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$n = 1$ surface excitons and LO-TO splittings of bulk excitons in solid rare gases

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The energies of the $n = 1$ surface excitons in solid rare gases have been calculated by an extension of the standard exciton model for weakly bound molecular crystals. For neon, the repulsive interactions were deduced from *ab initio* potential curves of excited states, whereas for argon, krypton, and xenon they were deduced from experimental values for bulk excitons or gas-phase dimer excited potential curves. Good agreement with experimental results is obtained for all rare gases. Calculations of LO-TO splittings are also presented.

I. INTRODUCTION

It has recently been proposed that the $n=1$ (n is the principal quantum number) excitons in solid neon could be described by the standard exciton theory[1] and in this parameter-free calculation good agreement was obtained with experiment.[2] In contrast to earlier theories,[3,4] this model brings out the close correlation which exists between the first excited states of the free atom, and those of the dimer and the pure crystal, bound by weak Van der Waals forces.

The surface excitons for rare-gas solids were first observed by Saile *et al.*[5] under ultrahigh-vacuum conditions. They are distinguished from the bulk excitons by their constant transmittance with increasing film thickness from 5 to 100 Å. In contrast the transmission of the bulk excitons decreases. From the thickness dependance the authors estimate that the absorption due to surface excitons is confined to one or two layers at the sample-vacuum boundary. Also the surface excitons disappear on coating with an extremely thin film of different rare gas. Instead the surface excitons of the cover layer appear. Since then the surface excitons of solid neon and of the heavier rare gases have been observed by reflection techniques.[6] Surface excitons have also been observed in organic molecular crystals by this technique.[7] Also the surface excitons have been observed in MgO,[8] with energy-loss spectra using 100-eV electrons whose penetration depth does not exceed 4–5 Å.

These surface excitons are quite distinct from surface polarization states observed at infrared frequencies in many inorganic materials and usually expressed in terms of a set of macroscopic Maxwell equations.[7] The surface excitons described in this paper are also different from the surface effect originating from a thin dead layer at the surface proposed by Andreoni which may be described as Hopfield-Thomas interference.[9] The surface excitons are caused by changes in the spatial environment while approaching the surface. They are localized in the first one on two planes at the surface. Recently, Ueba[10] has reported qualitative discussion of surface excitons in terms of the environmental shift term and exciton exchange term as for molecular crystals. This is somewhat similar to our model for bulk excitons.[1]

So we considered it interesting to present an extension of our model to the case of surface excitons. We assumed the surface exciton to be confined to the first surface layer which was taken to be either a (100) plane or a (111) plane. We find a rather good agreement with experimental data for $n=1$ surface excitons of rare gases. Wolff calculated[11] the unobserved A_1 mode to coincide or to lie at slightly lower energies with respect to the active E mode in argon, while we find them to occur in neon at slightly higher energies. On this basis we believe that this will be the same for other rare gases as it is mainly due to resonance interactions as for LO-TO modes of the bulk.

The longitudinal (LO)–transverse (TO) splittings of $n=1$ bulk excitons in solid rare gases have been measured by optical-absorption and -reflection measurements.[6] These have been calculated by previous theories,[3,4] but in our model[1] the correction of shielding by a background (dielectric) polarization and local-field effects are made according to Ref. 12.

II. OUTLINE OF THE CALCULATION FOR SURFACE EXCITONS

If the atom at n on the surface is in the fth excited state, the wave functions will have the form

$$\Psi_n^f = C\phi_n^f \prod_{m=1}^{N}{}' \phi_m^0, \quad m \neq n \tag{1}$$

with

$$C=\prod_{p=1}^{P}\phi_p^0,$$

where ϕ_n^f and ϕ_m^0 are, respectively, the excited (f) and ground-state (0) eigenfunctions of the atom.[13] In the total wave function we have separated out the factor C which corresponds to the P atoms not on the surface from the N atoms on the surface. Since only atoms on the surface layer are equivalent for the excited state, the N new orthonormal functions are taken as

$$|kf\rangle=CN^{-1/2}\sum_{n}\Psi_n^f e^{i\vec{k}\cdot\vec{n}} \tag{2}$$

which differ in wave vector $\vec{k}$. But in contrast with bulk exciton the excitation can pass from atom n only to atom m on the surface. Except for this difference, the formulation is exactly the same as for bulk excitons which is restated as we noticed some typographical errors in Eq. (3) of Ref. 1. The excitation energy for transition from the ground state to the excited state is given by

$$E_f(k)=\Delta\epsilon_f+D_f+L_f(k), \tag{3}$$

where $\Delta\epsilon_f$ is the excitation energy of the free atom;

$$D_f=\sum_{m=1}^{N+P}\left(\langle\phi_m^0\phi_n^f|V_{mn}|\phi_n^f\phi_m^0\rangle-\langle\phi_m^0\phi_n^0|V_{mn}|\phi_n^0\phi_m^0\rangle\right) \tag{4}$$

is the environmental shift in interaction energy of one excited atom with all the surrounding atoms both on the surface and inside layers; L_f gives the resonance interaction with the surface atoms only; V_{mn} is assumed to be the sum of the repulsive and attractive parts of the pair potential both for the ground and the excited states.

In contrast to the case of the bulk, the lowered local symmetry of the surface introduces essentially an anisotropy in the interaction which removes the degeneracy of the triply degenerate F_{1u} state of the bulk. The splitting of the states by the anisotropy of the crystal field at the surface depends on the crystallographic orientation of the surface layer.

The shift also depends on this orientation. So we calculated the shifts and the splittings for two orientations (100) and (111) of the surface layer, which have the largest density of packing of atoms. In the former case the symmetry is C_{4v} and in the latter C_{3v} and in both cases the F state is split into A_1 and E states. In order to get the crystal wave functions defined in Eq. (1) for these A_1 and E states one has to take a proper linear combination of the 0_u and 1_u states of the dimer for the surface pairs and 0 and 1 states of the dimer for pair interactions with the atom in the inside layer. 0 and 1 states refer to the average of u and g states.

In the case of a (100) surface there are four nearest neighbors of the excited atom n on the surface and four on the next layer. The total isotropic repulsive interaction is given by $8V_{\text{rep}}^f$ where

$$V_{\text{rep}}^f=\frac{1}{2}\,\frac{0_u+21_u}{3}+\frac{1}{2}\,\frac{0+21}{3}. \tag{5}$$

The anisotropic repulsive interaction is given by

$$V_{\text{rep}_{A_1}}^f=-\frac{4(0_u-1_u)}{3}+\frac{2(0-1)}{3}, \tag{6}$$

$$V_{\text{rep}_E}^f=\frac{2(0_u-1_u)}{3}-\frac{0-1}{3}. \tag{7}$$

The anisotropic terms were calculated assuming that the anisotropic overlap energy varied as $\cos^2\theta$ where θ is the angle between the dimer axis and the electric vector characterizing the transition moment. The corresponding terms of Eqs. (5), (6), and (7) for the (111) plane are given in Table I.

As for the bulk, the attractive part for the surface exciton is given by

$$D_f=9.54(C_6^f-C_6^0)R^{-6}; \tag{8}$$

the factor 9.54 in place of 14.45 for the bulk arises from lattice sum for the surface and the inner layers (i.e., there are 9.54 effective nearest neighbors for an r^{-3} dependance) with (100) plane at the surface. According to Allen and de Wette[14] the interplanar spacing is perturbed at the surface and they have calculated the static relaxation for the first four layers. Taking this into account the lattice sum turns out to be 9.20. In view of the unknown accuracy of the C_6 coefficient, it was not considered worthwhile to take into account the small C_8 coefficient. Following Cohen and Schneider[15] we also have ignored the anisotropy of the long-range interaction.

The resonance interaction $L^f(k)$ of Eq. (6) is given by

$$L_f(k)=\sum_{m=1}^{N}{}'\,M_{nm}^f\exp[i\vec{k}\cdot(\vec{n}-\vec{m})], \tag{9}$$

where M_{nm}^f is the matrix element of the excitation transfer between atoms n and m.[13] The interaction is considered to arise only from the dipole-dipole interaction. Then it depends on the magnitude and direction of the transition moment. It is parallel to the surface for the E states and perpendicular to it for the A states. This interaction falls off as $1/R^3$. For the plane it gives a finite result but the convergence is slow. In order to calculate this lattice sum, we summed up to a certain distance and then integrated to infinity as suggested by Born and

TABLE I. Schematic calculation of the energies of surface excitons for different surface orientations.

	Bulk exciton	Surface exciton			
	O_h site symmetry	(111) C_{3v} site symmetry		(100) C_{4v} site symmetry	
	$A_g \rightarrow F_{1u}$	$A_1 \rightarrow A_1$ Isotropic	and $A_1 \rightarrow E$ Anisotropic	$A_1 \rightarrow A_1$ Isotropic	and $A_1 \rightarrow E$ Anisotropic
Repulsive part	$12(V_r^f - V_r^0)$	$9(V_r^f - V_r^0)$	$V^f_{rA_1} = -2(0_u - 1_u)$	$8(V_r^f - V_r^0)$	$V^f_{rA_1} = -\frac{4(0_u-1_u)}{3} + \frac{2(0-1)}{3}$
	$V_r^f = \frac{(0_u + 21_u)}{3}$	$V_r^f = \frac{2}{3}\frac{(0_u+21_u)}{3}$	$V^f_{rE} = (0_u - 1_u)$	$V^f_{rE} = \frac{1}{2}\frac{(0_u+21_u)}{3}$	$V^f_{rE} = \frac{2(0_u-1_u)}{3} - \frac{(0-1)}{3}$
		$+\frac{1}{3}\frac{(0+21)}{3}$	$-\frac{1}{2}(0-1)$	$+\frac{1}{2}\frac{(0+21)}{3}$	
Attractive part	$14.45(C_6^f - C_6^0)/R^6$	$10.40(C_6^f - C_6^0)/R^6$ unrelaxed lattice	$\cdots$	$9.54(C_6^f - C_6^0)/R^6$ unrelaxed lattice	$\cdots$
		$10.23(C_6^f - C_6^0)/R^6$ relaxed lattice		$9.20(C_6^f - C_6^0)/R^6$ relaxed lattice	
Resonance	LO: $\frac{\epsilon+2}{3\epsilon}\frac{8\pi d^2\sqrt{2}}{3R^3}$	$\cdots$	$A_1 = 11.033\frac{\epsilon+2}{3\epsilon}\frac{d^2}{R^3}$	$\cdots$	$A_1 = 9.033\frac{\epsilon+2}{3\epsilon}\frac{d^2}{R^3}$
	TO: $-\frac{\epsilon+2}{3\epsilon}\frac{4\pi d^2\sqrt{2}}{3R^3}$		$E = -5.516\frac{\epsilon+2}{3}\frac{d^2}{R^3}$		$E = -4.517\frac{\epsilon+2}{3}\frac{d^2}{R^3}$

Huang[16]

$$\sum_{S=1}^{\infty}\frac{1}{R_S^3}=\sum_{S=1}^{M}\frac{1}{R_S^3}+\frac{1}{R^2}\int_{\rho}^{\infty}\frac{2\pi R_S}{R_S^3}\,dR_S\,, \qquad (10)$$

where $\rho=[(M+1)/\pi]^{1/2}R$ and R is the nearest-neighbor distance. We obtained the lattice sum for the A_1 states to be 9.033 and −4.517 for the E states. These sums agree perfectly with those evaluated by Mahan and Obermair[17] in connection with polaritons at surfaces. These are not far from the numerical factors $\frac{8}{3}\pi\sqrt{2}$ and $-\frac{4}{3}\pi\sqrt{2}$ which occur in LO-TO splittings. As pointed out by Mahan and Obermair[17] this is closely related to the fact that the atoms in one or two layers near the surface see a local field which is appreciably different from that of the bulk. We introduced the dielectric background effect in the same way as in LO-TO splitting. Hence we get

$$L_{fA_1}=9.033\,\frac{\epsilon+2}{3\epsilon}\,\frac{d^2}{R^3}\,, \qquad (11)$$

$$L_{fE}=-4.517\,\frac{\epsilon+2}{3}\,\frac{d^2}{R^3}\,. \qquad (12)$$

We have summarized all these results in Table II with comparison to bulk exciton calculation. As for TO modes the E mode is lowered by resonance interaction. In fact there is a close connection between TO bulk and surface E modes and LO bulk and surface A_1 modes. Similar calculations for the (111) surface plane are also presented in Table II.

The $^3P_2$ state of the atom correlates with several molecular states (see Fig. 1 of Ref. 1) of which only the transition to 1_u from the ground state becomes slightly allowed. But in the bulk solid it correlates with E_u+F_{2u} states to which transitions are strictly forbidden.[1] But at the surface transitions to E states becomes allowed while those to A_2 are forbidden. So we report also calculations of the shift of $^3P_2$ states for the surface excitons.

III. THEORETICAL RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

A. Neon

As in the case of the bulk crystal we made use of the *ab initio* calculation of the repulsive part for the excited state of Ne_2 formed by the pair interaction $Ne^*(^{1,3}P)+Ne(^1S)$.[15] For the attractive part, C_6^f

TABLE II. Collective contribution of the various interactions for surface excitons in rare solid gases: (a) for a (111) surface (9 nearest neighbors); (b) for a (100) surface (8 nearest neighbors).

(a)

(111) 9 atoms		Isotropic part	ΔV_{rep} Anisotropic part E	Anisotropic part A_1	ΔV_{att}	L_f L_{fE}	L_{fA_1}
Ne	$^3P_1$	1.0496	0.0097	−0.0193	−0.3306	−0.081	0.1037
	$^1P_1$	1.0625	−0.0737	0.1474	−0.3554	−0.090	0.1152
Ar	$^3P_1$	0.7866			−0.4856	−0.062	0.124
	$^1P_1$	0.8180			−0.5311	−0.069	0.138
Kr	$^3P_1$	0.5160			−0.4003	−0.065	0.130
	$^1P_1$	0.5373			−0.3915	−0.054	0.108
Xe	$^3P_1$	0.5414			−0.5654	−0.058	0.116
	$^1P_1$	0.760			−0.7184	−0.051	0.102

(b)

(100) 8 atoms		Isotropic part	ΔV_{rep} Anisotropic part E	Anisotropic part A_1	ΔV_{att}	L_f L_{fE}	L_{fA_1}
Ne	$^3P_1$	0.9107	0.0064	−0.0129	−0.2534	−0.0663	0.1327
	$^1P_1$	0.9369	−0.0492	0.0983	−0.2757	−0.0739	0.1479
Ar	$^3P_1$	0.7920			−0.4367	−0.0508	0.1016
	$^1P_1$	0.8180			−0.4777	−0.0565	0.1130
Kr	$^3P_1$	0.5160			−0.3600	−0.0532	0.1064
	$^1P_1$	0.5373			−0.3521	−0.0441	0.0882
Xe	$^3P_1$	0.5415			−0.5085	−0.0475	0.0950
	$^1P_1$	0.7600			−0.6460	−0.0418	0.0835

and C_6^0 were taken from Ref. 1. So no adjustable parameter was used and the results for $n=1$, $1'$ excitons are displayed in Tables II and III. The $^3P_2$ and $^3P_1$ levels are too close to be resolved for neon. Agreement between the calculated and experimental results for $^{3,1}P$-^1S transitions is reasonable for a parameter-free calculation. The calculated values are slightly higher than the observed values. This probably arises mainly from an overestimation of the repulsive part. The wave function for the excited state is perhaps flattened out on the surface by resonance interaction and some kinds of relaxation process as postulated for rare-gas solids luminescence.[10] Also the wave function could be more localized on the outside of the crystal. These effects would reduce the overlap interaction with the inner layer without any change in the attractive part. So the repulsive term in Tables II and III column should be reduced by about 25%.

It should be remarked that repulsive part anisotropy is very small ($A_1 - E \simeq 0.02$ eV for $^3P_1$ and -0.02 eV for $^1P_1$) compared to the resonance term. It is the resonance term that is primarly responsible for the splitting between A_1 and E levels ($A_1 - E \simeq 0.18$ eV for $^3P_1$ and 0.20 eV for $^1P_1$ in our

TABLE III. Comparison between experimental and calculated energies for the surface excitons in rare gas solids for (a) (111) and (b) (100) surface planes.

(a)

(111) 9 atoms	Atomic transition	$\Delta\epsilon$	$D_E=(\Delta V_{\text{rep}}+\Delta V_{\text{att}}+L_f)_E$	$D_{A_1}=(\Delta V_{\text{rep}}+\Delta V_{\text{att}}+L_f)_{A_1}$	$E=\Delta\epsilon+D_E$	E observed
	$^3P_2$-$^1S_0$	16.619			17.290	
Ne	$^3P_1$-$^1S_0$	16.671	0.6706	0.8845	17.342	17.14
	$^1P_1$-$^1S_0$	16.848	0.5856	1.0767	17.434	17.37
	$^3P_2$-$^1S_0$	11.548			11.921	11.71
Ar	$^3P_1$-$^1S_0$	11.624	0.3730	0.5590	11.997	11.81
	$^1P_1$-$^1S_0$	11.828	0.3519	0.5589	12.179	11.93
	$^3P_2$-$^1S_0$	9.915			10.150	9.95
Kr	$^3P_1$-$^1S_0$	10.032	0.2355	0.4305	10.267	10.02
	$^1P_1$-$^1S_0$	10.644	0.2766	0.4458	10.921	10.68
	$^3P_2$-$^1S_0$	8.315			8.439	8.21
Xe	$^3P_1$-$^1S_0$	8.440	0.1238	0.2978	8.564	
	$^1P_1$-$^1S_0$	9.569	0.1964	0.3494	9.765	

(b)

(100) 8 atoms	Atomic transition	$\Delta\epsilon$	$D_E=(\Delta V_{\text{rep}}+\Delta V_{\text{att}}+L_f)_E$	$D_{A_1}=(\Delta V_{\text{rep}}+\Delta V_{\text{att}}+L_f)_{A_1}$	$E=\Delta\epsilon+D_E$	E observed
	$^3P_2$-$^1S_0$	16.619			17.216	
Ne	$^3P_1$-$^1S_0$	16.671	0.5974	0.7774	17.268	17.14
	$^1P_1$-$^1S_0$	16.848	0.5381	0.9073	17.386	17.37
	$^3P_2$-$^1S_0$	11.548			11.853	11.71
Ar	$^3P_1$-$^1S_0$	11.624	0.3045	0.4569	11.929	11.81
	$^1P_1$-$^1S_0$	11.828	0.2838	0.4533	12.112	11.93
	$^3P_2$-$^1S_0$	9.915			10.018	9.95
Kr	$^3P_1$-$^1S_0$	10.032	0.1028	0.2624	10.135	10.02
	$^1P_1$-$^1S_0$	10.644	0.1411	0.2734	10.785	10.68
Xe	$^3P_2$-$^1S_0$	8.315			8.300	8.21
	$^3P_1$-$^1S_0$	8.440	−0.0145	0.1280	8.425	
	$^1P_1$-$^1S_0$	9.569	0.072	0.1976	9.641	

model and A_1 levels should be slightly higher than the E levels.

B. Argon and krypton

Encouraged by this result we extended this model to argon and krypton. As no *ab initio* calculations have been made for the repulsive interaction of the excited dimer, we inverted the procedure for calculating the energies of bulk excitons[1] in order to deduce the repulsive part for the excited state. We made use of the experimental results and of attractive and resonance interactions in the excited state and attractive and repulsive interactions in the ground state. As in neon we found the anisotropic repulsive interaction to be very small; we assumed this also to held for other rare gases so we ignored this anisotropy. In order to calculate C_6^f of the excited state, in the case of argon we used the same procedure as for neon.[1] As the oscillator strength of the transitions from the excited state of krypton are not known, it was not possible to calculate the polarizabilities. So we made use of the polarizabilities given in Ref. 18 to calculate C_6^f. Then following the same procedure of Table I we derived the energies of the $n=1$ surface excitons in argon and krypton. In order to obtain the energy of the surface exciton corresponding to the ${}^3P_2$ state we assumed that the splitting of the ${}^3P_2$, ${}^1P_1$ states is practically the same in the gas as in the solid. We assigned the first three observed peaks to the transitions to ${}^3P_2$, ${}^3P_1$, and ${}^1P_1$ states. Our assignment agrees with that of Wolff for argon.[10] We find as for neon the calculated values to be higher than the observed values by roughly 0.1 – 0.2 eV and this can be explained in the same way as for neon.

The unobserved A_1 modes are always slightly higher than E modes as this arises only from the resonance interaction in our model. This is analogous to the LO mode being higher than TO modes for bulk excitons. We have ignored the anisotropic attractive and repulsive interaction. But Wolff in his crystal field calculation finds the A_1 mode to lie slightly lower than E modes at the equilibrium distance in the crystal of argon. This difference may be due to the fact that the anisotropic overlap interaction is included in his calculation. If the A_1 modes could be observed experimentally by oblique angle excitation then it could decide between the two results.

In all these lighter rare gases both the bulk and first surface excitons lie on the high-frequency side of the resonance line in the gas, the surface excitons lying between the bulk exciton and resonance line of the atom. This is also the conclusion of Ueba.[9]

The ratios of the intensities of doublet in the gas are very small whereas in the bulk and surface exciton for lighter rare gases it is nearly the same. This is qualitatively explained in Sec. IV.

C. Xenon

In the case of xenon we calculated the repulsive part of the excited state as explained earlier from experimental bulk results. This repulsive part at this internuclear distance in the solid ($d=4.335$ Å) is in good agreement with the complete repulsive interaction obtained experimentally in gas phase studies by Castex.[19,20] She also obtained the repulsive anisotropic interaction for the states correlated to ${}^1P_1$ atomic states.[20] In this case, bulk excitons lie on the low-frequency side but close to their respective resonance lines. So the expected ${}^{3,1}P$ surface excitons would be to close to the bulk structure to be distinguishable. So we propose that the observed sharp structure could be assigned to ${}^3P_2$-${}^1S_0$ transition.

IV. LO-TO SPLITTINGS OF BULK $n=1$ EXCITONS

The bulk excitons in a cubic crystal are split by the long-range dipole-dipole interaction into longitudinal ($\parallel \hat{k}$) (LO) and transverse ($\perp\hat{k}$) (TO) excitons. In normal-incidence optical absorption, only transverse modes are observed as they alone interact with the incident transverse electromagnetic field. On the other hand the longitudinal mode may be observed in electron-loss spectroscopy[21] or in optical absorption at non-normal incidence as demonstrated recently.[6] The LO-TO splitting depends mainly on the oscillator strength of the transition involved and the lattice parameter. The earlier theories took into account only the shielding effect of the background dielectric constant ϵ in both LO and TO modes. Philpott[12] has shown that the shielding is not a simple division by ϵ. In addition the local-field correction due to all higher transitions enhances the interaction by a factor of $(\epsilon+2)/3$. The long-range exchange terms are given by Eqs. (9) and (10) in Ref. 1.

$$L^{\perp}=-\frac{\epsilon+2}{3}\,\frac{4\pi d^2\sqrt{2}}{3R^3} \tag{13}$$

and

$$L^{\parallel}=\frac{\epsilon+2}{3\epsilon}\,\frac{8\pi d^2\sqrt{2}}{3R^3}\,. \tag{14}$$

Then the LO-TO splitting is given by

$$L^{\parallel}-L^{\perp}=\frac{1}{\epsilon}\left(\frac{\epsilon+2}{3}\right)^2\frac{4\pi d^2\sqrt{2}}{R^3}\,. \tag{15}$$

In Table IV we report these splittings for $n=1,1'$ excitons of rare-gas solids and compare them with the available experimental values. Agreement with experiment is fairly good. According to Philpott[12]

TABLE IV. Comparison between calculated and experimental energies for LO-TO splittings in rare gas solids: (a) from Refs. 3 and 4; (b) present work; (c) experimental data extracted from Ref. 19 by comparison between optical measurements and less accurate electron energy-loss measurements; (d) experimental data obtained by non-normal incident light absorption measurements at Desy from Ref. 8.

			$^3P_1$-$^1S_0$		
		LO-TO		Experiment	
	f	(a)	(b)	(c)	(d)
Ne	0.11	0.004	0.2362	not observed	or probably overlaps with $^1P_1$
Ar	0.17	0.05	0.1648	0.11	⋯
Kr	0.158		0.1496	0.07	0.165
Xe	0.16		0.1439	0.13	0.06

			$^1P_1$-$^1S_0$		
		LO-TO		Experiment	
	f	(a)	(b)	(c)	(d)
Ne	0.11	0.232	0.2522	0.26	0.24
Ar	0.17	0.16	0.1638	0.17	0.27
Kr	0.135		0.1212		0.135
Xe	0.13		0.1036	0.33	

the oscillator strength of an oriented molecule or atom is modified by the local-field correction due to all higher transitions by a factor $[(\epsilon+2)/3]^2$. But according to Davydov[13] the dielectric constant ϵ must be evaluated at the exciton frequency excluding its own contribution. For the lowest exciton this would increase considerably its oscillator strength and this might explain why the ratio of intensities of the doublet $n=1,1'$ lies closer to unity as compared to that of the gas.

V. CONCLUSION

The close correlation of atomic, molecular, and lowest excitonic states is clearly seen in our simple model. As the surface and bulk excitons have the same origin, the atomic absorption cross section should be nearly equal for both excitons. Indeed according to Saile this has been verified for krypton by plotting the bulk exciton absorption coefficient as a function of film thickness.

Finally our model leads to fair agreement with experiment as it contains the essential physics of the problem.

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[1] E. Boursey, M. C. Castex, and V. Chandrasekharan, Phys. Rev. B 16, 2858 (1977).

[2] D. Pudewill, F.-J. Himpsel, V. Saile, N. Schwentner, M. Skikowski, and E. E. Koch, Phys. Status Solidi B 74, 485 (1976).

[3] W. Andreoni, M. Altarelli, and F. Bassani, Phys. Rev. B 11, 2352 (1975).

[4] W. Andreoni, F. Perrot, and F. Bassani, Phys. Rev. B 8, 3589 (1976).

[5] V. Saile, M. Skibowski, W. Steinman, P. Gürtler, E. E. Koch, and A. Kozevnikov, Phys. Rev. Lett. 37, 305 (1976).

[6] V. Saile, W. Steinman, and E. E. Koch, Fifth International Conference on Vacuum Ultraviolet Radiation Physics, Montpellier, France, 5-9 September 1977; and V. Saile (private communication).

[7] M. R. Philpott and J. M. Turlet, J. Chem. Phys. 64, 3852 (1976).

[8] V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, Phys. Rev. Lett. 36, 158, (1976).

[9] W. Andreoni, M. de Crescenzi, and E. Tosatti, in Ref. 6.

[10] H. Ueba, J. Phys. Soc. Jpn. Lett. 43, 353 (1977); H. Ueba and S. Ichimura, J. Phys. Soc. Jpn. 42, 355 (1977).

[11] H. W. Wolff, in Ref. 6.

[12] M. R. Philpott, J. Chem. Phys. 56 (1972); Phys. Ref. B 14, 3471 (1976). G. Venkataraman, L. A. Feldkamp, and V. C. Sahni, *Dynamics of Perfect Crystals* (MIT, Cambridge, 1975), p. 388. G. Zumofen and K. Dressler, J. Chem. Phys. 64, 5198 (1976). G. Zumofen, International Conference on Matrix Isolation Spectroscopy West Berlin, 21–24 June 1977.

[13] A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).

[14] R. E. Allen and F. W. de Wette, Phys. Rev. 179, 873 (1969).

[15] J. S. Cohen and B. Schneider, J. Chem. Phys. 61, 3230 and 3240 (1974).

[16] Born and Huang, *Dynamical Theory of Crystal Lattices* (Oxford University, Oxford, 1966).

[17] G. D. Mahan and G. Obermair, Phys. Rev. 183, 838 (1969).

[18] J. Granier and R. Granier, J. Quant. Spectrosc. Radiat. Transfer 13, 473 (1973).

[19] M. C. Castex, J. Chem. Phys. 66, 6584 (1977).

[20] M. C. Castex, in Ref. 6.

[21] B. Sonntag, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, 1977), Vol. II; I. T. Steinberger, P. Maaskant, and S. E. Webber, J. Chem. Phys. 66, 4722 (1977).