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Xenon 5d Emission in Pure Xenon and Xenon Doped Argon

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Abstract

The radiative decay of Xe 5d(3/2)$_1$ states in photo-excited Xe and Xe doped Ar is investigated. The Xe 5d fluorescence contains new information about the deactivation of highly excited states of Xe and about the energy transfer from Ar to Xe.

Now at Projektgruppe für Laserforschung der MPG, D-8046 Garching, Germany

1. Introduction

The vacuum-ultraviolet (VUV) fluorescence spectra of rare gases consist of atomic resonance lines and molecular emission bands. The relative intensities sensitively depend on pressure and on excitation energy [1]. For pressures above ~1000 Torr only the "second continuum" persists. It stems from vibrationally relaxed $^{1,3}\Sigma_u^+$ excimer states. At lower pressures the radiative decay of vibrationally excited excimers ("first continuum") and resonance emission of $^3P_1$, $^1P_1$ atoms compete with the second continuum.

Recently it was shown that the Xe 5d(3/2)$_1$ state is also a possible fluorescence channel provided an appropriate excitation energy is chosen [2]. The properties of this "Xe 5d emission" will be discussed in more detail in this paper. Xe 5d emission is of particular interest not only in pure Xe but also in Xe doped Ar because it yields new information on the energy transfer (ET) from excited Ar to Xe. This ET plays an important role in VUV laser physics for two reasons.

(i) Even a minimal amount of Xe in Ar leads to quenching of the Ar fluorescence and thus decreases the efficiency of the Ar_2^* excimer laser.

(ii) Controlled doping of Ar with Xe results in efficient Xe_2^* excimer lasers which are pumped via the Ar buffer gas [3-5].

2. Experiment

The experiment is described in Ref. [2] and Ref. [6]. Here only the essentials are given. Fluorescence is excited with monochromatic VUV light from the electron storage ring DORIS at DESY. The exciting light is focused into a LiF gas cell. The illuminated part of the cell serves as entrance slit for a VUV monochromator for the spectral analysis of fluorescence. The whole illuminated part of the cell is accepted by the analysing monochromator. The width of the exciting light beam limits the band pass in the fluorescence spectra to ~30 Å.

The excitation wavelength can be chosen arbitrarily for $\lambda > 1040$ Å (LiF cut off) with a band pass of ~4 Å. In this way well defined states can be excited. Measuring a fluorescence spectrum the excitation wavelength is kept constant. In an excitation spectrum, however, the intensity of a wavelength selected fluorescence band is measured as a function of excitation wavelength. The excitation spectra in this paper are normalised to the intensity of exciting light penetrating the gas cell.

3. Pure Xenon: Results and Discussion

Under resonant excitation of Xe $5d(3/2)_1$ states (1192 Å) three fluorescence bands are observed (Fig. 1).

(i) Xe $5d(3/2)_1$ emission (1192 Å).

(ii) The first continuum (1470 Å - 1520 Å, dependent on pressure) including Xe $6s(3/2)_1$ $^3P_1$ atomic emission not resolved here.

(iii) The second continuum (~1700 Å).

The Xe $^1P_1$ band at ~1300 Å [1,2] is absent in pure Xe under Xe $5d(3/2)_1$ excitation.

For pressures above ~30 Torr the Xe 5d band could no longer be detected. Below ~10 Torr it may even dominate in the spectra. This is difficult to be measured because of lack of intensity (only a small fraction of exciting light is absorbed at low pressures). The width of the Xe 5d band in Fig. 1 is due to the band pass of the analysing monochromator.

The excitation spectrum of the Xe 5d band is shown in Fig. 2, together with a transmission curve. The Xe 5d band can be excited in the absorption band A (Xe $5d(3/2)_1$ absorption), its blue wing B, and in the red wing C of Xe $7s(3/2)_1$ absorption D. C obviously stems from Xe $7s(3/2)_2$ states [7]. Excitation of higher Rydberg states of Xe does not lead to Xe 5d emission (see also Fig.5 and [2]).

The survival of Xe 5d emission against competing deactivation processes like molecule formation via collisions is obviously due to its very large oscillator strength. The radiative lifetime of Xe $5d(3/2)_1$ states (1.4 ns, [8]) is much smaller than, e.g., the radiative lifetimes of Xe $6s(3/2)_1$ $^3P_1$ (3.46 ns, [8]) or $6s(1/2)_1$ $^1P_1$ (3.44 ns, [8]) states.

The excitation spectrum is explained by an interaction of molecular Xe_2^* states terminating in the atomic $5d(3/2)_1$ and $7s(3/2)_2$ states (insert in Fig. 2). The avoided crossing of molecular 1_u states was proposed by Castex [7], based on a high resolution analysis of the absorption bands B and C. The minimum of the upper 1_u state approximately coincides with the Van der Waals minimum of the 0_g^+ ground state of Xe_2. Absorption C is due to transitions into vibrational levels of the $1_u(7s(3/2)_2)$ state [7]. Via collisions, the upper 1_u state can be relaxed into the lower one. If the attractive part of the potential curve is reached, the molecule survives and the Xe $5d(3/2)_1$ state is bypassed. If the dissociative part of the 1_u state is reached, atomic $5d(3/2)_1$ states are populated and Xe 5d emission shows up. The Xe 5d band may also contain a contribution from the $1_u(7s(3/2)_2)$ state itself not resolved here.

The survival of the Xe 5d emission under monochromatic excitation of the very few states discussed above and its absence under excitation of higher Rydberg states, Xe^{**}, is important for a better understanding of the deactivation of Xe^{**} in dense pure Xe.

The deactivation model for Xe^{**} presently under discussion [9] (electron impact excited dense Xe) is based on the assumption of successive formation of highly excited excimers, Xe_2^{**} and dissociation into lower excited states ($Xe_2^{**} \rightarrow Xe + Xe^*$) via potential curve crossing. It essentially predicts the transient population of lower excited atoms after excitation of a high Rydberg state. The absence of Xe 5d emission (and also Xe $^1P_1$ emission [2]) under excitation of Xe^{**} indicates that lower excited atomic states are bypassed and that the deactivation model of [9] cannot be applied to our experimental conditions (pressure below 100 Torr, photon excitation, neutral system).

Our results are better explained by intramolecular cascading of excitation energy [2] and it should be proved whether intramolecular cascading plays also an important role in electron impact excited rare gas lasers.

4. Xenon Doped Argon: Results and Discussion

$5d(3/2)_1$ states of Xe in Xe doped Ar can be excited either directly or via E T from Ar to Xe. In Fig. 3, fluorescence spectra of 700 Torr Ar doped with 100 ppm Xe are shown. The dotted curve has been obtained under direct excitation of Xe 5d states (1192 Å). The full curve is found under Ar $4s(3/2)_1$ excitation (1066 Å). In both cases Xe 5d emission is found, together with the first and second Xe continuum and the Xe $^1P_1$ band (~1300 Å, absent in pure Xe under Xe 5d excitation). The existence of the Xe 5d band in Xe doped Ar is in contrast to results obtained under electron impact [10], excitation with α-particles [11] or in an electric discharge [12].

In Fig. 4, the concentration dependence of the fluorescence spectra is shown (Ar 4s(3/2)$_1$ excitation, Ar pressure 700 Torr, partial pressure of Xe between ~0.004 Torr and 10 Torr). Even with the smallest amount of Xe, Xe $^3P_1$ emission at 1470 Å is found. Xe $^1P_1$ emission at ~1300 Å is superimposed to the second continuum of Ar excimers (~1280 Å). The blue tail of the Ar continuum could either be due to the first continuum of Ar or to Xe 5d emission.

With increasing Xe concentration, the Ar fluorescence is quenched in favour of the Xe bands. If we subtract the Ar background in the region of Xe $^1P_1$ emission it turns out that the Xe 5d and Xe $^1P_1$ bands have similar intensities.

The excitation spectrum of the Xe 5d band in Xe doped Ar demonstrates that excitation of higher Xe Rydberg states leads to Xe 5d fluorescence (Fig.5, curve in the middle) in contrast to the case of pure Xe (lowest curve of Fig.5).

The existence of Xe 5d emission under Ar 4s(3/2)$_1$ excitation gives new insight into E T from Ar to Xe. Gedanken et al [12] considered two different mechanism.

(i) Atom-atom E T to highly excited states of the acceptor. A dipole-dipole type E T requiring near resonance energy level coincidence, was considered.

(ii) Molecule-atom E T. It is assumed that the excitation energy cascades down within the Ar sub-system and that Ar_2^* ($^{1,3}\Sigma_u^+$) excimers are created before E T takes place. The Ar_2^* second continuum perfectly overlaps with Xe 6s'(1/2)$_1$ absorption. An efficient dipole-dipole type E T with Ar_2^* ($^{1,3}\Sigma_u^+$) as donors and Xe 6s'(1/2)$_1$ as acceptors was stated.

Chesnovsky et al [11] excluded case (i) at high total pressures (~1000 Torr). The model (ii) was adopted in more recent papers [3-5,10].

According to our results additional transfer mechanisms must be considered.

(i) Molecule-atom transfer which directly results in Xe 5d atoms. A dipole-dipole type E T can be excluded because the spectral overlap between the second continuum of Ar (~1280 Å) and Xe 5d absorption (1192 Å) is bad compared to Xe 6s'(1/2)$_1$. We assume the formation of short lived complexes $(Ar_2Xe)^*$ via collisions of Ar_2^* ($^{1,3}\Sigma_u^+$) molecules and Xe ground state atoms. Predissociation of this complex may lead either to Xe* 5d or to Xe* 6s' atoms.

(ii) Interaction of Ar* 4s(3/2)$_1$ atoms with Xe atoms leading to a short lived Ar*Xe molecule. Via potential curve crossing this molecule may relaxe ($Ar^*Xe \rightarrow ArXe^*$) and dissociate. Among others Xe*5d states can be excited in this way.

The role of heteronuclear molecules is not simply an assumption but manifests itself in the pressure dependence of Xe impurity absorption which is proportional to $P_{Xe} \cdot P_{Ar}$ ($P_{Xe,Ar}$ being the partial pressures of Xe and Ar, respectively) [13]. Heteronuclear molecules can also account for the different behaviour of the excitation spectra of Xe 5d fluorescence in Xe doped Ar compared with pure Xe (Fig. 5). Obviously now the deactivation model of [9] works, however, with the heteronuclear molecular states which don't have deep potential curve minima.

Future investigations including energy and time resolved fluorescence spectroscopy under monochromatic excitation [6] will disentangle the various processes in more detail.

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Figure Captions

Fig. 1 Fluorescence spectra of pure Xe at different pressures obtained under Xe $5d(3/2)_1$ excitation.

Fig. 2 Excitation spectrum of the Xe 5d band of pure Xe (10 Torr) together with a transmission curve. The insert shows the potential curves of the Xe_2^* molecule which are essential for an understanding of the excitation spectrum (schematic).

Fig. 3 Fluorescence spectra of Xe doped Ar under Ar $4s(3/2)_1$ excitation (full curve) and Xe $5d(3/2)_1$ excitation. Partial pressure of Xe: 0.07 Torr, Ar pressure: 700 Torr.

Fig. 4 Concentration dependence of the fluorescence spectra of Xe doped Ar under Ar $4s(3/2)_1$ excitation. The Xe concentration is given in the figure. Ar pressure: 700 Torr.

Fig. 5 Excitation spectra of the Xe 5d band in pure Xe (10 Torr, lowest curve) and Xe doped Ar (100 ppm Xe in 700 Torr Ar). At the top, a transmission spectrum of 100 ppm Xe in 700 Torr Ar is given.

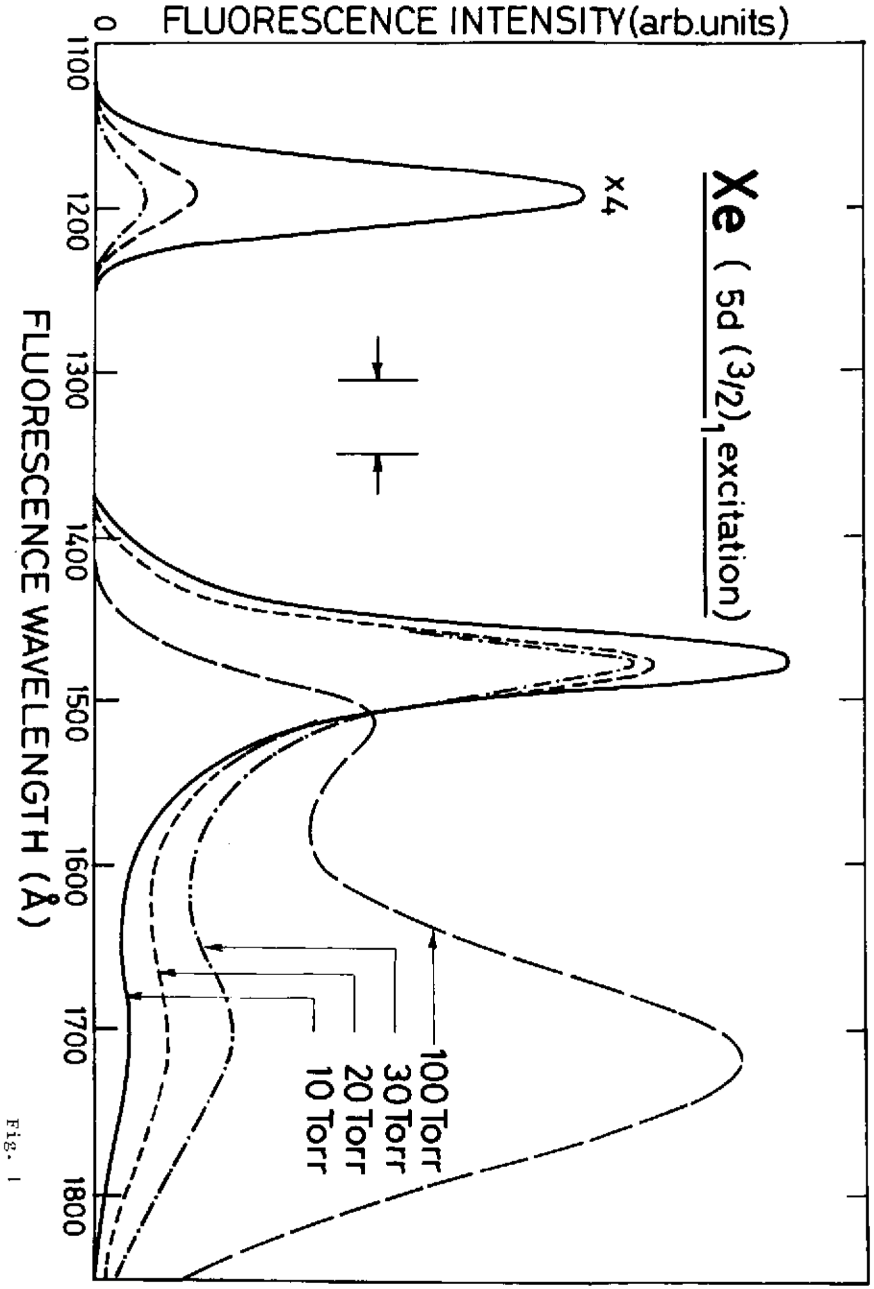

Fig. 1

270.3

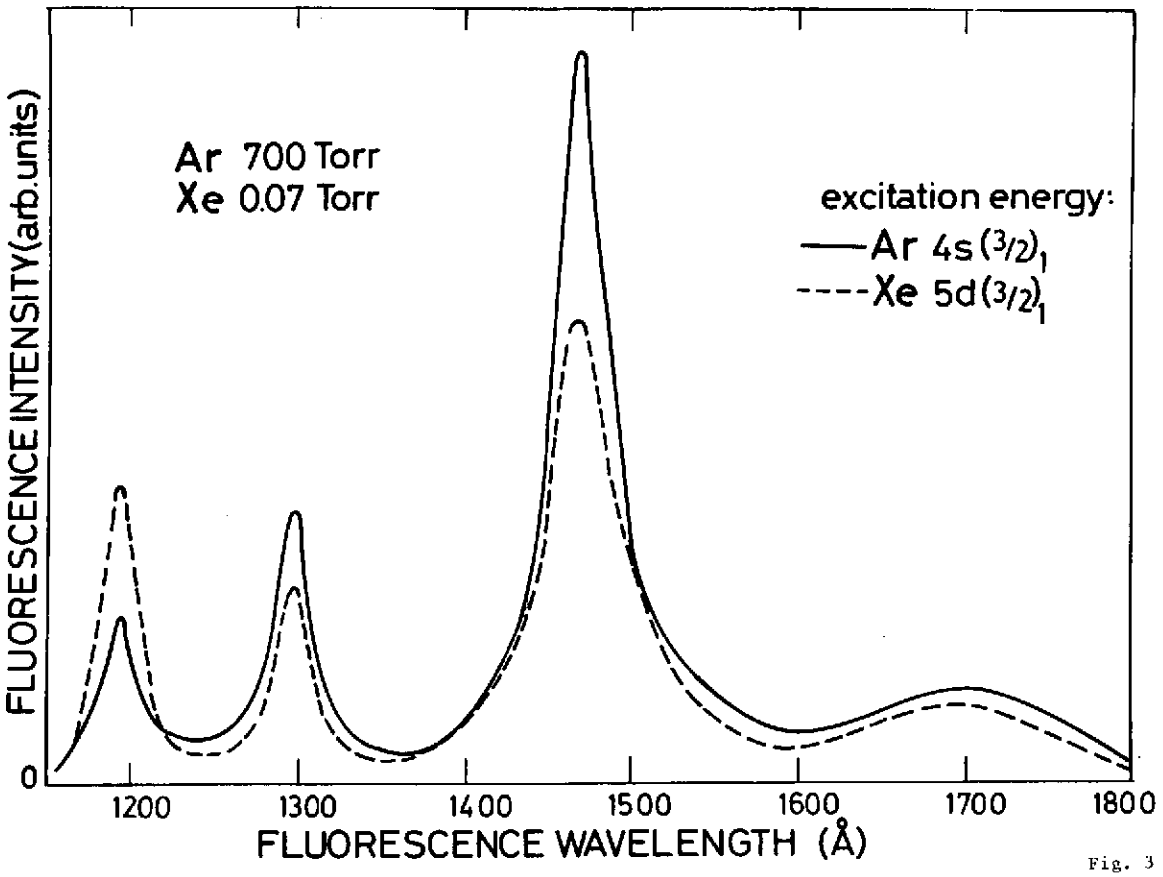

Fig. 3

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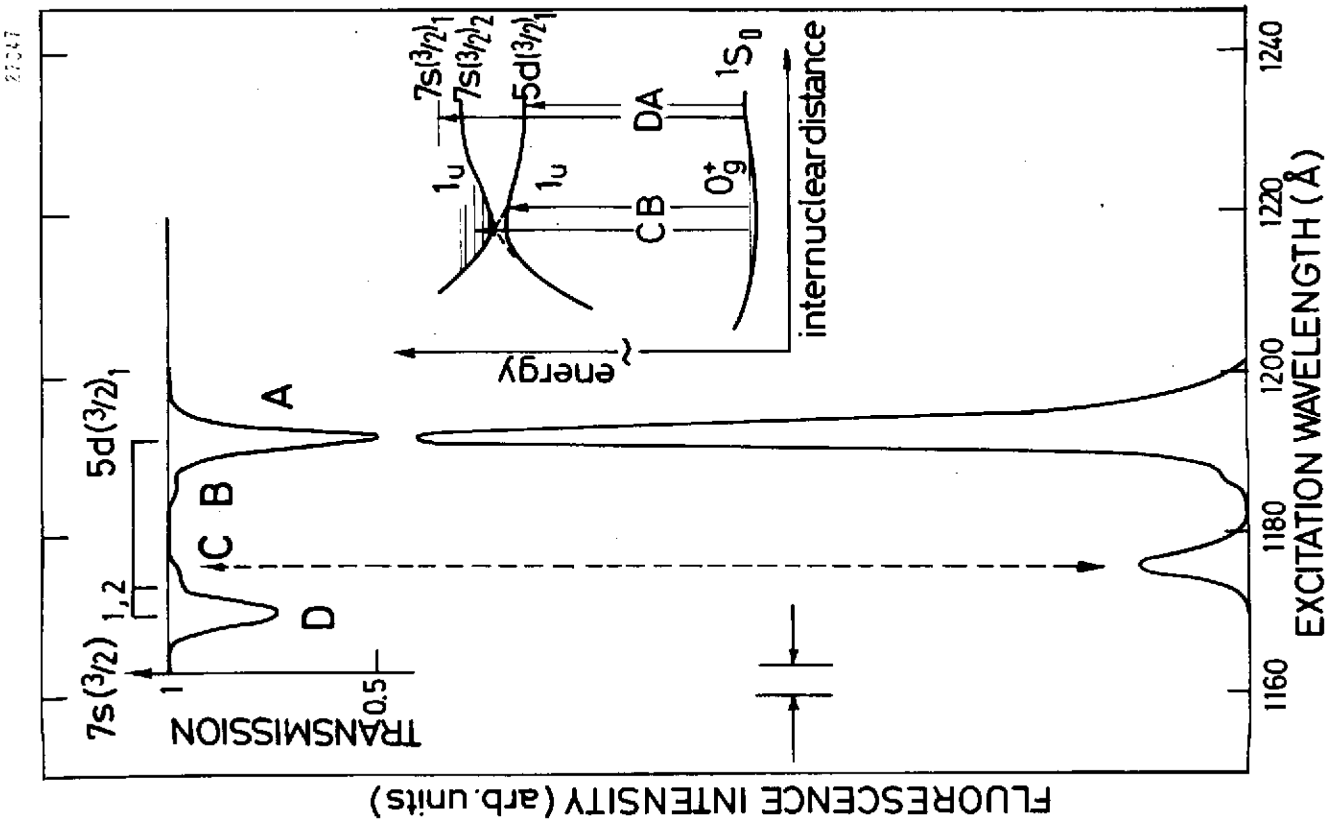


Fig. 2

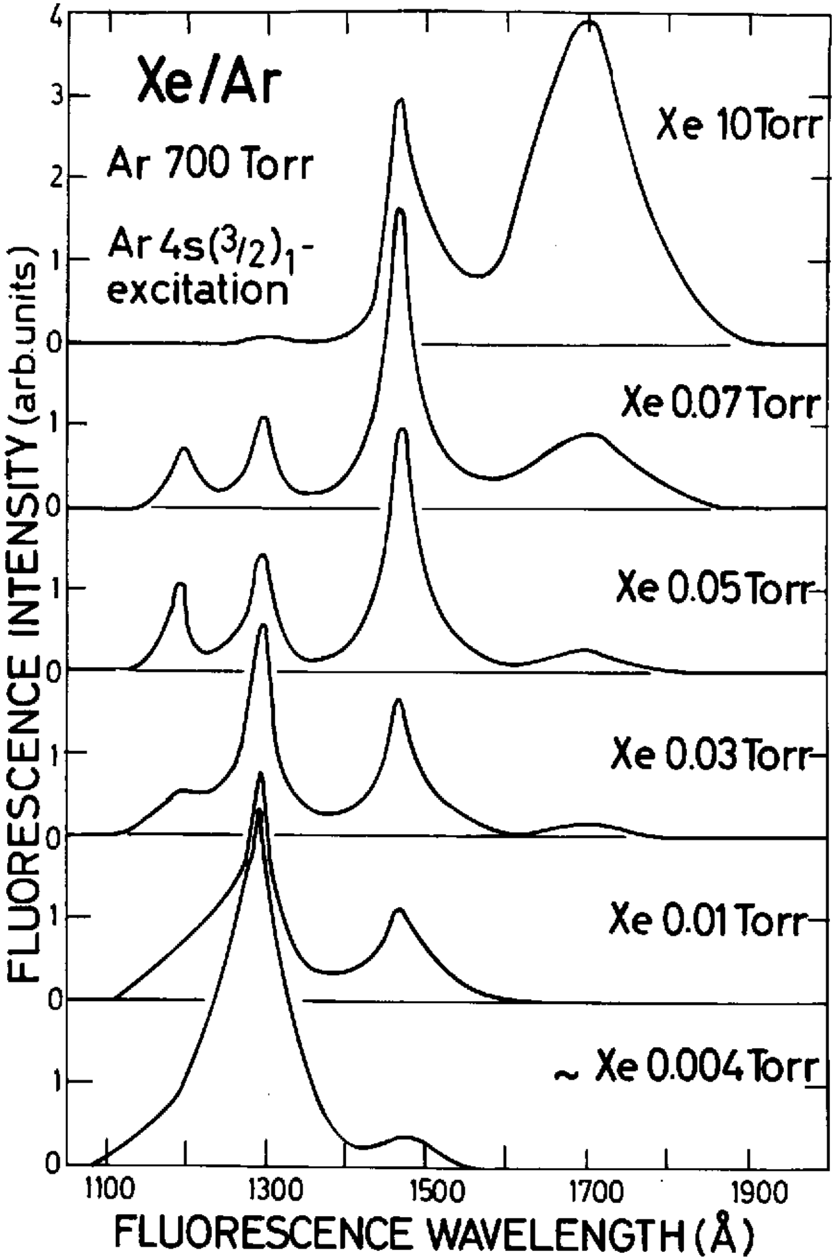
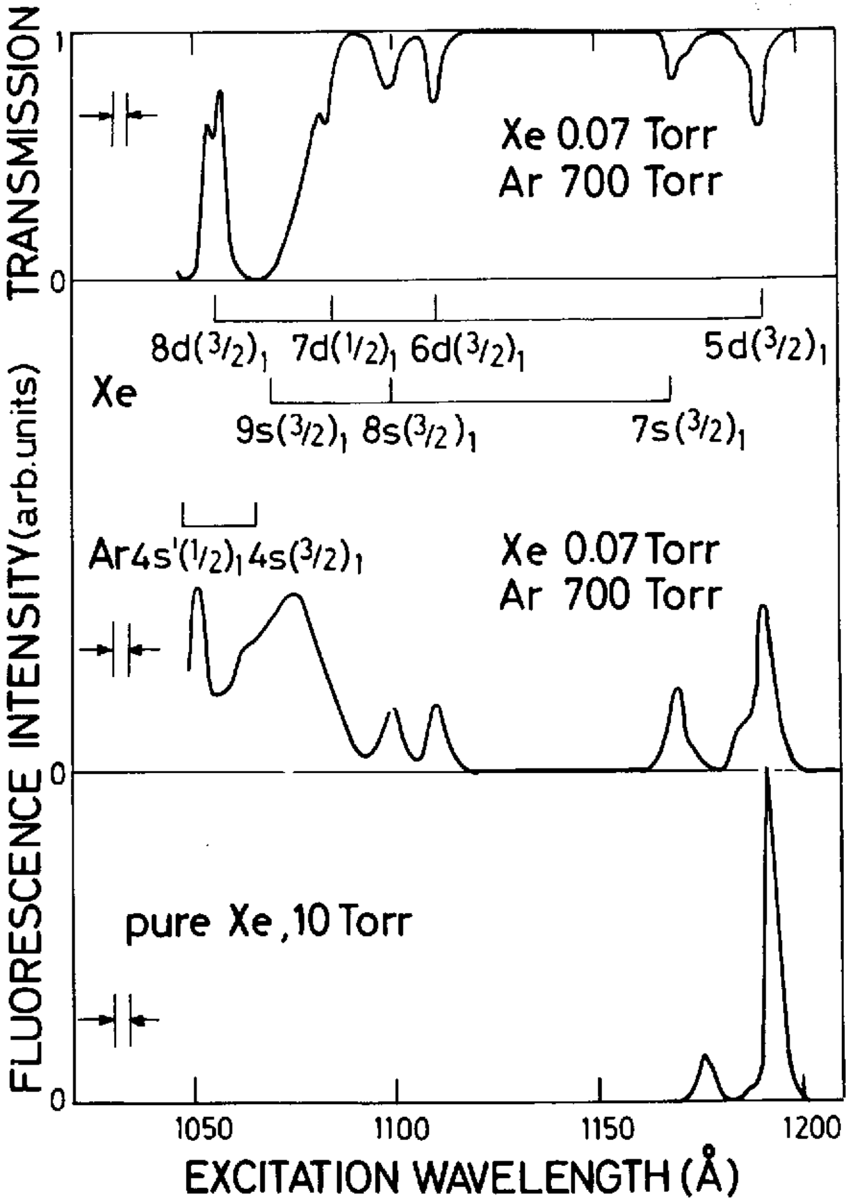

Xe/Ar
Ar 700 Torr
Ar 4s(3/2)1-excitation
Xe 10Torr
Xe 0.07Torr
Xe 0.05Torr
Xe 0.03Torr
Xe 0.01Torr
~ Xe 0.004Torr
4
3
2
1
0
FLUORESCENCE INTENSITY (arb.units)
1100
1300
1500
1700
1900
FLUORESCENCE WAVELENGTH (Å)

Fig. 4


TRANSMISSION
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Xe 0.07 Torr
Ar 700 Torr
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7d(1/2)1
6d(3/2)1
5d(3/2)1
Xe
9s(3/2)1
8s(3/2)1
7s(3/2)1
Ar4s'(1/2)1
4s(3/2)1
Xe 0.07 Torr
Ar 700 Torr
pure Xe, 10 Torr
FLUORESCENCE INTENSITY (arb.units)
1050
1100
1150
1200
EXCITATION WAVELENGTH (Å)

Fig. 5