

$5s^2 5p^3 ({}^4S)nl$ Levels of Xe III

M. Gallardo*, C. A. Massone†, A. A. Tagliaferri† and M. Garavaglia*

Departamento de Física, Universidad Nacional de La Plata, La Plata, Argentine

and

W. Persson

Department of Physics, Lund Institute of Technology, Lund, Sweden

Received October 7, 1978

Abstract

$5s^2 5p^3 ({}^4S)nl$ levels of Xe III. M. Gallardo, C. A. Massone, A. A. Tagliaferri and M. Garavaglia (Departamento de Física, Universidad Nacional de La Plata, La Plata, Argentine) and W. Persson (Department of Physics, Lund Institute of Technology, Lund, Sweden). *Physica Scripta (Sweden)* 19, 538–544, 1979.

Analysis of recent observations of the Xe III spectrum has yielded revised and extended identifications for the $5s^2 5p^3 ({}^4S)6s, 7s, 6p, 5d, 6d$ and $4f$ levels. Four of the previously known twenty-two levels have been rejected whereas sixteen new levels have been added. The ionization energy has been determined from isoelectronic comparisons. The value arrived at, $250\,400 \pm 300\text{ cm}^{-1}$, is some 9000 cm^{-1} lower than the presently accepted value.

1. Introduction

The last ten years have seen the publication of a large number of papers concerned with the ionic assignment and classification of xenon laser lines, the first systematic study on a large scale being the paper by Gallego Lluesma et al. in 1973 [1]. In this work, which gives references to earlier papers, the spontaneous xenon spectrum was photographed in the 2400–8700 Å range. By comparing the relative intensities of the lines at different excitation energies Gallego Lluesma et al. were able to determine the ionization stage of the majority of the xenon laser lines reported in literature. In 1976 Hoffman and Toschek [2] confirmed and extended the assignments made in [1] by comparing the rise times and pulse widths of a large number of spontaneous lines emitted from a xenon discharge.

In 1974 the work of Gallego Lluesma et al. [1] was greatly extended by Tagliaferri et al. [3], who gave ionic assignments for 568 lines in the spontaneous spectrum of xenon, many of them being observed for the first time. Since the vast majority of the new lines were attributed to Xe III, it was judged worthwhile to try to improve on and extend the existing analysis of the Xe III spectrum with the goal to get a better insight into the origin of the xenon laser lines.

The ground state of the doubly ionized xenon atom has the electron configuration $5s^2 5p^4$, which yields three terms, namely ${}^3P, {}^1D$ and 1S , of even parity. The low excited configurations are $5s5p^5$, comprising a 3P and a 1P term, and configurations of the type $5s^2 5p^3 nl$. The latter can be considered as being built on the ground configuration of Xe IV, $5s^2 5p^3$, by addition of

an outer electron. The parent configuration gives three terms, namely ${}^4S, {}^2D$ and 2P . In the present paper the main emphasis is being put on the $5s^2 5p^3 ({}^4S)nl$ level systems of Xe III.

The description of the Xe III spectrum, as given in AEL [4], is based mainly on the 1936 papers by Humphreys [5] and Boyce [6]. The analysis, founded on observations in the 8900–600 Å range, comprises energy levels belonging to the $5s^2 5p^4, 5s5p^5, 5s^2 5p^3 6s, 7s, 6p, 5d$ and $6d$ configurations. However, for some of the configurations mentioned the analysis is very far from being complete: in $6d$, for instance, only five of the thirty-eight theoretically expected energy levels had been identified. The most significant contribution to the analysis of the Xe III spectrum since 1936 is that by Humphreys et al. in 1939 [7], who studied the Zeeman effect and reported g -factors for some thirty levels.

The present paper is concerned with the structure of the $5s^2 5p^3 ({}^4S)nl$ level system of Xe III. Based on the registrations and measurements reported in [3] and additional unpublished material about 80 lines, ranging in wavelength from 6730 Å to 2470 Å, have been classified as combinations between levels within the $({}^4S)nl$ level system. About one half of these lines had not previously been classified or have now been reclassified. As a result, all $5s^2 5p^3 ({}^4S)6s, 7s, 6p, 5d, 6d$ and $4f$ levels are now known.

2. Experimental methods

The wavelength data on which the present report is based were obtained in the atomic spectroscopy laboratory of Universidad Nacional de La Plata. The spectrum was excited in a Pyrex tube with inner electrodes and a bore diameter of 3 mm, originally designed for laser operation, by discharging through the tube a capacitor bank, and photographed with a 3.4 m Ebert plane grating spectrograph. By varying the capacitance and the voltage applied to the capacitor bank the degree of excitation in the discharge could be varied, thereby permitting a determination of the stage of ionization in which a line originates.

Spectrograms were recorded in the first and third orders of the grating. Thorium lines from an electrodeless discharge were superimposed on the spectrograms and served as reference lines [8]. Unresolved hyperfine structures and isotope shifts cause many lines to appear wide and hazy, thereby decreasing the obtainable wavelength accuracy somewhat. However, the probable error seldom exceeds 0.03 Å for lines measured in the first diffraction order and 0.01 Å for lines measured in the third diffraction order.

Full experimental details are given in [3], which also lists

* Present address: Centro de Investigaciones Ópticas, Casilla de Correo 124, 1900 La Plata, Argentine.

† Present address: Instituto de Física, Universidade Federal Fluminense, Niterói–24000 RJ, Brazil.

intensities, shapes and wavelengths for 512 lines newly attributed to Xe III.

3. Energy levels

To take full advantage of the new experimental material the original line list, containing not only the wavelengths listed in [3] but also revised wavelength values of the Xe III lines already classified by Humphreys [5] and a number of lines which could not with certainty be attributed to Xe III, has been used in the present work. This complete line list, together with the energy level values given in AEL [4], was used as input for a computer code searching for recurring wavenumber intervals in the line list. In this way most of the already known levels were confirmed and many new levels were established.

To determine "best" level values the observed wavenumbers of the classified lines, weighted in inverse proportion to the square of their estimated uncertainties, were used as input to a computer code determining the level values by a least-squares procedure. In this process all well-established 5s²5p³nl levels, i.e., not only those built on the ⁴S parent state, plus the 5s5p⁵ ¹P₁ level were included. The latter level was fixed at the value given in AEL, thus fixing the energy scale. Some 360 lines in the 6750–2250 Å wavelength range were included in the fitting procedure.

All Xe III lines classified as combinations between levels built on the ⁴S parent term are given in Table I. The fourth column of the table gives the wavenumbers calculated from the energy level scheme. The degree of agreement between observed and calculated wavenumbers illustrates the internal consistency of the excited level system.

Eighteen of the 5s²5p³(⁴S)nl levels given in AEL [4] have been confirmed, four have been rejected and sixteen newly identified levels have been added. Thus, thirty-four (⁴S)nl levels, belonging to the 5s²5p³6s, 7s, 6p, 5d, 6d, and 4f configurations, are now known. The results are summarized in Table II. The last column of the table, which shows the number of observed transitions to or from a certain level, does also include combinations with levels outside the (⁴S)nl system.

3.1. 5d + 6s

Of the 5d + 6s levels based on the ⁴S parent term all but 5d ⁵D₄ have previously been reported [4]. The missing level has now been established from a strong (⁴S)5d ⁵D₄–(⁴S)6p ⁵P₃ combination at 2717.326 Å. The identification, based on a single line, is strongly supported by a theoretical prediction of the level structure obtained by diagonalizing the 5s²5p³(5d + 6s) + 5s5p⁵ energy matrix. Values for the radial integrals to be used in the diagonalization procedure were obtained from Hartree–Fock calculations [9].

Humphreys' identification of the level at 112 693 cm^{−1} as (⁴S)5d ⁵D₀ was changed to 5s5p⁵ ³P₀ by Martin and Corliss in their paper on the analysis of the second spectrum of iodine [10]. They based their reassignment on a comparison of the distribution of the experimentally established 5s5p⁵ levels with the predictions of the intermediate coupling theory as formulated by Condon and Shortley [11]. However, this theory does not take effects of configuration interaction into account. Particularly, it neglects the effects of the 5s5p⁵ ↔ 5s²5p³5d interaction. The *R*¹(5p², 5s5d) integral can be expected to be very large, since all orbitals involved have the same principal quantum number. The importance of this type of interaction has recently been recognized for the corresponding

spectra in the preceding row of the periodic table [12]. The relative positions of the 5s5p⁵ and 5s²5p³5d configurations vary very rapidly in the beginning of the Te I isoelectronic sequence. In I II and Xe III the levels of the two configurations are intermingled. This means that not only the 5s5p⁵ terms as such are shifted by the 5s5p⁵ ↔ 5s²5p³5d interaction but also that the individual levels within a term are not necessarily shifted by equal amounts.

A diagonalization of the 5s²5p³(5d + 6s) + 5s5p⁵ matrix predicts the (⁴S)5d ⁵D₀ level very close to the experimentally established level at 112 693 cm^{−1}. The 5s5p⁵ ³P₀ level, on the other hand, is predicted some 5000 cm^{−1} below. Since, furthermore, the combination properties of the 112 693 cm^{−1} level resemble those of the (⁴S)5d ⁵D_{4,3,2,1} levels much closer than those of the 5s5p⁵ ³P_{2,1} levels, there is little doubt that the identification originally proposed by Humphreys is the correct one.

The eigenvectors obtained in the abovementioned diagonalization procedure reveal a substantial mixing of wavefunctions between the 5s5p⁵ ³P and (⁴S)5d ⁵D states, despite the fact that the levels in these two terms are not connected by any matrix element. The mixing, which is due to break-down of *LS* coupling, is of the order of 1% for the *J* = 2 levels and 5% for the *J* = 1 levels whereas it amounts to as much as some 20% for the *J* = 0 levels. The large mixing between the *J* = 0 states means that they should have somewhat similar combination properties, and attempts to establish the 5s5p⁵ ³P₀ level from combinations with (⁴S)5p ⁵D₁ and ³P₁ have been made. This search revealed a level at 108 334 cm^{−1}. It is, however, not possible to verify the identification until observations in the vacuum ultraviolet region become available.

All (⁴S)5d ³D levels given by Humphreys [5] have been confirmed. However, the level at 124 691 cm^{−1}, identified as (⁴S)5d ³D₂, is about 7000 cm^{−1} above the predicted position for (⁴S)5d ³D₂ and is rather the ³F₂ level built on the ²D parent. A new (⁴S)5d ³D₂ level has now been established at 117 240 cm^{−1} from combinations with 6p levels. A line at 852.950 Å, classified by Boyce [6] as the 5s²5p⁴ ¹S₀–(²P)6s ¹P₁ transition, might as well correspond to the transition to the ground level from the new (⁴S)5d ³D₂ level.

The 5p³5d configuration comprises as many ³D terms as parent states. In the discussion above it has been anticipated that the lowest of the ³D terms is based on the ⁴S parent. However, this can not be taken for granted: the lowest ³D₃ level has, in fact, as large (²D)³D as (⁴S)³D contribution to its eigenvector. Also for the ³D₂ and ³D₁ levels the parent mixing is considerable and the assignment of parentage to the ³D terms is somewhat arbitrary.

The (⁴S)6s ⁵3S levels given in AEL have been retained. Humphreys et al. [7] reported experimental *g*-factors for both levels. The *LS* *g*-factor for the quintet level is 2.00, the experimental value is 1.95 and the theoretical value obtained from the aforementioned diagonalization of the 5s²5p³(5d + 6s) + 5s5p⁵ matrix is 1.94. The deviation from the *LS* value arises from a slight contribution to the eigenvector from the (²P)6s ³P₂ state, which has a *LS* *g*-factor of 1.50. Also for the level labelled (⁴S)6s ³S₁ the agreement between observed and calculated *g*-factors is very good: the *LS* *g*-factor is 2.00, the observed *g*-factor is 1.77 and the theoretical value is 1.81. The low *g*-factor is for this level caused by eigenvector contributions from the (²P)6s ¹3P₁ and (²D)6s ³D₁ states, all of which have *LS* *g*-factors smaller than 2.00.

For the 5d and 6s levels built on the ⁴S parent the calculated

$5d \leftrightarrow 6s$ mixing is quite negligible. This comes about since there are no close coincidences between $(^4S)5d$ and $6s$ or $(^4S)6s$ and $5d$ levels. Due to the smallness of $ns \leftrightarrow (n-1)d$ interaction integrals such close coincidences are in general necessary for strong $s \leftrightarrow d$ mixing to take place.

3.2. $6d + 7s$

The $(^4S)6d\ ^5D$ and the $(^4S)7s\ ^5, ^3S$ levels were reported by Humphreys [5] with the comment that the identification for the $6d\ ^5D_4$ level might be regarded as doubtful. The level, originally proposed by deBruin [13], was established from a single line at 3023.80 \AA which, in addition, was doubly classified. This line has now been identified with the transition from the $(^4S)6p\ ^3P_1$ level to the new $(^4S)5d\ ^3D_2$ level, and a new $(^4S)6d\ ^5D_4$ level has been established at $182\,716\text{ cm}^{-1}$. This new identification, based on three lines, places 5D_4 above 5D_3 in analogy with their relative positions in $5d$ and in I II $(^4S)nd\ ^5D$ [10].

The $(^4S)6d\ ^5D_0$ level at $182\,840\text{ cm}^{-1}$ has been rejected. One of the two lines used to establish the level, the 2772.41 \AA line, has now been identified with the $(^4S)6p\ ^5P_3 - (^4S)6d\ ^3D_2$ transition. A new $(^4S)6d\ ^5D_0$ level has been established at $182\,521\text{ cm}^{-1}$ from combinations with $(^4S)6p\ ^5, ^3P_1$ and $(^4S)4f\ ^5F_1$. The new position for the 5D_0 level is below 5D_1 which is in full agreement with the order found in all $(^4S)nd\ ^5D$ terms in I II [10] but in disagreement with the order in Xe III $5d$. However, as pointed out earlier, the $(^4S)5d\ ^5D_0$ level in Xe III is perturbed by the $5s5p\ ^5P_0$ level positioned just below.

The identification given in Table II for the $(^4S)6d\ ^3D$ levels are entirely new. The relative positions of the levels are the same as in the corresponding $5d$ term.

The $(^4S)7s\ ^5S_2$ identification given AEL [4] has been confirmed whereas the 3S_1 identification has been rejected. There is no obvious reason for expecting an increase in the $^5S_2 - ^3S_1$ distance when going from $6s$ to $7s$, as would be the case if the identification for 3S_1 given in AEL is accepted, but rather a considerable decrease. A new $(^4S)7s\ ^3S_1$ level, based on several combinations, has been established at $183\,786\text{ cm}^{-1}$. With this new identification the $^5S_2 - ^3S_1$ interval decreases approximately by a factor of three when going from $6s$ to $7s$ both in I II and Xe III.

3.3. $6p + 4f$

A theoretical prediction of the level structure in the $5s^25p^36p$ configuration, obtained by diagonalization of the energy matrix with Hartree-Fock values for the radial integrals, confirmed the identifications reported by Humphreys [5] and Humphreys et al. [7] for all $(^4S)6p$ levels. The calculation also confirmed most of the identifications for levels ascribed to the 2D and 2P parents and facilitated an extension of the identifications to include many of the $6p$ levels given without term designations. These latter results are beyond the scope of this report. However, one inconsistency in the existing analysis turned out to be of great importance for the continued analysis: the reported position of the $(^2P)6p\ ^3D_3$ level was at $173\,946\text{ cm}^{-1}$ whereas the calculations predicted the level around $183\,000\text{ cm}^{-1}$. A new level has now been established at $182\,377\text{ cm}^{-1}$ and the configuration assignment for the $173\,946\text{ cm}^{-1}$ level had to be revised. This point will be further discussed later on.

The eigenvectors for the $(^4S)6p$ levels (Table III), obtained in a least-squares fit of the theoretical energy expressions to

all well-established $6p$ levels (only three $J=0$ levels were excluded from the fit), reveal that these levels have fairly high purities in the LS -coupling scheme. The agreement between calculated and observed g -factors is satisfactory in view of the approximations inherent in the theory and the fact that the experimental values were deduced from only partially resolved Zeeman patterns.

In the computer search for even energy levels three levels having $J=4, 3$ and 2 showed up at $166\,355$, $166\,699$ and $167\,066\text{ cm}^{-1}$, i.e., in the energy range covered by the $(^2D)6p$ levels. Since all $(^2D)6p$ levels (except the 3P_0 level) were well established the additional levels were ascribed to the $4f$ configuration. The $166\,355\text{ cm}^{-1}$ level was reported already by Humphreys [5], who pointed out that the combination properties of the level were very similar to those of the $(^2D)6p\ ^3F_4$ level at $166\,554\text{ cm}^{-1}$. Later, Humphreys et al. [7] commented that the level "may belong to a term caused by the binding of an f -electron" and in AEL [4] the level was tentatively designated $5s^25p^3(^2D)4f\ J=4$. Since another group of three levels appeared somewhat higher up, namely at $170\,250$, $173\,734$ and $173\,946\text{ cm}^{-1}$ we ascribed the first mentioned group to the $(^4S)4f\ ^5F$ term and the latter group to the $(^4S)4f\ ^3F$ term (the $173\,946\text{ cm}^{-1}$ level was established by Humphreys [5] but assigned $(^2P)6p\ ^3D_3$, as already mentioned).

The "natural" way to establish the $5s^25p^3(^4S)4f$ levels would have been via combinations with $(^4S)5d$ levels. However, in Xe III these combinations are to be found in the vacuum-ultraviolet wavelength region where no recent observations are available. The reason why the $(^4S)4f\ ^5F$ levels showed up in the present investigation is therefore somewhat fortuitous: strong mixing between the $(^4S)4f\ ^5F_{4,3,2}$ levels and the $(^2D)6p\ ^3F_4, ^3D_3$ and 3P_2 levels (at $166\,554$, $166\,374$ and $166\,880\text{ cm}^{-1}$) gives rise to a great number of "forbidden" combinations, for instance of the type $(^2D)5d - (^4S)4f$, which appear in the wavelength region covered in the present investigation.

The $4f \leftrightarrow 6p$ mixing is, as was also the case for the $ns \leftrightarrow (n-1)d$ mixing discussed earlier, caused by close coincidences between levels rather than by large matrix elements. This explains why the $(^4S)4f\ ^5F_1$ level did not show up in the computer search for even levels: the $(^4S)4f\ ^5F_4, ^5F_3$ and 5F_2 levels are only some 300 cm^{-1} from their nearest $(^2D)6p$ neighbour having the same J value whereas the 5F_1 level is about 900 cm^{-1} from the nearest $6p$ level having $J=1$. This means a substantial reduction of the mixing coefficient.

The $J=4$ levels at $166\,355$ and $166\,554\text{ cm}^{-1}$ may be used to exemplify the mixing between $(^4S)4f$ and $(^2D)6p$ states. Humphreys et al. [7] reported g values for both levels. The experimental g -factors are 1.31 and 1.28 while the LS g -factor for a 5F_4 level is 1.35 and for a 3F_4 level 1.25 . Both levels have strong combinations with $(^4S)5d\ ^5D_3$ in the vacuum ultraviolet [6], the intensities of the lines being seven and six respectively. Both the g -factors and the combinations with $(^4S)5d\ ^5D_3$ point towards a heavy mixing between the two states.

$(^2D)6p\ ^3F_4$ is the only level in the $(^2D)6p\ ^3F$ term that combines with the $(^4S)5d\ ^5D$ levels. The reason for this is the following: the splitting of the $(^2D)6p\ ^3F$ term is large whereas the splitting of the $(^4S)4f\ ^5F$ term is small. Thus, since the $(^4S)4f\ ^5F_4$ and $(^2D)6p\ ^3F_4$ levels are close together the rest of the levels in the $(^4S)4f\ ^5F$ and $(^2D)6p\ ^3F$ terms are far apart and do not mix. In this context it should be pointed out that the $(^2D)6p\ ^3D_3$ and 3P_2 levels are very close to $(^2D)6p\ ^3F_4$ and

do in fact have combinations with (⁴S)5d ⁵D; these lines can be interpreted as being caused by (⁴S)4f ⁵F₃ ↔ (²D)6p ³D₃ and (⁴S)4f ⁵F₂ ↔ (²D)6p ³P₂ mixings.

The (⁴S)4f ⁵F₅ and ⁵F₁ levels do not mix with (²D)6p levels and therefore one has to rely on much fewer lines for their identification than for the other (⁴S)4f levels. However, knowing the positions of the intermediate-*J* levels in the ⁵F term the positions of the *J* = 5 and *J* = 1 levels are fairly well predictable. In the (⁴S)4f ⁵F terms of I II and Xe III the relative order of the levels is exactly the same. In the ³F term the *J* = 3 level is low both in I II and Xe III. In I II, however, the *J* = 2 level is slightly above the *J* = 4 level whereas the order is reversed in Xe III.

4. Ionization energy

A revised value for the ionization energy of Xe III has been determined from isoelectronic comparisons. The main features of the method used are illustrated in Tables IV a, b and c for three different *l*-values. The first column of the table shows what members of a certain isoelectronic sequence have been studied and the second column their ionization energies. The third column gives the level value for the specific state followed along the isoelectronic sequence. This is for a given *l* value always a state in the configuration with the largest possible *n* value applicable to all spectra studied, i.e., 7s, 6p and 6d and is, further, the state with the largest possible *J* value based on the lowest parent state. No effort has been made to eliminate the effects of spin-dependent interactions by using, for instance, term energies instead of individual level values. The fourth column of the table gives the quantum defects of the levels studied and the last column the change in the quantum defect along the sequence. Between second and third spectra and for a given *nl* value the change is to a very good approximation the same in the Xe I and Cs I isoelectronic sequences. Thus, it seems reasonable to anticipate this same change to apply in the Te I sequence. In doing so one arrives at the ionization energies for Xe III given in parentheses in the second column.

The mean of the values for the ionization energy of Xe III derived in Table IV is 250 400 cm⁻¹. This value, which should be correct to ± 300 cm⁻¹, is some 9000 cm⁻¹ lower than the presently accepted value, which was determined by Humphreys [5] by assuming the quantum defects for the (⁴S)5d ⁵D₂ and

(⁴S)6d ⁵D₂ levels to be the same. However, for *pⁿd* configurations it has turned out that the assumption of a constant quantum defect throughout the whole *nd* series is reasonably well justified only for first spectra. For ionized species there is in general a considerable change in quantum defect between the first two members of a *d* series. This is due to the collapse of the wavefunction for the lowest *d*-state in ionized atoms. Table V illustrates the situation in the Xe I and Cs I isoelectronic sequences.

It has recently been pointed out by Hellentin [14] that the 4f states of Ba III are far from their hydrogenic positions, their quantum defects being about unity. The (⁴S)4f levels of Xe III now turn out to have quantum defects of the order of 0.5. Thus, for third spectra the penetrating character of the 4f orbitals appears to a certain extent already in xenon.

Acknowledgements

We gratefully acknowledge the financial support from Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentine, the Comisión de Investigación Científica of the Universidad Nacional de La Plata, Argentine, and the Organization of American States.

References

1. Gallego Llesma, E., Tagliaferri, A. A., Massone, C. A., Garavaglia, M. and Gallardo, M., J. Opt. Soc. Am. **63**, 362 (1973).
2. Hoffmann, V. and Toschek, P. E., J. Opt. Soc. Am. **66**, 152 (1976).
3. Tagliaferri, A. A., Gallego Llesma, E., Garavaglia, M., Gallardo, M. and Massone, C. A., Opt. Pura y Apl. **7**, 89 (1974).
4. Moore, Ch. E., Atomic Energy Levels, Natl. Bur. Stand. Circ. 467, vol. III. Washington, 1958.
5. Humphreys, C. J., J. Res. Natl. Bur. Stand. **16**, 639 (1936).
6. Boyce, J. C., Phys. Rev. **49**, 730 (1936).
7. Humphreys, C. J., Meggers, W. F. and deBruin, T. L., J. Res. Natl. Bur. Stand. **23**, 683 (1939).
8. Valero, F. P. J., J. Opt. Soc. Am. **58**, 1048 (1968); Goorwitch, D., Valero, F. P. J. and Clua, A. L., J. Opt. Soc. Am. **59**, 971 (1969).
9. Hansen, J. E., private communication.
10. Martin, W. C. and Corliss, C. H., J. Res. Natl. Bur. Stand. **64A**, 443 (1960).
11. Condon, E. V. and Shortley, G. H., The Theory of Atomic Spectra. Cambridge, 1957.
12. Hansen, J. E. and Persson, W., J. Opt. Soc. Am. **64**, 696 (1974).
13. deBruin, T. L., Zeeman Verhandelingen, p. 413 (1935).
14. Hellentin, P., Physica Scripta **13**, 155 (1976).

Table I. Xe III lines above 2000 Å classified as combinations between levels belonging to the 5s²5p³(⁴S)*nl* level system

Comments on line shapes: A = asymmetric; B = blended; H = hazy; W = wide

Symbols in column five: a = new classification; b = revised classification

Intensity and shape	Wavelength (Å)	Wavenumber (cm ⁻¹)		Classification	Comment
		Observed	Calculated		
3	6 722.751	14 870.76	.77	(⁴ S) 4f ³ F ₃ -(⁴ S) 6d ³ D ₂	a
2	6 530.171	15 309.31	.28	4f ⁵ F ₁ -6d ⁵ D ₂	a
1	6 513.628	15 348.19	.21	4f ⁵ F ₁ -6d ⁵ D ₀	a
3 B	6 501.130	15 377.69	.76	4f ⁵ F ₁ -6d ⁵ D ₁	a
1	6 484.793	15 416.43	.45	4f ⁵ F ₂ -6d ⁵ D ₂	a
1	6 456.105	15 484.94	.94	4f ⁵ F ₂ -6d ⁵ D ₁	a
1	6 341.275	15 765.34	.33	4f ⁵ F ₃ -6d ⁵ D ₃	a
2	6 333.903	15 783.69	.69	4f ⁵ F ₃ -6d ⁵ D ₂	a
3	6 259.047	15 972.46	.47	4f ⁵ F ₅ -6d ⁵ D ₄	a
3	6 205.966	16 109.07	.10	4f ⁵ F ₄ -6d ⁵ D ₃	a
0 Xe III ?	6 196.431	16 133.86	4.12	4f ³ F ₃ -6d ³ D ₃	a
1	6 110.360	16 361.12	.11	4f ⁵ F ₄ -6d ⁵ D ₄	a
5 W	4 723.597	21 164.39	.33	6s ³ S ₁ -6p ⁵ P ₁	
5 B	4 683.566	21 345.28	.24	6s ³ S ₁ -6p ⁵ P ₂	

Table I. Continued

Intensity and shape	Wavelength (Å)	Wavenumber (cm ⁻¹)		Classification	Comment
		Observed	Calculated		
4 W	4 050.067	24 683.97	.94	6s ³ S ₁ –6p ³ P ₁	
2	4 021.601	24 858.70	.68	5d ³ D ₁ –6p ⁵ P ₁	
0	3 992.547	25 039.58	.59	5d ³ D ₁ –6p ⁵ P ₂	a
5 W	3 950.593	25 305.49	.47	6s ⁵ S ₂ –6p ⁵ P ₁	
5 W	3 922.548	25 486.41	.38	6s ⁵ S ₂ –6p ⁵ P ₂	
3	3 884.988	25 732.81	.86	5d ³ D ₃ –6p ⁵ P ₂	a
5 B	3 781.022	26 440.36	.56	6s ³ S ₁ –6p ³ P ₂	
5 W	3 676.672	27 190.77	.99	6s ³ S ₁ –6p ³ P ₀	
5 H	3 624.076	27 585.38	.41	6s ⁵ S ₂ –6p ⁵ P ₃	
2	3 591.994	27 831.75	.89	5d ³ D ₃ –6p ⁵ P ₃	
4 H	3 522.830	28 378.16	.29	5d ³ D ₁ –6p ³ P ₁	
4 W	3 468.218	28 824.99	5.08	6s ⁵ S ₂ –6p ³ P ₁	
4 B Xe II	3 384.117	29 541.32	.64	5d ³ D ₂ –6p ⁵ P ₁	a
0 B	3 317.456	30 134.91	.91	5d ³ D ₁ –6p ³ P ₂	
4 W	3 301.551	30 280.08	.13	6p ³ P ₂ –7s ⁵ S ₂	
3 B	3 287.818	30 406.54	.65	6p ³ P ₂ –6d ⁵ D ₃	
3	3 285.828	30 424.97	5.01	6p ³ P ₂ –6d ⁵ D ₂	
2	3 278.447	30 493.46	.49	6p ³ P ₂ –6d ⁵ D ₁	
5 H	3 268.983	30 581.74	.70	6s ⁵ S ₂ –6p ³ P ₂	
5 H	3 242.855	30 828.13	.18	5d ³ D ₃ –6p ³ P ₂	
3 A	3 236.847	30 885.35	.34	5d ³ D ₁ –6p ³ P ₀	
3 A	3 227.159	30 978.06	.00	6p ³ P ₀ –7s ³ S ₁	a
4 B	3 150.825	31 728.53	.43	6p ³ P ₂ –7s ³ S ₁	a
2	3 141.615	31 821.54	.58	5d ³ D ₂ –6p ⁵ P ₃	a
2 Xe III ?	3 120.509	32 036.76	.75	6p ³ P ₁ –7s ⁵ S ₂	a
1	3 106.457	32 181.68	.63	6p ³ P ₁ –6d ⁵ D ₂	a
2	3 102.682	32 220.82	.56	6p ³ P ₁ –6d ⁵ D ₀	a
2	3 099.865	32 250.11	.11	6p ³ P ₁ –6d ⁵ D ₁	
3 W	3 023.807	33 061.27	.25	5d ³ D ₂ –6p ³ P ₁	b
2 W	3 023.637	33 063.13	2.94	6p ³ P ₂ –6d ³ D ₂	a
3	3 004.254	33 276.43	.42	6p ⁵ P ₃ –7s ⁵ S ₂	
3 W	2 992.874	33 402.96	.94	6p ⁵ P ₃ –6d ⁵ D ₃	
2 W	2 991.230	33 421.31	.30	6p ⁵ P ₃ –6d ⁵ D ₂	
2	2 985.514	33 485.30	.05	6p ³ P ₁ –7s ³ S ₁	a
4 W	2 970.467	33 654.91	.94	6p ⁵ P ₃ –6d ⁵ D ₄	a
3 B	2 959.339	33 781.46	.19	6p ³ P ₀ –6d ³ D ₁	a
2	2 932.736	34 087.88	.90	5d ⁵ D ₀ –6p ⁵ P ₁	
4 W	2 912.363	34 326.33	.29	6p ³ P ₂ –6d ³ D ₃	a
3 W	2 911.891	34 331.88	.89	5d ⁵ D ₁ –6p ⁵ P ₁	
3	2 896.624	34 512.83	.80	5d ⁵ D ₁ –6p ⁵ P ₂	
3 W	2 871.243	34 817.89	.87	5d ³ D ₂ –6p ³ P ₂	a
4 W	2 871.096	34 819.68	.56	6p ³ P ₁ –6d ³ D ₂	a
3	2 862.401	34 925.45	.46	5d ⁵ D ₂ –6p ⁵ P ₁	
3	2 847.652	35 106.33	.38	5d ⁵ D ₂ –6p ⁵ P ₂	
3	2 827.448	35 357.17	.23	5d ⁵ D ₃ –6p ⁵ P ₂	
2	2 825.986	35 375.47	.44	6p ⁵ P ₂ –7s ⁵ S ₂	
2 W	2 815.913	35 502.01	1.97	6p ⁵ P ₂ –6d ⁵ D ₃	
2 B	2 814.448	35 520.48	.33	6p ⁵ P ₂ –6d ⁵ D ₂	
0	2 811.605	35 556.40	.36	6p ⁵ P ₁ –7s ⁵ S ₂	
2 A	2 809.047	35 588.78	.81	6p ⁵ P ₂ –6d ⁵ D ₁	
2 A	2 800.195	35 701.27	.24	6p ⁵ P ₁ –6d ⁵ D ₂	
1	2 797.122	35 740.49	.17	6p ⁵ P ₁ –6d ⁵ D ₀	a
1	2 794.831	35 769.79	.72	6p ⁵ P ₁ –6d ⁵ D ₁	
1	2 772.397	36 059.22	.23	6p ⁵ P ₃ –6d ³ D ₂	b
1	2 754.878	36 288.52	.24	6p ³ P ₁ –6d ³ D ₁	a
5	2 717.326	36 789.99	.99	5d ⁵ D ₁ –6p ⁵ P ₃	a
2 B	2 714.853	36 823.49	.74	6p ⁵ P ₂ –7s ³ S ₁	a
1	2 701.562	37 004.65	.66	6p ⁵ P ₁ –7s ³ S ₁	a
3	2 686.978	37 205.48	.41	5d ⁵ D ₂ –6p ⁵ P ₃	
1	2 678.551	37 322.53	.58	6p ⁵ P ₃ –6d ³ D ₃	b
4	2 668.983	37 456.31	.26	5d ⁵ D ₃ –6p ⁵ P ₃	
2	2 658.250	37 607.54	.51	5d ⁵ D ₀ –6p ³ P ₁	
3	2 641.123	37 851.41	.49	5d ⁵ D ₁ –6p ³ P ₁	
1 Xe III ?	2 607.496	38 339.52	.17	6p ⁵ P ₁ –6d ³ D ₂	a
0 Xe III ?	2 535.939	39 421.27	.61	6p ⁵ P ₂ –6d ³ D ₃	a
1	2 523.973	39 608.17	.12	5d ⁵ D ₁ –6p ³ P ₂	
0 Xe III ?	2 511.290	39 808.18	7.85	6p ⁵ P ₁ –6d ³ D ₁	a
1	2 486.700	40 201.80	.69	5d ⁵ D ₂ –6p ³ P ₂	
2	2 471.285	40 452.56	.54	5d ⁵ D ₃ –6p ³ P ₂	

Table II. 5s²5p³(⁴S)nl levels of Xe III
The level values were determined in a least-squares fit including all well-established excited levels (i.e. not only those built on the (⁴S) parent term). In the fit the 5s5p⁵ ¹P₁ level was fixed at the value given in AEL [4]

Term	J	Level value	Total number of lines
Odd levels			
[5s5p ⁵ ¹ P	1	119 026.28]	
(⁴ S)6s ⁵ S	2	121 476.19	5
³ S	1	125 617.33	7
7s ⁵ S	2	182 338.01	5
³ S	1	183 786.31 ^a	7
5d ⁵ D	4	112 271.61 ^a	1
	3	111 605.34	6
	2	111 856.19	5
	1	112 449.77	4
	0	112 693.76	2
³ D	3	121 229.71	7
	2	117 240.01 ^a	4
	1	121 922.97	7
6d ⁵ D	4	182 716.54 ^a	3
	3	182 464.54	6
	2	182 482.90	9
	1	182 551.38	5
	0	182 521.83 ^a	3
³ D	3	186 384.18 ^a	4
	2	185 120.83 ^a	5
	1	186 589.50 ^a	6
Even levels			
(⁴ S)6p ⁵ P	3	149 061.60	13
	2	146 962.57	16
	1	146 781.66	15
³ P	2	152 057.89	21
	1	150 301.27	15
	0	152 808.32	5
4f ⁵ F	5	166 744.08 ^a	3
	4	166 355.43 ^a	8
	3	166 699.21 ^a	11
	2	167 066.44 ^a	5
	1	167 173.62 ^a	2
³ F	4	173 946.67 ^a	6
	3	170 250.06 ^a	5
	2	173 734.22 ^a	6

^a New identification

Table III. Calculated eigenvector compositions (percentage compositions) and g values for the (⁴S)6p levels of Xe III
Eigenvector components ≥ 5% are given

E (obs.)	g (obs.)	g (calc.)	LS Percentage composition
149 061	1.57	1.62	87 (⁴ S) ⁵ P ₃ + 10 (² P) ³ D ₃
152 057	1.50	1.49	67 (⁴ S) ³ P ₂ + 18 (⁴ S) ⁵ P ₂ + 6 (² P) ¹ D ₂
146 962	1.70	1.70	71 (⁴ S) ⁵ P ₂ + 13 (⁴ S) ³ P ₂ + 6 (² P) ³ P ₂ + 5 (² P) ³ D ₂
150 301	1.59	1.50	64 (⁴ S) ³ P ₁ + 9 (⁴ S) ⁵ P ₁ + 9 (² P) ¹ P ₁ + 7 (² D) ³ P ₁
146 781	2.28	2.27	80 (⁴ S) ⁵ P ₁ + 6 (⁴ S) ³ P ₁ + 5 (² P) ³ P ₁
152 808	—	—	91 (⁴ S) ³ P ₀ + 6(² P) ³ P ₀

Table IVa. Comparisons of experimental quantum defects δ for 7s levels in the Cs I, Xe I and Te I isoelectronic sequences

	E [limit]	E [7s $^2S_{1/2}$]	δ_{7s}	
Cs I	31 406	18 536	4.0800	0.4640 0.3115
Ba II	80 687	42 355	3.6160	
La III	154 664	82 347	3.3045	
	E [limit]	E [($^2P_{3/2}$)7s [$3/2$] ₂]	δ_{7s}	
Xe I	97 834	85 189	4.0541	0.4858 0.2947
Cs II	186 600	149 327 ^a	3.5683	
Ba III	289 100	217 975	3.2736	
	E [limit]	E [(4S)7s 5S_2]	δ_{7s}	
Te I	72 667	—	—	— (0.3031)
I II	154 304	118 608	3.4933	
Xe III	(250 382)	182 338	(3.1902)	

^a Corrected for configuration interaction: $E = E(\text{exp.}) + 106 \text{ cm}^{-1}$ (Reader, J., Phys. Rev. A13, 507 (1976)).

Table IVb. Comparisons of experimental quantum defects δ for 6p levels in the Cs I, Xe I and Te I isoelectronic sequences

	E [limit]	E [6p $^2P_{3/2}$]	δ_{6p}	
Cs I	31 406	11 732	3.6383	0.3720 0.2688
Ba II	80 687	21 952	3.2663	
La III	154 664	45 111	2.9975	
	E [limit]	E [($^2P_{3/2}$)6p [$5/2$] ₃]	δ_{6p}	
Xe I	97 834	78 404	3.6235	0.3869 0.2707
Cs II	186 600	129 117	3.2366	
Ba III	289 100	181 816	2.9659	
	E [limit]	E [(4S)6p 5P_3]	δ_{6p}	
Te I	72 667	54 537	3.5398	0.3935 (0.2698)
I II	154 304	100 403	3.1463	
Xe III	(250 296)	149 062	(2.8765)	

Table IVc. Comparisons of experimental quantum defects δ for 6d levels in the Cs I, Xe I and Te I isoelectronic sequences

	E [limit]	E [6d $^2D_{5/2}$]	δ_{6d}	
Cs I	31 406	22 632	2.4635	0.0288 0.1422
Ba II	80 687	46 155	2.4347	
La III	154 664	82 814	2.2925	
	E [limit]	E [($^2P_{3/2}$)6d [$7/2$] ₄]	δ_{6d}	
Xe I	97 834	88 912	2.4929	0.0838 0.1420
Cs II	186 600	152 558	2.4091	
Ba III	289 100	218 225	2.2671	
	E [limit]	E [(4S)6d 5D_4]	δ_{6d}	
Te I	72 667	—	—	— (0.1421)
I II	154 304	121 826	2.3237	
Xe III	(250 455)	182 717	(2.1816)	

Table V. Difference in quantum defect δ between corresponding levels in the 5d and 6d configurations of the Cs I and Xe I isoelectronic sequences

	δ [5d $^2D_{5/2}$]	δ [6d $^2D_{5/2}$]	$\delta_{5d} - \delta_{6d}$
Cs I	2.4449	2.4635	−0.0186
Ba II	2.5810	2.4347	0.1463
La III	2.4598	2.2925	0.1673
	δ [($^2P_{3/2}$)5d [$7/2$] ₄]	δ [($^2P_{3/2}$)6d [$7/2$] ₄]	$\delta_{5d} - \delta_{6d}$
Xe I	2.5056	2.4929	0.0127
Cs II	2.5703	2.4091	0.1612
Ba III	2.4355	2.2671	0.1684