

EMISSION SPECTRA FROM SOLIDS CONDENSED AT VERY LOW TEMPERATURES FROM THE ELECTRICAL DISCHARGE PRODUCTS OF NITROGEN-CARBON MONOXIDE AND NITROGEN- ACETYLENE MIXTURES

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INTRODUCTION

IN a previous report¹ on the spectrum of the condensed deposits (4.2° K.) of microwave discharge products of nitrogen and carbon monoxide mixtures, a set of closely spaced diffuse bands between 3000 and 4600 Å were described. The present paper describes a second set of widely spaced, relatively sharper bands obtained from these solids under slightly different conditions. These bands are designated as sharp bands to distinguish them from the above-mentioned diffuse bands, though in reality they are not very sharp. Both sharp and diffuse bands have been obtained as well from the condensed deposits of discharge products of nitrogen and acetylene mixtures. The spectra also have been obtained by isotopic substitution with the following molecules, N₂¹⁵, C¹²O¹⁸, C¹³O¹⁶ and C₂D₂. A shift of the bands (both sharp and diffuse) was found only for C¹³ and not for the other isotopes.

EXPERIMENTAL

The experimental arrangement, consisting of a microwave oscillator, a low temperature Dewar and a gas flow system, was similar to that described previously.¹ Spectra were recorded on two grating spectrographs (an *f*/0.6 spectrograph with glass optics and a dispersion of 330 Å/mm. and an *f*/2.0 spectrograph with quartz optics and a dispersion of 20 Å/mm.) and an *f*/4 quartz prism spectrograph. Kodak 103 *a*-O and 103 *a*-F films and plates were used and times of exposure varied from 5 seconds to

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4 minutes; longer exposures (8 or 10 minutes) did not bring out any additional bands.

The sharp bands were best obtained in this system with a nitrogen flow of 15 cm.³/min. (NTP) and a carbon monoxide or acetylene flow of 1 cm.³/min. (NTP). Even though higher carbon monoxide flow rates (up to 60% CO in the total mixture) bring out these bands, no definite advantage was found in using flow rates higher than 1 cm.³/min., which was the lowest value that could be reproducibly measured with the flow meters that were used. Pre-purified nitrogen (purity 99.996%) and CP grade carbon monoxide (99.5% purity) were used for these experiments.

Two methods were used successfully with nitrogen and acetylene. In one method, the acetylene was mixed with nitrogen before entering the discharge region, as in the CO case. In the other method the acetylene was added to the discharge products of nitrogen about 5 cm. away from the cold finger. In the latter case the usual atomic flame was observed in the gas phase and the method essentially consisted in "freezing the atomic flame". The two methods gave the same spectra.

Experiments with carbon dioxide and nitrogen did not show the sharp or the diffuse bands. In the case of the discharge products of carbon dioxide condensed in an argon matrix, the spectra have shown the A bands (Herzberg bands)² of O₂ and a group of four bands at 5320, 5715, 6190 and 6743 Å. These latter bands may be Atmospheric Bands of O₂.

In both the carbon monoxide and the acetylene experiments the luminescence from the condensed deposit was violet in colour. As soon as the carbon monoxide (or acetylene) flow was stopped, allowing the nitrogen flow to continue, the luminescence changed from violet to bluish-green. The spectrum of this solid glow showed the diffuse bands previously described.¹ The bluish-green glow could be continued for more than an hour, the length of time depending on the amount of carbon monoxide or acetylene initially deposited. It should be pointed out that during the deposition of the nitrogen and carbon monoxide (or acetylene) mixtures, there also was emission from the gas near the solid. A weak pink glow could be observed surrounding the bottom tip of the cold finger. The spectrum of this gas-phase glow showed the violet and red systems of CN.

Isotopic nitrogen 15 at 50% and 90% concentration was used. For the higher concentration case, the evaporated sample containing nitrogen and carbon monoxide was mass-spectrometrically analysed and gave a ratio

2.5:1.3:1 for the mass numbers 28, 29 and 30. The O^{18} and C^{13} * (used in the form of CO) each had an isotopic concentration of 65% which was determined mass-spectrometrically before using it in the experiments. The deuterated acetylene used had a nominal deuterium concentration of 98%.

Most of the present series of experiments were conducted at liquid hydrogen temperatures because of its lower evaporation rate and because no difference in wavelengths, relative intensities or breadth of the sharp or the diffuse bands was observed at liquid helium temperatures. The only difference in the spectra was that at liquid helium temperatures the α -line of nitrogen was much stronger than the β -line of oxygen, while at liquid hydrogen temperatures the reverse was the case. This temperature effect agrees with the earlier observations on α and β .

RESULTS

The spectrum of the violet glow which gave the sharp bands is shown in Fig. 1. The upper spectrum was obtained during condensation and the lower spectrum was obtained during the warming of the condensed solid, after the refrigerant in the Dewar had evaporated. These spectra show a group of six strong bands with weaker components approximately midway between them.

In Tables I *a* and I *b* estimated eye intensities, wavelengths of the center of bands, widths of the bands, wavenumbers and wavenumber intervals of the sharp bands are given. These measurements are average values taken from a number of spectra on all three spectrographs. Table I *a* presents the data for the stronger bands while Table I *b* gives the data for the weaker components. The wavenumber interval is roughly the same for the stronger and weaker bands and is 2280 cm.^{-1} (with a maximum deviation of 80 cm.^{-1}). This frequency probably represents a common ground-state frequency for bands arising from two different vibrational levels of the upper electronic state. The strong bands, because of their high intensity, might arise from the zero vibrational level while the weaker ones might arise from a single quantum excitation of a vibrational frequency of about 1320 cm.^{-1} (maximum deviation of 30 cm.^{-1}) in the upper electronic state.

Figure 2 shows the diffuse bands obtained when the flow of carbon monoxide (or acetylene) was stopped and the glow changed from violet to bluish-green. The band data are given in Table II. The wavenumber interval between these bands is of the order of 670 cm.^{-1} (maximum deviation

* We are grateful to Dr. Robert Ferguson for preparing and supplying us $C^{13}O$,

TABLE I
Sharp bands

Intensity	(Centre) A	Breadth A	ν cm. ⁻¹	$\Delta\nu$ cm. ⁻¹
(a) Stronger bands:				
4	3013	10	33180	
8	3238	10	30874	2306
10	3502	10	28547	2327
				2266
9	3804	10	26281	
5	4165	10	24003	2278
2	4594	10	21761	2242
(b) Weaker components:				
1	3108	5	32166	
2	3347	5	29869	2297
2	3619	5	27624	2245
1	3950	5	25309	2315
1	4327	5	23104	2205
0	4810	5	20784	2320

100 cm.⁻¹). The data on the diffuse bands is in agreement with that previously reported.¹

Of the isotopes studied, only C¹³ produced definite and measurable shifts. Shifts occur for both the sharp and the diffuse bands. Figure 3 shows a comparison of the spectrum of the sharp and diffuse bands obtained with C¹³ and with C¹². The band data for C¹³ are given in Table III with a comparison of C¹² obtained with the same spectrograph. There is no shift for the first member of the sharp bands, *i.e.*, the 3010 Å band, and thus this band probably is the origin of the system. The other members of this series show a gradual increase in the width of the band, and a gradual shift

TABLE II
Diffuse bands

Intensity	(Centre) A	Breadth A	ν cm. ⁻¹	$\Delta\nu$ cm. ⁻¹	Blend with sharp band
1	2895	20	34523		..
				644	
2	2950	20	33888		..
				675	
6	3010	20	33213		×
				628	
3	3068	25	32585		..
				767	
4	3142	25	31818		..
				694	
5	3212	25	31124		×
				673	
4	3283	25	30451		..
				707	
5	3361	25	29744		×
				649	
6	3436	25	29095		..
				678	
6	3518	25	28417		×
				739	
8	3612	25	27678		×
				651	
8	3699	25	27027		..
				705	
8	3798	25	26322		×
				642	
10	3893	25	25680		..
				643	
9	3993	25	25037		..
				654	
9	4100	25	24383		..
				654	
8	4213	25	23729		..
				566	
6	4316	25	23163		..
				667	
5	4444	25	22496		..
				711	
6	4589	25	21785		×
				689	
1	4739	25	21096		..
				664	
0	4893	25	20432		..

TABLE III
Carbon¹³ substitution

Intensity	Designation	(Centre) A	Breadth A	ν (C ¹³) cm. ⁻¹	ν (C ¹²) cm. ⁻¹	(C ¹³⁻¹²) cm. ⁻¹
5	Sharp	3010	10	33213	33213	0
1	Diffuse	3140	15	31838	31808	30
3	Diffuse	3204	15	31202	31115	87
10	Sharp	3232	18	30932	30889	48
2	Diffuse	3278	20	30498	30423	75
3	Diffuse	3349	25	29851	29745	106
2	Diffuse	3432	25	29129	29053	76
10	Sharp	3489	22	28653	28571	82
3	Diffuse	3599	30	27778	27708	70
2	Diffuse	3687	30	27115	27027	88
6	Sharp	3782	20	26434	26288	146
1	Diffuse	3876	25	25793	25680	113
1	Diffuse	3978	..	25131	25024	107
1	Sharp	4117	10	24283	24037	246
1	Sharp	4143	8	24130	24037	93

in the center of gravity of the band toward shorter wavelengths. The fifth member, *i.e.*, the band at 4170 Å (this was too weak to be reproduced in Fig. 3) shows two relatively broad components separated by 150 cm.⁻¹. The one at the shorter wavelength is nearly twice as strong as the one at the longer wavelength. The components are shifted toward shorter wavelengths by 93 and 246 cm.⁻¹ with respect to the C¹² spectrum. If there are two carbon atoms in the emitter, one would expect, for the C¹³ concentration is 65%, three components corresponding to C₂¹², C¹²C¹³ and C₂¹³. The component corresponding to C₂¹² should be unshifted. Surprisingly enough, in the present case no unshifted component was observed. The diffuse bands

show a broadening and a shift toward shorter wavelengths with the C^{13} substitution.

The present experiments with the isotopes do not indicate the presence of nitrogen, oxygen or hydrogen atoms in the emitter, since no shifts were observed with the appropriate isotopes. Thus the previous¹ assignment of the diffuse bands to NCO and the sharp bands to CO_2^+ is not confirmed. There is a definite effect of the C^{13} isotope and an indication that at least two carbon atoms might be present in the emitters. The fact that the vibrational frequency (2280 cm.^{-1}) of the sharp bands is much higher than the ground-state frequency (1640 cm.^{-1}) of C_2 molecule suggests that the emitter may not be a simple diatomic molecule, but that it might contain more atoms which increase the carbon-carbon stretching frequency. Unfortunately, additional experiments have not given more information and the data are not sufficient to permit a reasonable assignment to the emitters nor to understand the mechanisms by which the two sets of bands are formed.

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SUMMARY

Two unidentified series of emission bands (sharp and diffuse) between 2900 and 4900 Å were observed at 4.2° and 20.4° K. These bands were emitted from the condensed products of microwave discharges in nitrogen-carbon monoxide and nitrogen-acetylene mixtures. The sharp series are characterised by a frequency difference of 2280 cm.^{-1} and the diffuse series by a frequency difference of 670 cm.^{-1} . Isotopic substitution shows at least one carbon atom is present in the emitting species.

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EXPLANATION OF PLATE I

Fig. 1. Sharp bands. Liquid helium temperature; $f/4$ quartz spectrograph; 103a-F emulsion; slit width 350μ ; CO and N_2 each at a flow rate of $7.5\text{ cm.}^3/\text{min}$. Exposure time for the glow is 10 minutes and for the warm-up is 3 minutes. Hg arc comparison spectrum taken with 20μ slit.

- FIG. 2. Diffuse bands. Liquid hydrogen temperature; $f/4$ quartz spectrograph; 103a-F emulsion; slit width $100\ \mu$; N_2 flow $7.5\ \text{cm}^3/\text{min.}$ for 2 minutes. Exposures are from the same negative, the top and bottom parts are exposed for 3 and 6 minutes respectively. Hg arc comparison spectrum taken with $20\ \mu$ slit.
- FIG. 3. C^{13} isotope effect. Liquid hydrogen temperature; $f/2$ grating spectrograph; 103a-O emulsion; spectrum at the top obtained with nitrogen flow of $15\ \text{cm}^3/\text{min.}$ and carbon monoxide flow of $1\ \text{cm}^3/\text{min.}$; C^{13} isotopic concentration 65%; exposure time 40 seconds; spectrum at the bottom obtained with nitrogen flow $15\ \text{cm}^3/\text{min.}$ and carbon monoxide flow $1\ \text{cm}^3/\text{min.}$; exposure time 60 seconds; slit width $400\ \mu$; Hg arc comparison taken with the same slit width.