The Iodine Lamp: A Light Source for Selective Excitation of CO

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Dedicated to Prof. Dr. W. Groth *on his sixtieth birthday*

A light source has been developed for photochemical studies which emits the 2062 Å line of iodine. This lamp has been used to study reactions of CO excited in the a $^3\Pi$ level. Carbon monoxide was irradiated in an experimental lamp incorporating an arrangement of concentric cylinders. The output of this lamp was $2 \cdot 10^{18}$ quanta per second. The CO a$^3\Pi$ molecules react to form CO_2 with a quantum efficiency between a few tenths and unity.

A series of lamps exists for photochemical studies in the near and far ultraviolet. Most commonly used are the mercury lamps with the two resonance lines at 2537 and 1849 Å. These lamps are convenient in many cases but suffer from the disadvantage that the gases used must be extremely clean with respect to mercury to prevent interference with the overall process by reactions with excited mercury atoms.

Many years ago the xenon resonance lamp with its two resonance lines at 1470 and 1295 Å was developed[1]. Such lamps were used for many interesting investigations in Haber's institute, in Hamburg[2], and in Bonn [see, for example, references [3] and [4]], and are today extensively used by many experimenters. Later on the krypton lamp[5] and the hydrogen lamp using Lyman alpha radiation were developed along similar lines. All these lamps are very useful for investigations in the far ultraviolet; however, except for N_2 and CO which absorb only to a minor extent at these wavelengths, all gases have very high absorption coefficients and selective experiments cannot be performed.

There is a special interest in the photochemistry of CO because it has been shown by radiation chemistry[6] and by the work of von Weyssenhoff, Harteck, and Dondes[7] as well as the recent work of Groth, Pessara, and Rommel[8] that CO if excited, may react with another CO forming CO_2 and carbon suboxide:

$$\begin{aligned} CO + CO^* \rightarrow \text{a) } & CO_2 + C \\ \text{b) } & C_2O + O \end{aligned}$$

Such reactions are of interest in themselves but are of further interest in connection with the chemosphere of Venus where CO may be expected to be present as a result of photodissociation of CO_2[9]. In our recent investigation of ultraviolet absorption spectra[9, 10] we became aware that the transition of CO from its ground state to the a$^3\Pi$ level (Cameron Bands) has an average absorption coefficient of about 0.01 cm^{-1}. Previous work[6–8] has been concerned with excitation of CO to higher levels where both reactions a) and b) could occur. Excited a$^3\Pi$ molecules, however, should undergo only reaction a). On the basis of energetic considerations reaction b) should not be expected to occur. In discussing all possible light sources for producing CO a$^3\Pi$ molecules, we realized that a certain very strong transition in the iodine system $5p^5\ ^2P_{1/2} \rightarrow 6s\ ^2P_{3/2}$ fell just within the (0,0) band of this CO transition. We have therefore developed an iodine lamp for the special purpose of exciting the a$^3\Pi$ level of the CO system which thus enables us to investigate the behavior of this metastable excited CO species. The

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[1] P. Harteck and F. Oppenheimer, Z. Phys. Chem. B **16**, 77 [1932].

[2] See, for example, W. Groth, Z. Phys. Chem. B **37**, 307, 315 [1937]; ibid. B **38**, 366 [1937].

[3] W. Groth and H. Schierholz, J. Chem. Phys. **27**, 973 [1957]; Planetary Space Sci. **1**, 333 [1959].

[4] W. Groth and H. von Weyssenhoff, Naturwiss. **44**, 510 [1957]; Ann. Phys., Lpz. (7) **4**, 69 [1959].

[5] W. Groth, Z. Elektrochem. **58**, 752 [1954].

[6] See S. C. Lind, Radiation Chemistry of Gases, Reinhold Pub. Corp., New York 1961, pp. 112–116.

[7] H. von Weyssenhoff, P. Harteck, and S. Dondes, to be published.

[8] W. Groth, W. Pessara, and H. J. Rommel, Z. Phys. Chem., N. F. **32**, 192 [1962].

[9] P. Harteck, R. R. Reeves, and B. A. Thompson, NASA TN D-1984 [1963].

[10] B. A. Thompson, P. Harteck, and R. R. Reeves, J. Geophys. Res., in press.

absorption coefficient of CO for the 2062 Å radiation emitted by this lamp is 0.0075 cm^{-1} which is quite adequate because at one atmosphere the energy absorbed by CO in a reaction vessel of few centimeters in depth will be rather constant. Absorption coefficients of other gases which may be present, CO_2, O_2, N_2, H_2O, are all less than 10^{-4} cm^{-1} at this wavelength. It is therefore possible to study reaction of this excited species without interference.

Theory

The emission spectrum of atomic iodine contains many strong lines in the ultraviolet extending from 2062 Å to shorter wavelengths. The spectrum has been analyzed in detail by Kiess and Corliss[11] and the energy levels have also been tabulated by Moore[12]. Fig. 1 shows an energy level diagram for iodine constructed from these tabulations. Many of

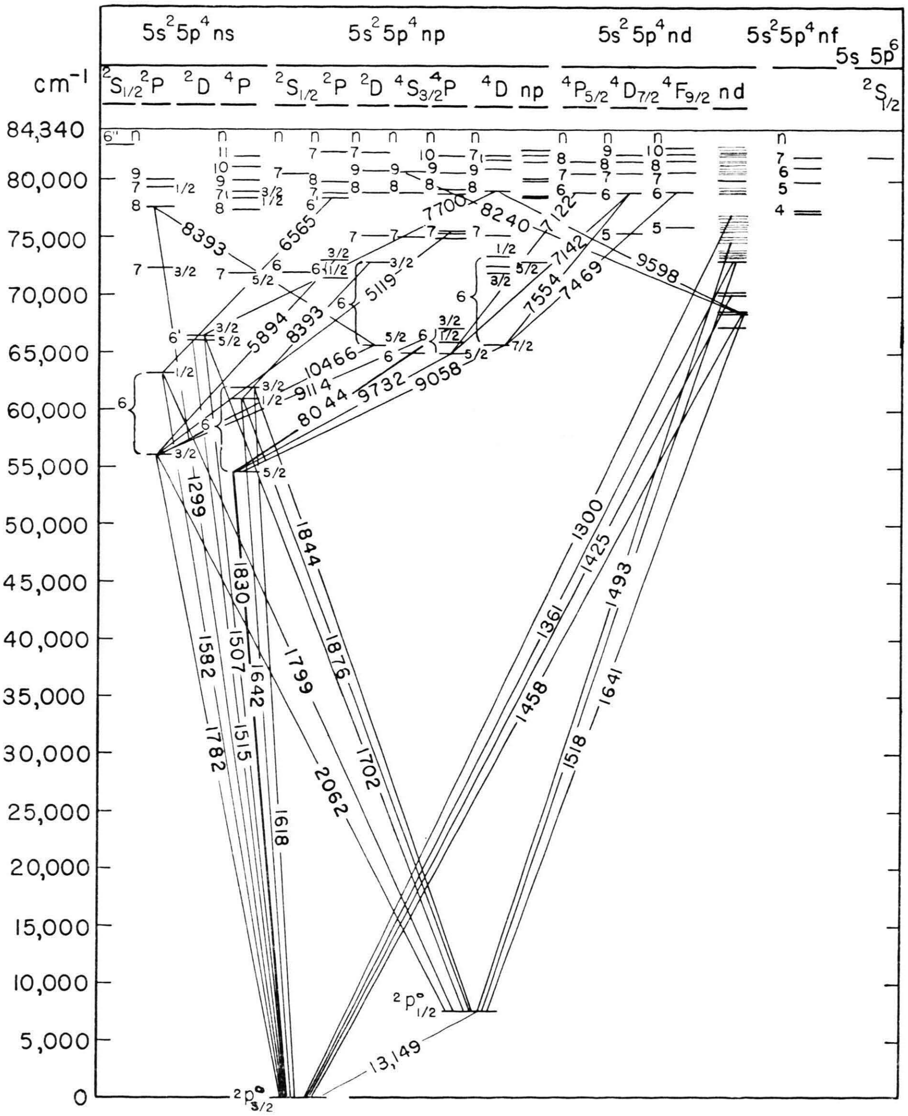

Fig. 1. Energy level diagram for iodine.

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[11] C. C. Kiess and C. H. Corliss, J. Res. Nat. Bur. Stand. **63** A, 1 [1959].

[12] C. E. Moore, Atomic Energy Levels, Vol. III, Nat. Bur. Stand. Circ. 567, 1958.

the close packed d and f levels are not resolved and only a few of the strongest transitions are shown. A detailed tabulation of all the observed transitions is given by Kiess and Corliss. From the diagram it can be seen that the intense line at 2062 Å corresponds to a transition between the $6s\ ^2P_{3/2}$ level and the $5p^5\ ^2P_{1/2}$ rather than the ground state $5p^5\ ^2P_{3/2}$ and thus is not a resonance line. It is also clear from the spacing of the levels that at wavelengths longer than 2062 Å there will be a large gap in the spectrum with no lines being observed. In fact, Kiess and Corliss report no lines between 2062 and 3552 Å. In addition, it is of interest that the next lines below 2062 Å are at 1876, 1844, and 1830 Å. Thus, by proper selection of window material, it should be possible to prepare a source of virtually monochromatic ultraviolet light.

A further advantage of the use of iodine is that its vapor pressure at room temperature is just under a millimeter which is ideal for use in a discharge.

Apparatus

Two types of lamps have been used for this work. The first was a small discharge tube about 6″ long with a quartz window at one end. Both electrode and electrodeless discharges could be applied to this tube. C. P. iodine was introduced into a side arm and was purified by fractional distillation. The most persistent impurity was water vapor, which not only caused high pressure in the lamp and made operation erratic, but also resulted in strong emission of the OH bands. When this had been removed, the lamp was quite constant in its output and the OH bands were no longer observed. This small lamp was used principally for the determination of absorption coefficients discussed below.

Photochemical experiments were carried out using a second type of lamp shown in Fig. 2. This consisted of an arrangement of concentric cylinders about 100 cm long, the inner one being made of quartz. Quartz windows were provided at each end for purposes of measuring the spectrum and monitoring the output intensity. The outer Pyrex jacket could be filled with any desired gas for photochemical studies. Argon was passed continuously through the inner cylinder and served the dual purpose of providing a stable discharge for excitation of the iodine and acting as a buffer to prevent chemical attack of the electrodes by iodine vapor. Earlier experiments had been carried out using a static system without addition of argon, but the flowing system proved to be much more satisfactory.

The emission spectrum of these lamps was measured with a Jarrel-Ash recording monochromator and was found to consist almost entirely of 2062 Å radiation with the 1876 Å line and the various continua near 3000 Å being weakly visible. The intensity of the 2062 Å line was about thirty times that of the 1876 Å line.

Absorption Coefficients

Absorption coefficients of CO, NH_3, N_2O for the 2062 Å line were determined using the small lamp mentioned above. The path length in each case was 94 cm. For CO the iodine emission at 2062 Å falls just within the 2059.6 Å (0,0) band of the $X^1\Sigma \rightarrow a^3\Pi$ transition (Cameron Bands). The ab-

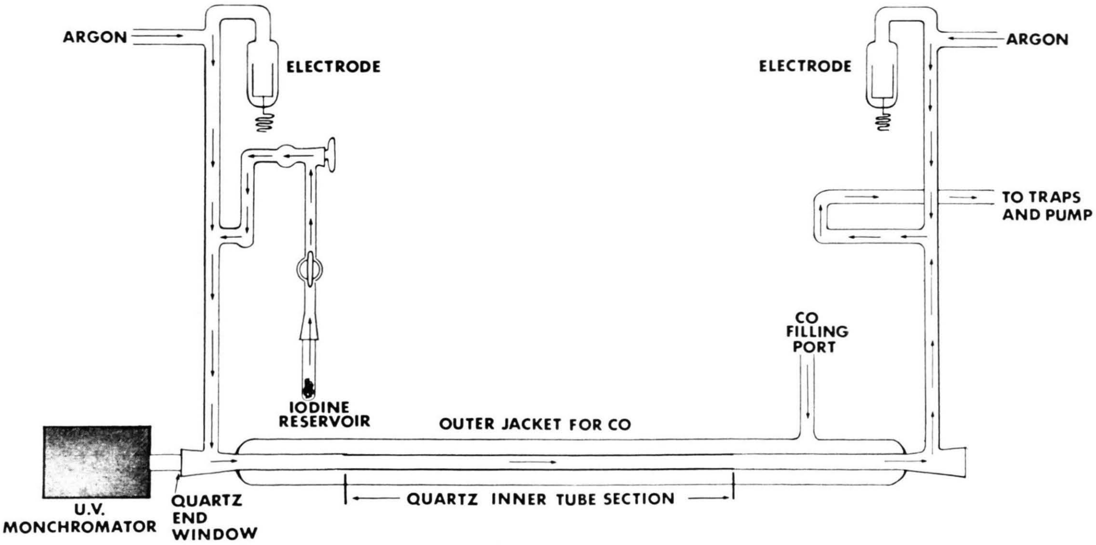

Fig. 2. Schematic diagram of iodine lamp.

sorption coefficient for CO for the 2062 Å line was found to be 0.0076 cm^{-1}. Those determined for NH_3 and N_2O were 23.8 and 0.374 cm^{-1} respectively. All those values are in good agreement with those reported elsewhere[10, 13]. For CO the 1876 Å line, present to a minor extent, is not absorbed since it falls between the (3,0) and (2,0) CAMERON bands.

Photochemistry

Calibration of Lamp Output

The output of the lamp shown in Fig. 2 was calibrated using the decomposition of ammonia as an actinometer. The quantum yield for this process has been determined at various pressures by WIIG[14] using zinc radiation of 2100 Å wavelength. The reaction products are reported to be only nitrogen and hydrogen in a 3 : 1 ratio. Since the absorption coefficient of NH_3 is less than 10^{-4} cm^{-1} at wavelengths longer than 2400 Å, the weak iodine continua near 3000 Å will not interfere with the calibration.

The calibration was carried out by filling the outer jacket of the lamp with purified NH_3 to a pressure of 150 mm. The lamp was then operated under normal conditions for 5 minutes. The intensity of the 2062 Å line was monitored continuously with the recording monochromator. At the end of a run a sample of the gas was analyzed mass spectrometrically and the increase in N_2 concentration was determined. From this and the quantum yield data of WIIG the output of the lamp was found to be 2×10^{18} quanta per second of 2062 Å radiation.

Irradiation of CO

Carbon monoxide was purified from iron carbonyl, CO_2, and other impurities by bubbling through concentrated sodium hydroxide solution followed by passing through successive cold traps. This purified CO was then introduced into the outer jacket of the iodine lamp and irradiated for various times. After irradiation the concentration of CO_2 in the CO was determined mass spectrometrically. In each case an analysis was made of the CO before irradiation to provide an accurate reference value. The difference between the two concentrations thus represented the CO_2 formed by the action of the iodine radiation. Fig. 3 shows a typical plot of CO_2 formed as a function of time. Clearly the CO_2 formation is linear with time. Knowing the volume contained in the lamp and the number of quanta absorbed, the quantum efficiency for CO_2 production can, in principle, be readily calculated. However, the rate of CO_2 production was found to be very sensitive to changes in temperature. This indicates that the absorption coefficient changes substantially with temperature, an effect which could be caused by broadening of the iodine line or changes in the relative population of CO rotational levels or to a combination of these factors. In an effort to evaluate the magnitude of this effect the absorption coefficient of CO was measured using light from the lamp shown in Fig. 2, thus providing a "high temperature" iodine line. The absorption coefficient varied somewhat with the operating power level of the lamp, but was about half that previously obtained at room temperature.

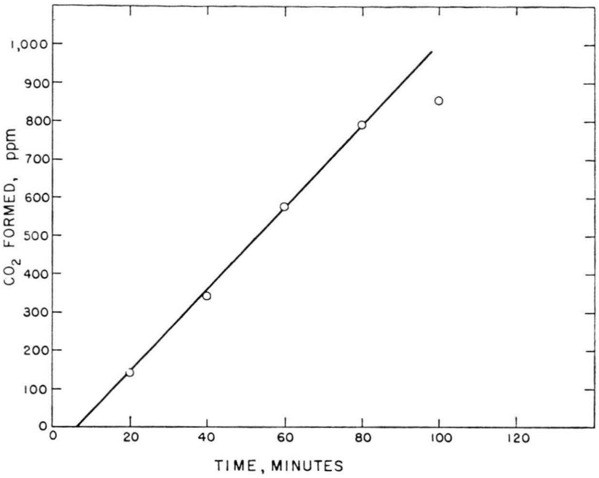

Fig. 3. Formation of CO_2 as a function of time.

These results show that changes in temperature of the lamp can lead to substantial changes in absorption by CO. Because the operating temperature of the lamp shown in Fig. 2 cannot be precisely con-

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[13] K. WATANABE, M. ZELIKOFF, and E. C. Y. INN, Absorption Coefficients of Several Atmospheric Gases, AFCRC Tech. Rpt. 53-23, 1953.

[14] E. O. WIIG, J. Amer. Chem. Soc. 59, 827 [1937].

trolled, we can only state that the quantum efficiency lies between a few tenths and unity. Experiments currently planned using a new lamp design should permit a more precise definition of this efficiency.

Irradiations were carried out at a variety of pressures between 200 and 700 mm and, as anticipated, no pressure effect was observed since in this region the absorption is linear and the collision lifetime is many of orders of magnitude shorter than the lifetime for light emission.

In this work other reaction products such as carbon and carbon suboxide polymer, which should also have been formed, were not investigated. In the static system shown in Fig. 2 such products would have accumulated on the vessel walls and would have been very difficult to detect under the experimental conditions employed.

Conclusions

The iodine lamp has been shown to be very useful for the photochemical study of excited CO ($a^3\Pi$) molecules. The lamp provides specific excitation to the $a^3\Pi$ level in its lowest vibrational level. The high quantum efficiency for reaction to form CO_2 provides an explanation for the fact that the CAMERON bands are never observed in emission except at very low CO pressures.

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Production of the Oxygen 5577 Å Emission by Polonium-210 Alpha Radiation*

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The production of the oxygen 5577 Å emission in purified nitrogen at atmospheric pressure by radiation with Po-210 alpha was studied spectroscopically. When the concentration of oxygen in the nitrogen was one part in ten thousand, the most intense emission observed was that of the forbidden atomic oxygen ($^1S \rightarrow {}^1D$) transition. This line emission at 5577 Å was seen to be associated with a continuum that extended from approximately 5600 to 5400 Å. To determine the reaction mechanism producing this emission, the effects of an electric field, temperature, and concentration of oxygen were examined. Several possible mechanisms are considered. The reaction producing oxygen atoms excited to the ^1S state which we found most favorable is shown below.

$$N^+ + O_2 \rightarrow NO^+ + O(^1S).$$

An understanding of the primary processes induced by ionizing radiation and of the reactions of the ions, atoms, and excited species formed are of paramount importance in radiation chemistry. An effective experimental approach to the problems in this field is to examine the emission spectra obtained by the irradiation of gaseous systems with the ionizing radiation of Po-210 alpha particles. It is the purpose of this paper to discuss an interesting observation which was made in an investigation of this type, namely, the presence of the forbidden auroral green line of atomic oxygen ($^1S \rightarrow {}^1D$) at 5577 Å in the spectra resulting from the irradiation of purified nitrogen containing small amounts of oxygen.

This auroral green line is observed when the oxygen concentration is about one part in ten thousand. The intensity of this line plus its associated continuum exceeds the intensity of any other spectra emitted under these conditions. Other than the associated presence of the 2972 Å ($^1S \rightarrow {}^3P$) line, no other lines of atomic oxygen (or atomic nitrogen) are seen.

The 5577 auroral green line is well-known from auroral and airglow studies in the upper atmosphere.

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