Time dependence of the vacuum-ultraviolet emissions in krypton excited by 250-keV electrons

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(Received 27 June 1973)

Time-dependent studies of the vacuum-ultraviolet emissions in krypton were performed using 250-keV electrons. Measurements as a function of pressure were made at the wavelengths of the $^1P_1$ and $^3P_1$ resonance lines and the 1250- and 1425-Å continuum emissions. The data suggest that at early decay times the $^3P_1$ atomic state is responsible for the 1250-Å molecular radiation. From the time-dependent studies it is proposed that the $^1P_1$ state is converted to a highly excited molecule by two-body collisions. This molecule undergoes rapid vibrational relaxation resulting from two- and three-body collisions. The vibrationally relaxed molecule then radiates the 1425-Å continuum. At high pressures (about 1000 torr) the vibrationally relaxed molecule decays with a nearly pressure-independent lifetime of about 0.30 μsec.

I. INTRODUCTION

The vacuum-ultraviolet (vuv) radiation from rare-gas atoms and diatomic molecules has been the subject of many experimental and theoretical investigations. Extensive experimental work on time-unresolved spectra was done using either electrical or microwave excitation[1-4] and, more recently, high-energy charged particles.[5-7] The noble-gas spectra in the vuv region are characterized by fairly sharp peaks at the wavelengths of the atomic resonance lines and by continuous emissions from diatomic molecules at longer wavelengths. In the heavier rare gases a first continuum is observed immediately following the lowest resonance state, and a second continuum is found at longer wavelengths. At gas pressures of a few hundred torr the second continuum dominates the emission spectra. On the other hand, in neon only the short-wavelength continuum increases strongly in intensity as gas pressure is increased.[2,6,8]

The physical processes leading to the continuous emissions are not yet fully understood and are the subject of vigorous investigation. It has been shown by Mulliken[9] and Tanaka *et al.*[10] that homonuclear diatomic molecules have a large number of bound and repulsive excited Rydberg states. In particular, the ground state is repulsive aside from a small van der Waals attraction, whereas the lowest excited state is bound. Time-resolved spectroscopic measurements are beginning to provide new information about the atomic precursors of the molecular radiation.

In recent experimental work, pulsed beams of energetic charged particles have been used to measure the time and pressure dependence of the resonance radiation and continuous emission in argon,[11] helium,[12] and neon.[8] Emission studies which utilize monoenergetic charged particles are reproducible and can be carried out over wider pressure ranges than gas-discharge experiments. Time-resolved vuv spectroscopy has proved to be valuable in providing new information about energy transfer processes between excited atomic and molecular states. Lifetime data on these states make it possible to examine the depletion of resonance states as a function of pressure, the pressure dependence of the continuous emissions, and the kinetic rates associated with the relaxation processes that lead to molecular radiation. Thus, one obtains useful information for assigning atomic precursors to the continuous emissions. Additional experimental input is obtained from such studies as the pressure dependence of the Jesse effect.[13]

In this work we report time-dependent studies of the vuv emissions in krypton stimulated by 250-keV electrons. Time-resolved measurements of the 1165- and 1236-Å resonance lines and the 1250- and 1425-Å continuum emissions are presented. These data are used to suggest models for the molecular radiation in krypton.

There is considerable current interest in vuv emissions from noble gases because of the potential that these elements have for new, efficient laser mechanisms.[14-17] Results such as reported here on the formation and decay of excited diatomic molecules are of value in determining optimum design parameters for high-power vuv lasers.[18]

II. EXPERIMENTAL METHOD

The experimental arrangement was similar to that used in the neon[8] and argon[11] work. A pulsed

beam of 250-keV electrons entered a cylindrical stainless-steel emission chamber through a 0.000025-in.-thick nickel foil and interacted with the krypton gas while traveling along the axis of the chamber. The electrons then left the chamber through a second nickel foil 0.0001 in. thick and were collected in a Faraday cup. Electron pulse widths[19] were adjustable from 50 nsec to 12 μsec. The repetition rate was continuously variable from 2 to 20 kHz. Maximum current was about 40 μA.

Photons emitted by the krypton gas were transmitted by a LiF window mounted perpendicular to the electron beam axis. Photons were dispersed using a scanning vuv monochromator and were detected with a channel electron multiplier. The intensity of the vuv radiation as a function of pressure was observed by scanning the monochromator through the wavelengths of interest. Time-dependent measurements at the wavelengths of the resonance lines and continuum emissions were performed by utilizing a time-of-flight technique. Further details on the apparatus can be found in Ref. 11.

Reagent-grade krypton gas with an assayed purity of 99.995% was used. Gas purity was maintained by using stainless-steel gas lines and valves, and an ultrahigh-purity pressure reducer. Gas pressure in the emission chamber was measured with a capacitance manometer. Before taking data the emission chamber and gas lines were evacuated to less than 10^{-6} torr for at least 48 hours. Krypton gas was flowed through the emission chamber at a rate of about 15 mliter/min when making measurements. No impurity emissions were observed. Gas pressure in the emission chamber ranged from 5 to 1000 torr, whereas the pressure in the monochromator always remained below 10^{-6} torr.

III. RESULTS

Typical vuv spectra of krypton as a function of of wavelength and pressure are displayed in Figs. 1 and 2. The low-pressure spectra are dominated by two fairly sharp resonance lines at 1165 and 1236 Å corresponding to the $^1P_1$ and $^3P_1$ atomic

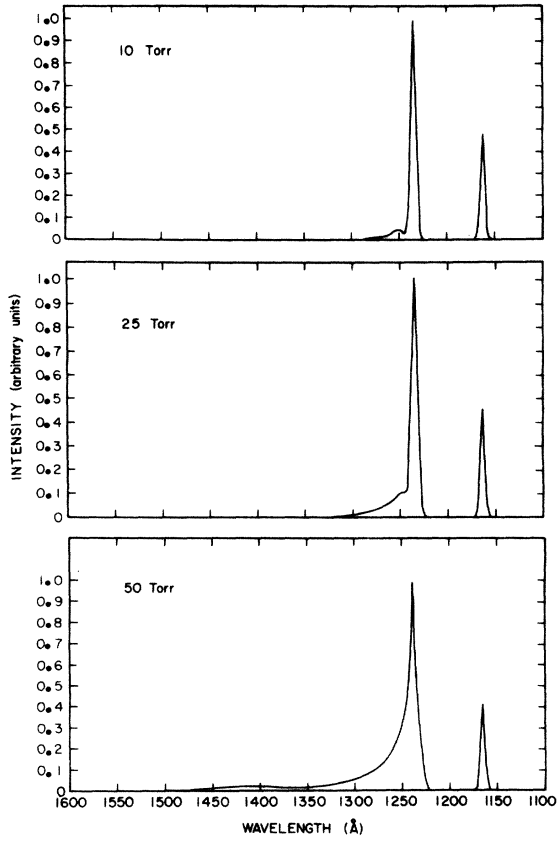

FIG. 1. Typical vuv spectra of krypton at low gas pressures.

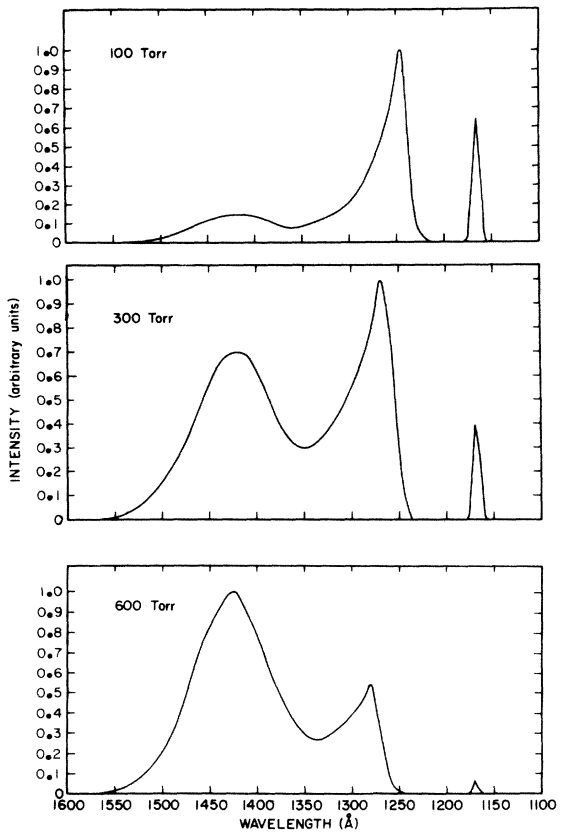

FIG. 2. Typical vuv spectra of krypton at high gas pressures.

states, respectively. The $^1P_1$ resonance line appears weaker because the transmittance of the LiF window decreases rapidly at the shorter wavelengths. At low pressures it was possible to spectrally resolve the first continuum at 1250 Å from the 1236-Å resonance line. The second continuum at 1425 Å was not observed for pressures below 50 torr.

As gas pressure is increased the first continuum rapidly increases in intensity. It is also considerably broadened and shifted toward the red. The total shift is about 45 Å in the pressure range 10–900 torr. A shift of 25 Å for pressures from 50–400 torr was previously observed in proton-induced spectra.[6] The high-pressure spectra clearly show a gradual growth of the second continuum and a decrease in intensity of the $^1P_1$ resonance line. At the highest pressure the second continuum dominates the spectrum.

Representative time-resolved spectra of the resonance lines and continuum emissions are shown in Figs. 3–6. The decay of the resonance lines and the first continuum is characteristic of the sum of two exponential terms. Tables I–III summarize the decay constants and coefficients obtained from computer fitting these data to an expression of the form

$$I(t)=\sum a_n e^{-u_n t}, \tag{1}$$

where the index n in each case refers to the two components of the particular time-dependent spectrum. Also tabulated are the wavelengths at which data were taken and the excitation pulse widths used. Time-dependent measurements of the $^3P_1$ resonance line were made over a limited pressure range (5–150 torr) because of intensity limitations.

Values of the rate coefficients for the fast-decay components (u_1, u_3, u_5) are quite reproducible, and it is estimated that the error in them is not more than 5%. The values of the slow-decay components are less reliable and are useful only in discussing general trends with pressure and spectral region. The origin of the slow decays is not completely understood. It has been suggested that these may arise from the recombination of ions.[20]

The time dependence of the 1425-Å continuum displays a feature that was also observed in neon[8]

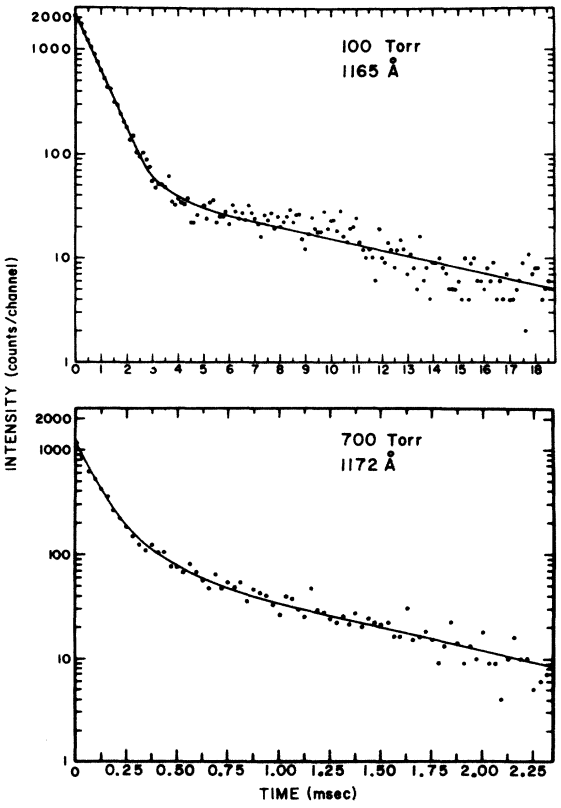

FIG. 3. Time-resolved spectra of the 1165-Å resonance line. The solid line represents a computed two-term exponential fit (see Table I).

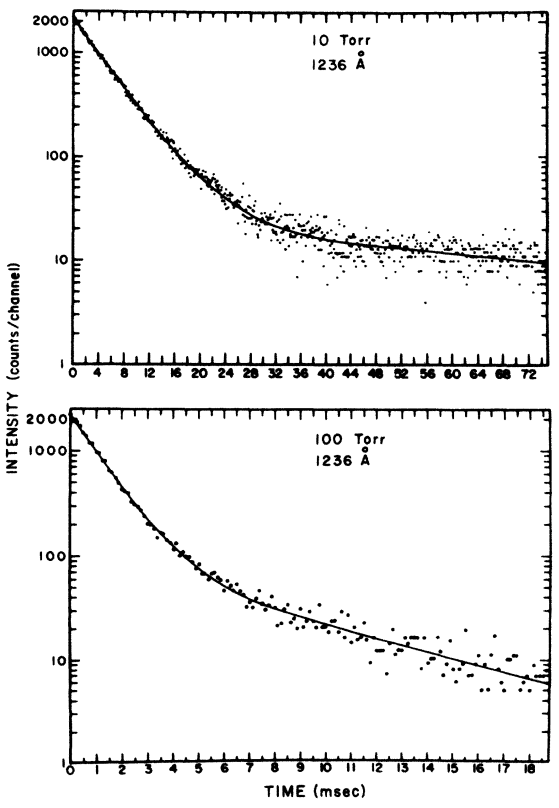

FIG. 4. Time-resolved spectra of the 1236-Å resonance line. The solid line represents a computed two-term exponential fit (see Table II).

and argon.[11] The intensity of the radiation continues to increase after termination of the excitation pulse. However, this increase takes place much more rapidly in krypton than in the lighter noble gases. Maximum intensity was reached approximately 0.9 μsec at 50 torr and 0.2 μsec at 300 torr after the beam pulse was terminated. Because of limitations in the time resolution of our apparatus we could not make reliable observations of the time delay in peak intensity for pressures above 300 torr. However, the decay was easily measured to 1000 torr. We note here that the measurements of Koehler *et al.*[17] show that in high-pressure xenon gas maximum intensity is obtained within nanoseconds. Table IV summarizes the decay constants and coefficients for the 1425-Å continuum obtained from fitting the data to the equation

$$I_4(t) = a_7 e^{-u_7 t} + a_8 e^{-u_8 t} + a_9 e^{-u_9 t} . \quad (2)$$

Excitation pulse widths and wavelengths are also tabulated. In this case the buildup and early decay are described by the difference of two exponentials. The late decay is given by the third term in Eq. (2). As before, absolute values of the late decays are not very reliable.

IV. INTERPRETATION OF THE RESULTS

In this section models are proposed to account for the time and pressure dependence of the vuv emissions in krypton. The construction of these models is facilitated by previous results obtained from gas-discharge and charged-particle excitations of the noble gases.

The time dependence of the resonance radiation may be interpreted in terms of Holstein's[21,22] theory of resonance-photon trapping and collision processes involving ground-state and excited atoms. The decay of trapped resonance photons is described by an exponential expression of the form

$$I(t) = N_0 e^{-\beta t} , \quad (3)$$

where β is Holstein's[22] pressure-independent decay constant given by

$$\beta = (0.2069/\tau)(\lambda/R)^{1/2} . \quad (4)$$

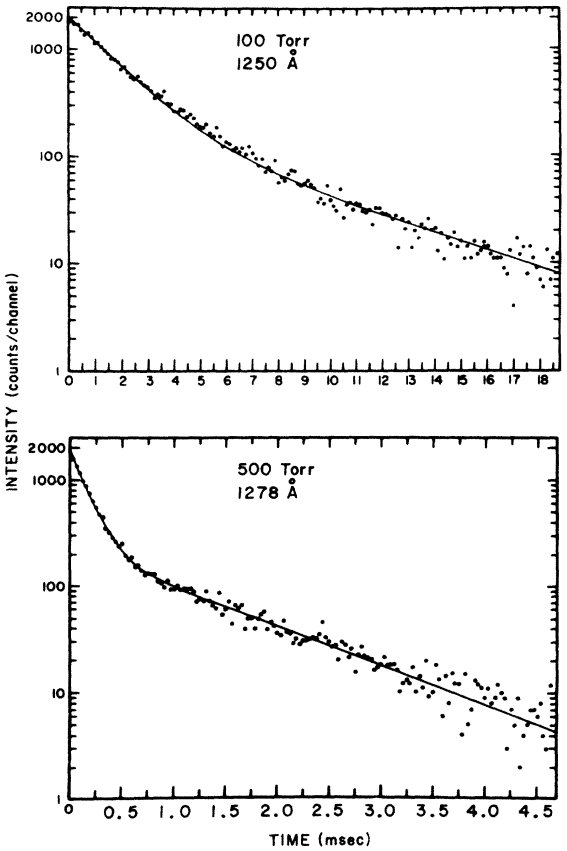

FIG. 5. Time-resolved spectra of the 1250-Å continuum. The solid line represents a computed two-term exponential fit (see Table III).

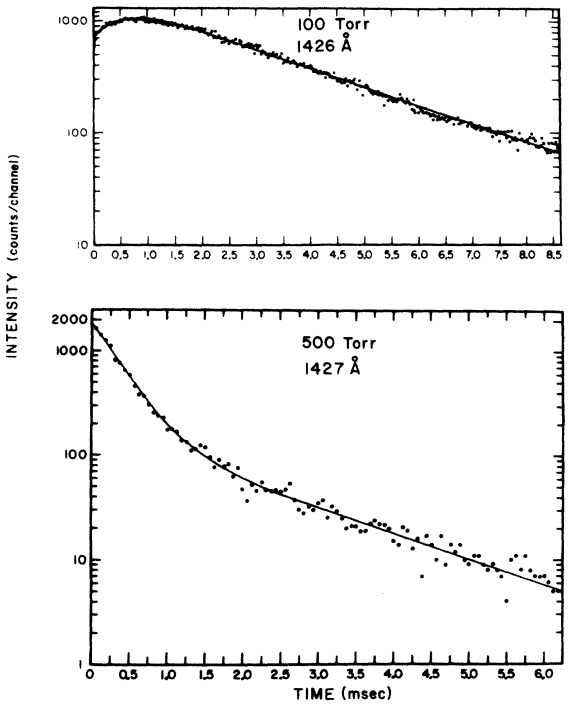

FIG. 6. Time-resolved spectra of the 1425-Å continuum. The solid line was obtained from fitting the data to Eq. (2). The rapid buildup in intensity was observed for pressures up to 300 torr. At higher pressures the time resolution of the apparatus was insufficient to reliably measure the initial buildup.

TABLE I. Calculated decay parameters for the $^1P_1$ time dependence. Data were fitted to the equation $I_1(t) = a_1 e^{-u_1 t} + a_2 e^{-u_2 t}$.

Pressure (torr)	λ (Å)	Pulse width (μsec)	a_1	a_2	u_1 (10^6 sec^{-1})	u_2 (10^6 sec^{-1})
5	1165	2.0	1023	26	0.242	0.0120
10	1165	1.0	1984	30	0.331	0.0297
20	1165	1.0	2017	32	0.496	0.0428
40	1165	1.0	1948	45	0.758	0.0773
60	1165	1.0	1955	57	1.01	0.0814
80	1165	1.0	1905	47	1.22	0.0857
100	1160	1.0	1012	29	1.43	0.0967
100	1165	0.5	2201	39	1.44	0.0969
100	1170	1.0	1016	28	1.43	0.0976
200	1167	1.0	1884	56	2.71	0.264
300	1168	0.3	864	22	4.20	0.394
400	1169	0.5	1934	84	5.59	0.572
500	1170	0.5	994	24	6.98	0.687
600	1170	0.5	1202	48	8.04	0.786
700	1172	0.5	1068	81	9.51	0.977

The quantity τ is the natural lifetime of the resonance state, λ is the corresponding wavelength, and R is the radius (equal to 2.22 cm) of the cylindrical emission chamber. Wilkinson[23] has measured the lifetimes of the $^1P_1$ and $^3P_1$ states to be 4.55 and 4.38 nsec, respectively. Using these values one obtains

$$\beta_1 = 0.105 \times 10^6 \text{ sec}^{-1} \quad (5)$$

for the $^1P_1$ state and

$$\beta_2 = 0.112 \times 10^6 \text{ sec}^{-1} \quad (6)$$

for the $^3P_1$ state. Knowledge of the pressure-independent decay constants is of significance in the following analysis.

A. 1250 - Å Continuum

The first continuum of the heavier rare gases begins near the $^3P_1$ resonance line and extends to longer wavelengths. Theoretical considerations[9,18,24] show that atoms in the $^3P_1$ and $^3P_2$ levels may be the atomic precursors of this continuum. Specifically, it has been suggested that the $^3P_1$ and $^3P_2$ states can form the $^1\Sigma_u$ and $^3\Sigma_u$ molecular states, respectively. This molecule formation can occur through collisions with ground-state atoms. The first continuum has been attributed to transitions from high vibrational levels of these molecules to the repulsive ground state. Experimental evidence[8,11,13] indicates that for the lighter rare gases these considerations may need modification, but it is generally conceded that the $^3P_1$ state is connected with the first continuum.

TABLE II. Calculated decay parameters for the $^3P_1$ time dependence. Data were fitted to the equation $I_2(t) = a_3 t^{-u_3 t} + a_4 e^{-u_4 t}$.

Pressure (torr)	λ (Å)	Pulse width (μsec)	a_3	a_4	u_3 (10^6 sec^{-1})	u_4 (10^6 sec^{-1})
5	1236	2.0	901	27	0.173	0.0107
10	1236	2.0	2105	67	0.202	0.0143
20	1236	1.0	2018	65	0.259	0.0168
40	1236	1.0	1869	53	0.362	0.326
60	1236	1.0	1997	57	0.508	0.0564
80	1236	1.0	2023	64	0.646	0.0968
100	1236	1.0	2182	69	0.831	0.119
125	1236	0.4	1574	42	1.12	0.208
150	1236	0.4	1435	47	1.52	0.277

The time-dependent measurements presented in Sec. III suggest that at early decay times the $^3P_1$ level gives rise to radiation in the 1250-Å region. This can be seen from an analysis of the time and pressure dependence of the $^3P_1$ and 1250-Å decay constants. The pressure-dependent part of the $^3P_1$ decay rate was determined by subtracting the constant β_2 from the fast-decay component u_3 given in Table II. Values of u_3-β_2 were then compared with the decay constant u_5 of the molecular radiation (see Table III). Over the pressure range for which comparison was possible, the quantities u_5 and $u_3 - \beta_2$ were the same within experimental error. In Fig. 7 we have plotted these decay rates vs pressure. The solid line was obtained from fitting the data to the equation

$$u = c_1 P + c_2 P^2, \quad (7)$$

where P is the pressure in torr. With $c_1 = 7.97 \times 10^3$ sec^{-1}/torr and $c_2 = 8.45$ sec^{-1}/(torr)^2 the above equation agrees with the data quite well. This analysis suggests that atoms in the $^3P_1$ state are depleted by the escape of resonance radiation to the walls of the emission chamber and by two- and three-body collisions with ground-state atoms. The fact that the pressure-dependent part of the $^3P_1$ decay constant and the decay rate of the con-

TABLE III. Calculated decay parameters for the 1250-Å continuum. Data were fitted to the equation $I_3(t) = a_5 e^{-u_5 t} + a_6 e^{-u_6 t}$.

Pressure (torr)	λ (Å)	Pulse width (μsec)	a_5	a_6	u_5 (10^6 sec^{-1})	u_6 (10^6 sec^{-1})
25	1250	1.5	862	48	0.156	0.00912
40	1250	0.5	1494	86	0.251	0.0425
60	1250	0.5	1472	84	0.399	0.0831
80	1250	0.5	1406	83	0.556	0.126
80	1250	1.0	1511	95	0.556	0.125
100	1250	1.0	1645	109	0.715	0.143
200	1260	1.0	1767	113	1.86	0.261
300	1270	1.0	1970	145	3.26	0.428
400	1274	1.0	1725	135	4.47	0.516
500	1278	1.0	1739	175	6.09	0.727
600	1285	1.0	1154	105	7.90	0.923
700	1290	1.0	1799	165	9.89	1.16
700	1290	0.2	1824	170	9.92	1.14
800	1292	0.2	1405	105	11.8	1.19
900	1294	0.2	1939	109	13.9	1.37

tinuum emission are nearly equal implies that $^3P_1$ atoms are converted by collisions to molecules which radiate the 1250-Å continuum. The decay of the molecular radiation at early times is thus governed by the rate of collisional conversion of the $^3P_1$ state.

We point out that the gas-discharge work of Turner[25] shows that $^3P_2$ atoms may also give rise to molecular radiation in the wavelength region of the first continuum. This gas-discharge study was carried out using long (60 μsec) excitation pulses at low gas pressures (up to 25 torr). The decay rates reported by Turner differ from those presented in this work. The reason for this may be that the gas-discharge measurements were made at relatively late times in the afterglow, whereas our data refer to the very early decay times. We return to this point in Sec. V. In summary, experimental evidence suggests that in krypton both the $^3P_1$ and $^3P_2$ atomic states may be responsible for the 1250-Å continuum.

B. 1425-Å Continuum

As discussed above, experiment and theory appear to be in agreement that in krypton the $^3P_1$ and $^3P_2$ states are the atomic precursors of the first continuum. This leaves open the possibility that the $^1P_1$ level may be responsible for the second (1425-Å) continuum. Additional arguments may be based on theory and on the results presented in Sec. III. The ratio of oscillator strengths of the $^1P_1$ to $^3P_1$ states is nearly equal to unity.[26] High-energy electrons would therefore be expected to richly populate both states so that the $^1P_1$ state should lead to emission in some form. The time-unresolved spectra (see Fig. 2) show that the $^1P_1$ resonance line decreases strongly in intensity at the higher pressures. This is accompanied by an increase in intensity of the second continuum at these same pressures. Thus, there is a qualitative correlation between the relative intensity of these emissions.

A significant feature is the time delay in the peak intensity of the second continuum. At 50 torr it amounted to about 0.9 μsec. Time delays were also observed in neon[8] and argon.[11] However, in the lighter gases the delays were much longer. For example, at 50 torr the time lag in neon was about 30 μsec and in argon it was about 10 μsec. This and other evidence led to the conclusion that an intermediate metastable molecule was involved in the emission mechanism for the continuum radiation. The metastable molecule was then converted to a radiative one by collisions with ground-state atoms. This radiative molecule gave rise to the continuum emission.

In view of the fast buildup of the intensity in krypton we do not believe that a metastable molecule is involved in this case. A possible mechanism is that energy may be transferred from the $^1P_1$ level through collisional processes to upper levels of the krypton molecule. There are several molecular states which have been mentioned as candidates for such an energy-transfer process.[9,18] This newly formed molecule may undergo many collisions which relax it to low vibrational levels of the lowest bound state. The radiation in the 1425-Å region would then correspond to transitions from these vibrationally relaxed levels to the repulsive ground state. Such a mechanism was suggested by Mulliken[9] who predicted that there are no metastable states in the heavier rare-gas molecules. A lucid presentation of this process for argon is given in Ref. 18.

We now attempt to make the above discussion more quantitative. If collisions are proposed to transfer energy out of the $^1P_1$ state, this should be reflected in the pressure dependence of the

TABLE IV. Calculated decay parameters for the 1425-Å continuum. Data were fitted to the equation $I_4(t) = a_7 e^{-u_7 t} + a_8 e^{-u_8 t} + a_9 e^{-u_9 t}$.

Pressure (torr)	λ (Å)	Pulse width (μsec)	a_7	a_8	a_9	u_7 (10^6 sec^{-1})	u_8 (10^6 sec^{-1})	u_9 (10^6 sec^{-1})
50	1425	0.6	−520	1278	•••	1.52	0.157	•••
100	1426	0.3	−1291	1841	13	1.80	0.398	0.001 03
200	1426	0.3	−2975	3981	24	3.17	0.927	0.004 34
300	1426	0.3	−3004	4219	24	6.14	1.39	0.0369
400	1427	1.0	•••	1962	68	•••	1.82	0.309
500	1427	1.0	•••	1776	73	•••	2.32	0.379
600	1430	1.0	•••	1545	65	•••	2.75	0.571
700	1430	0.1	•••	1732	112	•••	3.09	0.805
700	1460	0.1	•••	1797	115	•••	3.10	0.813
800	1430	0.1	•••	1883	135	•••	3.24	1.03
900	1430	0.1	•••	1912	136	•••	3.38	1.28
1000	1430	0.1	•••	1768	148	•••	3.39	1.34

fast-decay component u_1 (see Table I) of the $^1P_1$ resonance line. In Fig. 8 we have plotted u_1 vs pressure from 5–700 torr. The solid line was obtained from fitting the data to the equation

$$u' = \beta_1 + bP, \tag{8}$$

where β_1 is given by Eq. (5). With $b = 1.33 \times 10^4$ $\text{sec}^{-1}/\text{torr}$ the above equation gives good agreement with experiment over the entire pressure range. This shows that the $^1P_1$ resonance state is depleted by the escape of resonance radiation and by two-body collisions with ground-state atoms.

An examination of the fast-decay component u_8 (see Table IV) of the 1425-Å continuum reveals that the decay rate becomes nearly pressure independent at 1000 torr. This may be interpreted to mean that the second continuum arises from an allowed transition in the krypton molecule. The 1000-torr value of u_8 corresponds to a molecular lifetime of about 0.30 μsec. This is considerably shorter than the corresponding values for neon[8] and argon[11] molecules of 5.1 and 2.8 μsec, respectively.

A model for the emission mechanism of the 1425-Å continuum based on the above discussion is shown in Fig. 9. The two-body destruction rate of $^1P_1$ atoms is given by the term bP of Eq. (8). The intermediate upper-level molecular state is denoted by Kr_2**. This intermediate state is rapidly relaxed by two- and three-body collisions with ground-state atoms. Numerical values of the relaxation rate were obtained as described below. Radiation by upper-state molecules resulting from transitions to the lowest bound state occurs at much longer wavelengths[9,18,27] than we would observe. However, the vibrationally relaxed molecule, denoted by Kr_2*, emits photons in the 1425-Å region. The decay rate of the Kr_2* state by spontaneous emission is estimated from the 1000-torr value of u_8.

To arrive at rate equations for the energy transfer and relaxation processes, the following quantities are defined: $N_1(t)$ is the number of krypton atoms in the $^1P_1$ state, $M_1(t)$ is the number of molecules in the upper-level Kr_2** state, and $M_2(t)$ is the number of molecules in the vibrationally relaxed Kr_2* state. Further, let k_1 be the relaxation rate of Kr_2** molecules by collisions and by radiation and let k_2 be the decay rate of Kr_2* molecules by spontaneous emission. One then has the following equations:

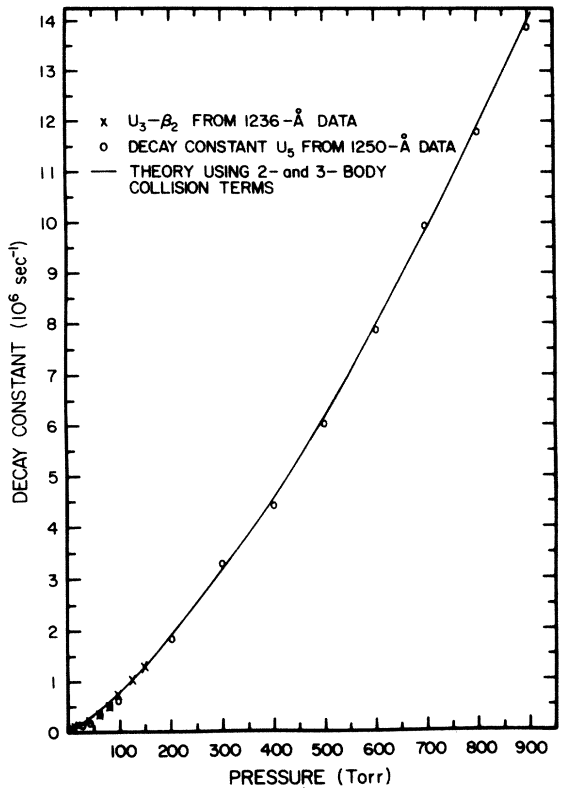

FIG. 7. Pressure-dependent part of the $^3P_1$ decay constant, u_3-β_2, and the decay constant u_5 of the 1250-Å continuum vs pressure. The solid line represents the equation $u = (7.98 \times 10^3)P + 8.45P^2$.

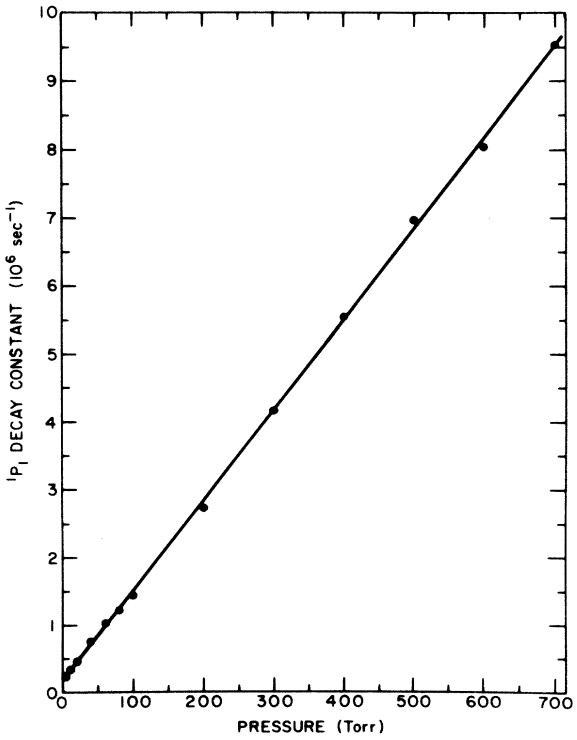

FIG. 8. Pressure dependence of the $^1P_1$ decay constant. The solid line was obtained from fitting the data to Eq. (8).

$$\frac{dN_1(t)}{dt} = -u' N_1(t), \tag{9}$$

$$\frac{dM_1(t)}{dt} = bPN_1(t) - k_1 M_1(t), \tag{10}$$

$$\frac{dM_2(t)}{dt} = k_1 M_1(t) - k_2 M_2(t). \tag{11}$$

In Eq. (10) we have included the decay of Kr_2^{**} molecules by radiation and by collisions in one rate constant k_1. We know of no simple way of estimating the radiation term, and there appear to be no measurements of the decay rate of these molecules by spontaneous emission. It would be useful to have more spectroscopic information on upper-state transitions. However, one can make the following observations: At high pressures collisions provide the dominant relaxation mechanism and upper-state decay by radiation is probably negligible. The rapid buildup in intensity of the 1425-Å radiation (see Fig. 6) indicates that even at relatively low pressures upper-state molecules may relax predominantly by collisions. As more experimental evidence becomes available the model will have to be refined, but we believe that the basic framework is correct.

From Eqs. (9)–(11) one finds

$$M_2(t) = \frac{k_1 bPN_0}{k_1 - u'}\left[\frac{e^{-u't}}{k_2 - u'} - \frac{e^{-k_1 t}}{k_2 - k_1} + \frac{(u' - k_1)\, e^{-k_2 t}}{(k_2 - u')(k_2 - k_1)}\right]. \tag{12}$$

The time evolution of Eq. (12) is determined by the quantity in square brackets, which contains the relaxation rate k_1 as an unknown. This rate was determined from normalizing to the 1425-Å data at 50, 100, 200, and 300 torr. Good agreement with the initial rise and decay of the continuum radiation was obtained for values of k_1 given by

$$k_1 = (2.05\times 10^3 P + 21.6P^2). \tag{13}$$

The slow exponential "tail" of the data is not included in the model or the equations. This fairly-low-intensity component whose origin is not understood was relegated to the status of "background." Calculations were carried out for pressures up to 1000 torr using the above value of k_1. At the higher pressures the computed decay agreed well with the observed one. Thus, it appears that the model shown in Fig. 9 can adequately account for the time evolution of the 1425-Å continuum.

V. SUMMARY AND DISCUSSION

Based on the analyses of experimental data in the preceding sections it was suggested that the $^3P_1$ state of krypton undergoes collisions with ground-state atoms and gives rise to emission in the 1250-Å region. Because of intensity restrictions, data on the 1236-Å resonance line were taken over a limited pressure range (5–150 torr). These data indicate that at early decay times $^3P_1$ atoms are depleted by the escape of resonance radiation and by two- and three-body collisions. Within experimental error, the pressure-dependent decay of the $^3P_1$ level was found to be equal to the fast-decay constant of the 1250-Å radiation. This implies that under the experimental conditions that prevailed in this work the decay of the first continuum at early times is determined by the collisional destruction of the $^3P_1$ state.

The gas-discharge work of Turner[25] has shown that at relatively late times in the afterglow the $^3P_2$ state can be connected to the 1250-Å continuum. Turner's study was performed using long excitation pulses for gas pressures up to 25 torr. The decay rates that he has reported differ from those measured in this work. In particular, his model does not include a three-body destruction process for the $^3P_1$ state. This can be understood qualitatively from the work of Thonnard and Hurst,[11] who observed that short excitation pulses were needed to measure the early decays reliably. We point out that analogous findings have been

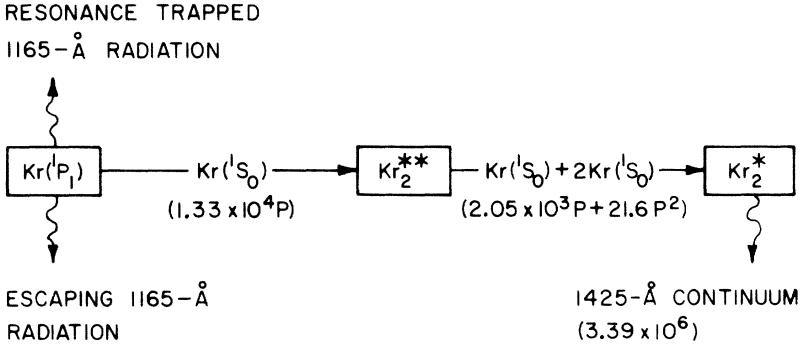

FIG. 9. Model for the 1425-Å continuum emission. The $^1P_1$ state is converted to an upper level molecule which is relaxed by two- and three-body collision. The relaxed molecule gives rise to the 1425-Å continuum. The numbers in parentheses are in units of inverse seconds, obtained as explained in text.

reported for neon. The gas-discharge data of Phelps[28] were analyzed late in the afterglow and revealed a final decay frequency of the neon $^3P_1$ state consistent with two-body collisions. These data also indicated that early in the afterglow $^3P_1$ atoms are depleted much more rapidly than late in the afterglow. A subsequent charged-particle study[8] has established that at early times the $^3P_1$ level is destroyed by three-body collisions and by the escape of resonance radiation.

On the other hand, gas-discharge experiments are well suited for measurements of the decay of metastable atoms. As mentioned above, Turner's data have shown that the $^3P_2$ state of krypton gives rise to molecular radiation in the wavelength region of the first continuum. The fact that the pressure dependence of the 1250-Å decay determined by Turner is different from that reported in this work may mean that different molecular states are involved, as discussed in Sec. IV A. Figure 7 shows that the decay rate of the 1250-Å continuum continues to increase at high pressures. This is a further indication that the $^3P_1$ atomic state may connect to the $^1\Sigma_u$ molecular state. The $^1\Sigma_u$ level represents an allowed transition at all internuclear distances. It will have a transition probability of the same order as that of the atomic level. Therefore, its lifetime is expected to be in the nanosecond range. A pressure-independent decay would be observed at much higher pressures than were used in this work.

Based on these ideas we have proposed that the $^1P_1$ atomic state of krypton is the precursor of the 1425-Å continuum. This model includes an intermediate upper-level molecular state which is rapidly relaxed by collisions. The relaxed molecule then radiates the 1425-Å continuum with a lifetime of about 0.30 μsec.

ACKNOWLEDGMENTS

The authors are very grateful to R. E. Knight for many informative discussions and for reading the manuscript. Numerical calculations were carried out with facilities of the University of Kentucky Computing Center.

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