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Spectroscopic Study of the Early Afterglow in Helium: Visible Bands and Hopfield Continuum*

DON VILLAREJO,† RONALD R. HERM,‡ AND MARK G. INGHRAM
Department of Physics, The University of Chicago, Chicago, Illinois 60637
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Measurements of the time-resolved early afterglow of the helium spectrum show that the Hopfield continuum and the visible bands occur primarily as an afterglow following pulsed excitation. Following a relatively rapid build-up, the slower afterglow decay of both the Hopfield continuum and the molecular transition $3p\pi$, $E^1\Pi_g \rightarrow 2s$, $A^1\Sigma_u^+$ is an exponential function of time, for approximately 50 μsec. Within the range of experimental variables, the decay rate is found to depend on the He pressure, but not on other discharge conditions. The kinetic constant associated with the exponential decay increases linearly with the He pressure, indicative of a two-body process. Separate studies of two regions of the Hopfield continuum, near 825 Å and 680 Å show that, for fixed pressure, the kinetic constant associated with 825 Å is the same as that observed for the transition E–A within experimental error. The kinetic constant at 680 Å is slightly smaller. The rate of change of the kinetic constant with pressure is the same in all three cases. The two-body rate constant obtained is $38\pm2\times10^{-15}$ cm^3/atom·sec. Both the magnitude and form of the pressure dependence of the observed rate constant indicate that the three-body process $He^+ + 2He \rightarrow He_2^+ + He$ is not the dominant process of He_2^+ production in the early afterglow. The data are consistent with the rapid production of He_2^+ in a two-body collision of an excited and a ground-state atom. Residual-impurity quenching by H_2, Ne and N_2 did not affect the afterglow decay. Values of quenching rates for all three gases are reported. Possible interpretations of the observed afterglow kinetics are discussed.

INDEX HEADINGS: Spectra; Molecular spectra; Helium.

THE afterglow emission excited in gaseous helium discharges has been extensively studied.[1] The kinetics of the afterglow atomic emission at low pressures appears to be governed by a collisional radiative-recombination mechanism.[2,3] In general, observations of the molecular emission have referred to the late afterglow, i.e., $>100\,\mu$sec after termination of the excitation pulse. They indicate that the molecular emission is governed by recombination of electrons with He_2^+.[4–7] Only a few studies of the early molecular visible afterglow have been reported.[8–13] The Hopfield continuum[14] near 825 Å also appears as an early afterglow emission.[15]

This paper reports the observation of the time dependence of molecular emission produced in the early afterglow of a pulsed helium discharge. Observations are reported for the Hopfield continuum and for several molecular transitions as functions of helium pressure and excitation conditions.

EXPERIMENTAL

Apparatus

The vacuum ultraviolet and visible measurements were recorded simultaneously by means of two monochromators. The source was mounted on the 1 m Seya-Namioka vacuum-ultraviolet monochromator described previously.[16] In this case the monochromator was equipped with a fast two-stage differential pumping assembly. A 600-line/mm Bausch & Lomb grating, blazed for 1200 Å as used in the Seya–Namioka mounting, coated with MgF_2, provided a first-order reciprocal dispersion of ~32 Å/mm. For the present study, a 250-μ entrance slit and a 1000-μ exit slit were used; symmetrical 250-μ slits provide a 5-Å band-pass full width at half maximum. A sodium-salicylate-coated photomultiplier served as detector. The pressure in the monochromator and the detection chamber was maintained below 10^{-6} torr. A Spex Industries Inc. 1.5-m Czerny–Turner spectrometer[17] was employed to observe the visible emission. A 1200-line/mm Bausch & Lomb grating blazed for 7500 Å provided a first-order reciprocal dispersion of ~10 Å/mm. The adjustable entrance and exit slits were varied in accordance with

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‡ National Academy of Science—National Research Council Postdoctoral Research Fellow supported by the Air Force Office of Scientific Research.
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[15] R. E. Huffman, J. C. Larrabee, Y. Tanaka, and D. Chambers, J. Opt. Soc. Am. 55, 101 (1965).
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[17] Model 1700-II Czerny–Turner Spectrometer, Spex Industrie Inc., Metuchen, New Jersey, 08841.

the requirements of a specific measurement. A photomultiplier with S-11 response served as detector. This instrument was also used as a spectrograph to photograph the visible spectrum. The time-resolved emissions from the pulsed source were observed by displaying the photomultiplier outputs on the screen of two oscilloscopes.[18]

The source was a water-jacketed quartz discharge tube (15 mm i.d., 25 cm long) as shown in Fig. 1. The vacuum monochromator viewed the discharge along the discharge-tube axis while the observations in the visible region were made at right angles to that axis. The experimental arrangement is shown in Fig. 2.

Helium was excited using a pulsed high-voltage power supply, see Figs. 2 and 3, which permitted independent variation of the pulse width, pulse-repetition frequency, and pulse power. For the measurements reported, a range of pulse durations between 0.1 and 1.0 μsec was employed. The pulse-repetition frequency was varied from 10 cps to 60 kc/sec. From voltage- and current-pulse shapes observed on an oscilloscope, it is estimated that peak pulse power was as high as 200 kW. "Ringing" of the current pulse was observed: with a 0.15-μsec (fwhm) voltage pulse, the current often did not attain zero until 0.7 μsec after onset. The pulsed high-voltage power supply was triggered from a Hewlett–Packard pulse generator[19] whose pulse output was delayed 0.1 μsec. The oscilloscopes used in conjunction with both monochromators were triggered from the pulse-generator trigger output. Thus, a typical oscilloscope trace

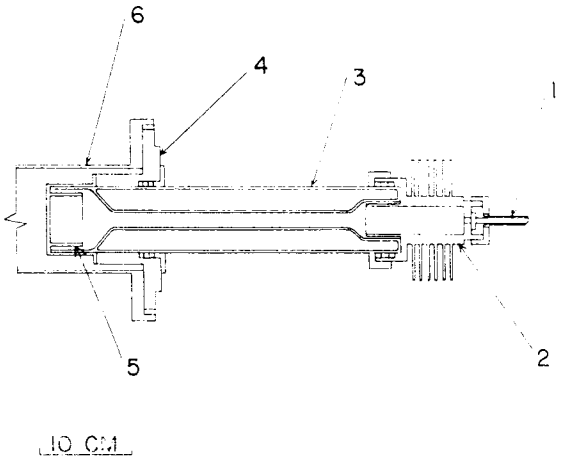

FIG. 1. Cross-sectional view of the quartz discharge tube: (1) gas inlet tubing; (2) air-cooled cathode, 2 S grade aluminum; (3) water-jacketed discharge tube, quartz; (4) water-cooled flange; (5) anode, 2 S grade aluminum; (6) monochromator and differential pumping system. The water taps in parts (3) and (4) are not shown.

[18] Tektronix 541A Oscilloscopes equipped with Type L fast-rise-time preamplifiers were used. The oscilloscope sweep was checked and found to be accurate within the manufacturer's specifications.

[19] Model 214A Pulse Generator, Hewlett–Packard Co., Palo Alto, California.

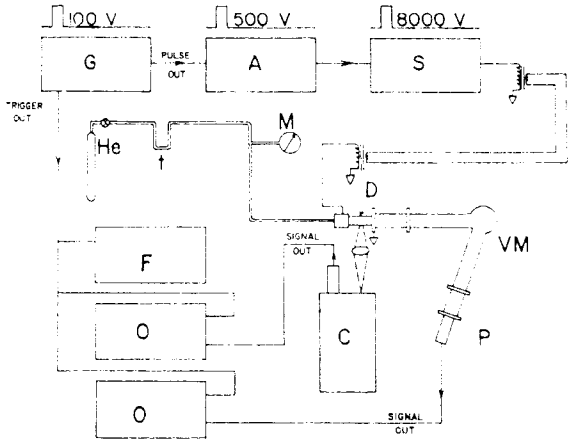

FIG. 2. Schematic diagram of apparatus. The diagram does not indicate that it was also possible to measure the time-averaged intensity from the photomultiplier of either monochromator while simultaneously observing the time dependence of both monochromator outputs. Legend: (G) pulse generator, 200-W peak power; (A) pulse amplifier, 2000-W peak power; (S) dc supply and trigger, 200 000-W peak power; (T) charcoal trap at 77°K; (M) manometer; (D) discharge tube; (VM) vacuum monochromator; (F) frequency counter; (O) oscilloscopes; (P) sodium salicylate converter and photomultiplier; (C) Czerny–Turner Spectrometer.

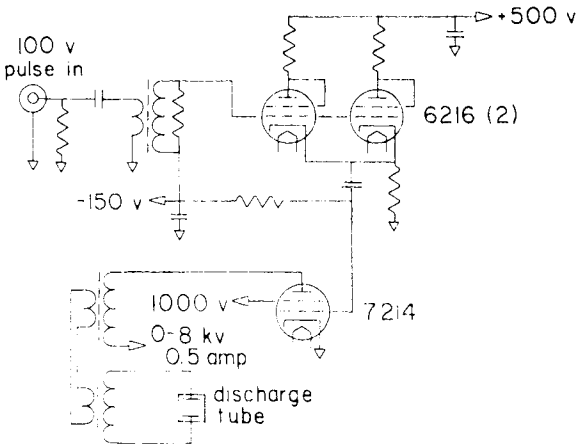

FIG. 3. Schematic diagram of the pulsed excitation unit. The input pulse was obtained from a Hewlett-Packard Model 214 A pulse generator.

exhibited a 0.1-μsec spur, the emission observed during the excitation pulse, and the afterglow emission.

Commercial tank helium was purified by passage through an outgassed charcoal trap immersed in a liquid-nitrogen bath. The effect of residual impurities present is discussed in a later section.

Procedure

The helium spectrum between 3100 Å and 7200 Å was photographed; an iron arc provided the comparison spectrum. Analysis of the plates showed a well-developed He_2 spectrum in addition to He I lines. It was possible to identify most of the previously reported

molecular-helium bands. In addition, many lines of the Ne I spectrum and a weak 4861.3-Å H line were present. We were unable to find molecular bands not attributable to He_2. A search for lines attributable to N, O, C, and Ar did not reveal presence of these impurities; further, no He II or Ne II lines were identified. The Ne I lines and the 4861.3 H line were positively identified by admitting trace quantities of research-grade Ne and H_2 into the flowing He stream and monitoring these lines. A similar experiment using N_2 revealed N I lines at spectral positions where, prior to the addition, no N I lines could be found. This does not imply that impurity species other than Ne and H_2 were absent, but rather that, if present, no visible spectra attributable to such species could be found.

Since it was necessary to increase the band pass of the Czerny-Turner spectrometer to ~20 Å in order to attain sufficient intensity to study the molecular afterglow, a careful choice of the He_2 bands studied was imperative. No atomic lines should be included. No lines belonging to a different band system should be included, either. One band system that satisfies these criteria was found to be $3p\pi$, $E^1\Pi_g \rightarrow 2s$, $A^1\Sigma_u^+$ (with Q-branch head of the 0–0 band near 5133 Å). More than thirty lines of the 0-0 band were identified, as well as a number of members of the 1–1 band.[20] We estimate that any extraneous lines which might have fallen within the band pass of our spectrometer were not more than 1/1000 of the signal level of the lines of the E–A band studied. By similar reasoning it was possible to study the transition $4p\pi$, $i^3\Pi_g \rightarrow 2s$, $a^3\Sigma_u^+$,

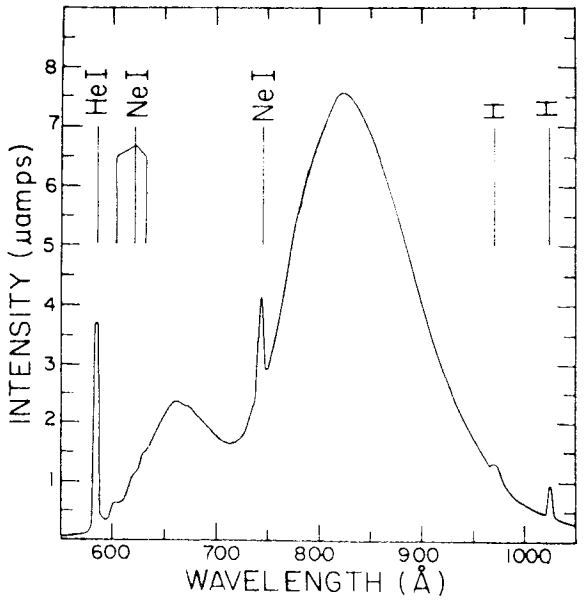

FIG. 4. Helium continuum obtained under the following conditions: pressure, 39 torr; PRF, 30 kc/sec; average power, 740 W; photomultiplier voltage, 980 V; band pass ~5 Å.

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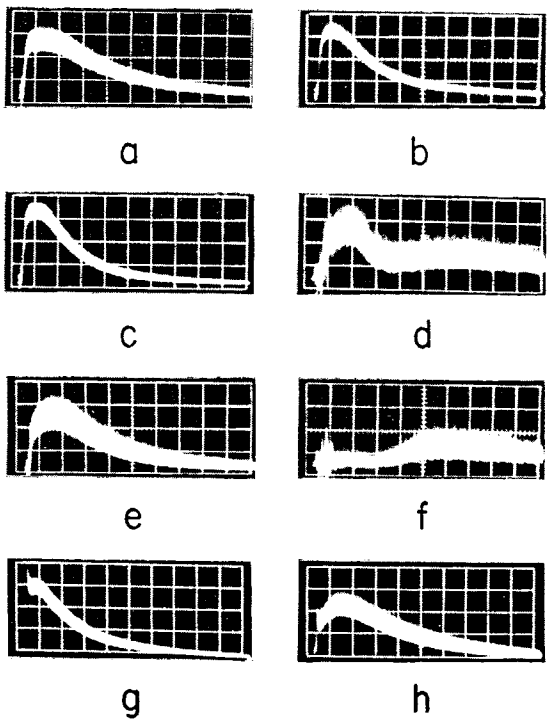

FIG. 5. Oscilloscope traces of emission for a variety of experimental conditions. The wavelengths, sensitivities, time scales, pressures, PRF's, average powers, and circuit time constants were as follows: (a) 825 Å, 0.5 V/div., 5 μsec/div., 24.8 torr, 4.45 kc/sec, 140 W, 1 μsec; (b) 825 Å, 1 V/div., 5 μsec/div., 56.3 torr, 11.5 kc/sec, 340 W, 1 μsec; (c) 825 Å, 1 V/div., 5 μsec/div., 76.8 torr, 15.5 kc/sec, 440 W, 1 μsec; (d) 825 Å, 0.1 V/div., 2 μsec/div., 39.0 torr, 4.57 kc/sec, 130 W, 1 μsec; (e) 680 Å, 0.2 V/div., 5 μsec/div., 53.2 torr, 11.1 kc/sec, 320 W, 1 μsec; (f) 680 Å, other conditions as in (d); (g) 5133 Å, 0.05 V/div., 10 μsec/div., 29.8 torr, 8.08 kc/sec, 240 W, 0.1 μsec; (h) 3676 Å, 0.02 V/div., other conditions as in (g).

with Q-branch head of the 0-0 transition near 3676 Å. In this case, more than thirty lines of the 0–0 and 1–1 bands were readily identified.[21,22]

A time-averaged photoelectrically measured intensity of the 600–1000 Å continuum is shown in Fig. 4. We did not observe the 600-Å band of the He_2 molecule at the resolution employed.[23]

The He pressure was measured with a Wallace and Tiernan absolute-pressure manometer[24] below 50 torr and a simple mercury manometer above 50 torr. Because of pressure drops in the tubing leading into the discharge tube and the impedance of the He discharge to gas flow, all pressures cited have been corrected to give the pressure within the discharge tube. To determine this correction, a special discharge unit was constructed with a Wallace and Tiernan absolute-pressure manometer mounted on glass tubing leading through

[21] W. E. Curtis and R. G. Long, Proc. Roy. Soc. (London) **108**, 513 (1925).

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[24] Absolute pressure indicator, Model No. FA 160, Wallace and Tiernan, Inc., Belleville, New Jersey.

the water jacket directly into the middle of the discharge tube.

Fast electronic circuit techniques were employed to study the emission afterglow displayed on the oscilloscopes. Since the sodium salicylate fluorescent-decay time is known to be less than 10 nsec[25] and the photomultiplier delay times are small, the limiting time constants of the visible and vacuum ultraviolet instruments were determined by the detection circuit. Circuit time constants up to 2 μsec were employed; in all cases, a time constant was chosen which was small compared to the decay constant of the light pulse studied.

At fixed pressure, the pulse power delivered to the discharge tube could be varied by controlling the power available from the dc high-voltage supply. Since the voltage drop across the discharge tube was determined by the pressure and pulse repetition frequency, excitation was varied in this way. The intensity of the observed spectrum could be changed by more than an order of magnitude by this means alone. While no electron densities were directly measured, it is believed that a change of the pulse power producing this variation results in a corresponding variation in the electron density.

The light pulse accompanying and following excitation was recorded simultaneously in the visible and vacuum-ultraviolet regions by photographing oscilloscope traces of the gated photomultiplier outputs. Typical photographs are shown in Fig. 5.

OBSERVATIONS

Hopfield Continuum

In agreement with previous studies of pulsed discharges in helium at moderate pressures, we find two distinct maxima in the continuum, one near 825 Å and one near 680 Å as shown in Fig. 4.[26–30] The two regions at 825 Å and 680 Å were separately studied. The time dependence of the continuum afterglow at selected wavelengths in the region from 825 Å to 960 Å show no departure from the time dependence at 825 Å. No significant deviation from the behavior observed at 680 Å was found when the region between 680 Å and 610 Å was scanned. However, differences did appear between the 825 Å and 680 Å regions. Hereafter, we discuss the two regions at 825 Å and 680 Å on the basis of measurements made at these wavelengths only.

We find that the emission observed at both 825 Å and 680 Å is principally an afterglow following termination of the pulsed excitation, in agreement with the observations of Huffman *et al.*[15] Under all experimental conditions, the afterglow decay has been observed to vary exponentially with time for approximately 50 μsec. Analysis of photographs of some oscilloscope traces has shown the decay to be exponential over more than an order of magnitude; two examples of this exponential decay are shown in Fig. 6. The exponential decay is well-represented by the equation

$$I(t)=I_0e^{-kt}, \tag{1}$$

and the integrated intensity per pulse may in most cases be well represented by I_0/k. The rates of the exponential decays, $k(680)$ and $k(825)$, are independent of pulse width, pulse-repetition frequency, and excitation. We find these quantities to be functions of the pressure only. The quantities $k(825)$ and $k(680)$ are both linear functions of the pressure p and can be represented by the equation

$$k=\alpha+\beta p, \tag{2}$$

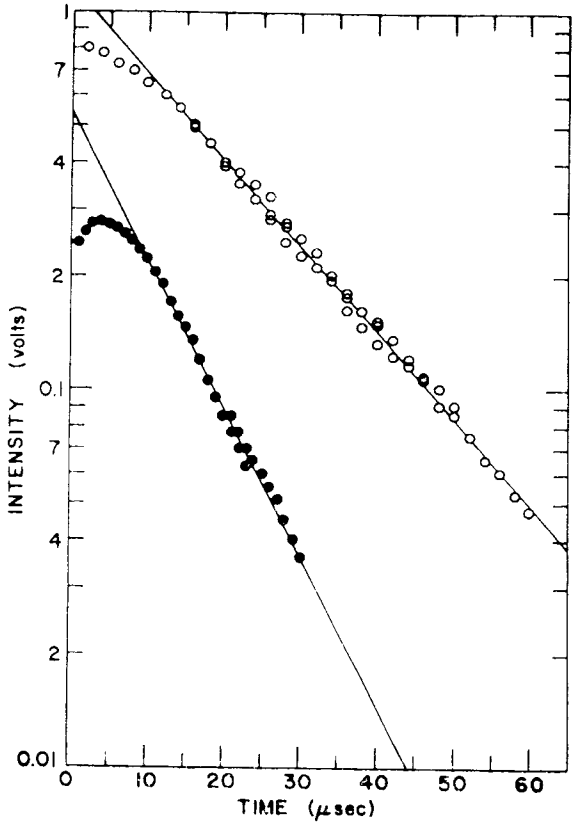

FIG. 6. Exponential decays of the Hopfield continuum in the early afterglow: open circles, 825 Å, 20.5 torr; closed circles, 680 Å, 58.2 torr. Two or three data points plotted at the same time coordinate indicate that the intensities were determined from two or three oscilloscope traces employing different sensitivities.

[25] G. K. Herb and W. J. Van Sciver, Rev. Sci. Instr. 36, 1650 (1965).
[26] Y. Tanaka, Sci. Pap. Inst. Phys. Chem. Res. (Tokyo) 39, 465 (1942).
[27] Y. Tanaka, A. S. Jursa, and F. J. LeBlanc, J. Opt. Soc. Am. 48, 304 (1958).
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[29] P. H. Metzger and G. R. Cook, J. Opt. Soc. Am. 55, 516 (1965).
[30] R. E. Huffman, J. C. Larrabee, and D. Chambers, Appl. Opt. 4, 1145 (1965).

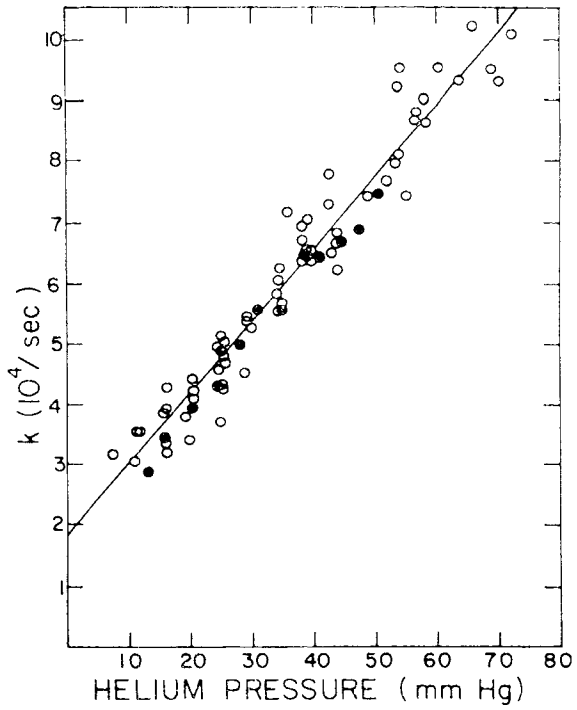

FIG. 7. Pressure dependence of the rate constant $k(680)$ characterizing the exponential decay of emission at 680 Å; open circles, He at 298°K; closed circles, He at 373°K. The pressures measured with He at 373°K have been converted to equivalent pressures at 298°K. The data plotted were collected under a wide variety of excitation conditions. The least-squares linear fit to the data at 298°K is also shown.

with equal slopes β. This behavior is shown in Figs. 7 and 8 where measured values of $k(680)$ and $k(825)$ are given as functions of the He pressure. The points show results obtained under a wide variety of pulse-repetition frequencies, pulse-power levels and pulse widths, illustrating the insensitivity of k to variables other than the pressure. Least-squares lines of the form of Eq. (2) have been fitted to the data and the derived values of α and β are given in Table I.

The detailed shape of the afterglow pulse was found to depend on both excitation conditions and pressure. As shown in Figs. 4 and 5, following onset, the afterglow emission rises rapidly, reaches a maximum, and decays in the manner described above. The time delay between termination of the discharge voltage pulse and onset of the afterglow emission was found to vary inversely with the pressure and to depend on excitation as well. The rate of rise of the afterglow was found to be a strong function of the excitation. The quantities $I_0(825)/k(825)$ and $I_0(680)/k(680)$ are approximately linear functions of the pressure at constant excitation. At constant pressure these quantities are strongly sensitive to excitation and the ratio $I_0(825)\times k(680)/I_0(680)\times k(825)$ increases with increasing excitation. Thus, the relative amplitude of the intensity maxima at 680 Å and 825 Å measured in a time-averaged

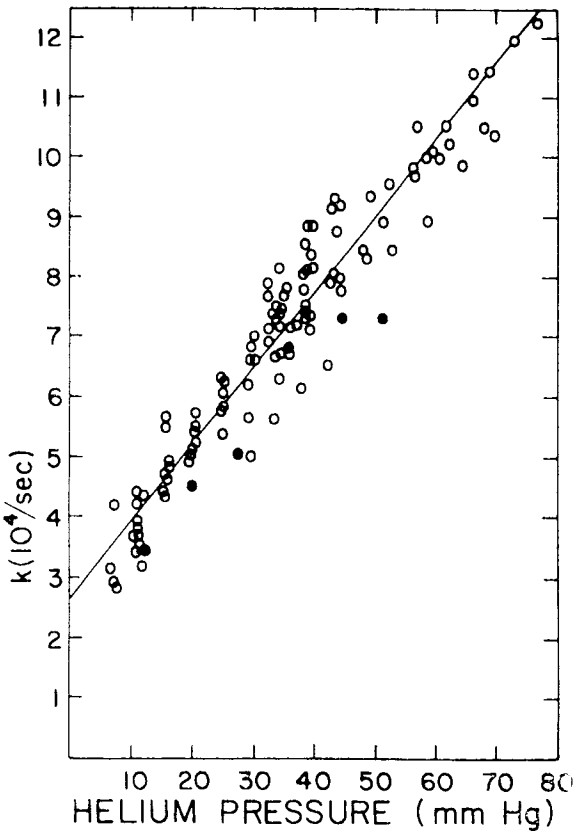

FIG. 8. Pressure dependence of $k(825)$ measured under a wide range of excitation conditions: open circles, He at 298°K; closed circles, He at 373°K. The least-squares linear fit to the data at 298°K is also shown. Pressures measured at 373°K have been converted to 298°K.

TABLE I. Pressure dependence of rate constant characterizing early-afterglow decay.[a]

λ Wavelength (Å)	α Intercept at zero pressure (10^3/sec)	β Slope (mm^{-1} sec^{-1})	β[b] Slope (10^{-15} cm^3/atom·sec)
680	18.2±1.5	1180±37	36.5±1.1
825	26.7±1.4	1270±37	39.3±1.1
5133	23±3.3	1300±87	40.0±2.7

[a] The quoted errors are the standard deviations of the least-squares fit.
[b] Calculated assuming a gas temperature of 298°K.

manner, as in Fig. 3, can be expected to depend on both pressure and excitation.

Visible Region

It has previously been suggested that the transition $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ is responsible for the principal maximum in the continuum near 825 Å.[27] A check of this suggestion would naturally include observations of the strong molecular emissions terminating in the $A^1\Sigma_u^+$ state. We find that the molecular emission at 5133 Å (E–A) consists primarily of an extended afterglow

which appears after termination of the excitation pulse. As in the case of the Hopfield continuum, the afterglow exhibits a rapid buildup to the maximum followed by a simple exponential decay; the decay rate $k(5133)$ is independent of all discharge conditions except pressure. Observations of the emission at various positions along the length of the discharge tube indicated that this decay rate was independent of position within the discharge. Within our experimental accuracy (reproducibility of about 20%), this pressure dependence of the rate followed the linear relation of Eq. 2. Measurements of $k(5133)$ as a function of He pressure are shown in Fig. 9 together with the least-squares fitted line. The derived quantities α and β are presented in Table I. The variations with changing excitation of $I_0(5133)/k(5133)$ follow closely the variations of $I_0(825)/k(825)$.

Observations of the 0-0 band of the system $4p\pi$, $i^3\Pi_g \rightarrow 2s$, $a^3\Sigma_u^+$ showed similar features including an exponential decay of the afterglow emission. The decay slope $k(3676)$ observed was substantially smaller than that found to characterize the E–A decay at a given pressure. In addition to this difference in the exponential decay, we also find that the trace observed at 3676 Å differed in another significant manner from that observed at 5133 Å; the time position of the maximum amplitude of the afterglow emission of i–a was substantially delayed in comparison with the E–A system, as shown in Figs. 5(g) and 5(h).

Effect of Tube Geometry and Temperature

In addition to the measurements employing a quartz discharge tube, experiments were attempted using a Pyrex discharge tube with a capillary section of substantially different geometry: 4 mm i.d., 12 cm long. The required helium flow rates produced a substantial pressure drop across the length of the discharge tube, thereby preventing a strict comparison of the results of this experiment with the results obtained employing the quartz discharge tube. At low helium pressures and consequent low flow rates, experiments in this narrower tube were found to agree with the quartz tube studies. At higher pressures the decay rates obtained with the Pyrex tube were somewhat faster. While these differences are considered to be beyond experimental error, the very large change of geometry (factor of 20 in volume and 14 in diffusion time) indicates that there is no large systematic variation attributable to geometry alone.

The effect of the temperature of the helium gas entering the discharge tube on the quantities k and I_0/k was studied. This was achieved by flowing the purified helium through a spiral trap contained in an oven; further, the Pyrex tubing connecting the spiral trap to the quartz discharge tube was heated. The water-cooling system surrounding the discharge tube was turned off and the water in the jacket was heated.

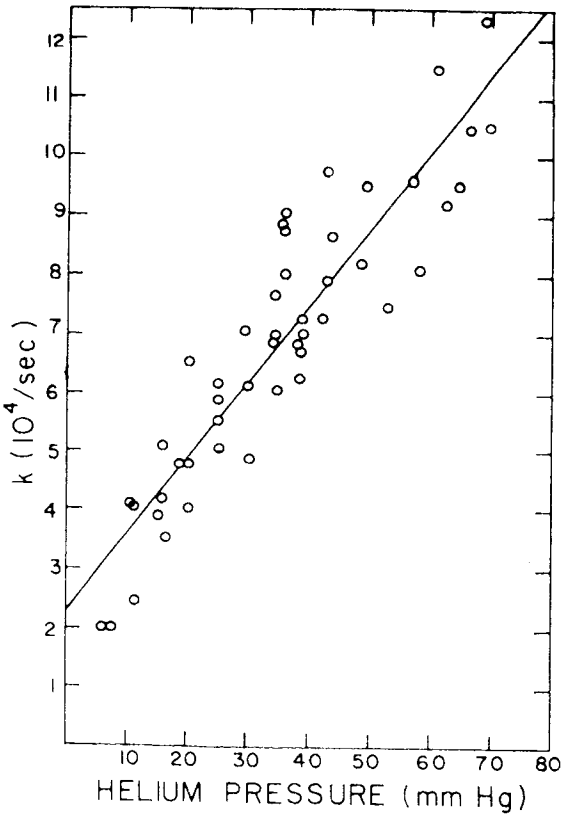

FIG. 9. Pressure dependence of $k(5133)$ measured under a wide range of excitation conditions at 298°K; the least squares linear fit to the data is also shown.

Measurements of the wall temperature of the helium inlet system and the water jacket indicated that the temperature of the flowing gas was roughly 373°K. The measured pressures of the heated helium were converted to equivalent pressures at 298°K. Both the quantities k and I_0/k exhibited the same pressure dependence as was observed in the absence of heating at both 680 Å and 825 Å (see Figs. 7 and 8). Under the unfavorable assumption of low gas pressure and maximum discharge power converted into heating of the gas, the ambient temperature rise per pulse is calculated to be 25°C. This calculation, the experiment employing externally heated helium, and the insensitivity of the decay rate to pulse repetition frequencies from 10 cps to several kc/sec imply the absence of an appreciable activation energy for the process determining the kinetics of the helium afterglow. While we have not determined the ambient gas temperature in the early afterglow, the above considerations support treatment of the data presented for an ambient gas temperature of 298°K.

Effect of Impurities

It has long been known that low impurity levels are sufficient to quench the molecular bands as well as the

Hopfield continuum.[14] As mentioned earlier, spectroscopic evidence indicated the presence of trace amounts of Ne and H_2 in the purified tank helium employed in these experiments. In a separate experiment, additional quantities (up to 400 ppm) of Ne, H_2, and N_2 were separately added to the flowing helium and the quenching of the Hopfield continuum was studied as a function of the partial pressure of the admitted gas. Research-grade samples of the indicated foreign gases were admitted to the discharge tube and, in the absence of helium flow, the steady-state pressure was measured. For Ne and H_2 the flow rate was measured in the absence of helium, and agreed with rates calculated from the geometry of the system. In the case of N_2, the flow rate was not measured; rather, the calculated flow rate was assumed. The helium flow was then turned on and the discharge initiated. Upon achievement of diffusion equilibrium of the foreign gas in the helium flow, the afterglow decay rates were determined. Measurement of the helium flow rate permitted evaluation of the true foreign-gas partial pressures. The residual levels of these foreign gases in the purified tank helium were estimated by monitoring the appropriate spectral lines in the visible region vs total added partial pressure and extrapolating to zero added partial pressure. The residual H_2 and Ne impurity levels correspond to 0.1 and 6.2 ppm, respectively. The estimated residual N_2 impurity level is less than 0.2 ppm.

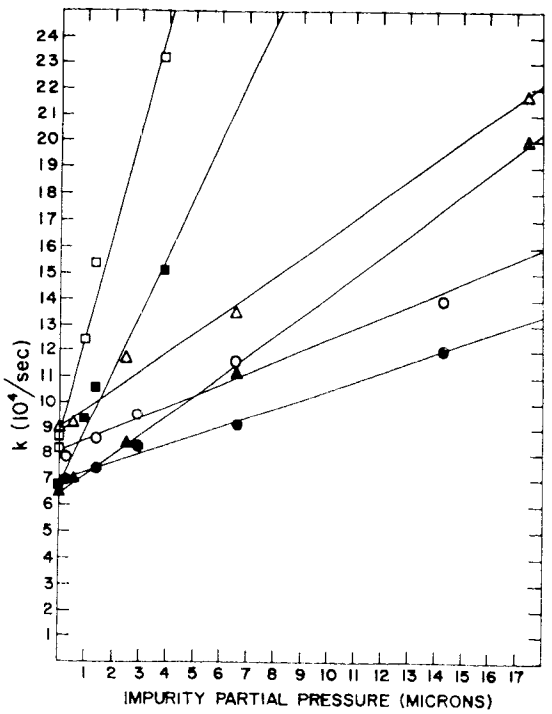

FIG. 10. Dependence of $k(825)$ (open symbols) and $k(680)$ (closed symbols) on H_2 (squares), N_2 (triangles), and Ne (circles) partial pressures at a fixed helium pressure (39 torr) and constant excitation conditions. The six lines are linear least-squares fits to the data.

At all partial pressures of the impurities studied, a purely exponential decay of the afterglow was found. The quantities $k(680)$ and $k(825)$ were linearly increasing functions of the partial pressures, at fixed total pressure, as shown in Fig. 10. The quenching rates derived from the slopes of these curves are: N_2, 2.2×10^{-10} cm^3/atom·sec; Ne, 1.2×10^{-10} cm^3/atom·sec; H_2, 9.0×10^{-10} cm^3/atom·sec. We conclude that the effect of residual impurities is such as to increase the true values of k roughly 1.5%, as compared with pure He. To further check this point, a sample of research-grade helium was used.[31] The results obtained at 825 Å, 680 Å, and 5133 Å (E–A) agree with the data obtained using the purified tank helium. Since electrode outgassing cannot explain the observed dependence of decay rates on pressure and excitation conditions, we believe that the observations described in this report refer to pure helium.

Prompt Molecular Emission

In addition to the afterglow emission, a pulse is observed at 825 Å with time constants comparable to those observed for the voltage pulse. By employing a sufficiently short detection-circuit time constant, it was possible to resolve this pulse from the afterglow pulse. No evidence was found for the existence of a similar prompt pulse accompanying the excitation at 680 Å. Under conditions when the apparent ratio of the maximum amplitudes of the afterglow emission at 680 Å with respect to that at 825 Å was 0.3, the corresponding ratio for pulses possibly accompanying the excitation was <0.07. The relative amplitude of the pulse accompanying the discharge with respect to the afterglow pulse is independent of wavelength for the region 1000 Å to 825 Å and is very nearly so between 825 Å and 760 Å. Below 760 Å the pulse accompanying the discharge rapidly decreases and approaches noise level near 700 Å. There is no positive evidence indicating the existence of such a pulse below 700 Å. Observation at 5133 Å (E–A) also showed a similar prompt pulse. The amplitude of this pulse as compared with the amplitude of the afterglow was found to be a function of position of observation along the axis of the discharge tube. This ratio was somewhat larger near the cathode than the anode.

The relative amplitude of the prompt emission with respect to the afterglow was found to be dependent on both pressure and excitation. It was possible, by lowering the excitation, to create conditions in which the afterglow pulse was a minor feature compared to the pulse accompanying the excitation. Oscilloscope traces obtained under these conditions are shown in Figs. 5(d) and 5(f).

[31] The Matheson Company, Inc., Joliet, Illinois 60434 quoted 2 ppm N_2 and less than 1 ppm levels of other gases.

TECHNOLOGY

The pulsed helium discharge has been studied as it relates to the over-all intensity of the Hopfield continuum. Empirical properties for fixed geometry are described. The peak amplitude of the voltage pulse is found to be an increasing function of the gas pressure p at fixed pulse-repetition frequency (PRF) and fixed pulse width. Measurements with the smaller tube indicate that the variable of relevance is not the pressure alone, but, analogous to the case of the dc discharge, the product pd, where d is the electrode separation. Also, the peak amplitude is a decreasing function of the PRF at fixed pressure and pulse width. A further feature is the apparent invariance of the magnitude of the voltage pulse at fixed pressure and PRF with respect to the pulse width. For pulse widths between 0.15 μsec and 1 μsec (fwhm), the amplitude of the voltage pulse is constant to within 10%.

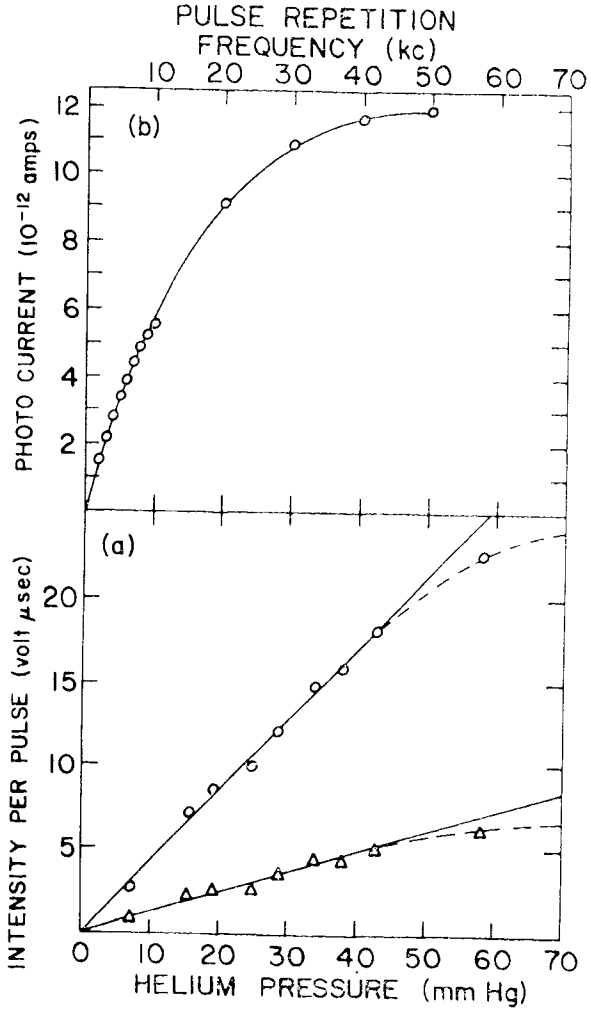

FIG. 11. (a) Dependence of the integrated emission intensity per pulse at 825 Å (circles) and 680 Å (triangles) on the pressure at fixed excitation conditions (15 kc/sec, 470 W). (b) Dependence of the time-averaged emission intensity at 825 Å on the PRF at fixed pressure (11.3 torr) and fixed nominal pulse power.

To describe the variation of the over-all light intensity it is convenient to speak separately of the output per pulse, I_0/k, and the product of this quantity with the PRF f. For our geometry, at fixed pressure, PRF, and nominal pulse power, the quantity I_0/k is essentially independent of pulse width for widths between 0.25 μsec and 1 μsec although the average power drawn from the dc supply increases linearly with pulse width. For pulse widths less than 0.25 μsec the quantity I_0/k decreases as the pulse width is diminished. At fixed pressure and PRF, I_0/k is found to be linear with the pulse power. At fixed frequency and pulse power the intensity I_0/k increases linearly with increasing pressure, provided that sufficient voltage is available, see Fig. 11(a).

The variation of the time-averaged intensity as a function of the pulse repetition frequency is shown in Fig. 11(b). The departure from linearity at low PRF is thought to be characteristic of the power supply. At higher values of the PRF the time constant associated with the afterglow kinetics becomes an important consideration. The circuit shown in Fig. 3 was developed to overcome the frequency limitation of the usual thyratron pulse supply. We have compared the light output resulting from the use of this circuit with that obtained when a spark-gap-controlled condensed-discharge unit is substituted. The improvement in intensity obtained is consistent with what would be expected on the basis of the higher PRF values accessible using our circuit.

In a separate experiment we have replaced the pulsed capillary discharge tube with an electrodeless Pyrex vessel (dimensions: 35 mm long, 25 mm i.d.) and a pulsed magnetron microwave excitation unit. The microwave power (X band, 10 kMc) was delivered to the lamp through a conventional wave guide placed against the face of the vessel. Pulse widths between 0.2 and 2 μsec were employed with PRF between 500 and 5000 cps, consistent with the recommended duty cycle of the magnetron. When operated in this manner, the Hopfield continuum was obtained. The intensity varied linearly with the pressure at constant PRF and pulse power and was found to be linear in PRF at fixed pressure and pulse power. However, owing to poor coupling of the microwave power to the gas phase system, the over-all intensity was substantially less than typical intensities obtained with the pulsed excitation unit.

CONCLUSIONS AND INTERPRETATION

General Remarks

The observations at 825 Å and 680 Å indicate that time-averaged measurements of the intensity distribution of the Hopfield continuum previously reported are strongly influenced by excitation conditions as well as impurity levels and possibly tube geometry. Differ-

ences[29,30] concerning the relative intensities at 825 Å and 680 Å can be understood in terms of these variables as well as other instrumental variables.

The observations demonstrate that at least two processes are operative in producing the radiation at 825 Å and that one of these is absent or strongly inhibited at 680 Å. This can explain the observation of the 825 Å continuum but the absence, or weak excitation, of the 680 Å continuum in an uncondensed discharge.[32] The observations also suggest that the 680 Å region of the continuum is a result of an electronic transition from a single excited electronic state or from several excited states which exhibit the same kinetics of formation.

The similarity of the time-resolved behavior of the transition $3p\pi$, $E^1\Pi_g \rightarrow 2s$, $A^1\Sigma_u^+$ with the 825-Å region of the continuum suggest that states at the level $3p\pi$, $E^1\Pi_g$ or higher are significant contributors to cascading radiation processes which result in the Hopfield continuum as a terminal process. This observation is consistent with a model which includes recombination of helium molecular ions with electrons to form excited neutral molecules at the level $3p\pi$, $E^1\Pi_g$ or higher. This observation also supports the suggestion that the 825-Å region of the Hopfield continuum is produced by the electronic transition A–X.[27]

The results reported here agree well with observations of the early helium afterglow previously reported by Anderson.[10] He was also able to show that mild heating of the electrons in the afterglow temporarily inhibited the molecular emission. We interpret this as showing that the electron temperature relaxes rapidly at moderate helium pressures and that the recombination step is substantially faster than the rate-determining step in the early afterglow. Janin and Eyraud[33] studied the early molecular afterglow in helium, following pulsed excitation, at pressures up to 15 torr. They report, at 15 torr, that the $3d\delta$, $f^3\Delta_u \rightarrow 2p\pi$, $b^3\Pi_g$ emission exhibited the same general features reported here for the E–A and the 825-Å region of the continuum, i.e., they report an emission pulse accompanying discharge followed by an extended afterglow with a buildup relatively rapid compared to the decay.

Bayet[8] has interpreted his results in terms of the variation of the recombination probability with changes of both electron density and electron energy. These variations are important at low pressures and high excitation.[2] However, there is substantial evidence that the decay rate of the electron energy at the pressures employed in the present study is substantially faster than the observed rate of molecular afterglow decay.[10,33,34]

[32] R. G. Newburgh, L. Heroux, and H. E. Hinteregger, Appl. Opt. 1, 733 (1962).
[33] H. J. Oskam, Philips Res. Rep. 13, 335 (1958).
[34] L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of Calif. Press, Berkeley, 1955), p. 477 *et seq.*

Prompt Emission

The observation reported here of molecular emission accompanying the excitation pulse implies a mechanism producing excited He_2 within a few hundred nanoseconds. Re-excitation of metastable He_2 molecules formed during a previous pulse cannot account for this observation. This hypothesis was rejected as a result of observation of the radiation at 825 Å using a pulse repetition frequency of 10 cps. In addition to quenching of long-lived species by processes such as diffusion to the discharge tube wall, the flow rates employed in this experiment were such as to replace all of the gas in the discharge tube within about 0.025 sec. The observed time dependence of the afterglow emission at 10 cps was identical to that observed using excitation frequencies of a few kc/sec. This experiment ruled out the possibility that any of the observed features of the molecular emission were produced by re-excitation of a long-lived excited species, molecular or atomic. From the observation of this prompt light pulse at E–A, we conclude that the light pulse accompanying excitation is produced by formation of a molecule in the zeroth or possibly first vibrational state, as the emission is too fast to allow relaxation processes from higher vibrational states to be operative.

A process which results in the initial random population of high Rydberg levels would be expected to populate both the E and D states. Consequently, assuming the 680-Å region of the continuum is produced by $D \rightarrow X$,[27] we interpret this rapid emission in terms of a primary formation of the E state or possibly a higher state from which radiation to the E state is strongly allowed. The electronic term values of the states E and D with respect to the A state are 19 476.5 cm^{-1} and 18 695.3 cm^{-1}, respectively. The difference, namely 781.2 cm^{-1}, is about 4% of the term value of the E state and, since the cube of the frequency enters into the spontaneous emission probability, plainly leads to a small value of the branching ratio. Then, although the $E \rightarrow D$ transition is allowed, the branching ratio of E–D/E–A is sufficiently small for this prompt emission to be observable at 5133 Å and 825 Å, but not 680 Å.

Afterglow Emission

The buildup and subsequent decay of the early molecular afterglow requires a separate interpretation. The data indicate that He_2^+ is the intermediary involved in the formation of He_2^*. The only other molecule-forming process consistent with our observations would be direct formation by a two-body collision between an excited helium atom and a ground-state atom. However, the persistence of the molecular emission well into the afterglow, in contrast to the more rapid atomic afterglow decay, suggest that only the metastable species 2^3S or 2^1S could be participants. The features of the relevant molecular-potential curves,

as they are now understood,[35] appear to preclude direct molecular formation of any states except possibly the $A^1\Sigma_u^+$ or $a^3\Sigma_u^+$ states from these species.

In contrast to the apparent low probability of direct molecule formation, substantial experimental evidence supports the efficient production of He_2^+ in gaseous discharges.[36–39] Two efficient processes seem well established

$$He^* + He \rightarrow He_2^+ + e^-, \quad (3)$$

$$He^+ + 2He \rightarrow He_2^+ + He. \quad (4)$$

Recent experimental determinations[40–42] of the rate of Eq. (4) are in good agreement with the theoretical value deduced by Mahan.[43] Thus, at a pressure of 10 torr, the rate corresponding to Eq. (4) is 10^4 sec^{-1}, somewhat smaller than the observed afterglow-decay rate of 3×10^4 sec^{-1} reported here. In contrast, at 60 torr the rate is 4×10^5 sec^{-1}, substantially faster than the corresponding decay rate of 9×10^4 sec^{-1} reported here. Moreover, the rate of Eq. (4) varies as the square of the helium pressure. Consequently, the observations reported here are inconsistent with the formation of He_2^+ predominantly by this mechanism; for times later in the afterglow, it is not unlikely that this three-body process assumes the dominant role in the production of He_2^+. The rate corresponding to Eq. (3) is known to be rapid; it has recently been suggested that the cross section for the two-body destruction of He (3^1P) atoms is 2 Å^2, a value interpreted as being consistent with the rate of production of He_2^+ by the mechanism of Eq. (3).[44] Assuming a relative velocity appropriate to a translational temperature of 300°K, this process is expected to proceed at a rate of $\sim2\times10^7$ sec^{-1} at 25 torr. Hornbeck's[45] value of $\sigma\tau\sim5\times10^{-23}$ cm^2 sec, where σ is the effective cross section for production of the molecular ion and τ is the radiative lifetime of the excited atomic level, predicts that at 35 torr roughly 10% of the excited atoms should be converted to molecular ions. Consequently, we conclude that the process should result in the efficient formation of He_2^+ within a few hundred nanoseconds after initiation of the discharge. This is further supported by the observation of Craggs, who reported[46] that, at 50 torr, the He_2^+ concentration reaches a maximum about 0.3 μsec after termination of excitation.

The quantity I_0/k is understood to represent an initial concentration of He_2^+ formed by the two-body process at time zero. The approximate linear dependence of I_0/k on current is consistent with mass-spectrometric investigations of He_2^+ formation which show a linear dependence of the molecular-ion concentration on bombarding current.[47] The observed impurity quenching is also consistent with this interpretation. If we interpret the observed quenching rates in terms of cross sections for He_2^+ destruction at 300°K, the derived cross sections are 11 Å^2, 22 Å^2, and 45 Å^2 for Ne, N_2, and H_2, respectively. In view of the uncertainties in our determination of the foreign-gas partial pressure, the absolute magnitude of these cross sections are believed to be correct within a factor of two; however, the relative values for the three gases should be more precise. These cross sections can be used to rule out three of the five known long-lived helium species as being responsible for the early afterglow molecular emissions described here. Table II presents a summary of experimental data on the destruction of He ($1s2s$, ^1S), He ($1s2s$, ^3S), He^+, and He_2^+ together with the results of the present study. The very large quantitative discrepancies and variations between the various foreign-gas species permit elimination of He (2^1S), He (2^3S), and He^+ from further consideration. In contrast, the good agreement between Oskam's value of 15 Å^2 for the destruction of He_2^+ by Ne[48] and our value of 11 Å^2 for the observed quenching by Ne further supports the interpretation

TABLE II. Cross sections (Å^2) for quenching of long-lived species in helium.

Foreign gas	$2s$, ^3S	$2s$, ^1S	He^+	He_2^+	Present study[b]
Ne	0.28[a]	4.1[b]	...	15[g]	11
N_2	7[a]	7[b]	110[c]	...	22
	6.4[b]		100[d]		
H_2	3[a]	2[b]	<0.6[e,f]	...	45
	6.0[b]				

[a] F. E. Benton, E. E. Ferguson, F. A. Matsen, and W. W. Robertson, Phys. Rev. 128, 206 (1962).
[b] E. E. Muschlitz, Jr., "Collisions of Electronically Excited Atoms and Molecules" in *Advances in Chemical Physics, Molecular Beams*, Vol. X, J. Ross, Ed. (Interscience Publishers, New York, 1966).
[c] J. Sayers and D. Smith, Discussions Faraday Soc. 37, 167 (1964).
[d] E. E. Ferguson, F. C. Fehsenfeld, D. B. Dunkin, A. L. Schmeltekopf, and H. I. Schiff, Planet. Space Sci. 12, 1169 (1964).
[e] C. F. Giese and W. B. Maier II, J. Chem. Phys. 35, 1913 (1961); J. Chem. Phys. 39, 739 (1963).
[f] L. Friedman and T. F. Moran, J. Chem. Phys. 42, 2624 (1965).
[g] See Ref. 48.
[h] The cross sections reported were derived from the experimental quenching-rate constants by assuming that the process was the quenching of He_2^+ at 300°K.

[35] R. S. Mulliken, Phys. Rev. 136, A 962 (1964).
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[44] R. G. Fowler, T. M. Holzberlein, and C. H. Jacobson, Phys. Rev. 140, A1050 (1965).
[45] J. A. Hornbeck, Phys. Rev. 84, 1072 (1951).
[46] J. D. Craggs, in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases, Paris, 1963* (North-Holland Publishing Co., Amsterdam, 1964), p. 423.
[47] J. A. Hornbeck and J. P. Molnar, Phys. Rev. 84, 621 (1951).
[48] H. J. Oskam, Philips Res. Rep. 13, 401 (1958).

that the long-lived species primarily responsible for the Hopfield continuum is in fact He_2^+.

The insensitivity of the afterglow-decay rate to excitation conditions and the linear pressure dependence of this rate strongly suggests that recombination of molecular ions with electrons is not the rate-controlling step in the early afterglow. The data may be interpreted as reflecting the slower two-body conversion of He_2^+ from a nonrecombining to a recombining form. This may be consistent with the recent discovery by Madson *et al.* of two He_2^+ species, distinguished according to mobility.[38] They suggest that one species is a freshly formed molecular ion while the second species is an ion which has been aged. Such a model would predict all of the features reported in the present study: rapid buildup of molecular light intensity, buildup sensitive to excitation, exponential decay in the early afterglow, decay rate insensitive to excitation, quenching due to collisions of He_2^+ with foreign-gas species, and similar kinetics for several singlet molecular transitions. This model is also consistent with the very different phenomena observed in the late afterglow since the recombination rate constant depends on the electron concentration and could become the rate-determining step at a later time in the afterglow.

A plausible physical interpretation of the two-body conversion suggested above could be the vibrational relaxation of vibrating helium molecular ions. Mulliken has recently advanced arguments[35] indicating that formation of He_2^+ by the two-body process, Eq. (3), should result in vibrational excitation of the ions formed. Curran,[49] using electron bombardment, finds that the two-body process is considerably enhanced when the principal quantum number of the He* excited is $n=4$ as compared with $n=3$. This is true in spite of the fact that St. John *et al.*[50] report that the excitation cross sections for the $n=3$ level of He* are larger than those for excitation to the $n=4$, 5, or 6 levels.

If recombination of vibrationally excited molecular ions occurs, we would expect to observe either dissociative recombination or transitions from higher vibrational states of the He_2^* produced, or both. There is no conclusive evidence supporting dissociative recombination in the helium afterglow.[1] The observed spectrum of He_2^* is well known to be characterized primarily by 0–0 and 1–1 transitions. Since recombination seems to be efficiently accomplished only in the low vibrational levels of the molecular ion, it is necessary to invoke a mechanism for vibrational relaxation operative in the early afterglow. We suggest that the two-body process described in this report is the vibrational relaxation of the He_2^+ formed initially. In this model, assuming a translational temperature of 300°K, the observed pressure dependence of the afterglow-decay rates yields an apparent cross section of about 3.5×10^{-19} cm^2 for this vibrational relaxation. While an alternative interpretation of the early molecular afterglow may be possible, the experimental results reported here severely restrict speculations regarding the dominant mechanisms.

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[49] R. K. Curran, J. Chem. Phys. 38, 2974 (1963).

[50] R. M. St. John, F. L. Miller, and C. C. Lin, Phys. Rev. 134, A888 (1964).