Emission spectra of homonuclear diatomic rare gas molecules in solid neon

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We report the vacuum ultraviolet $^{1,3}\Sigma_u - {}^1\Sigma_g$ emission of vibrationally relaxed $Ar_2{}^*$, $Kr_2{}^*$, and $Xe_2{}^*$ in solid neon at 6°K. The inhibition of the formation of $Ne_2{}^*$ in solid Ne is attributed to the retardation of vibrational relaxation for this diatomic molecule, which is characterized by a relatively high vibrational frequency.

It is well established that fluorescence from deep exciton states in most pure liquid and solid rare gases is not amenable to experimental observation because of efficient exciton trapping processes.[1,2] The optical emission spectra of solid and liquid Ar, Kr, and Xe result from the formation of electronically excited homonuclear diatomic rare gas molecules, which decay radiatively to the repulsive ground state.[1-6] These emission spectra from the pure condensed phases practically coincide with the second continuum of the rare gas diatomic molecules (observed at moderate ~100 torr pressures) in the gas phase. These continua are ascribed to transitions from the vibrationally relaxed $^1\Sigma_u$ and $^3\Sigma_u$ states[3] (originating from the $^3P_1 + {}^1S_0$ and $^3P_2 + {}^1S_0$ configurations, respectively) to the ground state, i.e., $Y_2^*(^{1,3}\Sigma_u) \rightarrow 2Y(^1S_0)$. The negligibly small medium spectral shift on these transitions from a Rydberg type excited state[3] was attributed to medium relaxation resulting in the formation of a microscopic cavity around the excited diatomic molecule.[4]

Solid neon is unique in this respect, as its emission spectrum is characterized by a relatively sharp emission band peaking at 743 ± 1 Å which was attributed by Packard, Reif, and Surko[5] to the emission from the lowest exciton state which can be described in terms of the $n=1$ Wannier states (or alternatively from the $^3P_1$ and $^1P_1$ Frenkel type states). In order to elucidate the nature of the inhibition of the formation of $Ne_2^*(^{1,3}\Sigma_u)$ in solid Ne, it is interesting to enquire whether other rare gas diatomics are formed in this matrix. Recent studies have demonstrated that in solid Xe/Ar and Xe/Kr alloys the Xe_2^* emission is exhibited at Xe concentration exceeding 0.1%, originating from efficient energy transfer to impurity pairs.[4,6] In the present work we have studied the emission spectra of impurity pairs of Ar, Kr, and Xe in solid Ne in order to clarify the nature of the formation of excited diatomic rare gas molecules in this matrix.

The emission spectra of solid neon and of Ar, Kr, and Xe impurities in solid neon excited by α particles were monitored by a 1-meter normal incidence vacuum spectrograph (McPherson 225).

The spectral region 600–2000 Å was scanned using a gold coated grating (600 lines per nm) blazed at 800 Å. The light was detected by a convertor consisting of a Pyrex plate coated with sodium salicylate which was mounted in front of an EMI 9514S photomultiplier cooled to 220 °K. Slit widths were 2 mm resulting in a spectral resolution of 18 Å.

A 0.5 mC americium α source was mounted on a helium flow cryostat. The gaseous mixtures (Matheson research grade) containing 1% of the impurity were injected throughout an injection nozzle on the source at 6 °K. The pressure in the spectrograph sample chamber prior to injection was 2×10^{-7} torr. The thickness of the deposited films was $0.1–1\mu$. The emission spectra were measured at 6 °K.

The absorption spectrum of solid Ne was measured by depositing a 1000 Å thick film at 6 °K on a sapphire window which was coated with a converter (sodium salicylate or liumogen) and using a windowless He discharge operated at 35 torr.

In Fig. 1 we display the absorption and the emission spectra of solid Ne. The absorption data confirm results of Haensel[7] and Boursey et al.[8] The emission spectrum exhibits a well-defined band at 742 Å (16.70 eV) and a broad shoulder peaked at 770 Å (16.10 eV). We have not observed a band at ~880 Å (14.08 eV). This band which appears in the gas phase corresponds to the second continuum emission from the vibrationally relaxed $Ne_2^*(^{1,3}\Sigma_u)$. These results concur with those of Packard et al.,[5] however, they do not agree in some important details with the recent high resolution work of Fugol et al.[9] who managed to resolve the 742 Å band into four components (which cannot be detected under our spectral low resolutions), but who failed to detect the broad shoulder at 770 Å. The emission at 743 Å was originally assigned by Packard et al.[5] to the $^1P_1 \rightarrow {}^1S_0$ and the $^3P_1 \rightarrow {}^1S_0$ transitions (or alternatively to emission from the relaxed $n=1$ Wannier excited state). The position of the main emission peak of solid Ne is very close to the gas phase atomic transitions (736 Å for $^1P_1 \rightarrow {}^1S_0$ transition and 744 Å for the $^3P_1 \rightarrow {}^1S_0$ transition), so that the medium effect on the exciton emission is small. It
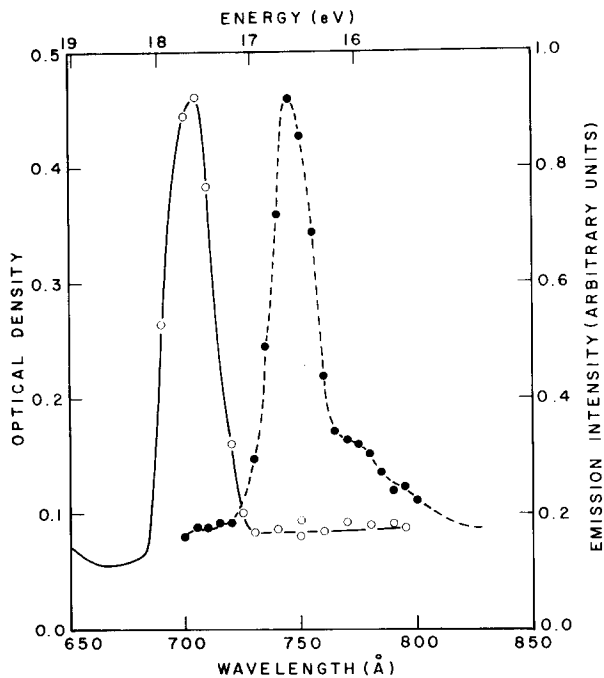
FIG. 1. Absorption (—O—) and emission (-- • --).
Spectra of pure solid Ne at 6 °K.

should be noted (see Fig. 1) that the Stokes shift between the absorption and emission of the $n=1$ state is 0.9 eV. (This large Stokes shift for the lowest exciton state of pure neon brings the emission band in the solid very close to the gas phase transition energy.) This result can be adequately rationalized in terms of medium relaxation (i.e., strong exciton-phonon coupling) which originates from large short range exchange repulsions resulting in the formation of a "microscopic cavity" surrounding the excited state. This effect of medium dilation surrounding a $n = 1$ Wannier exciton state is analogous to the behavior of Xe impurity states in solid and liquid argon.[4]

Finally, the broad shoulder at 770 Å in the emission spectrum of solid Ne (Fig. 1) is assigned to the radiative decay from high vibrational levels of the Ne_2^* molecule. We thus conclude that vibrational relaxation of this diatomic molecule in solid Ne is slow on the time scale of the radiative decay ($\sim 10^{-8}$ sec) for the $^1P_1$ state and $\sim 10^{-7}$ sec for the $^3P_1$ state). The mechanism of formation of electronically excited rare gas molecules involves the following steps:

(a) Population of the $^1P_1$ and $^3P_1$ allowed states either by direct excitation or by radiative decay and electronic relaxation from higher states. In the case of Ne direct optical excitation of the $^3P_1$ state is expected to be inefficient in view of the weak spin orbit coupling. The emission spectra in Fig. 1 demonstrate the efficiency of these popula-

tion processes.

(b) Electronic relaxation of the $^1P_1$ state to yield the $^3P_1$ state. The $^3P_1-^1P_1$ energy gap in solid Ne is 1850 cm^{-1} and this process may be inefficient.

(c) $^3P_1 \rightarrow {}^3P_2$ radiationless electronic relaxation characterized by an energy gap of 420 cm^{-1}.

(d) Formation of highly vibronic excited $^1\Sigma_u$ molecule originating from the $^3P_1 + {}^1S_0$ configuration and of the $^3\Sigma_u$ molecule from the $^3P_2 + {}^1S_0$ configuration.

(e) Vibrational relaxation of the diatomic molecule.

The inhibition of the formation of the vibrationally relaxed Ne_2^* $(^{1,3}\Sigma_u)$ molecule in solid Ne can result from either the retardation of the electronic relaxation processes (b) and (c) or alternatively it may originate from the inefficiency of the vibrational relaxation process (e). To elucidate this interesting point we have studied the emission spectra of Xe, Kr, and Ar impurities in solid neon. The impurity concentration was relatively high, $\sim 1\%$, insuring the formation of impurity dimers. Efficient electronic energy transfer from the electronically excited Ne matrix to the impurity is expected to occur resulting in autoionization of the impurity followed by electron capture, or alternatively by excitation of metastable impurity states (located above the conduction band) followed by electronic relaxation to lower excited impurity states. The experimental data are displayed in
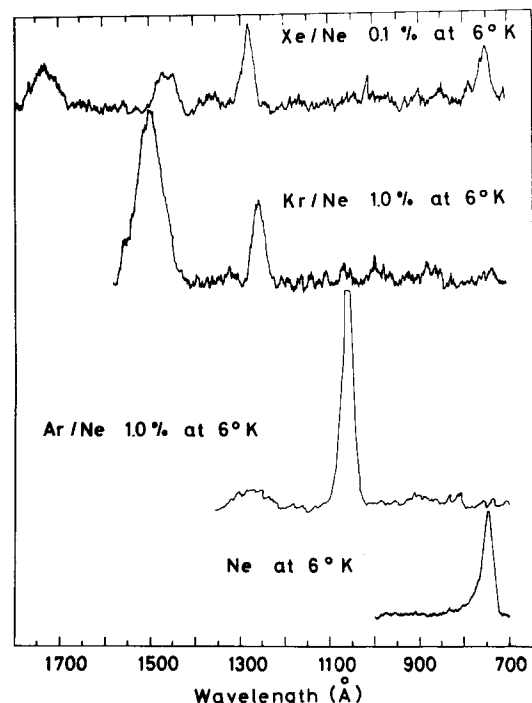

FIG. 2. Emission spectra of neon—rare gas alloys at 6 °K.

TABLE I. Emission spectra of rare gas impurities in solid Ne.[a]

| System | Emission | | | Absorption | | | | |
| | | | | Gas phase | | Impurity states in solid Ne | | |
	Wave length (Å)	Energy (cm^{-1})	Assignment	Wave-length (Å)	Energy (cm^{-1})	Wave-length (Å)	Energy (cm^{-1})	Stokes shift for solid Ne (cm^{-1})
Xe/Ne	742		Ne($^1P_1 \rightarrow {}^1S_0$)	736	135870			
	1270	78740	Xe($^1P_1 \rightarrow {}^1S_0$)	1296	77160	1099	91010	
			[or Xe/Ne $n=2$ ($^2P_{3/2}$)]					
	1465	68260	Xe($^3P_1 \rightarrow {}^1S_0$)	1470	68027	1365	73260	5000
	1725	57970	Xe$_2^*$ $^{1,3}\Sigma_u$ $\rightarrow \Sigma_g$					
Kr/Ne	1240	80650	Kr($^3P_1 \rightarrow {}^1S_0$)	1238	80917	1167	85680	5030
	1480	67570	Kr$_2^*$ $^{1,3}\Sigma_u$ $\rightarrow {}^1\Sigma_g$					
Ar/Ne	1070	93460	Ar($^3P_1 \rightarrow {}^1S_0$)	1067	93750	991	100850	7390
	1280	78125	Ar$_2^*$ $^{1,3}\Sigma_u$ $\rightarrow {}^1\Sigma_g$					

[a]The assignment of single impurity and exciton states in $n(^2P_{3/2})$ or $n(^2P_{1/2})$ in the Wannier scheme where n is the quantum number and $(^2P_{1/2})$ or $(^2P_{3/2})$ correspond to the hole state. Alternatively, we can use the tight binding scheme for labeling the atomic lowest excited $^3P_1$ and $^1P_1$ states. Thus, $n = 1(^2P_{3/2}) \equiv {}^3P_1$ and $n = 1(^2P_{1/2}) \equiv {}^1P_1$.

Fig. 2 and analyzed in Table I. These spectra exhibit the emission from the $n = 1$ Wannier states of Ar, Kr, and Xe, which are very close to the corresponding $^3P_1 \rightarrow {}^1S_0$ atomic gas phase transition and which exhibit large red Stokes shifts relative to the corresponding absorption bands. These single impurity emission bands exhibit again the effect of medium relaxation around the excited state.

Most important for the present discussion is the observation of the broad emission bands of the vibrationally relaxed Xe$_2^*$, and Ar$_2^*$ diatomics in solid Ne whose positions (see Table I) and widths coincides with the second continuum of rare gases in the gas phase[19] and in dense Ar, Kr, and Xe.[6] We thus conclude that solid Ne does not inhibit the formation of the heavier rare gas diatomic molecules. As the $^1P_1$–$^3P_1$ (and $^3P_1$–$^3P_2$) electronic energy gap is larger for Xe, Kr, and Ar than for Ne we assert that the solid Ne Matrix does not appreciably retard the electronic relaxation processes (b) and (c). The inhibition of the formation of Ne$_2^*$ in solid Ne is attributed to the slowing down of the vibrational relaxation process (e). In Table II we summarize the available information concerning the vibrational frequencies $\hbar w$ of the diatomics and the Debye temperatures $\hbar w_D$ of solid rare gases.

For Ar$_2^*$, Kr$_2^*$, and Xe$_2^*$ $\hbar w/\hbar u_L \sim$ 3–6 and the multiphonon vibrational relaxation process of the diatomic molecule in the solid is expected to be efficient. For the case of Ne$_2$, $\hbar w/\hbar w_D \sim 20$ the vibrational relaxation is slow on the time scale of the radiative decay. Thus the inhibition of molecular formation in pure solid Ne is a consequence of the energy gap

TABLE II. Molecular frequencies of rare gas diatonics and the Debye temperature ($\hbar w_D$) for the solids.

System Y	$\hbar v$ for Y_2^* cm^{-1}	$\hbar w_D$ for the solid Y cm^{-1}
Xe	140[a] 140[b]	38
Kr	190[c]	42
Ar	310[b] 290[c]	55
Ne	800[a]	44
He	1800[c]	...

[a]Estimates following Mulliken's theoretical arguments [Ref. (3)].
[b]Reference (6).
[c]Reference (11).

law for vibrational relaxation which is retarded with increasing the vibrational frequency. The observation of the first continuum of Ne_2^* in solid Ne is consistent with this of the first continuum of Ne_2^* in solid Ne is consistent with this interpretation. Finally we would like to point out that in view of the high vibrational frequency of He_2^* ($\hbar w \simeq 1800$ cm^{-1})[11] the vibrational relaxation of this molecule in liquid He will be inefficient and the broad emission spectrum reported by Sienko, Packard, Dick, and Reiff[12] from electron bombardment of liquid the originates from continuum–continuum transitions as proposed by Mies and Smith[13] for the corresponding gas phase spectra.

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