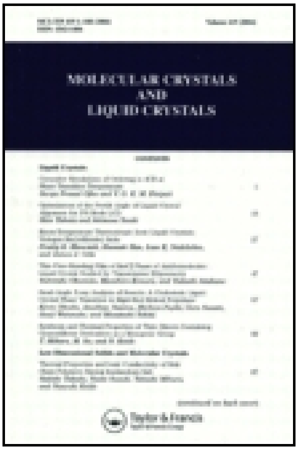

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Synthetic Three-and Lower-Dimensional Semiconductors Based on Inorganic Units

G. C. Papavassiliou [a]

[a] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48, Vassileos Constantinou Ave., Athens, 116 / 35, Greece

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SYNTHETIC THREE-AND LOWER-DIMENSIONAL SEMICONDUCTORS BASED ON INORGANIC UNITS

G.C. PAPAVASSILIOU
Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48, Vassileos Constantinou Ave., Athens 116 / 35, Greece.

Abstract. The structural, optical and related properties (i.e. photoluminescence, photoconductivity etc) of some synthetic (i.e. unconventional) three- and lower -dimensional semiconductor systems, which are based on inorganic units (:metal -halides, metal-chalcogenides etc), are briefly reviewed and some new results are reported. A blue shift of the excitonic bands as well as enhancements of their binding energy and intensity were observed by decreasing the dimensionality or the size of the materials active part. The results are similar to those obtained from conventional semicomductors, such as GaAs, CdS, PbI_2, by decreasing the dimensionality or the size.

INTRODUCTION

During the last few years, rapid advances in materials science and technology have led to the fabrication of novel electronic, optoelectronic and nonlinear optical devices based on low-dimensional (LD) systems, i.e. quantum wells (2D), quantum wires (1D), and quantum dots (0D). Artificial systems are fabricated by using conventional semiconductors, such as GaAs, GaAlAs, and applying several techniques, such as molecular beam epitaxy (for 2D systems) or a combination of epitaxy, etching and lithography (for 1D and 0D systems) [1]. However, in addition to manmade structures, natural LD compound semiconductor systems have long been known. These are based on single- or mixed-valency metal-halides (see [2-47]), metal-oxides (see [48-50], metal-chalcogenides (see [7, 45, 49-53]) etc. There is a large number of single-valence metal-halide complexes with the general formulae $Z_xA_yX_{z+y+x}$ [where M=Ga(I), In(I),Tl(I); Cu(I), Ag(I) Au(I);Z=K,Rb, Cs, $MeNH_3$ etc.; A=(amine-H) or $(\text{diamine-2H})_{0.5}$; X=F, Cl,Br, I], $Z_xA_yM_zX_{2z+y+x}$ or $Z_xM_{z+w}X_{2z+x}X'_{2w}$ or $Z_xM_zM'_wX_{2z+2w+x}$ [where M, M′=Ge(II), Sn(II), Pb(II); Zn(II), Cd(II), Hg(II); Cu(II), Ni(II), Co(II), Fe(II), Mn(II) etc] and $Z_xA_yM_zX_{3z+y+x}$ [where M=As(III), Sb(III), Bi(III); Ga(III), In(III), Tl(III)][2-45]; in all cases z,w=1,2,3..; x,y=0,1,2... Also, there is a number of mixed-valency metal-halide complexes with the general formulae $[(A)_2MX_2\text{-}(A)_2MX_4]$, $[(A)_4M\text{-}(A)_4MX_2]Y_4$, $Z_2[AMX_3\text{-}AMX_5]$, $Z_2[MX_4\text{-}MX_6]$, and $Z_2[AuX_2\text{-}AuX_4]$, where A=amine or $(\text{diamine})_{0.5}$; M=Ni, Pd, Pt etc; Y=X, ClO_4, BF_4 etc (see [46,47]). Some single-valency metal chalcogenide complexes have the general formulae $Z_x[X_yM_z(XR)_w]$, $[X_yM_z(XR)_w]Y_x$, where $Z=Me_4N$, Et_3NH etc; $Y=ClO_4$, HSO_4 etc; X=S, Se, Te; M=Cd, Zn etc; $R=CH_2CH_2OH$, Ph etc (see [7, 45,46, 52]. Recently, some oxide-sulfide complexes, such as $(Bu_4N)_4[Mo_8Cu_{12}O_8S_{24}]$, have been synthesized [50]. Most of them are inorganic-organic hybrid solids, in which the inorganic part is the active part of the system (semiconductor), while the organic part, i.e., amine, SR etc, plays the role of barrier.

In this paper the structural, optical and related properties of some of these synthetic(:unconventional) 3D and LD semiconductor systems based on single-valency metal-halides and metal-chalcogenides are briefly reviewed and some new results are reported. The room temperature (RT) results are mainly discussed.

RESULTS AND DISCUSSION

Compounds of the formula ZMX_3 (M=Pb, Sn, Ge) are built up of all-corner-sharing octahedra (MX_6) forming a 3D network with a cubic-perovskite structure, as it is shown in Fig. 1a for $MeNH_3PbI_3$. Z(small cycles in Fig. 1a) is placed in the centre of cube formed from M-atoms. Some of them were found to be 3D semiconductors [2-10, 14, 18-30, 46]. Compounds of the formula A_2MX_4 (A=alkylamine-H, phenylethylamine-H etc; M=Pb, Sn, Cu, Cd, Mn etc)are built up of four-coplanar-corner- sharing octahedra forming a 2D network with layered-perovskite structures, which alternate with layers of A-chains, as it is shown in Fig. 1b for $(C_9H_{19}NH_3)_2PbI_4$. Some of them (mainly those with M=Pb, Sn) were found to be 2D semiconductor(:quantum-well) systems [2-19, 46]. Compounds of the formula $[NH_2C(I)=NH_2]_3MI_5$ are built up of two-opposite-corner-sharing octahedra as it is shown in Fig. 1c for $[NH_2C(I)=NH_2]_3PbI_5$ [16]. These compounds were found to be 1D semiconductor (:quantum- wire) systems. Compounds of the formula $Z_4PbX_6{\cdot}xH_2O$ [31,32] consist of isolated PbX_6 octahedra, as it is shown in Fig. 1d for $(MeNH_3)_4PbI_6{\cdot}2H_2O$. They were found to be 0D semiconductor (: quantum dot) systems.

Electronic band structure calculations were performed by using the formalism of extended Hueckel theory and the room temperature crystallographic data [3, 6]. Fig. 2 shows the calculated band structures of $MeNH_3PbI_3$(3D), $(C_9H_{19}NH_3)_2PbI_4$(2D),$[NH_2C(I)=NH_2]_3PbI_5$(1D)and $(MeNH_3)_4PbI_6.2H_2O$(0D).One can see that the energy-gap value (E_g) of the systems increases as the dimension -

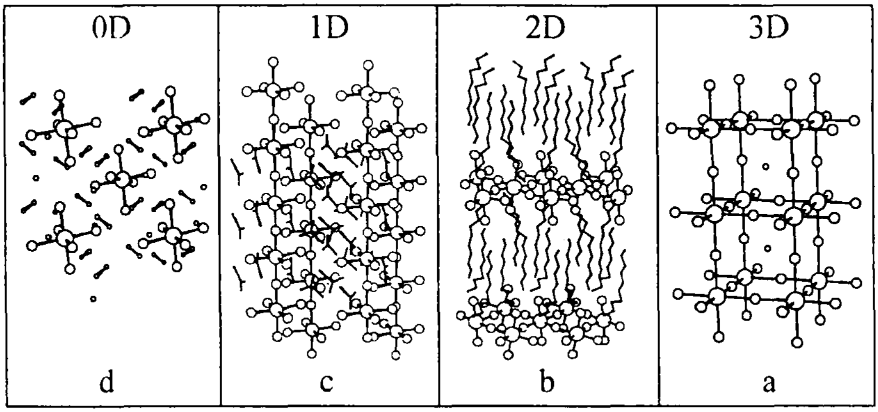


Figure 1. Crystal structures of $MeNH_3PbI_3$(a), $(C_9H_{19}NH_3)_2PbI_4$(b), $[NH_2C(I)=NH_2]_3PbI_5$ (c), and $(MeNH_3)_4PbI_6{\cdot}2H_2O$ (d): where large spheres = Pb atoms, medium spheres= I atoms, and small spheres = O, N, C atoms.

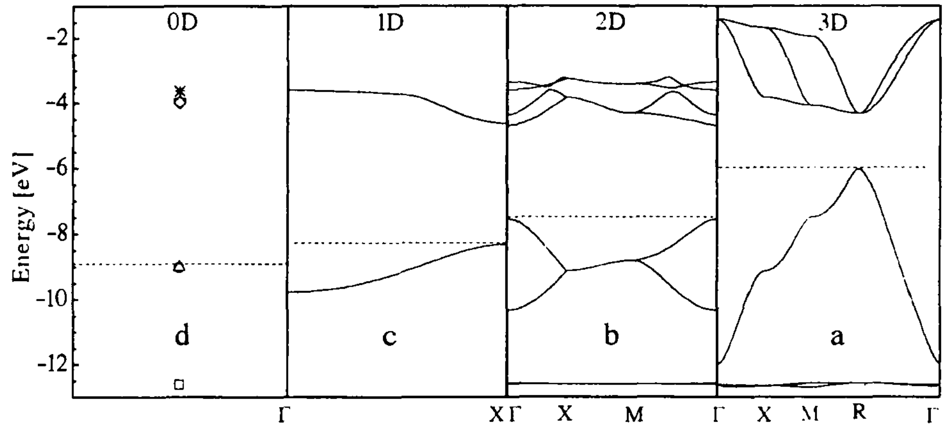


Figure 2. Calculated electronic band structures of $MeNH_3PbI_3$(a), $(C_9H_{19}NH_3)_2PbI_4$(b), $[NH_2C(I)=NH_2]_3PbI_5$(c), and $(MeNH_3)_4PbI_6{\cdot}2H_2O$ (d). Dashed lines indicate the highest occupied levels.

ality decreases (3D → 2D → 1D → 0D).

Fig. 3 shows the absorption coefficient *vs* the wavelength (λ) obtained from Kramers-Kronig transformation of the corresponding reflectance spectra of $MeNH_3PbI_3$ (black polycrystalline pellet), $(C_9H_{19}NH_3)_2PbI_4$ (orange single crystal) [20], $[NH_2C(I)=NH_2]_3PbI_5$ (yellowish polycrystalline pellet) [15,16,32] and $(MeNH_3)_4PbI_6.2H_2O$ (white polycrystalline pellet). By decreasing the dimensionality the colour changes gradually from black to white and the low energy peaks, which are due to the lowest free- excitonic states, are shifted to higher energies (i.e., to shorter wavelengths). The intensity of excitonic peaks of LD systems is higher than that of the corresponding 3D system. In other words, the excitonic binding energy (E_b) and oscillator strength (f) of LD systems are increased, in comparison to those

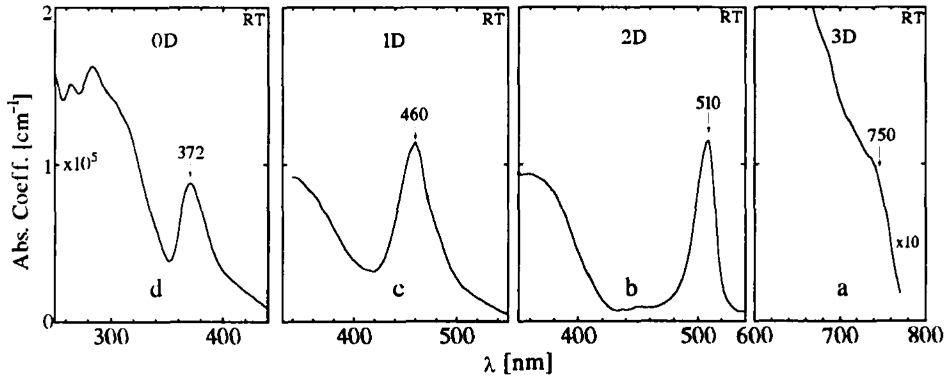
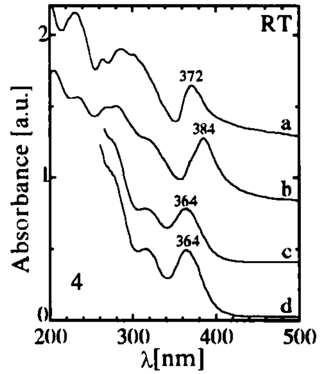


Figure 3. Absorption coefficient *vs.* the wavelength (λ) of $MeNH_3PbI_3$(a), $(C_9H_{19}NH_3)_2PbI_4$(b), $(NH_2C(I)=NH_2)_3$ PbI_5 (c) and $(MeNH_3)_4PbI_6.2H_2O$ (d).

of 3D one. As it is shown in Fig. 4, the optical absorption (OA) spectrum of $(MeNH_3)_4PbI_6{\cdot}2H_2O$ (0D) (see also [13] for low temperature results) is almost the same as the OA spectra of $(Et_4N)PbI_3$ [32], $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ in CH_3CN-solution and PbI_2 colloidal solution in CH_3CN [34]. It is similar to the spectrum of $(PbI_2)_1$ - clusters in zeolite [33]. The excitonic peaks of these compounds occur at higher energies than that of PbI_2 (see Fig. 4a′). The excitonic peak of bulk PbI_2, small particles (40-60 Å) [35, 36] and that of PbI_2-amine intercalated compounds (semiartificial systems) [37] occur at intermediate positions. Compounds of the formula $Z_{n-1}A_2M_nI_{3n+1}$ (with M=Pb, Sn and n=1,2,3...) are "monolayer" (n=1), "bilayer" (n=2), "trilayer" (n=3) and "multilayer" (n>3), semiconductor (quantum-well)systems. In these systems mixed MX and Z layers alternate with layers of A-chains. Compounds with $n \geq 3$ can not be isolated in a pure form. Fig. 5 shows the OA spectra of $(C_9H_{19}NH_3)_2PbI_4$(orange), $(MeNH_3)(C_9H_{19}NH_3)_2Pb_2I_7$(red), $(MeNH_3)_{n-1}(C_9H_{19}NH_3)_2Pb_nI_{3n+1}$($n \geq 3$) (red-violet), $(MeNH_3)PbI_3$ (black) and the OA spectrum of PbI_2 (pale orange), for comparison [4].



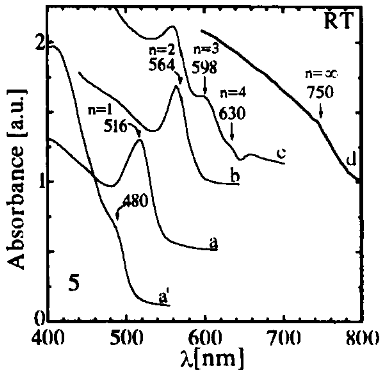
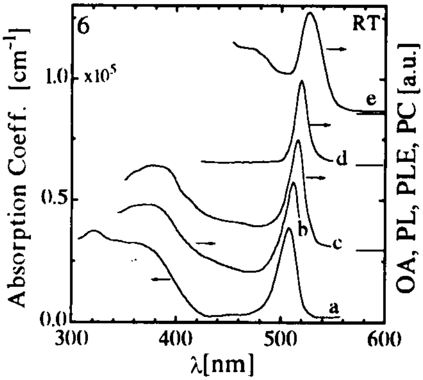


Figure 4. OA spectra of 0D systems: $(MeNH_3)_4PbI_6{\cdot}2H_2O$(a), $(Et_4N)PbI_3$(b), $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ in CH_3CN-solution (c), and PbI_2 colloidal solution in CH_3CN (d).

Figure 5. OA spectra of PbI_2 (a′), $(C_9H_{19}NH_3)_2PbI_4$ (a), $(MeNH_3)(C_9H_{19}NH_3)_2Pb_2I_7$(b), $(MeNH_3)_{n-1}(C_9H_{19}NH_3)_2Pb_nI_{3n+1}$ ($n \geq 3$), (c), and $MeNH_3PbI_3$ (d) deposits.

One can see that the excitonic peaks are shifted to lower energies (larger wavelengths) as the layer-thickness increases (n=1 → 2 → 3...). The exitonic peak of PbI_2 is weaker than that of A_2PbI_4 and $ZA_2Pb_2I_7$ because of the interlayer interactions in the PbI_2 crystals and the absence of dielectric confinement.

Similar effects have been observed in the photoluminescence (PL), photoluminescence excitation (PLE), and photoconductivity (PC) spectra of PbI containing complexes as well as in the spectra of complexes with PbBr, PbCl, SnI and SnBr units [5-19, 23-32]. Fig. 6 shows the PL, PLE and PC spectra of some materials with PbI units, in comparison to the corresponding absorption spectra. One can see that the absorption spectra are almost the same as the PLE spectrum. Also, that the PL spectrum is the same as the electroluminescence spectrum [11]. Fig.7 shows the



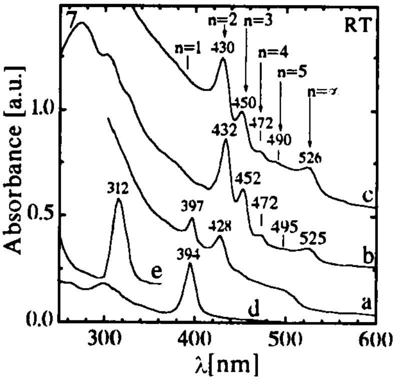


Figure 6. Absorption coefficient of $(C_9H_{19}NH_3)_2PbI_4$ (a), PLE(b), OA(c), PL(d) and PC(e) spectra of $(C_6H_5CH_2CH_2NH_3)_2PbI_4$.

Figure 7. OA spectra of three samples (a,b,c) of $(MeNH_3)_{n-1}(C_9H_{19}NH_3)_2Pb_nBr_{3n+1}$ thin deposits and OA spectra of $(C_9H_{19}NH_3)_2PbBr_4$ (d) and $(MeNH_3)_4PbBr_6{\cdot}2H_2O$ (e).

OA spetra of three different samples $(MeNH_3)_{n-1}(C_9H_{19}NH_3)_2Pb_nBr_{3n+1}$(2D) [4] as well as the OA spectra of $(C_9H_{19}NH_3)_2PbBr_4$ (2D) and $(MeNH_3)_4PbBr_6.2H_2O$ (0D) [32]. One can see that, as in the case of iodides, the excitonic peaks are shifted to lower energies as n increases. For all 3D and LD systems, it was found that the excitonic peaks of bromides occur at shorter wavelengths than those of the corresponding iodides and the peaks of chlorides at shorter wavelengths than those of bromides. The excitonic peaks of plumbates occur at shorter wavelengths than those of the corresponding stannates. Using the compounds reported above and those based on the corresponding mixed-metal and mixed-halides [2-32] one can observe sharp excitonic peaks in any required position from *ca* 300 to *ca* 850 nm. Figs. 3-7 show that the binding energy values (E_b) and the intensity values (i.e. oscillator strength, f) of excitonic peaks in LD systems are higher than those of the corresponding 3D systems. Using several models (e.g. image charge) and applying variational methods [3,11] for some materials of Pb and Sn, one finds that the calculated E_b values are close to the experimental values [3]. The results are summarized in Table I . The E_b values increase as the dimensionality and/ or size decrease. Also, E_b-values of stannates are smaller than those of the corresponding plumbates. It was found that by changing the amine (A) the E_b value is changed, because of the dielectric confinement effect (see [11, 13]). Also, for PbI_2 -amine(semiartificial) systems the calculated E_b values (250-280 meV)[3, 32] were found to be close to experimental ones [37]. The results are similar to those obtained from artificial systems based on conventional semiconductors [1]. The OA spectra of compounds based on Bi [39, 40] and Sb [39] (dielectric or ferroelectric materials) show large E_b- values, but in these cases the (free) excitonic luminescnce peaks are weak and difficult to be observed at room temperature. Instead, broad luminescence bands are observed at low frequencies which could be attributed to trapped excitons. Similar effects have been observed in the spectra of some other metal-halide complexes based on TI, Cu, Mn , Cd etc. [41-43] (ferroelectric or magnetic materials) as

TABLE I. Experimental E_g-, E_b-, f-, and α-values (α is the exciton Bohr radius) of PbI-, PbBr-, and SnI-systems at RT; calculated values [3] are given in parentheses.

Compound	Dimensionality	E_g (eV)	E_b(meV)		f	α(Å)
$(C_1)_1PbI_3$	3D	$1.70^a(1.70)$	$30^a,45^b$	(29)	0.014^c	(38.0)
$(C_1)_3(C_9)_2Pb_4I_{13}$	2D(4-layer)	$2.03^a(2.07)$	60^a	(130)		(22.9)
$(C_1)_2(C_9)_2Pb_3I_{10}$	2D(3-layer)	$2.17^a(2.19)$	96^a	(161)		(20.5)
$(C_1)_1(C_9)_2Pb_2I_7$	2D(2-layer)	$2.38^a(2.37)$	$181^a, \geq 220^b$	(218)		(17.5)
$(C_9)_2PbI_4$	2D(1-layer)	$\geq 2.82^a(2.85)$	$\geq 388^a, \geq 330^b$	(377)	0.7^d	(12.4)
$(C_1I)_3PbI_5$	1D	$3.10^a(3.67)$	410^a	(715)		
$(C_1)_4PbI_6 \cdot 2H_2O$	0D	$3.87^a(5.04)$	545^a			
$(C_1)_2(C_{6-2})_2Pb_3I_{10}$	2D(3-layer)			(145)		(16.9)
$(C_1)_1(C_{6-2})_2Pb_2I_7$	2D(2-layer)	2.36^a	170^a	(188)	0.3^c	(14.5)
$(C_{6-2})_2PbI_4$	2D(1-layer)	$2.58^a(3.00)$	220^a	(285)	0.5^c	(11.5)
$(C_1)_1PbBr_3$	3D	$2.48^a(2.47)$	150^a			(14.5)
$(C_9)_2PbBr_4$	2D(1-layer)	3.87^a	733^a	(897)		(6.2)
$(C_{6-2})_2PbBr_4$	2D(1-layer)	$\geq 3.49^a(3.89)$	$\geq 430^a$	(610)		(7)
$(C_1)_4PbBr_6 \cdot 2H_2O$	0D	$\geq 4.77^a$	$\geq 799^a$			
$(C_1)_1SnI_3$	3D	1.63^a	20			
$(C_1)_1(C_{6-2})_2Sn_2I_7$	2D(2-layer)	1.95^a	130^a	(146)		(26.6)
$(C_{6-2})_2SnI_4$	2D(1-layer)	2.19^a	$160\text{-}190^a$	(168)		(23.4)
$(C_1\text{-}I)_3SnI_5$	1D	≥ 3.02	≥ 380	(650)		
$(C_1)_4SnI_6xH_2O$	0D	3.54	656			

Here, C_1 is $MeNH_3$, C_9 is $C_9H_{19}NH_3$, C_1I is $NH_2C(I)=NH_2$, C_{6-2} is $C_6H_5CH_2CH_2NH_3$; [a] from OA spectra; [b] from temperature dependence of PL intensities; [c,d] f-values at low temperature [2]; [d] that of $(C_{10}H_{21}NH_3)_2PbI_4$ [2].

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well as in the spectra of oxides and chalcogenides. Fig. 8 shows the OA spectrum of $(C_8H_{17}NH_3)_2CuBr_4$(2D) [44] and the OA spectrum of $Mo_8Cu_{12}O_8S_{24}$ - clusters (0D) [50]. Fig. 9 shows the OA spectrum of $Cd_yS_x(SPh)_w$-clusters (0D) [7, 46, 52] and the spectra of CdS-particles (natural quantum dots) and bulk-CdS [7, 26,45, 53], for comparison. Some complexes described above have been proposed as components of optoelectronic and nonlinear optical devices [12, 18, 50]. Better results are expected from compounds with GaAs, InP etc (i.e., more covalent) units [1, 26, 54].

In conclusion, there is a large number of compounds with inorganic-organic hybrid structures which could be considered as 3D or LD semiconductor systems with properties and some possible applications similar to those of the corresponding systems based on conventional semiconductors [1, 45, 53].

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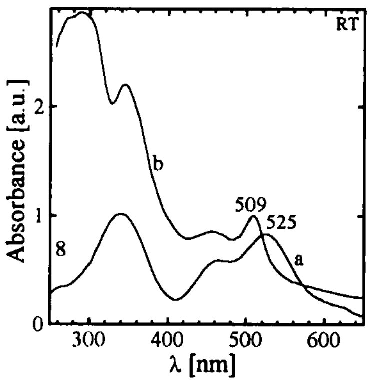

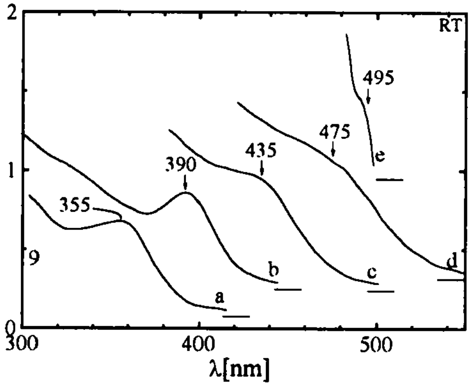

Figure 8. OA spectra of $(C_8H_{17}NH_3)_2CuBr_4$ (a) and $Mo_8Cu_{12}O_8S_{24}$ - clusters (b).

Figure 9.OA spectra of $Cd_yS_x(SPh)_w$-clusters with diameter (2R) $\leq$ 15 Å (a), CdS particles with: 2R $\leq$ 30 Å (b), 2R $\leq$ 45 Å (c) 2R $\leq$ 100 Å (d), and bulk CdS (e).

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