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Enhancement of the 2062-Å Atomic-Iodine Line in an Iodine Inert-Gas Flashlamp

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The spectral output of flash-discharge lamps containing iodine, and mixtures of iodine and the inert gases were studied at selected wavelengths and discharge voltages. It was found that addition of xenon or krypton to iodine produced a marked enhancement of the 2062-Å iodine line compared to the output from a pure iodine discharge. The enhancement of this line was found to be a maximum at approximately 130 torr and 3.0-kV discharge voltage with either of the inert gases. An enhancement factor of about 400 was found with added xenon and about 700 for a lamp filling containing krypton. It was postulated that, with xenon, energy-transfer collisions between metastable xenon and ground-state iodine atoms were responsible for the enhanced 2062-Å radiation. With krypton–iodine mixtures an additional mechanism for producing excited iodine atoms was the reaction of metastable krypton atoms with iodine molecules producing one ground-state iodine atom and one in the $6p^4P_{3/2}$ state.

INDEX HEADINGS: Iodine; Xenon; Krypton; Sources; Atomic spectra.

PULSED light sources have generally been confined to gas fillings containing mercury,[1] xenon,[2,3] and the other inert gases.[2,4] The spectral output of xenon flashlamps is well known[5] and approximates a 5000°K to 9000°K blackbody in the visible region with some characteristic lines of the gas filling superimposed on the continuum. The output in the ultraviolet region, below 3000 Å, is usually a small percentage of the visible and infrared output.

Intense light sources at wavelengths less than 2200 Å but greater than the oxygen cutoff in air (~1900 Å)

[1] S. A. Pollack, J. Appl. Phys. **36**, 3459 (1965); T. H. Rautenberg, Jr., and P. D. Johnson, Appl. Opt. **3**, 487 (1964).
[2] G. D. Hoyt and W. W. McCormick, J. Opt. Soc. Am. **40**, 658 (1950).
[3] P. M. Murphy and H. E. Edgerton, J. Appl. Phys. **12**, 849 (1941).
[4] G. A. Freeman, Westinghouse Engr. **8**, 90 (1948); V. I. Vasil'ev, M. S. Levchuk, and I. S. Marshak, Opt. i Spektroskopyia **11**, 118 (1961); J. N. Aldington, Endeavour **7**, 21 (1948).
[5] John H. Goncz and P. Bruce Newell, J. Opt. Soc. Am. **56**, 87 (1966).

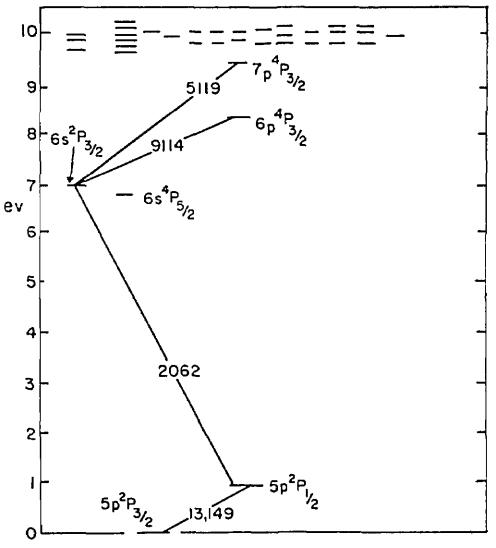


FIG. 1. Atomic-iodine energy-level diagram.

are not common; however, recently a continuous-operation iodine lamp emitting the intense 2062 Å atomic-iodine line was reported.[6] A mixture of argon and iodine flowed through the lamp and an ac discharge was used to excite the gas. Another lamp with pure iodine was also described and could be operated in an electrode or an electrodeless mode. It was found that argon was useful for protection of the electrodes from attack by the iodine and for producing a steady discharge.

The strong emission of the iodine lamp at 2062 Å was desirable, but we wished to operate the lamp in a pulsed mode. We found that a flashlamp filled with pure iodine operated erratically; therefore, an inert gas was introduced into the lamp to stabilize its operation. In addition, it was thought that a proper choice of inert gas and pressure in admixture with iodine might also enhance the output of 2062 Å.

Apparatus

The flash lamps were constructed in our laboratory of 9-mm-diam Suprasil quartz tubing with tungsten electrodes. Each lamp was attached through a greaseless ball joint to a mercury-free, oil-diffusion-pump vacuum system capable of maintaining a constant pressure of 5×10^{-6} torr or better.

Degassed and purified C.P. iodine was stored in a side tube and condensed through a greaseless stopcock into the flashtube as needed. Linde research-grade gases were stored in one-liter bulbs and admitted to the lamp as desired. Gas pressure was monitored with a Wallace and Tiernan gauge.

Lamps were flashed by discharging a 150-μF capacitor bank across the lamp through a 150-μH inductor and were triggered by imposing a high-voltage pulse on an externally wrapped wire.

The lamp was positioned 45 cm from the entrance slit of a Spex, Czerny–Turner recording spectrometer which had been set previously at the desired wavelength by means of a separate pure-iodine, ac discharge lamp. The spectrometer contained a 1200-lines/mm replica grating blazed at 5000 Å in the first order; the reciprocal dispersion was 10 Å/mm. The output of the photomultiplier, either an RCA 1P28 for visible and ultraviolet wavelengths or an RCA 7102 for the infrared, was fed into one channel of the type CA plug-in preamplifier of a Tektronix 555 dual-beam oscilloscope (with a transient-response time of 15 nsec). The signal from an EG&G model 560 Lite Mike (sensitive between 4000 Å and 11 000 Å with a typical response time of 5 nsec) fed into the second channel of the oscilloscope, was used to trigger the trace and to monitor the overall behavior of the discharge. Current and voltage were measured separately for several discharge conditions by means of a Tektronix model P6015 high-voltage probe and a Power Designs pulse-current-viewing transformer, model CVT-1, with a M-1 multiplier. When it was desired to operate the lamp on ac a 3-kV, 30-mA neon-sign transformer was used as a power supply.

In a few cases photographic spectra of the flashlamps were obtained on Kodak SWR ultraviolet plates through a Jarrell–Ash $f/6.3$ Czerny–Turner spectrograph blazed at 5000 Å in the first order.

Experiments

Pure-iodine flash discharges were initially studied in sealed-off flashtubes of the type described. The photographic spectrum between about 4000 Å to 2000 Å revealed only an atomic iodine line spectrum. When operated continuously on ac, the discharge spectrum of the same lamp contained iodine molecular bands as well as the atomic line spectrum, including the 2062-Å line.

In order to stabilize the firing voltage and also to produce a more intense 2062-Å line, experiments were carried out with krypton and xenon added to the iodine lamp at various pressures ranging from 5 to 240 torr and at firing voltages of 1, 1.5, 2, and 3 kV. Xenon was studied initially because its first metastable state, at 8.31 eV, is close in energy to the $6p^4P_{3/2}$ iodine state, which could be populated by collisions of the second kind between these xenon metastables and the iodine atoms formed in the discharges. A simplified iodine energy-level diagram is presented in Fig. 1, which shows only the pertinent energy levels and transitions.[7] Since the $6p^4P_{3/2}$ iodine state spontaneously decays to the $6s^2P_{3/2}$ state with the emission of 9114 Å and this state then decays to the $5p^2P_{1/2}$ ground state with the emission of 2062 Å, both of these wavelengths were

[6] P. Harteck, R. R. Reeves, Jr., and B. A. Thompson, Z. Naturforsch. 19a, 2 (1964).

[7] A more complete energy-level diagram for iodine can be found in Ref. 6. The exact energies and state designations of iodine were obtained from C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. Circ. 467, Vol. III (1958).

monitored. As an additional check of the mechanism, 5119-Å radiation, which results from the decay of the $7p^4P_{3/2}$ state at 9.4 eV to the $6s^2P_{3/2}$ state, was also observed. Since the $7p^4P_{3/2}$ state has considerably higher energy than the first xenon metastable state, we thought that it would not be readily populated by collisions with xenon atoms. These experiments were subsequently repeated with similar pressures of krypton.

We found that any iodine which remained condensed on the tube walls or electrodes would be evaporated into the discharge, yielding erratic results which depended on the amount of iodine evaporated. This problem was alleviated by condensing the excess iodine into the cool spaces behind the electrodes and by partially condensing it into a small appendage tube, thereby maintaining the iodine vapor at its room-temperature pressure (~0.3 torr). Consecutive reproducible discharges could then be obtained.

The spectrometer slits were set at 20 μ for the 2062 Å and 10 μ for the 5119-Å iodine lines, but were widened to 100 μ to record a greater part of the broader 9114-Å iodine line. Intensity vs time oscilloscope traces of the photomultiplier output of the spectrometer were photographed at each firing voltage and for each gas pressure. Traces were first taken of the pure-gas discharge at each wavelength. The inert-gas was pumped from the system, pure iodine condensed into the side tube and the experiments repeated. They were repeated again with the iodine–inert-gas mixture.

RESULTS

Light pulses followed the current pulses closely. In general, pulse durations were of the order of 0.6 msec but were lengthened to about 0.7 msec in the higher-pressure discharges of krypton-plus-iodine, especially at 9114 Å. Some structure, noticeable in the light pulses of the pure-iodine discharge at 2062 Å, was found also in the pulses of the inert-gas–iodine mixtures. In both cases, the structure became more prominent with increasing pulse energy. However, as gas pressure increased, structure became less prominent. Relative spectral line intensities were determined by measuring the areas under the recorded intensity–time traces.

No differences could be seen in the current and voltage characteristics of flash lamps containing inert gases with and without added iodine. A pure-iodine flashlamp had the same electrical characteristics as a lamp filled with 10 or 20 torr of inert gas. Although the general shapes of the current and voltage curves were the same in all cases, the peak current depended on the total pressure and decreased by about 20% between 10 and 200 torr.

Xenon+Iodine

Photographic spectra of an iodine-plus-20-torr-xenon sealed-off flashlamp, obtained on the Jarrell Ash spectrograph, revealed that the character of the discharge spectrum had changed as compared with a pure-iodine discharge. In this case, the line spectrum was characteristic of xenon radiation and was similar to a pure-xenon lamp at 20 torr pressure; only a few iodine lines appeared. However, several ultraviolet lines near 2000 Å were more intense in the mixture and one line could be identified as the 2062-Å iodine line while others were tentatively identified as silicon lines.

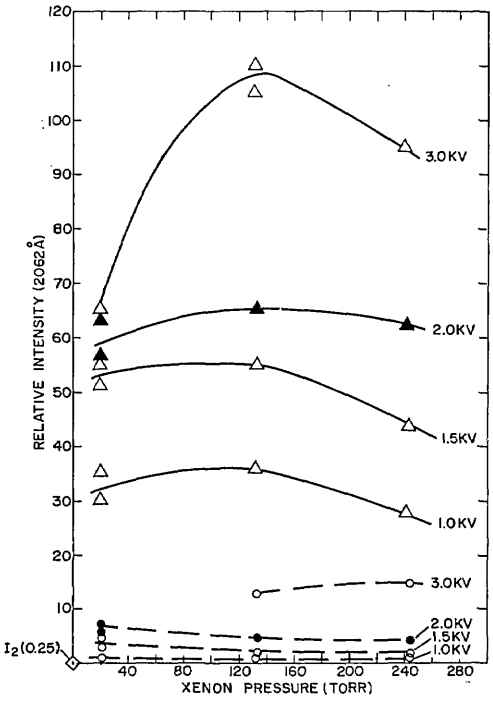


FIG. 2. Relative intensity of the 2062-Å atomic-iodine line in arbitrary units for flash discharges containing xenon. Broken curves: Xe, solid curves: Xe+I_2.

Relative pulse intensities at 2062 Å, obtained using the Spex spectrometer, are shown in Fig. 2 with the relative intensities of the pure gas and gas–iodine mixtures at various voltages plotted against inert-gas pressure. We determined that the xenon–iodine 2062-Å and 9114-Å intensities resulted from the iodine line and not from an increase of the xenon-continuum intensity, by scanning through this wavelength region at small wavelength increments. Since the intensity of the iodine lines was quite low in discharges in the pure material, large errors were possible in the measurements. We found that the intensity of the pure-iodine lamp at these wavelengths did not vary much with firing voltage; any variations were within the large (50%) estimated error of the measurement. This was true even at higher firing voltages when the lamp was heated to permit operation up to 3000 volts. The average value of the intensity of the 2062-Å line in the pure-iodine discharge has been indicated on the ordinate of Figs. 2 and 3 for comparison.

The enhancement of the iodine lines in the inert-gas–iodine mixtures was calculated by subtracting the

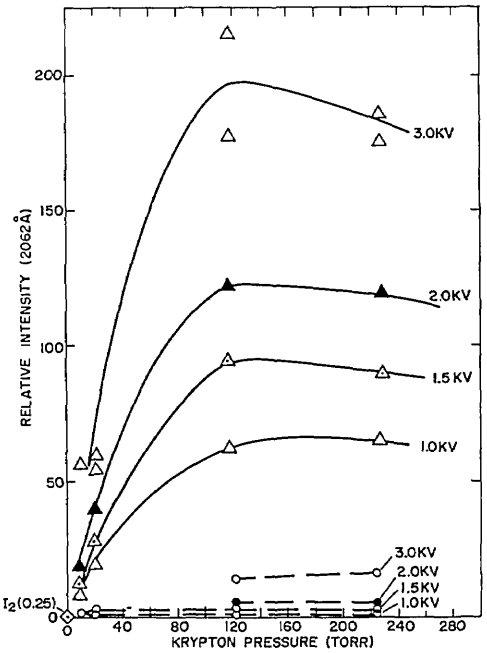


FIG. 3. Relative intensity of the 2062-Å atomic-iodine line in arbitrary units for flash discharges containing krypton. Broken curves: Kr, solid curves: Kr+I_2.

intensity of the pure inert-gas continuum from the intensity of the mixture and then dividing by the intensity of the line from the pure-iodine lamp.

From Fig. 2 it is possible to see that the 2062-Å iodine line was greatly enhanced. For example, at 130 torr xenon and 3.0-kV firing voltage, the enhancement factor was about 400 while at the same pressure, but at 1.0 kV, the enhancement was still about 140. Even when the large error in the pure-iodine-lamp intensity is taken into account, the enhancements are still extremely great at all the indicated pressures and firing voltages.

In the case of an ac discharge, only the 2062-Å line was monitored and only with 5 and 20 torr of added xenon, while the lamp was operated at 7-mA rms. We found that the output from a pure-xenon discharge at this wavelength was too low to be measured; but the strong emission from the xenon-plus-iodine mixture indicated that 60- and 73-fold enhancements of the 2062-Å iodine line were obtained at 5 and 20 torr, respectively.

There seemed to be a small enhancement of the 5119-Å iodine line in discharges containing xenon and iodine, especially at the higher firing voltages. No enhancement was evident at 240 torr or at 1.0-kV firing voltage; however, at 1.5- and 2.0-kV firing voltage and 120 torr of xenon the enhancement was about two while at 20 torr the enhancement was about 1.25.

The results obtained at 9114-Å clearly showed, at all firing voltages, an enhancement of this iodine line in discharges containing xenon and iodine. We could not quantitatively compare the enhancements at 2062-Å with those at 9114-Å since only a small portion of the broad 9114-Å line was allowed to pass through the slits of the monochromator during the intensity measurements while a much larger portion of the narrower 2062-Å line was collected. Furthermore, the relative responses of the monochromator and the photomultiplier tubes were not known for the two wavelengths. Representative enhancements obtained at 9114 Å in discharges containing 10 torr of xenon added to the iodine were 17, 36, and 57 at 1.0-, 2.0-, and 3.0-kV firing voltages, respectively, and were 29, 64, and 89 for the same voltages at 20 torr of added xenon. At higher pressures of added xenon, for example 120 torr, the enhancement seemed to be much less: 4.5, 26, and 15 for 1.0- 2.0-, and 3.0-kV firing voltages, respectively.

The comparatively low enhancement of the 9114-Å iodine line, especially at high pressures of added gas, was expected since the flashtube is known[8] to become opaque to this wavelength at peak current densities in excess of about 2500 A/cm^2. In the present experiments, the current densities were found to be between 2100 to 8800 A/cm^2, depending only on the pressure of the gas and the firing potential; these discharges were clearly in the high-absorption region for 9114 Å. In general, a high-pressure xenon flashtube has a continuum absorption produced by free–free and bound–free transitions in the xenon plasma. At constant peak current, the flashtube is quite transparent to the short-wavelength radiation around 2000-Å, but the continuum absorption increases with increasing wavelength and is very high at about 10 000 Å. Furthermore, at low gas pressures the continuum emission is very weak, and the discharge exhibits mainly a line spectrum characteristic of the excited gas; therefore, the continuum absorption would have to be quite weak as well. In the present experiments the enhancements of the 9114-Å iodine line in discharges containing 10 and 20 torr of added xenon would not be appreciably reduced by absorption by the plasma; however, with gas fillings at 120 torr and greater pressures, the plasma would be essentially opaque. In that case the intensity of 9114 Å from the xenon discharge and from the xenon–iodine discharge would be similar; only a small additional contribution to the intensity would originate from iodine atoms emitting 9114 Å close to the walls of the flashtube. Under these conditions the observed enhancement of this iodine line would be low although the true enhancement could be great.

Strong absorption of 5119 Å by the flashtube was also possible; therefore, no enhancement may have been expected at this wavelength at high pressures of added gas. However, since little or no enhancement was observed even at low pressures of the added gas, where the continuum absorption is weak, the intensity of this line was not affected greatly by absorption. Very little effect was expected in the case of the 2062-Å line, since

[8] J. L. Emmett, A. L. Schawlow, and E. H. Weinberg, J. Appl. Phys. 35, 2601 (1964).

the continuum absorption of this wavelength is quite small in the discharge.

Krypton+Iodine

The relative intensity of the 2062-Å atomic-iodine line in mixtures of iodine and krypton is shown in Fig. 3. The enhancements can be calculated by using the method described for the xenon–iodine mixtures. The enhancements at 2062-Å were found to be much higher in this case than in the xenon mixtures; they approached a maximum of about 700 at 3.0 kV and 120 torr of krypton. In contrast to this extremely great enhancement at 2062-Å, no enhancement was found for the 5119-Å iodine line; in fact, the intensity of the line from the mixture was the same as the intensity from the pure-gas discharge with no contribution from iodine.

The apparent enhancements of the 9114-Å line in discharge mixtures containing krypton were not as great as the enhancements obtained at 2062-Å; however, based on the reasoning presented in the case of xenon discharges, this low enhancement was expected. Representative enhancements of the 9114-Å iodine line in discharges containing 120 torr of added krypton were 10, 42, 74, and 54 at 1.0-, 1.5-, 2.0-, and 3.0-kV firing voltages, respectively, and 11, 21, 47, and 61 at the same voltages but at 220 torr of added krypton. The greater enhancements obtained in these discharges, compared to the discharges with added xenon could be explained by the weaker absorption continuum expected in the case of krypton discharges.[9]

DISCUSSION

The results obtained with these flash lamps can be explained by considering that iodine atoms in a specific excited state can be produced by energy-transfer collisions between the inert gas and unexcited iodine. These energy-transfer collisions, usually called collisions of the second kind, can take place with an inert-gas atom in any excited state; however, it is most likely with the more highly populated lower excited states. The energies of the first four excited states of xenon, krypton and argon[10] are shown in Table I. The efficiency of collisional energy transfer between excited inert-gas atoms and iodine would depend on the concentration of excited atoms, the decay time of the state, the energy resonance between the colliding atoms and, perhaps, the necessity for spin conservation in the reaction.[11] In the cases of the inert gases used in these experiments, the decay of the $1s_4$ and $1s_2$ states can be spread over several hundred microseconds[12]; however, the decay time of the highly populated metastable $1s_5$ state, and probably the $1s_3$ state, is quite long, extending over several milliseconds.[13] Inert-gas atoms in metastable states therefore would seem to be the species most likely to participate in energy-transfer collision in the inert-gas–iodine flashlamp, since they are highly populated states and can exist long enough to provide many opportunities for collisions with transfer of energy. During a flash discharge in pure iodine the distribution of excited states is governed by the electron bombardment of the gas during the flash and by the rate of decay of upper excited states. With inert gases at much higher pressures in the discharge, the direct excitation of the upper excited states of iodine by the electrons may not be as important and excitation by collision with excited inert-gas atoms may become much more important.

TABLE I. Lower excited states of inert gases.

State (Paschen notation)	$1s_5$ (eV)	$1s_4$ (eV)	$1s_3$ (eV)	$1s_2$ (eV)
Ar	11.548	11.623	11.723	11.828
Kr	9.914	10.032	10.562	10.643
Xe	8.315	8.436	9.447	9.569

In a flash discharge containing either pure iodine or a combination with an inert gas, no molecular spectrum was expected, since the low dissociation energy of I_2, (1.54 eV)[14] would permit the molecules to be dissociated easily in the discharge. In confirmation of these ideas, photographic spectra between 4000 Å–2000 Å showed only atomic-iodine lines with no indication of molecular bands.

A preliminary experiment with 20 torr of argon in the flash lamp, along with the iodine, indicated that approximately a 10-fold enhancement of 2062-Å could be obtained in a 1.0-kV discharge. This enhancement indicated energy transfer; however, no preferential population of any iodine atomic state could be identified. Since the energy of the $1s_5$ level of argon is far above the ionization potential of iodine atoms, energy-transfer collisions would produce the ion, which could have a complex decay scheme after neutralization and produce a general, relatively weak enhancement of many lines in the spectrum. In addition, the efficiency of energy-transfer collisions was probably low, because no close energy resonance was possible between the excited argon atoms and the unexcited iodine.

In general, the condition for efficient energy-transfer collisions is $a|\Delta E|/hv=1$, where a is the range of interaction of atoms, v is the relative velocity of the colliding atoms, and ΔE is the energy change involved in the reaction. Usually a close match between the energy of the excited atom and some particular energy level in the other species has been found to be a sufficient

[9] W. Thouret, Licht-Technik **2**, 107 (1950).
[10] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. Circ. 467, Vol. I (1949), Vol. II (1952), and Vol. III (1958).
[11] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, 1934, Reprinted 1961), Ch. II.
[12] R. Turner, Phys. Rev. **140**, A426 (1965).
[13] D. S. Smith and R. Turner, Can. J. Phys. **41**, 1949 (1963).
[14] R. D. Verma, J. Chem. Phys. **32**, 738 (1960).

condition for efficient transfer of energy during a collision.[11,15]

For any of the inert gases, the $1s_5$ metastable level was always too energetic to elevate iodine directly to the $6s^2P_{3/2}$ state at 6.96 eV above the ground state; however, a very close energy resonance, within 6 cm^{-1}, could be obtained between the xenon $1s_5$ level and the $6p^4P_{3/2}$ level of iodine. In addition to the close energy match, this exchange is spin-allowed. As expected on the basis of these considerations, both the 2062-Å, $6s^2P_{3/2} \rightarrow 5p^2P_{1/2}$, and 9114 Å, $6p^4P_{3/2} \rightarrow 6s^2P_{3/2}$, iodine lines were found to be enhanced at all xenon pressures and discharge voltages. The apparent small enhancement of the 5119-Å iodine line could be explained by the close energy resonance between the second xenon metastable energy level, $1s_3$, at 9.447 eV and the $7p^4P_{3/2}$ iodine state at 9.376 eV. However, the population of the $1s_3$ state during the flash is probably low, limiting the magnitude of the enhancement.

In discharges containing krypton, the $1s_5$ level of the inert gas was in close energy resonance with many of the upper excited states of iodine; therefore, many of these states could be populated through energy-transfer collisions. Subsequently, many of the excited iodine atoms could decay down to the $6s^2P_{3/2}$ state and yield an enhanced 2062-Å iodine line. Furthermore, in krypton-plus-iodine discharges, a greater enhancement of all the iodine lines might be expected, since the greater ionization potential of krypton would allow proportionately more iodine atoms to be ionized than in xenon-plus-iodine discharges. However, the magnitude of the enhancements of the 2062-Å and 9114-Å iodine lines and the absence of any enhancement of the 5119-Å line with added krypton indicated that some additional energy-transfer process must be considered. In addition to energy-transfer collisions with iodine atoms, the excited krypton atoms may participate in collisions with transient iodine molecules. In discharges containing xenon, energy-transfer collisions are energetically possible between the inert-gas atoms in the $1s_5$ state and iodine molecules, producing one ground-state iodine atom and one in the $6s^4P_{5/2}$ state,[16] below the $6s^2P_{3/2}$ state. This reaction would tend to reduce any enhancement of 2062 Å since the energy from a $1s_5$ xenon atom would be consumed without contributing to the excitation. When krypton is the added inert gas, the energy of the Is_5 krypton level at 9.91 eV is sufficient for the reaction producing one ground-state iodine atom and one excited to the $6p^4P_{3/2}$ state, which together require 9.85 eV. The optical emission from the decay of this excited iodine atom could produce the observed enhancements of the 2062-Å and the 9114-Å lines. The absence of any enhancement in the 5119-Å iodine line, and the apparent absence of any contribution from iodine at this wavelength could be interpreted to mean that the majority of the $1s_5$ krypton atoms are used up in reactions with iodine molecules. Unfortunately it is not known definitely that any upper excited state of iodine dissociates into one ground-state atom and one $6p^4P_{3/2}$ atom; but neither is such a transition ruled out.[16]

V. CONCLUSIONS

A flash lamp producing intense emission at 2062-Å has been described. Addition of xenon or krypton to a flashlamp containing iodine enhanced the output of the 2062-Å atomic-iodine line by means of energy-transfer collisions between the excited inert-gas atoms and iodine atoms or molecules. In addition, a similarly great enhancement of this line could be obtained in an ac discharge containing xenon and iodine. The strong emission of this lamp at 2062-Å should make it a useful source for photochemical studies or as an intense spectroscopic source at this wavelength. In addition, this lamp may be useful for certain laser-pumping operations if the pumping bands are in the ultraviolet near 2062 Å.

ACKNOWLEDGMENTS

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[15] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford Univ. Press, London, 1952), Ch. VII.

[16] L. Mathieson and A. L. G. Rees, J. Chem. Phys. **25**, 753 (1956).