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# Observation of surface sensitive luminescence in solid argon; relation to self-trapping and relaxation of excitons

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## Abstract

The luminescent emission of solid argon was measured under state selective excitation using synchrotron radiation. With the aid of excitation spectra and surface coverage experiments it was possible to show that the higher-energy emission bands at 1090 Å and at 1067 Å are produced by centers located at the surface of the sample. The interpretation was confirmed by time-resolved measurements and theoretical considerations relative to i) vibrational relaxation rates ii) effect of dimensionality on the stability of an exciton in a deformable lattice.

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## I. Introduction

The luminescence spectrum of pure solid argon is known from measurements with electron- (Fugol 1978, Hanus *et al* 1974), x-ray- (Heumüller 1978, Kink *et al* 1981), α-particle- (Cheshnovsky *et al* 1972) and photon-excitation (Brodmann *et al* 1974). The bands seen correspond closely to those observed in the dense gas phase (Cheshnovsky *et al* 1972, Wilkinson 1967) and have been interpreted in a similar way. Figure 1 shows a typical emission spectrum and relates it to exciton levels and potential curves of the argon excimer molecule Ar$_2^*$. After excitation in the exciton region the system can relax into atomic centers (atomic type self trapped exciton, a-STE) and decay radiatively. This process results in the emission band "a" at 1067 Å which is close to the emission line of the $^3P_1$-state in the gas phase. Another mechanism of lattice relaxation is the formation of a diatomic molecular center (excimer, m-STE) in the crystal. The main emission of the excimer is from the relaxed molecular states $^3\Sigma_u^+$ and $^1\Sigma_u^+$ yielding the broad band "M" centered at 1278 Å. Our experimental results have confirmed that the emission at 1090 Å (band "W") is from the vibrationally excited molecular states (hot luminescence).

In addition to the luminescence spectra themselves, in our experiments we measured the excitation spectra of the different emission bands. Such measurements assist greatly in discriminating between different possible formation mechanisms for the emitting centers. With the aid of time resolved measurements (decay curves) we obtained additional information about the relaxation mechanisms of these centers.

## 2. Experiment

The measurements were carried out at the experimental station Superlumi at HASYLAB Hamburg. The entire set-up has been described previously (Wilcke *et al* 1983, Gürtler *et al* 1983). Spectrally selected synchrotron radiation with a band pass of 2.5 Å was used to excite the sample in the wavelength range 500 - 1200 Å. The fluorescence was analysed by a VUV-monchromator with a band pass of 12 Å. The pulsed structure of the exciting light, which has a repetition rate of 1 MHz was exploited to provide time resolved data. With a channel-plate detector and the fast timing electronics used, time resolution to about 100 ps was obtained.

The solid argon samples were prepared from argon gas with a nominal purity of 99.9997 %. This gas was condensed on a LiF substrate cooled to temperatures near 10 K. The film thickness was determined from observation of the interference effects in the reflected light during deposition. Samples with a thickness of about 10000 Å were used. For the surface coverage experiments, a thin neon layer approximately 1000 Å thick was deposited on the argon film at 6 K. This layer could be removed by warming the sample to 15 K.

## 3. Results and Interpretation

The emission spectrum, excited with photons in the n = 1 exciton region (full curve in figure 2), shows the same features as observed most clearly by Fugol (1978), except that our resolution was insufficient to resolve the splitting of band "a".

In order to get information about the population channels, excitation spectra were measured for the three different emission bands. The spectra of band "a" and band "W" show a close correspondence, whereas the excitation spectrum of the main emission band at 1278 Å is completely different. Details will be published elsewhere (Roick *et al* to be published). The lower part of figure 3 shows the ratio of the excitation spectra of band "W" and band "M". For comparison, an absorption spectrum of a thin Ar film (30 Å) (Saile *et al* 1976) is shown in the upper part. From this comparison we see that the centers responsible for band "W" (the same is true for band "a") are mainly formed following primary excitation of surface excitons (as was already shown by Inoue *et al* (1982)) and with excitation energies where the absorption coefficient is high and therefore the penetration depth of the exciting light is short. This relationship suggested to us the possibility that these centers are located at the surface of the sample.

We then made a surface coating experiment which strongly corroborated this assumption. When the argon sample was coated by a thin neon layer (transparent in the energy range under discussion), the emission bands "a" and "W" disappeared (figure 2, dashed curve). The new peaks at 1040 Å and 1062 Å can be identified with emission of argon atoms in a neon matrix (Hahn and Schwentner 1980). After removal of the neon layer by warming the sample, the emission bands "a" and "W" reappeared with the same intensity as before.

From these experimentally observed facts we conclude,

(i) the vibrational relaxation rate is very different for molecular STE's in the bulk and at the surface.

(ii) The ratios of the emission intensities of the atomic and molecular STE's are very different in the bulk and at the surface.

In the bulk, vibrational relaxation of excimers is so fast that there is only one emission band, "M", emitted by the relaxed molecular STE. At the surface, relaxation is considerably slower so that emission is observed from high vibrational levels of the excimer, too (W-band). In section 4, a theory of the vibrational relaxation of a molecular center is described and applied to our experimental results.

The decay times derived from our time-resolved measurements also support the correctness of this interpretation. In figure 4, a decay curve of the M-band is shown. We measure two decay times of 1.8 ns and 1.2 μs which are ascribed to the $^1\Sigma_u^+$ and the $^3\Sigma_u^+$ state, respectively, and which are in close correspondence with other results (Carvalho and Klein 1979). The decay times of all emission bands are listed in table 1. The value of 7.5 ns for the a-band is equal to the radiative lifetime of the $^3P_1$ state in the gas phase (Keto *et al* 1979).

For the W-band we also measure two decay times which are associated with high vibrational levels of the $^1\Sigma_u^+$ and $^3\Sigma_u^+$ state. The short component is to within experimental error equal to the short component of the M-band. The long decay component is shortened considerably by the effect of vibrational

relaxation compared to the long component of the M-band. For a rough estimate of the rate of vibrational relaxation $\Gamma_v$ we may ignore the r-dependence of the transition moment of the $^3\Sigma_u^+$ state (Castex *et al* 1983). Then we obtain $\Gamma_v \approx 2.8 \times 10^6 s^{-1}$. This value will be discussed in more detail in the next section.

The differences in the ratio of the intensities of luminescence from a-STE's and m-STE's is considered in section 5 where evidence is presented that they may be due to a fundamental difference in the effect of the exciton-phonon interaction at the surface as compared to that in the bulk.

## 4. Relation of experimental results to a theory of the vibrational relaxation of the molecular STE

The results described require for their complete interpretation a theory of the dependence on proximity to a bounding surface of the vibrational relaxation of a molecular STE. Such a theory can be extracted from one developed by Yakhot *et al* (1975) and by Yakhot (1976 a-c) (referred to hereafter as YT) to describe radiationless transitions, and in particular the vibrational relaxation of an excimer within a condensed medium.

The subject of YT is an excimer (here Ar$_2^*$) embedded in and interacting with a host solid (here solid argon). Consider the vibrational displacements of all the atoms in this system. The internuclear distance of the excimer is called x (equilibrium value $x_o$); the vibrational energies of the excimer (henceforth regarded as an anharmonic oscillator) are denoted by $E_n$. (Note that $E_n - E_{n-1} \neq E_{n'} - E_{n'-1}$ due to anharmonicity.) The displacement of a typical host atom adjacent to the excimer is represented by y (see figure 1 of Yakhot *et al* (1975)). The potential energy of the excimer-crystal interaction is taken to be of the form

$$V = -\xi\beta x \exp(-\beta y) + V_o(y) \qquad (1)$$

where $V_o$ is the part not depending on x. For a given system, $\xi$ and $\beta$ are constants; thus for solid argon, $\xi = 5000\ \mathrm{cm}^{-1}$ (energy) and $\beta = 6.0 \times 10^8\ \mathrm{cm}^{-1}$ (inverse length). YT is strongly dependent on the assumption

$$|(E_n - E_{n-1}) / \hbar\omega_D| >> 1 \qquad (2)$$

in which $\omega_D/2\pi$ is the frequency of the most energetic mode of the solid (which may be a localized mode associated with the presence of the excimer in the crystal). This condition (the essential part of the definition of a multiphonon process) implies that the excimer oscillates much more rapidly than any of the host atoms.

Using this condition Yakhot obtains for the rate $P_{n,n-1}$ of the transition from vibrational level n to vibrational level n-1 (of the excimer interacting with the host solid):

$$P_{n,n-1} \equiv (\tau_{n,n-1})^{-1}$$

$$= [\xi^2\beta^2|x_{n,n-1}|^2/\hbar] \quad \exp(C^2)\ (2\pi/F)^{1/2} \exp[-(E_n-E_{n-1})^2/2F] \qquad (3)$$

with

$$|x_{n,n-1}|^2 = \hbar^2 n/2\mu\hbar\omega_{ex} \qquad (4)$$

$$C^2 = 2\beta^2\sum_q \frac{\hbar}{2m\omega_q N}\ (2N_q+1) \qquad (5)$$

$$F = \beta^2\sum_q \frac{\hbar^3\omega_q}{2mN}\ (2N_q+1) \qquad (6)$$

in which

$$N_q = [e^{\hbar\omega_q/kT} - 1]^{-1} \quad , \qquad (7)$$

N is the number of atoms in the crystal sample of unit volume, m is the mass of an atom of the host crystal, $\omega_q/2\pi$ is the frequency of the q-th phonon mode of the crystal, $\omega_{ex}/2\pi$ is the frequency of the lowest vibrational level of the excimer oscillator and $\mu$ is the reduced mass of the excimer.

$P_{n,n-1}$ can be regarded as a product of two factors, which we abbreviate by A and L:

$$P_{n,n-1} = A \cdot L \quad , \tag{8}$$

in which

$$A = \frac{\xi}{\hbar} \cdot \beta^2 \; |X_{n,n-1}|^2 \cdot \exp\,(C^2) \;\; \frac{\xi}{\hbar\,\omega_D}\sqrt{\frac{4\pi}{\kappa}} \tag{9}$$

(with $\kappa \equiv 2F/(\hbar\omega_D)^2$ and factors between dots dimensionless except for $\xi/\hbar$ which has dimension $s^{-1}$); and

$$L = \exp\,[-(E_n-E_{n-1})^2/2F] = e^{-\nu^2/\kappa} \tag{10}$$

with $\nu \equiv (E_n-E_{n-1})/\hbar\omega_D$.

A very important feature of equation (3) which this resolution emphasizes is that the L-factor is extremely sensitive to changes in the ratio $(E_n-E_{n-1})^2/2F$, whereas the A-factor is only very weakly dependent on this ratio. Thus a small fractional change in $(E_n-E_{n-1})$ or in F changes $P_{n,n-1}$ by orders of magnitude. This is the key to understanding our experimental results: both $(E_n-E_{n-1})$ and F can be expected to have (at least slightly) different values for excimers near the surface of the solid (s-STE) as compared to excimers inside the bulk (b-STE). Then equation (8) implies that the time required for vibrational relaxation (i.e., for the excimers to reach a thermal equilibrium or steady- state distribution with respect to their vibrational states) changes by a factor *orders of magnitude* greater than the fractional change in $(E_n-E_{n-1})^2/2F$. Thus is it possible that vibrational relaxation for a s-STE is slow, so that it has time to radiate light from its vibrationally excited states, whereas an excimer in the bulk relaxes much more rapidly and hence only radiates light from its lowest vibrational level.

Let us consider the specific example of argon, inserting in equations (8) - (10) values for the parameters used by Yakhot (1976 c) for the bulk case: $(E_n-E_{n-1}) = 310\ \text{cm}^{-1}$, $F = 0.6\ (\hbar\omega_D)^2$, $\hbar\omega_D = 64\ \text{cm}^{-1}$, $\xi = 5 \times 10^3\ \text{cm}^{-1}$, $\beta = 6 \times 10^8\ \text{cm}^{-1}$, $\mu = 20$ atomic mass units, $\hbar\omega_{ex} = 310\ \text{cm}^{-1}$ and $C^2 = 1$. With these values we obtain $P_{n,n-1} \simeq 2 \times 10^8\ s^{-1}$. Changing F to, e.g., $0.5\ (\hbar\omega_D)^2$ (which changes A from $6.48 \times 10^{16} s^{-1}$ to $7.08 \times 10^{16} s^{-1}$ and L from $3.24 \times 10^{-9}$ to $6.45 \times 10^{-11}$) changes $P_{n,n-1}$ to $4.6 \times 10^6 s^{-1}$. That such a change in F is associated with moving an excimer from a bulk to a surface position in argon seems entirely reasonable. At present it is not certain which of $(E_n-E_{n-1})$ and F is most sensitive to a change in the surroundings of the STE, though preliminary estimates suggest that it is F. Obtaining experimental or theoretical confirmation of that proposition seems to us an achievable as well as a worthwhile goal for future work.

Another avenue of theoretical investigation suggested by the present work is the search for useful analogies between the YT treatment of multiphonon vibrational relaxation and the treatment of spin relaxation in paramagnetic (or electron-spin) resonance experiments, such as the ones performed by Kanzig *et al* in the 1950's (see, e.g., Kanzig and Woodruff (1958) and references therein) which were followed by the work of a host of other investigators that led eventually to the "discovery" of self-trapped holes ($V_k$-centers) and STE's in alkali halide crystals.

## 5. Self-trapping of excitons in the bulk and at the surface

The surface sensitivity of the ratio of a- and m-STE luminescence as described in section 2 could in principle originate from

(i) differences between bulk and surface of interconversion rates of the two types of centers

(ii) differences between bulk and surface of the self-trapping behaviour.

Interconversion of two types of centers with such dramatic consequences as displayed in figure 2 should also show up in the time resolved spectra. If, e.g., a-STE's could decay into m-STE's, the time-resolved m-STE luminescence would be of the type generated by cascades. However, neither in a sample with nor in a sample without a surface coating were cascading effects observed (under primary excitation in the excitonic region). Therefore, category (i) effects, - if any - can be of minor importance at most.

There is strong evidence that the self-trapping process itself is drastically different in the bulk from that at the surface. Recently, Toyozawa and Shinozuka (1980) investigated the influence of *dimensionality* on the self-trapping process. They classified exciton-phonon interactions into three categories (the theory is developed for the more general case of a charged particle interacting with the phonons; we restrict ourselves to its application to excitons).

In the *"stiff"* case, the free exciton state is locally stable. Depending on the strength of the exciton-phonon coupling, there may be an additional energy minimum higher or lower in energy than the free exciton state. In either case, the two minima are separated by a potential barrier. In the *"limp"* case, no potential barrier exists. There is a continuous change from the free to the self-trapped state with increasing coupling strength. In the *"marginal"* case, the free state can be locally stable or not. Whether the free exciton is locally stable or unstable is determined by the coupling strength.

If the exciton-phonon interaction is of the short range (deformation potential) type (as is the case in rare gas solids), the three types of exciton-phonon interaction are directly related to dimensionality. The "stiff" case corresponds to three-dimensional systems, the "marginal" case to two-dimensional systems, and finally the "limp" case, to one-dimensional systems.

For our sample of solid argon, we may tentatively regard self-trapping at the surface as self-trapping in a two-dimensional system. Of course, to do so is not perfectly correct because we are dealing with a two-dimensional boundary of a three-dimensional system. Thus, if the coupling strength is sufficiently large, the situation is as displayed in figure 5. In the upper part, the potential curves of the a- and m-STE in the bulk are sketched as a function of the respective configuration coordinates (Fugol 1978, Zimmerer 1979). Both self-trapped species are separated from the free exciton state by a potential barrier. The heights of the barriers as estimated by Fugol (1978) are very different: ~2 meV for the m-STE, ~10 meV for the a-STE*. Hence the overwhelming majority of the excitons in the bulk are trapped in the molecular configuration - which would explain our experimental result that a-STE emission in the bulk is practically absent.

The lower part of figure 5 displays the situation in a two dimensional system (surface). Here both barriers are absent so that both self-trapping configurations are populated, giving us a natural explanation of the observed coexistence of a-STE's and m-STE's at the surface.

The stability (or instability) of the free exciton state at the surface is determined by the size of the coupling constant

* The heights of the barriers were estimated on the assumption that band "a" originates in the bulk. This asssumption may no longer be justified in view of the results reported here. Therefore it cannot be ruled out that in the bulk the local minimum of the a-STE potential surface is higher than the free exciton energy.

g defined in Toyozawa and Shinozuka 1980. For our particular case, $g = E_{LR}/B$, $E_{LR}$ being the lattice relaxation energy and B the half width of the exciton band. For self trapping, g must be larger than a numerical constant of the order of unity. For the m-STE, we can be sure that g exceeds unity because of the extremely large Stokes shift of the band "M" compared to the energy of surface exciton absorption. Concerning the a-STE, an independent estimate of g is not possible because the Stokes shift measured for band "a" is so small (~.2 eV) that a change in the ground state potential could account for this shift. (Note, that the Stokes shift energy is composed of a contribution from the excited state potential, $E_{LR}-B$, and a contribution from the ground state potential). However, if $E_{LR}$ were $<$ B for the a-STE, this state would not be populated at all because of the instability of the free exciton against m-STE formation.

## 6. Concluding remarks

In summary, the principal results of the work reported here are:

(i) we are able to detect luminescence from self-trapped excitons at or near the surface of solid argon;

(ii) near the surface, the m-STE's undergo vibrational relaxation at rates which are smaller by orders of magnitude than for the isoelectronic centers in the bulk;

(iii) our results appear to confirm the theoretical expectation (Toyozawa and Shinozuka 1980) of a qualitative difference in the effects of exciton-phonon interaction between the bulk and the surface which is directly related to the dimensionalities of the system and its parts.

Moreover, our results suggest an explanation of why different groups have observed such different luminescence spectra in solid argon. Those who used bulk excitation (e.g., x-rays (Heumüller 1978)) or who used a closed cell (Kink *et al* 1981) did not observe bands "a" and "W". The same is true for α-particle excitation where the sample was evaporated onto the α-source (Cheshnovsky *et al* 1972). In all of these cases, emission from the free surface of the sample was impossible. On the other hand, the results of those experiments in which surface sensitive excitation techniques were used, such as slow electrons (Fugol 1978) or photons (Brodmann *et al* 1974,the work reported here) agree quite well.

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Table 1. The decay times of the different emission bands of solid argon. The accuracy of the numerical results is about 10 %. All results are obtained with primary excitation of n = 1 excitons.

| Emission band | Wavelength (Å) | $\tau_1$(ns) | $\tau_2$(ns) |
|---|---|---|---|
| M | 1278 | 1.8 | 1200 |
| W | 1090 | 1.7 | 275 |
| a | 1067 | 7.5 | - |

## Figure Captions

Fig. 1 Schematic representation of the excitonic energy levels of solid argon in the unrelaxed lattice (I) and of the molecular type self-trapped excitons (II). In the lower part, a typical luminescence spectrum with bands "M", "W", and "a" is shown. The origin of the bands is indicated in the potential energy diagram. The design of the figure is taken from Fugol (1978). $Q_m$: internuclear distance.

Fig. 2 Luminescence of solid argon under photon excitation (excitation wavelength 102 nm, excitation of n = 1 excitons). The full curve is obtained from an uncoated sample. The dashed curve is obtained from a sample coated with a thin neon layer.

Fig. 3 Upper part: absorption spectrum of a thin Ar layer (30 Å) with n = 1,2,3 and n' = 1,2 bulk excitons, and n = 1,2 , n' = 1 surface excitons (after Saile et al 1976).

Lower part: intensity ratio of the W and M bands as a function of excitation energy.

Fig. 4 Typical decay curve of the M band under primary excitation of the n = 1 excitons at 102 nm (high energy side). The insert shows the fast decay component on an enlarged scale.

Fig. 5 Schematic configuration coordinate diagram of the a-STE and the m-STE in the bulk (upper part). $Q_a$ is the configuration coordinate of the atomic center, $Q_m$ is the configuration coordinate of the molecular center. Note the existence of self-trapping barriers. In the lower part the configuration coordinate diagrams for both centers at the surface are in accordance with an interpretation of the work of Toyozawa and Shinozuka (1980). Note the absence of self-trapping barriers.

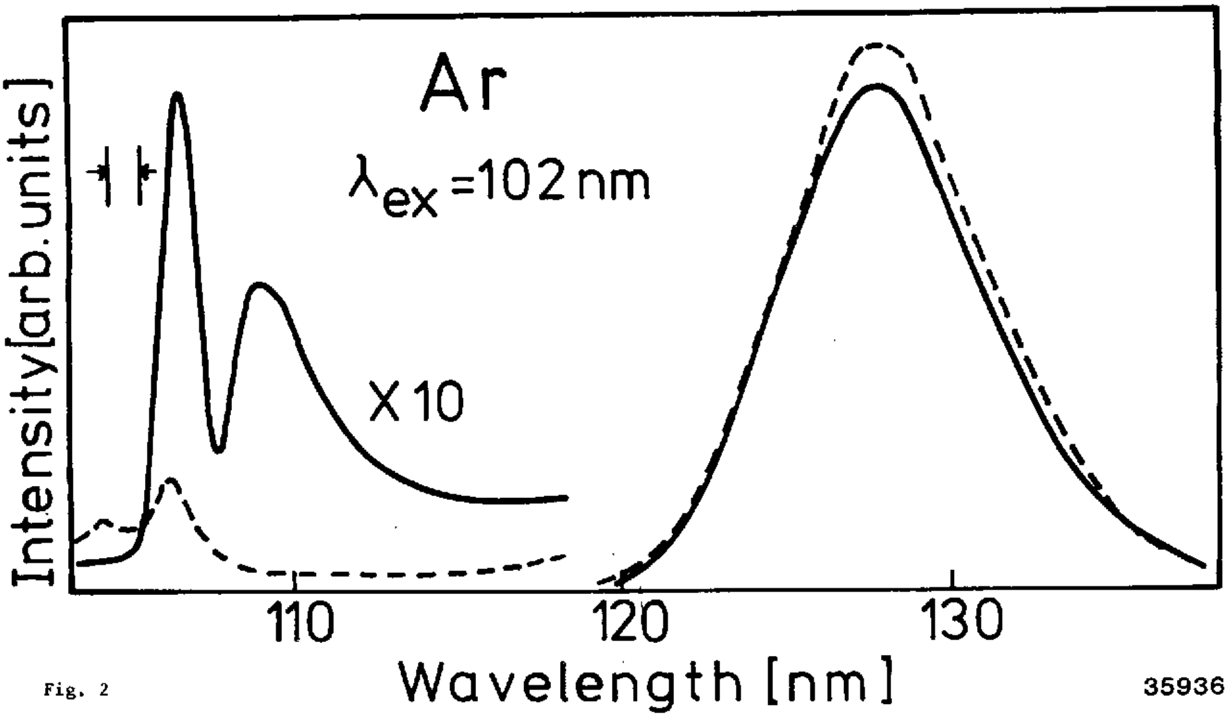

Fig. 2

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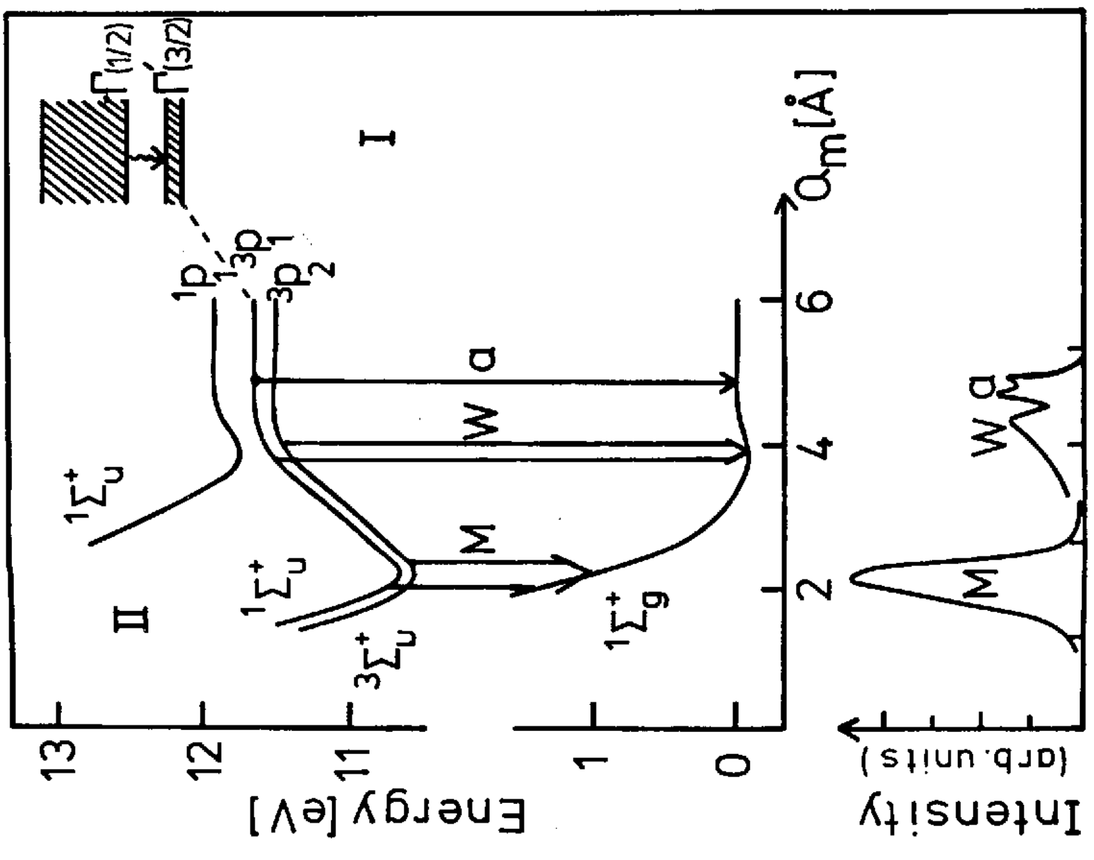

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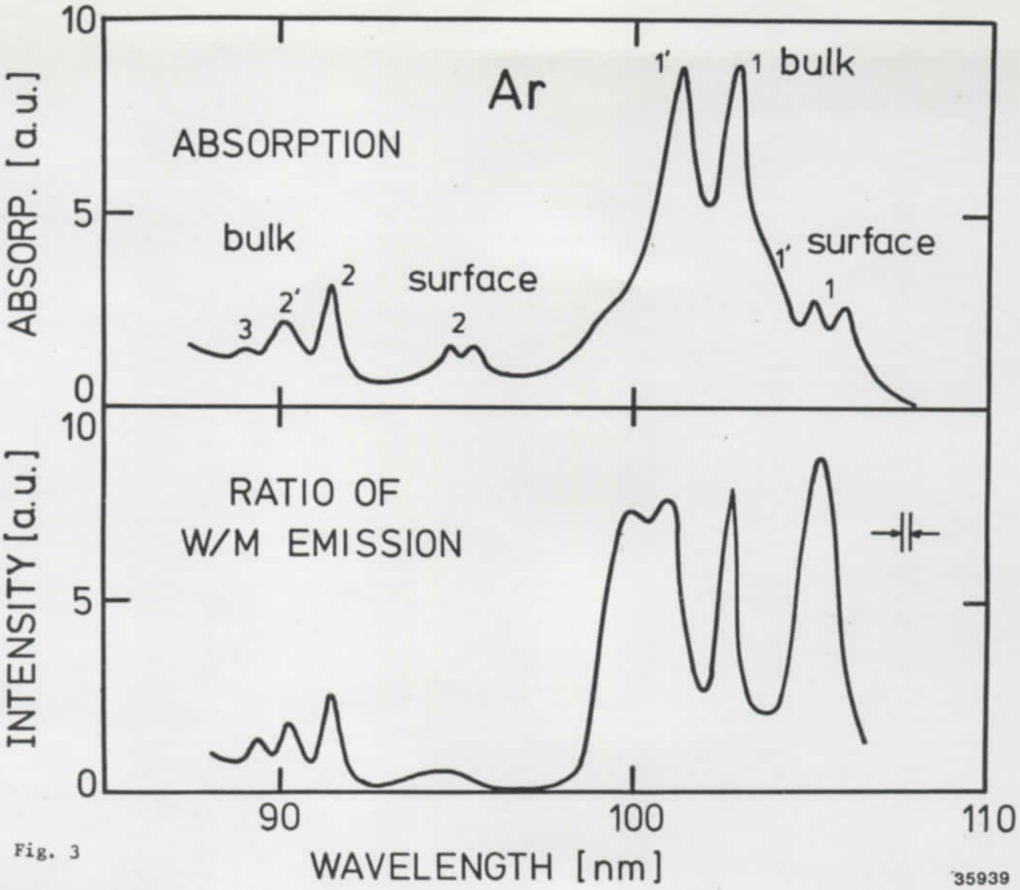
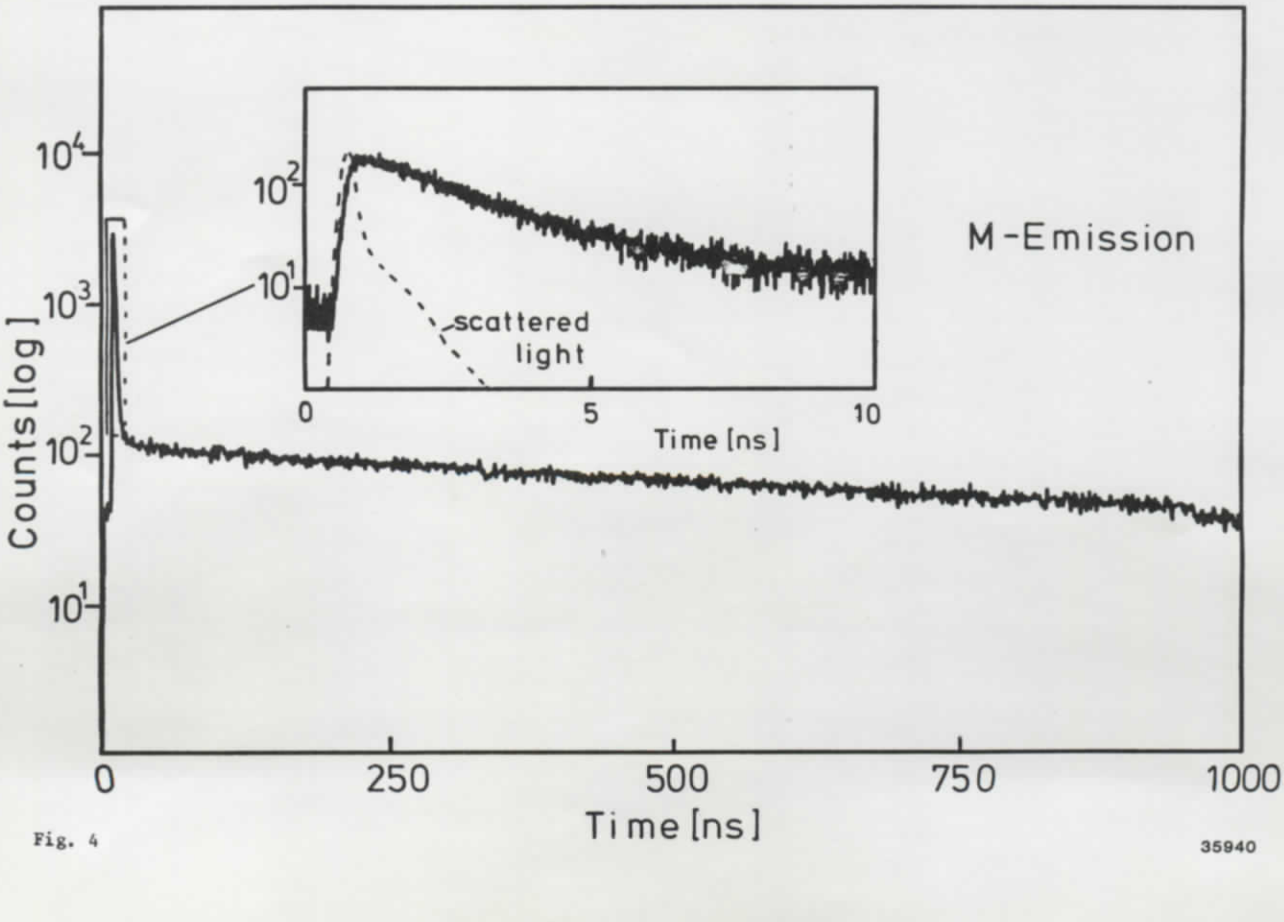
Fig. 1



Ar
ABSORPTION
ABSORP. [a.u.]
bulk
surface
3
2'
2
1'
1 bulk
1' surface
1
RATIO OF W/M EMISSION
INTENSITY [a.u.]
0
5
10
90
100
110
WAVELENGTH [nm]
35939

Fig. 3



M-Emission
Counts [log]
10¹
10²
10³
10⁴
0
250
500
750
1000
Time [ns]
scattered light
Time [ns]
0
5
10
35940

Fig. 4