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Localized Excitations in Condensed Ne, Ar, Kr, and Xe

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Experiments are reported which lead to the conclusion that electronic excitation energy in solid and liquid Ne, Ar, Kr, and Xe can be trapped by the formation of excimers. The consistency of this conclusion with other electronic properties of these substances is briefly discussed.

I. INTRODUCTION

DESPITE extensive study of the optical properties of ionic and molecular crystals,[1] very little is known of the properties and behavior of localized excitations. It is well known that impurities (guests) in a crystalline medium (host) may trap excitation energy if the lowest excited state of the guest is at lower energy than the lowest excited state of the host, and this phenomenon has been studied in a number of systems.[2] Herein we wish to direct attention to the study of the trapping of excitation energy by nonadiabatic processes, i.e., by configurational changes in the medium. In a low order of approximation, such trapping might be expected to occur whenever the lifetime of the excited state of a molecule or atom is longer than the time required for configurational changes and when the new configuration of the medium represents a state of lower energy.

Recent studies by Vala and Rice[3] have shown that excitation energy is trapped in the polymers polystyrene and polyvinylnaphthalene. In these cases, the lifetimes of the excited states of the molecules are long compared to the rotational relaxation time of a side group ($\sim 10^{-10}$ sec) and there exist stable excimers of the aromatic hydrocarbons. Indeed, it is found that the emission spectra from these polymers are red shifted 6000 cm^{-1} from the normal fluorescence spectra, the same shift as is observed when excimers of benzene or naphthalene are formed in solution.[4]

It is obviously desirable to examine the trapping of excitation energy in the simplest systems for which suitable observations can be made. As part of a program to study the electronic properties of simple liquids and solids, we have investigated the emission spectra of liquid and solid Ne, Ar, Kr, and Xe. These substances were chosen for study because the gas-phase emission spectra are attributed to the excited diatomic molecules[5] (excimers) Ne_2^*, Ar_2^*, Kr_2^*, and Xe_2^*, thereby suggesting that trapping of the excitation by molecule formation should occur in a condensed phase. This deduction, which follows from the conditions cited above (that the lifetime of an excited atom is long compared to the time required for small atomic displacements in a liquid or solid and that stable new configurations exist), is indeed supported by the experiments reported herein.

II. EXPERIMENTAL DETAILS

Light emitted from condensed Ne, $\cdots$, Xe bombarded with α particles was observed with a 0.5-m McPherson Seya–Namioka vacuum spectrometer. The light detectors were EMI 9514B photomultiplier tubes coated with sodium salicylate. The spectrometer was sensitive in the region 1100 Å (the LiF cutoff) to 6000 Å, while the monitor detector was sensitive to much shorter wavelengths. A lithium fluoride window separated the cryostat from the spectrometer. Slitwidths between 0.2 and 2.0 mm were used. Lithium fluoride, quartz, and Pyrex filters between the system and the monitor detector allowed a rough estimate to be made of the intensity of the light in different spectral regions.

The cryostat is shown schematically in Fig. 1. Radiation shields are not shown. All cold parts were wrapped with superinsulation ($\frac{1}{2}$-mil Al-coated Mylar). The source (approximately 5-mCi ^{210}Po) is mounted at the bottom of a vacuum-tight container which can be cooled externally at the lower end from a Dewar containing the refrigerant. The refrigerants used to condense sample around the source were, respectively, hydrogen for neon, oxygen for argon, Freon 14 for krypton and Freon 13 for xenon. The temperatures were adjusted by controlling the pressure of the refrigerant in the reservoir. The temperature difference between the condensate around the source and the refrigerant in the reservoir was a fraction of a degree, as determined by vapor-pressure measurements.

The gases used were obtained from the Air Reduction Company. The content of impurities, such as nitrogen, hydrogen, or the other rare gases, was less than 0.01%. The several gases were condensed in purged $\frac{1}{2}$-liter stainless-steel containers in amounts which yielded about 1500-lb/in.^{2} pressure at room temperature. The cryostat was filled from these bombs, and, after an

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[1] See, for example, R. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1964).

[2] See, for example, G. C. Nieman and G. W. Robinson, J. Chem. Phys. **39**, 1298 (1963).

[3] M. T. Vala and S. A. Rice, J. Chem Phys. (to be published).

[4] J. B. Birks, Proc. Roy. Soc. (London) **A277**, 571 (1964); **A280**, 289 (1964); R. Williams, J. Chem Phys. **28**, 577 (1958).

[5] Y. Tanaka, J. Opt. Soc. Am. **45**, 710 (1955).

experiment, the gases were recondensed back in the containers, thereby avoiding all possible contamination.

III. RESULTS AND DISCUSSION

The following observations were recorded:

(1) The emission spectra of all the liquids and solids consist of broad structureless bands, considerably displaced towards lower energy from the corresponding atomic absorption lines. A summary of the relevant data is displayed in Table I, and sample spectra are exhibited in Fig. 2.

(2) The band shapes are independent of slitwidth (over the range 0.20 to 2.0 mm), thereby indicating that the observations are not instrumentally distorted.[6]

(3) The efficiency of energy conversion is very high. Crude calculations indicate that (for Kr and Xe) between 10% and 100% of the energy of the α particles is accounted for by the intensity of the emission spectrum. This calculation, when taken together with the reproducibility of the measurements on cycling between the gaseous, liquid, and solid phases or on refilling, supports the deduction that the emission spectra arise from intrinsic structures and not from impurities. Indeed, impurities seem to quench, rather than to enhance, the emission. For example, solid xenon was cooled to 78°K and the pressure over the solid found to be higher than the known vapor pressure of xenon at 78°K. Since only 100 ppm of nitrogen or hydrogen would be needed to produce the observed pressure, we pumped on the solid for about 10 min, thereby reducing the pressure to the known vapor pressure of xenon. As a result, the intensity of the emission in the 1750-Å range was enchanced by a factor of 4. Mass-spectroscopic analysis of the pumped xenon showed, indeed, that the nitrogen content has been reduced to less than 10 ppm. Presumably, our solid was in small enough grains that diffusion of the N_2 to surfaces permitted this purification to occur.

(4) The emission spectrum of liquid Ar is quenched by the addition of O_2 or N_2 (1300-Å band).

Consider first the identification of the trapping mechanism. As can be seen from the entries in Table I and from Fig. 2, the emission spectra of the gaseous and condensed phases of Ne, ···, Xe are similar. We therefore interpret the observed emission spectra as arising from the transition between a bound excited state of a diatomic molecule and a repulsive (unbound) ground state. This interpretation agrees with the coincidences between the high-energy bands in our spectra and those found by Tanaka.[5] Other transitions, between bound excited states of the excimer, are probably responsible for the lower-energy emission bands (i.e., the continuum in gaseous Ar and the 2000-Å band in liquid and solid Ar).

The reader should note the striking environmental effects evident in the Xe spectrum. On passing from the gas phase to the solid phase, the emission spectrum is blue shifted; but on passing from the gas phase to the liquid phase, the emission spectrum is red shifted. These observations illustrate the delicate balance between competing changes in energy.[7] In both cases, the net shift observed arises from the sum of the changes in van der Waals energy, Coulomb and exchange energies, etc., all conditioned by the effects of extensive overlap of the surrounding medium by the wavefunction of the excimer. The fact that the liquid is red shifted relative to the solid is consistent with the greater ease of atomic displacement in a liquid than in a solid. Similar trends are evident, but less marked, in the spectra of other systems (see Table I).

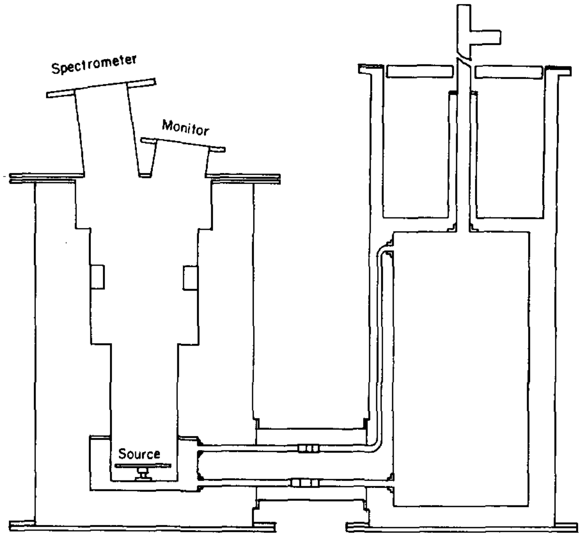

FIG. 1. Schematic drawing of the cryostat. The right-hand side of the cryostat is a refrigerant reservoir.

From the data presented in Table I, it is possible to make a very crude estimate of the binding energy of the excimer as $D \approx E_{\text{atomic excitation}} - E_{\text{emission}}$. This estimate is inaccurate because of the neglect of the (unknown) repulsive energy of the ground-state configuration. It is found that

$$D_{\text{Ne}_2^*} \sim 6 \text{ eV},$$

$$D_{\text{Ar}_2^*} \sim 2.2 \text{ eV},$$

$$D_{\text{Kr}_2^*} \sim 1.9 \text{ eV},$$

$$D_{\text{Xe}_2^*} \sim 1.9 \text{ eV},$$

to be compared with $D_{\text{He}_2^*} \sim 5.9$ eV from Tanaka's data.[5] In making the preceding calculation, we have used the average of the singlet and triplet energies, an adequate approximation for the present purposes.

The reader will note that the emission spectrum of liquid Kr differs markedly from that of the solid. At

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[6] J. R. Kane, R. T. Siegel, and A. Suzuki, Phys. Letters **6**, 256 (1963).

[7] A. Gold, J. Phys. Chem. Solids **18**, 218 (1961); Phys. Rev. **124**, 1740 (1961); H. Y. Sun, S. A. Rice, and J. Jortner, J. Chem. Phys. **41**, 3779 (1964).

TABLE I. Emission spectra of rare gases under α-particle excitation.

	α-particle excitation[a]			Electric discharge in gas (Tanaka)[c]	Atomic lines (gas)	Atomic lines (solid)[d]
	Gas[b]	Liquid	Solid			
Ne	vw	...	$\nu = 80\ 970\ \mathrm{cm}^{-1}$ $\Delta\nu = 4500\ \mathrm{cm}^{-1}$ $T = 20°\mathrm{K}$	...	$135\ 500\ \mathrm{cm}^{-1}$ $136\ 320\ \mathrm{cm}^{-1}$	...
Ar	$\nu = 76\ 920\ \mathrm{cm}^{-1}$ (vw) continuum $62\ 500\text{–}40\ 000\ \mathrm{cm}^{-1}$ $T = 300°\mathrm{K}$	$\nu = 77\ 220\ \mathrm{cm}^{-1}$ $\Delta\nu = 6000\ \mathrm{cm}^{-1}$ $\nu = 49\ 380\ \mathrm{cm}^{-1}$ $\Delta\nu = 5000\ \mathrm{cm}^{-1}$ $T = 85°\mathrm{K}$	$\nu = 79\ 370\ \mathrm{cm}^{-1}$ $\Delta\nu = 5000\ \mathrm{cm}^{-1}$ $\nu = 50\ 000\ \mathrm{cm}^{-1}$ $\Delta\nu = 5000\ \mathrm{cm}^{-1}$ $T = 77°\mathrm{K}$	$80\ 000\ \mathrm{cm}^{-1}$ (Second continuum maximum)	$93\ 730\ \mathrm{cm}^{-1}$ $95\ 420\ \mathrm{cm}^{-1}$	$96\ 790\ \mathrm{cm}^{-1}$ $99\ 200\ \mathrm{cm}^{-1}$
Kr	$\nu = 67\ 570\ \mathrm{cm}^{-1}$ $\Delta\nu = 6000\ \mathrm{cm}^{-1}$ $T = 300°\mathrm{K}$	$\nu = 56\ 500\ \mathrm{cm}^{-1}$ Shoulder at $60\ 600\ \mathrm{cm}^{-1}$ $T = 120°\mathrm{K}$ $\Delta\nu = 4000\ \mathrm{cm}^{-1}$	$\nu = 66\ 450\ \mathrm{cm}^{-1}$ $\Delta\nu = 5300\ \mathrm{cm}^{-1}$ Shoulder at $59\ 520\ \mathrm{cm}^{-1}$	$66\ 670\ \mathrm{cm}^{-1}$ (Second continuum maximum)	$80\ 900\ \mathrm{cm}^{-1}$ $84\ 930\ \mathrm{cm}^{-1}$	$81\ 870\ \mathrm{cm}^{-1}$ $87\ 100\ \mathrm{cm}^{-1}$
		Solid and liquid present	$\left\{\begin{array}{l}\nu = 66\ 230\ \mathrm{cm}^{-1}\\ \nu = 59\ 170\ \mathrm{cm}^{-1}\\ T = 77°\mathrm{K}\end{array}\right.$			
Xe	$\nu = 57\ 300\ \mathrm{cm}^{-1}$ $\Delta\nu = 4900\ \mathrm{cm}^{-1}$ $T = 300°\mathrm{K}$	$\nu = 56\ 180\ \mathrm{cm}^{-1}$ $\Delta\nu = 4500\ \mathrm{cm}^{-1}$ $T = 160°\mathrm{K}$	$\nu = 58\ 140\ \mathrm{cm}^{-1}$ $\Delta\nu = 4900\ \mathrm{cm}^{-1}$ $T = 140°\mathrm{K}$ $\nu = 59\ 000\ \mathrm{cm}^{-1}$ $\Delta\nu = 4900\ \mathrm{cm}^{-1}$ $T = 77°\mathrm{K}$	$57\ 140\ \mathrm{cm}^{-1}$ (Second continuum maximum)	$68\ 000\ \mathrm{cm}^{-1}$ $77\ 190\ \mathrm{cm}^{-1}$	$68\ 800\ \mathrm{cm}^{-1}$ $77\ 590\ \mathrm{cm}^{-1}$

[a] ν is the band maximum ($\pm 200\ \mathrm{cm}^{-1}$); $\Delta\nu$ is the half-height bandwidth ($\pm 500\text{-}\mathrm{cm}^{-1}$ error); vw indicates a very weak band, so close in intensity to noise level that caution must be used; w indicates a weak band. If not otherwise marked, bands are *moderately intense*.

[b] Observed in the same apparatus, $p \approx 1$ atm.

[c] Reference 2.

[d] Reference 4.

the present time, we do not understand the origin of this difference. Further experiments, including direct optical excitation of the fluorescence spectra of condensed Ne, Ar, Kr, and Xe, are now in progress. It should be noted that we believe it unlikely that the binding energy of the diatomic species exceeds 1–2 eV. We therefore interpret the values of $D_{\mathrm{Ne}_2}{}^*$ and $D_{\mathrm{He}_2}{}^*$ as evidence of large ($\sim$4 eV) ground-state repulsions.

We now turn to an examination of the theoretical implications of the results reported herein. First, we note that any argument based on the rigid-lattice approximation will be invalid. Thus, although the lifetime on any one site of a localized exciton in a rigid lattice of solid Ar is predicted to be shorter than a vibrational period,[8] that calculation is not appropriate because of the neglect of configurational changes which lead to a *qualitative* alteration of the predictions. A similar situation exists in the theory of trapped holes in alkali halide crystals, where trapping is impossible in the rigid lattice but occurs when ionic polarizability and lattice deformation are included in the description.[9] As is well known, self-trapped holes in KCl and other alkali halides have been observed by Castner and Kanzig.[10a] Excimers are also observed in the alkali halides.[10b]

Recent calculations indicate that the solids Ne, ···, Xe have conduction bands that are almost perfectly free electron in character.[11] It is a direct consequence of this conduction-band structure that a Wannier function defining a localized excitation will be confined to one atomic cell. It is then apparent that:

(a) The lowest excitation of the solid should be only slightly shifted from the free-atom excitation.

(b) If there exists an easily reached geometric configuration which has a lower energy than the energy corresponding to the localized excitation, then that configuration will be stable.

The first deduction (a) has been demonstrated to be correct by Baldini[12] and is in agreement with the calculations of Webber, Rice, and Jortner.[13] Now, if a Wannier function is so compact as to be confined to an atomic cell, as is the case in these solids, then it is very much like an atomic function. Therefore, the construction of a molecular orbital for a bound state of the excimer represents a large charge delocalization, and hence a likely lowering of the energy. Since the lifetime of the atomic state is long compared with a vibrational period, such excimer formation should be favored, as indeed we have observed.

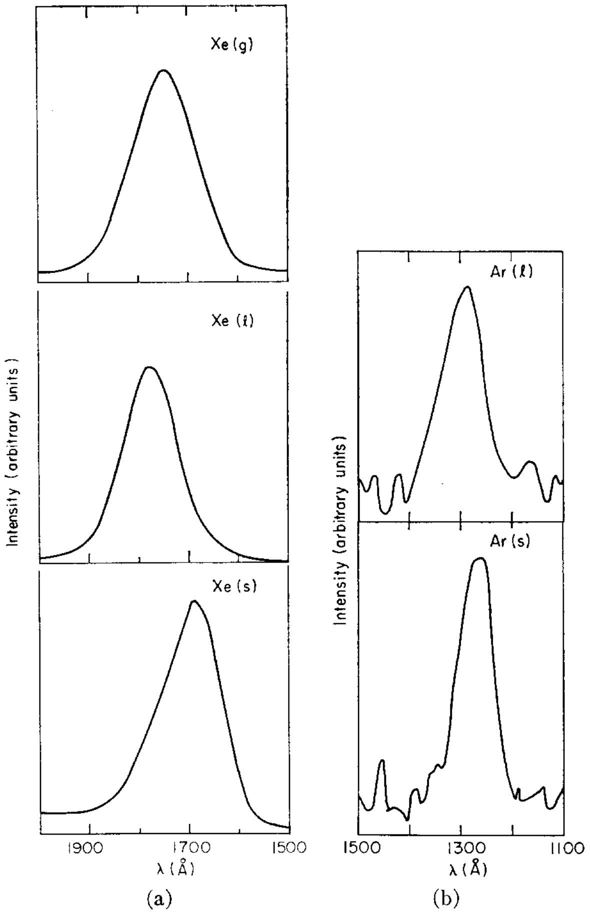

FIG. 2. Emission spectra of α-particle excited (a) Ar and (b) Xe in several states of aggregation.

An analysis of the formation of excimers in the liquid would proceed along similar lines. Here we merely note that the postulation of excimers in liquid Xe, ···, Ne is in complete agreement with the existence of the ions Xe_2^+, ···, which ions provide a quantitative description of positive ion motion in these liquids.[14]

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[8] A. Gold and R. S. Knox, J. Chem Phys. **36**, 2805 (1962).

[9] S. J. Nettel, Phys. Rev. **121**, 425 (1961).

[10] (a) T. G. Castner and W. Kanzig, J. Phys. Chem. Solids **3**, 178 (1957); C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958); (b) See, for example, M. N. Kabler, *ibid.* **136**, A1296 (1964), and references cited therein.

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[14] H. T. Davis, S. A. Rice, and L. Meyer, J. Chem. Phys. **37**, 947 (1962).