Three-photon excitation of autoionizing states of Ar, Kr, and Xe between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits

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Three-photon excitation of autoionizing states between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits of atomic argon, krypton, and xenon has been investigated using multiphoton ionization in combination with supersonic expansion techniques. As the result of the high signal-to-noise ratios and energy resolution achieved in these experiments, we have been able to study autoionizing states in argon with multiphoton excitation, and have considerably augmented the knowledge of the autoionizing states of krypton and xenon. All atoms show (in $j_c l$ coupling notation) the odd $ns'[1/2]_1$, $nd'[3/2]_1$, and $ng'[7/2]_3$ autoionizing series, while the $nd'[5/2]_3$ series can only be observed in xenon. The analysis of the line profile of the autoionizing resonances has enabled a detailed comparison of the present results with those obtained with other experimental techniques and predictions by theoretical studies.

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I. INTRODUCTION

The photoionization of rare gases between their $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits has been studied extensively in the past, both experimentally and theoretically. The observed and calculated spectra are dominated by the presence of $(mp^5)^2P_{1/2}nl'$ autoionizing resonances, which have been observed for the first time in the pioneering work of Beutler [1]. When a one-photon absorption process from the ground state is used to excite these resonances, only the members of the two autoionizing series, viz., $ns'[1/2]_1$ and $nd'[3/2]_1$, can be accessed. These series have been characterized with steadily increasing resolution by synchrotron studies and vacuum ultraviolet (vuv) experiments [2–14]. Extremely high resolution has been achieved in experiments where excitation is performed from an excited state of the atom [15–23]. Ionization from these states has in some cases allowed for the study of autoionizing states with $J \neq 1$.

For the investigation of autoionizing series with $J \neq 1$ multiphoton excitation would seem the method of choice, since the angular momentum selection rules would no longer restrict the change in total angular momentum to 1. Moreover, one should obtain a superior energy resolution in comparison with the resolution obtained with synchrotron radiation. Nevertheless, the number of multiphoton excitation studies on autoionizing states of rare-gas atoms with tunable lasers is, as yet, rather limited and restricted to Kr and Xe [24–28]. Obtaining a fundamental understanding of the multiphoton ionization dynamics via autoionizing levels by theoretical methods has represented an even more complex challenge [29–31].

In the present study we have investigated the $ns'[1/2]_1$, $nd'[3/2]_1$, $nd'[5/2]_3$, and $ng'[7/2]_3$ autoionizing series in Ar, Kr, and Xe using three-photon excitation. The observation of these series in Ar constitutes the first study of autoionizing states in this atom with multiphoton excitation. Additionally, the present experimental conditions have allowed for a considerably more extensive characterization of these series in Kr and Xe with respect to previous three-photon excitation studies [26,27]. Excitation has been performed with linearly as well as circularly polarized light. An advantage of the application of circularly polarized light is that under these circumstances only the $J=3$ autoionizing series can be excited. As a result, we have been able to assign the various series uniquely and to investigate the members of the $J=3$ series up to high quantum numbers under conditions of no overlap with other series.

The results of our study will show that there are considerable differences between the excitation spectra of the three rare-gas atoms, in particular with respect to the intensity of the $nd'[5/2]_3$ series. An analysis of the line profiles of the observed autoionizing resonances will be presented and the results of this analysis will be used for a comparison with previous experimental one- and three-photon excitation studies, and the results of theoretical work. It will be shown that under the high-resolution conditions of the present experiments (0.08 cm^{-1} at the fundamental wavelength) linewidths of the autoionizing resonances can be determined, which, for some series, are smaller than observed before. Finally, we shall consider the three-photon ionization dynamics on the basis of the observed cross sections and line profile indices q.

II. EXPERIMENT

The experimental setup has been described in detail previously [32] and will only be summarized here. Briefly, the laser system consists of an excimer laser (Lambda Physik EMG103 MSC), operating on XeCl, which pumps a dye laser (Lumonics HyperDye 300) operating on the coumarin dyes C460, C500, or C540 or the rhodamine dye R590. For frequency doubling of the fundamental laser light (energy width 0.08 cm^{-1}) and for tracking of the doubling crystal an Inrad Autotracker II unit is used. The polarization of the excitation light can be modified continuously from linearly polarized light

with a purity of 1000:1 to circularly polarized light with a purity of 300:1 by a Pockels cell (Electro Optic Developments PC105). In the present study wavelength calibrations have been performed using the sharp resonances of the $s'[1/2]_1$ series as given by Yoshino for Ar [2], by Yoshino and Tanaka for Kr [5], and by Wang and Knight for Xe [19].

The laser output is focused by a quartz lens with a focal length of 10 cm, reaching a maximum average power density in the focal point of about 10^{10} W/cm^2. At this point it intersects at right angles a molecular beam produced by a free-jet expansion of pure Ar, Kr, or Xe gas. This expansion is generated by either a homebuilt pulsed valve, whose design allows for ionization extremely close to the nozzle aperture, or a General Valve Iota One System. The ions produced at the intersection point are focused by homebuilt ion optics into the entrance aperture of a quadrupole mass spectrometer set at the appropriate mass.

In our experiments the experimental parameters, such as the backing pressure, the laser power, and the distance from the nozzle to the ionization point, turned out to be of considerable importance. On the one hand, these parameters had to be optimized such that a sufficient signal-to-noise ratio could be achieved. On the other hand, pressure and power broadening effects and Stark shifts had to be avoided as much as possible. Excitation spectra have therefore been recorded under varying conditions in order to estimate the influence of these parameters. From these trial runs it could be concluded that the autoionizing resonances in Ar were most susceptible to variations in the experimental conditions. The autoionizing resonances in Kr were much less influenced, while in Xe they could be studied over a large range of experimental conditions without significant changes in the results. The excitation spectra discussed in the present paper have been obtained under the conditions of 4, 2, and 0.5 bars of backing pressure, and with excitation at 0.5, 3, and 10 mm from the nozzle for Ar, Kr, and Xe, respectively. These spectra have not been corrected for variations in the laser output resulting from the dye gain curve.

A last point of concern is third-harmonic generation, which, if present, might dramatically alter the excitation spectra [28,33–35]. Experimentally it is well known that the efficiency of such processes is strongly dependent on the gas pressure. In our experiments we have not observed any changes in the line shapes and relative peak intensities when the backing pressure or the distance from the nozzle to the point of excitation was changed. We therefore conclude that the role of third-harmonic generation in the present study is negligible.

III. RESULTS

In Fig. 1 the three-photon excitation spectrum of Ar between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits using linearly polarized light is shown. At the photon energies used there is no resonant enhancement at the one- or two-photon level. The excitation spectrum shows three series of autoionizing Rydberg states converging to the $^2P_{1/2}$ ionic limit: the $ns'[1/2]_1$, $nd'[3/2]_1$, and $ng'[7/2]_3$ series. The $J=1$ series show broad $nd'[3/2]_1$ and relatively sharp $ns'[1/2]_1$ resonances, in agreement with previous observations with one-photon excitation techniques [10,14]. The $J=3$ series are limited to the $ng'[7/2]_3$ series, whose members appear as extremely sharp resonances. On the basis of the selection rules for three-photon excitation a fourth series, the $nd'[5/2]_3$, would also be allowed. This series, however, is not observed in the excitation spectrum. From the signal-to-noise ratio it can be concluded that the peak intensity of this series is at least an order of magnitude smaller than the intensity of the transitions to the members of the $ng'[7/2]_3$ series.

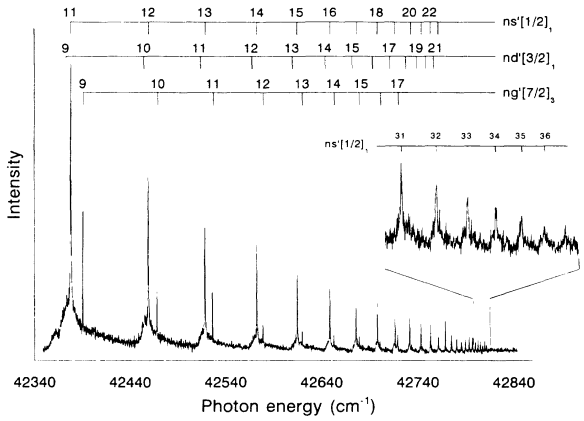

FIG. 1. Three-photon excitation spectrum of autoionizing series in Ar between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits obtained with linearly polarized excitation light.

Careful examination of the excitation spectrum in Fig. 1 reveals that the signal intensity increases slightly approximately 12 cm^{-1} before the three-photon energy exceeds the $^2P_{3/2}$ ionization limit at a one-photon energy of 42 370.0 cm^{-1}. A similar increase has previously been observed by Radler and Berkowitz [4]. In this study it was proposed that an explanation might be found in the collision-induced ionization of very high Rydberg states. Probably it is also this mechanism which is responsible for the considerable difference in the reduced linewidth between the first and the higher members of the $ns'[1/2]_1$ series, the first member having an anomalous linewidth.

A high-resolution excitation spectrum of the $12s'[1/2]_1$, $10d'[3/2]_1$, and $10g'[7/2]_3$ autoionizing states of Ar is shown in Fig. 2, together with a fit (*vide infra*) of the spectrum, which has been constructed using the summation of three line profiles. Good agreement is observed between the fitted and the experimental spectrum. Also shown in Fig. 2 is the excitation spectrum obtained with circularly polarized light, as well as a fit to this spectrum. Using circularly polarized light only states with J equal to the number of absorbed photons, i.e., 3, can be excited. In agreement with this selection rule only the $10g'[7/2]_3$ state is observed. The line shape of this resonance, however, seems to be independent of the polarization of the excitation light.

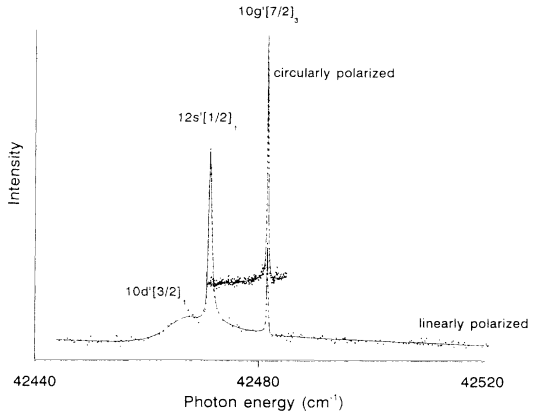

FIG. 2. High-resolution three-photon excitation spectrum of the $10d'[3/2]_1$, $12s'[1/2]_1$, and $10g'[7/2]_3$ autoionizing resonances of Ar obtained with linearly and circularly polarized excitation light. With the latter polarization only the $10g'[7/2]_3$ resonance is observed. The solid lines through the experimental data points represent fits according to Eq. (1).

The three-photon linearly polarized excitation spectrum of autoionizing states between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits of Kr is depicted in Fig. 3. Again, resonant enhancement at the one- or two-photon level is unimportant. Similar to what has been observed in the excitation spectrum of Ar, only three series of autoionizing resonances are present, corresponding to the $ns'[1/2]_1$, $nd'[3/2]_1$, and $ng'[7/2]_3$ series. The spectrum is in good agreement with previous three-photon excitation results of Dehmer, Pratt, and Dehmer [27], who were able to observe, however, only the two lowest members of each series. Our spectrum does not show rapid distortions in going from the first to the second ionization limit, as predicted by Dehmer, Pratt, and Dehmer [27].

In contrast to the excitation spectrum obtained for Ar, the excitation spectrum in Fig. 3 exhibits a rising background. This background can be attributed to direct ionization processes into noninterfering ionization continua, demonstrating that such processes are of more importance in Kr than in Ar. Since the energy difference between the two ionic limits is larger in Kr than in Ar, and as the dye gain curve reaches its maximum at the second ionization limit, part of the dependence of the background signal on the excitation wavelength should certainly be attributed to these experimental conditions. A consequence of the rising background signal is that the line shapes of the lower-lying resonances are slightly distorted. Such distortions are not present for higher members, which have therefore been used for the analysis of the line shapes discussed below.

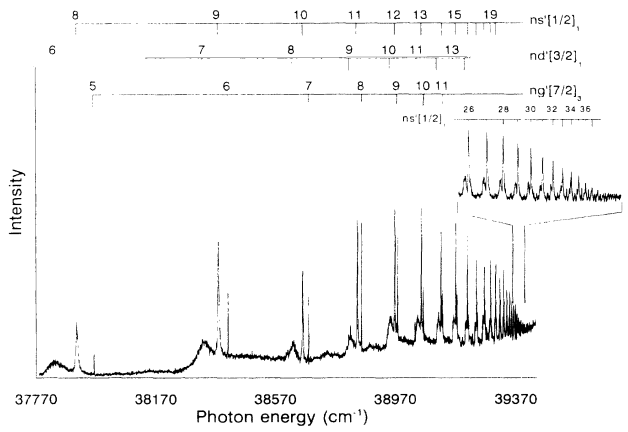

FIG. 3. Three-photon excitation spectrum of autoionizing series in Kr between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits obtained with linearly polarized excitation light.

A high-resolution wavelength scan of the $10d'[1/2]_1$, $12s'[3/2]_1$, and $9g'[7/2]_3$ resonances is shown in Fig. 4(b). The spectrum can be fitted very well with the sum of three line profiles, as can be observed in the same figure. The figure shows that the $9g'[7/2]_3$ resonance has an extremely small width. Indeed, the width obtained for this member of the $ng'[7/2]_3$ series amounts to only 0.39 cm^{-1}, caused predominantly by the instrumental bandwidth of 0.08 cm^{-1} at the fundamental wavelength.

In our measurements with linearly polarized light the formally allowed $nd'[5/2]_3$ series is not observed. Using circularly polarized light this series should be allowed as well, and the intensity of its resonances should be 2.5 times larger than with linearly polarized excitation light. Moreover, using circularly polarized light, transitions to

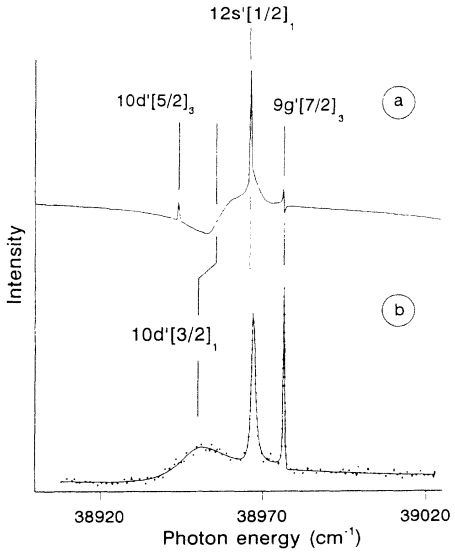

FIG. 4. High-resolution three-photon excitation spectrum of the $10d'[5/2]_3$, $10d'[3/2]_1$, $12s'[1/2]_1$, and $9g'[7/2]_3$ autoionizing resonances of Kr for linearly polarized excitation light. (a) Three-photon excitation spectrum calculated by L'Huillier, Tang, and Lambropoulos [30] (see text for details). (b) Experimentally obtained three-photon excitation spectrum. The solid line through the experimental data points represents a fit according to Eq. (1).

the $ns'[1/2]_1$ and $nd'[3/2]_1$ series become forbidden, allowing for a search of members of the $nd'[5/2]_3$ series under optimal conditions. Despite these favorable conditions, none of the members of the series could be observed. From Fig. 5, where a high-resolution scan with circularly polarized light of the region around the $5g'[7/2]_3$ resonance is shown, it can be concluded that the peak intensity of the $nd'[5/2]_3$ series is at least two orders of magnitude lower than the intensity of the $ng'[7/2]_3$ series.

The three-photon excitation spectrum obtained for Xe with linearly polarized light is shown in Fig. 6 and is in reasonable agreement with the three-photon excitation spectrum obtained previously for the lower members of these autoionizing series by Pratt, Dehmer, and Dehmer [26]. As before, resonant enhancement at intermediate photon levels is absent. One striking difference between this excitation spectrum and our spectra obtained for Ar and Kr is that for Xe, apart from the $ns'[1/2]_1$, $nd'[3/2]_1$, and $ng'[7/2]_3$ series, the $nd'[5/2]_3$ series can now be observed with considerable intensity. Similar to the excitation spectrum of Kr, a rising background, resulting from the important role of direct ionization into noninterfering ionization continua, can be seen. The two broad bands present at 34 145 and 34 370 cm^{-1} do not derive from any of the above-mentioned autoionizing series. The pressure dependence of these signals indicates that they most probably originate from Xe clusters, and are therefore not of interest for the present paper.

Previously [26] it has been suggested that the three-photon transitions to the members of the $nd'[3/2]_1$ series exhibit a line shape with $|q|>1$. The present results show unambiguously that the members of this series manifest themselves as window resonances, in contrast to what has been observed before in Ar and Kr. In the case of Xe the line shapes of the lower members of this series are distorted by the presence of the two broad bands attributed to Xe clusters, and by the rapid change of laser intensity over the wavelength region. For the higher members, however, reliable line shapes can be obtained.

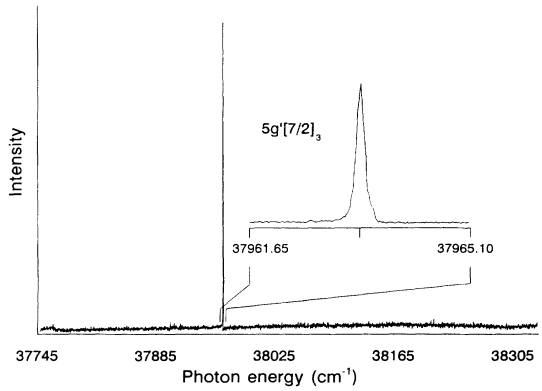

FIG. 5. High-resolution three-photon excitation spectrum of Kr with circularly polarized excitation light. Only a member of the $ng'[7/2]_3$ autoionizing series can be observed and no indication is found for the presence of a member of the $nd'[5/2]_3$ autoionizing series.

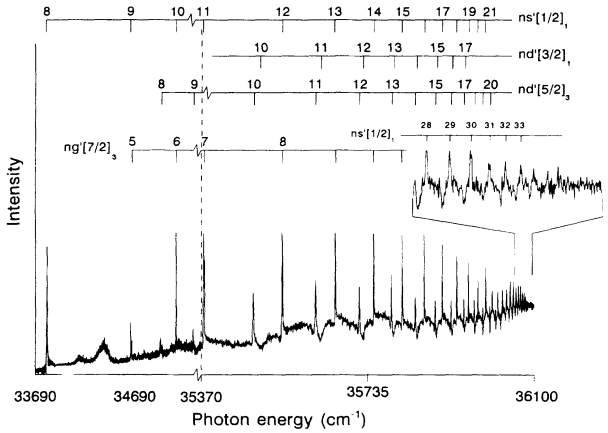

FIG. 6. Three-photon excitation spectrum of autoionizing series in Xe between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits obtained with linearly polarized excitation light.

Figure 7 shows a high-resolution wavelength scan of the $12d'[5/2]_3$, $12d'[3/2]_1$, $14s'[1/2]_1$, and $10g'[7/2]_3$ resonances using linearly (b) and circularly (c) polarized light, together with the fits to these spectra. It appears that with linearly polarized light the $14s'[1/2]_1$ and $10g'[7/2]_3$ resonances cannot be resolved as the result of insufficient resolution. The members of the two series

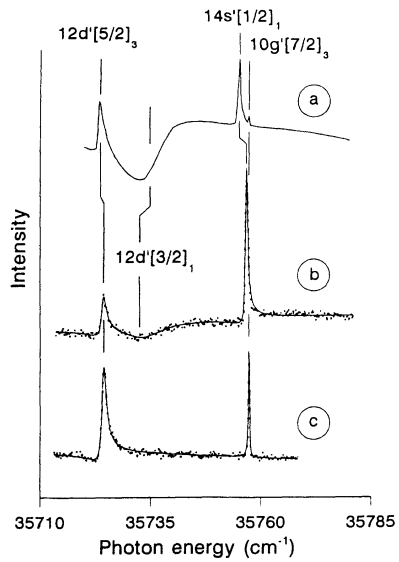

FIG. 7. High-resolution three-photon excitation spectrum of the $12d'[5/2]_3$, $12d'[3/2]_1$, $14s'[1/2]_1$, and $10g'[7/2]_3$ autoionizing resonances of Xe. (a) Three-photon excitation spectrum calculated by L'Huiller, Tang, and Lambropoulos [30] for linearly polarized excitation light (see text for details). (b) Experimentally obtained three-photon excitation spectrum with linearly polarized excitation light. (c) Experimentally obtained three-photon excitation spectrum with circularly polarized excitation light. The solid lines through the experimental data points represent fits according to Eq. (1).

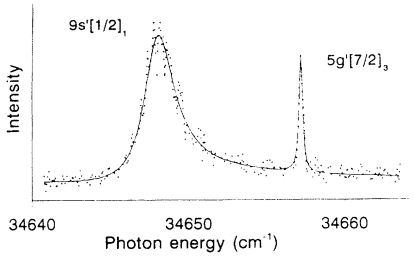

FIG. 8. High-resolution three-photon excitation spectrum of the $9s'[1/2]_1$ and $5g'[7/2]_3$ resonances of Xe with linearly polarized excitation light.

can indeed only be observed separately for $ng'[7/2]_3$, $n<8$ as a wavelength scan of the $9s'[1/2]_1$ and $5g'[7/2]_3$ resonances in Fig. 8 demonstrates. Application of circularly polarized light, on the contrary, allows for an accurate study of the resonance energies and line-shape parameters of the members of the $ng'[7/2]_3$ series up to $n=20$, since under such conditions excitation of the members of the overlapping $J=1$ series is forbidden. The width of these extremely sharp resonances could only be obtained reliably for the lowest member, since for higher members the width is determined by the instrumental resolution. For all the members of the $J=3$ series the line shapes measured with linearly and circularly polarized light do not exhibit measurable differences.

IV. DISCUSSION

The results presented above show that in the present multiphoton ionization study, using three-photon excitation with linearly and circularly polarized light, we have been able to investigate in great detail the $ns'[1/2]_1$, $nd'[3/2]_1$, $nd'[5/2]_3$, and $ng'[7/2]_3$ autoionizing series in Ar, Kr, and Xe. In this section the observed line shapes will be parametrized by means of a line-shape formula derived by Ueda [36]. The parameters thus derived from the observed resonances will be compared, when possible, to parameters obtained in previous experimental and theoretical studies. Finally, the role of the two-photon virtual level in the three-photon ionization dynamics will be discussed.

In the past one-photon excitation of the $J=1$ autoionizing series has been studied extensively, both experimentally and theoretically [1–23,37–40]. In these studies thorough comparisons have been made between the various experimental studies and between experiment and theory. Our study on Ar represents the first observation of autoionizing series using three-photon excitation in this atom. The discussion will therefore have to be restricted to a comparison with previous one-photon excitation data. In the cases of Kr and Xe we shall concentrate on a comparison of the present results with those obtained in previous experimental and theoretical three-photon studies. A comparison with one-photon excitation studies will only be made insofar as our results differ from one-photon data.

A. Parametrization of autoionizing resonances

From a theoretical point of view it would be preferable to analyze the measured excitation spectra from first principles using a complete multichannel quantum defect theory (MQDT) approach, as has been done previously in a number of pioneering one-photon excitation studies on Rydberg states of rare gases [38,39,41,42]. Such a treatment is rather involved and will not be pursued in the present experimental paper. We have chosen, instead, an analysis in which the spectra are parametrized by means of the line-shape formula derived by Ueda [36] within the framework of MQDT theory for the case of many uncoupled closed channels l with many open channels i:

$$\sigma(E)=\sigma_{\rm nr}+\sum_l \sigma_{{\rm rc},l}(q_l+\varepsilon_l)^2/(1+\varepsilon_l^2)\ , \tag{1a}$$

where $\sigma_{{\rm rc},l}$ represents the resonant contribution to the cross section involving the transition to the open channels which interact with the closed channel l, $\sigma_{\rm nr}$ the portion of the cross section for the transition to the nonresonant background continuum, and q_l the asymmetry parameter. The periodic energy scale ε is given by

$$\varepsilon_l=\tan[\pi(\nu_{1/2}+\mu_l)]/W_l\ , \tag{1b}$$

$$\nu_{1/2}=[R/(I_{1/2}-E)]^{1/2}\ , \tag{1c}$$

in which R is the mass-corrected Rydberg constant, $I_{1/2}$ is the second ionization limit, and E is the energy of interest. The formula in Eq. (1a) has the same form as the generalized Fano resonance formula [43–45]; the parameter ε, however, accounts for the periodicity of the Rydberg spectrum implicit in multichannel quantum defect theory [46]. For relatively narrow resonances ($W_l \ll 1$), the quantum defect μ_l and width parameter W_l are related to the resonance energy E_n and resonance width Γ_n by the following relations [36,47]:

$$I_{1/2}-E_n=R/(n-\mu_l)^2\ , \tag{2a}$$

$$\Gamma_n/2=2RW_l/\pi(n-\mu_l)^3\ . \tag{2b}$$

The parametrization of the excitation spectrum according to Eq. (1) is *only* valid if closed-channel interactions can be neglected, i.e., in terms of the coupling matrix $\mathcal{R}'$, defined by Dubau and Seaton [48], the relations $\mathcal{R}'_{ll'}=0$ and $\sum_i \mathcal{R}'_{il}\mathcal{R}'_{il'}=0$ should hold [36]. Only under these conditions can the parameters W_l, q_l, μ_l, $\sigma_{{\rm rc},l}$, and $\sigma_{\rm nr}$ appearing in Eq. (1) be related to the MQDT coupling matrix $\mathcal{R}'$ and the MQDT dipole matrix elements D'_i and D'_l by the relations [36]

$$W_l=\sum_i \mathcal{R}'^2_{il}\ , \tag{3a}$$

$$q_l=-D'_l/\sum_i \mathcal{R}'_{il}D'_i\ , \tag{3b}$$

$$\sigma_{{\rm rc},l}=B\sum_i(\mathcal{R}'_{il}D'_i)^2/W_l\ , \tag{3c}$$

$$\sigma_{\rm nr}=B\sum_i |D'_i|^2-\sum_l \sigma_{{\rm rc},l}\ , \tag{3d}$$

in which B is a constant.

We emphasize once again that an analysis of the excitation spectrum by means of Eq. (1) will only give rise to meaningful results provided the conditions stated above are valid. If closed-channel interactions would be significant, such an analysis would at best be a phenomenological parametrization of line shapes yielding the width and position of spectral features, rather than the more fundamental channel interaction strengths and quantum defects. The theoretical study performed by Maeda, Ueda, and Ito [14] on the $ns'[1/2]_1$ and $nd'[1/2]_1$ Rydberg series of Ar, Kr, and Xe, accessed by one-photon excitation from the ground state, has demonstrated, however, that the neglect of closed-channel interactions is justified for the systems presently under investigation. In this study the width and quantum defect parameters have, on the one hand, been determined from a fit by means of Eq. (1) to excitation spectra reproduced from calculated MQDT parameters at certain energies, and, on the other hand, by direct transformation of the calculated MQDT parameters using complex quantum defect theory. Comparison of the parameters obtained by both methods showed that the differences are within 0.2% [14]. Since these parameters can be determined considerably less accurately from our experimental spectra (2–20%), we conclude that the neglect of closed-channel interactions will, to a first approximation, not significantly influence the analysis of the present excitation spectra.

Under the neglect of closed-channel interactions Eqs. (1) and (3) demonstrate that the width and quantum defect parameters, as determined from the excitation spectra by a fit with Eq. (1), are independent of the initial state and the excitation mechanism, as has been confirmed in various other experimental studies [16,23]. From Eq. (3b) it can be concluded, on the other hand, that the q_l parameters are dependent on the initial state from which excitation is performed, and on the excitation scheme [16,23].

In Figs. 4 and 7 the present experimental spectra for Kr and Xe, respectively, are compared with the three-photon excitation spectra as predicted by MQDT calculations [30]. In order to allow for a more quantitative comparison of these theoretical spectra with our experimental spectra, we parametrized the theoretical spectra by means of Eq. (1), while we determined W_l and μ_l as well using complex quantum defect theory [47].

Our fits presented in Figs. 2, 4, and 7 demonstrate that Eq. (1) gives an excellent description of the autoionizing profiles. In these fits ionization potentials $I_{1/2}$ of 128 541.8, 118 284.5, and 108 370.8 cm^{-1} have been used for Ar[2], Kr[49], and Xe[19], respectively. As discussed above, some of the narrower autoionizing resonances, viz., $ns'[1/2]_1$ and $ng'[3/2]_3$, might be subject to serious pressure, power, and instrumental broadening effects. Under such circumstances the values derived from the fits for W_l should be considered with some caution. However, the values obtained for μ_l and q_l will to a first approximation still be reliable, since these parameters are insensitive to instrumental broadening [13]. Of course, the above considerations gain importance, as the observed resonances are narrower.

B. Autoionizing resonances in Ar

The analysis of the line shapes of the autoionizing series observed in Ar (Fig. 1) by means of Eq. (1) results in values for the q_l, μ_l, and W_l parameters as given in Tables I, II, and III. With respect to the quantum defects given in Table II, it can be concluded that the values for the $ns'[1/2]_1$ and $nd'[3/2]_1$ series determined in the present three-photon excitation study are in good agreement with the results of previous one-photon excitation work [14,23]. The only notable exceptions concern the studies of Wu *et al.* [10] and Radler and Berkowitz [4]. Although the quantum defects obtained for the $ns'[1/2]_1$ series in these studies are identical to the ones obtained in the present work, a value of 0.25 was determined for the quantum defects of the $nd'[1/2]_1$ series. A possible explanation for this apparent discrepancy might be found in the fact that in both these one-photon excitation studies the line shapes have been analyzed using the original Fano formula, which is only valid for isolated resonances. Such an explanation is corroborated by the observation that our value agrees very well with the value given by Maeda, Ueda, and Ito [14] determined in a one-photon excitation study with a line-shape analysis similar to ours.

In our experiments we have been able to observe the $ng'[7/2]_3$ series up to $n=17$. The line shapes of these resonances are almost symmetrical, indicating a large value for $|q|$. A precise analysis of the line shapes is hin-

TABLE I. Line profile parameters q obtained for the $ns'[1/2]_1$, $nd'[3/2]_1$, $nd'[5/2]_3$, and $ng'[7/2]_3$ autoionizing series in Ar, Kr, and Xe by the analysis of the three-photon excitation spectra according to Eq. (1). The top of the table gives the parameters obtained from the present experimental results; at the bottom of the table the parameters are given for Kr and Xe as determined from the three-photon excitation spectra calculated by L'Huillier, Tang, and Lambropoulos [30].

	$ns'[1/2]_1$		$nd'[3/2]_1$		$nd'[5/2]_3$		$ng'[7/2]_3$	
			Present experimental results					
Ar	$n=11$:	43(10)	$n=11$–16:	3(0.8)			$n=9$:	−25(20)
	$n=12$–14:	14(3)						
Kr	$n=8$–20:	12(4)	$n=10$–16:	7(4)			$n=5$:	−30(25)
Xe	$n=8$–14:	6.5(1)	$n=10$–15:	0(0.1)	$n=8$–20:	3.3(0.5)	$n=5$:	−30(20)
			Theoretical results obtained from spectra in Ref. [30]					
Kr	$n=10$:	10(4)	$n=8$:	0.75(0.10)				
Xe	$n=9$–10:	13(5)	$n=7$–8:	0.45(0.06)	$n=7$–8:	4.4(0.4)		

TABLE II. Quantum defects μ obtained for the $ns'[1/2]_1$, $nd'[3/2]_1$, $nd'[5/2]_3$, and $ng'[7/2]_3$ autoionizing series in Ar, Kr, and Xe from the analysis of the three-photon excitation spectra according to Eq. (1). The top of the table gives the quantum defects as obtained from the present experimental results, while in the middle of the table the quantum defects are given for Kr and Xe as determined from the three-photon excitation spectra calculated by L'Huillier, Tang, and Lambropoulos [30]. At the bottom of the table the quantum defects at the two ionic limits, $I_{3/2}$ and $I_{1/2}$, are given as calculated by complex quantum defect theory [47] from the results of previous MQDT calculations.

	$ns'[1/2]_1$		$nd'[3/2]_1$		$nd'[5/2]_3$		$ng'[7/2]_3$	
				Present experimental results				
Ar	$n=11$–34:	2.14(0.006)	$n=9$–14:	0.21(0.02)			$n=9$–17:	0.000(0.005)
Kr	$n=8$–24:	3.097(0.005)	$n=6$–24:	1.25(0.03)			$n=5$–16:	0.003(0.0015)
Xe	$n=8$–30:	4.021(0.006)	$n=10$–15:	2.33(0.03)	$n=8$–29:	2.43(0.025)	$n=5$–20:	0.006(0.003)
				Theoretical results obtained from figures in Ref. [30]				
Kr	$n=8$–10:	3.099(0.015)	$n=8$:	1.198(0.015)	$n=8$:	1.321(0.015)		
Xe	$n=9$–10:	4.045(0.030)	$n=7$–8:	2.30(0.015)	$n=7$–8:	2.438(0.015)		
				Theoretical results with complex quantum defect theory using $U_{l\alpha}$ and μ_α				
Ar	$I_{1/2}$:	2.128[a]	$I_{1/2}$:	2.193[a]				
Kr	$I_{1/2}$:	3.0729[a]	$I_{1/2}$:	1.2061[a]	$I_{3/2}$:	1.314[b]		
	$I_{3/2}$:	3.0978[b]	$I_{3/2}$:	1.2205[b]	$I_{1/2}$:	1.348[b]		
	$I_{1/2}$:	3.0881[b]	$I_{1/2}$:	1.2468[b]				
Xe	$I_{1/2}$:	3.981[a]	$I_{1/2}$:	2.286[a]	$I_{3/2}$:	2.419[c]		
	$I_{3/2}$:	4.033[d]	$I_{3/2}$:	2.299[d]	$I_{1/2}$:	2.418[c]		
	$I_{1/2}$:	3.987[d]	$I_{1/2}$:	2.299[d]				

[a]Obtained from [40].
[b]Obtained from [42].
[c]Obtained from [30].
[d]Obtained from [39].

TABLE III. Width parameters W obtained for the $ns'[1/2]_1$, $nd'[3/2]_1$, $nd'[5/2]_3$, and $ng'[7/2]_3$ autoionizing series in Ar, Kr, and Xe from the analysis of the three-photon excitation spectra according to Eq. (1). The top of the table gives the width parameters obtained from the present experimental results, while in the middle of the table the width parameters are given for Kr and Xe as determined from the three-photon excitation spectra calculated by L'Huillier, Tang, and Lambropoulos [30]. At the bottom of the table the width parameters at the two ionic limits, $I_{3/2}$ and $I_{1/2}$, are given as calculated by complex quantum defect theory [47] from the results of previous MQDT calculations.

	$ns'[1/2]_1$		$nd'[3/2]_1$		$nd'[5/2]_3$		$ng'[7/2]_3$	
				Present experimental results				
Ar	$n=11$:	0.014(0.002)	$n=9$–14:	0.23(0.02)			$n=9$:	<0.001 3
	$n=12$:	0.0075(0.002)						
	$n=13$–14:	0.0076(0.002)						
Kr	$n=8$–12:	0.015(0.003)	$n=6$–20:	0.23(0.05)			$n=5$:	<0.000 26
Xe	$n=8$:	0.0062(0.0004)	$n=10$–15:	0.22(0.05)	$n=8$–14:	0.021(0.003)	$n=5$:	0.000 51(0.000 10)
	$n=9$:	0.0062(0.0004)						
	$n=10$:	0.0063(0.0004)						
				Theoretical results obtained from figures in Ref. [30]				
Kr	$n=8$:	0.013(0.002)	$n=8$:	0.165(0.020)				
Xe	$n=9$–10:	0.0095(0.0004)	$n=7$–8:	0.21(0.02)	$n=8$:	0.024(0.003)		
				Theoretical results with complex quantum defect theory using $U_{l\alpha}$ and μ_α				
Ar	$I_{1/2}$:	0.0087[a]	$I_{1/2}$:	0.260[a]				
Kr	$I_{1/2}$:	0.014[a]	$I_{1/2}$:	0.239[a]	$I_{3/2}$:	0.027[b]		
	$I_{3/2}$:	0.014[b]	$I_{3/2}$:	0.152[b]	$I_{1/2}$:	0.027[b]		
	$I_{1/2}$:	0.015[b]	$I_{1/2}$:	0.194[b]				
Xe	$I_{1/2}$:	0.0096[a]	$I_{1/2}$:	0.296[a]	$I_{3/2}$:	0.038[c]		
	$I_{3/2}$:	0.0074[d]	$I_{3/2}$:	0.223[d]	$I_{1/2}$:	0.037[c]		
	$I_{1/2}$:	0.0070[d]	$I_{1/2}$:	0.225[d]				

[a]Obtained from [40].
[b]Obtained from [42].
[c]Obtained from [30].
[d]Obtained from [39].

dered to a large extent by their extremely small widths. Since fits with a large negative value for q gave slightly better results than fits with large positive values, we tend to favor the former value of q. The quantum defect of these resonances is established as 0.000 ± 0.005, in agreement with the expectation of a small quantum defect for nonpenetrating orbitals with a large angular momentum. This value is similar to the value obtained in one-photon excitation studies from excited states of the Ar atom, in which it was determined as 0.004 ± 0.003 [22].

The widths of the broad $nd'[3/2]_1$ resonances are found to be in good agreement with those determined in the study of Maeda, Ueda, and Ito [14]. By means of Eq. (2b) the width parameter Γ_l can be determined from the W_l parameter and compared with the results of Wu *et al.* [10] and Radler and Berkowitz [4]. From this comparison it might appear that in the latter two studies smaller widths have been observed. Such is not the case, however, since we have checked that the difference is only caused by the fact that the spectra have been analyzed with different line-shape formulas (*vide supra*). While the widths of the $nd'[3/2]_1$ resonances can be determined accurately, the intrinsically much narrower $ns'[1/2]_1$ and $ng'[7/2]_3$ resonances are seriously broadened under our experimental conditions. It is, for example, observed that the width of the $12s'[1/2]_1$ resonance is 1.34 cm^{-1}, a value which is considerably larger than that of 0.52 cm^{-1} obtained by Klar *et al.* [23].

Figure 1 shows that the intensity of the autoionizing resonances decreases as n increases. Although the spectra have not been corrected for the changes in laser pulse energy caused by the dye gain curve, this cannot explain the decrease in intensity, since the dye used in this energy region has its maximum efficiency at the high-energy side of the excitation spectrum. For the $ns'[1/2]_1$ and $ng'[7/2]_3$ series the finite instrumental width might in principle be responsible for such a decrease, but even for the broad $nd'[3/2]_1$ resonances the same phenomenon occurs. A similar decrease has previously been observed in one-photon excitation studies of the $ns'[1/2]_1$ and $nd'[5/2]_1$ series [14]. A possible explanation could be that the line-shape parameters are strongly energy dependent, although for one-photon excitation this would be surprising. For three-photon excitation, however, one might in principle expect such a dependence, since here the three-photon transition amplitude contains contributions of the various energy levels in the atom weighted by the energy difference with the one- and two-photon levels. As the excitation energy is changed, the relative contributions of the different energy levels will consequently also change. Inspection of the energy levels of the lowest $4p$ and $4p'$ states, which are expected to be a major influence at the two-photon level, reveals, however, that even for three-photon excitation a strong energy dependence of the line-shape parameters is not expected.

Unfortunately our three-photon excitation spectrum cannot be compared with theoretically predicted spectra, since as yet no theoretical studies on three-photon excitation of autoionizing states in Ar have been performed. The widths and energies of the $ns'[1/2]_1$ and $nd'[5/2]_1$ resonances, on the other hand, can be compared with those obtained in theoretical studies of one-photon excitation from the ground state. Since such a comparison has already been carried out extensively in [14], we shall not discuss this issue further.

C. Autoionizing resonances in Kr

In Tables I–III the results of the analysis of the line shapes of the autoionizing states observed in Kr (see Fig. 3) are reported. Three-photon excitation to the autoionizing states of Kr has been studied previously by Dehmer, Pratt, and Dehmer [27], who reported, however, only the observation of the lowest members of the $ns'[1/2]_1$, $nd'[3/2]_1$, and $ng'[7/2]_3$ series. In the present study we have been able to study these series up to $n=35$, enabling a considerably improved characterization of the line shapes, in particular of the broad $nd'[5/2]_1$ resonances, and allowing for a better comparison with theoretically predicted three-photon excitation spectra.

Comparison of the present three-photon excitation spectra with the one reported by Dehmer, Pratt, and Dehmer [27] reveals a number of differences. First, in the present study the relative intensity of the $ng'[7/2]_3$ resonances is considerably larger. This might be due to a difference in resolution. Secondly, it has been concluded previously that the q parameter of the $nd'[3/2]_1$ series has a negative value. Our study, on the other hand, shows unambiguously that q is positive. This difference can probably be attributed in part to the fact that in the previous study only the lowest members have been studied, which, as shown in the present study, exhibit slightly distorted line shapes.

The quantum defects of the $ns'[1/2]_1$ and $nd'[3/2]_1$ series obtained from Fig. 4 agree reasonably well with those reported in one-photon excitation studies. Since Maeda and co-workers [11,14] have already compared the experimental and theoretical results for these series with one-photon excitation in great detail, we shall not discuss this topic any further.

As outlined in the experimental section, during the experiments great care has been exercised to avoid pressure and power broadening effects. For the measurements on Kr the signal-to-noise ratio of the spectra allowed for larger variations of the various experimental parameters than in the case of Ar. Despite this optimization procedure, the widths of the $ns'[1/2]_1$ resonances are still slightly larger than those measured by Klar *et al.* [23], indicating that broadening effects have not been eliminated completely. The $ng'[7/2]_3$ resonances have not been observed before under very-high-resolution conditions. In the present study they appear as extremely narrow peaks, with probably a major contribution to the observed linewidths due to the laser bandwidth. For the lowest member a width of 0.39 cm^{-1} is measured which, taking the laser bandwidth into account, results in a value of 0.000 26 for the width parameter W. Above it has been pointed out that the laser bandwidth is not the only factor contributing to the broadening of the resonances, and this value should consequently only be considered as an upper limit. Measurements with a much smaller bandwidth and lower pressures would be neces-

sary to achieve an accurate determination of the widths of these resonances.

The three-photon excitation spectra obtained for Ar reveal that the intensity of the broad $nd'[3/2]_1$ resonances decreases as higher members of the autoionizing series are accessed. Because of the strong power dependence in three-photon excitation processes, caution is needed when the line intensities of different members are compared. Nevertheless, it would appear from Fig. 4 that such a decrease in intensity does not occur in the case of Kr.

For a comparison with the results of theoretical calculations we shall primarily concentrate on the MQDT calculations performed by L'Huillier, Tang, and Lambropoulos [30] for three-photon excitation of autoionizing states in Kr. Figure 4(a) shows the autoionization spectrum as predicted by these three-photon excitation calculations. Because of the difficulties encountered in measuring undistorted line profiles, especially for those of the lower members of the broad $nd'[3/2]_1$ series, the comparison shown in this figure has been performed for higher members only, i.e., the $10d'[3/2]_1$, $12s'[1/2]_1$, and $9g'[7/2]_3$ resonances. The theoretical spectrum, which in the original paper has been given for the lowest members of these series, has for this purpose been extrapolated to these higher members under the assumption that the line-shape parameters are independent of energy. In order to allow for a quantitative comparison of the two spectra, the published theoretical spectrum has been subjected to an analysis using Eq. (1). The results of this analysis are given in Tables I–III.

One of the most striking differences between theory and experiment is clearly found in the intensities of the various series: while the $nd'[5/2]_3$ series is predicted with an intensity comparable to the other series, it cannot be experimentally observed; analogously, an intensity is predicted for the $ng'[7/2]_3$ series that is considerably smaller than observed in the experiment. Figure 4(a) and the values of the line-shape parameters show that for the $ns'[1/2]_1$ series the theoretical and experimental quantum defects and q parameters are in good agreement, while the width is obviously underestimated in the calculations. The differences between theory and experiment for the $nd'[3/2]_1$ series, on the other hand, are significantly larger, as can already be observed qualitatively in Fig. 4. For the $ng'[7/2]_3$ series the present study determines the quantum defect as 0.0030 ± 0.0015, and for q a large negative value is found. A comparison with theory is not possible for these series, since the resonances cannot be analyzed accurately from the calculated spectra.

D. Autoionizing resonances in Xe

In Tables I–III we report the results of the line-shape analyses of the four autoionizing series observed in the three-photon excitation of Xe (Fig. 6). Compared to Ar and Kr, the cross section for three-photon excitation of autoionizing states in Xe is relatively large. Consequently, the study of these series could be performed under almost ideal experimental conditions, i.e., low pressure at the point of excitation and low laser power. As a result we have been able to obtain linewidths which are smaller than or comparable to the linewidths obtained in recent high-resolution studies [13,14,19].

The spectra depicted in Figs. 6–8 and their analyses reported in Tables I–III differ in a number of aspects from the results obtained in the three-photon excitation study of Pratt, Dehmer, and Dehmer [26]. First, these authors observe a large difference in peak intensities between the members of the $ns'[1/2]_1$ series and the $ng'[5/2]_3$ series. Our results, on the contrary, give comparable peak intensities for these two series. This might result from the fact that in the study of Pratt, Dehmer, and Dehmer [26] a resolution at the fundamental wavelength of only 0.3 cm^{-1} was achieved, while our resolution is about 0.08 cm^{-1}. Secondly, it has previously been concluded that the q parameter of the broad $nd'[3/2]_1$ series is positive. Our analysis demonstrates that this q is almost zero, indicating a window resonance instead. In Ar and Kr the $nd'[5/2]_3$ series could not be observed, but in Xe it is clearly present. Pratt, Dehmer, and Dehmer [26] have reported that the width of this series was in reasonable agreement with the measurements of Wang and Knight ($W=0.043$) [19]. From the analysis of our spectra it can be concluded that this value is rather large, since we determine a width of 0.021. Finally, the application of circularly polarized light, by which the $ng'[7/2]_3$ series could be observed up to $n=20$, enables a more accurate determination of the quantum defect of this series, which is now established as 0.006 ± 0.003. The width parameter of these series is more difficult to obtain, since the resonances are extremely narrow. From the linewidth of the lowest member (0.89 cm^{-1}) a value of $W=0.000\,51\pm0.000\,10$ is found after correction for the laser bandwidth.

The width of the $ns'[1/2]_1$ series in Xe has been the subject of a large number of experimental studies. Recently Klar *et al.* [23] in a two-step excitation study determined the width as $W=0.0061\pm0.0002$, which was significantly smaller than the values reported before. The width observed in the present three-photon excitation study, $W=0.0062\pm0.0004$, is in excellent agreement with this value.

Before it has been noticed that in Ar the $nd'[3/2]_1$ resonances decreased in peak intensity for higher members, while in Kr these resonances retained the same intensity. For Xe the excitation spectrum in Fig. 6 shows that the $nd'[3/2]_1$ series exhibit the same behavior as for Kr.

Similar to the excitation spectrum obtained for Kr, the lowest members of the $nd'[3/2]_1$ series are slightly distorted by background fluctuations. The comparison of the present three-photon excitation spectra with those predicted by MQDT calculations of L'Huillier, Tang, and Lambropoulos [30] has therefore been performed for higher members only, i.e., the $12d'[5/2]_3$, $12d'[3/2]_1$, $14s'[1/2]_1$, and $10g'[7/2]_3$ resonances. The extrapolation, which results in the spectrum shown in Fig. 7(a), has again been carried out under the assumption that the line-shape parameters are independent of energy. The analysis of the theoretical spectrum using Eq. (1) leads to

values for the line-shape parameters given in Tables I–III.

The theoretical three-photon excitation spectrum of Kr showed clear discrepancies with the experimental spectrum when the relative peak intensities of the various series were compared. For Xe these differences are less pronounced, although the intensity of the $ng'[7/2]_3$ resonances is again underestimated. The line-shape parameters of the $ns'[1/2]_1$ series derived from the calculated spectra show that the q parameter is in good agreement with experiment, while the width parameter and the quantum defect are less satisfactorily predicted. For Kr the calculation of the excitation spectrum of the $nd'[3/2]_1$ series proved to be rather difficult. Figure 7 and the derived parameters show that such problems are also encountered in the calculation of the excitation spectrum of these series in Xe. Calculation of the $nd'[5/2]_3$ series, on the other hand, results in parameters which are in reasonable agreement with the experimental results, although we notice that the width as determined from the theoretical spectrum with Eq. (1) ($W=0.024$) appears to be somewhat different from that obtained with the complex quantum defect theory from their reported μ_α vector and $U_{l\alpha}$ matrix ($W=0.037$). The $ng'[7/2]_3$ resonances are not available from the calculated spectra, and a detailed comparison therefore cannot be carried out.

Finally we remark that the parameters as found in the present study for the two $J=1$ series in Xe compare well with the results of previous one-photon excitation studies. For a detailed comparison between theory and experiment for these series we refer to the studies of Maeda and co-workers [13,14].

E. Influence of the two-photon virtual level

For all three rare-gas atoms it has been observed that the three-photon excitation spectrum of the autoionization region between the two lower ionic limits does not display any rapid distortions of the resonances. Such distortions would indeed not be expected *a priori* when the energy levels of the rare-gas atoms are considered in relation to the one- and two-photon levels reached in our experiments.

The one-photon excitation spectra of the three rare-gas atoms between the lower ionic limits are reasonably similar. We might consequently have expected that the three-photon excitation spectra would also demonstrate such similarities. Such is roughly the case for Ar and Kr, but certainly not for Xe. For the latter atom the members of the $nd'[3/2]_1$ series manifest themselves as window resonances, and it is the only atom which shows a measurable peak intensity for the $nd'[5/2]_3$ resonances. In previous three-photon excitation studies of Kr and Xe [26,27] this difference in intensity of the $nd'[5/2]_3$ series has been attributed to a difference in the composition of the two-photon virtual level, where the lowest np and np' levels are of major influence. In the present study we have seen that also in Ar the $nd'[5/2]_3$ series cannot be observed, which would be in agreement with such an explanation. Inspection of the excitation energies of the lowest np and np' levels reveals that indeed the contributions of these states are expected to be different in Xe compared to both Kr and Ar. The energy difference between the two-photon energy used in our experiments and the $6p$ level in Xe varies between 12 000 and 5000 cm^{-1}, while for the $6p'$ level energy differences between 23 000 and 16 000 cm^{-1} occur. The ratio of these energy differences is therefore between 1.9 and 3.2, which is significantly different from the ratio obtained for Kr(~ 1.45) and Ar(~ 1.15).

The influence of the two-photon virtual level on the excitation dynamics of the autoionizing series is also reflected in the profile index q. Equation (3b) implies that q is dependent on the ratio of direct and indirect ionization. As has been discussed in a previous study [16], in which autoionizing states are excited by a one-photon process from an excited state of the atom, the absolute magnitude of q is strongly dependent on the character of the core of that initial excited state. If the core of the initial state is mainly of $^2P_{1/2}$ character, the absolute value of q is expected to be high, implying a predominant role of indirect ionization. On the other hand, for states with a $^2P_{3/2}$ core the direct ionization rate is large, and a small q is expected. Above we have reasoned that in Xe the two-photon virtual level contains more $^2P_{3/2}$ character than the two-photon virtual levels of Kr and Ar. Such a conclusion is supported by the comparison of the q parameters of the autoionizing resonances in the three atoms, since they are indeed smaller for Xe than for the other two atoms.

V. CONCLUSIONS

The $ns'[1/2]_1$, $nd'[3/2]_1$, $nd'[5/2]_3$, and $ng'[7/2]_3$ autoionizing series of Ar, Kr, and Xe between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic limits have been studied using three-photon excitation with linearly and circularly polarized excitation light. For Ar this study has enabled observation of such series using multiphoton excitation, while for Kr and Xe previous three-photon excitation results have been improved significantly and extended to higher members.

All rare-gas atoms show very regular autoionizing profiles in going from the first to the second ionization limit. From an analysis of the three-photon excitation spectra by means of the line-shape formula Eq. (1) the parameters μ_l, W_l, and q_l of the various resonances have been obtained. A comparison of the parameters from the present work which, under the assumption of negligible closed-channel interactions, are independent of the excitation scheme, i.e., the quantum defects and the widths, with the results of one-photon excitation studies shows a good agreement for the quantum defect. With respect to the widths, values have been obtained that are comparable to and in some cases even smaller than previously observed. The three-photon excitation spectra predicted by MQDT for Kr and Xe, on the other hand, differ significantly in a number of aspects from the present experimental spectra.

Previously, three-photon excitation studies of Kr and Xe gave reason to believe that the appearance of the $nd'[5/2]_3$ series is critically dependent on the nature of the two-photon virtual level. The present results ob-

tained for Ar are in agreement with such a picture. Moreover, it has been demonstrated that the measured q_l parameters also corroborate the importance of the two-photon virtual level.

In the present study we have applied three-photon excitation to investigate the autoionizing states in Ar, Kr, and Xe. As a result of the nature of this excitation process, only the odd $ns'[1/2]_1$, $nd'[3/2]_1$, $nd'[5/2]_3$, and $ng'[7/2]_3$ autoionizing series could be accessed. In order to study the even autoionizing series such as $np'[1/2]_0$, $np'[3/2]_2$, $nf'[5/2]_2$, and $nf'[7/2]_4$ one would have to revert to an even-photon excitation process. In a forthcoming paper we shall report the results of such a study on Ar, Kr, and Xe using four-photon excitation.

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