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U. Hahn and N. Schwentner
Institut für Experimentalphysik der Universität Kiel

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ELECTRONIC RELAXATION CASCADES IN WANNIER AND FRENKEL TYPE EXCITON STATES

U. Hahn[+] and N. Schwentner

Institut für Experimentalphysik der Universität Kiel, Germany.

Excitation spectra, emission spectra and decay curves for Xe and Ar atoms in solid Ne matrix have been investigated with Synchrotron radiation. The excited impurity states involved and the rate constants - between 10 psec and 1 μsec - for the radiative and nonradiative relaxation cascades have been determined.

The fate of excitons in insulators and organic crystals is still an open field concerning the dynamics of localisation processes and the quantitative analysis of relaxation in the manifold of free and trapped exciton states. In pure rare gas solids the lowest excitons are of the Frenkel type, the higher excitons are of the Wannier type. For isoelectronic dopands like Xe, Kr and Ar atoms in a solid Ne matrix, excitons belonging to the guest atoms are observed which have the same binding energies as those of the Ne host [1] . These states provide a link between Frenkel excitons, Wannier excitons, and Rydberg states of molecules in rare gas matrices.

We have measured luminescence emission spectra after exciting step by step higher exciton states of Xe, and Ar guest atoms in a Ne matrix, using pulsed monochromatized Synchrotron radiation [2] . For Xe and Ar three emission bands have been observed due to the decay of n=1, n'=1 and n=2 excitons (inset of Fig.1). The dependence of the intensity in each emission band on excitation energy is shown in the three lines of Fig. 1 together with some decay curves. By

+ Now at Deutsches Elektronen Synchrotron DESY

exploiting all the information contained in the intensities, the rise times and the fall times of the luminescence for different excitation energies we derived the following conclusions.

1. Maxima in the excitation spectra (Fig. 1) correspond to maxima in the absorption coefficient. They are attributed to a hydrogenic series of Wannier states n = 1, 2 , 3, 4. The binding energies of these impurity states are the same as the binding energies of the Ne excitons. This pure solid state behaviour of the excited impurity states can be explained by an effective mass approximation for the binding energies [1] . Two exciton series are observed for each species of guest atoms separated by the spin orbit splitting of the guest atom and denoted by n and n' (Fig. 1).

2. The emission bands show large Stokes shifts of ≈0.5eV to the red. The energies of the emission bands correspond with a blue shift of ≈0,2 eV to the atomic (n+1)s ($^3P_1$), to the (n+1)s' ($^1P_1$) and to the (n+2)s or nd levels. The radiative life times of all three relaxed exciton states are close to the gas phase values of the atoms (table 1). The atomic like emission bands are explained by the formation of a bubble around the excited guest atom by receding matrix atoms due to the much larger electron orbits in the excited states compared to the ground states. The rise times of the emission after direct population of the emitting electronic states show, that this matrix relaxation is faster than our time resolution of 10 psec.

3. Radiative and non radiative relaxation takes place in the atomic like states after the fast matrix relaxation (Fig. 2, table 1).

Population of n=1 impurity states:

Due to matrix relaxation the atomic $^3P_1$ state ist formed. Only radiative decay to the ground state is observed (table 1). Radiationless quenching to the ground state or nonradiative

relaxation to the close lying $^3P_2$ state are unimportant.

Population of n'=1 impurity states:

Matrix relaxation leads to the atomic $^1P_1$ states followed by radiative decay to the ground state. For Xe and Ar guest atoms nonradiative relaxation to the lower lying excited states $^3P_0$, $^3P_1$ and $^3P_2$ has not been observed. Transitions to $^3P_0$ are forbidden by the triangle rule for the total angular momentum. In Xe intersystem crossing $^1P_1 \rightarrow {}^3P_1$ is hindered by the large energy gap of 1.13 eV. In Ar, with a much smaller gap, the corresponding matrix element is small due to the weak spin orbit coupling in the lighter rare gas atoms.

Population of n=2 impurity states:

In Xe pure nonradiative relaxation to the $^1P_1$ states in the manifold of 7s, 5d and 6p states competes with radiative decay of the 5d (1 1/2) state to the ground state. The rate constant for the nonradiative relaxation of 1 nsec is determined by the largest gap of 0.18 eV between the lowest 5d and the highest 6p state. No relaxation to the $^3P_0$, $^3P_1$ and $^3P_2$ states is observed. In Ar (Fig. 2) fast nonradiative relaxation to the lowest 3d states takes place. The nonradiative decay from the lowest 3d state to the highest 4p' state takes 10 - 20 nsec due to the quite large gap ($\approx$ 0.5 eV) and radiative decay to the ground state can compete even when the decay time is long (420 nsec). After crossing this gap radiative decay from the 4p' and 4p states to $^1P_1$, $^3P_0$, $^3P_1$ and $^3P_2$ populates the 4s' and 4s states and radiative decay of 4s' and 4s to the ground state completes the relacation cascade.

[1] D.Pudewill, F.-J. Himpsel, V. Saile, N. Schwentner, M.Skibowski and E.E. Koch, phys. stat. sol (b) 74 (1976) 485.

[2] U. Hahn, N. Schwentner and G. Zimmerer, Nuclear Instruments and Methods ~~(1978)~~. 152 (1978) 261.

Fig. 1. Excitation spectra (hatched area) for the three emission bands (I, II, III) of Xe in Ne matrix. For some excitation energies (a, b, c, d, e) decay curves of the emission are shown. Inset: overview of emission spectra.

Fig. 2. Excitation and decay channels for Ar atoms in Ne matrix in a configuration coordinate scheme (left). Atomic levels and radiative lifetimes of free Ar atoms (right).

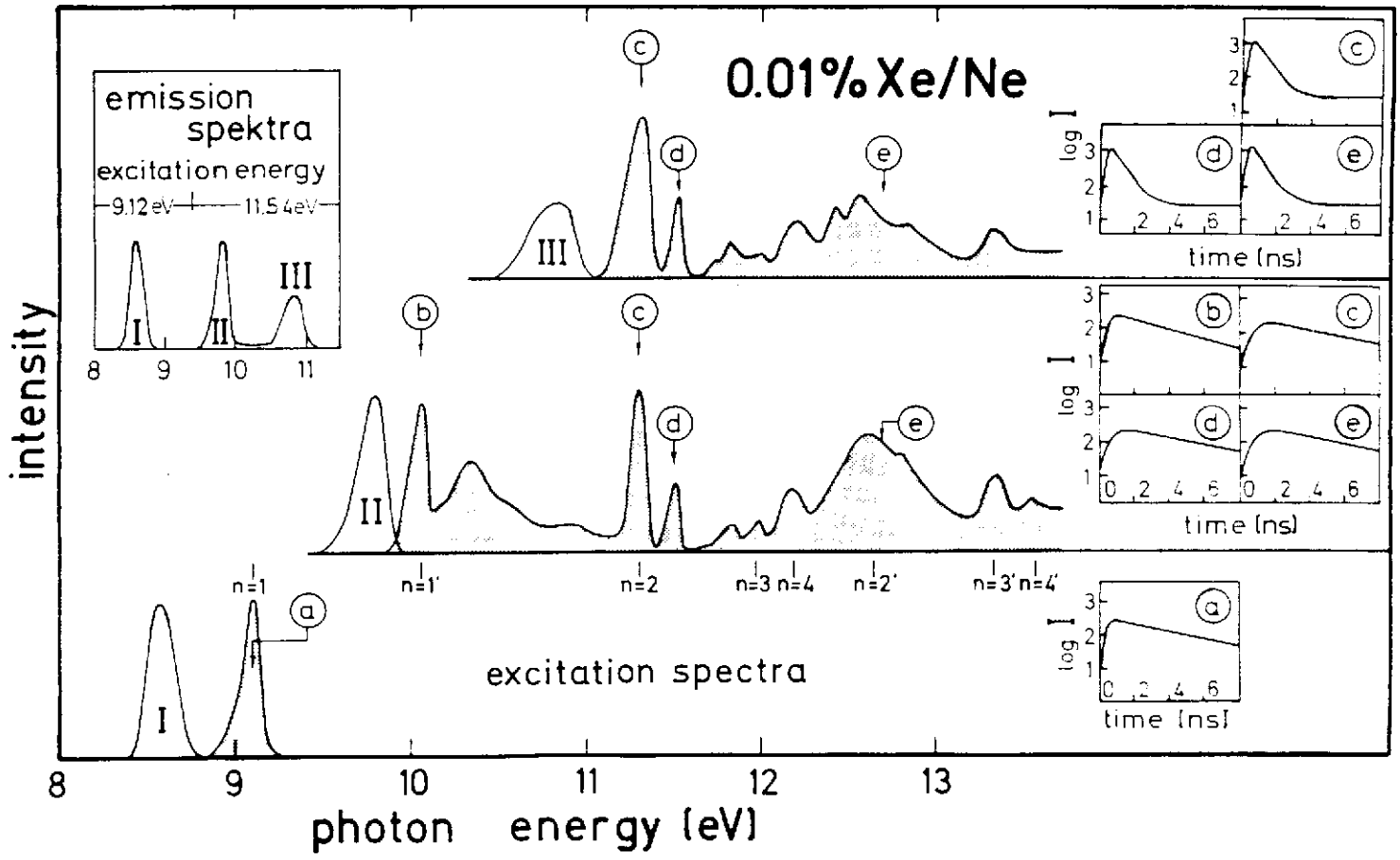

Fig. 1

Table 1. Life times and relaxation times between excited states in Ne matrix

exciton	life times [nsec] total in Ne	life times [nsec] radiative in Ne gasphase	life times [nsec] (other authors)		relaxation times [nsec] non radiative		relaxation times [nsec] radiative	
Xe n=1	2.4	2.4	$^3P_1$	3.4	$^3P_1 \rightarrow {}^3P_2$	not observed		
Xe n'=1	3.5	3.5	$^1P_1$	3.5	$^1P_1 \rightarrow {}^3P_o, {}^3P_1, {}^3P_2$	>100		
Xe n=2	0.57	1.3	5d	1.4	5d $\rightarrow {}^1P_1$	1		
					5d $\rightarrow {}^3P_o, {}^3P_1, {}^3P_2$	>100		
Ar n=1	5.5	5.5	$^3P_1$	8.4	$^3P_1 \rightarrow {}^3P_2$	not observed		
Ar n'=1	1.2	1.2	$^1P_1$	1.9	$^1P_1 \rightarrow {}^3P_o, {}^3P_1, {}^3P_2$	>100		
Ar n=2	13	420			3d $\rightarrow$ 4p', 4p	10-20	4p' $\rightarrow {}^1P_1$	71
							4p' $\rightarrow {}^3P_o$	82
							4p $\rightarrow {}^3P_1$	63
							4p $\rightarrow {}^3P_2$	32

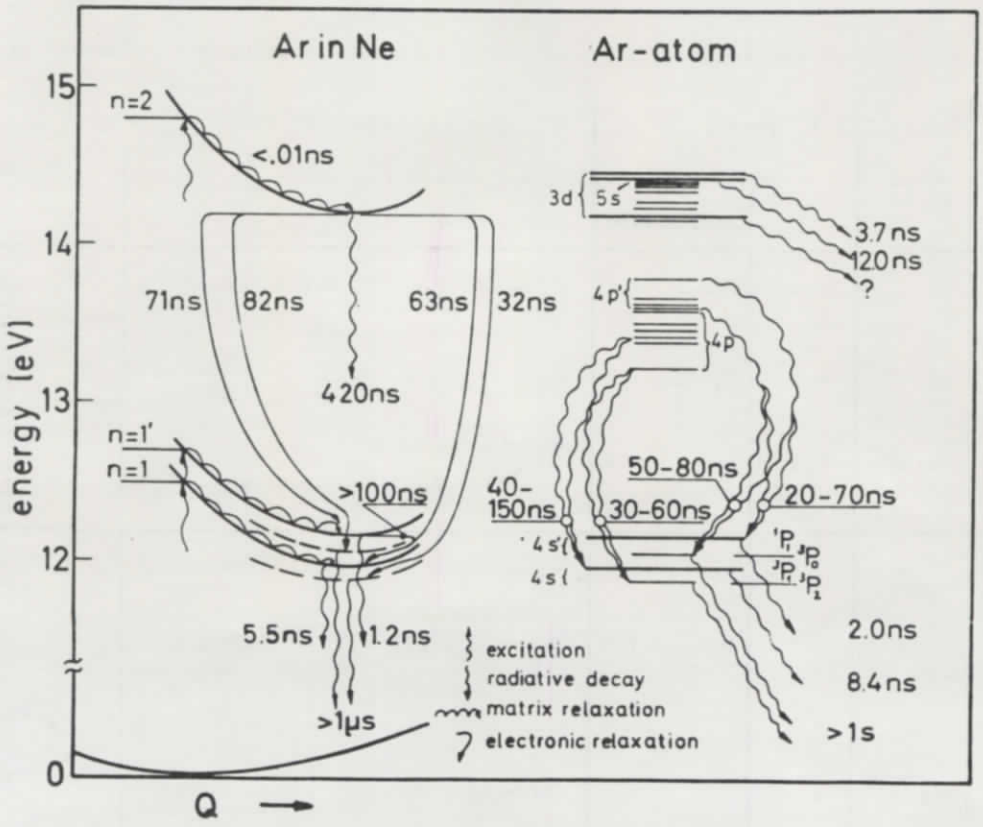
Ar in Ne
Ar-atom
energy (eV)
15
14
13
12
0
Q
n=2
<.01ns
71ns
82ns
63ns
32ns
420ns
n=1'
n=1
>100ns
5.5ns
1.2ns
>1μs
3d
5s
3.7ns
120ns
?
4p'
4p
50-80ns
40-
150ns
30-60ns
20-70ns
4s'
4s
2.0ns
8.4ns
>1s
excitation
radiative decay
matrix relaxation
electronic relaxation

Fig. 2