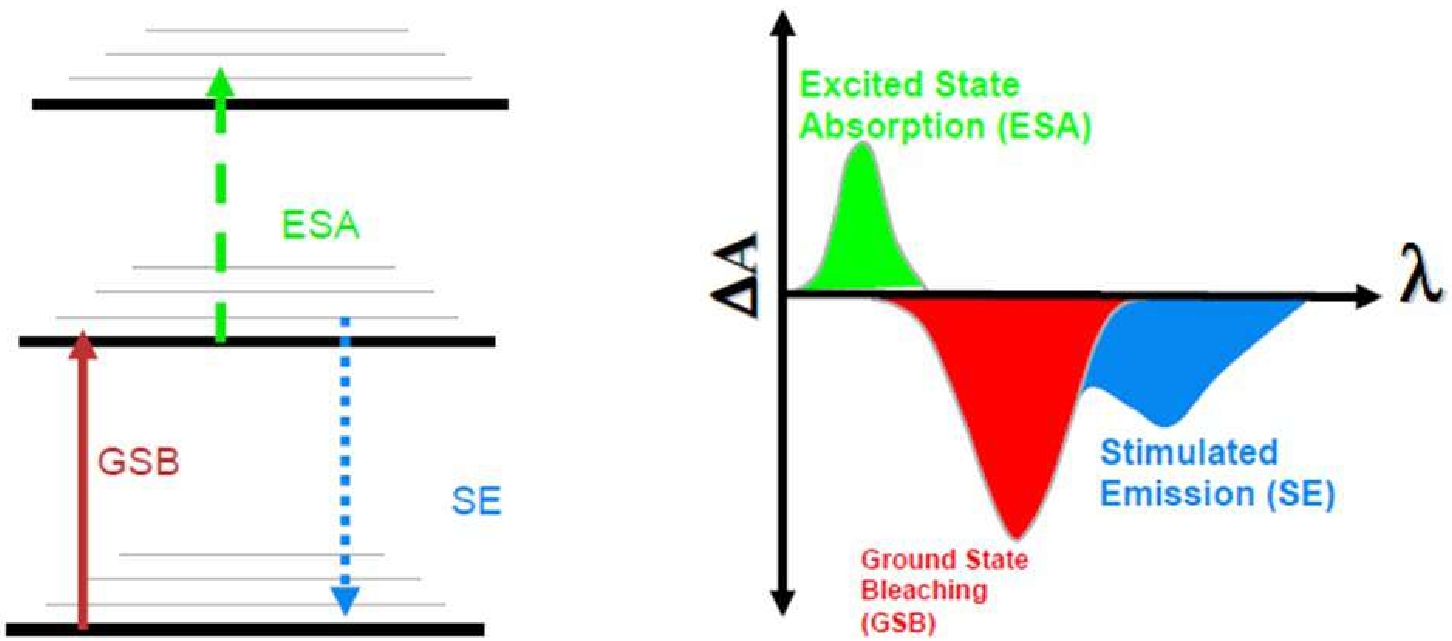


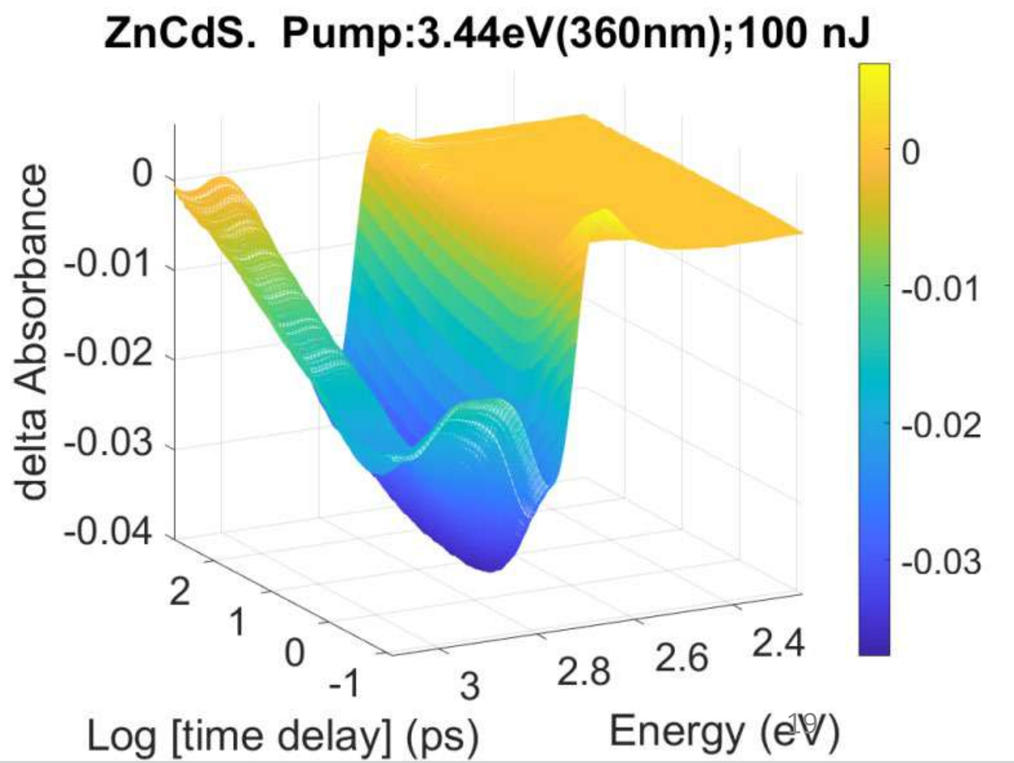


Transient absorption spectra
Дифференциальные спектры

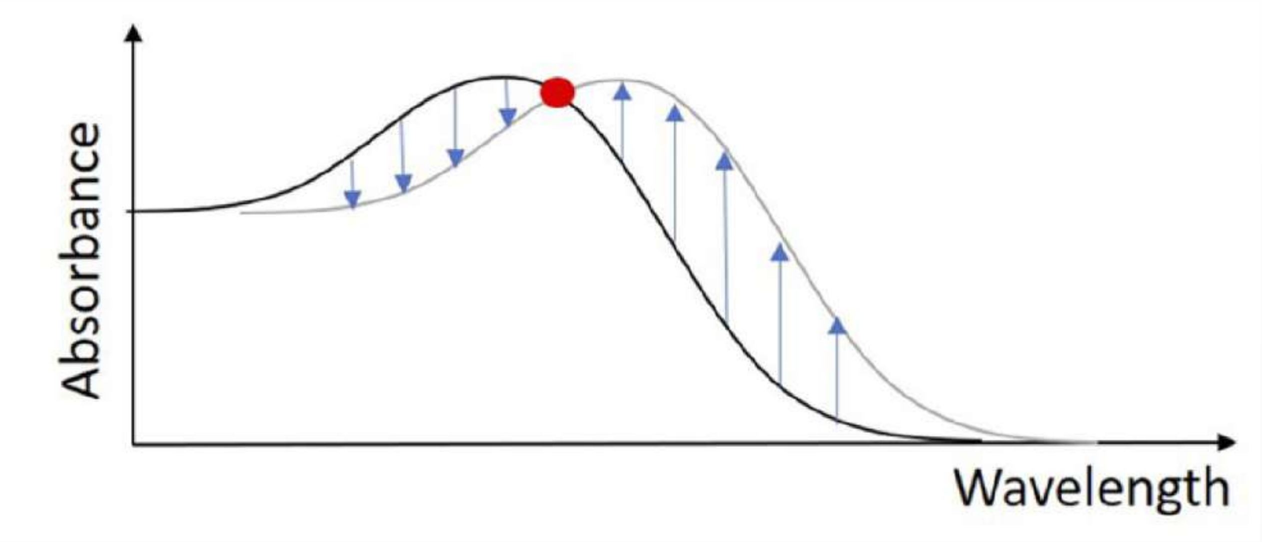
$$\Delta A(\lambda, t) = A(\lambda, t) - A(\lambda, t = -\infty)$$

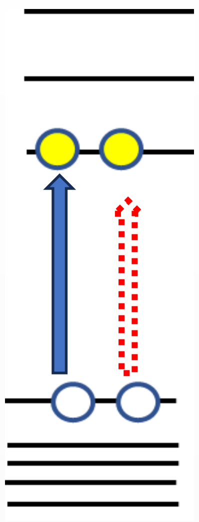
$$\Delta A = \Delta A(t, \lambda)$$ Difference between the sample absorption with and without pump pulse

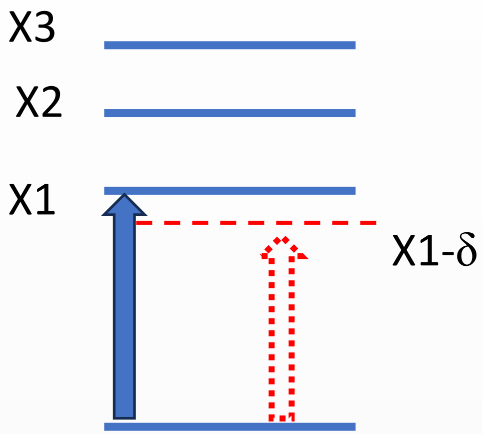




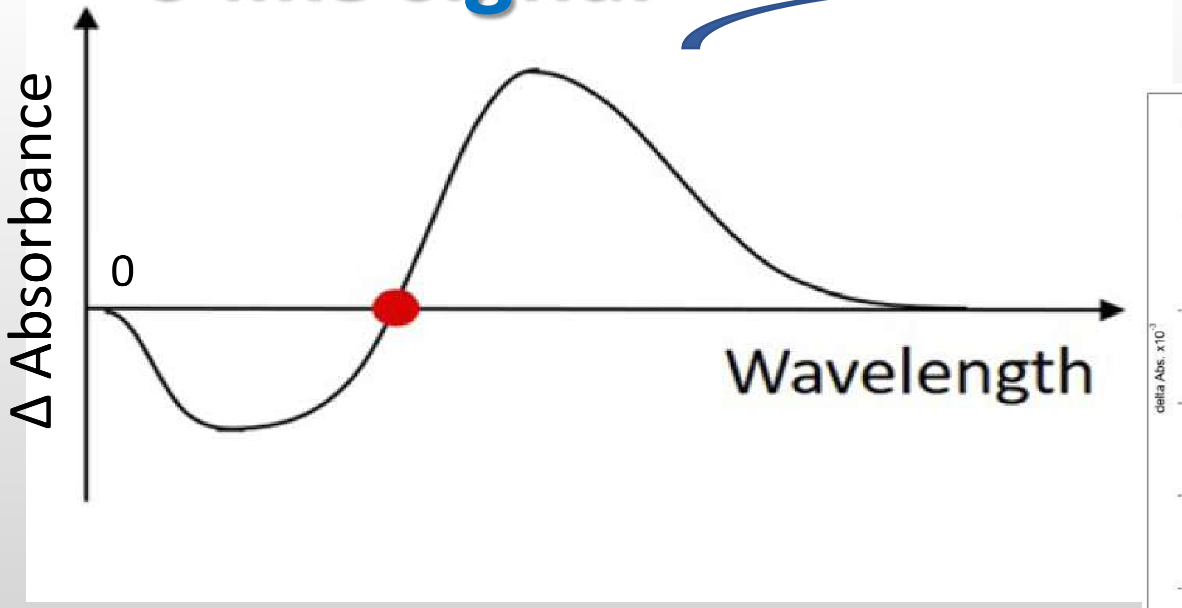
Biexciton shift / Stark shift

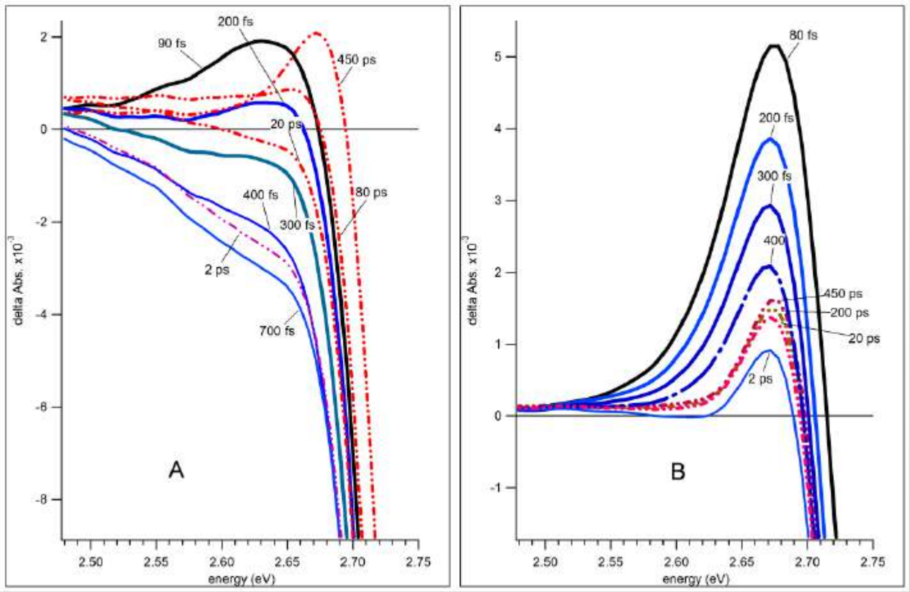






S like signal



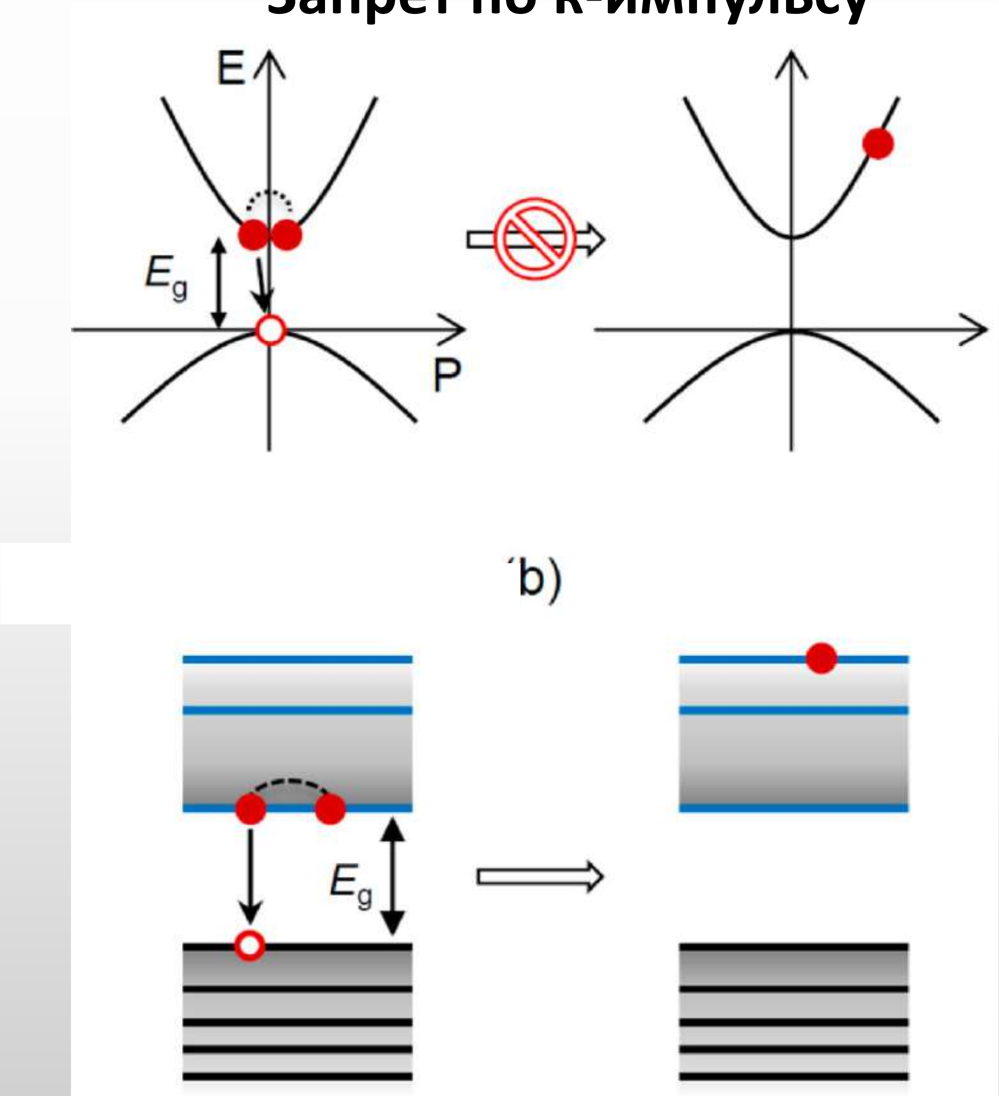


ОЖЕ РЕКОМБИНАЦИЯ
ГЕНЕРАЦИЯ ГОРЯЧЕГО ЭЛЕКТРОНА/ДЫРКИ

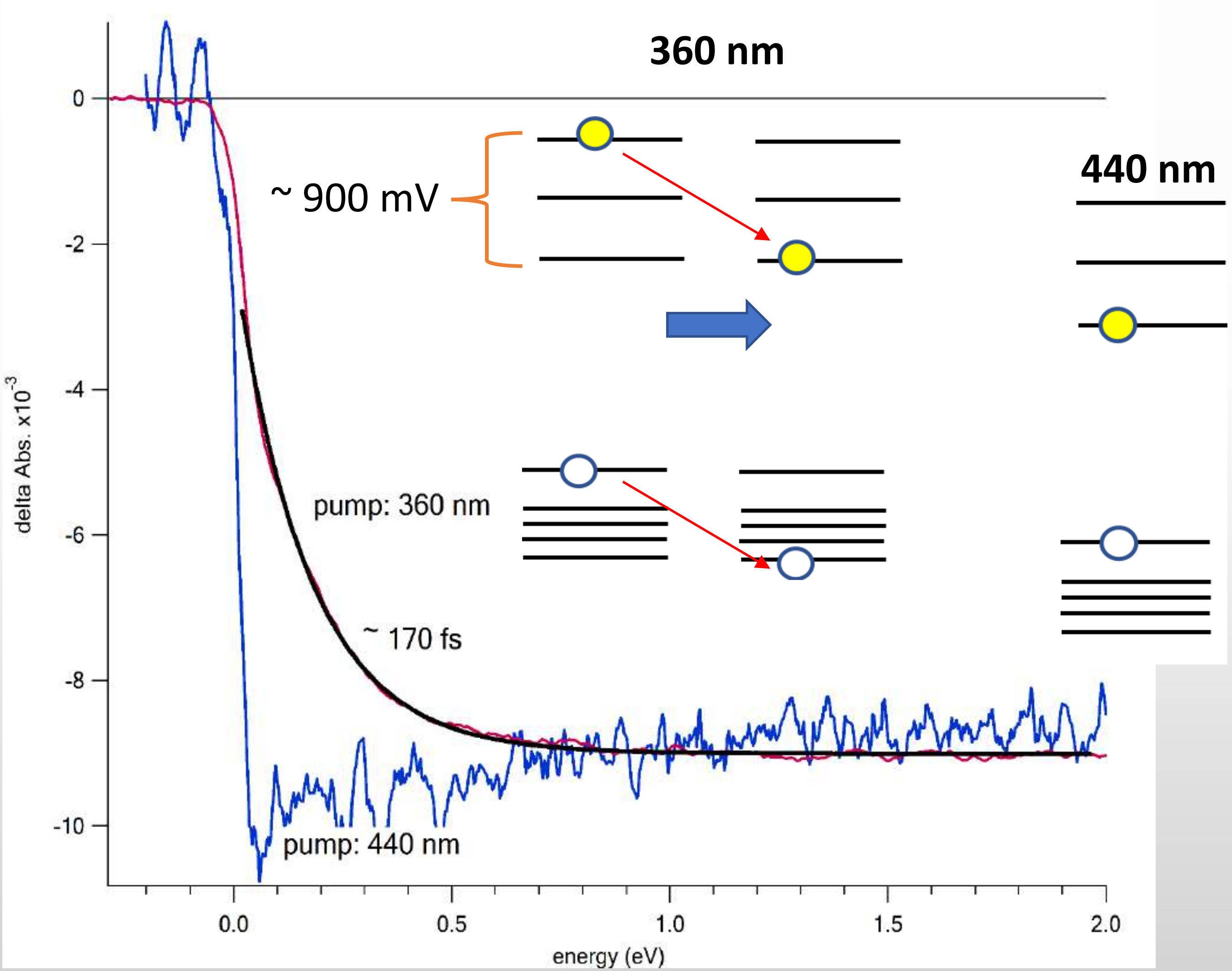
Запрет по к-импульсу

ОБЪЕМНЫЙ ПОЛУПРОВОДНИК

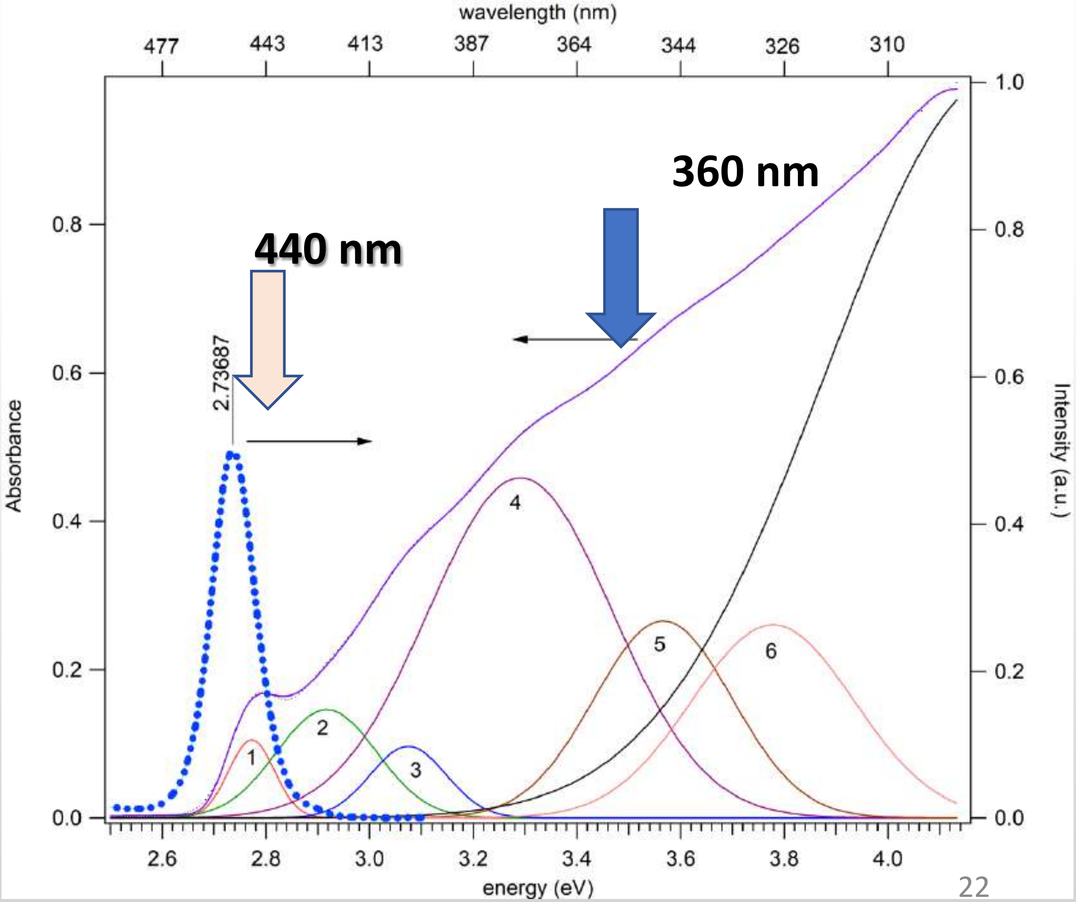
КВАНТОВАЯ ТОЧКА



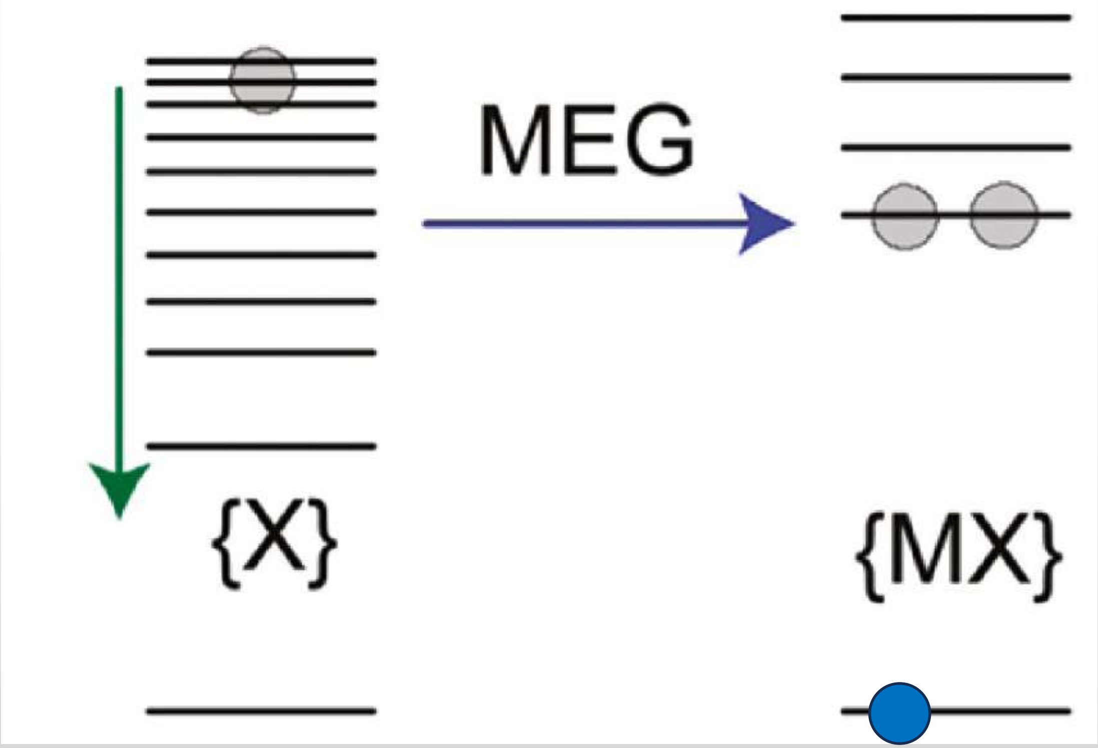
Релаксация горячего электрона

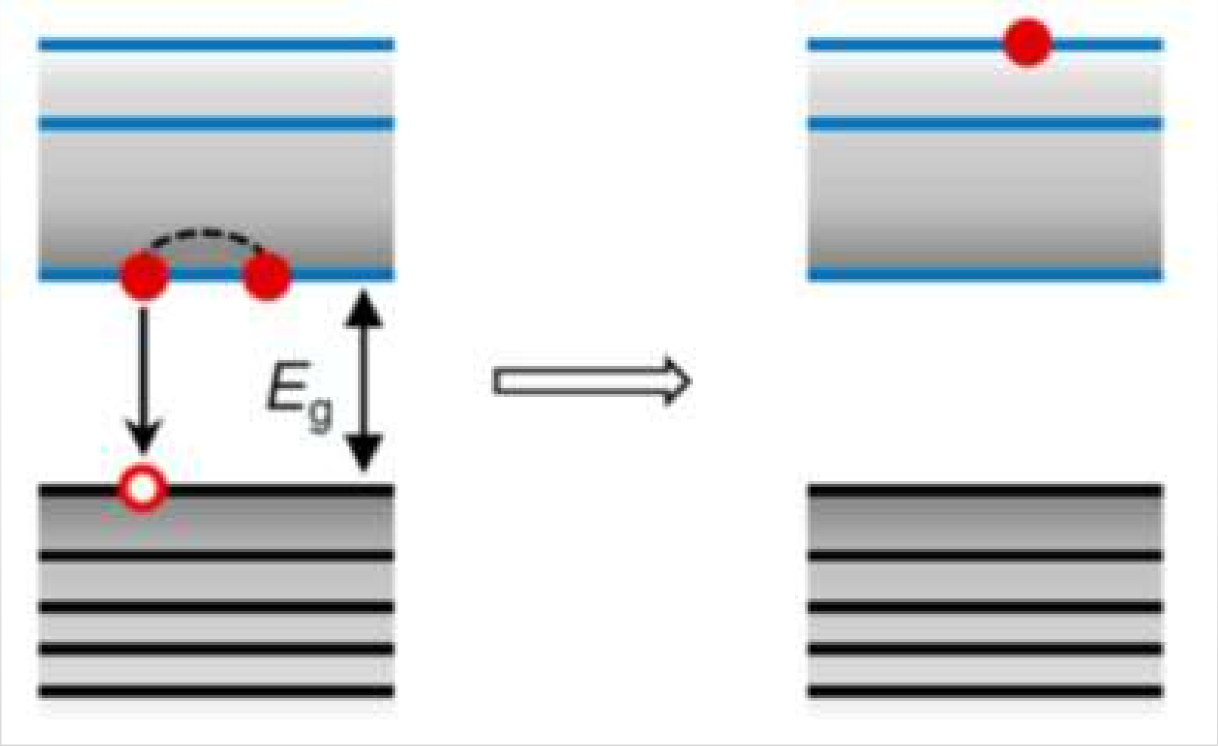


ZnCdS

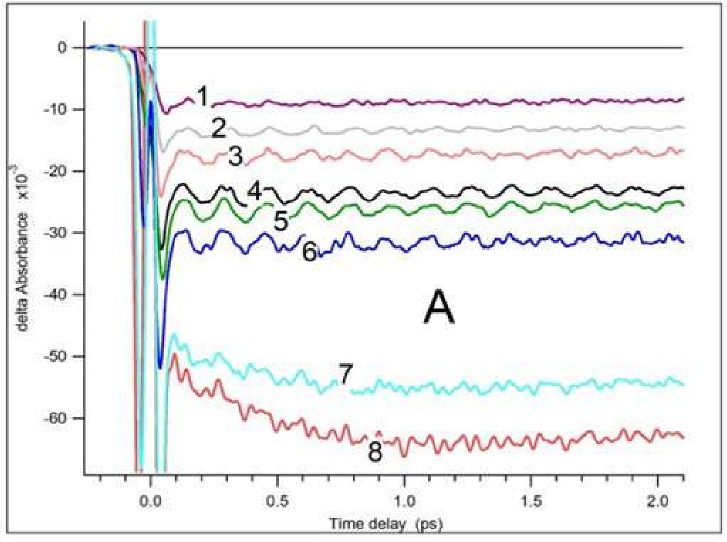


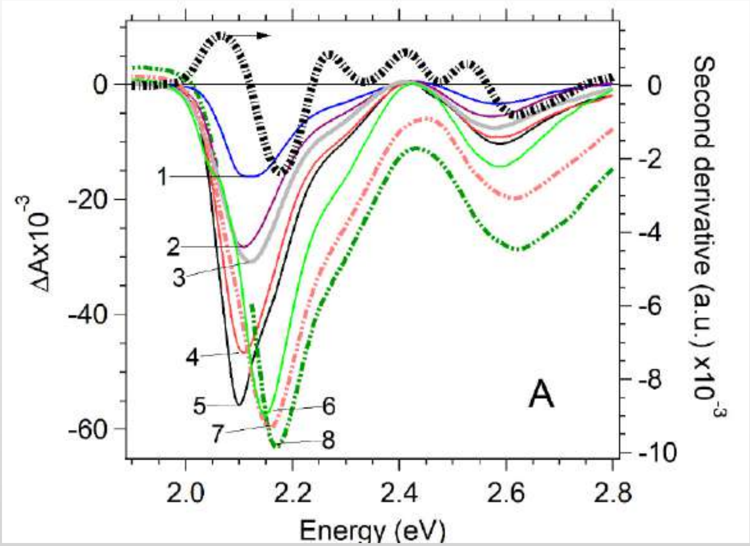
РЕЛАКСАЦИЯ ГОРЯЧЕГО ЭКСИТОНА
ОЖЕ ПРОЦЕСС: ГЕНЕРАЦИЯ МУЛЬТИЭКСИТОНОВ



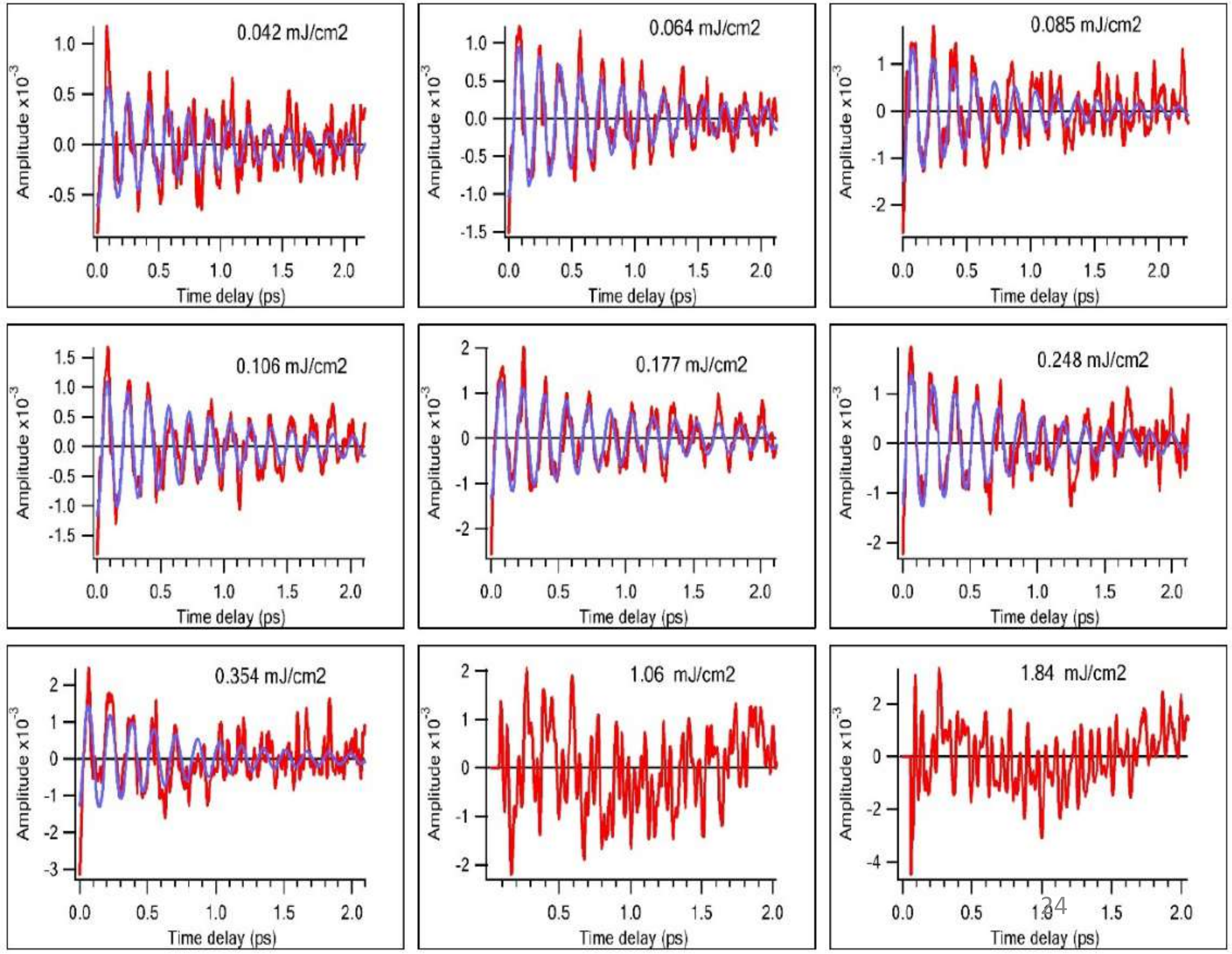


CdSe QDs:
когерентные волновые пакета как функция энергии возмущения.

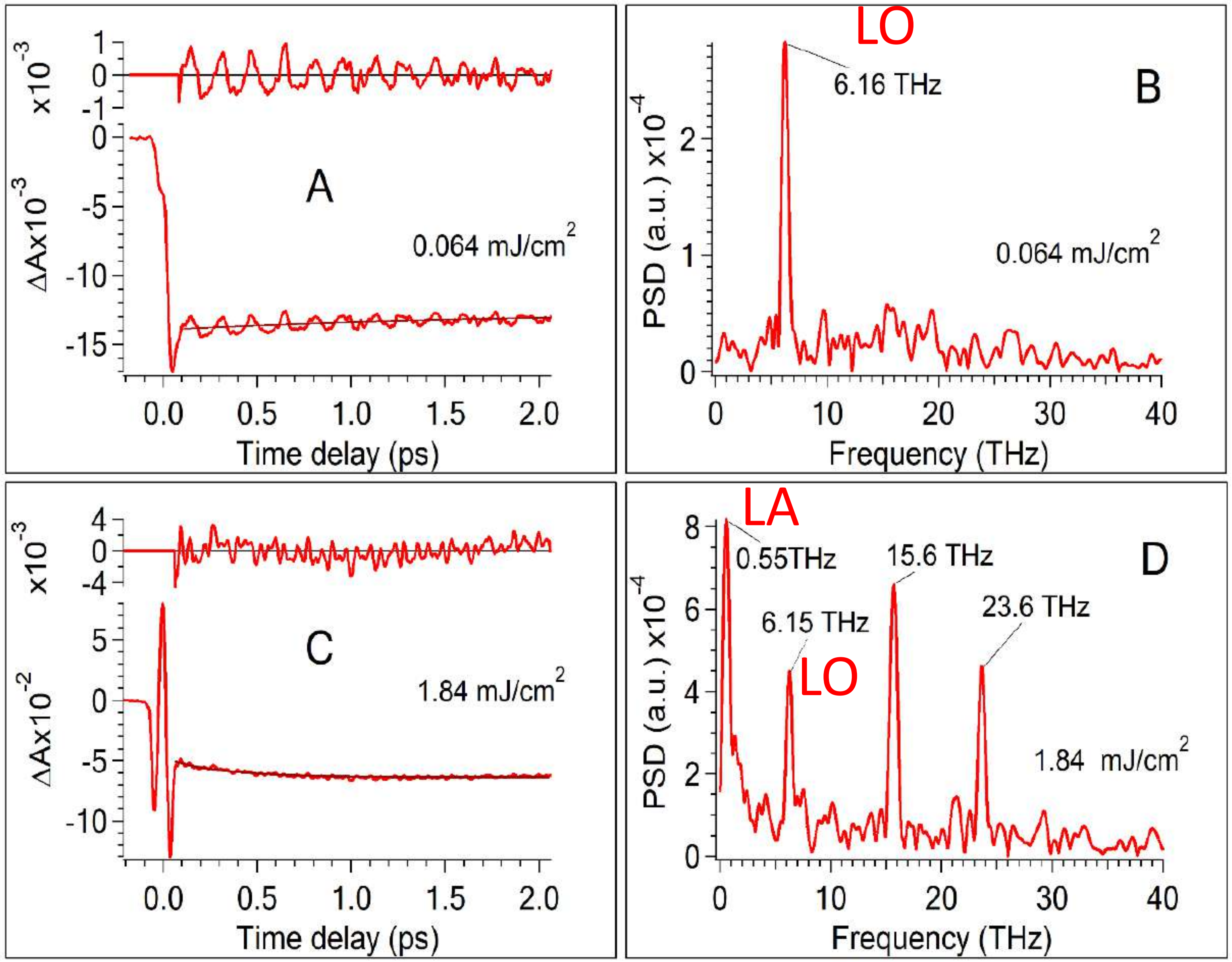




V. Nadtochenko et al. Nanomaterials **2017**

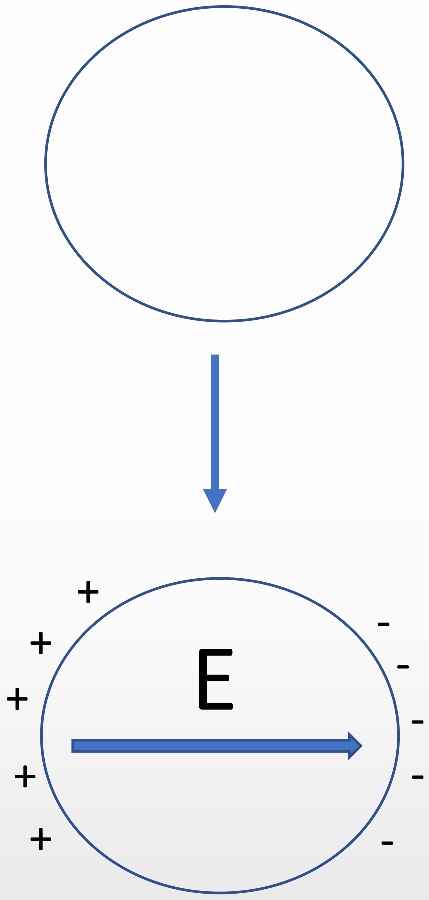


FFT спектры



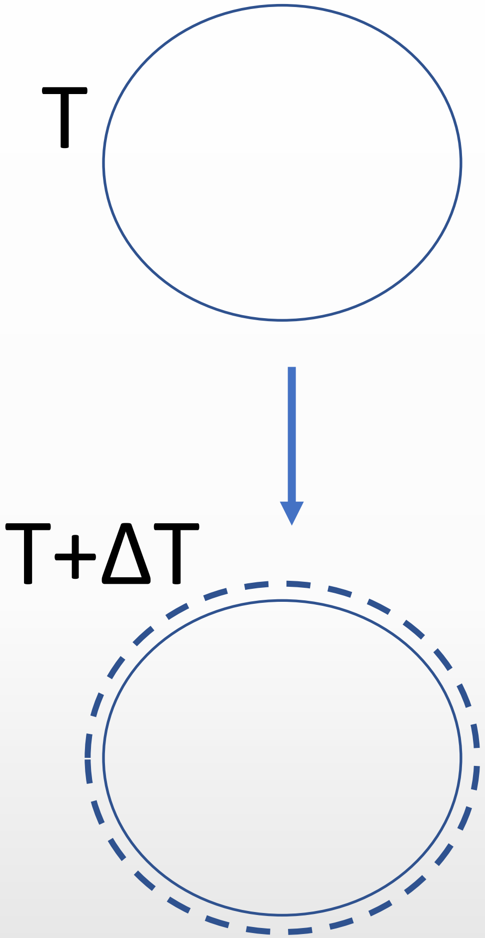
x10^{-3}
ΔAx10^{-3}
A
0.064 mJ/cm^2
Time delay (ps)
LO
6.16 THz
B
PSD (a.u.) x10^{-4}
0.064 mJ/cm^2
Frequency (THz)
x10^{-3}
ΔAx10^{-2}
C
1.84 mJ/cm^2
Time delay (ps)
LA
0.55THz
15.6 THz
D
6.15 THz
LO
23.6 THz
PSD (a.u.) x10^{-4}
1.84 mJ/cm^2
Frequency (THz)

Piezoelectric screening



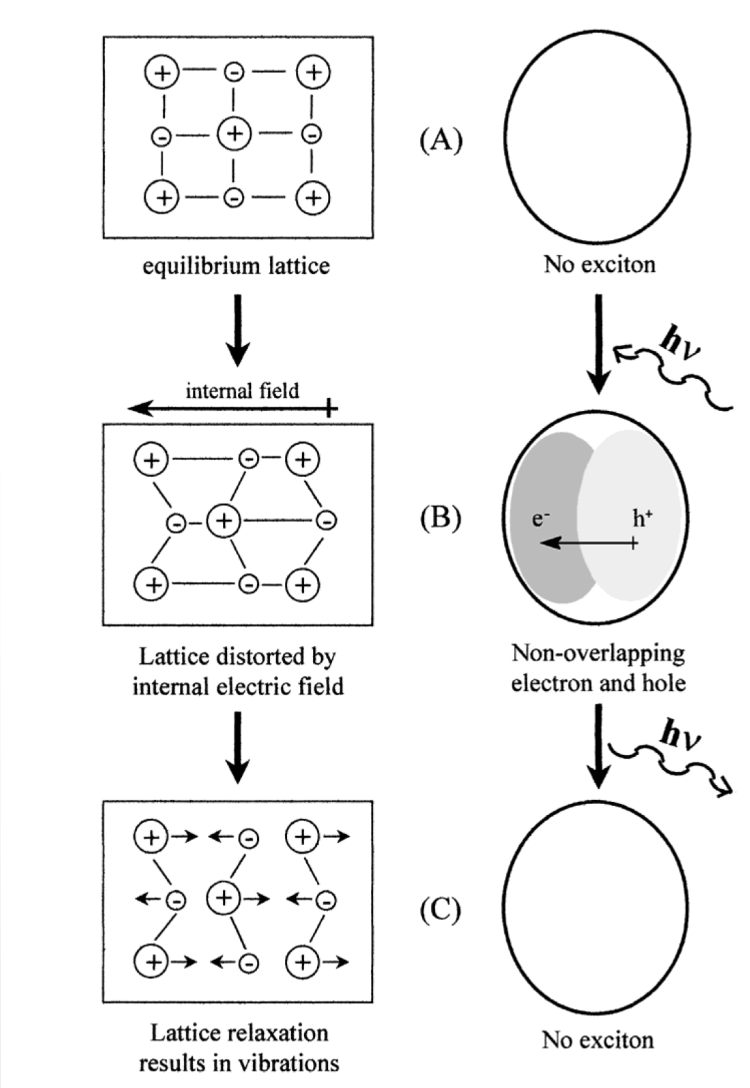
LA

Thermoelastic effect



LA

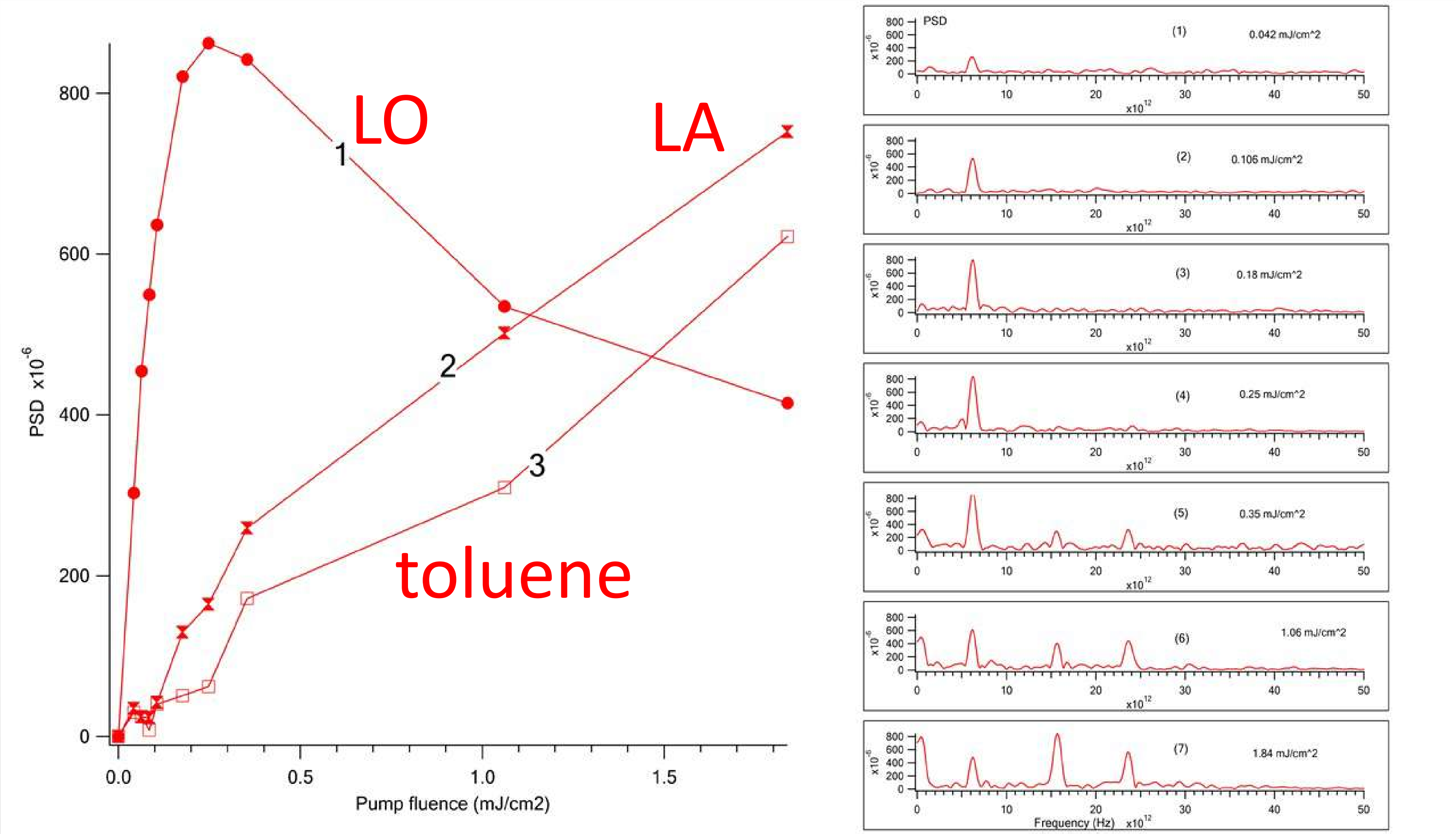
Frohlich mechanism



LO

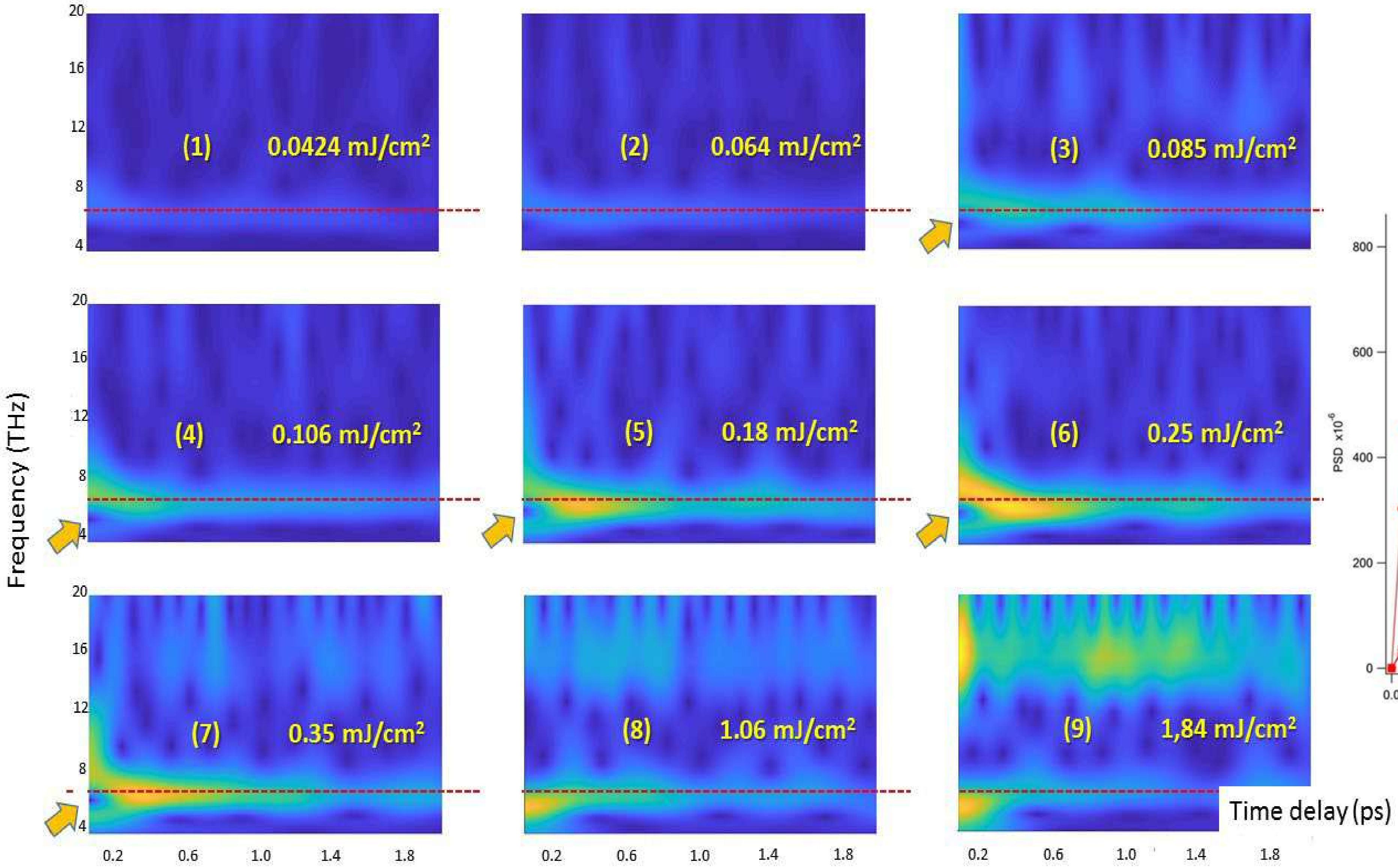
Stephen A. Empedocles, et all

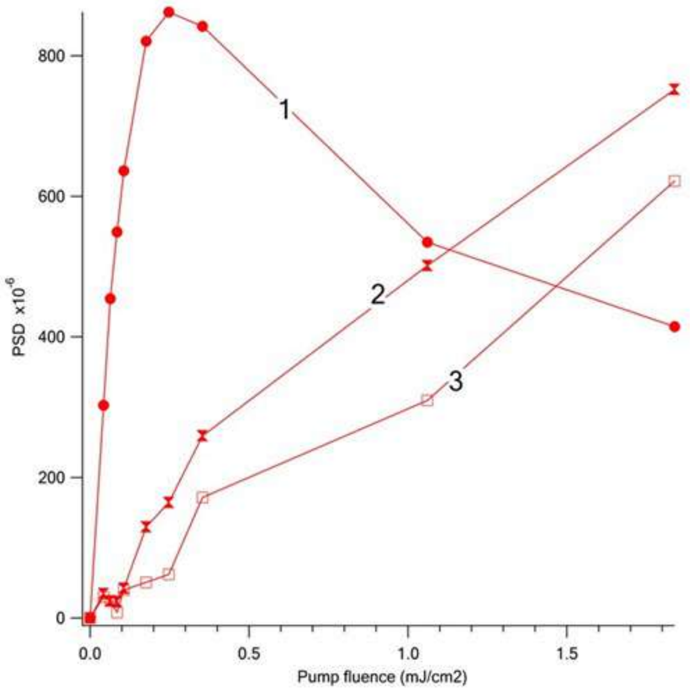
Амплитуда LO фонона относительно энергии импульса возбуждени



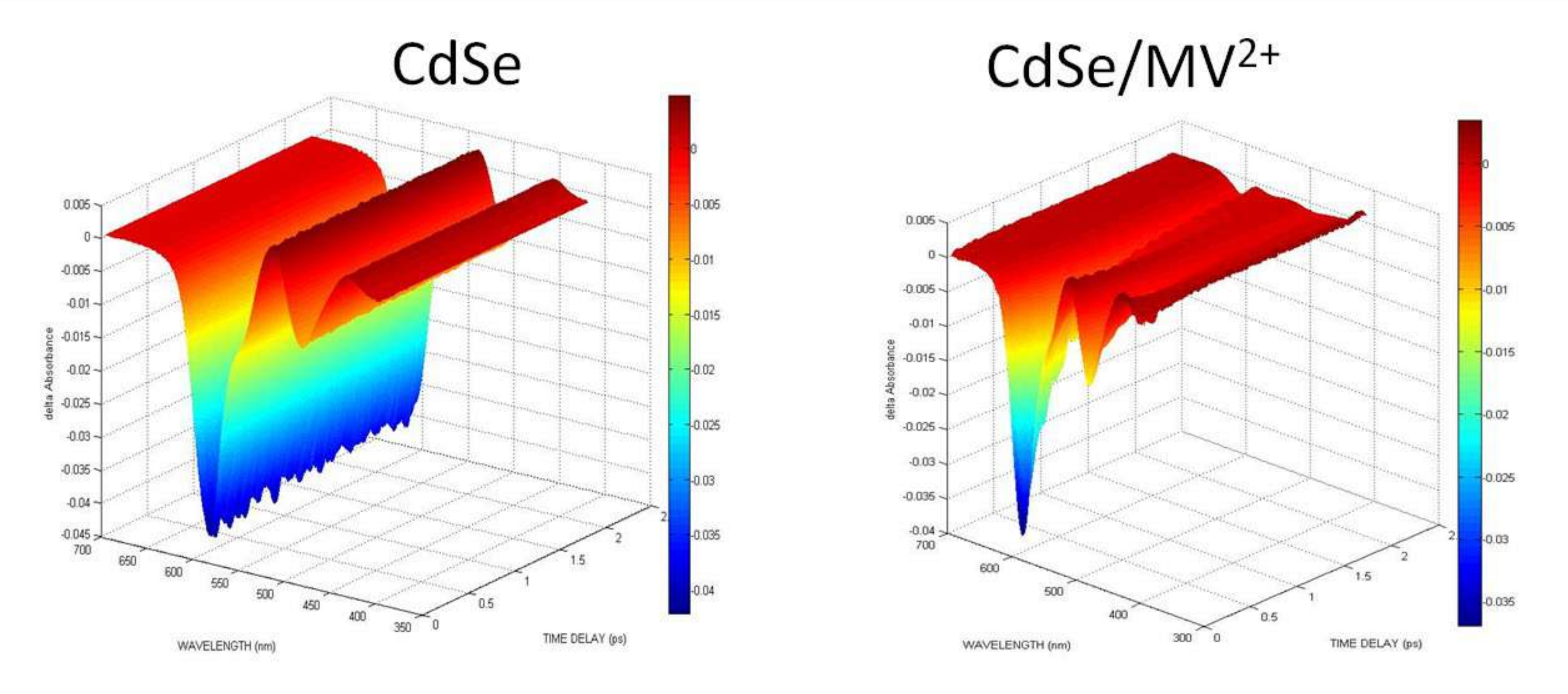
CONTINUOUS WAVELET TRANSFORM (CWT)

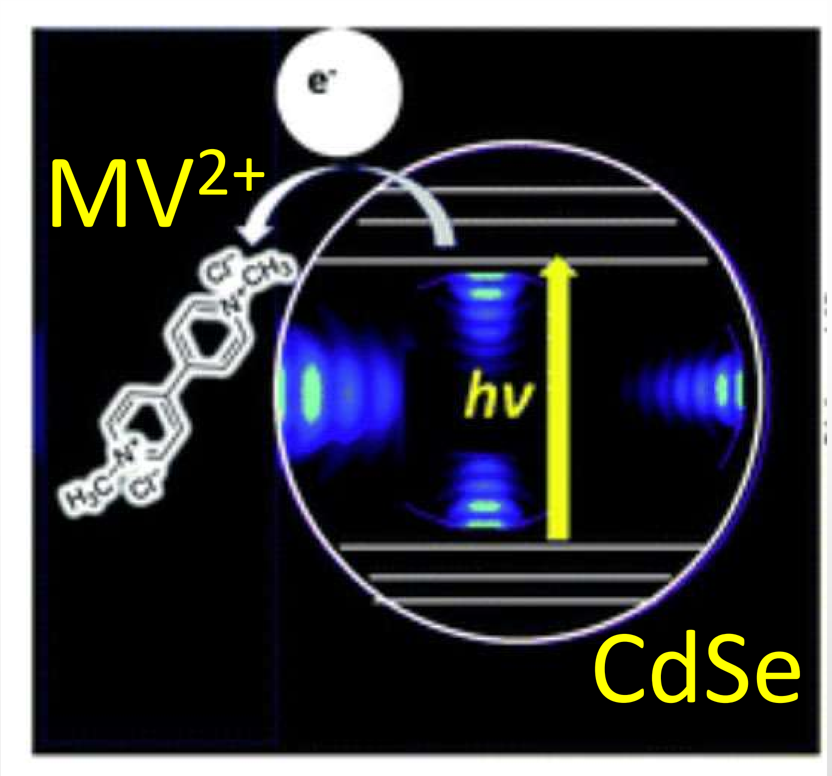
временная зависимость частоты от времени : чирп





Реакция переноса электрона с участием ЭКСИТОНА

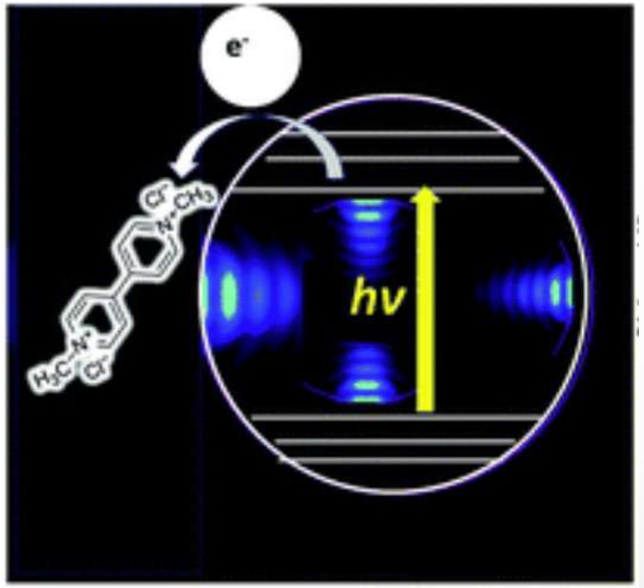


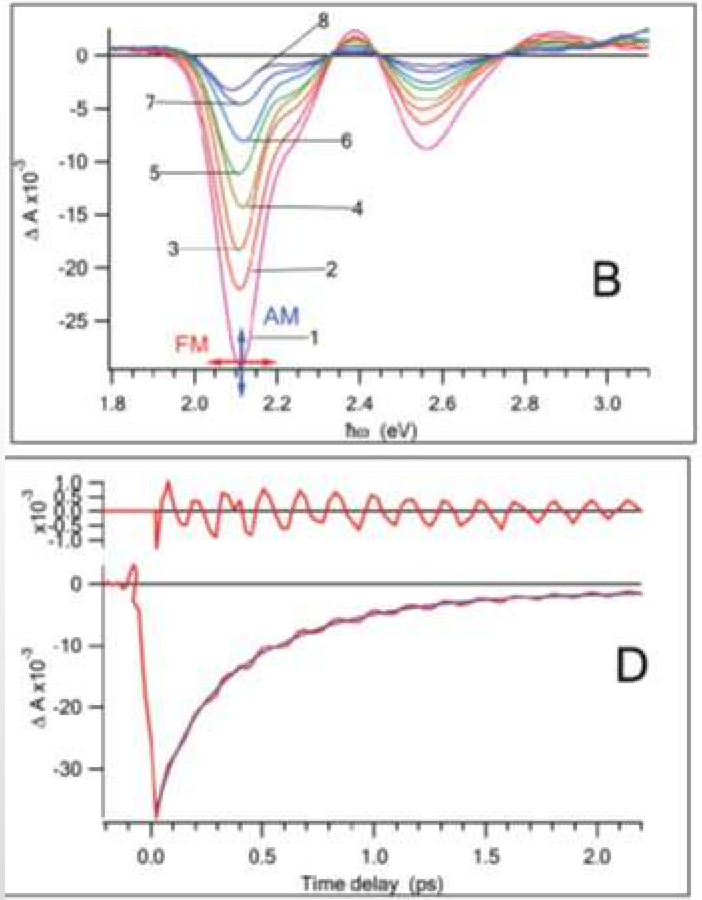


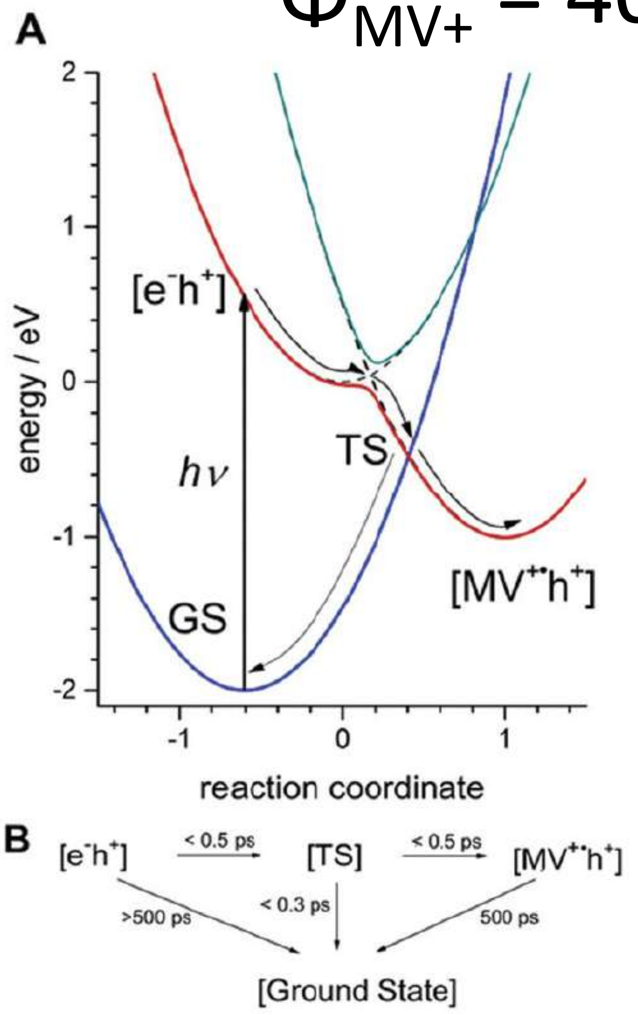
Cherepanov et al. *Nanoscale 2018*

mechanism of MV^{2+} reduction by excited QDs

$\Phi_{MV+} = 40\%$





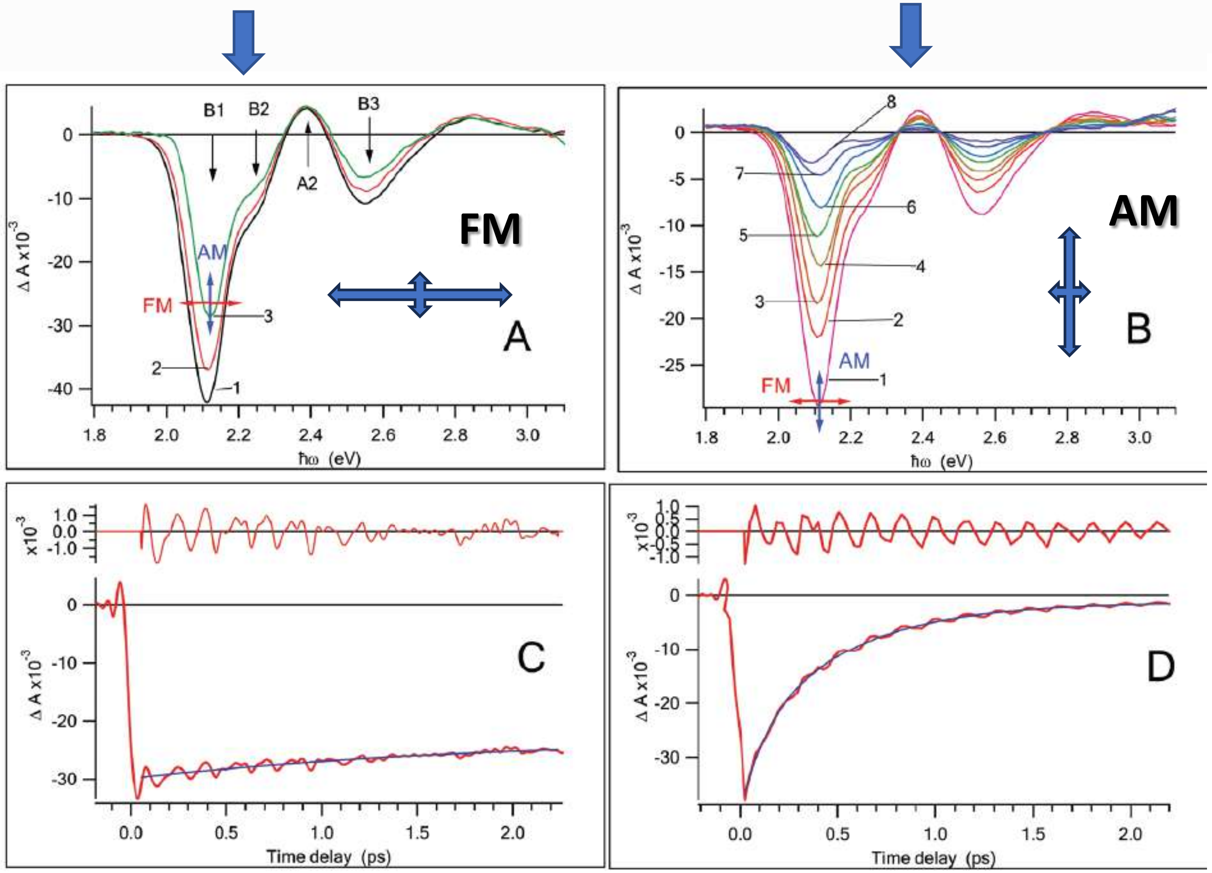


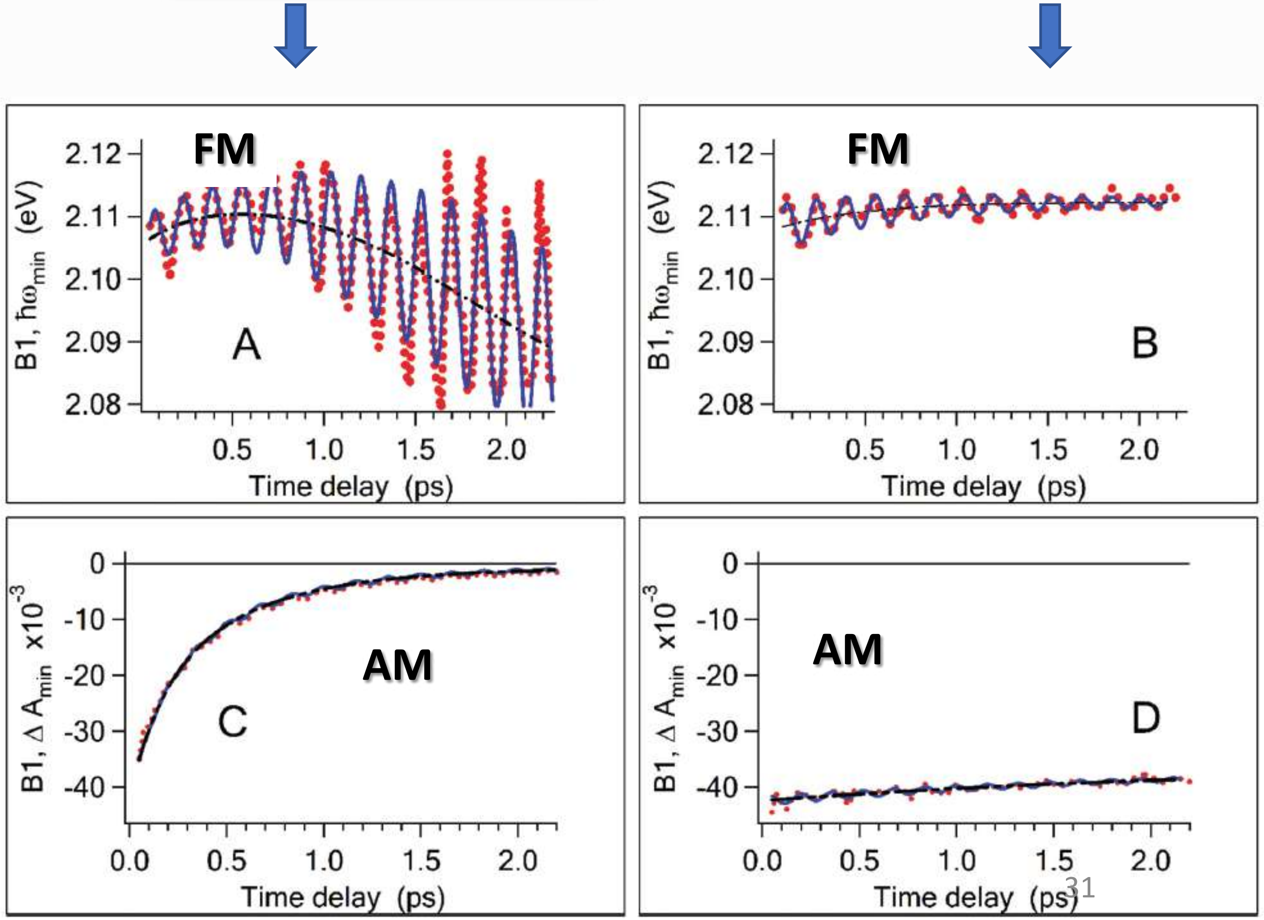
2 exp decay 164 fs (~30%) and 540 fs (~70%)

Cherepanov et al. *Nanoscale 2018*

КОГЕРЕНТНЫЙ ВОЛНОВОЙ ПАКЕТ В CdSe: эффект быстрого переноса электрона

CdSe **$CdSe/MV^{2+}$** **$CdSe/MV^{2+}$** **CdSe**





Inverse piezoelectric effect and LA phonon excitation

T_{AO} ~1.7-2.0 ps

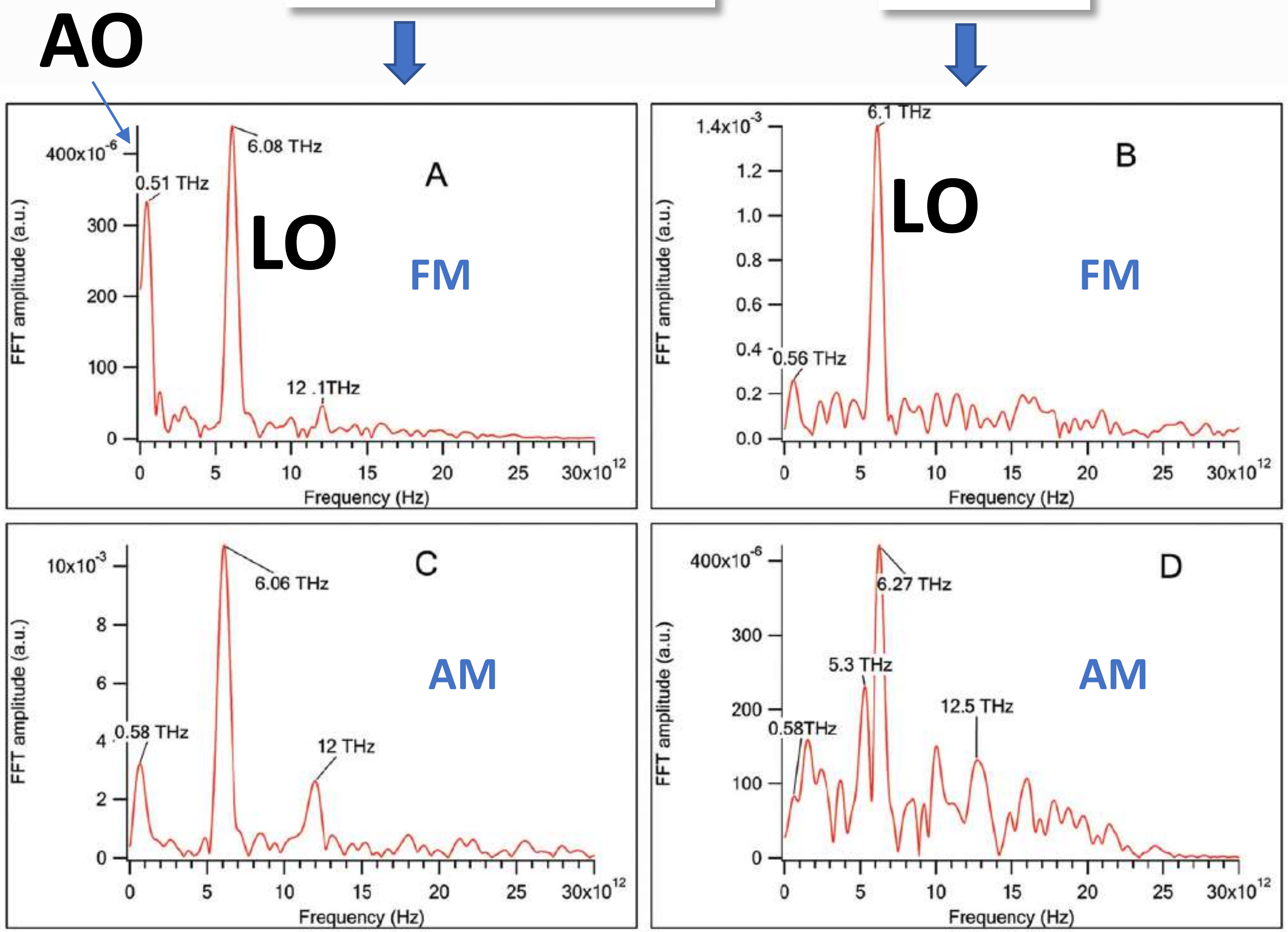
τ_{MV+} <0.5 ps

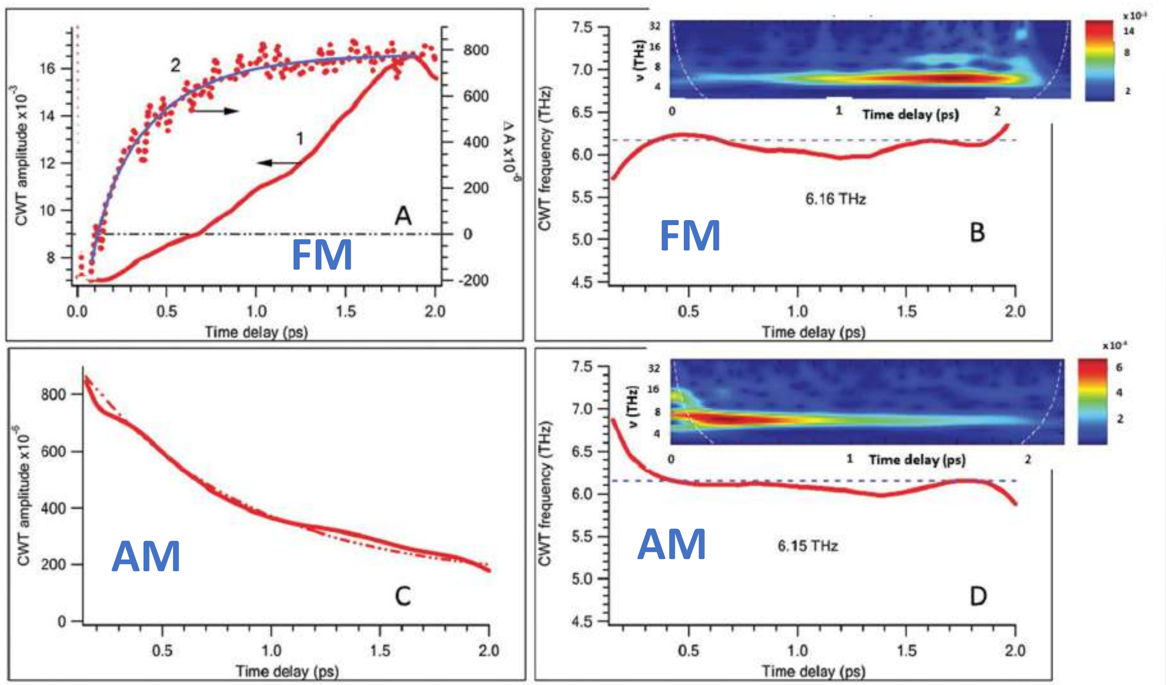
F= 5×10^6 V cm^{-1}

CdSe/MV^{2+}

CdSe

CdSe/MV^{2+}





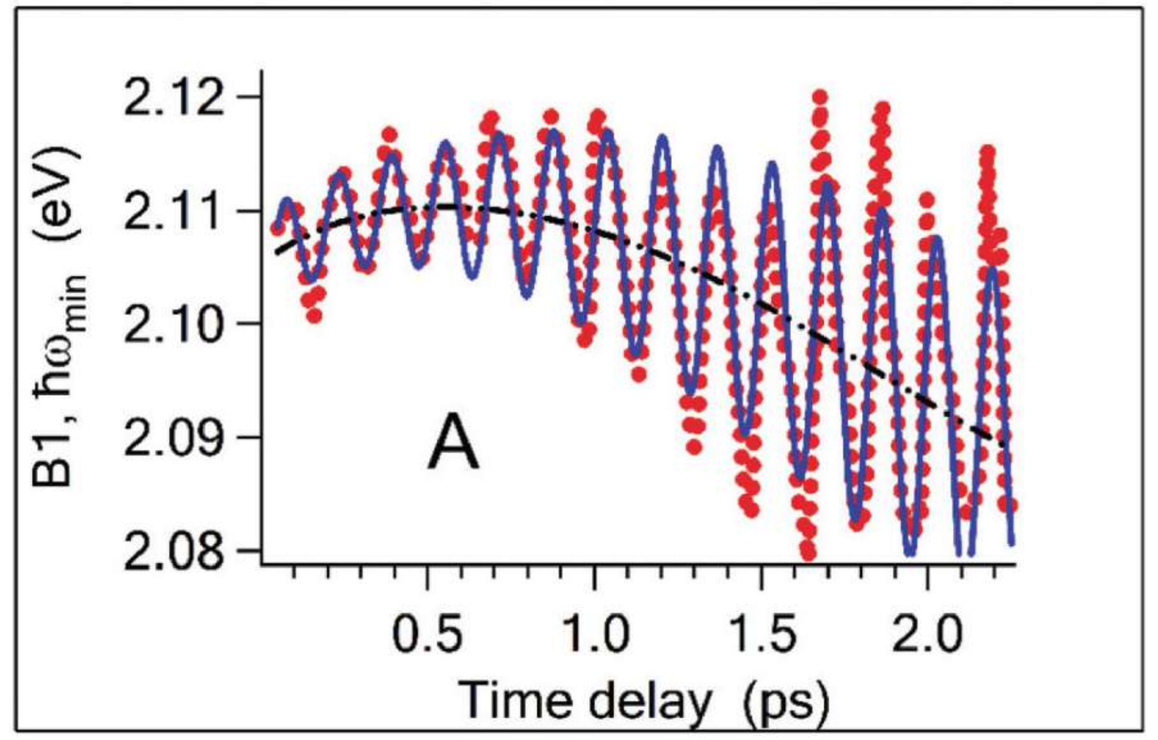
Electro-absorption effects

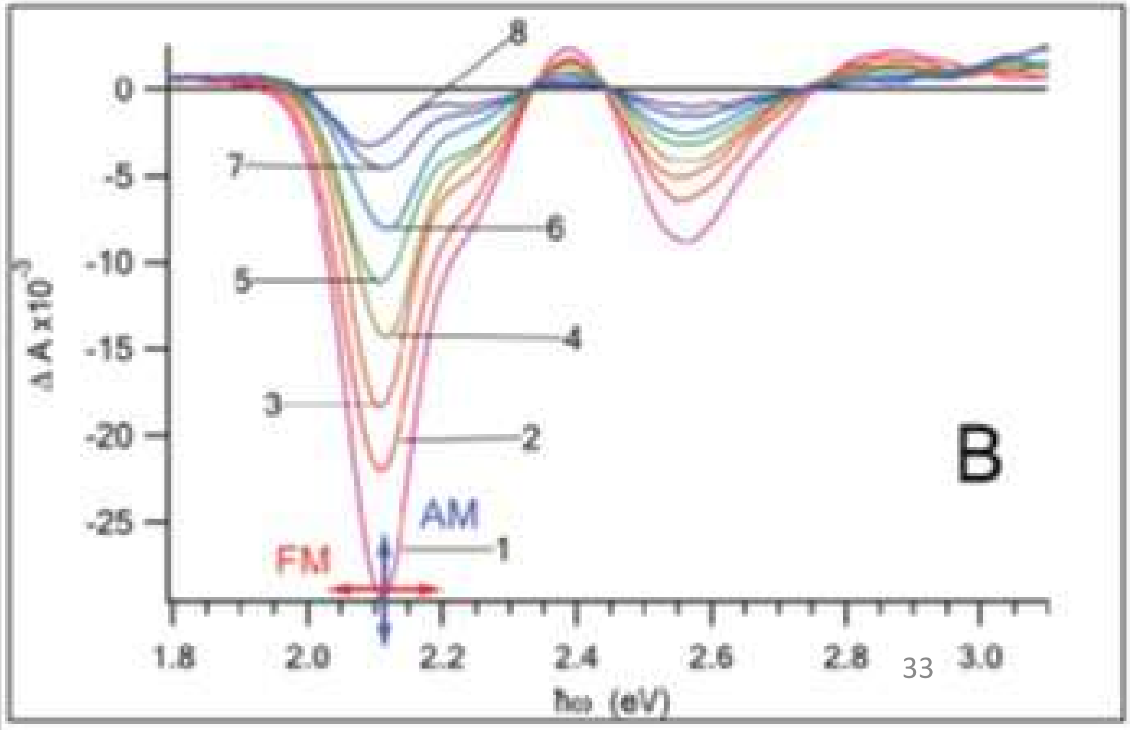
F= 5×10^6 V cm^{-1}

$\mu_0 = 76$ D

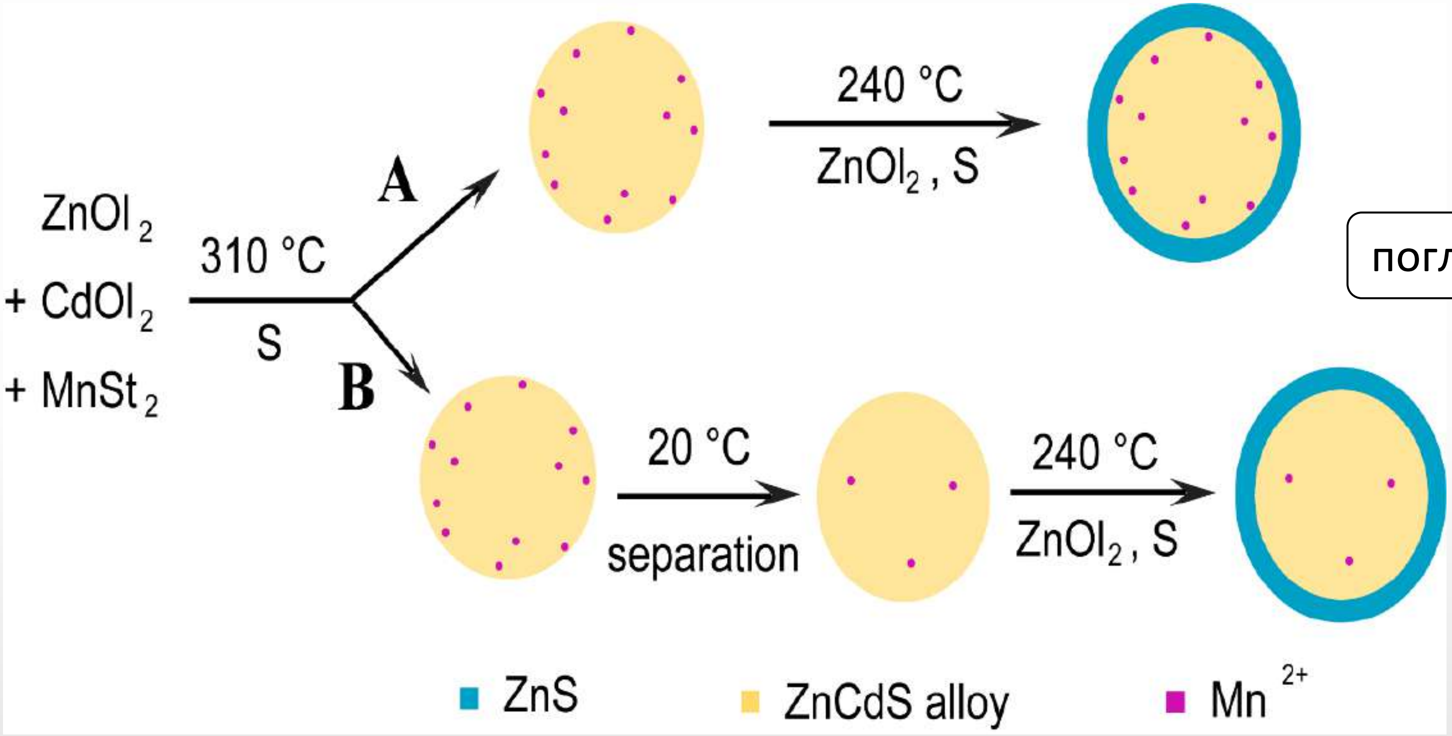
$$\Delta E = \mu_0 \cdot F - \frac{1}{2}\alpha_0 \cdot F^2.$$

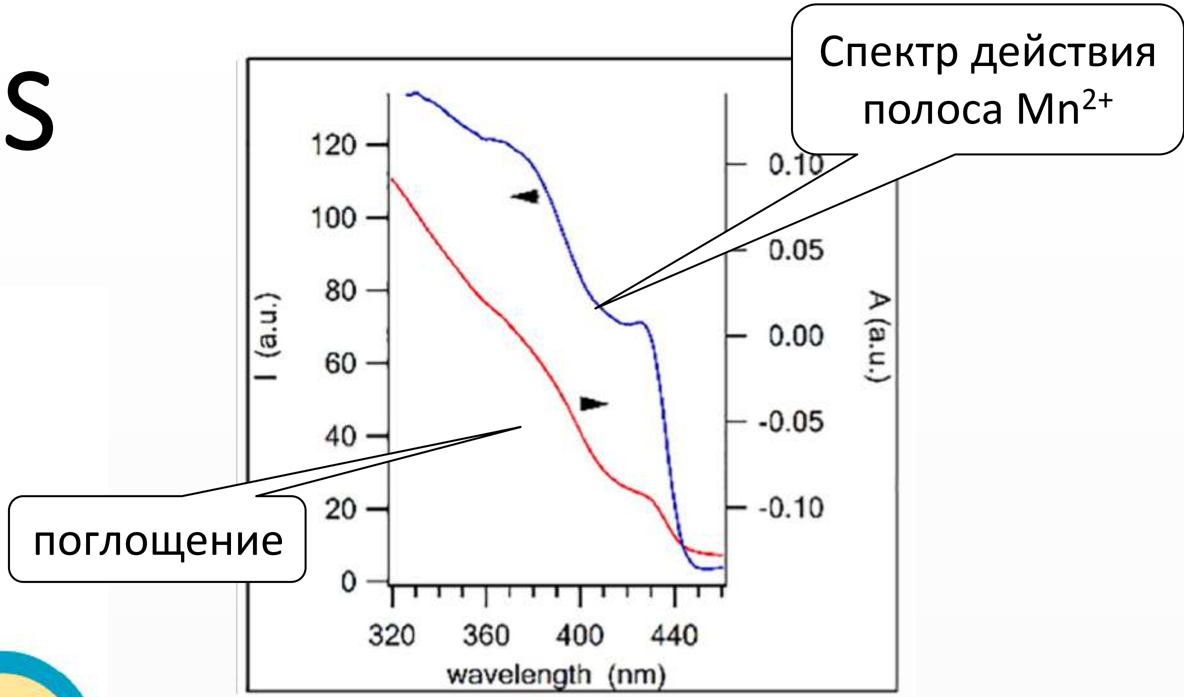
образование [h⁺…MV•+] вызывает красное смещение полосы B1 и увеличивает амплитуду FM колебаний.



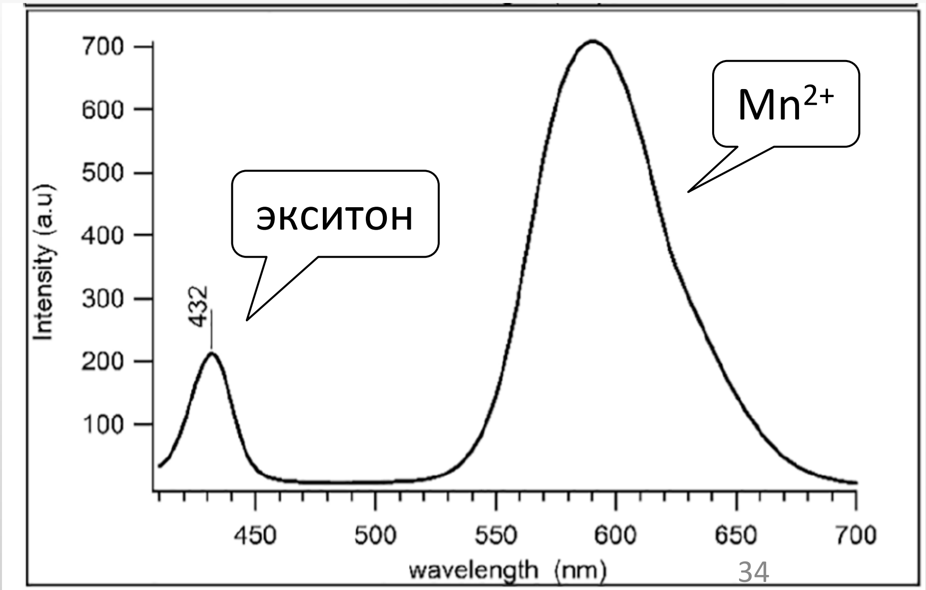


Синтез Mn:$Zn_xCd_{1-x}S$/ZnS





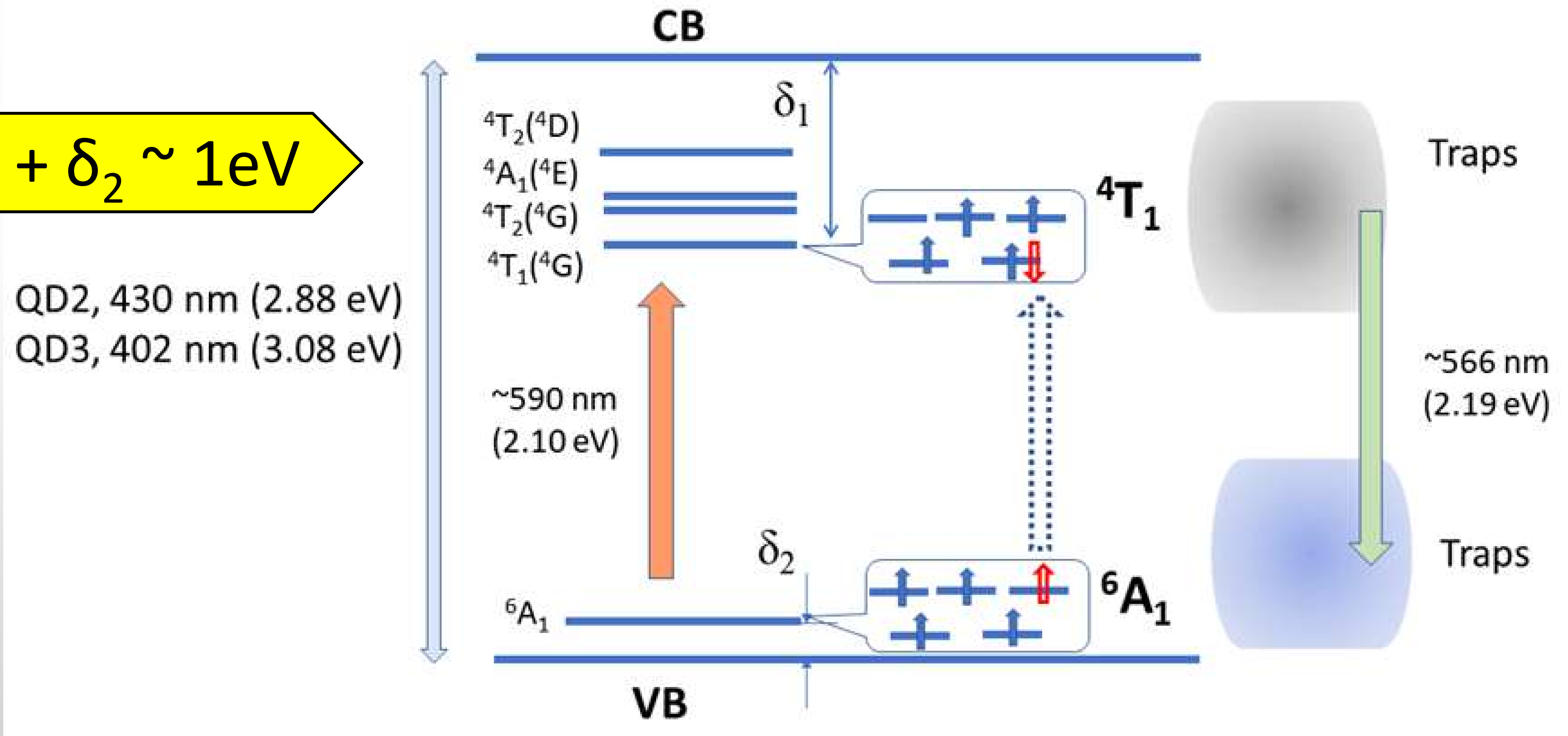
Флуоресценция

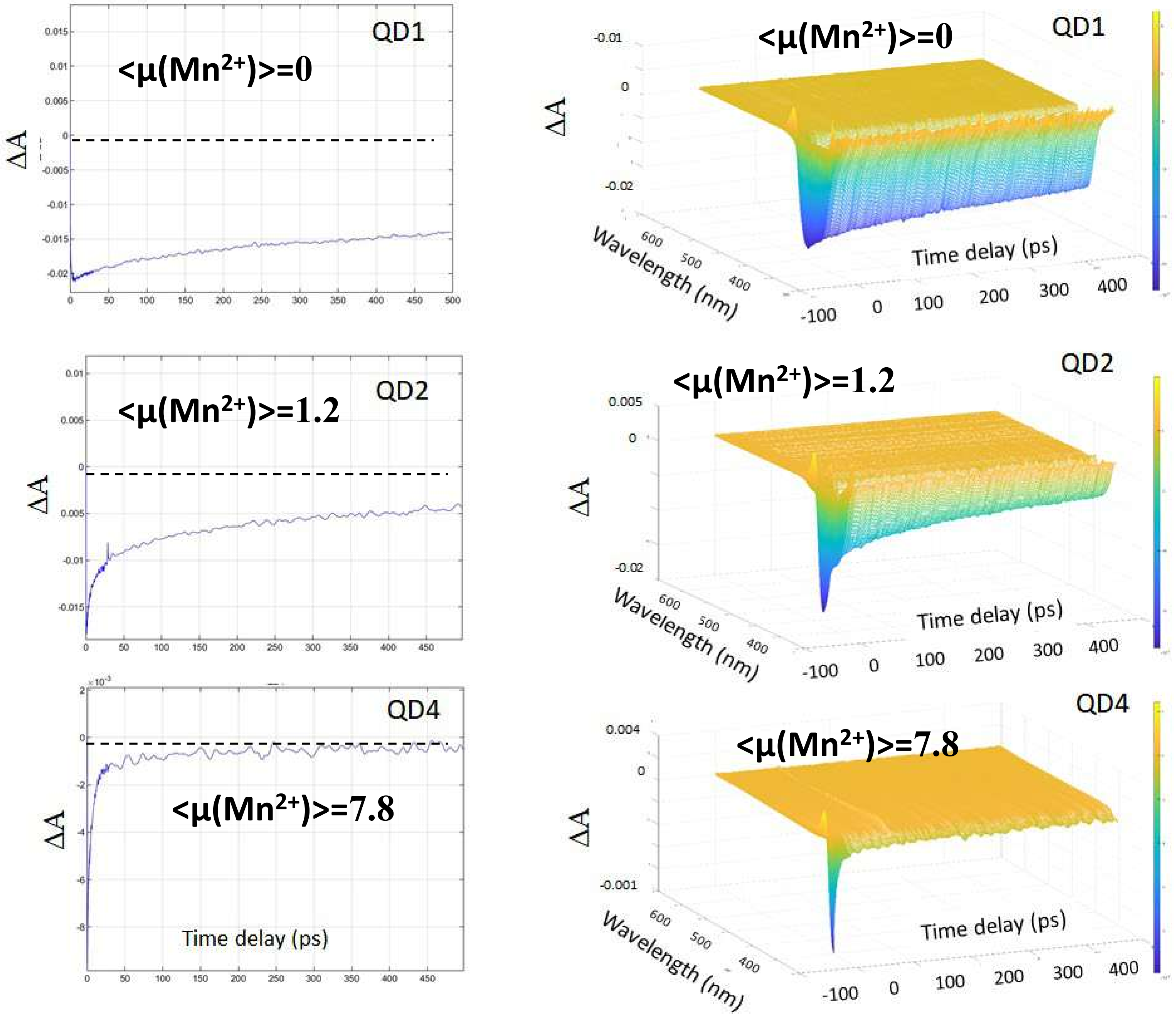


V. Nadtochenko et al. Appl. Phys. A Mater. Sci. Process. 2023
V. Nadtochenko et al. *J. of Photochem. and Photobiol. A: Chemistry* 2022
V. Nadtochenko et al. *Current Opinion in Chemical Engineering* 2021
D.Cherepanov et al. Nanomater. 2021
Y.A. Kabachii MENDELEEV Commun. 2021
V. Nadtochenko et al. Appl. Phys. A Mater. Sci. Process. 2020
V. Nadtochenko et al. Chem. Phys. Lett. 2020
A.Gulin et al Appl. Surf. Sci. 2019

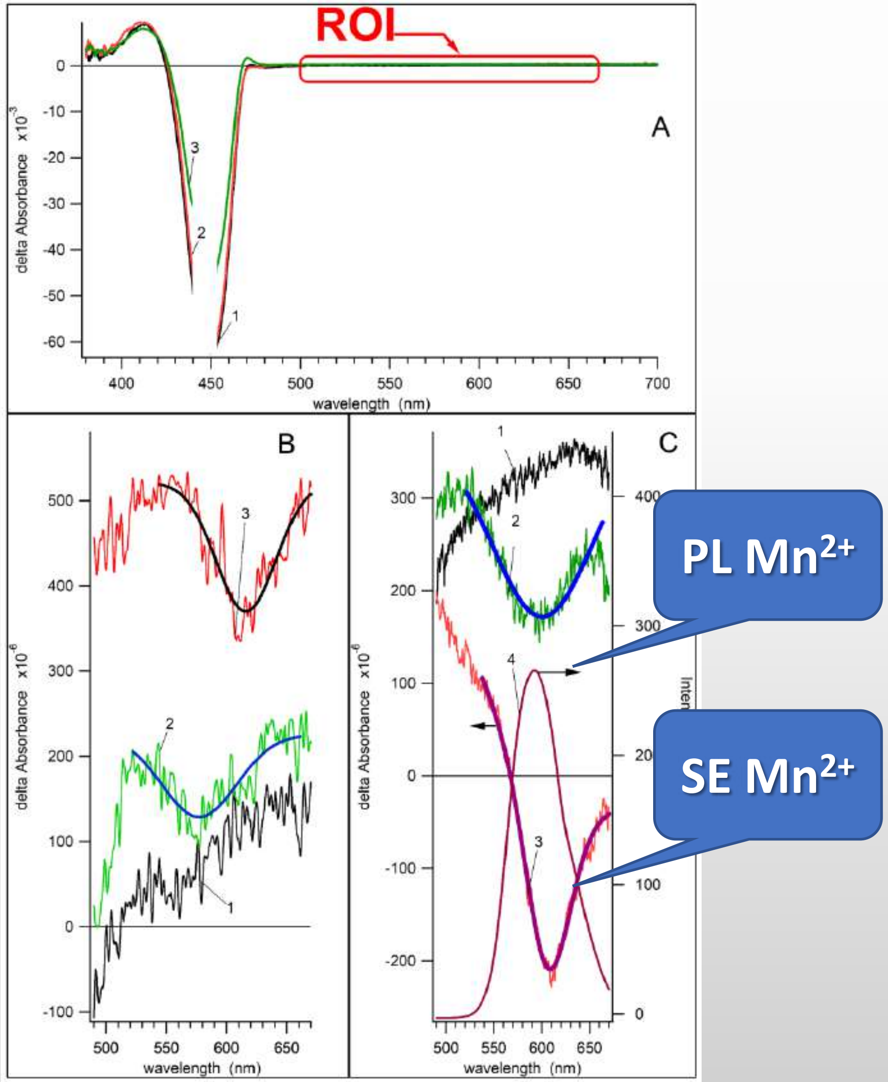
Alloy $Zn_{0.5}Cd_{0.5}S$ & $Zn_{0.5}Cd_{0.5}S/ZnS$ QDs doped with Mn^{2+}

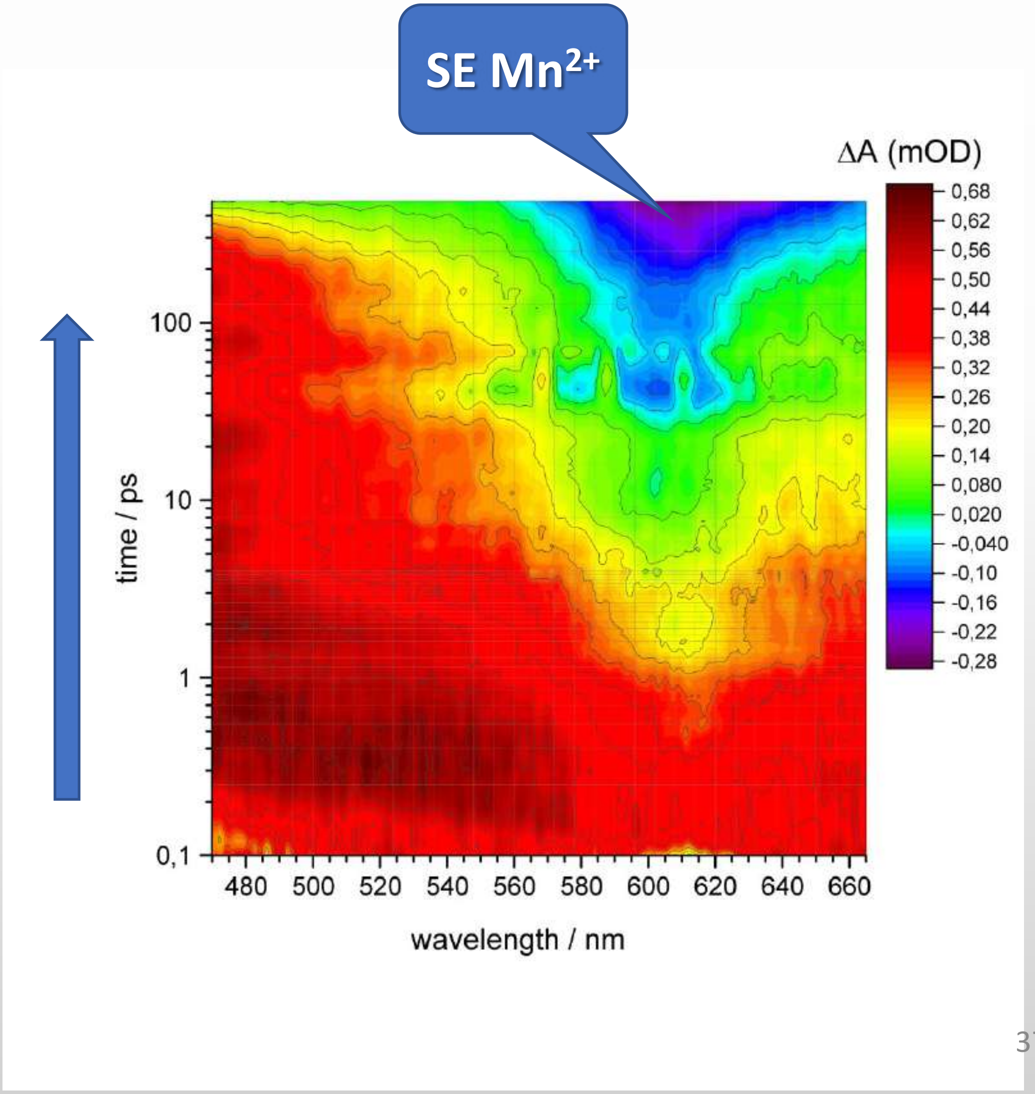
$\delta_1 + \delta_2 \sim 1eV$



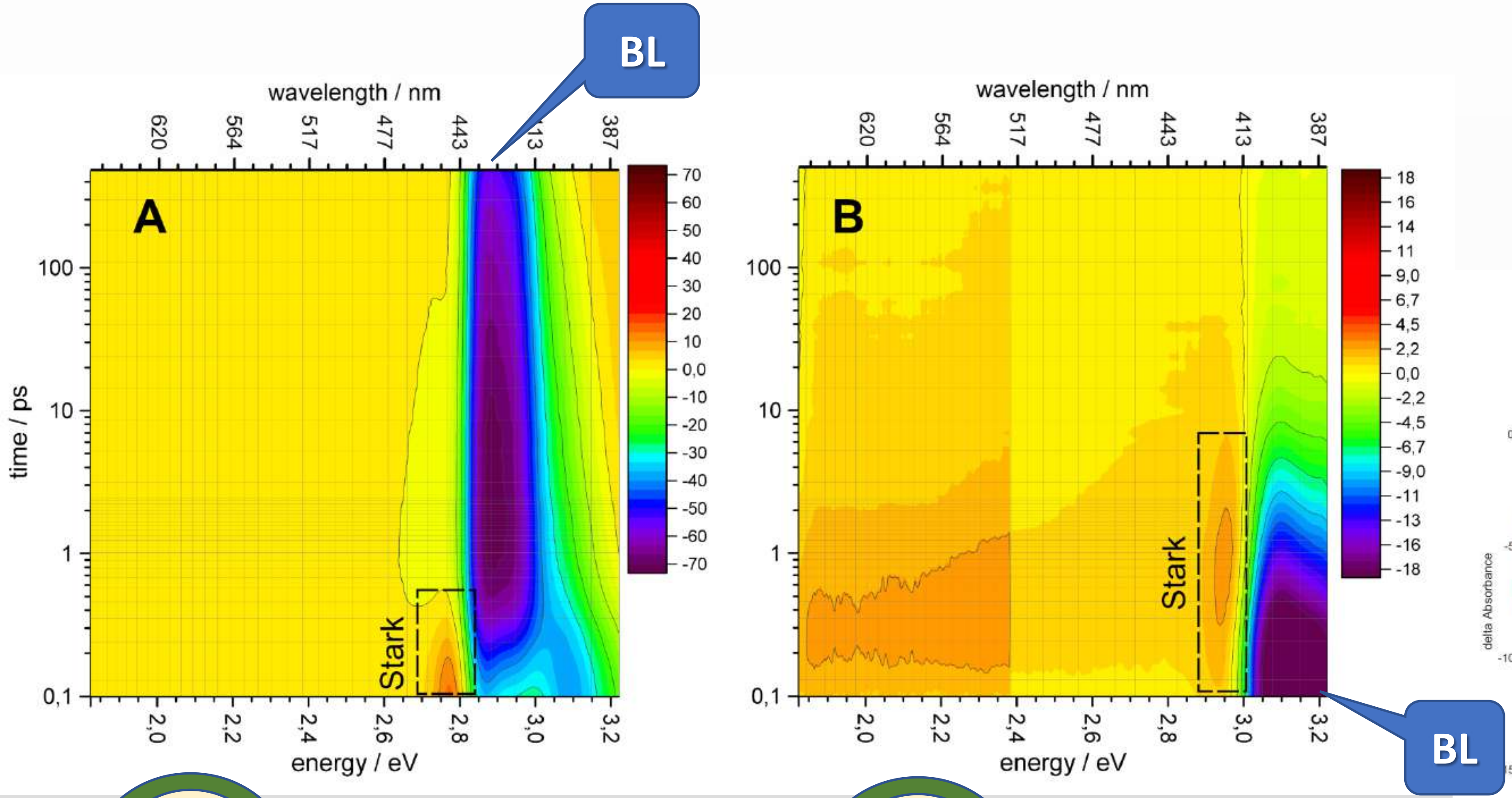

QD1
<μ(Mn2+)>=0
ΔA
QD2
<μ(Mn2+)>=1.2
QD4
<μ(Mn2+)>=7.8
Time delay (ps)
Wavelength (nm)

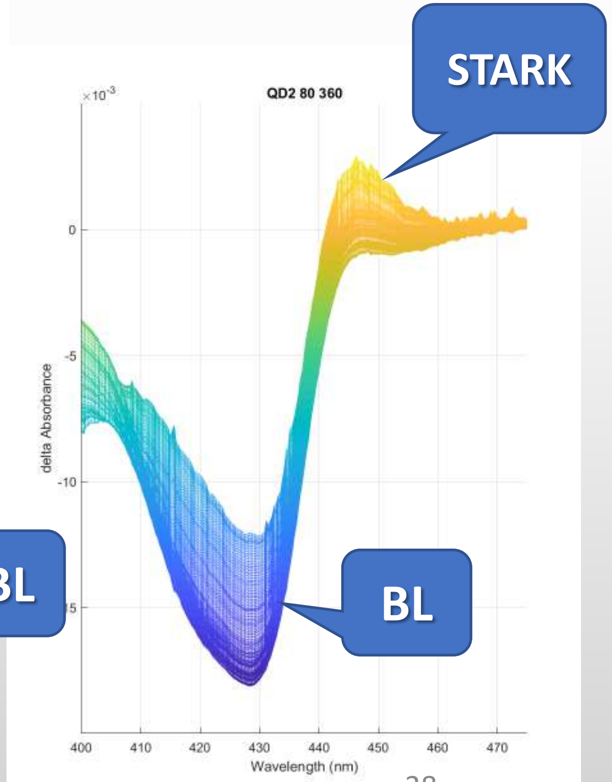
Stimulated emission of Mn(II)

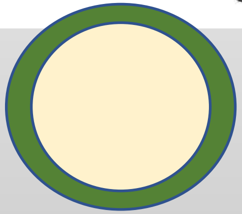


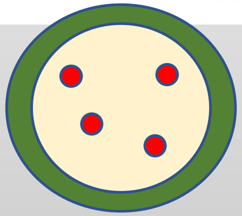


Delayed Stark peak

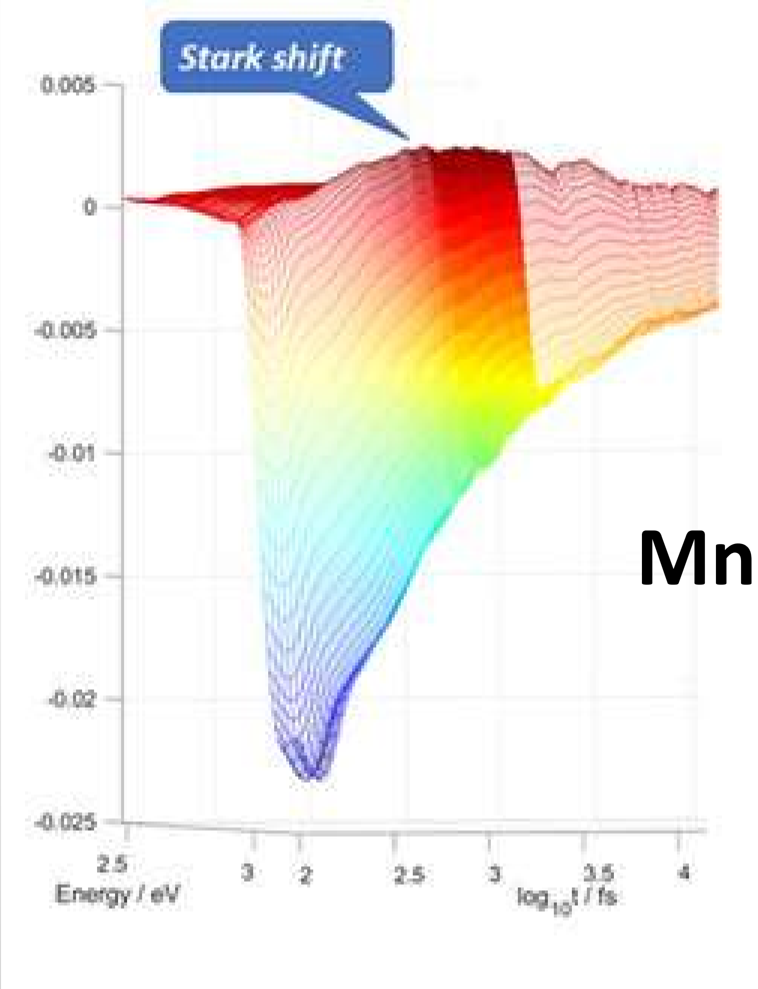


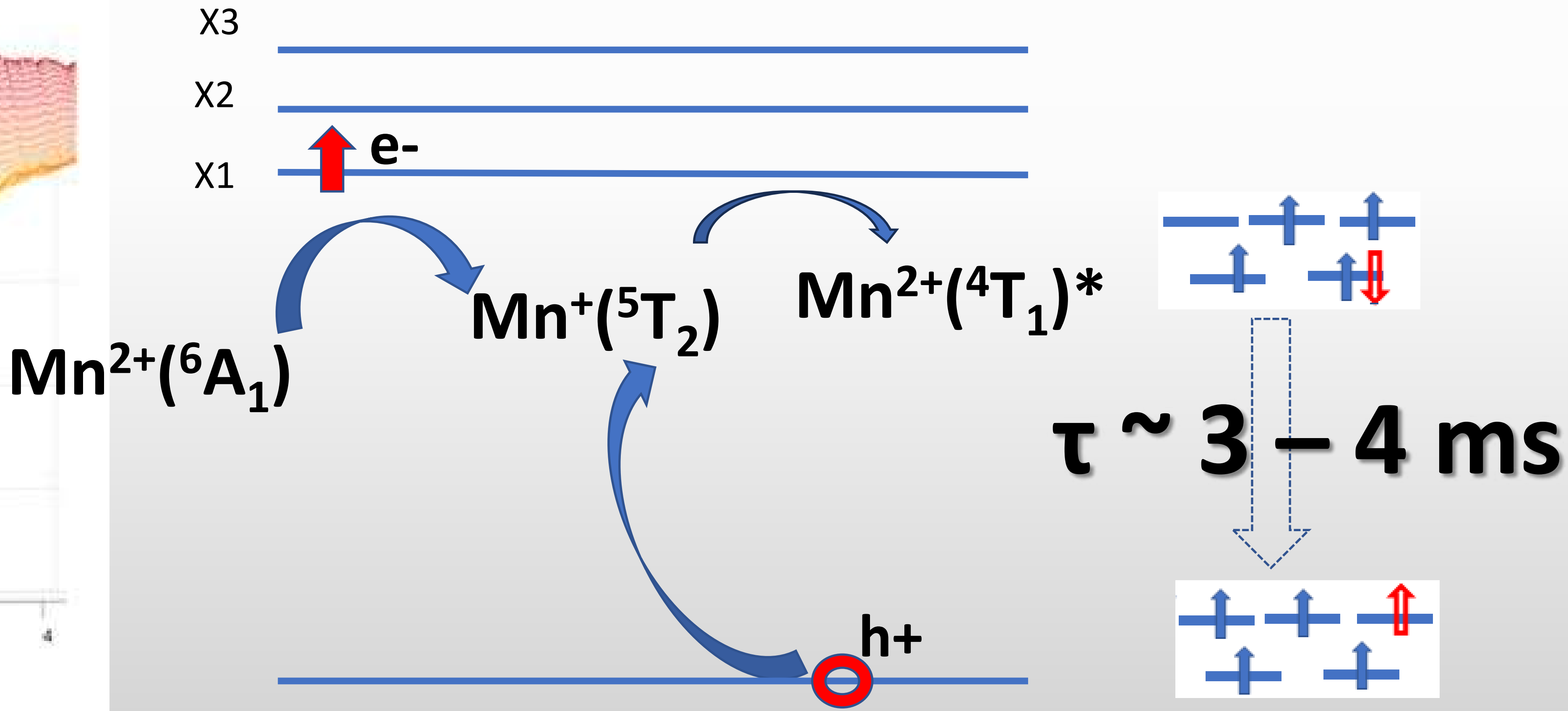




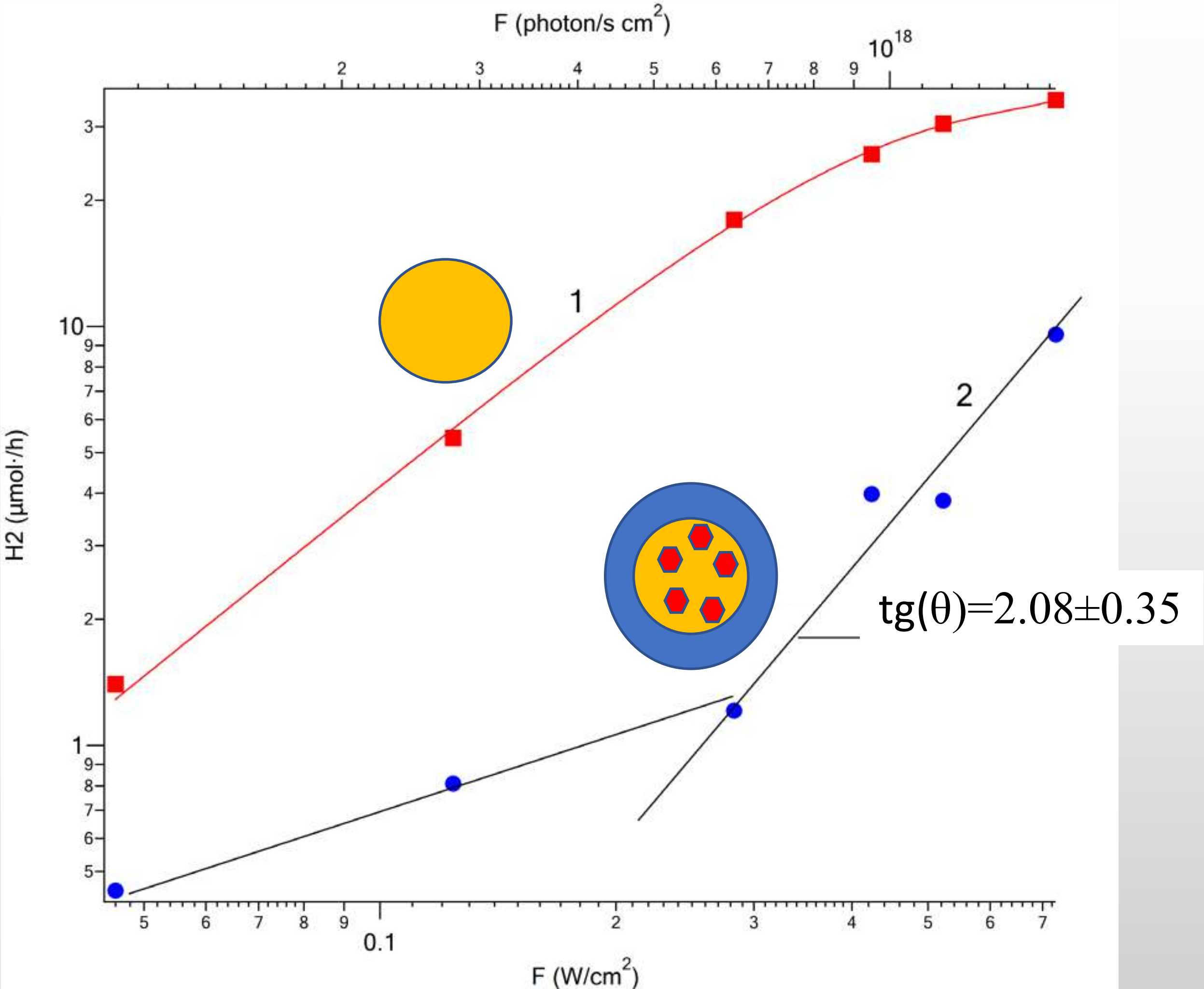


Mn^{2+} excitation scheme





H_2 rate vs flux F

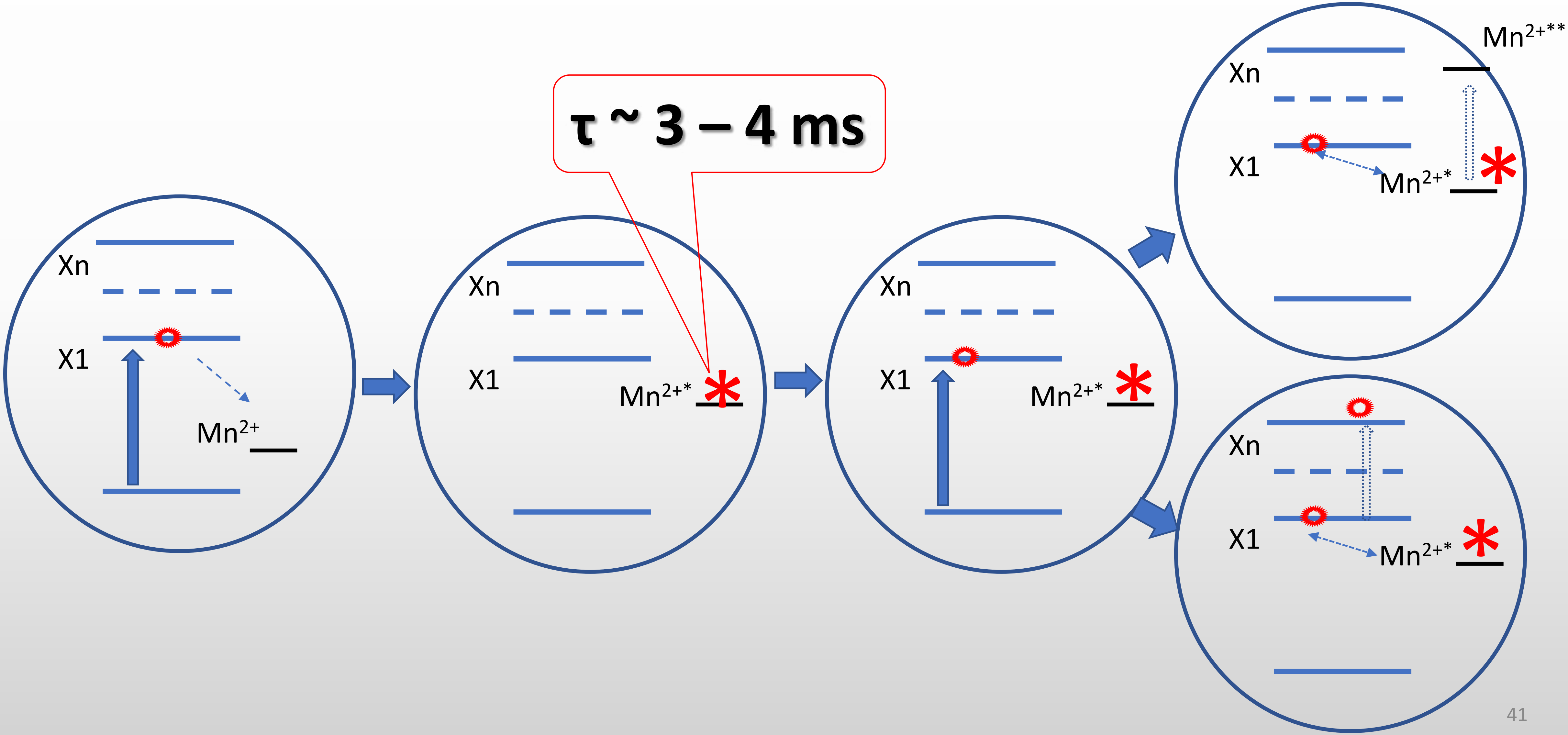


$F \sim 7\ 10^{17}$ photons/(sec cm^2)

$\sigma_{abs} \sim 5\ 10^{-16}$ cm^2

$\sigma_{abs} \cdot F = 350 \sim 1/\tau = 250\text{-}330$ (1/sec)

Mn^{2+} participation in the hot states generation



Оптические измерения

Гостев Ф.Е.
Шелаев И.В.
Костров А.Н.
Айбуш А.В.
Гулин А.А.
Астафьев А.А.
Шахов А.М.
Васин А.А.
Корозникова К.

Анализ фс спектров

Черепанов Д.А.
Добряков А.Л.

Теория

С.Я.Уманский

ЭПР

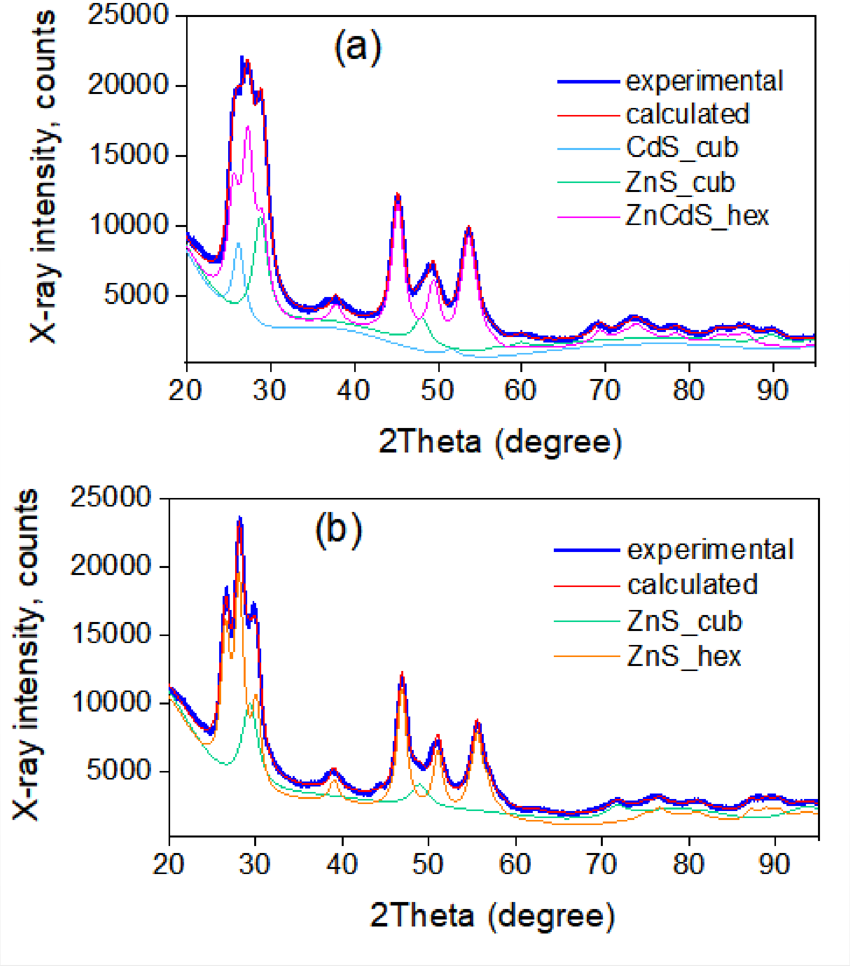
Мотякин М.В.

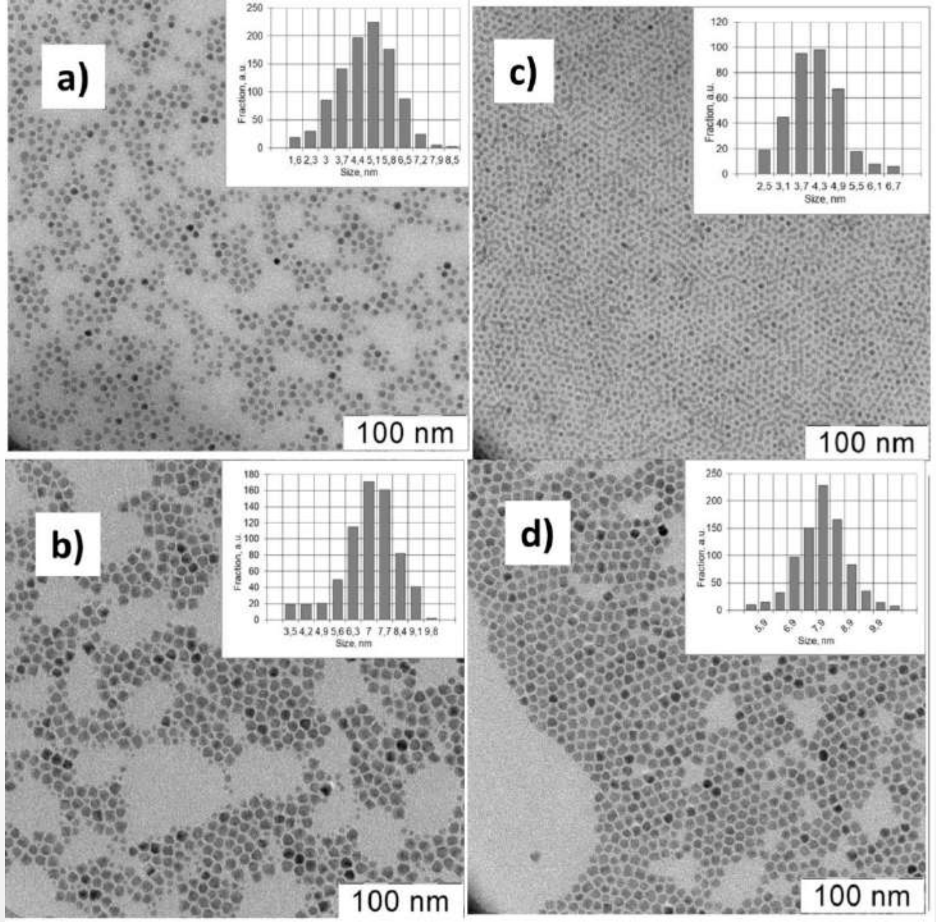
Синтез

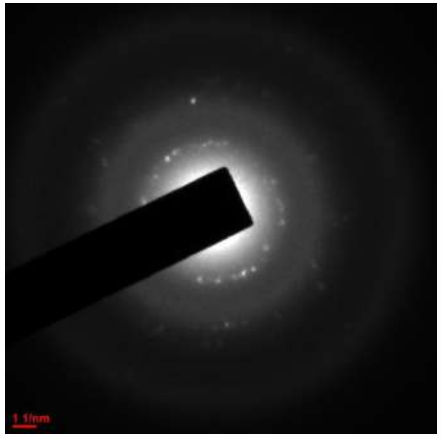
Кочев С.Ю.
Кабачий Ю.А.
Антонова О.

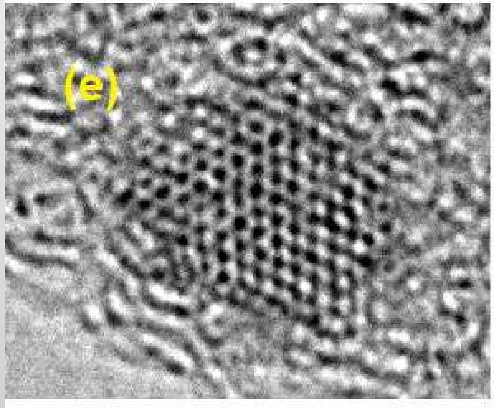
И особое спасибо А.А.Берлину

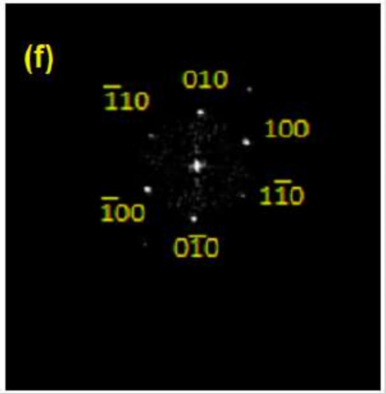
за то, что познакомил меня с П.М. Валецким

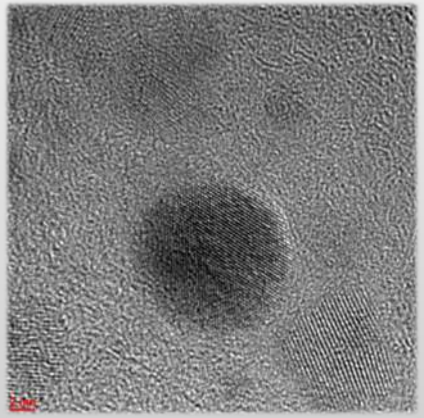

(a)
X-ray intensity, counts
25000
20000
15000
10000
5000
20
30
40
50
60
70
80
90
2Theta (degree)
experimental
calculated
CdS_cub
ZnS_cub
ZnCdS_hex
(b)
X-ray intensity, counts
25000
20000
15000
10000
5000
20
30
40
50
60
70
80
90
2Theta (degree)
experimental
calculated
ZnS_cub
ZnS_hex

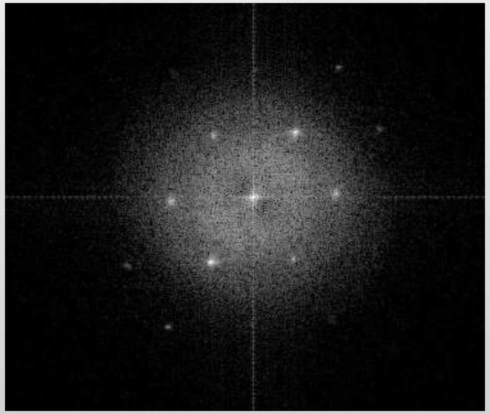

a)
b)
c)
d)
100 nm
100 nm
100 nm
100 nm




(e)


(f)
010
$\bar{1}10$
100
$1\bar{1}0$
$\bar{1}00$
$0\bar{1}0$





degrees of freedom	dispersion (kinetic energy)	density of states (close to the conduction band)	effective density of states (at the conduction band)
3D (bulk)	$E = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2)$	$\rho_{3D} = \frac{1}{2\pi^2}\left(\frac{2m*}{\hbar^2}\right)^{\frac{3}{2}}(E - E_c)^{1/2}$	$N_c^{3D} = \frac{1}{\sqrt{2}}\left[\frac{m^* kT}{\pi\hbar^2}\right]^{3/2}$
2D (film)	$E = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2)$	$\rho_{2D} = \sum^{n} \frac{m^*}{\pi\hbar^2} H(E - E_c)$	$N_c^{2D} = \frac{m^* kT}{\pi\hbar^2}$
1D (wire)	$E = \frac{\hbar^2}{2m^*}(k_x^2)$	$f_B(E_c) = N_c e^{-(Ec-EF)/kT}$ 2 $m^* \pi\hbar\left(2(E - E_c)\right)$	$N_c^{1D} = \sqrt{\frac{m^* kT}{2\pi\hbar^2}}$
0D (dot)	a	$\rho_{0D} = 2\delta(E - E_c)$	$N_c^{0D} = 2$

$$f_B(E_c) = N_c e^{-(Ec-EF)/kT}$$