RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 2 15 JULY 1987-I

# Electronic excitations of pure and doped rare-gas fluids: Theory and experiment

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(Received 2 February 1987; revised manuscript received 8 April 1987)

It is shown that a mean-spherical model with no adjustable parameters developed by Chandler, Schweizer, and Wolynes [Phys. Rev. Lett. **49**, 1100 (1982)] is in rough agreement with the experimentally observed shifts of photoconductivity thresholds in pure and doped rare gases. This holds for a wide density range. However, the theory always yields a red shift for discrete absorption lines and bands, while in the experiments blue shifts are dominant, essentially as a result of correlation effects.

For pure and doped fluids of the rare gases Xe, Ar, and Kr, there exists a profusion of experimental data[1-7] describing the evolution of electronic states from densities of a dilute gas to that of a triple-point liquid. These data have been interpreted mainly by drawing on the similarity and continuity with the respective gas and solid samples: They were discussed in terms of broadened and shifted atomic lines influenced by molecular interactions, free and trapped excitons, as well as valence and conduction bands. However, in spite of the basic importance of the rare-gas fluids and the wide scope of results available, the data have not yet been used for comparison with fundamental theories on electron states formulated specifically for fluids. The present Rapid Communication intends to bridge this gap between theory and experiment.

We shall compare experimental results with a linear response theory of the dielectric properties of liquids. Many such theories can be viewed as mean-field theories of the atomic dynamic polarizability; the induced dipole in the atom is acted on by a local field produced, in turn, by the polarized surrounding medium. Adopting the simplest possible model for the dynamic polarizability $\alpha(\omega)$ of an isolated atom ($\alpha_0$ being the static atomic polarizability)

$$\alpha(\omega)=\frac{\alpha_0}{1-(\omega/\omega_0)^2} , \tag{1}$$

with a single resonance at the frequency $\omega_0$, such theories can predict a frequency shift due to the solvent effect.[8] We have chosen to make a comparison with a more recent version of the linear response theory developed by Chandler, Schweizer, and Wolynes[9] (CSW) based on a quantum reformulation[10] of the statistical mechanics of molecular liquids, and utilizing the "mean-spherical" scheme of approximation (MSA).[11,12] This theory has the advantage of being essentially free from adjustable parameters.[1,7] As usual in MSA theories, the liquid structure is approximated by assuming hard-core repulsion between the molecules. It predicts, for the pure fluid, an absorption band within a finite range of frequencies ($\omega_- < \omega < \omega_+$, see below), corresponding to the "atomic line" at $\omega_0$.

The boundaries of the absorption band are given by Eq. (8) of CSW:

$$\omega_\pm^2=\omega_0^2[1+\alpha_0 b\pm(8\alpha_0^2 a)^{1/2}] . \tag{2}$$

For the parameters $a$ and $b$ we used the formulas

$$a=\frac{2\pi}{3}\rho\sigma^{-3}I_2(\rho\sigma^3) , \tag{3a}$$

$$\frac{a}{b}=\frac{8}{5}\frac{I_2^2(\rho\sigma^3)}{I_3(\rho\sigma^3)\sigma^3} , \tag{3b}$$

where $\rho$ is the number density, $\sigma$ is the hard-sphere diameter, and the functions $I_2(x)$ and $I_3(x)$ are given in Ref. 13. Equations (3a) and (3b) differ from the corresponding Eqs. (6a) and (6b) of Ref. 9 by the numerical factors: They were obtained by using the Padé approximant [Eq. (5) in Ref. 9]

$$E(\alpha)=a\alpha/(1+b\alpha) , \tag{4}$$

consistent with the expression for the dipolar part $-3(\alpha/\beta)E(\alpha)$ of the internal energy ($\beta=1/k_BT$, $k_B$ being the Boltzmann constant and $T$ the absolute temperature) and on taking the parameter $y$ appearing in Ref. 13 as $y=4\pi\alpha\rho/3$. Only with the numerical factors resulting from this assumption [and appearing in Eqs. (3a) and (3b)] could the shapes of the absorption curves presented in Fig. 1 of Ref. 9 be reproduced.[14]

The most convenient experimental system for comparison is that of fluid xenon; for this substance data are available[2-4] on the evolution of electronic states with density, ranging from that of the dilute gas up to the triple-point liquid; this includes the photoconductivity threshold $E_{\mathrm{PC}}$, and the minimum energy of the conduction electron $V_0$ (the bottom of the conduction band). Moreover, it was shown[5] that the polarization energy $P_+$ of the medium due to the hole created simultaneously with the photoelectron can be satisfactorily estimated by means of the simple formula ("Born charging energy formula"[15]):

$$P_+=\frac{e^2}{2\sigma_0}\left(1-\frac{1}{\epsilon}\right) , \tag{5}$$

$\sigma_0$ being a hard-core diameter and $\epsilon$ the (optical) dielectric constant.

The above quantities are related to each other through the relation[16]

$$E_{\mathrm{PC}} = I + V_0 + P_+ + E' , \tag{6}$$

$I$ being the first-atomic-ionization potential and $E'$ a correction term (not known), due to the fact that the top of the "valence band" in the dense fluid is shifted with respect to the ground state of the atom. Since $V_0$ and $P_+$ are essentially final-state corrections due to the interaction of the free electron or hole with the medium, the CSW theory cannot be expected to account for them properly. In Fig. 1, we compare, as a function of the density, the low-energy threshold of the absorption band developing from the first-ionization limit of the isolated xenon atom (12.127 eV) with $E_{\mathrm{PC}} - P_+$ and with $I + V_0$. It is seen that $I + V_0 > E_{\mathrm{PC}} - P_+$, implying [see Eq. (6)] that $E' < 0$ as expected. Moreover, the theoretical curve is bracketed between the two experimental estimates, and the total variation with density is similar in the three cases (0.5–1 eV). It should be pointed out also that the $E_{\mathrm{PC}}$ values measured at low pressures are limited by an essentially molecular process, with a threshold of 11.10 eV. This process is the creation of a molecular-ion–free-electron charged pair;[17] it is not dealt with in the CSW theory and it prevents the extrapolation of the measured $E_{\mathrm{PC}}$ values at low densities from being equal to the first-atomic-ionization potential, 12.127 eV.

According to the CSW theory, all excitations should shift toward lower frequencies with increasing density in a pure rare-gas fluid. Experimental data on the evolution of pure fluid xenon,[2] krypton,[2] and argon[6] absorption spectra with density show that above a characteristic threshold density, excitonic bands also appear at the wings of the broadened and shifted atomic lines. This feature complicates comparison with theory. Even so, the overall tendency of all bands is a slight red shift at the lowest densities, followed by a blue shift of the order of a few tenths of an eV at the highest ones. Thus the CSW theory implies a shift mostly in a direction opposite to the experimental one in these cases.

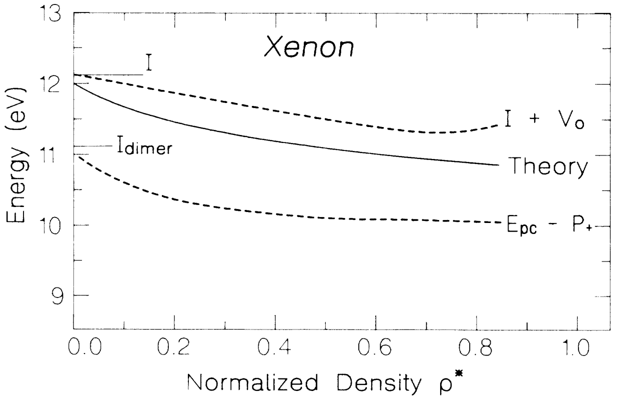

FIG. 1. The absorption-band threshold as calculated from the CSW theory (solid line), compared with experimental data (see text, dashed lines) for fluid xenon as a function of the normalized density $\rho^* = \rho\sigma^3$, with $\sigma = 0.398$ nm.

The CSW theory predicts for an impurity at low concentration in a fluid, with $\omega_{0,I} < \omega_0$, $\omega_{0,I}$ being the impurity atomic absorption line, $\omega_0$ that of the host, an absorption spectrum of the form of a $\delta$ function (it does not take into account the various interactions causing broadening). The position of the $\delta$ function is given by the zero of the equation[9]

$$\omega_{0,I}^2 - \omega^2 - 2\alpha_{0,I} E'(\omega) = 0 . \tag{7}$$

$\alpha_{0,I}$ is the zero-frequency atomic polarizability of the impurity, and $E'(\omega)$ is defined in Ref. 9.

If $\omega_{0,I} < \omega_0$, the solution of Eq. (7) yields a consistent red shift with density. This is illustrated in the lower part of Fig. 2 for the first resonance line of xenon (at 8.437 eV) calculated with $\alpha_{0,I} = 0.0016\ \mathrm{nm}^3$ and $\omega_0 = 15.56$ eV. It is seen in the figure that again the experimentally measured[1] shift of the absorption peak for xenon in argon is mainly toward the blue, though at small densities a slight red shift is discernible.

The upper part of Fig. 2 deals with the shift of the ionization energy of xenon (at 12.127 eV) with argon density. The theoretical curve has been calculated as indicated above. The relevant experimental data are those on impurity photoconductivity thresholds $E^i_{\mathrm{PC}}$ provided a correction is made for the polarization energy $P^i_+$ of the hole attached to the impurity. However,[16]

$$E^i_{\mathrm{PC}} - P^i_+ = I^i + V_0 , \tag{8}$$

$I^i$ being the ionization potential of the (free) impurity atom and $V_0$ the minimum energy of a conduction electron. In fact, the experimental curve in the upper part of Fig. 2 represents $I^i + V_0$ based on the experimentally determined $V_0$ values for fluid argon. It is seen that there is a rough correspondence between theory and experiment, though the theory does not reproduce the minimum of the $I^i + V_0$ curve; this minimum is known to be due to competition between long-distance attractive and short-distance repulsive interactions between the free electrons

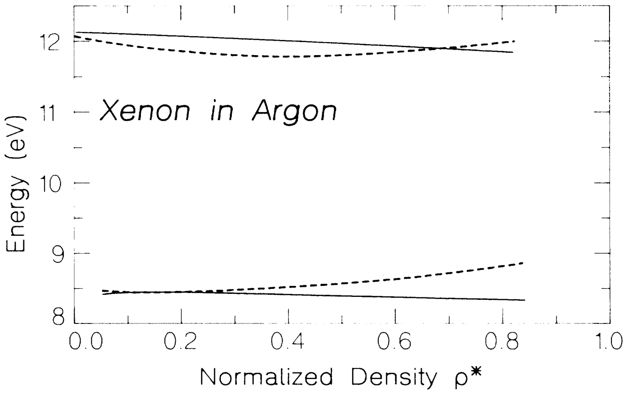

FIG. 2. Impurity-absorption-band positions as calculated from the CSW, theory (solid lines) for low concentrations of xenon in fluid argon, as a function of the normalized argon density $\rho^* = \rho\sigma^3$, with $\sigma = 0.34$ nm. Experimental curves (dashed): upper part, $I^i + V_0$ from Ref. 4; lower part, impurity-absorption-band peak, Ref. 1.

and the host atoms.[18,19]

The above comparisons can be extended to include numerous other pure- or doped-rare-gas absorption levels:[1-7,9] In all cases the magnitude of the density-induced shift is similar in theory and experiment, but for discrete levels the theory predicts a consistent red shift with density both in pure and doped materials (provided the dopant excitation energy is smaller than that of the host), while blue shifts are dominant in such systems. For levels corresponding to the first atomic ionization potential (and involving intrinsic or extrinsic photoconductivity), however, the theory is in rough agreement with experiment. This marked difference in the applicability of the theory in its basic form[9] can be traced to the different excited states involved. Both for impurity excitations and for the excitons in pure fluids considered above (having many traits of a Frenkel exciton[2]), the excited wave function is roughly confined to one atom. Thus such systems should be very sensitive to the local liquid structure and the detailed interactions[1,7] with the neighboring atoms due to the effects of orbital overlap, etc. On the other hand, the CWS theory is in rough agreement with experiment when the excitation leads to photoconduction, i.e., an essentially free electron in the final state. Thus it seems that the MSA model as presented in Ref. 9 and variants thereof[20-22] are reasonably successful in reproducing the dielectric response in cases when the excited-state wave function extends over spatial regions sufficiently large so that the microscopic details of the liquid structure and correlation effects become relatively unimportant. To deal with the blue shifts when excitation is confined, extensions of the theory[19-21] should be considered. These require a more realistic account of nearest-neighbor correlations and of the repulsive interactions going beyond the MSA. Replacement of the hard core by a soft repulsion would be in conformity with suggested[21] effects of interatomic exchange forces on the electronic properties of the system.

Finally, a further interesting prediction of the CSW theory on a doped simple fluid should be mentioned. When the impurity absorption band is very near to that of the host, this "resonance" should be manifested by dramatically varying absorption profiles (Fig. 2 in Ref. 9). An experimental test of these predictions seems to be rather difficult because of the much stronger absorption of the host as compared to that of a dilute solute. A combination of near-normal incidence and oblique incidence reflectivity spectra, using polarized light excitation, might furnish the necessary experimental data.[23]

One of us (I.T.S.) acknowledges the partial support of this research by Grant No. 85-0080 from the U.S.-Israel Binational Science Foundation, Jerusalem, Israel.

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