

Evolution of excitonic bands in fluid xenon

P. Laporte*

Laboratoire des Interactions Moléculaires et des Hautes Pressions, Centre National de la Recherche Scientifique-Bellevue, 92190, Meudon, France

I. T. Steinberger

Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

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Reflection spectra of homogeneous fluid xenon are presented for the wavelength region $115 < \lambda < 165$ nm and densities ranging from that near the critical point to that at the triple point. For each atomic line in this spectral region two bands are observed: one broadened and somewhat shifted band corresponding to the atomic transition, and another distinct band corresponding in position to that of the exciton observed in the triple-point liquid. Dispersion analysis of the two (atomic and excitonic) 3P_1 bands yielded the optical constants ϵ' , ϵ'' , n , and k as a function of photon energy as well as parameters of the absorption bands. The results are interpreted in terms of exciton transitions appearing in momentary clusters of the fluid. The analysis of the parameters of the absorption bands was compared with the statistical fluctuations of the fluid density. It was estimated from this comparison that the 3P_1 exciton can be formed in a momentary cluster of atoms provided two conditions are fulfilled: the cluster has at least the volume of 1.5×10^{-21} cm³ and contains at least ten atoms.

I. INTRODUCTION

The conditions for the appearance of Wannier excitons in a liquid and their properties were discussed by Rice and Jortner.¹ Rice and coworkers²⁻⁴ subsequently predicted many features of Frenkel excitons in simple liquids. Wannier excitons (both free⁵⁻⁷ and bound⁸⁻¹⁰) have been experimentally observed in rare-gas liquids as well as excitons of "intermediate" type.⁵⁻¹⁰ For liquid xenon it has also been shown^{11,12} that the exciton bands are closely related to those observed in the solid; i.e., the solid-liquid shift of the excitonic bands is that as expected from the density change on melting.

For the creation of any excitonic band¹³ (either Wannier or Frenkel type) a number of neighboring atoms have to cooperate. In the case of a solid, the dimensions of a small crystallite have to be larger than the exciton Bohr radius in order that the excitonic absorption band should be observable in it. Moreover the excitonic band in such a crystallite will have a shape similar to that observed in a large crystal only if its phonon spectrum will also be approximately that of the large crystal. These two conditions set a lower limit to the dimensions of the solid sample for the observation of excitons. In the case of a liquid, the sample dimensions have to be again larger than the excitonic Bohr radius; the band shape and width should be determined principally by the electron scattering in the liquid.¹ For Frenkel excitons, effects of sample size might also be caused by the collective translational excitations of the liquid and their coupling to the excitons.

For a dense fluid another question also arises, closely related to the above discussion of the effects of the sample size. Do excitonic levels evolve continuously, by gradual shift and/or broadening, from the corresponding states in the gas, or are they inherently different and distinct states? In the latter case excitonic bands should be observable alongside the corresponding perturbed atomic bands at some fluid densities, probably smaller than the density at the triple point. "Free" excitons in liquids have been hitherto reported only for densities near that at the triple point.⁵⁻⁷

The present work concerns the development of excitonic bands in fluid xenon at states near and above the critical density along thermodynamic paths crossing the critical isotherm above the critical point, i.e., along the continuous transition gas \leftrightarrow liquid. Accordingly, this work is relevant to the determination of atomic interactions and aggregations needed for the appearance of exciton bands in a noncrystalline substance.

II. EXPERIMENTAL

The experiments near and above the critical density were performed in Bellevue with a double-beam spectrometer, using a deuterium discharge lamp, a special pressure chamber and a photoelectric recording system, as reported previously.¹⁴ The measurements near the triple point were made in Jerusalem using a McPherson 1-m monochromator, a krypton-filled Tanaka lamp and simultaneous photoelectric monitoring of both the incident and reflected light intensity.⁶ The im-

proved methods used for obtaining the correct values of the reflectivity of the MgF_2 window/liquid xenon interface will be published shortly.¹⁵ Parts of the calculation were performed at the Daresbury Laboratory.¹⁶

III. RESULTS

This work deals with the atomic transitions in Xe which are observed at wavelengths above the MgF_2 cutoff: 119.20, 129.56, and 146.96 nm. Corresponding, but greatly broadened excitonic bands were observed in liquid xenon in the liquid near the triple point⁵⁻⁷ at 119.9, 132.6, and 152.6 nm. These latter wavelengths are those of reflectivity maxima.

Figure 1 shows the reflectance of fluid xenon at several densities, starting with a density just below the critical density ($\rho_c = 185.2$ amagat¹⁷). Results on lower densities are presented in Ref. 14.

For all bands a gradually increasing red shift is evident. At the lowest density presented here the 119.20-nm band is already considerably broadened. Moreover, the bands which appear on both the blue and red sides of the atomic transition even at lower densities^{14,18-20} are already considerably overlapping with the atomic line. It is also seen that at $\rho = 241$ amagat these bands are superimposed on a much broader band, centered at about the same point. Increasing the density causes this broad band to grow in amplitude (but not in width), until the narrow one is completely swallowed. The position and width of the broad band is as that of a reflection band in liquid-xenon samples near the triple point.⁵ The latter exists as an exciton band in the solid as well; a recent discussion of its origin is given in Ref. 21.

The behavior of the bands observed at and around 129.6 nm is somewhat more involved. As stated before,¹⁴ several narrow bands (of molecular origin mostly) appear at the red wing of the atomic line. The steep edge on the blue side of the 182-amagat curve is formed by the superposition of several such bands. At a higher density, the blue side of this system decreases in intensity and an approximately symmetric band emerges, shifted to the red. With increasing density this symmetric band increases in intensity (but not in width) and shifts nearer and nearer to the position of the 132.6-nm excitonic band, observed in liquid xenon near the triple point. The widths of the bands observed in the present work were similar to those reported at the triple point. The corresponding exciton in the solid is an "intermediate exciton", which can either be denoted as the $n = 1$ member of the $\Gamma(\frac{3}{2})$ series in the Wannier notation or as the 1P_1 Frenkel exciton.

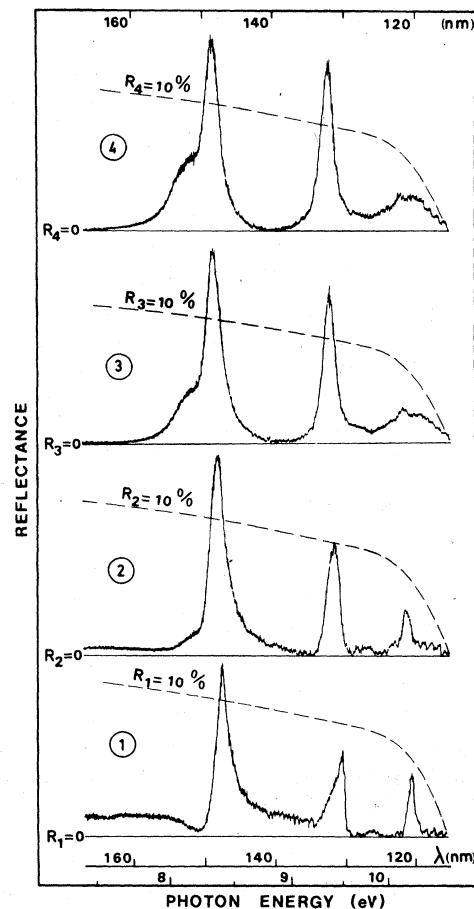


FIG. 1. $6s(\frac{3}{2})_1^0$, $6s'(\frac{1}{2})_1^0$, and $5d(\frac{3}{2})_1^0$ bands in fluid xenon, observed by reflection, as a function of density. Conditions: 1—292.7 K, 61.8 bar, 182 amagat; 2—293.9 K, 65.7 bar, 241 amagat; 3—283.4 K, 61.8 bar, 306 amagat; 4—274.4 K, 61.8 bar, 338 amagat.

The 146.96-nm line is already considerably broadened and shifted at 182 amagat. At 241 amagat, a further band is already evident on the red side, increasing gradually with density. Both the original—shifted and broadened—"atomic" band and this further band stay, however, distinct at all densities of observation. The further band is again very near to the position of the 152.6-nm exciton band observed in liquid xenon near the triple point. This correspondence has been mentioned previously.²² The exciton band in question is again an "intermediate exciton", $n = 1$ $\Gamma(\frac{3}{2})$ in the Wannier and 3P_1 in the Frenkel scheme.

All three bands have thus in common the appearance of the "liquid exciton" bands at densities far below that of the density of liquid xenon near the triple point ($\rho = 523$ amagat). Phenomenologically, the differences are due mainly to the difference in the rela-

tive positions of the atomic line and the corresponding exciton in the triple point liquid; while the atomic $5d(\frac{3}{2})_1^0$ line at 119.2 nm is very near to the center of the corresponding exciton band there is a shift of 2.7 nm for the $6s'(\frac{1}{2})_1^0$ line (129.56 nm in the dilute gas) and a shift of 5.6 nm in case of the $6s(\frac{3}{2})_1^0$ line (146.96 nm in the dilute gas). The chief qualitative result of this work is the fact that the bands corresponding to the excitonic bands of the triple point liquid appear already at much lower densities and the "dense gas" bands do not transform gradually into the "liquid" bands. This is true even along the thermodynamic paths chosen, where the system is a single-phase one and there is no discontinuity in the gas/liquid transition.

A more detailed analysis was made of the behavior of the $6s(\frac{3}{2})_1^0$ line (146.96-nm atomic line). For this case the transparency of the MgF_2 window is higher than at the other two bands and therefore the spectrum is less noisy. Moreover the dense-gas line is distinct and well-separated from the corresponding exciton band at all densities.

Figure 2 represents the reflectivity spectra of a xenon/ MgF_2 interface at several densities near the critical point as well as near the triple point. The gradual rise of the excitonic band (at 8.33 eV) at the expense of the perturbed atomic band (at 8.14 eV) is evident from Fig. 2.

The reflectivities of these spectra were analyzed as follows in order to obtain the optical constants. It was assumed that the real and imaginary parts of the dielectric constant ϵ' and ϵ'' can be represented in this region by the Lorentz formulas

$$\epsilon'(E) = n_0^2 + \sum_{i=1}^2 \frac{A_i E_i g_i (E_i^2 - E^2)}{(E_i^2 - E^2)^2 + g_i^2 E^2}, \quad (1)$$

$$\epsilon''(E) = \sum_{i=1}^2 \frac{A_i E_i g_i^2 E}{(E_i^2 - E^2)^2 + g_i^2 E^2}. \quad (2)$$

E being the photon energy corresponding to the frequency $\nu_f = E/h$, E_1 , and E_2 the respective energies of the resonance frequencies, n_0^2 the contribution of higher absorption bands; n_0 was allowed to vary linearly with E , in order to allow for the decay of the tails of higher bands, A_i is the amplitude, and g_i the damping constant of the resonance curve. Calculated values of the reflectivities $R(E)$ (at normal incidence) were obtained as follows

$$R(E) = \frac{(\epsilon'^2 + \epsilon''^2)^{1/2} - n_1 [2(\epsilon'^2 + \epsilon''^2)^{1/2} + \epsilon']^{1/2} + n_1^2}{(\epsilon'^2 + \epsilon''^2)^{1/2} + n_1 [2(\epsilon'^2 + \epsilon''^2)^{1/2} + \epsilon']^{1/2} + n_1^2}. \quad (3)$$

n_1 being the (average) refractive index of the MgF_2 window in this region. The parameters $n_0, A_i, E_i, g_i (i=1, 2)$ were chosen, by trial and error, in such a manner as to obtain a good fit of the R values cal-

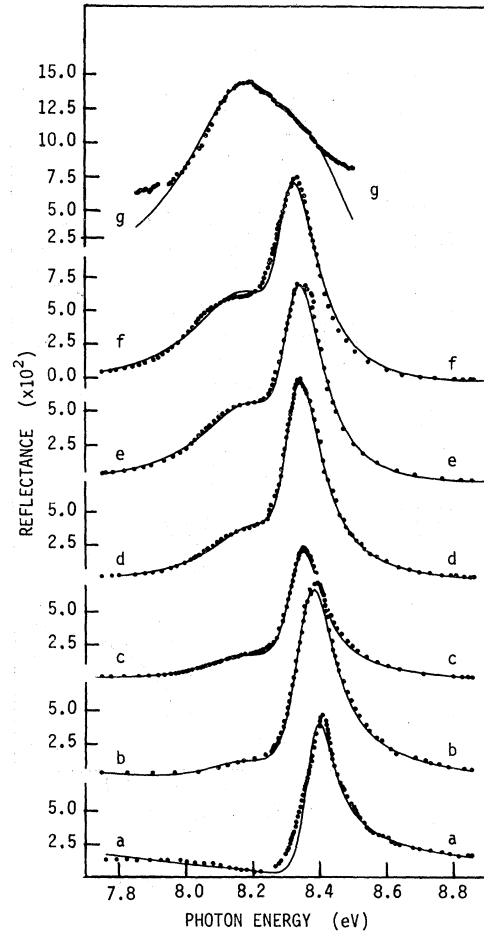
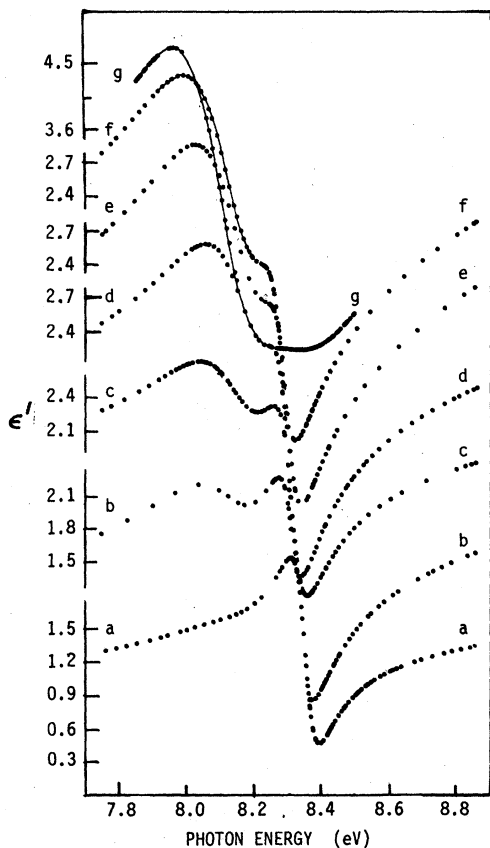


FIG. 2. $6s(\frac{3}{2})_1^0$ reflection bands in fluid xenon at various densities. The points are experimental, the curves calculated by means of dispersion analysis (see text). The curves a to g correspond here and in graphs 3-7 to densities increasing from 182 to 500 amagat, according to Table I.

culated from (3) to the experimental reflectivity spectrum. The fitted spectra also appear in Fig. 2. The fit is excellent for most densities, but it becomes worse at the two ends of the high-density (500 amagat) curve. It is likely that in this case further bands, reported for the solid²³ may contribute to the reflectivities. The dependencies of ϵ', ϵ'', k , and n on photon energy at the various densities appear in Figs. 3-7. In Fig. 4, the respective contribution of the two bands are also indicated.

Values of A_i, g_i, E_i as well as n_{or} and n_{ob} [denoting n_0 at the "red" end (160 nm) and "blue" end (140 nm), respectively, of the presented bands] are listed in Table I. It is seen that E_1, E_2 and g_2 are roughly constant, n_{or}, n_{ob} , and A_2 increase monotonously with density, A_1 is roughly constant up

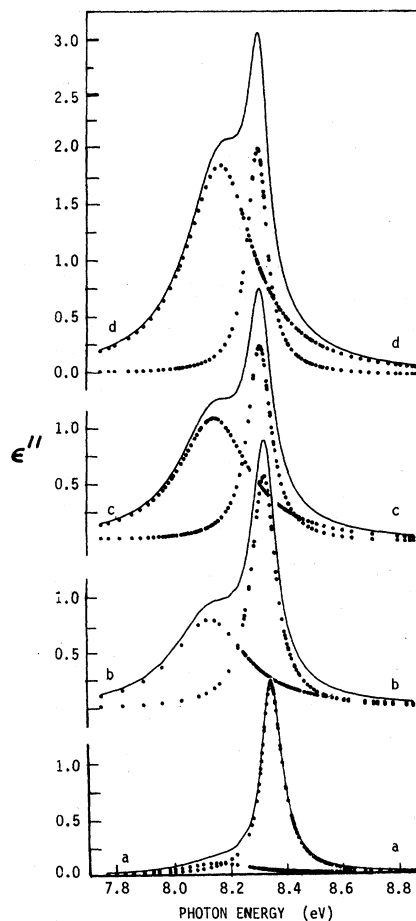
FIG. 3. ϵ' vs photon energy.

to 306 amagat and decreases subsequently. g_1 is approximately constant up to 350 amagat but it becomes three times larger at 500 amagat. However, part of this increase may be due to the difficulty in establishing the width of a band which appears only as a shoulder in the reflection spectrum; the bad fit at the wings also contributed to the inaccuracy.

IV. DISCUSSION

The results presented above indicate that the excitons appear in fluid xenon already at comparatively low densities and that the relative weight of the excitonic transition increases with the increase of density. We suggest that it is possible to extract from the spectroscopic information presented above the necessary and sufficient condition for the appearance of the exciton in the fluid.

The results are interpreted by assuming that some of the atoms are in a "gaslike" environment;

FIG. 4. ϵ'' vs photon energy. The contributions of the two bands according to Eq. (2) are indicated.

these atoms contribute to the perturbed atomic/molecular absorption bands.¹⁴ Other atoms are in an environment where the local density and number of nearest neighbors are sufficiently similar to the conditions in the liquid; these atoms contribute to the excitonic absorption band. On the basis of the quantum mechanical treatment of dispersion²⁴ one may thus write

$$A_i = \frac{4\pi e^2 f_i \rho_i}{m \omega_{0i} G_i}, \quad i=1,2, \quad (4)$$

ρ_i being the number density of atoms which take part in transition i , f_i the oscillator strength of this transition, ω_{0i} and G_i correspond to E_i and g_i , but are expressed in terms of angular frequency, m and e are the electron mass and electron charge, respectively. Since $A_i \omega_{0i} G_i$ is known for both bands ($i=1,2$), the densities ρ_1 and ρ_2 can

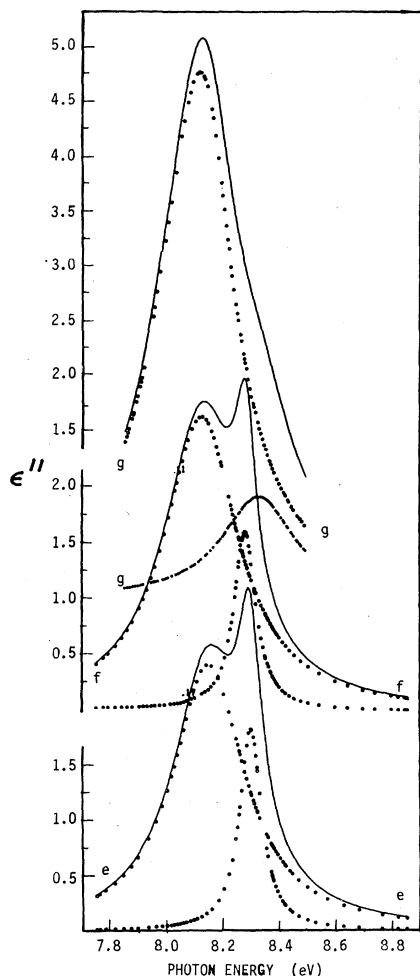


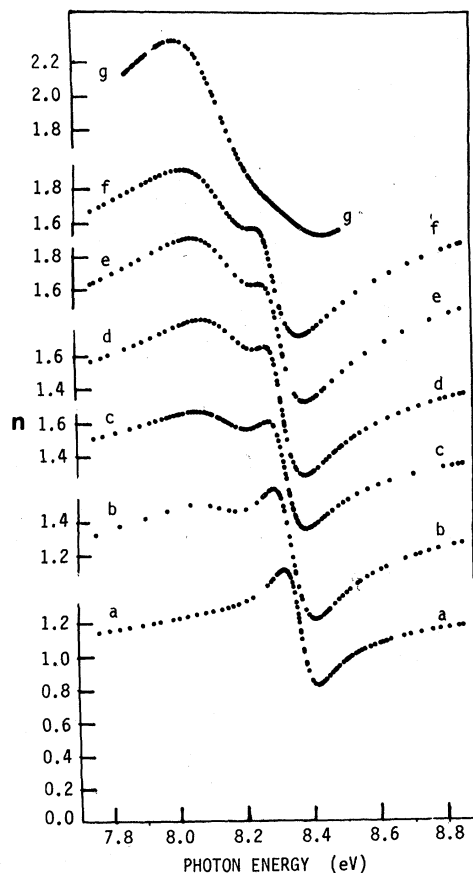
FIG. 5. Same as in Fig. 4. but for higher densities.

be calculated provided the oscillator strengths f_1 and f_2 are known. It is reasonable to assume that $f_1 \approx f_2$.^{25,26} With this assumption the ratio

$$\alpha = \frac{A_2 E_2 g_2}{A_1 E_1 g_1 + A_2 E_2 g_2} \quad (5)$$

is equal to the ratio of the number of atoms being in "liquid" environment to the total number of atoms. α vs density is represented in Fig. 8. It is seen that α rises from about 0.17 at 182 amagat to a saturation value of ~ 0.8 . It should be emphasized that the accuracy of α is lowest at the two extreme densities (182 and 500 amagat) since in these cases α is determined by the parameters of weak, poorly resolved bands.

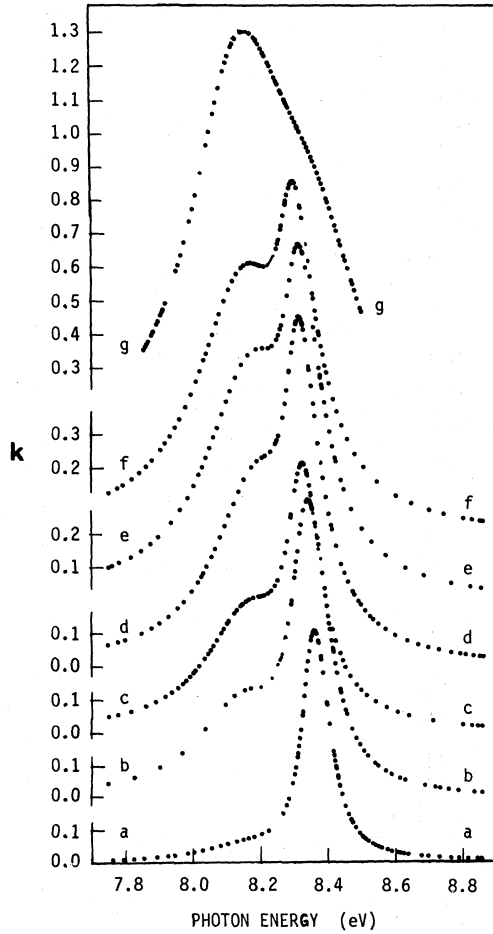
According to the above assumption, α is equal to the probability that an atom should be a member of an appropriate cluster of atoms; this cluster should be large enough both to accommodate the ex-

FIG. 6. n vs photon energy.

citon orbit and cause the interaction between the atoms necessary for the observation of the exciton. For the present purposes an "appropriate cluster" may be any, however short-lived aggregate of atoms, where each atom has at least a certain minimum coordination number (say ν nearest neighbors in the random-close-packing sense). Ideally, if detailed structure data for Xe near the critical point were known,²⁷ the present data should yield both the size of the cluster as well as ν . As a rather crude approximation of the real problem we calculated the mean-square fluctuation $\langle \Delta N \rangle^2$ on the number of atoms in the volume V_0 according to the thermodynamic formula²⁸

$$\langle \Delta N \rangle^2 = (k T N_A^2 / V_0) \kappa, \quad (6)$$

k being Boltzmann's constant, T the absolute temperature, N_A the average number of atoms in the volume V_0 , and κ the isothermal compressibility.^{29,30} If $w(N_0)$ is the probability that the volume V_0 should contain at least N_0 atoms, $w(N_0)$ can be estimated from the area under the Gaussian,

FIG. 7. k vs photon energy.

$$w(N_0) = \int_{N_0}^{\infty} \frac{1}{2\pi\langle\Delta N\rangle^2} \exp\left(-\frac{(N-N_A)^2}{2\langle\Delta N\rangle^2}\right) dN. \quad (7)$$

Values of V_0 and N_0 were sought to obtain a fit with

TABLE I. Parameters obtained from curve-fitting of reflectivities of the $6s(\frac{3}{2})_1^0$ transitions. For the definitions of the parameters see text.

	P (bar)	T (K)	ρ (amagat)	E_1 (eV)	A_1	g_1 (eV)	E_2 (eV)	A_2	g_2 (eV)	n_{or}	n_{ob}
(a)	61.8	292.7	182	8.352	1.71	0.087	8.15	0.10	0.30	1.068	1.23
(b)	65.7	293.9	241	8.325	2.10	0.105	8.137	0.80	0.312	1.13	1.40
(c)	61.8	287.8	283	8.310	1.75	0.100	8.150	1.10	0.30	1.32	1.48
(d)	61.8	283.4	306	8.30	2.00	0.087	8.170	1.85	0.29	1.31	1.55
(e)	61.8	274.4	338	8.297	1.82	0.095	8.15	2.40	0.31	1.29	1.68
(f)	83.4	275.0	350	8.28	1.60	0.094	8.125	2.62	0.32	1.29	1.68
(g)	0.8	163.0	500	8.33	0.91	0.320	8.10	4.68	0.32	1.25	2.00

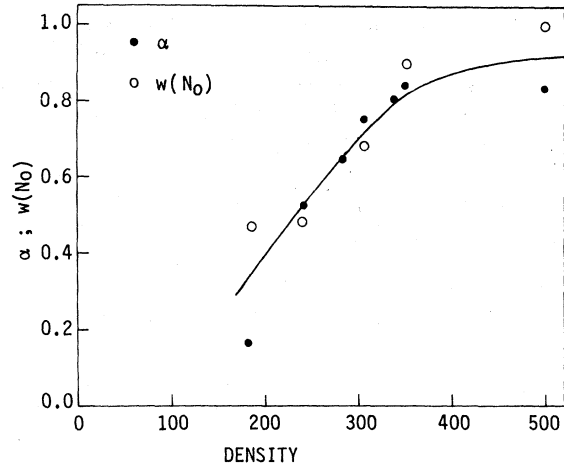


FIG. 8. The relative number α of atoms in a "liquid-like" environment and the probability $w(N_0)$ that in a volume of $1.5 \times 10^{-21} \text{ cm}^3$ there should be at least $N_0 = 10$ atoms as a function of the density.

the α vs. density curve (Fig. 8). In this graph the values of $w(N_0)$ also appear, with $V_0 = 1500 \text{ \AA}^3$ and $N_0 = 10$. This corresponds to a local density which is about half of that of the triple-point liquid (523 amagat). Taking the volume V_0 as a sphere, its radius would be 7.1 \AA . This value should be compared with the Bohr radius of the $n=1 \Gamma(\frac{3}{2})$ exciton in liquid Xe, namely 3.52 \AA , calculated from the parameters of Ref. 12 without central cell correction. Moreover in the pair distribution function $g(r)$ of liquid Xe³² the first and second peak are 4.34 and 7.92 \AA , respectively. Thus the exciton has to be regarded as a tightly bound state; for its existence a few atoms (≥ 4 , see above the estimate for ν) have to be close-packed neighbors to the atom in question and a similar number has to be not further away than in the position of second nearest neighbors.

The fit of Fig. 8 for intermediate densities is

good, but it becomes poor for the lowest and highest densities. The reason may be the inaccuracy in determining α for these cases (see above), but it may also be due to the invalidity of the thermodynamic-statistical reasoning leading to Eq. (6). In the critical point region coupling with fluctuations in the neighborhood of the volume in question may also be significant. Using $g(r)$ from experiment³² for the triple-point region and from liquid structure theory in the critical point region should yield a better means to correlate the evolution of the band with the structure of the fluid.

V. CONCLUSIONS

It has been shown that "free" excitons may exist not only in solids and liquids, but also in a dense

fluid. The fact that distinct exciton absorption bands appear already at densities much lower than that at the triple point shows clearly the distinction between perturbed and overlapping atomic/molecular states and excitons. The statistical considerations indicate that the $n=1$ $\Gamma(\frac{3}{2})$ exciton can appear already in a rather small and loose momentary cluster of atoms.

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*Present address: Equipe UV, Laboratoire associé au C. N. R. S. no. 171, Ecole Nationale Supérieure des Mines, 42023 Saint Etienne Cedex, France.

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²⁵If $f_1 = f_2$ is calculated from Eq. (4) using the fact that $\rho_1 + \rho_2$ is the total density, improbably large (≥ 0.5) f values result. However, in fact, a correction of the local Lorentz field has to be taken into account (Ref. 26). As a result the true f value denoted by f' is related to the one obtained from (4) by the relation $f' = [9/(n_0^2 + 2)^2]f$, where n_0 is the contribution of higher bands to the refractive index. With this correction $f'_1 = f'_2 \sim 0.3$ for all densities except that of 182 amagat, but in this case the accuracy is very low.

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²⁷Using results on liquid argon (Ref. 31), scaled to the ratio of densities at the triple point, and taking into account the position of the sharp rise in Fig. 2, one would infer $\nu \approx 4$ for the minimum number of nearest neighbors necessary for the observation of the exciton band.

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