SIMULTANEOUS IONIZATION AND EXCITATION OF DIATOMIC MOLECULES BY IMPACTS WITH POSITIVE IONS AND EXCITED ATOMS

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Abstract

A study of mixtures of helium, neon, and argon with carbon monoxide and nitrogen is made wherein it is demonstrated that impacts occur between a rare gas ion and a diatomic molecule leading to ionization and excitation of the latter. It is also shown that impacts of the second kind between excited helium and neon atoms and neutral carbon monoxide molecules, resulting in the simultaneous ionization and excitation of the latter, are possible. Experiments are described which show the effectiveness of either type of impact to be greatest when the energy difference is the least. These impacts are shown to explain several previously observed but unexplained effects in similar mixtures in glow dicharges. Two new bands in the Baldet-Johnson band system due to ionized carbon monoxide with edges at λ4454.95, 4458.94, 4480.24, 4485.00; and 4494.30, 4498.31, 4519.89, 4524.89 are reported and six new edges and a new band at λ3413.14, 3414.60; 3584.20, 3600.75; 4116.69, 4348.08; 5856.30, 5860.37, 5900.21, 5905.85 in the comet-tail system. The wave-lengths of the heads of all bands of these two systems observed in this investigation have been measured and an analysis of the systems is given. From a study of the intensity distribution of the negative band systems of carbon monoxide excited in He-CO and Ne-CO mixtures, the following deductions relative to the degree of excitation of the CO-ion in the two mixtures are made: In Ne-CO mixtures there are many more CO-ions in the 16.8 volt state than in the 20 volt state, but in He-CO mixtures the reverse is true. A study of the intensities of the individual comet-tail bands excited in He-CO and in Ne-CO mixtures under the same conditions shows that the exciting processes in He-CO mixtures are more effective in exciting the higher vibrational states of the comet-tail bands than they are in Ne-CO mixtures. The spectrum of carbon dioxide recently observed and reported by Fox, Duffendack and Barker has been shown to be due to the carbon dioxide ion.

EVERY now and then some unusual and interesting effect observed in an electrical discharge through a mixture of gases at low pressure is reported. The conditions under which most of the effects have been noted were those of the ordinary glow discharge. One of the most interesting of these effects is the modification of the spectra of the components of the mixture.

A series of investigations on the effect of helium, neon, and argon on certain diatomic gases has been conducted by Merton and Johnson;[1] Johnson;[2,3] Johnson and Cameron;[4] and Cameron.[5] The results of these investigations are summarized clearly in the Table I taken from Cameron's paper.

[1] Merton and Johnson, Proc. Roy. Soc. **A103,** 383 (1923).
[2] Johnson, Phil. Mag. **48,** 1069 (1924).
[3] Johnson, Proc. Roy. Soc. **A108,** 343 (1925).
[4] Johnson and Cameron, Proc. Roy. Soc. **A106,** 195 (1924).
[5] Cameron, Phil. Mag. **1,** 405 (1926).

TABLE I. *Summary of the observed effects of rare gases on the spectra of diatomic gases.*

System	Emitter	In helium	In neon	In argon
Comet-tail bands	CC^+	strong	less strong	absent
Associated bands (Baldet-Johnson)	CO^+	fairly strong	weak	absent
Negative carbon bands (1st negatives)	CO^+	very strong	moderately strong	very weak
Carbon arc lines	C	present	absent	absent
Negative nitrogen bands	N_2^+	strong	strong	absent
Nitrogen arc lines	N	present	present in part	absent
Triplet system	C	present	present	present
Ultra-violet oxygen bands	O_2^+	weak	weak	absent
Negative oxygen bands	O_2^+	fairly strong	very weak	absent
Oxygen O I	O	present	present	present
Oxygen O II	O^+	?	strong members present	absent

TYPES OF IMPACTS

The foregoing examples of mixture effects, together with many others not mentioned, make a systematic spectroscopic study of electrical discharges in gas mixtures desirable. It is the purpose of this investigation to make such a spectroscopic study, with a simple discharge, in order to demonstrate types of impacts which will explain many of the afore-mentioned effects.

Most of the mixture effects mentioned in the beginning have been observed in glow discharges. This type of discharge is unsatisfactory if an explanation of the observed effects is sought on the basis of impacts, because of the complexity of the phenomena occurring in the discharge. A type of discharge must be chosen wherein the conditions under which the discharge takes place are rather easily controlled. The low voltage arc meets this requirement.

Another most important reason for using the low voltage arc is that it permits the use of two filaments or hot cathodes, separately controlled both as far as electron emission and electron speeds are concerned. The use of such an auxiliary filament in the present investigation has aided materially in demonstrating the types of impacts just discussed above.

APPARATUS

A cross section of the discharge tube together with side and end views of the filaments and the plate is shown in Figure 1.

The discharge tube was made of Pyrex glass throughout. The stoppers S_1 and S_2 and the quartz window W were sealed in with hard deKhotinsky cement and the joints water-cooled to prevent softening when the tube was hot. The side tubes A and B were placed diametrically opposite to avoid reflection from the glass wall at the back of the tube. The filaments were made by winding five turns of 12 mil tungsten wire about another of the same diameter used as an arbor. These spirals were welded to the 100 mil tungsten leads. The U shaped tungsten plate P was placed about 8 mm from

the filaments. The entire tube was placed in an electrically heated oven so that it could be thoroughly outgassed.

The circuit used was similar in many respects to the low voltage arc circuit. The important differences were that the two filaments F_1 and F_2 were on separate circuits, and by means of a potential divider, it was possible

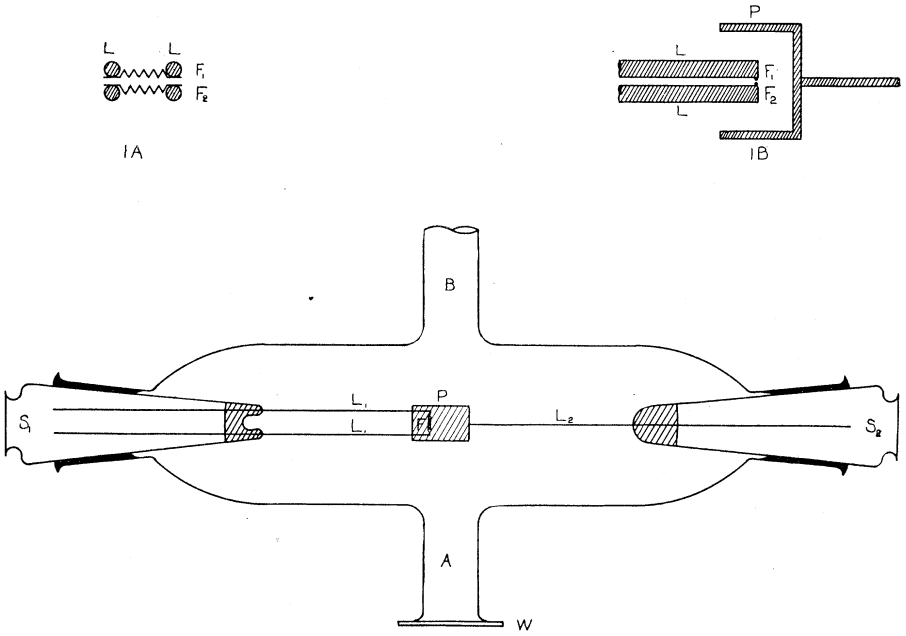

Fig. 1. The discharge tube.

to apply a smaller potential difference between F_2 and the plate than between F_1 and the plate. The necessary voltage for the filament and the plate circuits was supplied by storage cells.

The usual apparatus for purifying, circulating, and storing the gases used was employed in conjunction with the discharge tube. The entire system was exhausted by a single stage mercury diffusion pump backed by a Cenco-Hyvac oil pump.

Manipulation of the Apparatus

In evacuating the system preparatory to the admission of gas, the usual methods of pumping, and baking out of the discharge tube and charcoal traps were employed.

The helium was obtained from the Bureau of Mines at Washington, D. C. Impurities were removed by circulating the gas several times through charcoal traps at liquid air temperatures. Magnesium discharge tubes were also operated during this time to aid in purifying the gas.

The neon came from the Linde Air Products Company. This was admitted to the system and circulated through charcoal traps as in the case of helium. The neon was found to be very pure.

The argon was obtained from the Nela Research Laboratory at Cleveland. This gas was known to contain nitrogen. A calcium arc purifier was used successfully in removing the nitrogen from the argon.

The carbon monoxide was prepared outside the system by heating chemically pure oxalic acid crystals in the presence of concentrated sulphuric acid. This yields carbon monoxide with some carbon dioxide and water vapor. The mixture was passed through a wash bottle containing a concentrated solution of potassium hydroxide to remove the CO_2. The remaining gas was passed over phosphorus pentoxide to remove the water. Any water vapor and carbon dioxide not removed at this time was condensed in the liquid air traps. The dried gas was allowed to flow into an evacuated bulb which filled up to atmospheric pressure. This bulb was sealed on to the system and the gas admitted through a stop-cock as desired.

In producing mixtures of a rare and a diatomic gas the rare gas was admitted first to the required pressure and the diatomic gas added very slowly and the two allowed to mix for some time.

Mixtures of the Rare Gases with Carbon Monoxide and with Nitrogen

The spectra of carbon monoxide excited by electron impacts[6] have recently been investigated in this laboratory. Nine band systems are now known. Six of these originate in the neutral molecule and the remaining three in the ionized molecule. The names of the bands and their respective excitation potentials are given in the accompanying energy level diagram.

Comparative runs were made, using mixtures of each of the rare gases with first, carbon monoxide and later nitrogen, under the same conditions. There were five important variable factors to be considered, namely: partial pressures of the rare gas and the diatomic gas, total gas pressure, potential difference between electrodes, current density, and region of the arc photographed.

After a considerable number of trials with total gas pressures ranging from 0.5 mm to 10 mm and with partial pressures of CO varying from one half to one fiftieth of the total, an optimum total pressure was found at 2.4 mm, with a partial pressure for the CO at 0.2 mm. Under these conditions an arc current of 40 milliamperes could be maintained under a potential difference of from 23 to 25 volts.

A region of the discharge about 4 mm from the filament was focussed on the slit of the spectrograph. It is in this region that the greatest concentration of positive ions produced by direct electron impacts is to be expected. Spectrograms made with the Hilger E2 quartz spectrograph under the above conditions showed in the He-CO mixture a beautiful development of the three band systems of CO, to the practical exclusion of the bands due to the neutral molecule. In the Ne-CO mixtures the first negative bands were present, but weak, the comet-tail bands were fairly strong, and the Baldet-

[6] Duffendack and Fox, Astrophys. J. **65**, 214 (1927).

Johnson bands absent. In the A-CO mixtures all of the band systems due to the ionized molecule were entirely absent.

Simultaneous Ionization and Excitation of Molecules by Positive Ions

In order to account for the development of the band systems of ionized CO in He-CO and Ne-CO mixtures the following three possible processes must be considered: (1) Direct electron impacts, (2) Impacts of the second kind with excited rare gas atoms, (3) Impacts by slow positive ions.

1. *Direct electron impacts.* The simultaneous ionization and excitation might be due to direct electron impacts as Duffendack and Fox[6] have shown to be possible.

That this process is not operative was shown by taking two spectrograms with an He-CO mixture in the tube. In the first, the applied potential difference between the cathode and the plate was 24.7 volts. The second filament was hot but no potential difference was applied between it and the plate. The arc current was 40 milliamperes. In the second, a voltage greater than the excitation potential of the first negative bands, 20 volts, but less than the ionization potential of helium, 24.5 volts, was applied between the auxiliary filament and the plate. The arc current was then 120 milliamperes. The current from the auxiliary filament being now twice as great as from the cathode, the possibility of excitation of the negative bands by direct electron impact was thereby increased threefold, while the concentration of helium ions was increased very little. The intensity of the first negative bands in the second case was not noticeably greater than in the first. It is to be concluded then that under the above conditions the CO molecule is not ionized and excited by direct electron impacts.

2. *Impacts of the second kind with excited rare gas atoms.* The helium spectrum is made up of singlets and triplets. The singlet series belongs to parhelium and the triplet series to orthohelium. The lowest term of parhelium is a 1^1S term corresponding to the normal helium atom; the lowest term of orthohelium is a 2^3S corresponding to an energy of 19.8 volts. The 2^1S term corresponds to an energy of 20.5 volts. The neon atom has its lowest excited state at 16.6 volts.

From the accompanying energy level diagram for carbon monoxide, Fig. 2, it is to be noted that the 19.8 volt level of orthohelium and the 16.6 volt level of neon almost exactly coincide with the minimum excitation potentials of the first negative and comet-tail bands respectively. Hence it is to be expected that in He-CO and Ne-CO mixtures, collisions of the second kind may occur between the excited rare gas atoms and the CO molecules, wherein the latter are simultaneously ionized and excited. The small energy difference of 0.2 to 0.3 of a volt may be expected to come out of the relative kinetic energy of translation of the two colliding molecules, as Franck has shown to be possible. However a study of the first negative bands excited in He-CO mixtures and the comet-tail bands excited in Ne-CO mixtures shows an absorption of energy in the vibrational states of 0.8 volt and 0.7 volt re-

spectively, thus increasing the total energy necessary to excite the band system in the one case to 20.8 volts and in the other to 17.5 volts. While these values increase the amount of energy to come out of translational energy to rather large values, still the possibility of simultaneous ionization and excitation of CO molecules by excited He and Ne atoms must be considered.

When nitrogen is substituted for carbon monoxide the situation is somewhat changed, since the excitation potential of the negative band system of nitrogen, which is less than the ionizing potential of neon, lies far enough above the strong radiating potentials of neon to preclude the simultaneous ionization and excitation of nitrogen molecules by excited neon atoms. However, spectrograms taken with Ne-N_2 mixtures in the discharge tube under the same conditions used for Ne-CO mixtures showed a strong development of the negative bands of nitrogen. As a result it must be concluded that the appearance of the negative bands is not due to collisions of the second kind between excited rare gas molecules and the molecules of N_2, but that the N_2 molecule is ionized by contact with the neon ion.

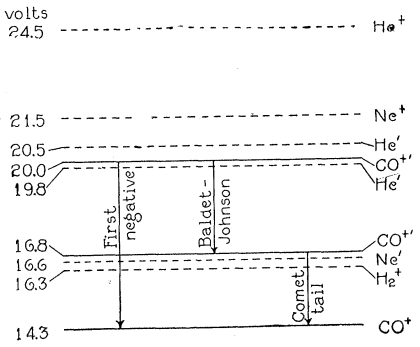

Fig. 2. Energy levels of H_2, Ne, He, and CO^+.

In case both positive ions and excited atoms are present, each possessing sufficient energy to ionize a neutral molecule, then it is to be expected that both types of impacts will occur. Presumably that impact will be most effective wherein the energies are most nearly the same.

3. *Impacts by slow positive ions.* The results of the preceding considerations indicate that the rare gas ion is an effective agent in producing the bands of the ionized diatomic molecule. If the rare gas ion is effective in exciting the negative bands, two possibilities suggest themselves, namely: 1. The rare gas ion upon contact with the molecule might ionize and excite the latter simultaneously, or 2. The excitation of the molecule-ion by direct electron impact might follow as a later event after the molecule had been ionized by the rare gas ion.

That this latter process was not operative was demonstrated by introducing into the discharge, electrons from the auxiliary filament at a voltage sufficiently great to excite the CO ions on collision. Here again the electron current from this filament was twice as great as from the cathode, the total

current being 120 milliamperes. *However, no increase in the intensity of the negative bands was observed.* On the other hand, the electrons from the auxiliary filament were effective in developing the bands due to the neutral CO molecule, especially the third positive bands. These bands, not present in the original discharge, appeared with moderate intensity in the discharge with the auxiliary filament in operation, when the difference of potential between the auxiliary filament and the plate was equal to their excitation potential. In mixtures containing nitrogen the second positive bands of nitrogen were present even though the auxiliary filament was not used, but their intensities increased enormously when the voltage of the auxiliary filament reached their excitation potential. This suggests a new method for determining the excitation potentials of positive bands and arc lines.

Simultaneous Ionization and Excitation of Monatomic Molecules by Positive Ions

In some recent experiments by Duffendack and Black, as outlined in a preceding paper, it is demonstrated that positive ions of high ionization potential may simultaneously ionize and excite monatomic molecules. In neon-copper mixtures those lines originating in levels lying between 21.0 and 21.4 volts were greatly enhanced due to the fact that these levels are in resonance with the neon ion at 21.5 volts.

The reaction may be written:

$$Ne^{+}+Cu \rightarrow Cu^{+\prime}+Ne$$

The failure of the excited neon atoms, 16.6 volts, strongly to excite the Cu^{+} levels lying between 15.9 and 16.8 volts is probably due, as suggested by Professor J. Franck, to the presence of molecular hydrogen, which, with an ionization potential of 16.3 volts, quenched the excited neon atoms.

The reaction may be written:

$$Ne^{\prime}+H_2 \rightarrow H_2^{+}+Ne+e$$

Impacts by Slow Positive Ions vs. Impacts by Excited Atoms

Since in a discharge through a He-CO mixture there are He ions and excited He atoms, it is important to determine, at least in an approximate way, which is more effective in exciting the bands of CO, the He ion or the excited He atoms. A similar statement may be made for Ne-CO mixtures. Professor J. Franck has suggested that by adding hydrogen it should be qualitatively possible to say which is more effective in exciting a given band system, a positive ion or an excited atom.

The following table shows the possible reactions in mixtures of He-CO-H_2 and Ne-CO-H_2, listed presumably in the order of their probabilities. It is assumed that the probability of the impact is greatest when the energy difference is the least. The energy values of the various components may be obtained from the accompanying energy level diagram, Fig. 2.

The experimental work was carried out as follows:—Hydrogen was prepared by the electrolysis of water carefully dried over P_2O_5 and de-oxidized

by being in contact with a hot tungsten filament in the presence of P_2O_5 for several hours. Helium was introduced into the system to a pressure of 2 mm, then CO was added until the total pressure was 2.2 mm. With a plate voltage of 26 volts and an arc current of 40 m. a., a spectrogram was made in 30 minutes with a Hilger E2 spectrograph. A second exposure was made

TABLE II. *Possible reactions in He-CO-H_2 and Ne-CO-H_2 mixtures.*

Reactions	Energy difference (volts)
(a) $He' + CO \rightarrow CO_{20}^{+'} + He + e$	$-.2$ to $.5$
(b) $He' + CO \rightarrow CO_{16.8}^{+'} + He + e$	3.0 " 3.7
(c) $He' + H_2 \rightarrow H_2^+ + He + e$	3.5 " 4.2
(d) $He^+ + CO \rightarrow CO_{20}^{+'} + He$	4.5
(e) $He^+ + CO \rightarrow CO_{16.8}^{+'} + He$	7.7
(f) $He^+ + H_2 \rightarrow H_2^+ + He$	8.2
(g) $Ne' + CO \rightarrow CO_{16.8}^{+'} + Ne + e$	$-.2$
(h) $Ne' + H_2 \rightarrow H_2^+ + Ne + e$	.3
(i) $Ne^+ + CO \rightarrow CO_{20}^{+'} + Ne$	1.5
(j) $Ne^+ + CO \rightarrow CO_{16.8}^{+'} + Ne$	4.7
(k) $Ne^+ + H_2 \rightarrow H_2^+ + Ne$	5.2

with all conditions the same except that 0.01 mm of H_2 was added. In a third exposure the partial pressure of H_2 was 0.05 mm, and in a fourth hydrogen pressure was 0.1 mm, that is, there was one half as much hydrogen as carbon monoxide.

Next, two exposures were made with Ne-CO mixtures in the discharge tube, the first with no hydrogen present and the second with 0.1 mm of hydrogen added. The plate voltage was 25 volts and the arc current 40 m.a.

The results of these experiments are summed up in the following table:

TABLE III.

No.	Partial pressures (mm)				Intensities of the band systems		
	He	Ne	CO	H_2	First negative	Baldet-Johnson	Comet-tail
1	2		0.2	—	strong	strong	strong
2	2		0.2	0.01	"	"	"
3	2		0.2	0.05	weaker	weaker	much weaker
4	2		0.2	0.10	"	"	very weak
5		1.85	0.18	—	weak	absent	fairly strong
6		1.85	0.18	0.10	no change	"	very weak

The reduction in intensity of the comet-tail bands, as shown in No. 4 above, is presumably due to the fact that reactions (*b*) and (*c*) are about equally probable. The smaller reduction in intensity of the first negative and Baldet-Johnson bands indicates that reaction (*a*) is much more probable than (*c*) and that (*d*) is more probable than (*f*). The first negative and Baldet-Johnson bands are no doubt largely excited through reaction (*a*) and to a lesser degree through reaction (*d*).

The failure of the Baldet-Johnson bands to appear in Ne-CO mixtures may be due to the fact that the transition probability from the 20 volt level

of CO^+ to the normal level of the ion is greater than that to the 16.8 volt level. In Ne-CO mixtures the 20 volt level is reached through reaction (*i*) only, which does not seem to be extremely probable; since the first negative bands do not have a great intensity in these mixtures. Number 6 in Table III shows that the addition of hydrogen does not affect the intensity of the first negative bands, which indicates that reaction (*k*) is quite improbable. In Ne-CO mixtures there appears to be a greater reduction of intensity of the comet-tail bands when H_2 is added than there is in He-CO mixtures. This is probably due to the fact that the 16.8 volt of CO^+ is the final level for the Baldet-Johnson bands and the intitial level of the comet-tail bands, hence in He-CO mixtures where the Baldet-Johnson bands are strong the addition of H_2 can only effect the direct excitation of the 16.8 volt level while in Ne-CO mixtures the excitation of the 16.8 volt level is due almost entirely to a direct process (*g* in Table II), but since (*h*) may be expected to be equally probable, the addition of H_2 should greatly affect the intensity of the comet-tail bands. This is in agreement with the results shown in Table III.

Conclusion

The results of the fore-going experiments demonstrate conclusively two types of impacts, wherein a neutral molecule is simultaneously ionized and excited.

1. An ion of one kind may, upon collision with a molecule of another gas, ionize that molecule and excite the resulting molecule-ion to the degree that the work of ionization of the one exceeds that of the other. This means that an ion may rob a molecule of an electron, and at the same time give to the resulting ion the excess energy made available by its recombination with the electron over the amount needed to take that electron out of the molecule. Since the energies of excitation are quantized there is usually some energy to be accounted for, and this probably goes into increased kinetic energy of one or both particles involved in the collision.

2. An excited atom of one kind may, upon collision with a molecule of another gas, ionize that molecule and excite the resulting molecule-ion to the degree that the energy of excitation of the one exceeds the work of ionization of the other. In this process an electron is liberated and must take up its share of any excess energy as kinetic energy of translation.

It is also demonstrated that the effectiveness of these impacts in ionizing and exciting a molecule depends upon the energy difference between the states involved, that type of impact being most effective wherein the energy differences are the least.

There is no reason to believe that the method of excitation either by a positive ion or an excited molecule is limited to the ions or excited molecules of the rare gases or to multi-atomic molecules. The same processes may be expected to occur in any mixtures of gases or vapors and should find some application in the production of the first spark spectra of atomic ions to the exclusion of higher spark spectra or even of higher levels in the first spark spectra, and in the approximate determination of the excitation potentials of the spark lines.

Simultaneous Investigations

During the progress of this investigation two other investigations of a somewhat similar nature, but attacking the problem from a different standpoint were being carried on, one by Harnwell[7,8] at Princeton and the other by Hogness and Lunn[9] at the University of California.

It is very evident that, while the results of these two investigations are in harmony with those obtained by the writers, they are not as specific regarding the disposition of the energy in excess of that necessary to produce ionization.

Band Systems of Ionized Carbon Monoxide

The First Negative Bands

The appearance of the first negative bands of carbon monoxide when excited in the helium mixtures is different from that when the bands are excited by direct electron impacts. In the latter case the fine structure seems to be continuous right up to the head of the band, while in the former there is a break in the fine structure just back of the head which indicates an absence of transitions originating in low rotational states.

Baldet-Johnson and Comet-Tail Band Systems

Two bands in the Baldet-Johnson system, one comet-tail band and several band edges in this system not previously reported were observed in

Table IV. *Baldet-Johnson bands. n', initial vibrational levels; n'', final vibratinal levels.*

	n''	$n'=0$	1	2	3
Int.		7	5		
λ	0	3978.29	3729.88	3515.8	3331.9
ν		25129.3	26803.5	28434.9	30004.3
		1674.2	1631.4	1569.4	
$\Delta\nu$		1530.8			
Int.		5			
λ		4236.36			
	1				
ν		23598.5			
$\Delta\nu$		1504.7			
Int.		3	1		
λ		4524.89	4205.74		
	2				
ν		22093.8	23770.3		
		1676.5			
$\Delta\nu$			1480.0		
Int.			1		
λ			4485.00		
	3				
ν			22290.3		

[7] Smyth and Harnwell, Nature, Jan. 15, (1927); Harnwell, Phys. Rev. **29,** 683 (1927).
[8] Harnwell, Phys. Rev. **29,** 830 (1927).
[9] Hogness and Lunn, Phys. Rev. **30,** 26 (1927).

spectrograms of the helium-carbon monoxide mixture. The wave-lengths of all the bands of both systems found on the spectrograms taken with the Hilger E1 quartz spectrograph have been carefully measured by interpolation between lines of the iron comparison spectrum. The wave-lengths and wave-numbers of the band edges of both systems together with their intensities are given in Tables IV and V. The two new bands in the Baldet-Johnson system are both of longer wave-length than those previously reported, and two bands of short wave-length observed by Johnson were not observed by the writers.

TABLE V. *Comet-tail bands.*

n''	$n'=0$	1	2	3	4	5	6
	Int 2	8	10	9	7	4	2
	λ 4879.72	4539.4	4248.66	3997.43	3777.86	3584.20	3413.14
0	ν 20487.4	22023.2	23530.0	25009.2	26462.2	27892.3	29290.5
	1535.8	1506.8	1479.2	1453.0	1430.1	1398.2	
	$\Delta\nu$ 2180.1	2183.6	2183.1		2177.7		
	Int 2.5	3	4		1		
	λ 5460.83	5039.03	4682.20		4116.69		
1	ν 18307.3	19839.6	21346.9		24284.5		
	1532.3	1507.3					
	$\Delta\nu$ 2154.3	2154.0					
	Int 2.5	1					
	λ 6189.06	5652.75					
2	ν 16153.0	17685.6					
	1532.6						
	Int		00				
	λ		5856.3				
3	ν		17071				

The addition of new bands to the Baldet-Johnson system aids in the analysis of the system. According to Birge,[10] these bands constitute a combination system between the initial states of the first negative and the comet-tail systems. The new Baldet-Johnson bands fit into the analysis made on this basis. The appearance of the bands excited in the various mixtures is in agreement with the above.

Not all the bands of the comet-tail system reported by Baldet[11] were observed either by Johnson or by the writers, in particular the band at λ5281A, corresponding to a wave-number 18,930 which in Baldet's analysis is taken as the 0—0 band. If this band is excluded and the band at λ4879.72A taken as the 0—0 band, as Birge has done, then both the comet-tail and the Baldet-Johnson band systems may be analyzed to include the new bands.

DEDUCTIONS FROM INTENSITY DISTRIBUTION OF NEGATIVE BANDS OF CO EXCITED IN HE-CO AND NE-CO MIXTURES

It is supposed that the CO ion possesses only two energy levels above the normal state, namely at 20 volts and at 16.8 volts, and that the CO ion

[10] Birge, Nature **117,** 230 (1926).

[11] Baldet, Comptes Rendus **180,** 272 (1925).

when once excited loses energy only by radiation. In He-CO mixtures all three band systems are strongly developed with almost equal intensity, the comet-tail bands the most strongly. Since the first negative and the Baldet-Johnson bands have the same initial level, there must have been many more CO ions in the 20 volt state than in the 16.8 volt state. In Ne-CO mixtures, the first negative bands are weak, the Baldet-Johnson bands absent and the comet-tail bands fairly strong. This indicates that in the Ne-CO mixtures there are many more CO ions in the 16.8 volt state than in the 20 volt state.

Vibrational States

The ratio of the intensity of a band excited in a Ne-CO mixture to the intensity of the same band excited in a He-CO mixture may be expected to be the same for all bands with a common initial level.

If one now takes the ratio of intensities of the individual comet-tail bands from the same initial level excited in He-CO and Ne-CO mixtures under the same conditions it is found that the ratio is approximately constant for a given value of n', but as one goes to larger values of n', the ratio decreases. This means that the exciting processes in He-CO mixtures are more effective in exciting the higher vibrational states of the comet-tail bands than they are in Ne-CO mixtures.

The Spectrum of Ionized Carbon Dioxide

Fox, Duffendack, and Barker[12] have recently devised a method for obtaining the spectrum of a gas while it flows continuously through the discharge tube. This method was applied to carbon dioxide and revealed a band spectrum not previously reported, which they assigned to the CO_2 molecule.

This same band spectrum has been obtained in He-CO-O_2, and Ne-CO-O_2 mixtures but not in A-CO-O_2 mixtures. A reduction in the total gas pressure during the exposure was noted in all cases which suggests a clean-up of the CO_2 molecules in the liquid air trap near the discharge tube. The failure of the spectrum to appear in A-CO-O_2 mixtures accompanied by the pressure reduction suggests that CO_2 molecules were formed but not excited.

Several runs were made using He-CO-O_2 and Ne-CO-O_2 mixtures with the auxiliary filament in use at voltages varying from 12 to 19 volts. No increase in the intensity of the bands was noted. This behavior suggests the simultaneous ionization and excitation of the CO_2 molecule by He and Ne ions, by excited He and Ne atoms or both. The immediate conclusion is that the so-called CO_2 bands are really due to ionized CO_2 molecules. In view of the fact that the bands appeared in neon but not in argon the excitation potential of the negative bands of CO_2 must lie between 15.4 and 21.5 volts, the ionization potentials of argon and neon respectively.

[12] Fox, Duffendack and Barker, Proc. Natl. Acad. Sci. **13**, 302 (1927).

The type of positive ion impact which has been demonstrated in this investigation obviously has very little effect on the number of charged carriers in the discharge tube since the process always results in the loss of a positive ion of one kind and a gain of one of another kind. If the newly formed ion has a different mobility than the ion instrumental in its formation a modification of the space charge may result as a secondary effect which may tend to change the value of the current through the tube. The ion formed in the impact while having the same charge will usually have a smaller energy than the ion making the impact, and since some of the energy of the latter is used in exciting the former, and since this energy of excitation is lost by radiation it is thus seen that more energy will be dissipated in the body of the gas than would otherwise be if the conditions were such that the impact could not occur. In this latter case more of the energy of the positive ions would be dissipated by recombination at the cathode where they are collected.

Ionizing impacts by excited molecules will, however, have an effect in cases of conduction of electricity through gases. These effects may be expected to appear in regions like the positive column of a glow discharge when an electric field must be maintained of sufficient intensity to produce ions by electron collisions in order to maintain a neutral space charge in the column. If ionization results from impacts with excited atoms a reduction of the intensity of the field may result and should be observed when a slight amount of a suitable gas or vapor is introduced into the discharge tube.