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Optically Excited Emission and Excitation Spectra of Solid Xenon

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The luminescence of solid xenon at 20 K has been excited optically in the wavelength range 1550 Å to 1150 Å. The 1760 Å emission band due to a $^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ *transition of the* Xe_2^* *molecule is found in agreement with that obtained from* α*- or* e^-*-excitation. The excitation spectrum yields a relatively high quantum efficiency of the* $\Gamma(3/2)$ *exciton series indicating an efficient self trapping. The* $\Gamma(1/2)$ *exciton series and conduction band states have a low quantum efficiency.*

In the last few years interest in the vacuum ultraviolet luminescence of gaseous, liquid, and solid xenon has increased considerably, because this rare gas seems to be a promising material for vacuum ultraviolet lasers[1]. In most cases, the xenon emission has been excited either by α-particles[2], x-rays[3] or electron beams[4]. To our knowledge, only gaseous xenon has been excited optically[5]. Excitation by monochromatic light offers the great advantage that the luminescent material is excited to definite states. In this case, the decay of the excited states, i.e. the emission via relaxation and energy transfer can be investigated. We have measured the monochromatically excited emission spectra as well as the excitation spectra of pure xenon using the synchrotron radiation of the Deutsches Elektronen-Synchrotron DESY. The synchrotron radiation was monochromatized by a near normal incidence monochromator[6] (grating blazed at 1200 Å, band width ∿8 Å) connected to a UHV sample chamber. A toroidal mirror focused the monochromatic light onto the sample. The emitted light was analyzed by a Seya Namioka monochromator with a grating blazed at 1500 Å. The illuminated part of the sample (∿1 mm^2) served as entrance slit of the analyzing system. Photoelectronic detection of the emitted light was used. A detailed description of the experimental setup will be given elsewhere[7].

The samples were prepared by evaporation onto a sapphire substrate (T ≈ 20 K). Xenon of a purity of 99.997 % (L'Air Liquide) was used as sample material. Before evaporation, in a separate UHV system this gas was purified by sputtering titanium. The thickness of the layers was controlled by interference oscillations during evaporation and ranged from .8 to 1.5 µm.

In Fig. 1 the emission band of solid xenon for an exciting wavelength of 1510 Å is shown. Together with the emission band the stray light peak of the exciting light can be seen. The observed emission band is centered at about 1760 Å in good agreement with the α-excited emission[2]. Similar results could be obtained for other exciting wavelengths. In all cases, the emission peak centered at 1760 Å remained unchanged in shape and position.

The similarity of the 1760 Å emission band with the intrinsic xenon emission measured under α-[2] and e^--excitation[4] as regards energetic position and shape indicates that the same mechanism for luminescence takes place also under optical excitation. The optically excited emission band, therefore can be explained by the radiative decay of an excited $Xe_2^{\neq}$ molecule. This molecule can be created in solid xenon either by self trapping of an exciton state[8] or by a self trapped hole (V_k-center like) which captures a free electron[9]. The relaxation process leading to the self trapped exciton takes place along a {110} direction of the lattice. Though the center has D_{2h} symmetry it may be treated in a good approximation as a diatomic molecule with $D_{\infty h}$ symmetry as has been pointed out by Molchanov[10]. Thus the emission is due to a transition $^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ where the $^3\Sigma_u^+$ state is built up from the atomic $^3P_2 + {}^1S_0$ states[10].

The excitation spectrum of the 1760 Å emission band as shown in Fig. 2 exhibits rich structure. The emission intensity is normalized to the spectral distribution of the exciting light. The curve, therefore, yields the quantum efficiency in relative units. It was checked that a correction due to reflection does not influence significantly the spectral behaviour of the excitation curve.[11] Therefore, the reflection of the sample was neglected. For comparison of the peak positions an absorption spectrum of xenon measured by Scharber and Webber[12] is included.

The main features of the excitation spectrum are: At the long wavelength side of the n=1 $\Gamma(3/2)$ exciton (absorption peak at 1485 Å) the excitation spectrum shows a pronounced maximum at 1510 Å. At the position of the exciton itself the relative quantum efficiency (RQE) decreases to about 10 % of the maximum efficiency. At higher energies, between the n=1 and n=2 $\Gamma(3/2)$ exciton (∿1360 Å), the excitation spectrum has a broad maximum with two peaks at 1400 Å and 1430 Å. At the n=2 $\Gamma(3/2)$ exciton a dip in the excitation spectrum is found followed by a maximum at the short wavelength side. In the region of the n'=1 $\Gamma(1/2)$ exciton (∿1300 Å) and in the region of fundamental absorption the RQE for the 1760 Å emission is very low.

The high RQE in the region of the $\Gamma(3/2)$ exciton series indicates that the relaxation to the Xe_2^{+} ${}^3\Sigma_u^+$ state is much more probable than in the region of the $\Gamma(1/2)$ exciton series and the fundamental absorption where the RQE is low. The overall behaviour of the excitation spectrum in the region of excitonic transitions can be explained with the theoretical considerations of Molchanov[10]. He showed that only excited states with a hole of total angular momentum j=3/2 can relax to the molecular state. Excited states with a hole of j=1/2 lead to potential curves of the Xe_2^{+} molecule which are mainly repulsive or have a shallow minimum only for rather large internuclear distances.

The low RQE when exciting conduction band states ($\lambda < 1330$ Å) implies either great amount of nonradiative transitions or extrinsic emission which could not be detected till now. Moreover, the photoelectric yield of solid xenon is relatively high in the fundamental absorption region.[13] Perhaps photoemission is a competitive process to luminescence.

Up to now no conclusive explanation can be given for the excitation minima at the energy position of the n=1 and n=2 Γ(3/2) exciton. Similar minima have also been observed in the excitation spectra of alkali halides[14-16]. In some cases they are explained by the reflectivity of the sample[15,16]. As mentioned above this is not the case for xenon. Perhaps competitive radiationless recombination processes in the surface of the layers play an important role when the penetration depth of light is very small as is the case for the exciton absorption maxima in xenon. A similar explanation has been suggested by Ramamurti and Teegarden for KI[14].

The high RQE at the low energy tail of the n=1 Γ(3/2) exciton possibly indicates that not only the allowed n=1 exciton (equivalent to the atomic $5p^5 6s\ ^1P_1$ state) but also the forbidden triplet exciton ($5p^5 6s\ ^3P_2$) is excited. In Ref. 17 it is pointed out for KI that the first phonon side band of the triplet state with total angular momentum J=2 is roughly as intense as the first phonon side band of the singlet state with J=1. Because our layers were rather thick the phonon assisted excitation of the forbidden exciton may not be neglegible. For xenon even in absorption spectra sometimes structure below the n=1 Γ(3/2) exciton is observed, which also has been discussed possibly to be due to excitations of the forbidden exciton[18]. According to Molchanov[10], the forbidden exciton state with the total angular momentum J=2 relaxes directly to the $^3\Sigma_u^+$ state without crossing any other potential curves. Therefore a high RQE is to be expected.

We hope to get further information by measuring the temperature dependence of the emission and excitation spectra as well as the dependence on the thickness of the layers. These investigations, together with measurements on other rare gases, are in progress.

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Figure Captions

Fig. 1 Luminescence spectrum of solid xenon at 20 K for an exciting wavelength of 1510 Å. The exciting light leads to the stray light peak of the spectrum. The constant background level of the spectrum is due to dark pulses of the multiplier.

Fig. 2 Intensity of the 1760 Å luminescence band of solid xenon at 20 K vs. exciting wavelength (solid line). The long wavelength tail is due to dark pulses of the multiplier. The dashed line yields the absorption curve of solid xenon at 20 K measured by Scharber and Webber (Ref. 12).

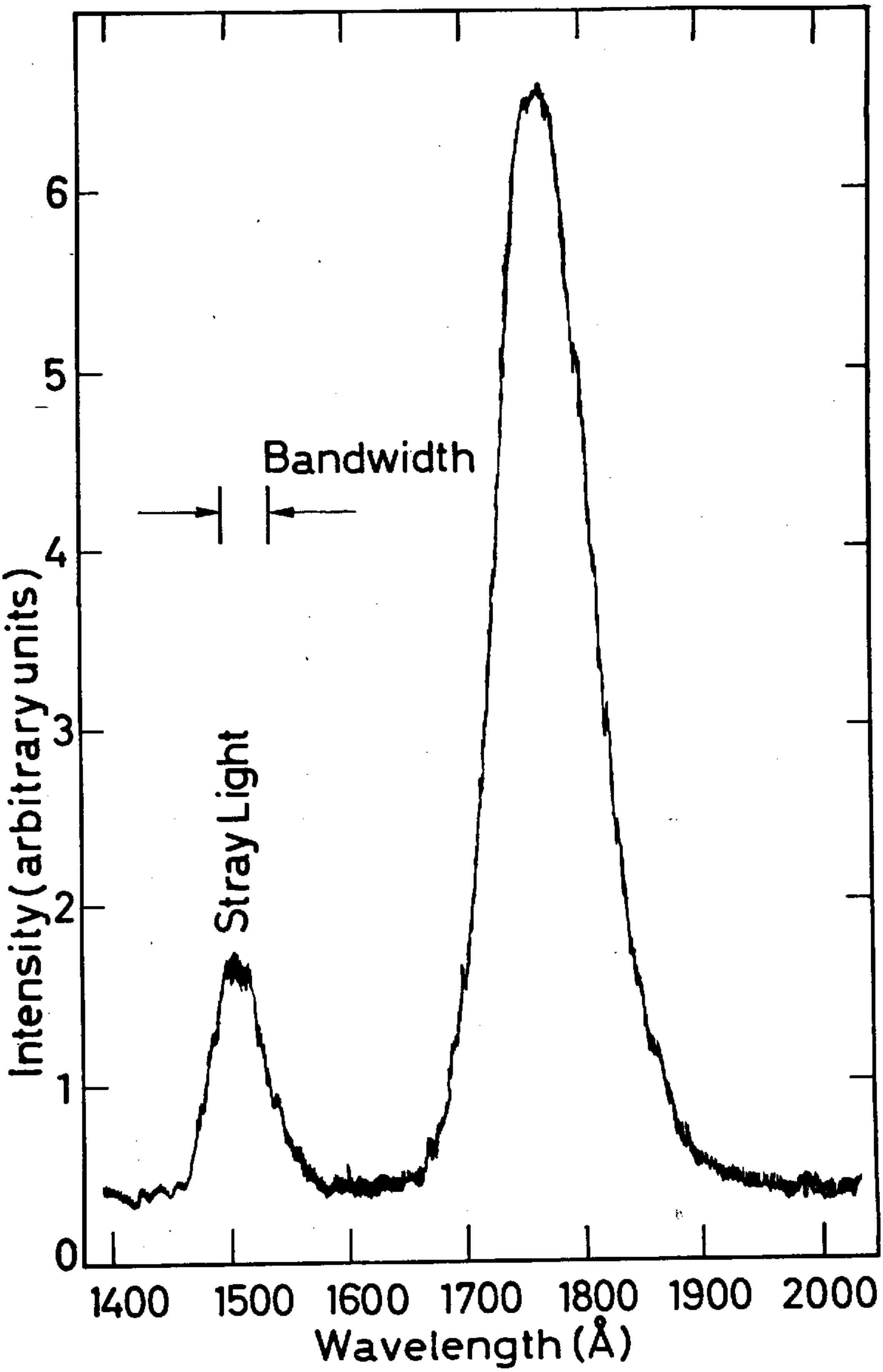
Bandwidth
Stray Light
Intensity (arbitrary units)
0
1
2
3
4
5
6
1400
1500
1600
1700
1800
1900
2000
Wavelength (Å)

Fig. 1

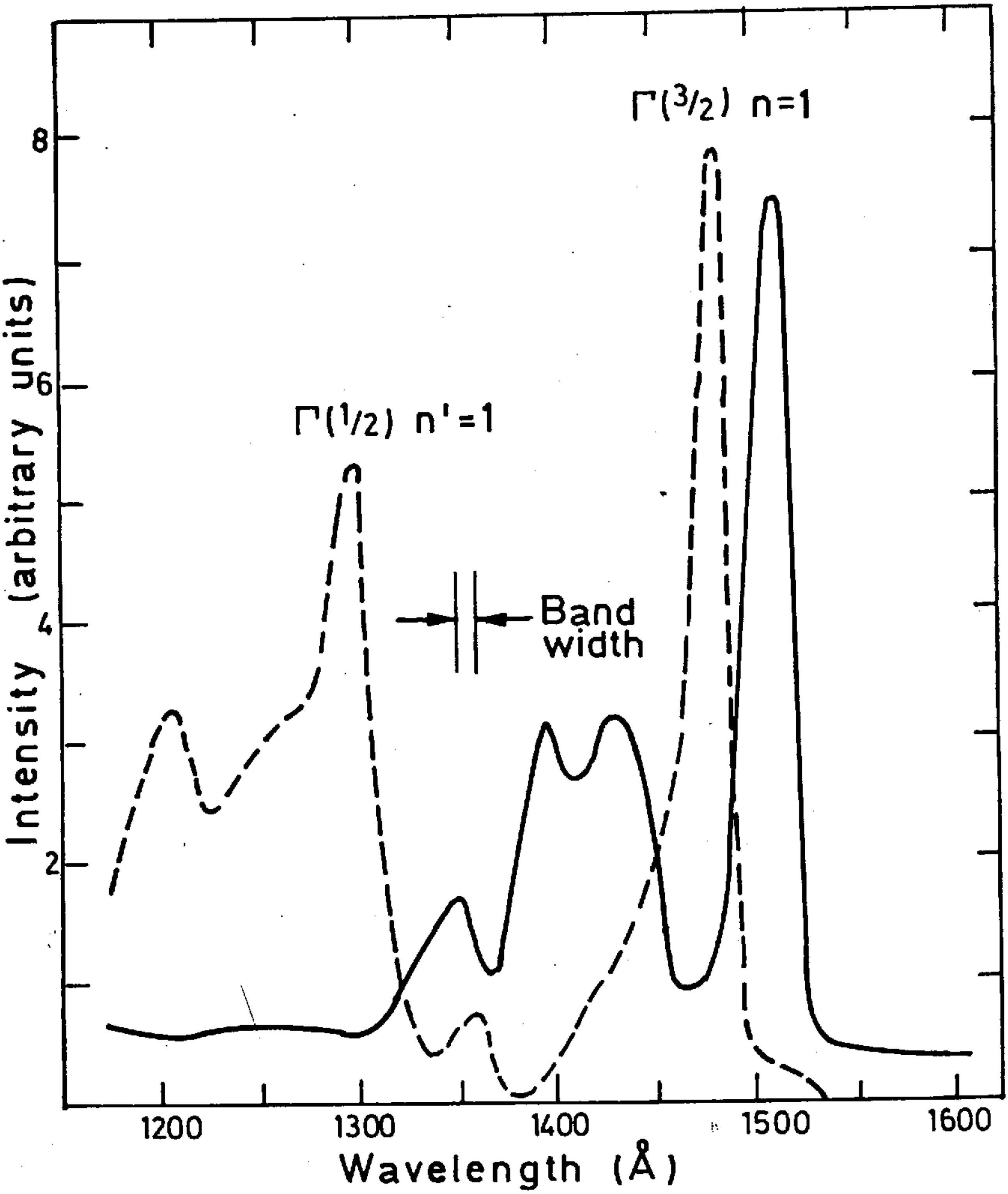
Intensity (arbitrary units)
2
4
6
8
Γ(1/2) n'=1
Γ(3/2) n=1
Band width
1200
1300
1400
1500
1600
Wavelength (Å)

Fig. 2