DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-80/17
October 1980

DYNAMICS OF LOCALIZED EXCITATIONS FROM ENERGY AND TIME RESOLVED SPECTROSCOPY

by

Nikolaus Schwentner
University of Kiel
Institut für Experimentalphysik

NOTKESTRASSE 85 · 2 HAMBURG 52

DESY SR-80/17
October 1980

Dynamics of Localized Excitations from Energy and Time Resolved Spectroscopy

Nikolaus Schwentner, University of Kiel,
Institut für Experimentalphysik, 2300 Kiel,
Germany/W.

The electronic structure and the excited state relaxation phenomena in condensed rare gases have been studied by absorption spectroscopy, photoelectron spectroscopy and time resolved luminescence spectroscopy all using selective excitation by monochromatized synchrotron radiation. Radiationless and radiative electronic transitions in excited states and the rearrangement of surrounding matrix atoms will be discussed for excited rare gas atoms in rare gas matrices. Furthermore experimental results concerning the scattering of excitons within the free exciton branches, localization of excitons, relaxation within the selftrapped exciton states and energy transfer to guest atoms and boundaries will be presented.

to be published in "Applied Optics" in December 1980.

1) Introduction

Excitation of a solid or liquid sample leads to a conversion of the deposited energy into phonons, photons and in some cases to the emission of electrons or desorption of ions. Upon excitation a nonequilibrium configuration of the electronic and nuclear structure is prepared. The new electron distribution at the excited site initiates nuclear rearrangements around this site. These structural changes cause nonradiative transitions to lower lying electronic states.[1-13] Therefore structural changes and electronic transitions are strongly coupled. During the time elapsing between the fast ($\approx 10^{-16}$s) electronic excitation process and the radiative decay process which takes place after 10^{-9}s or longer for VUV radiation, an interesting cascade of nonradiative electronic transitions and of structural changes is passed. A complete experimental investigation should provide the following set of informations:

1) electronic and geometric structure in the ground state
2) electronic structure in the primary excited state
3) new nuclear equilibrium configuration for this electronic state
4) rate constants for the relaxation to this structure
5) all intermediate electronic states and all rate

constants for the corresponding radiative and nonradiative transitions in the relaxation cascade to lower states

6) all intermediate nuclear configurations and all rate constants involved in their formation
7) electronic states and
8) equilibrium configurations from which finally radiative decay to the ground state is observed.

Compared to these high aims the available experiments yield only some parts of the whole cascade. The structural changes in excited states are in general beyond the scope of direct structure investigation techniques like X-ray diffraction and extended X-ray absorption fine structure analysis (EXAFS).[14] The difficulties arise from the short lifetimes and small densities of the excited states. To get a safe ground concerning the structure in the excited states the development of time resolved EXAFS[15] with a time resolution of 10^{-10}s will be of prime importance. Up to now the information concerning the points 3, 4, 6 and 8 has to be extracted from spectroscopic investigations in an indirect way. More data are available concerning the electronic states and the rate constants involved in electronic transitions. Absorption and photoelectron spectroscopy[16] provide a safe ground for point 2. But only some of the

intermediate states (point 5 and 7) are accessible. Easy of access are those states from which enough light is emitted to be detected by time resolved luminescence[17] spectroscopy or states which live long enough to be studied by transient absorption spectroscopy.[18] Due to these difficulties many questions remain open in the description of even a simple relaxation cascade in electronically excited states. From the experimental point of view it seems worthwhile to search for systems where the central process i.e. the coupling of electronic excitations with structural changes might be accessible. This for example will be systems where electronic excitation initiates large geometric rearrangements. Furthermore there should be an easy way to modify the electronic states and the rate constants to allow for a derivation of general trends. During the last years it turned out that pure and doped condensed rare gases are convenient systems for these studies[7] because of the following reasons:

- Electronic excitation breaks up the closed shell configuration. The chemical nature changes from inert to reactive[19] and the excited electron interacts strongly with the surrounding.
- The lattice is very soft[20] which allows quite large structural changes in response to the new electronic configuration.

- The lattice phonon energies are extremly small[21] (some meV). The dissipation of electronic energy to heat needs in general the emission of many phonons. Thus nonradiative electronic relaxation processes are slowed down.
- The chemical nature is similar in the gas, liquid and solid phase. Thus relaxation processes and their dependence on density and on structural order can be investigated in all three phases at comparable conditions.
- Different rare gases and molecular gases can be easily mixed in the gas phase and codeposited as doped samples.[22] This allows a systematic variation of electronic and structural parameters at comparable conditions.
- Rare gases are transparent up to 17 eV photon energy. Therefore they are favorable matrices for matrix isolation spectroscopy[22] in general.

In the following some examples of experimental progress towards an understanding of the dynamics in electronically excited states of pure and doped condensed rare gases will be presented. Reviews have been prepared by Fitzsimmons,[23] Jortner[7], Zimmerer[24], Schwentner[25], Fugol'[26], Bondeby and Brus[27] and Schwentner, Koch and Jortner[28]. In this issue the relevant theory is treated by Toyozawa and Bassani and a discussion of one and two photon absorption results is given by Saile.

2) Relaxation channels in condensed rare gases

For an introductory overview some electronic states relevant in the relaxation cascade in liquide He are shown in Fig. 1. The scheme describes atomic and molecular states in the gas phase. The arrows indicate transitions which have been observed in luminescence emission and in transient absorption experiments in the liquid phase.[23] According to these experiments the same electronic states with only minor changes in the energies appear in liquid and gaseous He. This close correspondence is due to a rearrangement of the liquid around the excited He atoms. After the rearrangement of the liquid the centers can be grouped into atomic like excited centers He^* and molecular like centers He_2^*. Both species are surrounded by empty bubbles. The radius of the bubble exceeds the nearest neighbour separation of 3 Å of He atoms in the ground state by far. The radius of the bubble (5 - 20 Å) and its shape which is nonspherical for states with symmetry unlike s, depend strongly on the main quantum number and the symmetry of the specific excited electronic state. The configuration around some of the excited atomic like states and its dependence on external pressure has been calculated.[34-38] Also the sizes and the shapes of bubbles around molecular centers have been estimated from electron density calculations in excited states of He_2^* molecules.[30] Despite the interesting experimental results concerning the dynamics in these excited states,[23,33] there exists no consistent description of the various relaxation channels neither from a theoretical nor from an experimental point of view even for this simple system consisting of He atoms with only two electrons. One of the main problems is the quite large manifold of channels which are possible due to the formation of two types of centers. In addition the atomic and molecular like centers interact via dissociation and recombination processes.

This example illustrates that in the case of pure liquid and solid rare gases we have to deal with[7,23-28]
- electronic relaxation of atomic like states in a bubble
- electronic, vibrational and rotational relaxation of molecular like states in a bubble
- interaction of these channels by dissociation and recombination.

In rare gas crystals excitation creates excitons which move free before the deformation of the lattice leads to localized centers described above. Therefore the fate of these free excitons until they are localized as atomic or molecular centers has to be analysed.

This includes[3,8]:
- scattering within a free exciton branch
- scattering to lower free exciton branches
- localization of excitons

In doped samples energy transfer processes become important. The competition of the processes listed above with[3]
- energy transfer by coherent or diffusive migration of free excitons
- energy transfer of localized excitons by a Förster-Dexter type interaction[39,40]

has to be considered.

To disentangle all these competing processes systems have been analysed where only a few of these channels are open. We will start with a discussion of rare gas atoms in rare gas matrices. In the excited states of the guest atoms only the first channel contributes to relaxation. In this way this channel can be studied separately. Next we turn to the localization processes of free excitons, the branching into the two types of localized states and to vibrational relaxation within the molecular type centers. Finally some experiments are described which represent a first attempt to tackle the problem of relaxation in the free exciton states and of localization of free excitons in competition to energy transfer.

3) Excited states of rare gas guest atoms in solid rare gas matrices

After a short characterization of the excited electronic states of the guest atoms, the rearrangement of the matrix atoms around the excited atoms and the nonradiative and radiative electronic transitions within the guest atom states will be described. The energetic positions of the occupied valence states of heavy rare gas guest atoms within the bandgap of the matrix have been derived from absorption experiments[41,42] from photoelectron yield[43,45] and from photoelectron energy distribution measurements[46,47]. Absorption[41,42] and luminescence excitation spectra[17] (Fig.2) yield the exited states of the guest atoms within the host band gap. The excited states form for each kind of guest atoms two series of excitons which are separated by the spin orbit splitting of the valence states and which will be denoted by n and n'. A survey of the valence states and the exciton states for Xe, Kr and Ar guest atoms in a solid Ne matrix is shown in Fig. 3. The binding energies of the exciton series where members up to $n = 5$ have been identified are determinded by the dielectric constant of the host and the effective mass of electrons in the conduction band of the host[17,41-45,48]. According to the experimental results these states are Wannier excitons which

obey the effective mass approximation. The electron orbit for $n \geq 2$ is large compared to the nearest neighbour separation. For the $n = 1$ excitons some corrections have to be included to account for the smaller electron orbit[42,48]. Relative to the corresponding Rydberg transitions of the free atom the absorption energies of the excitons in the matrix are strongly blue shifted by about 0.5 - 1 eV (table 1).

The emission bands have been studied first by α-particle[7] and X-ray[49] excitation. The relaxation channels have been investigated by time and energy resolved luminescence spectroscopy using monochromatized synchrotron radiation for excitation[17]. The emission spectrum for excitation of a specific exciton allows an identification of the corresponding emitting state and the energy difference yields the Stokesshift between absorption and emission (Fig. 2). For the guest atoms in Ne atomic type emission due to the fine structure components of ns and (n - 1)d states has been observed. n is the main quantium number of the lowest excited state. The emitting states are $1s_4$, $1s_2$ and $3d_5$ for Ar and Kr and $1s_4$, $1s_2$, $3d_2$ for Xe in Ne. The emission bands are redshifted compared to the excitation energies by about 0.5 - 1 eV. Therefore they are now close to the free atomic transitions (table 1). Furthermore the radiative lifetimes in the matrix[17] derived from decay curves

(Fig. 2) are similar to the free atomic values (table 1). From these observations the formation of a bubble around the excited atom has been postulated[7,17] similar to the case of He. In this bubble the electronic wave function resembles the free atomic limit. From the density dependence (Fig. 4) of the n = 1, n' = 1 and n= 2 exciton transition energies[17,55] an increase by about 30 % - 100 % of the nearest neighbour separation in the bubble compared to the groundstate configuration has been estimated[17]. The large Stokesshifts correspond to very strong differences in the electron lattice couplings between the ground state and the excited states. From the Stokesshift E_s and independently from the large line width H(T) in emission[49] a value of $S \approx 50$ for the Huang Rhys coupling constant[5,13] is derived for example for the $1s_4$ decay of Kr. From S again an increase in the nearest neighbour separation of about $Q \approx 2$ Å (i.e. 70 %) can be predicted. For these estimates the following relations have been used which are based on the harmonic approximation with linear coupling and a single characteristic phonon frequency $\hbar\omega_p$ in the strong coupling limit[4-13]. M is the reduced mass of the system.

$$E_s = 2\,S\hbar\omega_p \qquad (1)$$

$$H(T=0) = 2.36\,\sqrt{S}\,\hbar\omega_p \qquad (2)$$

$$S\hbar\omega_p = 1/2\,M\,\omega_p^2\,(\Delta Q)^2 \qquad (3)$$

A similar strong coupling has been derived for the n = 1 state of Xe in Ar from the temperature dependence of the absorption line[7,28]. The risetimes[17] in the time resolved emission spectra which are shorter than 10^{-11}s represent an upper limit for the time required for the rearrangement of the matrix. This upper limit is consistent with theoretical estimates[7] of 10^{-13}s.

From the total intensity of individual emission bands for excitation of the n =1, n' = 1 and n = 2 exciton states and from the corresponding time dependence of the intensity in the emission bands a quantitative cascade for electronic relaxation has been determined[17]. The relative intensities of the emission bands for one excitation energy yield the branching ratio for radiative and nonradiative decay to different lower lying electronic states. The rise and decay times in one emission band correspond to the times for population(for example via relaxation from higher states) and depopulation (for example due to relaxation to lower states). Thus the cascade can be built up consistently in populating first the lowest state and going up stepwise to higher primary excited states[17]. Since Ne does not form bound molecular states with Xe, Kr and Ar atoms the complications due to molecular states like in the pure gases (see He) are absent. Excitation of the n = 1 impurity state of Xe, Ar and Kr in solid Ne causes a rearrangement of the matrix leading to the formation of the $1s_4$ $(^3P_1)$ impurity state. On the basis of the experimental data (table 1) for the radiative decay, it is apparent that the major contribution to the lifetime of the $1s_4$ state originates from the radiative decay channel to the ground state which is much faster than the two competing radiationless processes (Fig. 5,6), i.e. radiationless relaxation either to the only lower lying exited state $1s_5$ $(^3P_2)$ or to the ground state[17]. Radiationless transitions rates W_{nr} for relaxation between electronic states which are separated by an energy difference ΔE of the two minima of the potential surfaces are determined by the coupling constant S which essentially describes the displacements ΔQ of the equilibrium coordinates of the two states involved (equ. 3) and the order $N = E/\hbar\omega_p$. N corresponds to the number of phonons which are emitted in the dissipation of the electronic energy difference ΔE[4-13]. For low temperatures an exponential decrease of the transition rates with increasing energy gap ΔE or order N is predicted provided that S is not too large,

$$W_{nr}(T \rightarrow 0) = \frac{A}{\sqrt{2\pi N}} \exp(-S)\exp(-\gamma N) \qquad (4)$$

$$\gamma = \ln\left(\frac{N}{S}\right) - 1 \qquad (5)$$

A contains the electronic matrix element. According to this well known "energy gap law" the radiationless relaxation to the ground state is hindered by the very large energy gap. The separation from $1s_4$ to the $1s_5$ state is only 0.1 - 0.2 eV requiring a radiationless transition of the order of N = 10 - 30. In the case that the corresponding S is not too large the radiationless $1s_4$ - $1s_5$ decay will be effectively blocked by the appreciable energy gap. The energy gap law is also manifested in the photoselection of the n = 1' impurity states of Xe and of Ar in solid Ne. This excitation process which populates the spin orbit mate of the n= 1 exciton, leads to the formation of the medium relaxed $1s_2(^1P_1)$ state (Fig. 5,6). The experimental lifetimes (table 1) are again dominated by the pure radiative decay channel[17], so that radiationless electronic relaxation from $1s_2(^1P_1)$ to $1s_3(^3P_0)$, $1s_4(^3P_1)$ and $1s_5(^3P_2)$ is not exhibited on the time scale of 10^{-6} sec. The energy gaps of 0.2 eV for Ar and 1.1 eV for Xe determined by the spin orbit coupling are sufficiently large to prohibit electronic relaxation. For Kr in solid Ne there is an interesting complication due to impurity-impurity energy transfer, as in this system there is an accidental energetic overlap between the medium relaxed $1s_2(^1P_1)$ state and the n = 1 $(^3P_1)$ state. The rise and decay times of the emission bands of the $1s_2$ and the

$1s_4$ states after excitation of n' = 1 exitons indicate that a resonant dipole-dipole energy transfer[39,40] takes place from an excited Kr atom in the $1s_2$ state to a nearby Kr atom in the ground state[17]. The Förster-Dexter radius for this transfer is 21 Å.

Next we consider the fate of n = 2 guest atom excitations in solid Ne. There are several characteristic differences for the n = 2 exciton relaxation cascades for Xe, Kr and Ar guest atoms in a Ne matrix. The origin is an increasing spread on an energy scale of the (n + 1)s, the (n - 1)d, the np and the ns' states in going from Xe to Ar. This spread results in groups of close lying levels which are separated by increasing gaps (Fig. 5,6). Excitation of n = 2 excitons in Xe leads to a population of the medium relaxed $2s_4$ and $3d_2$ states (Fig. 5). The $3d_2$ state is separated from the next state $3d_1$' by a gap of 0.18 eV. It was experimentally established that the $3d_2$ state decays radiatively to the ground state with a time constant of 1.3×10^{-9}s as well as nonradiatively to $3d_1$' with a time constant of 1.0×10^{-9}s. We note that in this case radiationless processes of the order of N = 30 can have time constants as fast as 10^{-9}s. This observation is incompatible with the considerations based on the energy gap law and can be rationalized in terms of the cancellation effect which is exhibited

when $N \approx S$ in eqs 4,5. The energy interval between the $3d_1$' and the $1s_2$ states is so densely populated with other states (Fig. 5) that the radiationless processes will be extremely fast. Radiative transitions, i.e. the dipole allowed decay from the $3d_5$ state, are not observed. In the $1s_2$ state the radiationless relaxation cascade terminates as has been previously noted. No relaxation to $1s_3$, $1s_4$ or $1s_5$ is observed.

The relaxation cascade for the n = 2 excitation of Ar in solid Ne (Fig. 6) results in an initial population of the medium relaxed $2s_4$ state which relaxes effectively to the lowest 3d states ($3d_5$ and$3d_6$). The gap between the 3d and (4p, 4p') states is sufficiently large to make nonradiative decay rather slow. There is branching between radiative decay of the $3d_5$ state (420×10^{-9}s) and slow nonradiative decay to 4p' and 4p states. The(4p', 4p) states are separated by a large energy gap from the 4s and 4s' levels. Therefore both the 4p' and 4p states are depopulated radiatively to the 4s as well as 4s' state with similar time constants. The intensity is distributed between radiative channels from the fine structure components of the 4p' ($1s_2$, $1s_3$) and the 4p ($1s_4$, $1s_5$) states with the branching ratios given in Fig. 6. The relaxation cascade of Kr in solid Ne is similar to that of the Ar impurity state in the same matrix[17].

The radiationless relaxation rates are strongly influenced by the matrix and by the temperature. The temperature dependence of the lifetime of the Kr $1s_4(^3P_1)$ state in an Ar matrix has been studied as an example[56]. The $1s_4$ state is depopulated by radiative decay to the ground state and by nonradiative decay to the $1s_5(^3P_2)$ state. Fig. 7 shows the temperature dependence of the decay rate of the $1s_4(^3P_1)$ state which exhibits the temperature independent relaxation to $1s_5$ at low temperatures and as activated process at higher tempratures. An analysis of the data with the expressions given in ref. 57 can be performed (fit in Fig.7) taking $\Delta E = 72$ meV and $\hbar\omega_p = 4$ meV, i.e. $N = 18$. The separation of $1s_4$ and $1s_5$ in the Kr matrix of 72 meV derived in this way is close to the separation in the free atom (table 1).

4) Exciton states of pure rare gas solids

The analysis of the dynamics in the excited states of pure rare gas solids requires the spectrum of exciton states[16] as input data.

4.1 Free and localized exciton states

The spectrum of free exciton states with wave vector $k = 0$ is well known from reflection and absorption spectroscopy[16,58,59]. It consists of two series of excitons which are separated by the spin orbit splitting of the valence bands. Up to 5 members of the series have been identified. For the $n = 1$ excitons the energy of the longitudinal excitons at $k = 0$ has been determined in addition to the transverse excitons[59]. The calculations of Knox[3,60] show that two additional $n = 1$ branches exist which are not accessible by optical absorption. The dispersion of the $n = 1$ exciton bands versus wave vector k has been calculated for Ar[3,60]. The bandwidth 2B has been estimated also from the width of the valence bands[61] for Xe, Kr, Ar and Ne by Fugol'[26] (table 2). A schematic illustration for the $n = 1$ and $n' = 1$ states in Kr is shown in Fig. 8. In addition to these bulk excitons also surface excitons have been observed[59].

Three types of localized exciton states have been observed in luminescence spectra[7,24-26,28]. They have been identified in analogy to emission spectra in the gas phase[7,26,28] at high and low pressure. Atomic type localized n = 1 excitons[7,24-26,28,65-68] are excited rare gas atoms where a cavity has been formed similar to He and similar to guest atom states in rare gas matrices. In molecular type localized states[7,24-26,28,63-76] a neighbouring rare gas atom moves to the excited atom and an excimer with a smaller equilibrium separation than the nearest neighbour distance in the undistorted crystal is formed (see He_2^* in Fig. 1). Two species of molecular type states with different lifetimes[24,25,28,67,68,73-75] in the 10^{-9}s and in the 10^{-6}s region have been identified. They belong to the $^1\Sigma_u$ and $^3\Sigma_u$ branches of the molecular potential curves (Fig. 8). The energy versus the internuclear distance in the molecular type states is sketched also in Fig. 8. By transient absorption spectroscopy[18] higher atomic states i.e. the fine structure components of the 2p states have been observed in solid Ne and higher molecular states have been found in solid Ne, Ar and Kr. Now we proceed to the dynamics in the exciton states.

4.2 Selftrapping of free excitons and relaxation in localized states

The emission bands and their relative intensities are summarized in table 2 in a tentative way[24,26,28,68,71]. "a" indicates emission from free excitons, "b" from atomic centers, "c" from vibrationally hot molecular centers and "d" from vibrationally relaxed molecular centers. It is immediately apparent from table 2 that 99 % of the luminescence intensity is emitted from localized states in all solid rare gases. This implies that the selftrapping process is at least a factor of 100 faster than the radiative decay time of free excitons. Selftrapping occurs within a time $<10^{-11}$s. Selftrapping can be treated by the theory developped by Toyozawa[8] and Rashba[11] which is presented also in the preceeding paper by Toyozawa. The Lorentzian line shape of the excitons in absorption[59] indicates that initially free excitons are created in solid rare gases. The free excitons are stable when the lattice relaxation energy E_{LR} is smaller than the exciton kinetic energy given by the bandwidth in k space i.e. $E_{LR} < B$ or vice versa. Furthermore this continuum theory[8] predicts a barrier of height E_m between the free and localized states which has to be crossed for localization either by thermal activation or by tunneling. Fugol' and Tarasova[26,66] derived in a semiempirical analysis

E_{LR}, H_m and 2B from spectroscopy data (see table 2). This analysis explains the experimental results in a qualitative way. It predicts the observed stability of the molecular type centers in Ne, Ar and Kr and it describes the trend to stronger emission from free excitons in going from Ne to Xe by an increasing barrier H_m. But the predicted instability of atomic type centers in Xe and the very large barrier for formation of molecular type centers are in disagreement with the weak free exciton emission band "a" (table 2).

This continuum theory[8] does not include the microscopic structure of the selftrapped centers without additional input data. A microscopic calculation[77,78] similar to that for selftrapping of holes in alkalihalides[79] can go further. In the case of rare gas solids the calculated molecular potential curves for excimers[19,29,30,80,81] provide information concerning the branching ratio into atomic and molecular centers. The potential curves for He_2^* [19,29,30] and Ne_2^* [81] show up humps around 2 - 4 Å which have to be crossed in the formation of molecular centers. These humps reduce the probability for the molecule formation. They push away neighbouring atoms thus favouring atomic centers as observed in solid Ne. Kunsch and Coletti[82] calculated the local structure around an excited Ne atom from these potential curves. The separation of the excited atoms from the first shell of neighbouring atoms increases by a factor of 1.37 compared to the undistorted lattice. This distortion extends up to the 16th shell causing still deviations of 1 %.

After formation of molecular centers vibrational relaxation in the molecular potential curve will reduce the energy of the centers further[7]. Vibrational relaxation follows an energy gap law similar to equ. 4. The rate constant decreases exponentially with the order N given by the ratio of the vibrational spacing and a characteristic phonon energy. N increases from 4 to 6 in going from Xe to Ar which explains the stronger hot luminescence band c. N jumps to 18 in the case of Ne thus vibrational relaxation will be incomplete[7]. Due to the anharmonicity in the potential curves of Ne the relaxation is stopped within the 4th or 3rd vibrational level[83].

4.3 Exciton scattering, selftrapping and energy transfer

Since strong luminescence emission is observed only from the lowest localized states it is necessary to search for faster processes than radiative decay to analyse relaxation processes in free and in higher selftrapped exciton states. Two photon spectroscopy can provide a tool for future investigations as will be discussed by Saile in the following contribution. It has been shown that energy transfer processes are fast enough to compete with localization[44,46,84-86] and free exciton scattering[46,86]. Two different ways of energy transport by excitons are possible apart from electromagnetic transport[3]: hopping transport of selftrapped excitons via a Förster-Dexter[39,40] type of energy transfer and wave packet transport of free excitons. In the case of wave packet transport either coherent or diffusive motion will dominate depending on whether the mean free path between scattering events with phonons and lattice imperfections is larger or of the order of the lattice constant. To distinguish between energy transfer from localized or free excitons three criteria have been used in the experimental investigations.

First the amount of transfered energy per exciton is characteristic for a specific exciton state. For example the energy of localized excitons is more than 1 eV lower than the energy of free excitons. Ar and Ne matrices have been doped with Xe atoms[46]. The ionisation energy of Xe atoms in these matrices is lower than the energy of the free n = 1 excitons of the matrices (see Fig. 1). Some of the free

electrons produced by ionisation of the guest atoms leave the sample and can be detected. The energy distribution of the emitted electrons has been measured. The electrons are ejected either by direct ionisation of the guest atoms via absorption of the exciting photons by the guest atoms or via absorption of the light in the matrix and creation of excitons of the matrix and subsequent energy transfer from the matrix excitons to the guest atoms. In the second case the energy of the emitted electrons carries the information about the status of relaxation of the matrix excitons at the moment of energy transfer. Fig. 9(lowest curves) shows the energy distribution of the emitted electrons for photon energies lower than the n = 1 exciton energy of the matrix where all the light is absorbed in the guest atoms which are directly ionised[46]. Further results are shown for photon energies corresponding to the n = 1, n' = 1 (not for Ne) and n = 2 and n' = 2 (not for Ne) excitons. In these cases essentially all the light is absorbed by matrix excitons and the observed electrons stem from energy transfer of the matrix excitons to the Xe guest. The electrons ejected by ionisation of 1 % Xe in Ar matrix carry the full energy of the free n = 1 and n' = 1 excitons of the Ar matrix when these excitons have been excited. Also a considerable number of n = 2 and n' = 2 excitons transfer the full free n = 2 (n' = 2) exciton energies. But also smaller energies due to partly relaxed exciton states are transfered. The low energetic electrons are attributed to transfer from localized n = 2 excitons. For 1 % Xe in Ne matrix and excitation of the n =1 and n = 2 excitons of the Ne matrix only the energy of the localized atomic Ne centers is transfered to Xe atoms. This shows that for example in the case of n = 2 excitons in Ne more than 3 eV of the free exciton energy have been dissipated to the Ne lattice and the exciton has been also localized before energy transfer is completed. From these experiments a time hierarchy for relaxation and energy transfer has been derived[25,46].

Secondly the range of the energy transfer process is typical for the exciton state involved. Localized excitons in solid rare gases are deeply trapped by about 1 eV and thermal activation can be excluded. In this case energy can be only transported via pairwise dipol-dipol interaction[39,40] between the localized exciton and a guest atom or an atom at a boundary. The efficiency of the transfer process decreases with r^{-6} or r^{-3} when r is the distance to the acceptor atom or metallic boundary respectively[39,40,86,87]. Free excitons are able to migrate to the vicinity of a guest atom or boundary. The range of energy transport can depend in this case on the wave vector and electronic state of the free exciton. For a diffusive motion the range is determined by the diffusion length l which follows from the diffusion constant D and the lifetime τ of the free exciton state.

$$l = \sqrt{D\tau} \tag{6}$$

τ is not the radiative lifetime but the selftrapping time or even shorter. When D is dependent on the specific free exciton state or even on the kinetic energy of the specific exciton than τ corresponds to the lifetime of this state concerning scattering to lower kinetic energies or to lower exciton states. In solid Xe films deposited onto an Au substrate exciton diffusion to the Au substrate has been observed[84]. At the metal surface electrons are ejected due to a Penning type transfer of the exciton energy to the metal. Part of the ejected electrons penetrates the solid Xe films, reaches the vacuum interface and can be detected. The energy transfer range has been determined from the thickness (100 Å to 1000 Å) dependence of the number of emitted electrons for different Xe excitons. An averaged diffusion length of 300 Å has been obtained[84]. Similar experiments have been performed for Kr overlayers on an Au substrate[86]. The efficiency for conversion of excitons to free electrons at the Au substrate is 10 times larger than the photoelectron emission efficiency at the same energy. This proves that the conversion is a true surface process similar to electron emission by decay of metastable rare gas atoms on metal surfaces[88]. Even more interesting the derived diffusion length is strongly dependend on the primary excited exciton state. The diffusion length increases monotonously with increasing energy of the free excitons[86], starting with about l = 30 Å at the low energy tail of the Kr n = 1 exciton and reaching about 300 Å in the n = 2 exciton (Fig. 10). Fig. 10 demonstrates that energy transport is conducted essentially by free excitons because in the transport by localized excitons only one type of excitons independend on the excitation process would be involved. Furthermore transport is faster than relaxation within the free exciton states and it is more efficient for higher exciton states as is evident from the monotonous increase of l from n = 1 to n' = 1 to n = 2 (Fig. 10). Finally the increase of l within each exciton band raises interesting questions concerning the relation between transfer probability and kinetic energy of excitons and concerning the rate constants for thermalisation in an exciton band and energy transfer.

Thirdly the investigation of the time dependence of the depopulation of the primary excited exciton states and the population of the acceptor states is

a powerful method to study the nature of energy transfer processes as has been shown for molecular crystals[90,91]. Such time resolved luminescences experiments have been carried out for rare gas solids only for energy transfer between Kr atoms in a Ne matrix[17]. A combination of time resolved techniques in the 10^{-12}s regime, using synchrotron radiation for excitation, with electron spectroscopy as discussed above will be a interesting diagnostic tool. The investigation of ejected electrons utilizes the advantages of a prompt process and avoids the restrictions due to the limited radiative decay rates involved in luminescence studies.

5) Summary

The dynamics of electronically excited states in pure and matrix isolated systems can be tackled now due to progress in experimental techniques by combining lineshape analysis in absorption and emission with time and energy resolved luminescence and electron spectroscopy and with transient and two photon absorption spectroscopy. These experiments profit from the tunability and time structure of synchrotron radiation[92]. The advent of structure analysis in the 10^{-10}s range will stimulate this field further.

Aknowledgement

This paper is based on investigations at the synchrotron radiation laboratory of DESY in Hamburg in collaboration of the author with several groups. It is a pleasure to thank U. Hahn, E.E. Koch, V. Saile and G. Zimmerer from the lab in Hamburg, H.-W. Rudolf and W. Steinmann from the University of Munich, J. Jortner, Z. Ophir and B. Raz from the Tel Aviv University and R. Haensel, M. Skibowski and H. Wilcke from the University of Kiel for their cooperation.

References:

1) Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) 20, 53 (1958)
2) H. Haken, Fortschr. Physik 6, 271 (1958)
3) R.S. Knox, in "Theory of Excitons", Academic Press, New York (1963)
4) Y.E. Perlin, Sov. Phys. Uspekhi 6, 542 (1963)
5) W.B. Fowler and D.B. Fitchen, in "Physics of Color Centers", ed. W.B. Fowler, Academic Press, London (1968)
6) R. Englman, J. Jortner, Mol. Phys. 18, 145 (1970)
7) J. Jortner, in "Vacuum Ultraviolet Radiation Physics" (ed. E.E. Koch, R. Haensel and C. Kunz), p. 263, Pergamon, New York (1974)
8) Y. Toyozawa, in "Vacuum Ultraviolet Radiation Physics", (ed. E.E. Koch, R. Haensel and C. Kunz), p. 317, Pergamon, New York (1974)
9) F.K. Fong in "Theory of Molecular Relaxation", Wiley (1975)
10) K.F. Freed in "Radiationless Processes in Molecules and Condensed Phases" (ed. F.K. Fong), Springer (1976)
11) E.I. Rashba, Izv. AN SSSR, Ser. Fiz. Bd. 40, 535 (1976)
12) L.A. Riseberg and M.H. Weber in "Progress in Optics XIV" (ed. E. Wolf), p. 91, North-Holland (1976)

13) F. Auzel in "Luminescence of Inorganic Solids" (ed. DiBartolo) Plenum Press, New York (1978)

14) e.g. P. Rabe and R. Haensel in "Festkörperprobleme XX" , ed. J. Treusch, Vieweg (1980)

15) D . R. Sandstrom, S.C. Pyke, F.W. Lytle and R.B. Greegor in SSRL Report No 79/05 p.12 from Stanford Synchrotron Radiation Laboratory (1979)

16) B. Sonntag in "Rare Gas Solids", (ed. M.K. Klein and J.A. Venables) vol. II, p. 1021, Academic Press, London (1977)

17) U. Hahn and N. Schwentner, J. Luminescence 18/19, 23 (1979)
U. Hahn and N. Schwentner, Chem. Phys. 48, 53 (1980)

18) T. Suemoto, H. Kanzaki, J. Phys. Soc. Jap. 46, 1554 (1979)

19) R.S. Mulliken, Phys. Rev. 136, 962 (1964)
R.S. Mulliken, J. Chem. Phys. 52, 5170 (1970)
R.S. Mulliken, Radiation Research 59, 357 (1974)

20) I.A. Barker in "Rare Gas Solids", ed. M.K. Klein and J.A. Venables, vol. I, p. 212, Academic Press, London (1976)

21) B.M. Powell and G. Dolling in "Rare Gas Solids", ed. M.K. Klein and J.A. Venables, vol. II, p. 921, Academic Press, London (1977)

22) B. Meyer "Low Temperature Spectroscopy", Elsevier, New York (1971)

23) W.A. Fitzsimmons in "Atomic Physics 3" (ed. J. Smith and G.K. Walters), p. 477, Plenum, New York (1973)

24) G. Zimmerer in "Proc. of Intern. Summer School on Synchrotron Radiation Research", (ed. A.N. Mancini and I.F. Quercia), vol. I, p. 453, Alghero (1976)
G. Zimmerer in "Luminescence of Inorganic Solids", (ed. B. DiBartolo), p. 627, Plenum Press, New York (1977)
G. Zimmerer, J. Luminescence 18/19, 875 (1979)

25) N. Schwentner in "Luminescence of Inorganic Solids", (ed. B. DiBartolo), p. 645, Plenum Press, New York (1978)

26) I.Ya. Fugol' "Excitons in Rare Gas Crystals", in Advances in Physics 27, 1 (1978)

27) V.E. Bondybey, L.E. Brus in "Advances in Chemical Physics", ed. S.A. Rice(1980)

28) N. Schwentner, E.E. Koch, J. Jortner in "Rare Gas Solids", ed. M.K. Klein and J.A. Venables, vol. III, (1981)

29) M.L. Ginter and R. Battino, J. Chem. Phys. 52 , 4469 (1970)

30) S.L. Guberman, W.A. Goddard, Phys. Rev. A 12, 1203 (1975)

31) M. Stockton, J.W. Keto, W.A. Fitzsimmons, Phys. Rev. A5, 372 (1972)

32) W.S. Dennis, E. Durbin, W.A. Fitzsimmons, O.Heybey and G.K. Wolters, Phys. Rev. Letters 23, 1083 (1969)
33) F.J. Soley and W.A. Fitzsimmons, Phys. Rev. Letters 32, 988 (1974)
34) J. Jortner, N.R. Kestner, S.A. Rice and M.H. Cohen, J. Chem. Phys. 43, 2614 (1965)
35) A.P. Hickman and N.F. Lane, Phys. Rev. Letters 26, 1216 (1971)
36) J.P. Hansen and E.L. Pollock, Phys. Rev. A 5, 2214 (1972)
37) W. Steets, A.P. Hickman, N.F. Lane, Chem. Phys. Letters 28, 31 (1974)
38) A.P. Hickman, W. Steets and N.F. Lane, Phys. Rev. B12, 3705 (1975)
39) Th. Förster, Ann. Phys. 6, 55 (1948)
40) D.L. Dexter, J. Chem. Phys. 21, 836 (1953)
41) G. Baldini, Phys. Rev. 137 A, 508 (1965)
42) E. Pudewill, F.J. Himpsel, V. Saile, N. Schwentner, M. Skibowski and E.E. Koch, Phys. Stat. Sol. (b) 74, 485 (1976)
43) Z. Ophir, B. Raz and J. Jortner, Phys. Rev. Letters 33, 415 (1974)
44) Z. Ophir, B. Raz, J. Jortner, V. Saile, N. Schwentner, E.E. Koch, M. Skibowski and W.Steinmann, J. Chem. Phys. 62, 650 (1975)

45) D. Pudewill, F.J. Himpsel, V. Saile, N. Schwentner, M. Skibowski, E.E. Koch and J. Jortner, J. Chem. Phys. 65, 5226 (1976)
46) N. Schwentner and E.E. Koch, Phys. Rev. B 14, 4687 (1976)
47) R. Nürnberger, F.J. Himpsel, E.E. Koch and N. Schwentner, Phys. Stat. Sol. (b) 81, 503 (1977)
48) W. Böhmer, R. Haensel, N. Schwentner, E. Boursey, Chem. Phys. (1980)
49) E. Schuberth and M. Creuzburg, Phys. Stat. Sol. (b) 90, 189 (1978)
50) C.E. Moore in "Atomic Energy Levels", NBS 467, vol. I, II, III (1949, 1952, 1958)
51) E. Matthias, R.A. Rosenberg, E.D. Poliakoff, H.G. White, S.T. Lee and D.A. Shirley, Chem. Phys. Letters 52, 239 (1977)
52) P.F. Gruzdev, A.V. Loginov, Opt. Spectrosc. 38, 611 (1975)
53) W.L. Wiese, M.W. Smith, B.M. Miles in "Atomic Transition Probabilities" II, 192, NS RDS-NBS22 (1969)
54) A. Gedanken, B. Raz and J. Jortner, J. Chem. Phys. 59, 5471 (1973)
55) I. Messing, B. Raz and J. Jortner, Chem. Phys. 23, 23 (1977)
56) U. Hahn, R. Haensel, N. Schwentner, G. Zimmerer, to be published

57) J. Jortner, J. Chem. Phys. 64, 4860 (1976)

58) G. Baldini, Phys. Rev. 128, 1562 (1962)

59) V. Saile and E.E. Koch, Phys. Rev. B 20, 784 (1979)
V. Saile, this issue

60) R.S. Knox, Phys. Chem. Solids 9, 265 (1959)

61) N. Schwentner, F.J. Himpsel, V. Saile, M. Skibowski, W. Steinmann and E.E. Koch, Phys. Rev. Letters 34, 528 (1975)

62) A.G. Molchanov, Fiz. Tverd. Tela Kratkie Soobshch, Fiz 4, 9, Sov. Phys. Usp. 106, 165 (1972)

63) F. Coletti and A.M. Bonnot, Chem. Phys. Letters 55, 92 (1978)

64) R.E. Packard, F. Reif and C.M. Surko, Phys. Rev. Letters 70, 1435 (1970)

65) E. Schuberth and M. Creuzburg, Phys. Stat. Sol. (b) 71, 797 (1975)

66) I.Ya Fugol', E.I. Tarasova, Fiz. Niz. Temp. 3, 366 (1977)

67) F. Coletti and J. Hanus, V. VUV Conference, Montpellier I 78 (1977)

68) U. Hahn, B. Jordan, N. Schwentner, K. Sommer and G. Zimmerer, to be published

69) J. Jortner, L. Meyer, S.A. Rice and E.G. Wilson, J. Chem. Phys. 42, 4250 (1965)

70) N.G. Basov, E.M. Balsahov, O.V. Bogdankevich, V.A. Danilychev, G.N. Kasnikov, N.P. Lantzov and D.D. Khodkevitch, J. Luminescence 1, 2, 834 (1970)

71) M. Creuzburg, Solid State Commun. 9, 665 (1971)

72) R. Brodmann, R. Haensel, U. Hahn, U. Nielsen and G. Zimmerer, Chem. Phys. Letters 29, 250 (1974)

73) U. Hahn, N. Schwentner and G. Zimmerer, Opt. Commun. 21, 237 (1977)

74) R. Kink ., A. Lôhmus, M. Selg, T. Soovik, Phys. Stat. Sol. (6), 84, K61 (1977)

75) M.J. Carvalho and G. Klein, J. Luminescence 18/19, 487 (1979)

76) R. Kink and M. Selg, to be published (1980)

77) S.D. Druger and R.S. Knox, J. Chem. Phys. 50, 3143 (1969)

78) K.S. Song, Canadian J. of Phys. 49, 26 (1971)

79) T.P. Das, A.N. Jette and R.S. Knox, Phys. Rev. 134, 1079 (1964)

80) For a review see Ch.K. Rhodes in "Excimer Lasers", Springer, Berlin (1979)

81) J.S. Cohen and B. Schneider, J. Chem. Phys. 61, 3230 (1974)

82) F.L. Kunsch and F. Coletti, J. Chem. Phys. 70, 726 (1979)

83) V. Yakhot, M. Berkowitz and R.B. Gerber, Chem. Phys. 10, 61 (1975)
V. Yakhot, Chem. Phys. 14, 441 (1976

84) Z. Ophir, N. Schwentner, B. Raz, M. Skibowski and J. Jortner, J. Chem. Phys. 63, 1072 (1975)

85) N. Schwentner, E. E. Koch, Z. Ophir and J. Jortner, Chem. Phys. 34, 281 (1978)

86) R. Rudolf and N. Schwentner, to be published

87) R.R. Chance, . . Prock and R. Silbey, J. Chem. Phys. 65, 2527

88) F.B. Dunning, R.P. Rundel, R.E. Stebbing, Rev. Sci. Instrum. 46, 697 (1975)

H. Conrad, G. Ertl, J. Küppers, K. Gerard and H. Haberland, Phys. Rev. Letters (1980)

89) I.T. Steinberger, P. Maaskant and S.E. Weber, to be published in J. Chem. Phys.

90) H.C. Wolf in "Advances, in Atomic and Molecular Physics" (ec. D.R. Bates), vol. 3, p. 119, Academic Press, New York, London (1967)

91) C. Powell and Z.G. Soos, J. Luminescence 11, 1 (1975)

92) N. Schwentner, U. Hahn, D. Einfeld, G. Mühlhaupt, Nuclear Instr. Methods 167, 499 (1979)

Table 1: Transition energies (in eV) and life times(in 10^{-9}s)of rare gas atoms in a Ne matrix and of free atoms (from ref. 17)

	exciton state	atomic state	energy in Ne matrix			energy in free atom^{c}	life time	
			absorption^{a},	emission^{a},	emission^{b}		in Ne matrix^{a},	of free atom
Xe/Ne		6s $1s_5$			8.34;8.47	8.31		
	n =1	6s $1s_4$	9.06	8.61	8.61	8.44	2.4$\pm$0.2	3.46$\pm$0.09^{d}
		6s' $1s_3$				9.45		
	n'=1	6s' $1s_2$	10.05	9.80	9.77	9.57	3.5$\pm$0.2	3.44$\pm$0.07^{d}
	n =2	5d $3d_2$	11.32	10.78		10.40	1.3$\pm$0.2	1.40$\pm$0.07^{d}
Kr/Ne		5s $1s_5$			10.02	9.91		
	n =1	5s $1s_4$	10.6	10.10	10.16	10.03	2.5$\pm$0.2	3.18$\pm$0.12^{d}
		5s' $1s_3$				10.51		
	n'=1	5s' $1s_2$	11.22	10.78		10.64	3.1$\pm$0.5	3.11$\pm$0.12^{d}
	n =2	4d $3d_5$	13.35	12.12		12.04	13.0$\pm$2	44.5^{e}
Ar/Ne		4s $1s_5$			11.63	11.54		
	n =1	4s $1s_4$	12.51	11.70	11.71	11.62	5.8$\pm$0.3	8.4^{f}
		4s $1s_3$			11.81	11.72		
	n'=1	4s' $1s_2$	12.74	11.92	11.92	11.83	1.2$\pm$0.2	2.0^{f}
	n =2	3d $3d_5$	14.82	13.93		13.86	420$\pm$20	

a) ref. 17 c) ref. 50 e) ref. 52
b) ref. 49 d) ref. 51 f) ref. 53

Table 2: Energies and intensities in luminescence bands of free excitons (a), atomic type (b), molecular type vibrationally excited (c) and molecular type vibrationally relaxed (d) localized excitons. The values have been estimated from experimental data for Ne from ref. 71 for Ar from ref.26 for Kr from ref.24,68 and for Xe from ref.26. $\hbar\omega_D$, 2B, E_{LR} and H_m are the Debeye energies, the free exciton bandwidth in k-space, the lattice relaxation energy and the barrier height for localization respectively according to ref.26. All energies in eV.

	energy				relative intensity						molecular center		atomic center	
	a	b	c	d	a	b	c	d	$\hbar\omega_D$	2B	E_{LR}	H_m	E_{LR}	H_m
Ne		16.5-17	13-16			1.0	1.0		0.0064	0.4	2.0	0.0003	1.25	0.0008
Ar	12.1	11.64,11.58	11.37	9.8	$1x10^{-4}$	$3x10^{-2}$	$5x10^{-2}$	1.0	0.008	0.7	1.86	0.002	1.05	0.001
Kr	10.15	10.05	9.7	8.4	$5x10^{-3}$	$5x10^{-3}$	10^{-2}	1.0	0.0062	0.9	1.38	0.01	0.77	0.01
Xe	8.35			7.6,7.1	10^{-3}			1.0	0.0055	0.9	0.85	0.02	0.05	5.6

Figure captions

1) Potential curves for He. The curves have been adopted from Ginter and Battino[29], except the singulet states above $C\ ^1\Sigma_g^+$ (Guberman and Goddard[30]). Arrows indicate observed transitions in liquid He. Transitions to the ground state: Stockton et al.[31]; radiative decay between excited states: Dennis et al.[32]; transient absorption: Soley and Fitzsimmons[33].

2) Excitation spectra (emission intensity versus excitation energy) for Xe in Ne (hatched curves) for each of the three emission bands I, II and III. Each emission band is shown infront of the corresponding excitation spectrum on the same energy scale. Prominent maxima in the excitation spectra are marked by a, b, c, d, e. Further the positions of excitonic states n = 1, 2, 3, 4 and n = 1', 2', 3', 4' ar marked. The inserts at the right hand side provide a survey about the time dependence of the intensity in the emission bands at prominent excitation energies. The left hand side insert shows the complete emission spectrum. From ref. 17.

3) Energy level scheme for a solid Ne host and Xe, Kr and Ar guest atom states. Arrows indicate the

exciton states $n = 1$, $n' = 1$, $n = 2$ of Xe for which the relaxation cascade (Fig. 4) has been determined.

4) Dependence of the energy position of the lowest states of Xe atoms on the density of surrounding Ne atoms (55). The density is expressed by the mean nearest neighbour separation between a Xe atom and surrounding Ne atoms. The Ne density ranges from 0 through liquid and solid phase. For solid Ne (density $1.44\ (\mathrm{g\ cm^{-3}}) \hat{=} 3.13$ Å) the maxima of the excitation spectra[17] (left hand side) have been included. The density around relaxed Xe atoms follows from a comparison with the emission spectra (right hand side, horizontal lines) From ref. 17.

5) Left part: experimental radiative (⇝) and non-radiative (→) electronic relaxation pathways and time constants (in 10^{-9}s) for Xe in Ne in a configuration coordinate diagram. The excitation channels $n = 1$, $n' = 1$ and $n = 2$ and the matrix relaxation (⟿) are included. Right part: atomic energy levels (Paschen notation) of Xe with some lifetimes for radiative transitions to the ground state (⇝). Long bars correspond to states with allowed, short bars to forbidden transitions to the ground state (from ref. 17).

6) Relaxation cascade for Ar in Ne similar to the results shown in Fig. 5. Important radiative transitions between excited atomic transitions are included (⇝) (from ref. 17).

7) Temperature dependence of the transition rate of Kr $n = 1$ excitons in an Ar matrix. Crosses, experimental points; solid line, fit (see text) (from ref. 56).

8) Scheme for exciton states in solid Kr. Right hand side: dispersion of the $n = 1$ and $n' = 1$ excitons versus the wave vector k of the excitons in analogy to the calculation for Ar[3,60]. T and L indicate transversal and longitudinal excitons and the dashed lines correspond to optical forbidden exciton branches. Center: exciton series at $k = 0$ observed in absorption experiments[16,59]. Left hand side: energy of molecular type localiced excitons versus the internuclear separation r of an excited Kr atom and a neighbouring Kr atom in analogy to molecular potential curves for Xe[62].

9) Electron energy distribution curves (counting rates versus kinetic energy) from films of 1 % Xe in Ar and 1 % Xe in Ne for several excitation

energies (below and within the n = 1, n' = 1 and n = 2, n' = 2 host exciton bands) (after ref. 46). The diagonal bars indicate the highest possible electron energies. Electrons up to this energy are expected when the whole free exciton energy is transfered.The two maxima are separated by the spin orbit splitting Δ_{so} of Xe (see Fig. 3)

10) Lower part: diffusion length of Kr excitons versus the excitation energy of the excitons. The dashed lines indicate the trend. The scattering of the points corresponds to the uncertainities involved in the evaluation of l (from ref. 86). Upper part: absorption coefficient k of Kr (imaginary part of the complex refractive index) versus photon energy (from ref. 89) used in the evaluation. The maxima correspond to the n = 1, n' = 1 and n = 2 excitons.

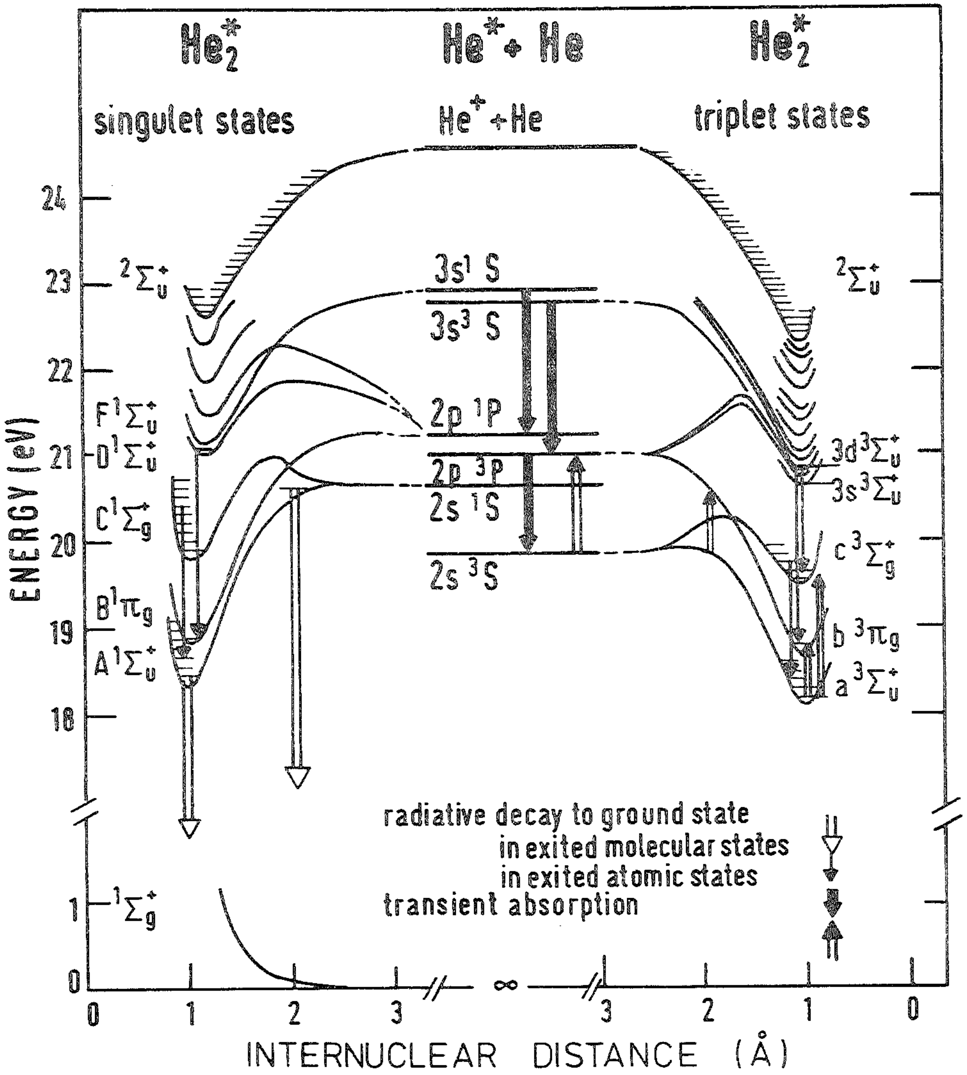


Fig. 1

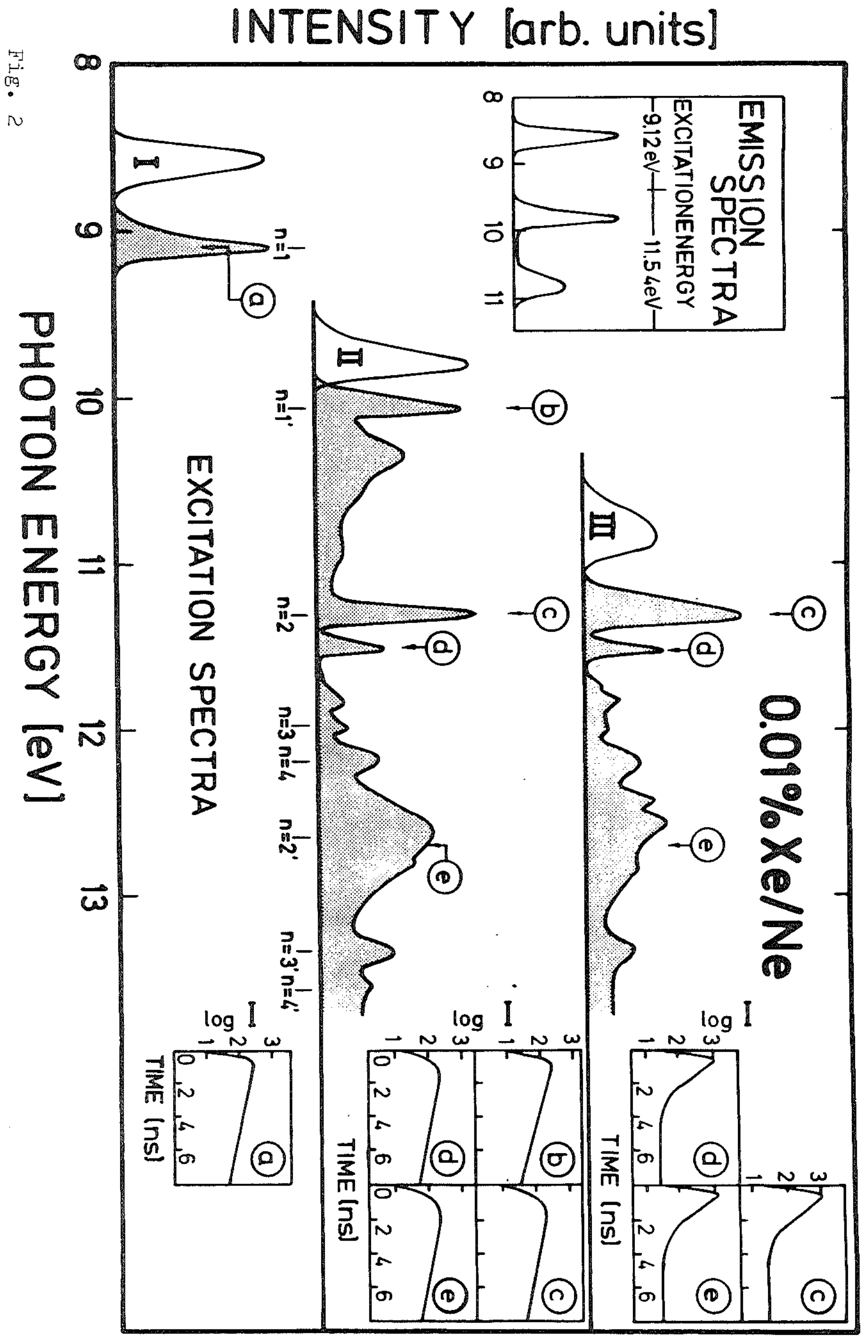

INTENSITY [arb. units]
PHOTON ENERGY [eV]
8
9
10
11
12
13
EXCITATION SPECTRA
EMISSION SPECTRA
EXCITATIONENERGY
9.12eV
11.54eV
0.01% Xe/Ne
I
II
III
n=1
n=1'
n=2
n=3 n=4
n=2'
n=3' n=4'
a
b
c
d
e
log I
TIME [ns]
0 2 4 6
1 2 3

Fig. 2

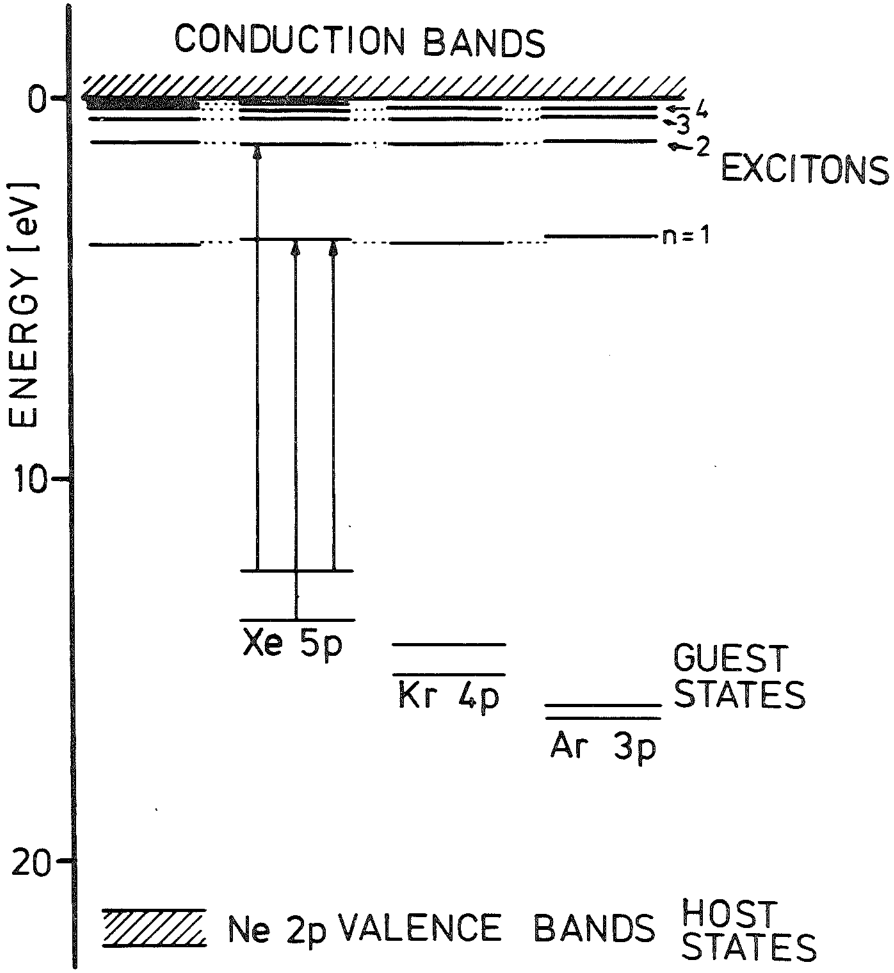

CONDUCTION BANDS
0
10
20
ENERGY [eV]
EXCITONS
4
3
2
n=1
Xe 5p
Kr 4p
Ar 3p
GUEST STATES
Ne 2p VALENCE BANDS
HOST STATES

Fig. 3

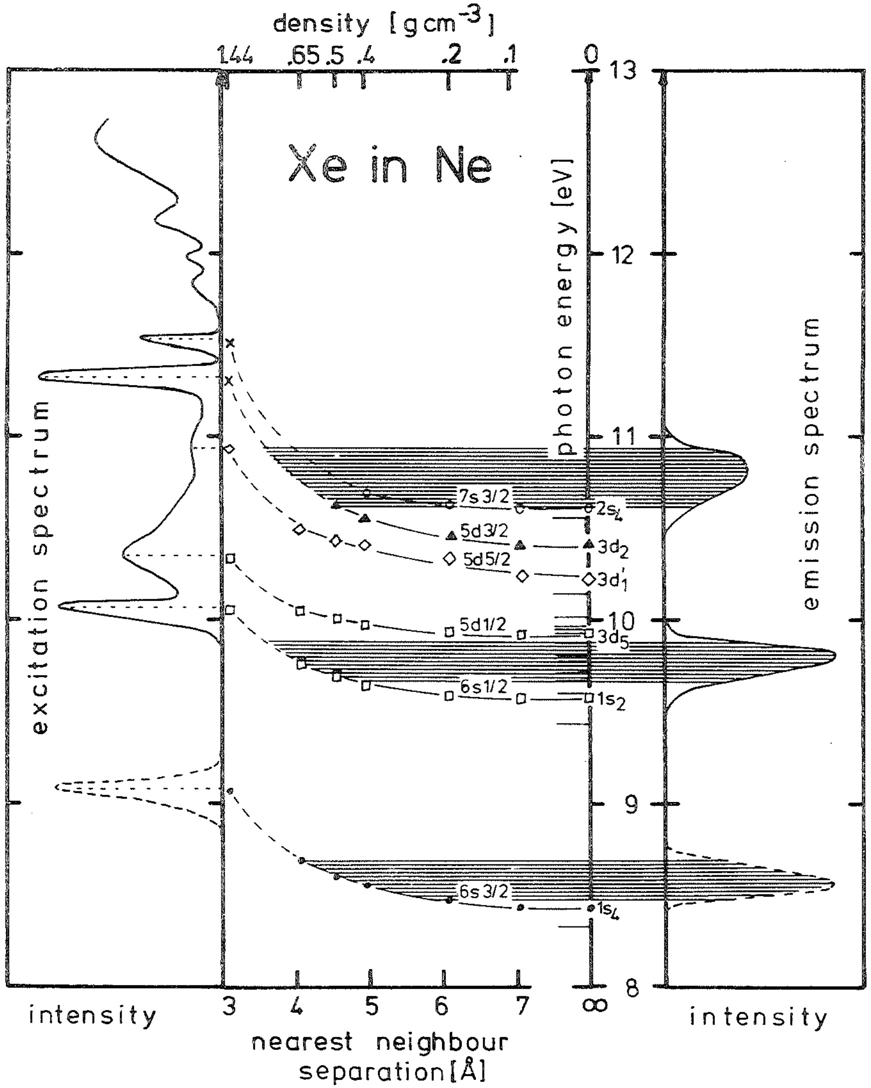

density [g cm^{-3}]
1.44
.65
.5
.4
.2
.1
0
Xe in Ne
excitation spectrum
photon energy [eV]
emission spectrum
13
12
11
10
9
8
7s 3/2
2s$_4$
5d 3/2
3d$_2$
5d 5/2
3d$'_1$
5d 1/2
3d$_5$
6s 1/2
1s$_2$
6s 3/2
1s$_4$
intensity
3
4
5
6
7
∞
nearest neighbour separation [Å]
intensity

Fig. 4

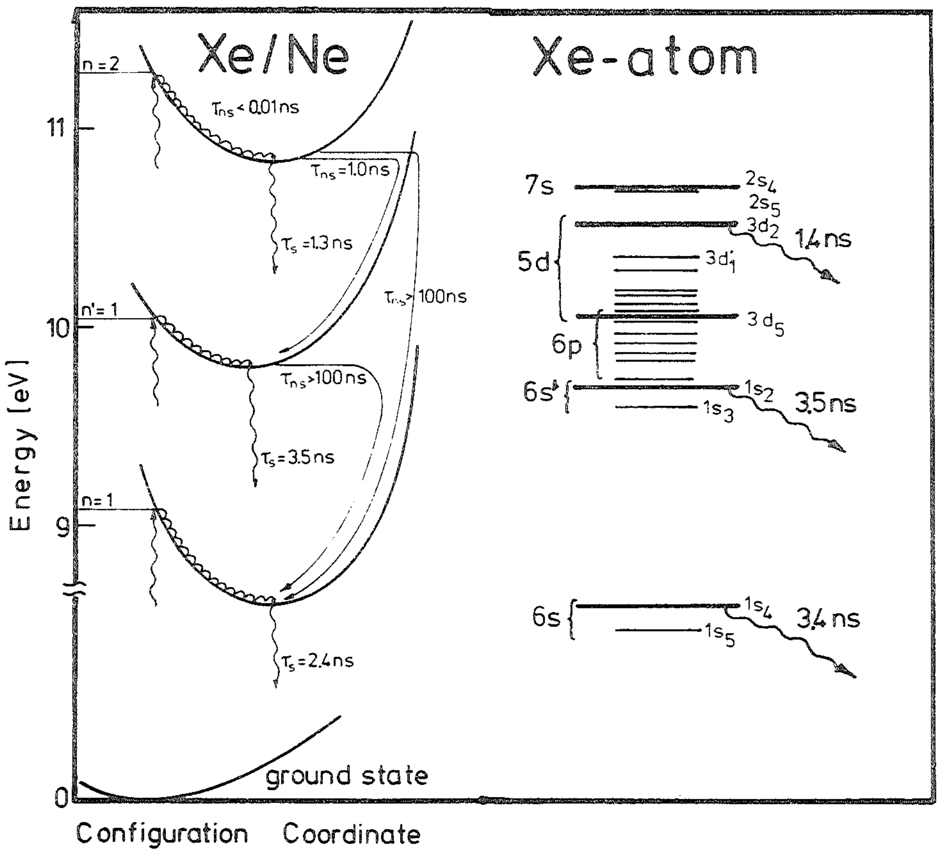
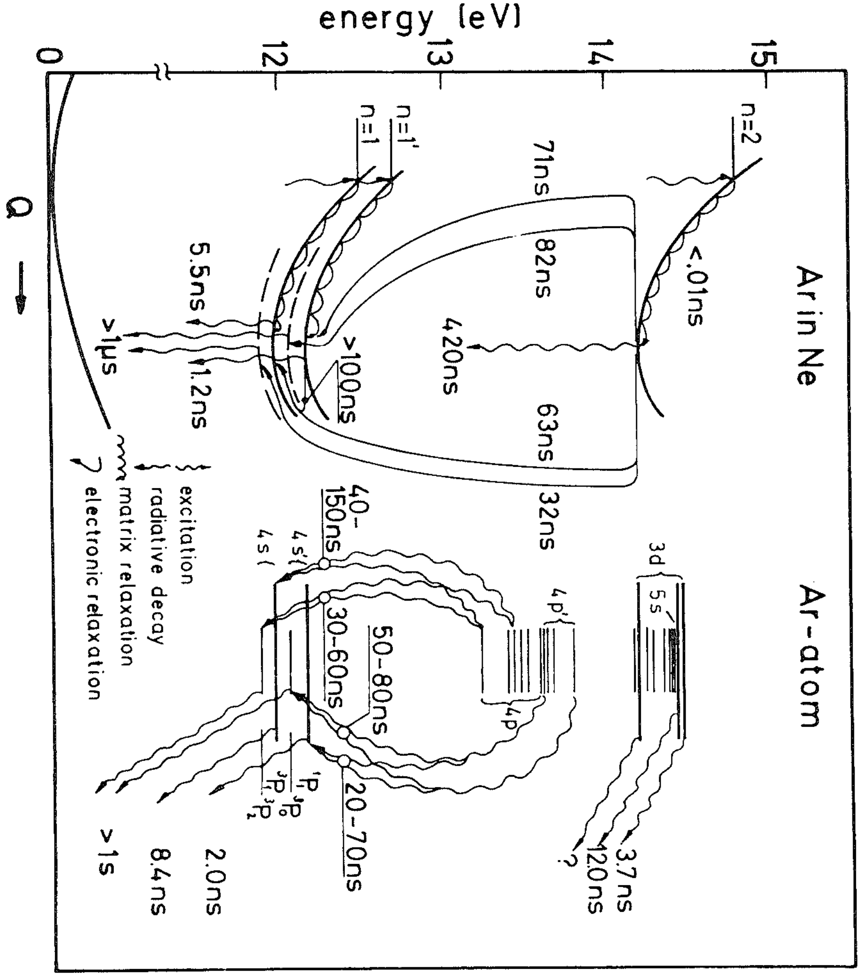

Xe/Ne
Xe-atom
Energy [eV]
11
10
9
0
n = 2
n' = 1
n = 1
τ_{ns} < 0.01 ns
τ_{ns} = 1.0 ns
τ_s = 1.3 ns
τ_{ns} > 100 ns
τ_{ns} > 100 ns
τ_s = 3.5 ns
τ_s = 2.4 ns
ground state
7s
2s$_4$
2s$_5$
3d$_2$
1.4 ns
5d
3d$'_1$
3d$_5$
6p
6s'
1s$_2$
1s$_3$
3.5 ns
6s
1s$_4$
1s$_5$
3.4 ns
Configuration Coordinate

Fig. 5

Fig. 6


energy (eV)
0
12
13
14
15
Ar in Ne
Ar-atom
n=2
n=1'
n=1
<.01ns
71ns
82ns
420ns
63ns
32ns
>100ns
5.5ns
1.2ns
>1μs
Q
3d
5s'
4p'
4p
4s'
4s
40-150ns
30-60ns
50-80ns
20-70ns
1P1
3P0
3P1
3P2
3.7ns
12.0ns
?
2.0ns
8.4ns
>1s
excitation
radiative decay
matrix relaxation
electronic relaxation

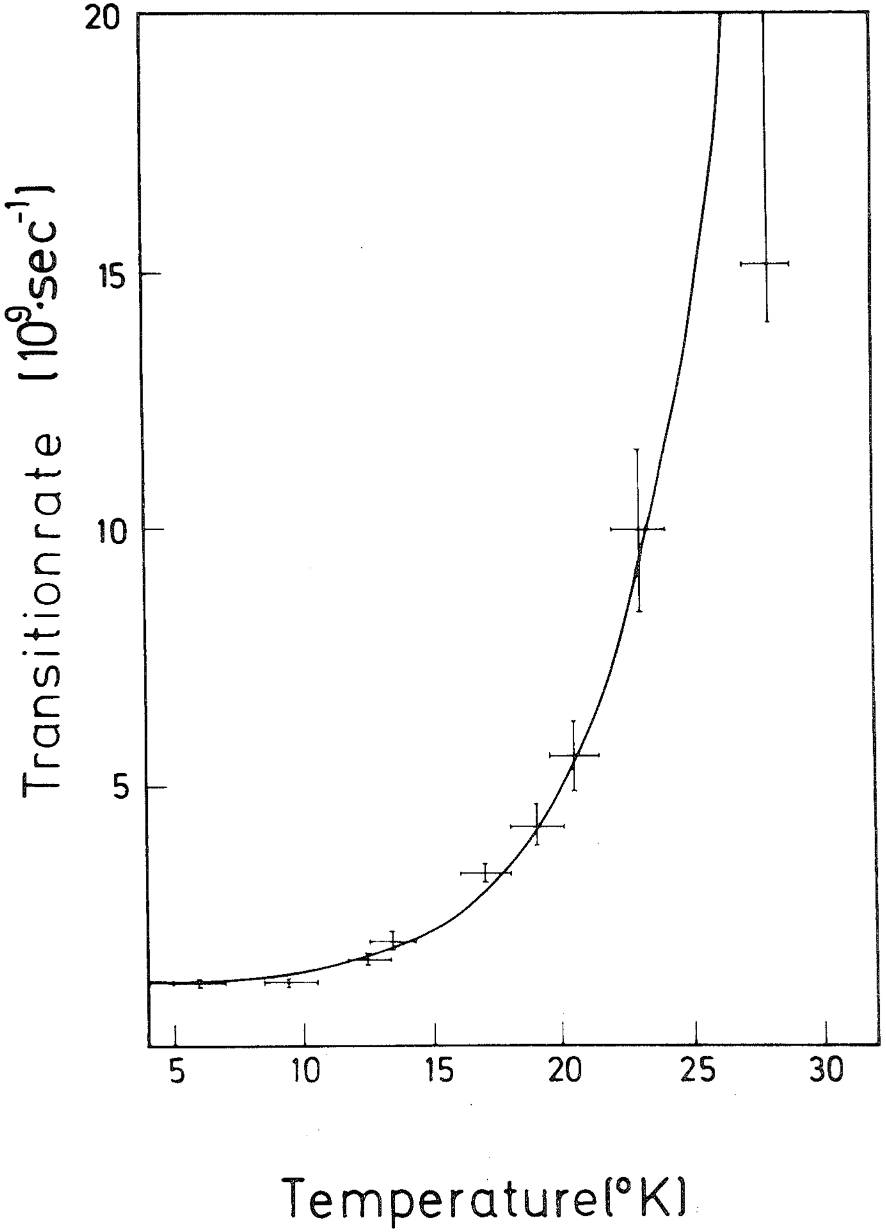

Transitionrate [10^9·sec^-1]
20
15
10
5
5
10
15
20
25
30
Temperature(°K)

Fig.

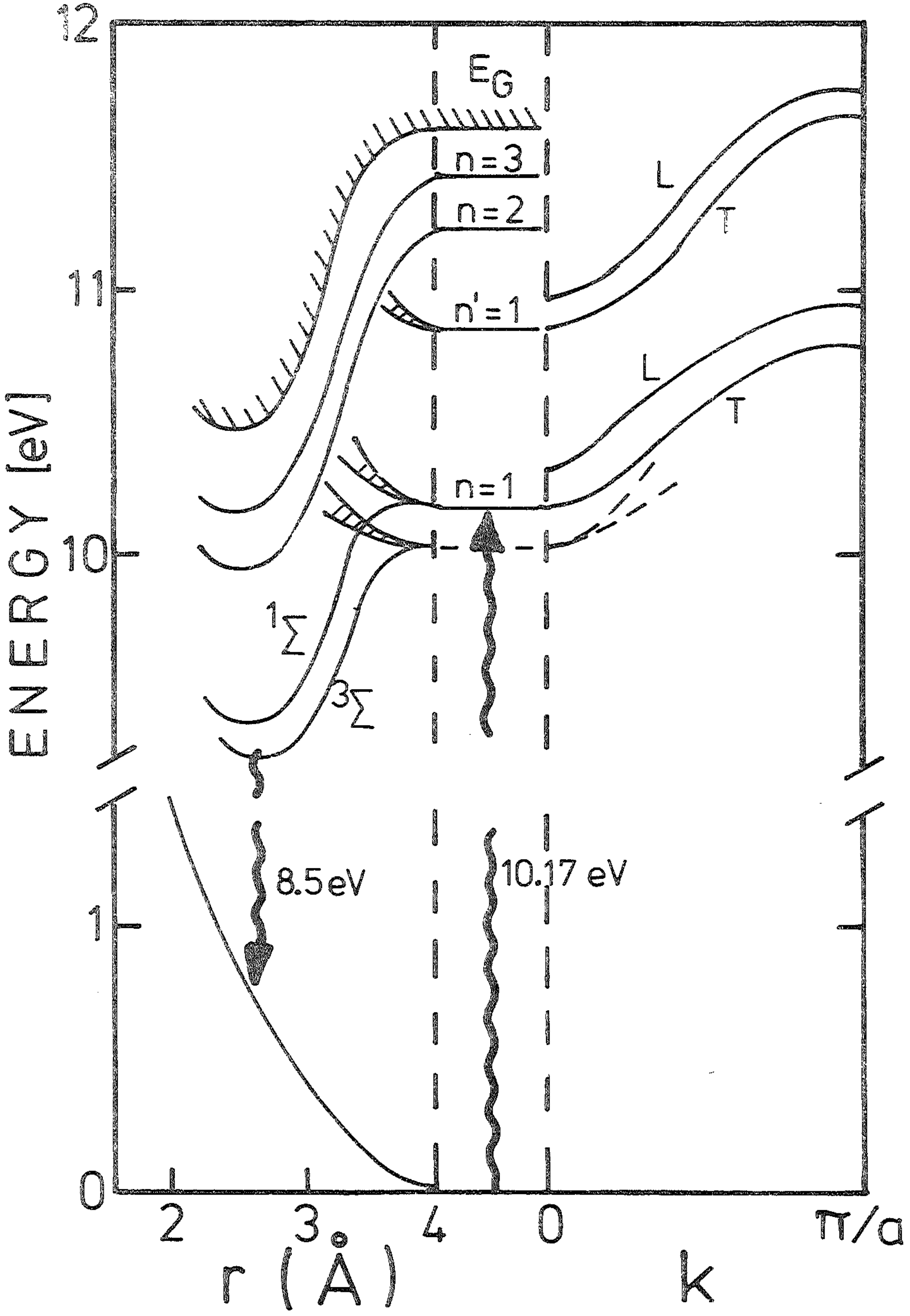

ENERGY [eV]
12
11
10
1
0
E_G
n=3
n=2
n'=1
n=1
L
T
L
T
$^1\Sigma$
$^3\Sigma$
8.5 eV
10.17 eV
2
3
4
0
π/a
r (Å)
k

Fig. 8

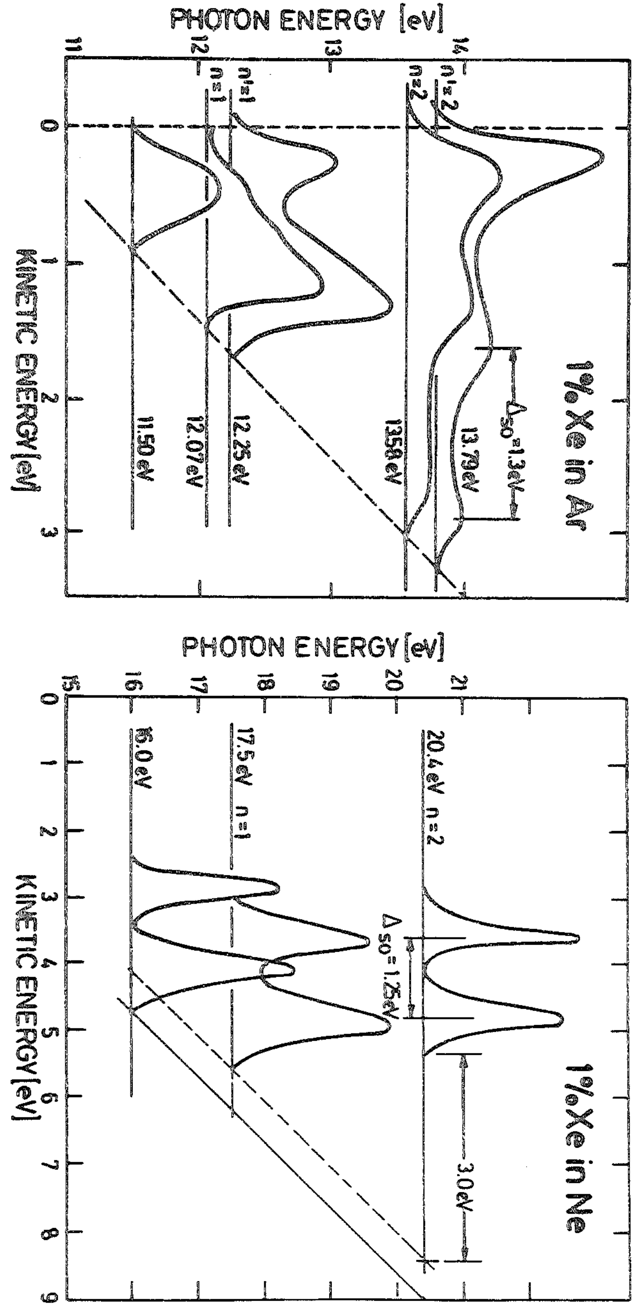

PHOTON ENERGY [eV]
11
12
13
14
n=1
n'=1
n=2
n'=2
KINETIC ENERGY [eV]
0
1
2
3
11.50 eV
12.07 eV
12.25 eV
13.58 eV
13.79 eV
Δ_{so}=1.3eV
1% Xe in Ar
PHOTON ENERGY [eV]
15
16
17
18
19
20
21
16.0 eV
17.5 eV n=1
20.4 eV n=2
Δ_{so}=1.25eV
3.0 eV
KINETIC ENERGY [eV]
0
1
2
3
4
5
6
7
8
9
1% Xe in Ne

Fig. 9

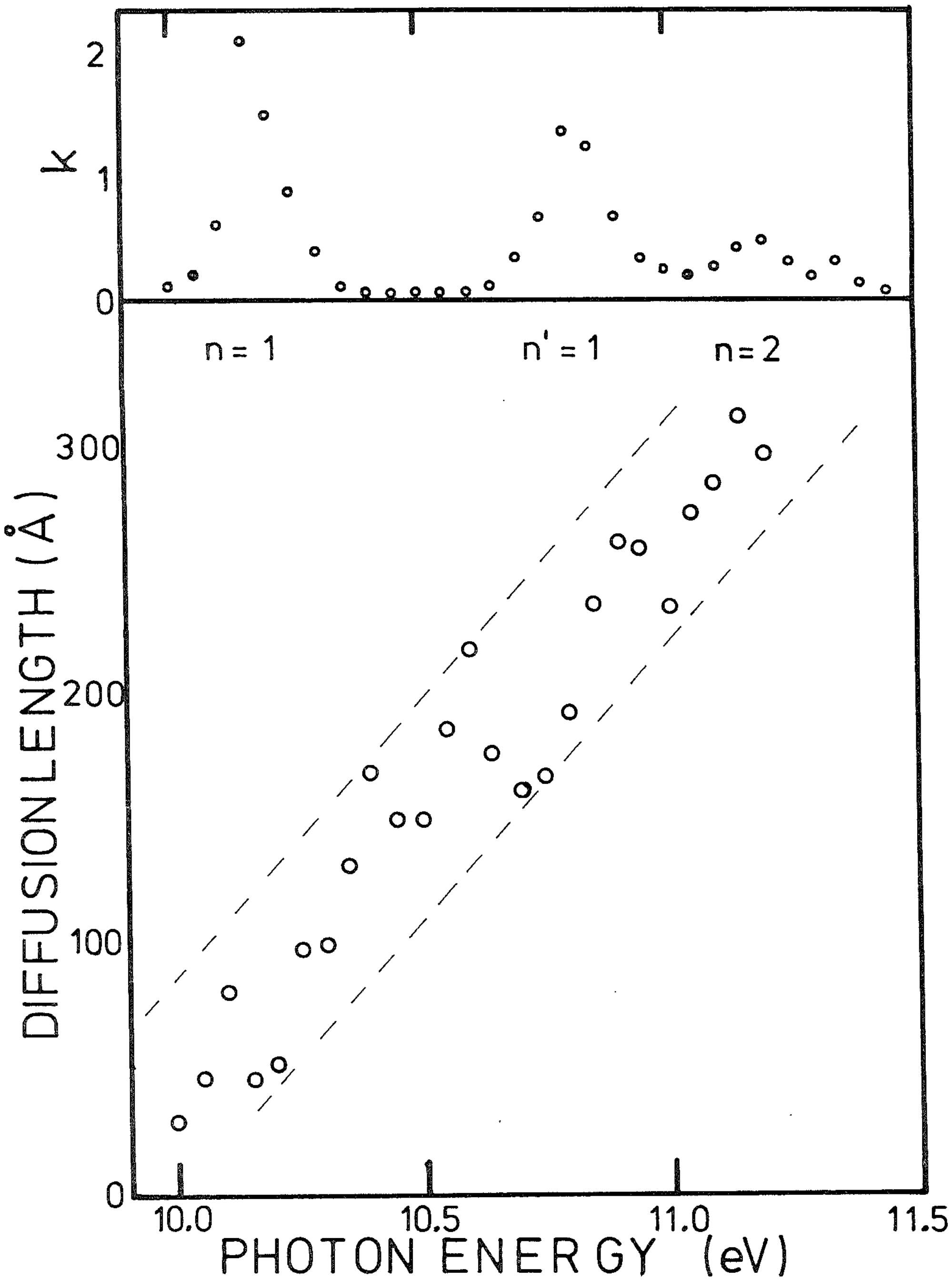

k
2
1
0
n = 1
n' = 1
n = 2
DIFFUSION LENGTH (Å)
300
200
100
0
10.0
10.5
11.0
11.5
PHOTON ENERGY (eV)

Fig. 10