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Citation: The Journal of Chemical Physics **60**, 3721 (1974); doi: 10.1063/1.1681603
View online: http://dx.doi.org/10.1063/1.1681603
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/60/9?ver=pdfcov
Published by the AIP Publishing

Light emission from an argon discharge containing an admixture of carbon monoxide

G. Bekefi*, P. Avivi, F. Dothan-Deutsch, L. Friedland, J. L. Hirshfield†, and H. Keren

Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem, Israel
(Received 12 December 1973)

The electrical transport in a noble gas discharge can be altered appreciably by the addition of small amounts of molecular impurities. Argon is known to be particularly susceptible, and investigators[1,2,3] have reported large changes of the electron drift velocity produced by minute concentrations of hydrogen or nitrogen. Calculations show[3,4] that this increase in drift velocity is accompanied by a reduction of the mean electron energy and by a depletion of hot electrons in the tail of the energy distribution function. From this, one infers that addition of the molecular gas reduces the rate of inelastic excitations, ν_x, of the ground state argon atoms. This in turn reduces the population of excited states and thus would be expected to produce a diminution of spectral intensities of ArI lines. We report circumstances under which an unexpected *increase* in the line emission occurs when CO is added to the filling gas.

The experimental arrangement is shown in Fig. 1. Spectroscopic grade Ar and CO gases, purified by passage through a 1 m long cold trap, are flowed continuously through the discharge tube at a speed of ~1 m/sec, thus assuring a fairly clean discharge environment. Two Langmuir probes[5] measure the axial electric field E, the charge density N, and the mean electron energy $\langle U\rangle$. Light from the central section of positive column is focused onto the slits of the spectrometer (Jarrell–Ash Model 78-467) and the output from the photomultiplier (EMI 9558QB) is displayed on a chart recorder. A slitwidth of 100μ is used, giving an instrumental line broadening of ~1 Å. All intensities are therefore integrated line intensities. The range of the observed spectra is 3300–8500 Å.

A given experiment is conducted by first taking a spectral run in a pure argon discharge at a fixed pressure p(Ar) and a fixed discharge current $i = 30$ mA. Then, an amount p(CO) of carbon monoxide is introduced, and with the *same* p(Ar) and the same $i = 30$ mA, a rerun of the spectrum is taken. After subtracting the underlying continuum, the intensity I(Ar) of an atomic line in a pure argon discharge is compared with the value I(Ar + CO) measured in the presence of the admixture of CO. All ArI lines show these properties:

At low argon pressures, $p(\mathrm{Ar}) \lesssim 1$ torr, the intensity I(Ar + CO) is *smaller* than I(Ar) for all partial pressures of CO, $p(\mathrm{CO}) \lesssim 20\times10^{-3}$ torr. When p(CO) becomes too high [$p(\mathrm{CO}) \gtrsim 50\times10^{-3}$], the lines of atomic argon disappear, and continuum and CO bands dominate. The discharge acquires new characteristics, as witnessed by the greatly increased electric field E.

At high pressures of argon, $p(\mathrm{Ar}) \gtrsim 5$ torr, I(Ar + CO) is *greater* than I(Ar) for all pressures of CO up to $p(\mathrm{CO}) \approx 4\times10^{-3}$ torr. The enhancement in the ratio $I(\mathrm{Ar}+\mathrm{CO})/I(\mathrm{Ar})$ increases monotonically with p(CO); when p(CO) is $\sim 5\times10^{-5}$ torr, the light is enhanced by ~5%. Eventually, when p(CO) reaches a few millitorr, a doubling or tripling of the light emission occurs. Relatively few ArI lines can be seen; only lines whose lower level is a metastable level can be positively identified. Presence of the small amounts of CO causes at most a 15% increase in E. As the pressure of CO is increased beyond $\sim 4\times10^{-3}$ torr, an abrupt change in the discharge characteristics takes place; E increases suddenly, and the plasma column becomes unstable. At this point, all measurements are ended.

The enhancement of the atomic lines depends on wavelength. We systematized this by exhibiting the ratio $I(\mathrm{Ar}+\mathrm{CO})/I(\mathrm{Ar})$ of a given optical transition $m \rightarrow n$ as a function of the energy of the upper level m. In Fig. 1, we plot the foregoing intensity ratio vs the energy dif-

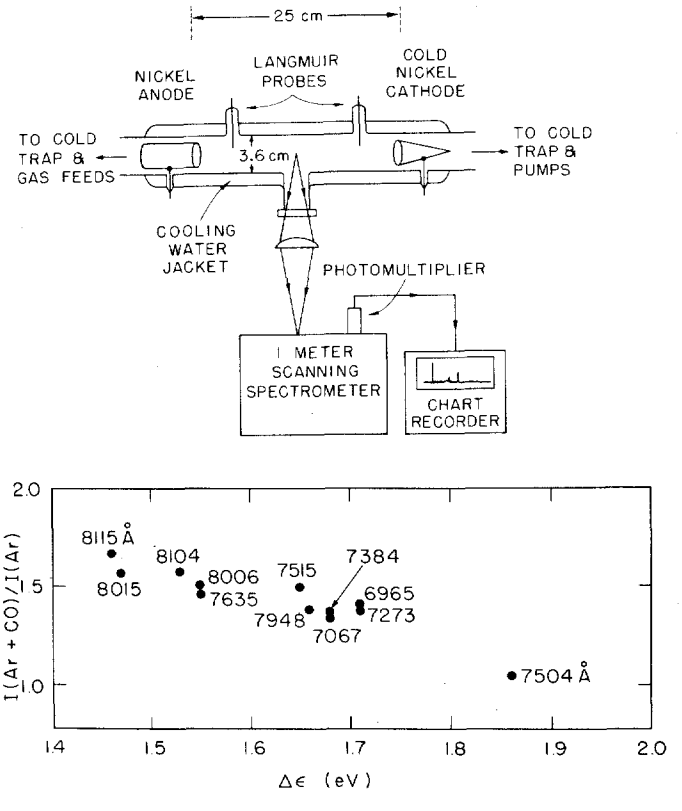

FIG. 1. Ratio of line intensity in an Ar–CO mixture to the line intensity in pure Ar, as a function of the energy gap between the upper radiating level of ArI and its upper metastable level. The numbers adjacent to the experimental points give the wavelengths of the lines; $i = 30$ mA; p(Ar) = 8.0 torr; p(CO) $= 2\times10^{-3}$ torr; $E = 5.4$ V/cm; $N = 6\times10^{10}$ cm^{-3}; $\langle U\rangle = 3.4$ eV; calculated $\nu_x \simeq 3.5\times10^5$ sec^{-1} with CO present; $\nu_x \simeq 6.4\times10^5$ sec^{-1} in pure Ar.

ference between state m and the upper argon metastable state, namely $\Delta\epsilon(\text{eV}) = \epsilon_m - 11.62$ eV. There is a monotonic decrease in the enhancement as $\Delta\epsilon$ increases. By way of contrast, one finds that at low pressures of argon (regime i, above) the reduction in the intensity caused by CO is about the same for all lines. The wavelength-dependent enhancement rules out the possibility of a geometric effect; that is, an alteration, upon introduction of CO, of the radial profile of the slightly "constricted"[6] argon column. The light increase is also seen at lower discharge currents ($i = 10$ mA) where the plasma column is unconstricted.[6]

The increase of the ArI lines induced by the presence of CO remains unexplained. One possibility is that CO destroys argon metastables, that ionization processes involving metastables are more important at the higher pressures (for argon, and our discharge tube diameter the metastable lifetime[7] peaks at $p(\text{Ar}) \simeq 1$ torr) and thus, in order to maintain the discharge, the number of high energy electrons increases. One may also ask whether the atomic levels are populated as a result of a nonresonant transfer of the vibrational energy contained in the CO molecule, where a vibrationally excited CO forms a temporary compound state with an argon metastable and transfers its energy. For this, the CO needs to be excited to moderately high vibrational states. Referring to Fig. 1, we note that $\Delta\epsilon$ equal to 1.51 eV requires 6 vibrational quanta to span it, and $\Delta\epsilon$ equal to 1.76 eV requires 7 quanta. Thus, the monotonic decrease in the light emission (Fig. 1) is not inconsistent with the progressive decrease in the expected population of the higher vibrational states. While no information is available concerning the magnitude of the energy exchange cross section, studies[8] of the quenching of vibrationally excited molecules by easily ionizable neutral atoms indicate large cross sections.

Finally we point out that a substantial concentration of CO metastables cannot be ruled out. Collisions of CO metastables with Ar atoms may produce higher excited states of Ar. Kenty,[9] working with high pressure rare-gas discharges, reports the appearence of line radiation upon the introduction of minute amounts of N_2. He tentatively blames this on the presence of N_2 metastables.

*Present address: Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139
†Present address: Mason Laboratory, Yale University, New Haven, CT 06511

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