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The fluorescence of Xe at a pressure of 10 Torr has been excited by monochromatic light in the wavelength region from 1040 Å to 1500 Å. Besides the well known first and second continuum additional emission bands appear at 1192 Å and 1300 Å. They are ascribed to an atomic transition $5d(3/2)_1 \rightarrow {}^1S_0$ *and a molecular transition* $0_u^+(6s'(1/2)+{}^1S_0) \rightarrow 0_g^+({}^1S_0+{}^1S_0)$. *The excitation spectra of the first and second continuum yield high fluorescence efficiency if higher Rydberg states are excited. Excitation of the first resonance line of Xe results in a low fluorescence intensity. Obviously the formation of highly excited molecules* Xe_2^{**} *and intramolecular relaxation plays an important role for the population of the vibrationally relaxed excited states* (0_u^+, 1_u) *of the* Xe_2^* *molecule.*

1. Introduction

In the last years the number of investigations of the vacuum ultraviolet (VUV) fluorescence of gaseous rare gases has grown rapidly. The current interest in this field is due to the fact that rare gases are suited for the development of high power VUV-lasers (1-3). Most of these investigations are concerned with Xe. The laser active level of Xe is the lowest excited state of the diatomic molecule (1). Information about the processes which populate the laser active level is rather poor because in most cases the fluorescence is excited either in a gas discharge or by high energy particles (electrons, α-particles). Only recently has the fluorescence of Xe been excited optically in a narrow wavelength region around the first resonance line using either the 1470 Å Xe emission itself or the fourth positive bands of CO around 1500 Å (4-6).

The intense continuum of synchrotron radiation from the electron storage ring DORIS at DESY, Hamburg, has enabled us to excite Xe for the first time monochromatically in an extended wavelength region from 1500 Å to 1040 Å (LiF cut off). In this paper we report on the monochromatically-excited fluorescence of Xe at a pressure of 10 Torr, where molecular emission bands and atomic emission lines co-exist. The excitation spectra of all fluorescence bands are given. The measurements yield information about the population of those excited levels which give rise to detectable fluorescence.

2. Experiment

Figure 1 shows the experimental set up. The synchrotron radiation was monochromatized by a near normal incidence monochromator, W, (grating Al+MgF_2 coated, 600 l/mm, blaze wavelength 1200 Å). A toroidal mirror, FM, focussed the monochromatic light (band pass ~3 Å) into a gas cell with LiF windows.

The special design of the cell enabled us to measure the transmitted light, T, and the fluorescence light, L, simultaneously. The illuminated part of the gas cell served as entrance slit of a second monochromator, SN (Seya-Namioka type, holographic grating, 1200 l/mm, blazed at 1200 Å, radius 0.4 m. In Fig. 1, the monochromator SN has been rotated by 90° around the axis of the entrance arm for a clearer understanding of the optical design. Because the whole illuminated path in the cell is imaged onto the exit slit of SN, independent of the penetration depth of exciting light, the same fraction of the fluorescence light is always monitored. In this way geometrical effects connected with the use of a mechanical entrance slit are avoided. The only disadvantage of the optical design is the limitation of the resolution of the SN by the geometrical width of the exciting light beam within the cell (band pass of SN typically 45 Å). The fluorescence light and the transmitted light were converted by a sodium salicylate phosphor to the visible and detected by a cooled multiplier. Photon counting techniques were used. The whole gas handling system, GI, was constructed for UHV conditions. Xe with a purity of 99.9997 % (L'Air Liquide) was investigated. Extrinsic fluorescence due to traces of other gases could not be monitored.

3. Results

In Fig. 2, typical emission spectra of Xe for different excitation wavelengths are shown. The excitation wavelength is indicated in each curve by an arrow. The measured width of the emission bands is partly caused by the band pass of the monochromator, SN. In the upper curve Xe was excited by 1171 Å light, inducing atomic $^1S_0 \rightarrow 7s(3/2)_1$ transitions. (For excited atomic states we use the notation of Moore's table (7)). In this case, only the well known first (1480 Å) and second (1720 Å) continuum of the Xe_2^*

molecule is observed. Apart from the relative intensities of the continua, the upper curve of Fig. 2 is typical of the overwhelming part of the wavelength region of excitation. There are, however, two very interesting exceptions. Excitation of the atomic $5d(3/2)_1$ state leads to an additional emission at 1192 Å. Excitation at the long wavelength tail of the second resonance line ($6s'(1/2)_1$) yields an additional emission band centered at 1300 Å. Due to the poor resolution of the analyzing monochromator we have not been able to decide definitely whether these emission bands are resonant with the exciting light or slightly shifted to longer wavelengths. No further emission could be detected up to 5500 Å.

Figure 3 shows the excitation spectra of the four emission bands. For the measurement of an excitation spectrum the analyzing monochromator SN was fixed to the maximum of the emission under consideration. For each excitation spectrum the emission wavelength is indicated in the figure. The fluorescence intensity is measured under continuous variation of the excitation wavelength. The excitation spectra are corrected for the characteristics of the monochromator, W, and for the transmission of LiF. The characteristics of the analyzing monochromator and self absorption (in the case of resonant emission) are not taken into account. At the top of Fig. 3, a transmission spectrum of the cell with 10 Torr Xe is included (a) together with the wavelengths of those excitations of atomic Xe which can be reached by optical excitation [7]. The transmission curve yields atomic as well as molecular type of absorption.
Curves (b) and (c) are the excitation spectra of the second (1720 Å) and first (1480 Å) continuum. The main features are

(i) The fluorescence intensity increases greatly on excitation of higher Rydberg states

(ii) Apart from excitation of the 6s and 6s' states, the ratio of the intensity of the first and second continuum is approximately constant.

(iii) There are striking differences between the spectra in the region of 6s and 6s' excitation. Excitation of the first resonance line results in a ratio of 1:160 between the second and first continuum, whereas excitation of 6s' results in a ratio of only 1:10.

The excitation spectrum of the 1300 Å emission band consists of one peak only. This peak is found at 1298 Å at the long wavelength side of the 1296 Å $6s'(1/2)_1$ absorption line. For the 1192 Å emission band we get an excitation peak at 1192 Å (excitation of the atomic $5d(3/2)_1$ state) and a peak at 1175 Å (long wavelength side of the $7s(3/2)_1$ level).

4. Discussion

According to Fig. 2 the Xe fluorescence at 10 Torr always contains both continua of the Xe_2^* molecule, independent of the wavelength of the exciting light. They are well known from gas discharges as well as from high energy particle excitation (1-3,8,9) and the previous fluorescence measurements with optical excitation (4-6). In the right upper part of Fig. 2 we have sketched schematically the lower excited atomic levels of Xe and some potential curves of the Xe_2 molecule versus internuclear distance. The first continuum with its maximum near 1480 Å is due to transistions from the high vibrational levels of the 0_u^+ and 1_u states of Xe_2^* to the ground state 0_g^+ (6,1o). (The molecular states are characterized by the notation of Hund, coupling case c). The broad second continuum (1720 Å) is ascribed to transitions from the vibrationally relaxed 0_u^+, 1_u states to the repulsive part of the ground state (9,10).

The 1192 Å emission is probably due to the direct recombination $5d(3/2)_1 \rightarrow {}^1S_0$ for the following reasons:

(i) Within the accuracy of our measurements the excitation peak at 1192 Å and the emission peak are resonant.

(ii) The excitation peak at 1192 Å is clearly connected to the ${}^1S_0 \rightarrow 5d(3/2)_1$ atomic excitation and not to a molecular tail of the $5d(3/2)_1$ absorption.

(iii) On increasing the pressure, the emission completely vanishes around 20 Torr. This is mainly caused by self-absorption, due to the geometry of the gas cell (see Fig. 1).

The excitation peak at 1175 Å also contributes to the 1192 Å emission. In this case we have molecular absorption at the long wavelength side of the $7s(3/2)_1$ state into vibrationally excited molecular states. The energy transfer to the $5d(3/2)_1$ atomic level is probably a collisionally induced process or is due to crossing of the molecular potential curves with repulsive potential curves connected to the atomic $5d(3/2)_1$ state.

The 1300 Å emission can be explained by a molecular transition $0_u^+(6s'(1/2)_1 + {}^1S_0) \rightarrow 0_g^+({}^1S_0 + {}^1S_0)$. According to recent absorption measurements of Castex et al. (11), the 0_u^+ state has a shallow minimum at a larger internuclear distance than that of the continuum of the lowest molecular excited states, as predicted by Mulliken (10). The excitation maximum (1298 Å) (see curve (d) of Fig. 3) at the long wavelength side of the second resonance line ($6s'(1/2)_1$) is therefore a transition from the ground state 0_g^+ into vibrational levels of the 0_u^+ state which decays either directly or after some vibrational relaxation. Another important proof of the molecular character of the 1300 Å emission is its pressure dependence. Even at 80 Torr Xe we can observe this emission. In the case of a resonant atomic transition the fluorescence should be completely self absorbed at this pressure.

Excitation of higher Rydberg states (up to the LiF cutoff) leads exclusively to the first and second continuum and not to shorter wavelength emission (at a pressure of 10 Torr). There may be a variety of processes which depopulate the higher Rydberg states and populate the lowest excited molecular state 0_u^+ and 1_u. If we restrict ourselves to initial atomic excitation, two mechanisms for the formation of the lowest excited molecular states should be considered:

(i) A highly excited atom (Xe^{**} (ns or nd)) undergoes radiative or collisionally induced transitions into atomic p states. These decay radiatively into the $6s(3/2)_1$ or $6s(3/2)_2$ state which can form the molecular state 0_u^+ or 1_u by three body collision with ground state atoms.

(ii) A highly excited Xe^{**} atom undergoes three body collisions leading to highly excited molecular states, Xe_2^{**}. These states can cascade down radiatively to the lowest excited states 0_u^+ and 1_u. Prior to the formation of Xe_2^{**}, Xe_2^+ ions may be produced by the Hornbeck-Molnar process $Xe^{**}+Xe \rightarrow Xe_2^+ + e^-$ [12]. As suggested by Mullikan [10], the Xe_2^+ ions may capture an electron resulting in Xe_2^{**}.

The excitation spectrum of the second continuum (b) of Fig. 3 gives strong evidence that (ii) is the preferred process for the population of vibrationally relaxed 0_u^+, 1_u states for the following reason: Excitation of the $6s(3/2)_1$ atomic states results in very little emission of the second continuum compared with excitation of higher Rydberg states. Since, then, all relaxation processes which include $6s(3/2)_1$ as intermediate state must lead to very little emission of the second continuum, the higher states must relax by a route that does not include $6s(3/2)_1$.

The population of vibrationally unrelaxed 0_u^+, ^1u states leading to the first continuum may involve process (i) also because the peak of excitation spectrum (c) of Fig. 3 is not drastically smaller than the peaks from higher Rydberg states.

As for the sum of the two radiative channels, the general increase with increasing excitation energy indicates a nonradiative quenching of the lowest excited atomic states. We assume that excited atoms in the $6s(3/2)_1$ state are metastable due to resonance trapping of radiation [14], which may lead to quenching at the walls.

Investigation of the pressure dependence of all emission bands, which gives more detailed information, is in progress now.

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Figure Captions

Fig. 1 Experimental set up of the fluorescence experiment. The whole system is designed for UHV-conditions because it is directly connected to the storage ring, DORIS

Fig. 2 Fluorescence spectra of Xe at 10 Torr, monochromatically excited with different wavelengths. The excitation wavelengths are indicated by arrows. The fluorescence intensities are given in arbitrary units. In the right upper part, some atomic and molecular states of Xe and Xe_2 are drawn schematically. The observed radiative transitions are indicated (see text).

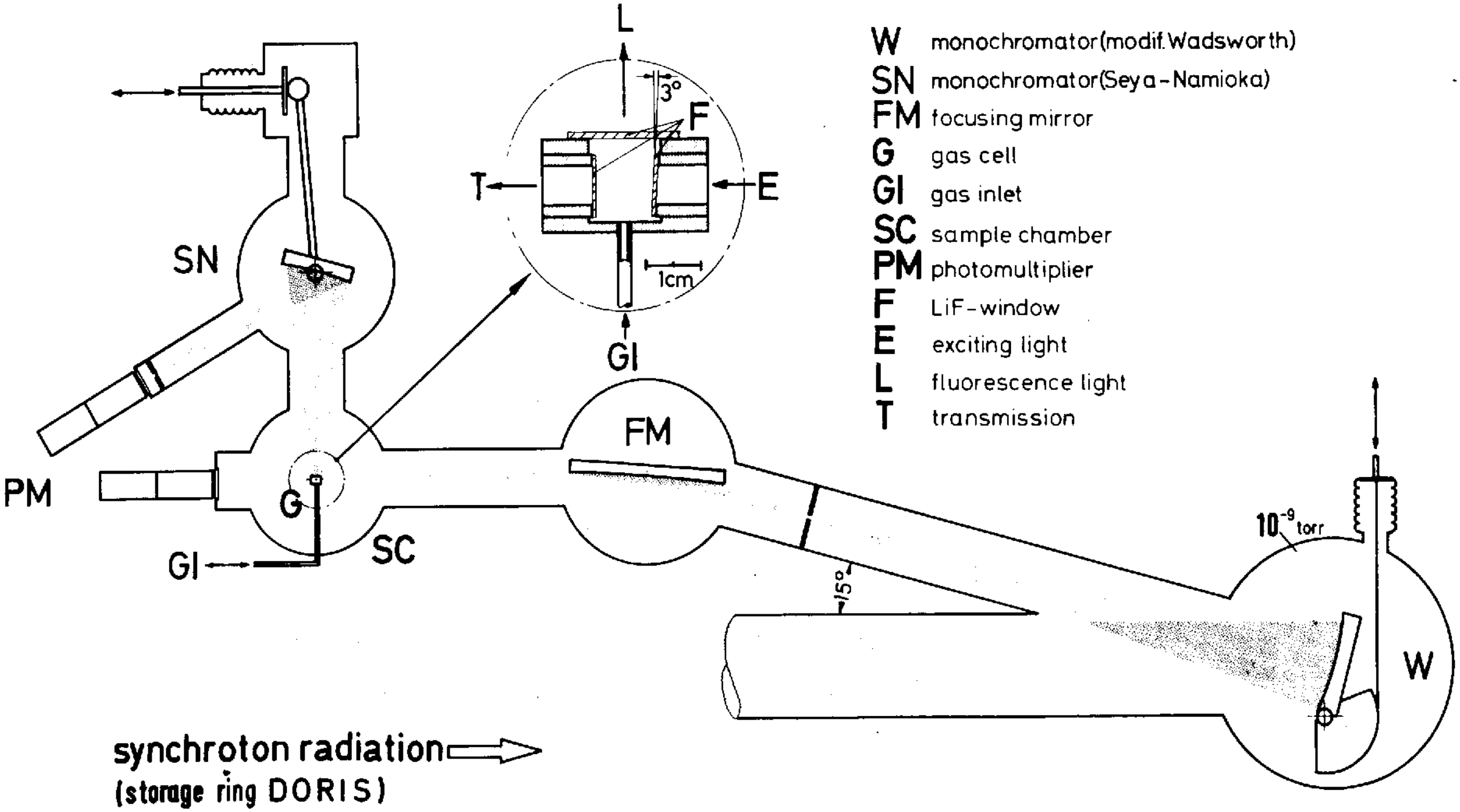
Fig. 3 (a) Transmission of Xe at 10 Torr, together with the associated Rydberg series taken from Ref. (7)

(b) - (e) Excitation spectra of the four emission bands shown in Fig. 2.

References

1. C.K. Rhodes, IEEE J. Quantum Electron. QE-10 (1974) 153
2. J.B. Gerado and A.W. Johnson, IEEE J. Quantum Electron. QE-9 (1973) 748
3. P.W. Hoff, J.C. Swingle and C.K. Rhodes, Appl.Phys.Letters 23, 245 (1973)
4. L.W. Sick, J.Phys.Chem. 72, 3129 (1968)
5. C.G. Freeman, M.J. McEwan, R.F.C. Claridge and L.F. Phillips, Chem.Phys. Letters 25, 190 (1974)
6. E.H. Fink, F.J. Comes, Chem.Phys. Letters 30, 267 (1975)
7. C.E. Moore, "Atomic Energy Levels", Natl.Bur.Std. (U.S.) Circ. No. 467 (1949)
8. R.E. Huffman, J.C. Larrabee and Y. Tanaka, Appl.Opt. 4, 1581 (1965) and references therein
9. O. Chesnovsky, B. Raz and J. Jortner, Chem.Phys.Letters 15, 475 (1972)
10. R.S. Mulliken, J.Chem.Phys. 52, 5170 (1970)
11. M.C. Castex and N. Damany, Chem.Phys.Letters 24, 437 (1974)
12. J.A. Hornbeck and J.P. Molnar, Phys.Rev. 84, 621 (1951)
13. T. Holstein, Phys.Rev. 72, 1212 (1947); 83, 1159 (1951)

Fig. 1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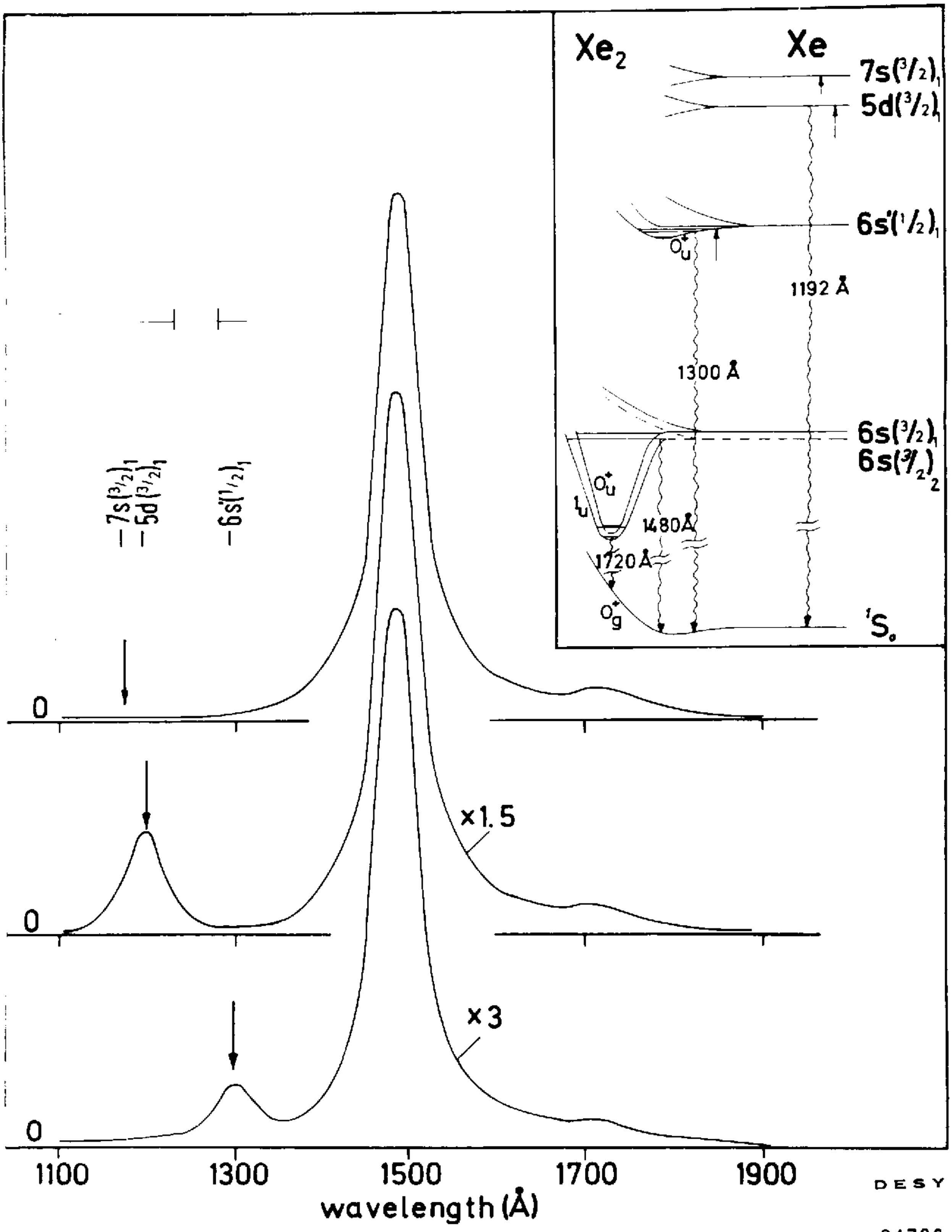

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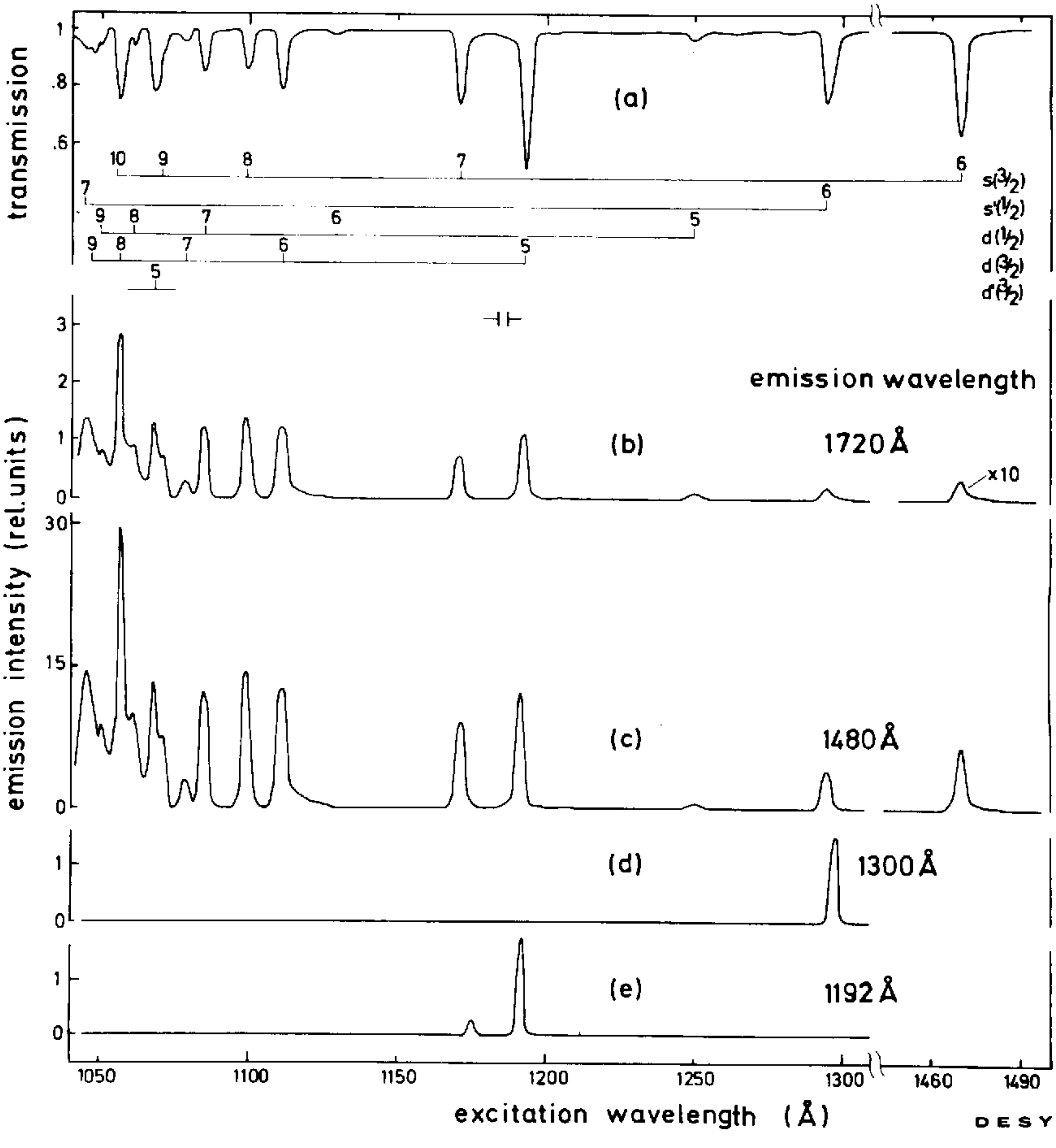
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.6
(a)
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7 6 s(1/2)
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emission intensity (rel.units)
emission wavelength
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(c)
1480 Å
(d)
1300 Å
(e)
1192 Å
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1050
1100
1150
1200
1250
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1490
excitation wavelength (Å)

Fig. 3