# Resonances in the Photoionization Continuum of Kr and Xe

K. Codling* and R. P. Madden
*National Bureau of Standards, Washington, D. C.* 20234
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A total of 153 krypton resonances in the spectral region 500–337 Å, and 254 xenon resonances in the spectral region 600–375 Å are reported. The disposition of the detailed line lists are indicated. The analysis is very incomplete and will require detailed theoretical calculations to advance. In krypton, 45 resonances and in xenon, 56 resonances have been grouped into probable Rydberg series, for which classifications are suggested. In general, the resonances observed are due to the excitation of the inner subshell "$s$" electron ($ns^2np^6 \rightarrow nsnp^6mp$) or to the excitation of two of the outer electrons simultaneously ($ns^2np^6 \rightarrow ns^2np^4mll'$). These high-lying excited states autoionize, resulting in resonances with window-, asymmetric-, and absorption-type profiles. The detailed lists for the subshell "$s$" electron excitations are given.

## INTRODUCTION

A number of years ago, resonances due to the autoionization of high-lying excited states were first observed in the photoionization continuua of He, Ne, and Ar [1] and of Kr and Xe. [2,3] These resonances, due to inner-shell excitations or to two electrons being simultaneously excited, were observed by absorption spectroscopy using the National Bureau of Standards (NBS) 180-MeV synchrotron as a continuum background source. Subsequently more detailed reports were published for He, [4] Ne, [5] and Ar. [6] In the case of Ar, strong configuration interaction was present and large departures from pure *LS* coupling were evident. As a result the analysis was difficult and necessarily incomplete. These complexities become more severe in Kr and Xe and considerable theoretical work is required before a thorough analysis can be made. This communication indicates the final disposition of our detailed experimental data on Kr and Xe, with spectral positions and some classification of the resonances. In the case of the more prominent resonances, a significant amount of intensity and profile data has been obtained using a 3-m grazing-incidence scanning monochromator with 0.06-Å resolution. These results are presented in the accompanying paper. [7]

## EXPERIMENTAL

The data reported here were obtained using a 3-m grazing-incidence spectrograph which has been described elsewhere. [8] The grating is 600 lines/mm and the slit is 10 $\mu$, yielding a spectral resolution of 0.055 Å. This spectrograph obeys the grating equation with great precision, and has a well-established calibration based on the known spectra of helium, and many known levels in ion spectra of the noble gases, to which the various Rydberg series converge in the limit.

## SPECTRAL DATA

Our catalog contains 153 resonances in Kr covering the spectral region 501–337 Å and 254 resonances in Xe covering the spectral region 600–375 Å. The estimated absolute accuracies vary from ± 0.03 to ± 0.2 Å, depending on the breadth and intensity of the resonance; the relative errors are smaller by nominally a factor of 2. The complete lists are available[9] in the NBS Journal of Research, where the wavelength, wave number, the profile type[10] of the resonance and a rough indication of its breadth are given.

In 1966, Samson summarized[11] his own measurements of the wavelengths of the resonances he observed in Kr and Xe for the case of excitation of the subshell "$s$" electron. His data are in agreement with the values reported here for those resonances. However, his error bars were considerably larger. More recently, Mansfield[12] has again photographed the subshell "$s$" electron excitation in Kr and Xe with an accuracy comparable to that of this experiment. The agreement is good for resonances below about 585 Å (within ± 0.05 Å). For resonances between 585 and 600 Å (which occur only in xenon) a consistent deviation appears between our data and that of Mansfield. At 600 Å our values are 0.2 Å larger than Mansfield's, while our quoted error is only ± 0.05 Å. Mansfield apparently has calibration difficulty in this region. Although our calibration and instrumental errors are greatest at the long-wavelength end also, we are in better agreement with Samson's data in this region.

In both Kr and Xe, quantum defects have been calculated for all of the resonances to the available[13,14] known limits (levels in Kr II and Xe II which could form $J=1$ final states of Kr I and Xe I with the addition of an appropriate running electron). As a result of this analysis, 45 resonances of Kr and 56 in Xe have been grouped into probable Rydberg series. These are also listed, with their effective quantum numbers, in Ref. 9.

The most prominent series in both Kr and Xe is due to the one-electron transitions $ns^2np^6\,{}^1S_0 \rightarrow nsnp^6\,({}^2S)\,mp$. This final configuration has available

TABLE I. One-electron excitation Rydberg series in Kr, $4s^2 4p^6\,{}^1S_0 \to 4s4p^6\,({}^2S_{1/2})np$.

| $n$ | Wavelength (Å) | Wave number (cm$^{-1}$) | $n^*$ |
|---|---|---|---|
| 5 | 496.07 (±0.05) | 201 584 | 2.323 |
| 6 | 471.23 (±0.03) | 212 211 | 3.363 |
| 7 | 462.71 (±0.03) | 216 118 | 4.351 |
| 8 | 458.69 (±0.03) | 218 012 | 5.303 |
| 9 | 456.12 (±0.03) | 219 241 | 6.406 |
| 10 | 454.73 (±0.03) | 219 911 | 7.399 |
| 11 | 453.73 (±0.03) | 220 395 | 8.498 |
| 12 | 453.15 (±0.03) | 220 677 | 9.42 |
| 13 | 452.68 (±0.03) | 220 907 | 10.43 |
| 14 | 452.34 (±0.03) | 221 073 | 11.41 |
| 15 | 452.07 (±0.03) | 221 205 | 12.43 |
| 16 | 451.86 (±0.03) | 221 307 | 13.44 |
| 17 | 451.69 (±0.03) | 221 391 | 14.47 |
| 18 | 451.56 (±0.03) | 221 455 | 15.44 |
| 19 | 451.45 (±0.03) | 221 508 | 16.43 |
| Second series of two available having $J=1$ final states | | | |
| 5 | 497.50 (±0.05) | 201 005 | 2.304 |
| 6 | 471.48 (±0.03) | 212 098 | 3.343 |

two $J=1$ levels $({}^{1,3}P_1)$, thus two series might be expected approaching a single limit. No more than two series are possible, however, since the selection rules $\Delta J=0,\ \pm 1,\ J=J'\neq 0$ hold rigorously regardless of the coupling scheme. The two series, if resolved in low members, would merge into a single observed series since the limit for both is a ${}^2S_{1/2}$ state of the ion. Primarily what has been observed is a single series of slightly asymmetric reduced-absorption (window-type) resonances. These are quite broad due to autoionization of the excited states into the $ns^2np^5\epsilon s, \epsilon d$ continuua. The series is given in Table I for Kr and in Table II for Xe.

From energy considerations, the remaining resonances must be due to two-electron excitations. The term possibilities are the same as those outlined previously[6] in the case of Ar. In general, the excited states form series of the type

$$ns^2np^4\ ({}^3P,\ {}^1D,\ {}^1S)\ mlm'l'\ ,$$

with $ll'=sp,\ pd,\ sf$, or $df$, and where either electron can have the running principal quantum number.

Higher-energy two-electron excitations, of the type $nsnp^5\,mlm'l'$ have been seen in Ar. However, all of the resonances reported here lie lower in energy than the limits $4s^2 4p^4$ in Kr III and $5s^25p^4$ in Xe III, and two-electron excitations involving the inner subshell "$s$" electron appear to be feasible only for the few resonances lying at wavelengths shorter than 400 Å in Xe for which no classification has been suggested. Most of these resonances are broad due to autoionization to the underlying continuua. The profiles vary, with window-, asymmetric-, and absorption-enhancement-type profiles all being represented.

TABLE II. One-electron excitation Rydberg series in Xe, $5s^25p^6\,{}^1S_0 \to 5s5p^6\,({}^2S_{1/2})np$.

| $n$ | Wavelength (Å) | Wave number (cm$^{-1}$) | $n^*$ |
|---|---|---|---|
| 6 | 591.77 (±0.03) | 168 985 | 2.359 |
| 7 | 557.83 (±0.02) | 179 266 | 3.409 |
| 8 | 546.08 (±0.02) | 183 123 | 4.433 |
| 9 | 540.54 (±0.02)[a] | 185 000 | 5.440 |
| 10 | 537.46 (±0.02) | 186 060 | 6.438 |
| 11 | 535.55 (±0.02) | 186 724 | 7.437 |
| 12 | 534.27 (±0.02) | 187 171 | 8.450 |
| 13 | 533.34 (±0.05)[b] | 187 498 | 9.52 |
| 14 | 532.76 (±0.02) | 187 702 | 10.44 |
| 19 | 531.21 (±0.02) | 188 249 | 15.47 |
| 21 | 530.93 (±0.02) | 188 349 | 17.48 |
| 22 | 530.83 (±0.03) | 188 384 | 18.41 |
| 23 | 530.74 (±0.03) | 188 416 | 19.39 |

[a]Alternate choice: 540.62 (±0.02) with $n^*=5.420$.
[b]Observationally judged to be perturbed.

TABLE III. Two-electron excitation Rydberg series in Kr.

| Series | Limit (cm$^{-1}$) | No. of members identified | Average $n-n^*$ |
|---|---|---|---|
| Unidentified[a] | 240 300 | 4 | 2.67 |
| $4p^4\ ({}^1S)5s\ ({}^2S_{1/2})np$ | 258 727 | 9 | 2.62 |
| $({}^1D)4d\ ({}^2D_{5/2})np$ | 262 429 | 2 | 2.64 |
| $({}^1D)4d\ ({}^2P_{1/2})np$ | 265 100 | 4 | 2.57 |
| $({}^1D)4d\ ({}^2S_{1/2})np$[b] | 273 710 | 7 | 2.71 |
| $({}^1S)4d\ ({}^2S_{5/2})np$ | 273 927 | 2 | 2.57 |

[a]The nearest known limit is $({}^1D)5s\ ({}^2D_{3/2})$ which, according to Minnhagen (Ref. 14), lies at 240 512 cm$^{-1}$.
[b]This $4p^4\ ({}^1D)4d\ ({}^2S_{1/2})$ limit was previously (Ref. 13) labeled $4p^4\ ({}^3P)5d\ ({}^4P_{1/2})$. It was given the present designation by Minnhagen in his recent analysis of the Kr II spectrum (Ref. 14).

TABLE IV. Two-electron excitation Rydberg series in Xe.

| Series | Limit (cm$^{-1}$) | No. of members identified | Average $n-n^*$ |
|---|---|---|---|
| $5p^4\ ({}^3P)6s\ ({}^4P_{5/2})np$ | 190 902 | 6 | 3.58 |
| $({}^3P)6s\ ({}^4P_{3/2})np$ | 192 898 | 4 | 3.54 |
| Unidentified[a] | 212 665 | 6 | 0.30 |
| $({}^3P)6p\ ({}^4D_{3/2})nd$[b] | 214 617 | 4 | 2.64 |
| $({}^3P)6p\ ({}^4S_{3/2})nd$ | 219 463 | 4 | 2.32 |
| $({}^1S)5d\ ({}^2D_{3/2})np$ | 222 136 | 3 | 3.65 |
| $({}^1D)6p\ ({}^2F_{7/2})nd$ | 227 898 | 7 | 2.26 |
| $({}^3P)7s\ ({}^4P_{1/2})np$ | 232 895 | 9 | 3.46 |

[a]The nearest Xe II levels according to Ref. 13 are the $({}^1D)5d\,{}^2F_{5/2,7/2}$ at 212 585 cm$^{-1}$ and 212 748 cm$^{-1}$, either of which would allow an $nf$ series.
[b]Although this series is labeled $nd$, the quantum defect is more appropriate for an $np$ series which would be parity forbidden *if* the limit at 219 463 cm$^{-1}$ is correctly assigned (Ref. 13) as $({}^3P)6p\ {}^4S_{3/2}$.

In Kr, the two-electron excitation series for which some evidence has been established appear in Table III. Similarly, such series in Xe, are given in Table IV. The average quantum defect $(n - n^*)$ for the observed members to the indicated limits is also given.

## CONCLUSIONS

The two-electron resonances listed into series for Kr and Xe represent only one-fourth of those cataloged. The principle problem is, of course, the complicated configuration interactions present which displace the levels from locations expected from simple theoretical considerations and produce intensity anomalies. For some series the profiles of the resonances vary with the principle quantum number. Other series appear fragmentarily, having observable strength only where they have borrowed sufficient intensity from an interacting configuration. As a result of these difficulties it appears at present that substantial theoretical calculations are required to analyze the spectra further. Prints of the spectra are available from the authors, and the reader is again reminded that the detailed lists are available in Ref. 9.

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*Present address: University of Reading, Physics Department, J. J. Thomson Physical Lab., White Knights Park, Reading, Berkshire, England.

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# Cross-Section Profiles of Resonances in the Photoionization Continuum of Krypton and Xenon (600–400 Å)

David L. Ederer
*National Bureau of Standards, Washington, D. C.* 20234
(Received 16 July 1971)

The cross-section profiles in krypton and xenon have been measured for one- and two-electron excitations of the type $ns^2np^6(^1S_0) \rightarrow nsnp^6(^2S_{1/2})mp$ or $ns^2np^6(^1S_0) \rightarrow ns^2np^4(^3P, {}^1D, {}^1S)mlm'l'$. These cross sections were assumed to have the form

$$\sigma(E) = C(E) + \sum_i \frac{(E - E_i)(\Gamma_i/2)a_i + (\Gamma_i/2)^2 b_i}{(E - E_i)^2 + (\Gamma_i/2)^2},$$

where the adjustable parameters $C(E)$, $b_i$, $a_i$, $E_i$, and $\Gamma_i$ were determined by a least-squares unfolding process which separated the smearing effect of the monochromator slit from the true optical density. Parameter values and cross-section curves are given for 12 krypton resonances and 11 xenon resonances.

## I. INTRODUCTION

Photoionization in noble gases and metallic vapors has been the object of a great deal of experimental and theoretical attention[1] recently. Experimentally, the noble gases have several distinct advantages over metallic vapors in that they are easy to handle, noncorrosive, and monoatomic. Theoretically, their strategic location throughout the periodic table is ideal for a systematic study of the photoionization process.

The development of continuum light sources[2] paved the way to the study of discrete excitation states lying in the photoionization continua of