PHOTOELECTRON ENERGY DISTRIBUTION MEASUREMENTS FROM BENEZENE

IN RARE GAS MATRICES

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Photoelectron energy distributions (PEDs) are presented for benzene molecules embedded in solid Ar, Kr and Xe rare gas matrices obtained with monochromatized synchrotron radiation for selective excitation in the range hν = 8 eV to 15 eV. For photon energies in the transparent region of the matrices direct emission from the occupied benzene initial states in the band gap of the matrix is observed. Energy transfer from the matrix exciton states to the benzene guest molecules takes place when the host exciton states are excited. The PEDs show that energy of unrelaxed excitons is transferred and that transfer to initial states just at the ionization threshold is favoured.

I. Introduction

The energetics and the dynamics of excited states of impurity states consisting of atoms or molecules isolated in rare gas matrices have attracted considerable interest [1]. While optical and luminescence spectroscopy has been applied for some time to investigate these systems [2] photoemission, in particular photoelectron energy distribution (PED) measurements, have only recently been successfully applied to atomic impurities in rare gas matrices [3].

In the present communication we report on PED-measurements for Ar, Kr and Xe matrices doped with benzene. When matrix excitons are excited energy transfer to guest molecules is observed. The energy transfer manifests itself in an increase of the photoemission yield although the matrix exciton states have energies below the vacuum level of the pure solid and cannot contribute directly to photoemission. The energy distribution of photoelectrons will immediately show the amount of transferred energy, provided the distribution of initial states of the benzene acceptor molecules is known. This method has been applied to rare gas matrices doped with atoms and it has been demonstrated that energy transfer takes place on a picosecond time scale from unrelaxed n=1 excitons [3]. Depending on the matrix either energy transfer from unrelaxed higher (n=2) exciton states or relaxation of higher excitons to the n=1 state as well as partial relaxation prior to energy transfer have been observed [3].

The interpretation of energy transfer processes has been a controversial topic even for the most thoroughly studied systems, namely doped organic crystals [4]. Recent detailed experimental investigations based on the analysis of the time dependence of the luminescence seem to have settled the problem of the analysis and interpretation of the results in this case [5].

In rare gas solids as a result of the strong lattice relaxation, the energies

of the lowest "free" excitons are larger by more than 1 eV than the energies

of the relaxed self trapped exciton states (2). For these systems energy

transfer has frequently been discussed by considering the amount of transferred

energy. Either diffusion of free excitons or a Förster-Dexter type dipole-dipole

interaction with relaxed electronically excited diatomics or a combination

of both have been invoked for a description of energy transfer processes, but

a detailed understanding of the mechanism is still missing. If the transferred

energy corresponds to the stokes shifted luminescence band of the matrix, the

Förster-Dexter mechanism is dominant. If the full energy of the free exciton

is transferred, diffusion of excitons has to be favoured (2).

Energy transfer in benzene doped rare gas matrices has been investigated until

now only by luminescence- (6,7) and photoemission yield spectroscopy (8,9).

In these experiments competition with surface quenching (6-9) and a transfer

rate increasing with exciton excitation energy (6) have been reported. From

PED-measurements one can hope to obtain information about the transferred

energy. Furthermore, PED curves allow to locate the initial states in the

band gap of the matrix, and to analyse the partial photoionization cross

section and the partial energy transfer cross section of the benzene initial

states.

II. Experiment

Benzene and rare gases have been mixed in the gas phase with partial pressures

according to the desired concentration. Thin films of these mixtures have been

frozen onto a gold substrate cooled by a liquid Helium flow cryostat. The back-

ground pressure was below 10^{-9} Torr. Monochromatized synchrotron radiation of

the DESY synchrotron was used for selective excitation of the samples. The

energy distribution of electrons emitted within a cone of 5° normal to the

sample surface has been analysed using a combination of retardation field and

static electron lenses. The total electron yield and the reflectance of the

samples have also been recorded. The thickness of the sample films has been

determined by measuring the interferences in the reflected light with in-

creasing film thickness during deposition. Details of the experimental arrange-

ment are given in Ref. 3.

III. Results and Discussion

In Fig. 1 representative PEDs are shown for C_6H_6 in Ar, Kr and Xe matrices.

Similar PEDs have been observed for various thicknesses and concentrations

without significant changes. Intensity versus electron kinetic energy is

shown, where the zero of the energy scale corresponds to the vacuum level of

the sample. The spectra are shifted upwards with respect to each other pro-

portional to the exciting photon energy. Thus structures due to a distinct

initial state will follow the diagonal lines shown in Fig. 1 provided that the

electrons get an energy equal to the photon energy $h\nu$. Two processes, the

escape process and electron emission from the Au-substrate which might con-

tribute to the PEDs are neglected in the discussion. The influence of the

escape function is considered to be small and it is not expected to produce

additional structure because (i) at the kinetic energies of the photoelec-

trons considered here, energy loss in the matrix due to electronic excitations

is not essential (10), (ii) due to the low concentrations used the density of

guest molecules is at least only 1/100 part of that of the matrix and (iii)

energy loss processes due to electronic excitations of the guest molecules are

only possible for electron energies above 3.5 - 5 eV (11) and (iv) the cross

sections for vibrational excitations are not expected to depend strongly on

electron kinetic energy. We note, however, that the excitation of intramole-

cular vibrations and phonons gives rise to the strong maximum of scattered

electrons in the PED's at kinetic energies below 0.5 eV. Electron emission from

the substrate should depend strongly on the thickness of the films and on the benzene concentration which was not observed for the main features to be discussed below.

The spectra will be discussed in two parts (A) the transparent region of the matrix where PEDs of electrons directly excited from C_6H_6 are observed and (B) the excitonic region of the matrix up to the band gap.

A. Transparent Region of the Matrix

The ionization energies $E_{Th}^{C_6H_6}$ for benzene in the different rare gas matrices are obtained from the extrapolation of the diagonal lines marking the highest kinetic energy of the photoelectrons for a given $h\nu$ to $E_{kin} = 0$. They are given in Table I together with other relevant energies. For the ionization energies determined in this manner we find good agreement with our previous results from photoemission yield experiments [12]. The transparent region of the matrix extends from the ionization energy $E_{Th}^{C_6H_6}$ in the particular rare gas matrix to the n=1 excitons of that matrix (≈12.0 eV for Ar, ≈10 eV for Kr and ≈8.3 eV for Xe). In order to identify the initial states of C_6H_6 in the matrix, PEDs for pure solid benzene [13] are also shown in Fig. 1 together with the MO-assignments. The density of the occupied benzene orbitals and the electronic states of the different matrices are shown schematically in Fig. 2. The small energy gap for Xe of ~0.15 eV between $E_{Th}^{C_6H_6}$ and the n=1 exciton states does not allow to draw any conclusion. In the case of C_6H_6 in Kr a maximum which is attributed to the uppermost $1e_{1g}$ states of benzene is growing up to the limiting photon energy of 10.05 eV. For Ar a maximum due to the $1e_{1g}$ orbital dominating the spectrum at $h\nu=10.31$ eV and a shoulder near zero kinetic energy due to the unresolved $1a_{2u}$ and $3e_{2g}$ orbital at $h\nu=11.3$ eV are observed. It should be noted that at $h\nu=11.3$ eV the relative intensity of the $1e_{1g}$ band is strongly reduced. This might be due to an enhancement of the partial ionization cross section of

the $1a_{2u}$, $3e_{2g}$ bands near threshold relative to the cross section of the $1e_{1g}$ state.

B. Excitonic Region of the Matrix

The excitonic region of the matrix is characterized by strong absorption by the host matrix. Therefore primarily the host states are now excited by photons. The major part of the photoelectrons is then produced by energy transfer to the occupied benzene states in the band gap (see the insert in Fig. 1).

The discussion below focuses on the following three questions: (i) does energy transfer from relaxed matrix excitons (R_2^* centers) as observed in luminescence occur or (ii) is energy transfer from the free exciton states observed and (iii) which benzene states are populated by the energy transfer mechanism?

In Xe the n=1,2 excitons and the spin orbit partner n'=1 have been excited. The maximum kinetic energy of the ejected electrons increases according to the increase in the photon energy from n=1 to n=2 and to n'=1. This shows that for these electrons the whole amount of excitation energy is transferred. We conclude that a relaxation of n=2 and n'=1 to n=1 and the relaxation of the n=1 exciton to a Xe_2^* self trapped exciton state is slow relative to the energy transfer rate. A contribution due to energy transfer from Xe_2^* centers can be excluded. This is evident by observing that the PED resulting from such a state would be below the vacuum level as indicated by curve L in Fig. 1, the result of folding the C_6H_6-$1e_{1g}$ band with the luminescence emission curve [6].

In Kr the n=1,2,3 exciton states and the spin orbit partners n'=1,2 have been excited. When the n=1 exciton state is populated the structures in the PEDs are similar to PEDs due to the $1e_{1g}$ state excited directly as is evident by comparison with PEDs immediately below the Kr n=1 exciton and those from pure ben-

zene. The same holds for the $n'=1$ exciton state. (The corresponding PED's for C_6H_6 in Ar for photon energies in this range are similar. Note, that in the Ar matrix there are no exciton states in this range.) For Kr at higher excitation energies ($n=2$) the contribution of the $1e_{1g}$ state is reduced and for $n=3$ and $n'=2$ this tendency is even stronger. A shoulder which can be correlated with the $1a_{2u}+3e_{2g}$ band appears. The general shift of the main intensity in the PEDs towards smaller kinetic energies could be associated with a relaxation of the exciton states prior to energy transfer. Complete relaxation to the self-trapped exciton state is unlikely as the experimental data are incompatible with the PED derived by folding the $1e_{1g}$ band with the Kr_2^* emission band L. Electronic relaxation within the exciton manifold to the $n=1$ exciton would lead to the same shape of the PED as observed by direct excitation into the $n=1$ exciton, which is not observed in the experiment. Thus we believe that the whole excitation energy is transferred. We explain the apparent shift to lower kinetic energies by the fact that this energy is transferred preferentially to the lowest possible benzene initial level which can be excited just above threshold.

In Ar matrices the $n=1,2$ excitons and $n'=1,2$ excitons have been excited. The convolution of the $1e_{1g}$ band with the Ar_2^* luminescence band (dashed curve) shows a maximum at ~ 1 eV kinetic energy. In the case of energy transfer from the Ar_2^* state a maximum at this energy independent of $h\nu$ should appear. Since this is not observed we argue that again energy is transferred directly from unrelaxed exciton states. The PEDs are determined by the partial cross sections of the C_6H_6 initial states for energy transfer. Again, states leading to final states just above the ionization threshold are prefered compared to higher lying initial states. Therfore the maxima respectively shoulders of the $1e_{1g}$, the $1a_{2u}+3e_{2g}$ and the $3e_{1u}$ bands appear and disappear with increased photon energy. This observation is confirmed by the spectrum taken with $h\nu = 13.05$ eV between the $n=1'$ and $n=2$ exciton state of the host, where Ar is highly transparent (14).

In this case electrons are predominantly excited directly from the C_6H_6 molecule excluding the relaxation mechanism within the matrix. Nevertheless this spectrum fits smoothly into the whole series of spectra.

IV. Conclusions

The occupied molecular orbitals of benzene isolated in rare gas matrices can be located and correlated with those from pure solid benzene as long as they are within the band gap of the host and do not overlap with the valence bands of the matrix. The partial cross section for ionizing these states are strongly dependent on the excitation energy, in particular near the ionization threshold. Those states leading to emission just above threshold are favoured. For a complete discussion of the PEDs from benzene doped rare gas solids the escape probability, electron emission from the gold substrate and the $h\nu$-dependence of the partial cross sections have to be taken into account in addition to detailed considerations of energy transfer and relaxation processes. The present preliminary discussion of the energy transfer problem results in qualitative conclusions. Energy transfer is observed from unrelaxed matrix excitons. Thus our results favour a diffusion of matrix excitons rather than a Förster-Dexter type energy transfer mechanism for a spatially localized excimer molecule.

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Table I Parameter for the C_6H_6 impurity states in Ar, Kr and Xe. All energies are in eV. A superscript i denotes values for the impurity states. E_n, excitation energies (Ref. 13); E_G, E_G^i band gap energy; E_{Th}, E_{Th}^i, threshold energy for photoemission = vacuum level.

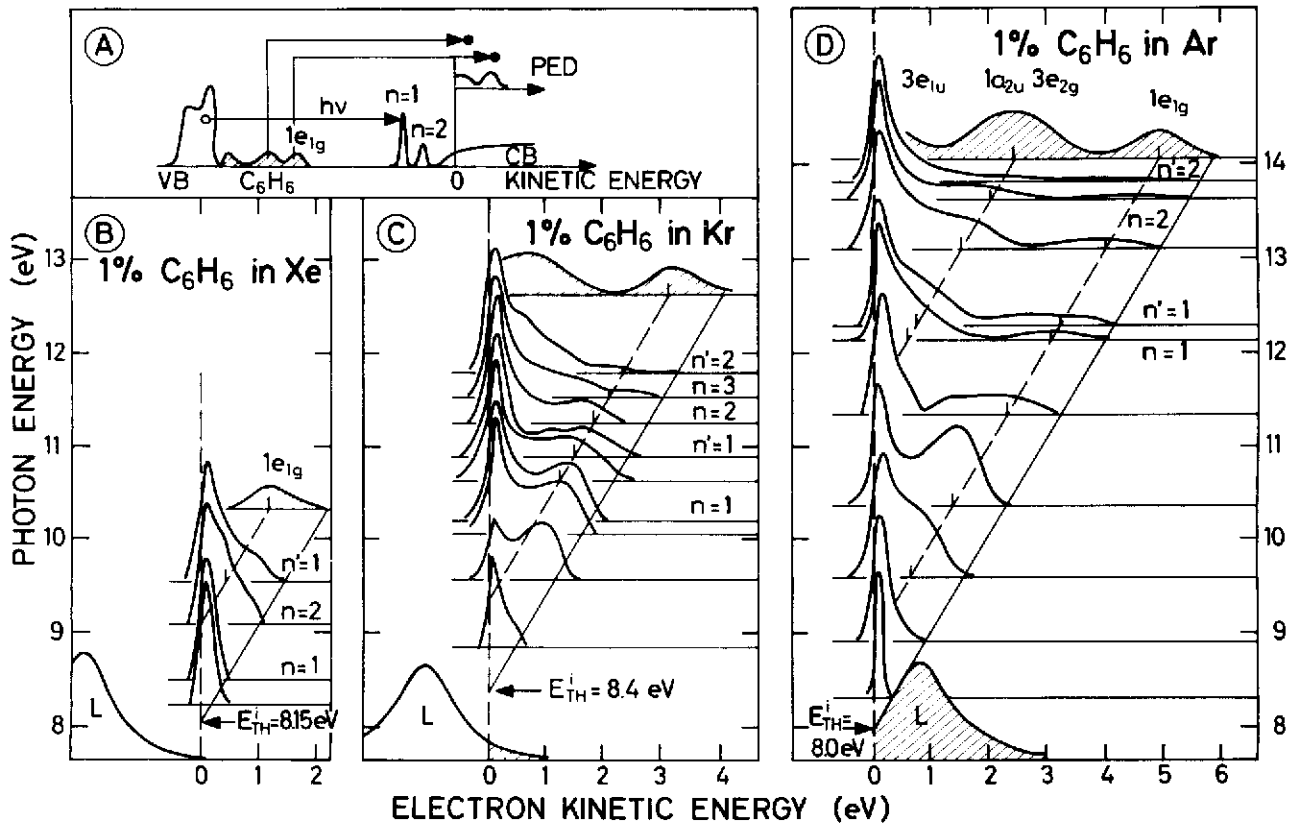|	$E_{n=1}$	$E_{n=1'}$	$E_{n=2}$	E_G or E_G^i	E_{Th} or E_{Th}^i
Ar	12.06	12.24	13.57	14.2	13.8
C_6H_6 in Ar				8.3	8.0
Kr	10.17	10.86	11.23	11.6	11.9
C_6H_6 in Kr				8.18	8.4
Xe	8.37	9.51	9.07	9.3	9.7
C_6H_6 in Xe				7.75	8.15

Fig. 1

Figure Captions

Fig. 1 Photoelectron energy distribution curves (counting rates versus kinetic energy) of 1 at % C$_6$H$_6$ in Xe, Kr and Ar for various photon energies. All curves have been normalized to the same counting rates. Panel A illustrates schematically the energy levels involved in photoelectron emission from doped solid rare gases. VB valence band of the host; CB, conduction band of the host. Panels B, C and D show the experimental results. Here L denotes the luminescence bands observed for the host matrix (see text). In panel B, C and D the uppermost curve gives the result for pure solid benzene (Ref. 13).

Fig. 2 Schematic energy level diagram as derived from the PED's for 1 at % C$_6$H$_6$ in Xe, Kr and Ar. The labeling is the same as in Fig. 1.
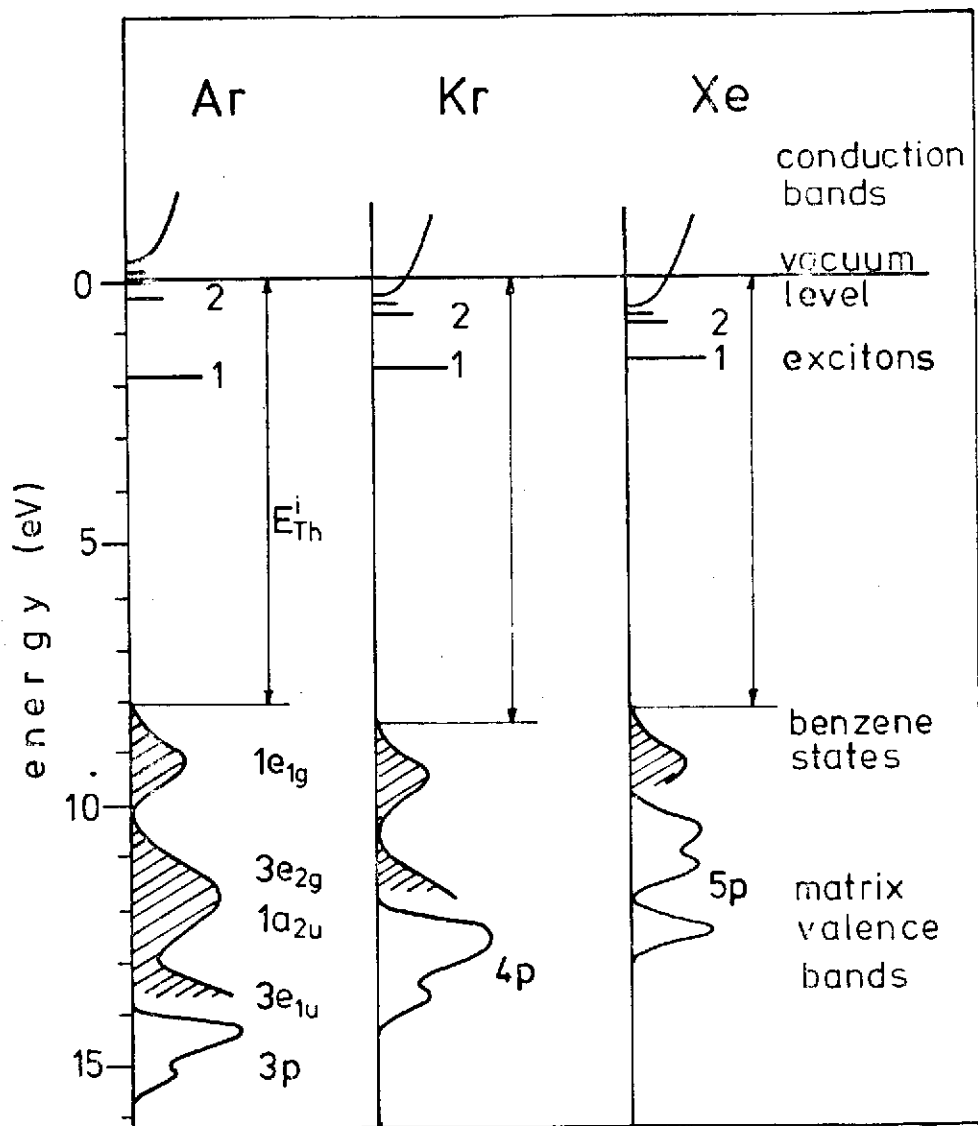
Fig. 2