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Observation of Cooper minima in excited-*s*-state photoionization cross sections in neon and argon

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Observations of Cooper minima in excited-state photoionization cross sections for the Ne 3*s* and Ar 4*s* levels are reported. Prebreakdown Ne and Ar discharges under irradiation by light in the 200—400-nm wavelength range yield spectral dependences of photoionization cross sections with minima at the ionization threshold of these states in Ne and slightly distant from them in Ar. They are in close agreement with certain theoretical predictions. Autoionization structure which exists between the two ionization limits $^2p_{3/2}$ and $^2p_{1/2}$ was not observed in any of the Ne or Ar photoionization spectra due to both low spectral resolution and the high density of levels in this spectral region. Application of these measurements to ultraviolet-radiation detection is examined. High detection sensitivity of ultraviolet light is indicated.

I. INTRODUCTION

Theoretical calculations and experiments for determining photoionization cross sections from ground states have been of great interest from the standpoints of both basic physics and practical application.

From the standpoint of theory, calculation of this cross section involves evaluation of the quantum transition rate of a bound electron of the atom into the ionization continuum. An interesting feature has been found for ground-state photoionization, i.e., "Cooper minima."[1,2] Several authors have also predicted the existence of such minima in the photoionization cross sections of excited states of rare-gas atoms and different calculations of wavelengths have been presented.[3–8] The agreement between these calculations is generally poor. Assessment of the theoretical results is difficult because of the scarcity of measurements. Measurements of cross sections for photoionization from excited states have been reported for metastable barium,[9] excited cesium,[10] metastable helium,[11] and magnesium.[12] We report here an experimental observation of Cooper minima in excited-state photoionization spectra. To the best of our knowledge, this is the first *experimental* observation of Cooper minima to be reported for photoionization from excited states. The excited states investigated are the *s* and *p* levels in neon and argon. Our results agree with Duzy-Hyman predictions.

Interesting features are added to the photoionization spectrum in the case of the existence of two close ionization limits of the atom, where autoionizing resonances can occur.[13,14] These are bound states of the electron embedded in the ionization continuum. Owing to configuration interaction these bound states are coupled to the ionization continuum and autoionize. The ground-state photoionization cross section or spectrum consequently exhi-

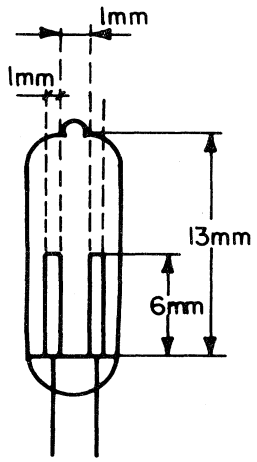

FIG. 1. Typical discharge lamp used in experiments. Direction of incident light is perpendicular to page.

bits additional features between the ionization limits[15,16] under the proper experimental conditions. These were not observed here in excited-state photoionization. Reasons for this are discussed in Sec. III.

From the standpoint of applications, the vigorous search for efficient high power for gas lasers in discharges or *e*-beam schemes naturally leads to the need for determination of photoionization cross sections both from the ground state and from excited levels of molecules or atoms. The aim is to determine the advantages of photoionization in laser discharges and the drawbacks due to the absorption of the laser light by the excited states. In particular, recent interest in photoionization of rare-gas atoms in excited states has resulted from the importance of such phenomena in laser breakdown of gases[17–20] and in photoionization processes[21] for transverse-excitation atmospheric-pressure (TEA) lasers and rare-gas-halide exciplex lasers.[22] By preionizing a prebreakdown discharge through photoionization, it is possible to break down the gas rather uniformly during the main discharge pulse with reduced fields (lower E/N) as required for population inversion.[23,24]

The potential of excited-state photoionization as an inexpensive and sensitive means of detection of near uv radiation[25] also appears worthy of exploration, particularly in view of high sensitivities[26] (1000 $\mathrm{V\,W^{-1}}$) already obtained at visible wavelengths by use of the optogalvanic effect.[27,28] Indeed, argon excited-state photoionization signals similar in magnitude to those of S-3 (Ag-O-Rb) and S-4 (Cs-Sb) photocathode emission under the same incident-light-irradiance conditions have been observed.[25,29] In this paper we report high excited-state photoionization responsivities for Ne and Ar, without any observable photocathode emission.

The purpose of this paper is to report near-uv photoionization spectra of excited atoms, namely, *s* and *p* states in neon and argon, and to compare the spectral dependences with theoretical predictions.[3–8] The significance of this work is that the predicted existence of Cooper minima in the *s*-state photoionization cross sections for excited Ne and Ar is indeed supported by experiment. The spectral results here are compatible in particular with those predicted by Duzy and Hyman.[3] Also, the fairly high responsivity to uv radiation measured over even very short path lengths ($\simeq$0.3 mm) indicates the potential usefulness of the technique for sensitive detection of near-uv radiation.

II. EXPERIMENT

Previous experimental work made use of photocathode emission to generate atomic excitation for excited-state photoionization.[25,29] In the present work high uv response is obtained by the use, instead, of Ni electrodes in simple indicator lamp tubes depicted in Fig. 1. The uv glass (GE 9823) envelopes exhibit flat transmittance down to about a 250-nm wavelength. The lamps were biased to a prebreakdown discharge. With this biasing, responsivities similar to and even higher than those of the optogalvanic effect[26–28] are obtained. Doing away with the fragile photocathode makes this photoionization technique much more feasible for the TEA laser photopreionization purposes and also permits observation of excited-state photoionization without cathode photoelectric effect distortions. The advantage of the prebreakdown rather than glow discharge is a highly significant noise reduction and thus signal-to-noise improvement. The prebreakdown discharge results from electron emission from the cathode. Bias is near breakdown, as shown in Table I. Free electrons emitted from the cathode produce excited states via inelastic collisions. The prebreakdown condition also permits low E/N biasing so as to generate most excitation only at the lowest levels. Thus, illumination of the prebreakdown discharges with *very* low intensity light at different wavelengths enables the spectral dependence of the *s*- and *p*-level photoionization cross sections to be observed with minimum distortions imposed by interactions of photons or photoionization electrons with atoms excited to higher energy states. It is also important for the light to be of very low intensity so as to permit minimum distortion of spectral dependence by photoionization-generated space charges.[30] These

TABLE I. Discharge gases, additives, and voltage characteristics. Electrode coating refers to BaSr. Radioactive additive is ^{85}Kr in units of millicurie per liter.

Test No.	Coating	Gas	Pressure (mm)	Radioactivity	$V_B(V)$	$V_D(V)$
1	No	Ne	90	No	142	130
2	Yes	Ne	90	No	116	106
3	No	Ne	90	0.1 mCi/l ^{85}Kr	142	133
4	Yes	Ne	90	0.1 mCi/l ^{85}Kr	123	117
5	No	No	0.001			500
6	Yes	No	0.001			500
7	No	98% Ar 2% H_2	90	1.0 mCi/l ^{85}Kr	198	182
8	Yes	98% Ar 2% H_2	90	1.0 mCi/l ^{85}Kr	203	194
9	No	100% Ar	90	No	236	223
10	Yes	100% Ar	90	No	183	157

have been known to distort the electric fields in discharges and thus to alter electron energy and consequent current carrier multiplication processes. As might be expected from the excited-state photoionization origin of such space charges, resulting nonlinearities of response exhibit a wavelength dependence, as described previously.[18,25,29] To minimize such nonlinear spectral effects, it is necessary to use a high sensitivity detection system so as to operate with minimal irradiance levels of incident light and thus minimal photoionization-generated space charge. In the present case, incident irradiance was only 600 nW/cm^2 at each wavelength. Indeed, at such light levels discharge current response ΔI was measured to be very close to being linear with incident radiometric irradiance H. No wavelength dependence to the order of nonlinearity γ could be determined, where $\Delta I \propto H^{\gamma}$. γ was within a few percent of unity for each discharge lamp. Measurements of spatial profile of response, using a focused Ar laser beam incident on different portions of the discharge, have indicated[30] the cathode fall as being the most responsive portion of the discharge, out to a distance of about 250 μm from the cathode. For discharge orientation such that electrode length is transverse to the direction of incident light, effective receiver area is 6 mm (electrode length)$\times\frac{1}{4}$mm$=1.5$ mm^2. In view of the glass-envelope transmission, actual light power received over the effective discharge receiving area for 600-nW/cm^2 irradiance is only about 6 nW, except at the 218-nm wavelength where it is reduced to 2.5 nW because of glass-envelope absorption.

The effects on responsivity and spectral response of standard barium strontium electrode coatings, used to increase electron emissivity, and krypton 85 radioactive-gas additives, are investigated here too. These are common additions to indicator lamps. The lamps, at 90-Torr pressure with the high-purity research grade gases indicated in Table I, were supplied by the Signalite Division of General Instrument Corporation. They contained parallel wire Ni electrodes about 1-mm thick. Closest electrode separation was approximately 1 mm. Effective discharge depth or path length between the electrodes has already been measured to be about 0.3 mm.[31] The BaSr electrode coatings features in some of the indicator lamps were investigated for photoelectric properties. For this purpose indicator lamps were also obtained with and without the electrode coatings. Some of these lamps contained a "vacuum" of 10^{-3}-Torr pressure air. Cathode photoemissive properties, if they exist, should be evident in vacuum too, although they should be somewhat reduced for lack of internal multiplication collisions. Experiments were carried out in vacuum tubes with the electrode coating (test no. 6 in Table I) and in tubes without it (test no. 5 in Table I). These experiments with vacuum tubes were carried out using unattenuated high-pressure Hg lamps over their whole spectrum of emission, including the high intensity lines in the visible. [There was no attenuation of intensity through calibrated neutral density filters (quartz) or narrowing of spectral width using interference filters for wavelength selection, as was indeed done with the "gas" tubes described below.] The absence of any response to light of such relatively high intensity in vacuum tubes as measured with a Princeton Applied Research Model 186 Synchro-Het Lock-in Amplifier, even with 500-V discharge bias, suggests that cathode photoemission played a negligible role, if any, in these experiments and that the responses reported here are almost entirely, if not completely, the result of excited-atom photoionization and current carrier multiplication of such photoionization resulting from the dc bias.

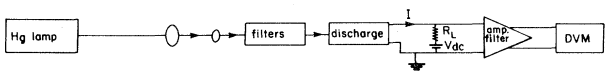

FIG. 2. Block diagram of experimental system.

The experimental system is described in Fig. 2. Radiation from a mercury lamp was electronically chopped at 100 Hz by the lamp power supply. This light was focused onto the filter box by quartz lenses. Filters included both interference filters [about 10-nm full width at half maximum (FWHM) linewidth] for wavelength selection and quartz neutral density filters for calibrated attenuation (discrete) of the incident irradiance. Irradiance incident on the discharges was measured with an International Light 325 radiometer. Through use of the quartz neutral density filters, curves of discharge response versus irradiance at each wavelength were obtained over the spectral range 218—400 nm. From the curves, discharge response for 600-nW/cm^2 irradiance levels was obtained and plotted in Figs. 3(a) and 3(b) for Ne and Ar, respectively. Two load resistors R_L were used to determine the effect of changing bias current. Such currents were on the order of a few nanoamps. The detected signal was amplified with a low noise Ortec Brookdeal 9452 filter amplifier (1000-MΩ input impedence). Limiting noise was from the amplifier, rather than from the Townsend discharge. The discharge noise was thus determined to be less than 16 nV/Hz$^{1/2}$. dc discharge bias voltage was as high as could be maintained for a stable discharge under the Hg lamp illumination conditions. The various discharge gases, breakdown voltages in the dark without photoionization (V_B), and operating voltages (V_D) for the experiments are listed in Table I. At higher bias levels, discharge instabilities set in as a result of the onset of gas breakdown conditions[25,30] resulting from the incident light, although the bias was still prebreakdown and thus lower than V_B. The discharge spectral responses are shown in Fig. 3.

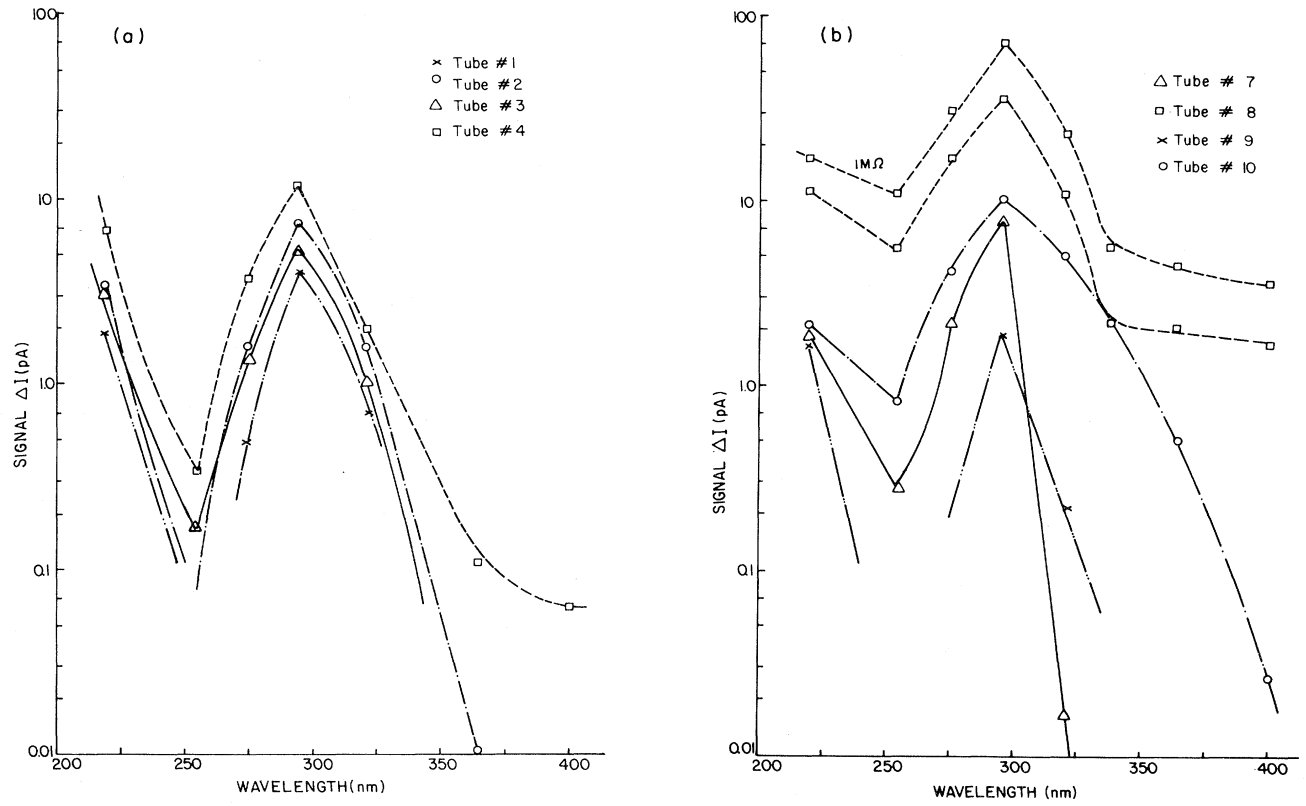

FIG. 3. Discharge signal as a function of wavelength per 0.3-mm effective path length for (a) Ne and (b) Ar lamps. Incident irradiance is 600 nW/cm^2, corresponding to 6 nW received by discharge itself, except at 218-nm wavelength where received power is only ≃2.5 nW because of increased absorption by glass. Except as otherwise noted, $R_L = 10$ MΩ.

III. DISCUSSION

In a discharge of such low E/p ($\simeq$12 V cm^{-1} Torr^{-1} for Ne and $\simeq$20 V cm^{-1} Torr^{-1} for Ar) most excitation is to the very lowest excited states. Average electron energy for discharge tubes of this type of electrode geometry and gas pressure has been measured to be on the order of 0.3 eV for an abnormal glow with significant space-charge distortion giving rise to fields on the order of 1000 V cm^{-1}, or $E/p \simeq 100$ V cm^{-1} Torr^{-1}.[31] Thus, for the present case of a prebreakdown discharge where E/p is much smaller, the assumption that *average* electron energy $\bar{\epsilon}$ is less than an electron volt would appear to be justified. Therefore, since $\bar{\epsilon}$ is much less than that energy required for even the lowest excitation (16.62 eV for Ne and 11.55 eV for Ar) almost all excitation that does exist from the higher energy tail of the electron energy distribution is to the s states, with the remaining excited states being confined almost entirely to p states.

The experimental results of Fig. 3 can be understood on the basis of two processes generated by the incident photons: (1) photoionization of excited states and (2) distortions in the electron energy distribution resulting from the initial electron energy ϵ_d of an electron produced by such photoionization. This initial electron energy is essentially the energy difference between that of the absorbed photon and that required to photoionize the excited state. For example, consider an $1s_5$ (16.62 eV) excited state (Paschen notation) in Ne. Since the ionization energy for Ne is 21.56 eV, photon energy of at least 4.94 eV (251-nm wavelength) is required for photoionization of the $1s_5$ level. If the incident photon energy is 5.89 eV, corresponding to 218-nm wavelength, then the initial electron energy after such a photoionization can be as high as 0.94 eV, which is at least on the order of $\bar{\epsilon}$ and most probably considerably larger on the basis of the arguments presented above. Thus, as wavelength decreases from that at threshold (251 nm for the Ne $1s_5$ state), more and more photoionization-assisted electron heating can take place as a result of increasing ϵ_d. This heating is reflected in multiplication of such photoionization signal through electron-impact collisions. In situations where $\bar{\epsilon}$ resulting from bias is low, as here, relatively high values of ϵ_d have been known to significantly affect electron-impact and ionization processes[19,21] and thus alter the excited-state population density. However, the electron energy enhancement depends not only on ϵ_d per excited-state photoionization event but also on the probability of such events taking place. For example, at the Cooper minima the photoionization cross section is essentially zero. This means that at such wavelengths very few, if any, such energetic photoelectrons are produced. A relative measure of actual average electron energy enhancement, therefore, is the product $\sigma\epsilon_d$, where σ is the photoionization cross section. Both σ and ϵ_d are functions of wavelengths. Because of the wavelength dependence of photoionization current carrier multiplication processes on ϵ_d, signal amplification is wavelength dependent and it is possible for discharge response maxima to exist at wavelengths other than those where the photoionization cross section (σ) are maxima. The photoionization-assisted electron heating can thus significantly affect measured discharge response as far as maxima are concerned. However, for Cooper minima $\sigma \simeq 0$ and consequently ϵ_d is essentially nonexistent since no such photoionization can take place. Photoionization-assisted electron heating cannot alter the wavelength of such discharge response minima since there is no photoionization signal to be amplified by the current carrier multiplication processes resulting from bias. Therefore, the results of Fig. 3 provide a simple method to determine the existence and wavelengths of Cooper minima.

On the basis, then, of these two processes—photoionization of excited states and photoionization-assisted electron heating—we will proceed to discuss the experimental data of Fig. 3.

Hazi and Rescigno[5] and McCann and Flannery[6] have predicted photoionization cross-section minima for s states at about 218-nm wavelength in Ne.[4] Hartquist[7] predicts the minimum for $1s_4$ and $1s_5$ states to be at slightly below 200 nm,[4] while Ranson and Chapelle[4] predict such minima to occur at slightly above 200-nm wavelength. Spectral comparisons of these excited-state photoionization cross-section calculations can be seen in Ref. 4. Our results in Fig. 3(a) appear to be most consistent with those of Duzy and Hyman,[3] who predict a Cooper minimum of essentially zero cross section around threshold for s states in Ne. Threshold is about 251- and 256-nm wavelengths for the metastable Ne $1s_5$ and $1s_3$ states, respectively, corresponding nicely to the minimum of response in Fig. 3(a). The FWHM of the filter at 253 nm is 248—263 nm. Considerations of electron heating do not change the closeness of our minima measurements with the Duzy-Hyman[3] prediction since at such minima, wherever they may be, σ should be essentially zero. Hence, the spectral location of measured Cooper minima cannot be altered by enhanced photoionization signal electron-impact amplification. Consequently, of all the various theoretical calculations of photoionization cross sections for Ne s states presented thus far, the experimental results of Fig. 3(a) concerning minima in discharge response are compatible pri-

marily with those of the Duzy-Hyman calculation. Note, for example, that in discharge tubes 1 and 2 where there are no gas additives there were no measurable responses whatever at around 253 nm.

For argon, Hartquist[7] and McCann and Flannery[6] predict minima in $1s_4$ and $1s_5$ photoionization cross sections at wavelengths below 200 nm. Ranson and Chapelle[4] predict the same minima to occur at even smaller wavelengths. An earlier model of Hyman[22] predicts minimum cross section at about 215-nm wavelength. The Duzy-Hyman calculation,[3] differing from the Hyman model with regard to core polarizability value, predicts Cooper minimum for s-state photoionization in Ar to occur at about 250-nm wavelengths with noticeable increases in cross section at 218 and 295 nm (threshold). Again, inspection of Fig. 3(b) suggests compatibility of our minimum response measurements with the Duzy-Hyman calculation. Unlike the case with Ne, all the various theoretical models for Ar predict relative *maxima* instead of minima at *threshold,* which, for $1s_5$ states in Ar, is at about 295 nm. For the $1s_4$ and $1s_3$ states, threshold in Ar is at 300 and 307 nm, respectively. These predictions of maxima at threshold are supported by the maximum in Fig. 3(b) at 294-nm wavelength (FWHM of filter is 291—299 nm).

It is important to discuss the effect of autoionization states on the photoionization spectrum. These levels are of two types, namely, one and two electron autoionizing levels. The two electron states of the type converging to the $ns(n+1)p^2L$ limit have very high excitation energies, on the order of 30 eV, and thus are out of the wavelength range of the Hg lamp radiation with regard to both neon and argon. The more interesting levels are those converging to the $np^5\,^2P_{1/2}$ ionization limits and lie above the $np^5\,^2P_{3/2}$ limit, namely, embedded in the first ionizaton continuum. Such autoionizing resonances have been observed by others in Ar, Kr, and Xe.[15,16,32] However, due to the resolution of the measurement, the high density of autoionizing levels, the broad linewidth inherently associated with these resonances, and the small energy gap between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization limits in neon, no structure is seen. These resonances in Ne are not expected to blur the Cooper minimum at 251 nm or below the ionization limit, i.e., up to 256 nm where the autoionizing resonances occur. This spectral range (251—256 nm) is a relatively narrow energy gap on the order of only 800 cm^{-1}, and thus the autoionizing structure is smeared. Similar results are obtained via the optogalvanic effect in neon.[33]

While discharge response at wavelengths shorter than s-state threshold within the spectral scope of Fig. 3 is attributed to s-state photoionization because of the low electron energy, response at longer wavelengths is primarily attributed to p-state photoionization. No Cooper minimum within the spectral range of our experiments is attributed to p states.[3] Consequently, photoionization cross sections from p states are expected to decrease noticeably with wavelength decrease from their threshold (389-nm wavelength in Ne). Therefore, the peak in Ne response in Fig. 3(a) at around 294-nm wavelength does *not* correspond to any of the excited-state photoionization calculation models by themselves but does appear attributable to the Duzy-Hyman calculation when electron heating is considered. As shown above, a relative measure of actual average electron energy enhancement is the product $\sigma\epsilon_d$. Calculations of this figure of merit using the Duzy-Hyman calculations for σ are shown in Table II. For p states in Ne, this electron velocity enhancement is a maximum at 294 nm, thus possibly explaining this peak in Fig. 3(a) as a function not only of p-state photoionization cross section but also of discharge current carrier multiplication processes enhanced by photoionization assisted electron heating. It is interesting to note from Table II that for Ne, $\sigma\epsilon_d$ for p states is essentially the same at 277- and 320-nm wavelengths, being slightly higher at the shorter wavelength. This also corresponds well with the experimental results of Fig. 3(a). At wavelengths where s-state photoionization *can* take place, p states are *not* considered in Table II in view of the very low p-state population in our prebreakdown case.

It is worthwhile to consider whether the measured minimum at 253-nm wavelength for Ne discharge response is a result of a minimum in the value of σ, as proposed by Duzy and Hyman, or a result of the fact that ϵ_d is zero at threshold. A comparison of results from Ar, as shown in Fig. 3(b), suggests that the Ne signal minimum at threshold is due to a minimum in σ rather than the minimum in ϵ_d. The experimental system is sufficiently sensitive to measure the Ar signal at 294 nm although there is no internal amplification provided at threshold by photoionization-assisted electron heating. This indicates that even where ϵ_d is small and there effectively is little internal signal amplification by the discharge, nevertheless the experimental system could measure the pure unamplified photoionization signal as long as σ is essentially nonzero. Therefore, the fact that no signal whatsoever for the unseeded Ne tubes could be measured at 253 nm suggests that the reason is due to σ being minimum there.

The data in Fig. 3 indicate generally sharp decreases in signal as wavelengths increase beyond 294 nm. Such responsivity decrease extends beyond the uv spectrum. At visible wavelengths prebreakdown discharge signals can be detected only at much

TABLE II. Calculations for average electron cloud relative energy enhancement from photoionization process per unit excited state.

Filter wavelength (nm)	Photon energy (eV)	Ionization energy (eV) Ne	Ar	$1s_5$ excitation level (eV) Ne	Ar	Photoionization Ne	Threshold energy (eV) Ar	ϵ_d (eV) Ne	Ar	$\sigma^a\epsilon_d$ (10^{-19} cm^{2}eV) Ne	Ar
					(a) s states						
218	5.887	21.564	15.759	16.62	11.55	4.944	4.209	0.943	1.678	0.282	0.177
253	4.900*	21.564	15.759	16.62	11.55	4.944	4.209	0[b]	0.691	0[b]	0
277	4.476	21.564	15.759	16.62	11.55	4.944	4.209	0	0.267	0	0.053 4
294	4.217	21.564	15.759	16.62	11.55	4.944	4.209	0	0.008	0	0.003 04
Wavelength (nm)	Photon energy (eV)	Ionization energy (eV) Ne	Ar	$2p_{10}$ excitation level (eV) Ne	Ar	Photoionization Ne	Threshold energy (eV) Ar	ϵ_d (eV) Ne	Ar	$\sigma^a\epsilon_d$ (10^{-19} cm^{2}eV) Ne	Ar
					(b) p states						
253	4.900	21.564	15.759	18.38	14.50	3.184	1.259	1.716			
277	4.476	21.564	15.759	18.38	14.50	3.184	1.259	1.292		18.09	
294	4.217	21.564	15.759	18.38	14.50	3.184	1.259	1.033		20.66	
320	3.874	21.564	15.759	18.38	14.50	3.184	1.259	0.690	2.615	17.15	222
365	3.397	21.564	15.759	18.38	14.50	3.184	1.259	0.213	2.138	10.6	235
400	3.100	21.564	15.759	18.38	14.50	3.184	1.259	0	1.841	0	230

[a]Photoionization cross-section value taken from the Duzy-Hyman calculation.
[b]For 248 nm (within filter FWHM) photon energy is 4.999 eV, $\epsilon_d=0.055$ eV, and $\sigma\epsilon_d=0$.

higher received power levels (milliwatt order instead of nanowatt order) except at resonant wavelengths where the optogalvanic effect rather than photoionization gives rise to increased responsivity.[30,34] This overall signal decrease at longer wavelengths is attributed to the very low value of $\bar{\epsilon}$ which renders the probability of excitation to higher levels prohibitively small. The signal minima at wavelengths such as 365 nm and longer are not minima, since photoionization signals continue to decrease even further as wavelength increases. Thus, these low signal levels at longer wavelengths are not attributed to Cooper minima but to the very low value of mean electron energy which, even within the p-state groupings, favors population primarily at the lowest excitation levels. Thus, for prebreakdown discharges the low responsivity at *longer* wavelengths is due *not* to minima in σ or *even* ϵ_d but to *lack* of *population* at excitation *levels* sufficiently *high* for photoionization. It is worthwhile to point out that Cooper minima have not even been predicted to exist at these longer wavelengths for p- states by any of the theoretical calculations thus far. The fact that no signal whatsoever could be measured at the 253-nm wavelength using the discharge tubes which contain no additives, even though the 253-nm filter passes s-state threshold wavelengths for Ne gas atoms, is attributed not to coincidence but to the Cooper minima that have been indeed predicted to exist at such wavelengths.

The data in Fig. 3 decrease much more rapidly away from the peaks than do the predictions from Table II. The calculations of ϵ_d are based upon the assumption that only the lowest possible states are occupied. These thresholds only are considered. For higher excitation levels ϵ_d correspondingly increases. For p states in Ne, for example, photoionization thresholds extend from 389-nm wavelength for $2p_{10}$ levels to 479-nm wavelength for $2p_1$ levels. Thus, even though the low value of $\bar{\epsilon}$ favors population of the lowest levels, the relatively small population of higher levels can nevertheless still be expected to affect the average value of ϵ_d and in this way to introduce some distortions to the calculations of Table II. Table II should therefore be considered a qualitative and not quantitative measure of signal gain stemming from photoionization-assisted electron heating and refers to initial electron energy at the instant following photoionization, before electron energy is influenced by bias field and collisions.

Except for the lowest levels, Fig. 3(b) indicates very little p-state population for the Ar tubes, apart

from tube 8 which contains gas additives, radioactivity, and electrode coatings. However, comparison of Figs. 3(a) and 3(b) suggests that *s*-state photoionization-assisted electron energy enhancement does appear to slow down the rate of decrease of Ar discharge response from the *s*-state cross-section maximum at threshold (295 nm) to the Cooper minimum (Duzy and Hyman) around 253 nm.

Some information concerning the effects of electrode coating and the radioactive additive can be obtained from the data in Fig. 3. Comparison of spectral results for discharge tubes 3 and 4 for Ne suggest that the BaSr electrode coating acts to increase discharge response at longer wavelengths. This is supported by comparison of spectral results for discharge tubes 7 and 8 for Ar. It would appear from comparison of spectral results for tubes 2 and 4 and for tubes 8 and 10 that the radioactive additive ^{85}Kr generates a similar effect. The mechanism may well be common to both the additive and the electrode coating. Both are introduced into the tubes for the same purpose of generating larger currents and thus lowering the breakdown voltage. Their effectiveness in this regard cannot be seen from breakdown voltage data in Table I since the electrodes in each lamp are not necessarily parallel to the same degree. Nevertheless, on the basis of experiments with a large number of tubes, these techniques are well known to be successful.[35] This increase in bias current affects the excited-state populations. In particular, current increases are known to increase the nonmetastable states more than the metastables.[36–40] Consequently, one would expect in such "seeded" lamps more excitation to higher energy states, thus permitting more photoionization at longer wavelengths. It is interesting to note that in tubes with *no* additives or coating, *no response whatsoever at wavelengths of Cooper minima (Duzy-Hyman calculation) could be obtained.* This opens the possibility that in the lamps with coatings and/or ^{85}Kr, the very small response *measured* at about 253-nm wavelength results from *p* rather than from *s* states in accordance with expected excitation increase to higher levels. However, even with such seeding, response minima are in accordance with the Duzy-Hyman calculation for *s*-state Cooper minima, thus suggesting the excitation increase is small.

No change in spectral response appears attributable to the small quantities of krypton themselves, since for Kr *s* and *p* states σ is expected to decrease with decreasing wavelength, with the (Cooper) minimum lying at wavelengths below 200 nm.[3–8] Krypton thus should decrease response at 218 nm in Fig. 3. Since this does not appear to be the case, the effect of the ^{85}Kr additive therefore is primarily that of increased bias current rather than spectral effects of Kr itself.

The effect of increased bias can be seen in Fig. 3(b) for different resistor values. Decreasing the load resistor decreases the $(\Delta I)R_L$ signal *voltage* output. However, the photoionization *current* signal, as a result of increased free-electron density, is increased. The ΔI increase is by a factor of about 2 at longer wavelengths, and only a factor of about 1.3 at 218 nm, thus being compatible with known effect of increased current increasing nonmetastable more than metastable populations.[36–40] The 2% H_2 additive does not appear to alter Ar spectral response.

One final comment is in order concerning the sensitivity of such a technique as a uv radiation detector. The low noise properties of such Townsend discharges have been discussed above. Despite the 1 mm diameter, because the shape of the electrodes is cylindrical, effective path length has been measured to be about 0.3 mm.[31] Thus, path lengths of 1 cm should result in a response increase by a factor of about 30. Even so, for 6 nW of received power, responsivity R in Fig. 3(b) is 0.012 nA/nW at 294 nm (*s*-state photoionization threshold). This corresponds to an effective quantum efficiency-gain coefficient

$$\eta=\frac{\Delta I}{q}\frac{h\nu}{P_r}=R\frac{h\nu}{q} \tag{1}$$

of 5% at 294 nm. For only 1-cm path length, one would expect $R=0.36$ nA/nW or an effective quantum efficiency-gain coefficient of 150%.

At 218 nm only about 2.5-nW power is received by the discharge because of glass-envelope absorption. Here, $R=0.007$ nA/nW and $\eta\simeq 4\%$. For 1-cm path length, one would expect $R=0.21$ nA/nW[1] and $\eta\simeq 120\%$. Since both ϵ_d and photoionization cross section increase as wavelengths decrease further beyond 218 nm,[3] discharge sensitivity should be even higher at shorter wavelengths. These parameters indicate fairly high sensitivity as a detector, competitive with any detector at *such* wavelengths except a photomultiplier. Detection sensitivity can be improved further by optimum biasing, increased path length, and increased additives. For lower intensities, sensitivity can be improved further by increasing bias voltage even further until gas breakdown instabilities begin to set in. The very low noise of the prebreakdown discharge can make this technique particularly desirable.

IV. CONCLUSIONS

Our measurements, particularly with the unseeded lamps, show good agreement with theoretical calculations of the spectral dependence of excited-state

photoionization cross sections and the predicted Cooper minima. Spectral effects of photoionization-assisted electron heating via current carrier multiplication impact can shift discharge response maxima to wavelengths other than those where photoionization is most likely. However, current carrier signal multiplication should not affect the spectral location of the Cooper minima since, because of strong cancellation effects in the radial matrix element, photoionization probability at such wavelengths should effectively be zero. Hence, there is no photoionization signal to be amplified by discharge current carrier multiplication. Autoionization structure does not obscure Cooper minima because of their broad linewidth close to the ionization thresholds, particularly under the low spectral resolution conditions here.

Our experimental results appear to be very compatible with the Duzy-Hyman excited-state photoionization cross-section calculations with regard to not only Cooper minima but also overall discharge response maxima, including effects of photoionization-assisted electron heating.

Use of prebreakdown discharges as sensitive and inexpensive uv detectors appears to be of promising potential, particularly for seeded tubes. Judicious mixing of gases to provide selective excitation may make possible almost any desired detector spectral response.

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