TABLE I. Spin–lattice relaxation times of solid deuterium above and below T_λ.

Above T_λ

% para-D_2	T (°K)	t_1 (sec)	t_1^{rot} (sec)	T_λ (°K)[a]
93	4.2	1.92	1.62	3.4
87	4.2	2.15	1.56	3.2

Below T_λ

% para-D_2	T (°K)	t_1 (sec)	t_1' (sec)	$f_{(\text{obs})}$	$f_{(\text{calc})}$
93	2.0	195±10	45±5	0.80±0.08	0.84
87	1.5	130±10	35±5	0.66±0.1	0.73

[a] The T_λ's were taken from the heat-capacity measurement of G. Grenier and D. White, J. Chem. Phys. **40,** 3015 (1964). The Pake splitting, on first cooling, occurs 0.1°–0.15° below the above T_λ's.

radio-frequency power was sufficient to cover the entire spin system with the 90° pulse.

Above the transition temperature T_λ, the difference between the signal amplitude after complete relaxation, $S(\infty)$, and the signal amplitude $S(\tau)$ is proportional to $\exp(-\tau/t_1)$. A single relaxation process is observed for both spin systems ($I=2$, $J=0$; $I=1$, $J=1$) presumably because of a very fast (compared to spin–lattice) adiabatic cross relaxation between $I=2$ and $I=1$. For this mechanism the spin–lattice relaxation for the rotating molecules, $I=1$, $J=1$, is given by[4]

$$t_1^{\text{rot}}=(2x/5-3x)t_1, \tag{1}$$

where x is the mole fraction of paradeuterium.

Below T_λ, the change in signal amplitude is described by

$$[S(\infty)-S(\tau)]/S(\infty)=f\exp(-\tau/t_1)+(1-f)\exp(-\tau/t_1'). \tag{2}$$

The pre-exponentials f, $(1-f)$, are the fraction of the total signal from the $I=1$, $J=1$ (para-D_2) and $I=2$, $J=0$ (ortho-D_2) spin systems, respectively, with corresponding spin–lattice relaxation times t_1, t_1'. The experimental results above and below T_λ are summarized in Table I below.

The present results confirm the large energy gap between the ground and excited states in the rotational excitation (libron) spectrum of the ordered state (arising from the intermolecular quadrupolar interactions) given by Homma, Okada, and Matsuda[5] as well as the long spin–lattice relaxation time predicted by Homma[6] on the basis of a relaxation mechanism caused by inelastic scattering of the rotation waves by the nuclear moments (Raman process). In the case of pure orthohydrogen ($J=1$), Homma's calculations predict a spin–lattice relaxation time of 10 to 100 sec in the ordered state near T_λ. This is 2 orders of magnitude larger than what has been observed in the rotationally disordered phase above T_λ.[7]

For the relaxation mechanism proposed by Homma,[5] an even longer spin–lattice relaxation time should be observed in pure para-D_2 ($J=1$). This is indeed borne out by the present experiments and is in part the result of a larger energy gap in the rotational excitation spectrum of deuterium due to a shorter nearest-neighbor distance in the solid.[8]

The present data show a decrease in t_1 with increasing ortho ($J=0$) concentration. This can be attributed to a decrease in the energy gap of the rotational excitation spectrum combined with a shift in the density of states[4] toward lower frequencies due to the ortho impurity.

A mechanism for the relaxation of the $I=2$ ($J=0$) spin system below T_λ has not been proposed. The present results strongly suggest that neither intramolecular dipole–dipole interactions modulated by the lattice nor cross relaxation with the $I=1$ spin system is a dominant factor. A possible explanation may be in an intramolecular dipole–dipole interaction modulated by an angular dependent intermolecular multipole–multipole interaction involving ortho–para nearest neighbors. In this model J is no longer a valid quantum number and both ortho and para species become oriented in the lattice under the influence of the crystal field.

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* This work is supported by the Chemistry Branch, Division of Research, U.S. Atomic Energy Commission.

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Trapped Exciton States in Liquid Argon

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(Received 27 May 1968)

Experimental studies of the electronic states of solid rare gases[1–5] led to the identification of Wannier exciton states in these systems. In connection with studies of the electronic structure of disordered systems, we enquire whether there exist exciton states in liquids. The present note reports experimental evidence for Wanniertype xenon impurity states in liquid argon. Studies of the structure and the scattering process of Wannier exciton states in a simple liquid[6] demonstrated that Coulomb electron-hole correlation leads to a hydrogenic manifold of levels, provided that the conduction band states can be described as quasifree particles. The linewidth $\Delta\nu$ of exciton states in a liquid[6] was accounted for in terms of electron scattering by fluid. The exciton can be related to the relaxation time $\tau(\mathbf{k})$ by $\Delta\nu = \Pi\tau(k)^{-1}$ and $\tau(k)^{-1} = \rho\hbar\tilde{a}^2k(m_e^*)^{-1}S(k)$, where ρ is the number density of the liquid, $\tilde{a}$ is the scattering length in the liquid,[7] m_e^* the effective mass, $\mathbf{k}$ the electron wave vector, and $S(k)$ the structure factor, which can be approximated by the long wavelength limit. The theory of Lekner and Cohen[7,8] for the low field electron mobility, μ, leads to[9] $\Delta\nu \propto e\hbar k m_e^{*-3/2}T^{-1/2}\mu^{-1}$. Liquid argon appears as a suitable system in view of the relatively low value ($\tilde{a} = +1.5$ a.u.) of the scattering length in the liquid.[7] Mobility data[10,11] indicate that (a) the excess electron in liquid argon behaves to a reasonable approximation as a quasifree particle and (b) the exciton linewidth in liquid argon will not be excessively broad to prohibit experimental observation.[12]

The absorption spectrum of liquid argon doped with xenon was measured at 85°K using a McPherson 0.3-m Czerny–Turner vacuum spectrograph. A Tanaka-type Krypton lamp (spectral range 1600–1300 Å) was used as a light source. A 1-cm optical cell sealed with 1-mm thick LiF windows was attached to a Dewar. The gases (Matheson Research Grade) were then liquified in the cell at a pressure of 550–600 torr.[13] The absorption spectrum of pure liquid argon was measured at the beginning of each experiment and used as a reference.[14] A 0.1% Xe/Ar gas mixture was liquified at 85°K.[15]

Figure 1 presents the optical spectrum of xenon-doped liquid argon. The absorption band at 1430 Å is identified as corresponding to the ${}^1S \rightarrow {}^3P_1$ transition. This band reveals an appreciable asymmetry on the high-energy side. The gross features of this effect are attributed to a spectral blue shift and possibly a (small) level splitting[16] of the ${}^3P$ state induced by short-range interactions with the fluid. An additional band at 1370 Å is observed which cannot be attributed to a perturbed atomic state[16,17] and is assigned to the $n=2$ Wannier state in the liquid. The following comments are in order:

(a) The exciton linewidth can be estimated from the electron mobility data in solid and liquid argon leading to $\Delta\nu$ liquid/$\Delta\nu$ solid$\simeq\mu$ solid/μ liquid$=2.2$ [10,11] so that $\Delta\nu$ liquid$\simeq 0.5$ eV,[9] in agreement with the optical data.

(b) Locating the $n=2$ trapped Wannier exciton level at 9.1 eV and employing the effective mass $m_e^* = 0.46m_e$ calculated by Lekner[7] for liquid argon and $\epsilon = 1.46$ for the dielectric constant, we can estimate the impurity gap[18] $E_G^L = 9.7 \pm 0.1$ eV in the liquid. This band gap is lower than the impurity gap in the solid $E_G^L = 10.3$ eV.

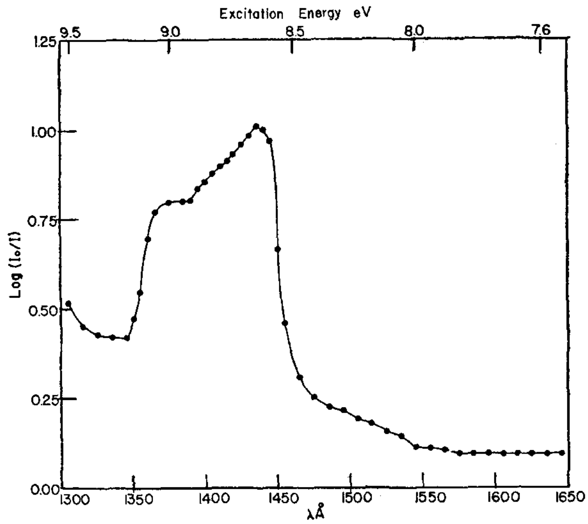

FIG. 1. The absorption spectrum of xenon-doped liquid argon.

(c) The onset for photoconductivity in Xe-doped liquid argon should be at 9.7 eV, while the onset for photoelectron emission should be located at $I = 9.7 - V_0$ where V_0 is the adiabatic barrier for electron injection into the liquid. Taking $V_0 = -0.5$ eV,[7] one gets $I = 10.2$ eV.

(d) The blue shift of the Xe ${}^3P_1$ state in liquid argon is comparable to the shift in Xe/Ar gas mixtures at 500 atm,[19] i.e., at about the same fluid density. Asymmetric broadening effects and the appearance of Wannier excitons are expected to occur. Our arguments concerning the electronic states of disordered systems are general, thus exciton states should be also observed in dense gaseous mixtures of rare gases.[20]

We are grateful to Mr. Uzi Even for his helpful advice and to Mr. Jacob Magen for his expert technical assistance. We wish to thank Professor S. A. Rice for helpful discussions and Professor O. Schnepp for penetrating comments.

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[13] To eliminate optical absorption due to O_2 impurity, all gas handlings were performed in a system evacuated prior to the experiment to pressures lower than 10^{-6} torr. The absorption spectrum of oxygen in liquid argon reveals a broad continuous absorption in the region 1600–1300 Å with a maximum at about 1520 Å and is appreciably red shifted in liquid argon relative to the gas phase.

[14] The absorption of pure liquid argon did not exceed O.D.= 0.1, serving as an adequate purity check.

[15] The gas composition was Xe/Ar$\simeq$0.001. The concentration of Xe in the solution is unknown because of the solidification of the xenon gas on the transfer tube and on the metal parts of the cell.

[16] Gaseous Xe/Ar mixtures reveal two blue satellites separated by 100–200 cm^{-1} from the main line [R. Granier, M. C. Castex, J. Granier, and J. Romand, Comp. Rend. **264**, 778 (1967)]. This result indicates that level splitting in a Xe/Ar contact pair is small.

[17] For the location of the $^3P_2$ and $^1P_0$ forbidden levels of Xe, see Ref. 1. The broad low-energy tail at 1500 Å cannot be assigned to xenon aggregates, as it increases linearly by a twofold increase in the xenon density. It can be due to the $^3P_2$ state. The non-negligible absorption in this range may arise from xenon absorbed on the LiF window which at 85°–120°K is characterized by a band at 1510 Å.

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Notes

Combination of External with Internal Vibrations in Molecular Crystals*, †

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General symmetry selection rules for the vibrational spectra of crystals have been derived by Winston and Halford.[1] Although only $\mathbf{k}\simeq 0$ vibrations may be optically active as fundamentals, essentially all crystal vibrations may be involved in combination transitions, which will have both infrared and Raman activity. More recently, Mitra[2] has pointed out quite explicitly that the only general selection rules for combinations in crystals are conservation of energy and of wave vector and that, although there is a continuum of lattice frequencies, maxima may be observed in the combination spectra due to singularities in the phonon frequency distribution.

In the case of ionic crystals, the need to consider $\mathbf{k}\neq 0$ modes in explaining experimental combination spectra has long been realized.[3] However, for molecular crystals the common practice[4–8] is to assign combinations of molecular vibrations with lattice modes as resulting from $\mathbf{k}\simeq 0$ motions; this procedure is often used to arithmetically deduce the frequencies of the optically active lattice vibrations from the combination spectra. The rationale is that no definite violation of the factor-group selection rules ($\mathbf{k}\simeq 0$) has been observed for such crystals. For example, it has recently been stated, "Although arguments have been proposed to the effect that factor-group selection rules are not rigorously obeyed by combination transitions, it is generally accepted that they may serve as a guide to their classification."[6] However, the fact that a correlation might be obtained between lattice frequencies observed in combination and those observed directly as fundamentals does not necessarily mean that $\mathbf{k}\simeq 0$ selection rules are being obeyed. The purpose of this note is to present clear violations of the factor-group selection rules for the internal plus external combination spectra of representative, simple molecular crystals.

Infrared spectra of thick films of CO_2 and N_2O in the bending region have been obtained by Dows,[5] and for CO_2 in all regions by Jacox and Milligan.[9] Since our recent measurement[10] of the librational frequencies of CO_2 and N_2O showed Dows' analysis of the combination spectra[5] to be incorrect, we decided to study the infrared spectra of thick films of these molecules further. Our CO_2 spectra are quite similar to those of Dows[5] and Jacox and Milligan.[9] No combinations are observed with the inactive symmetric stretch; the pattern of the combinations on each of the other two fundamentals is almost identical. This pattern is also observed in the N_2O combination bands, although the maxima are not as sharp. The analogy is not surprising in light of the similar molecular properties and crystal structures of these isoelectronic molecules. CO_2 crystallizes in a T_h^6 space group with four molecules per unit cell on S_6 sites.[11] From a microscopic point of view, the N_2O crystal has no strict symmetry since the sense of the molecules is random[12,13] (as would be the case for CO_2 if one oxygen were isotopically substituted). However, the average structure, as determined by x-ray diffraction, is the same as CO_2.[11] The strong similarity of the Raman lattice spectra[10] and infrared combination spectra indicate that the lattice vibrations of CO_2 and N_2O are closely related and that it is a reasonable

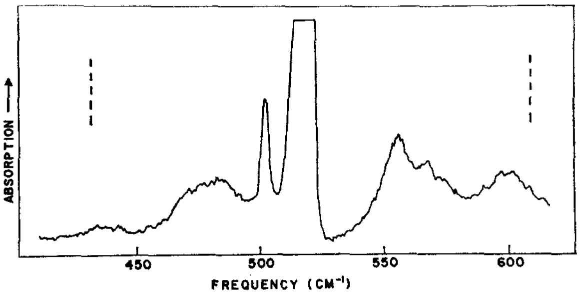

FIG. 1. ir spectrum of a thick film of OCS. Dotted vertical lines show positions of factor-group-predicted combination bands.