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## Abstract

This report summarizes project activity during the period 1 January 1971 to 31 March 1971. Experimental measurements of  $15\mu\text{m CO}_2$  data are described. Preliminary results of the analysis of some of the data is given. Progress in experimental measurements of  $\text{O}_3$  spectra and the method of processing these medium resolution data are described.

## 1. Introduction

This is the 6th Quarterly Progress Report on Contract No. NSR 23-005-376, covering the period 1 January 1971 to 31 March 1971.

The project effort during this time was divided among the following tasks.

- A. High resolution measurements of the  $15\mu\text{m}$  absorption band of  $\text{CO}_2$ . (L. W. Chaney).
- B. Analysis of high resolution  $15\mu\text{m}$  absorption band of  $\text{CO}_2$  spectra. (S. R. Drayson).
- C. Medium resolution measurements of the  $9.6\mu\text{m}$  absorption band of  $\text{O}_3$  (L. T. Loh and P. A. Titus).
- D. Report Writing

## II. High Resolution measurements of the $15\mu\text{m}$ Absorption Band of $\text{CO}_2$ .

L. W. Chaney.

### A. Long Path (20 meter) Measurements

During the previous reporting period a program was initiated to cover the entire  $15\mu\text{m}$  band at high resolution using the approximate 20 meter path through the complete instrument. These measurements were continued and completed by Feb. 1, 1971. The only problem encountered was due to the wavelength shift resulting from a change in the index of refraction of the gas as the pressure was increased. Fortunately, the solution was quite simple. Known calibration lines were included in every scan.

Supplementary data was taken with the 8.74 cm cell at low pressure near the main Q-branch lines. This was done to identify individual lines in the Q-branch.

## B. Isotope Measurements

Three isotope enriched carbon dioxide samples were obtained.

(1)  $C_{13}O_{16}O_{16}$ , (2)  $C_{12}O_{16}O_{18}$ , and (3)  $C_{12}O_{16}O_{17}$ . The measurements were made in the 8.74 cm sample cell. The gas manifold was modified to receive the sample and a provision was made to trap the sample after the measurement using liquid nitrogen.

The measurements on the  $C_{13}$  sample were carried out satisfactorily in about two weeks with no complications.

The  $O_{18}$  measurements were delayed slightly and not completed due to a leak in the sample bottle. A portion of the sample was lost, but has now been replaced by the supplier (Isomet Corp.).

The leak was difficult to find. The system was not leaking to the outside atmosphere but from the sample to the gas manifold. The helium leak detector was not usable for this condition.

Data was taken on the third sample enriched in  $O_{17}$ . The measurements were approximately 90% completed when the spectrometer S/N ratio began to deteriorate.

An investigation has shown that the problem was due to a grating location screw which had become loose and thus had slightly tipped the beam. The spectrometer must now be re-aligned and re-assembled.

## C. Detector Investigation

Two infra red detectors were received from Texas Instruments

(1) The Cu-Ge detector is intended for the  $15\mu$  study.

(2) The Indium-Antimonide detector is intended for the  $4.3\mu$  study.

The sensitivity of the detectors was checked with a set-up as close as possible to that reported by Texas Instrument. The check indicated that the sensitivity of the Cu: Ge was low and when used in the spectrometer the output voltage was identical to a unit belonging to the Willow Run Laboratories, but the noise was twice as large. After re-checking the detector several times it was returned to the manufacturer. The unit has now been returned to Michigan and will be checked in the spectrometer. The other detector seems to be satisfactory.

During the next quarterly work period it is planned to re-assemble the spectrometer and complete the isotope CO<sub>2</sub> data.

The new indium antimonide detector and a new grating will be installed in order to take data in the CO<sub>2</sub> 4.3 $\mu$  band and the CO 4.6 $\mu$  band.

### III. Analysis of high resolution 15 $\mu$ m CO<sub>2</sub> spectra. (S. R. Drayson)

The analysis was continued to determine accurate values for the vibrational and rotational constants for CO<sub>2</sub> in the 15 $\mu$ m region. Some of the preliminary results are shown for some of the bands in Table 1-5. It is anticipated that only minor modifications will be necessary for Tables 1-3, but more major changes will be made to Table 5 when the analysis of the isotope enriched samples is completed.

The following is a brief discussion of the results and the methods used to obtain them. A detailed description will be given in a Technical Report as soon as the analysis of <sup>12</sup>C<sup>16</sup>O<sub>2</sub> is complete.

The basic calibration for the work was obtained from the CO<sub>2</sub> measurements of Gordon and McCubbin (1965). Lines of the  $\nu_2$  fundamental were used as calibration for the (020:2)-(010:1) band. These were then used

to recalibrate lines of the  $\nu_2$  fundamental and an iterative procedure was thus established. Convergence was very rapid (2 iterations). Note that the band center of the  $\nu_2$  fundamental has been shifted slightly from Gordon and McCubbin's value ( $667.379 \text{ cm}^{-1}$ ) to  $667.381 \text{ cm}^{-1}$ . The rotational constants for the ground state were provided by Benedict 1970 (private communication).

Table 1 b gives results for the  $\nu_2$  fundamental, based on measurements from  $J=32$  to  $68$ . The band center cannot be accurately determined from these data, so that the value from the P- and R- branches was used.

For the (020:2) - (010:1) transition (Tables 2 a and b) a band center is obtained for the (c-c, odd J) and (d-d, even J) transitions. It is a very good check on accuracy to obtain the band center from each of these and to compare the result. For this band the difference was less than  $0.001 \text{ cm}^{-1}$ . The values shown in the tables were obtained by solving simultaneously both sets of data.

The accuracy of the data for the (030:3) - (020:2) band is considerably less since lines are much weaker and tend to become blended with other weak lines or influenced by random noise in the spectra. They represent the first such measurement for the band. The band centers differed by  $0.002 \text{ cm}^{-1}$  when each of the even and odd set of J-numbers was treated separately.

In Tables 1a, 2a and 2b the results were obtained from a least squares fit of the sum of P(J) and R(J). A least squares fit of the P(J) and R(J) without adding them gave results that agreed very closely. For Table 3a and b this later technique was used since there were very few J-values for which the P- and R- branch line positions could both be accurately measured. This also applies to Table 5.

Tables 4 and 5 are for the isotopic molecules  $^{13}\text{C}^{16}\text{O}_2$  and  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  respectively. The former seems to be in a very satisfactory state, while the later will be considerably improved when the analysis of the isotopic enriched samples is complete.

#### IV. Medium resolution measurements of the 9.6 $\mu\text{m}$ absorption band of $\text{O}_3$

##### A. Experimental Details (L. T. Loh)

During the measurement of the infrared transmissivity of ozone, the quantity of ozone in the White cell will be determined by ultraviolet spectroscopy. The U. V. measurement system consists of a mercury vapor lamp, a quartz lens system in the White cell, a monochromator, and a 1P28 photomultiplier tube with amplifier and power supply. All components except the RCA 1P28 photomultiplier and lenses were purchased from Jarrell-Ash. They worked together qualitatively very well, with plenty of signal and good resolution. The signals, however, drifted. A series of tests were performed to determine the cause of the drift.

Measurements showed that the output of the mercury vapor lamp changed with the line voltage and also with the time after being turned on. When operated through a constant voltage transformer, the lamp output slowly decreased to a stable value in about an hour. Upon turning off and then turning on again, the output approached a stable value in minutes.

Even though the strength of the mercury lines was kept constant, the signal from the photomultiplier tube still was not reproducible. It was suspected that this was due to the extreme sensitivity of the photomultiplier tube to the operating voltage and poor reproducibility of the operating voltage.

Table 1a Band center, rotational constants and wavenumbers of lines in the P and R branches of the  $^{12}\text{C}^{16}\text{O}_2$  fundamental (010:1)-(000:0).

BAND CENTER= 667.381  
 BL= 0.3902180 BU= 0.3906369 BU-BL= 0.0004189  
 DL= 13.31D-08 DU= 13.47D-08 DU-DL= 16.21D-10

J	P CALC	O-C	R CALC	O-C	P+R CALC	O-C
2	665.821	0.002	669.727	-0.003	1335.548	-0.001
4	664.264	-0.001	671.295	0.002	1335.559	0.001
6	662.711	-0.001	672.867	0.002	1335.578	0.001
8	661.161	-0.005	674.442	0.000	1335.603	-0.005
10	659.615	-0.002	676.020	0.002	1335.635	0.000
12	658.072	0.000	677.601	0.002	1335.673	0.002
14	656.532	-0.003	679.186	0.003	1335.718	-0.000
16	654.996	-0.000	680.774	-0.001	1335.770	-0.001
18	653.464	0.003	682.364	-0.001	1335.828	0.002
20	651.935	-0.003	683.958	-0.001	1335.893	-0.004
22	650.410	-0.001	685.555	0.001	1335.965	-0.000
24	648.888	0.003	687.155		1336.043	0.003
26	647.370	0.001	688.758	0.003	1336.128	0.004
28	645.856	-0.002	690.364	0.001	1336.220	-0.001
30	644.345	-0.000	691.972	0.001	1336.318	0.000
32	642.838	-0.002	693.584	0.002	1336.422	-0.000
34	641.335	0.002	695.198	0.001	1336.533	0.003
36	639.835	0.002	696.816	-0.003	1336.651	-0.001
38	638.339	-0.004	698.436	-0.001	1336.775	-0.005
40	636.847	0.004	700.059	-0.003	1336.905	0.002
42	635.358	0.002	701.684	0.000	1337.042	0.002
44	633.874	-0.001	703.312	0.002	1337.186	0.001
46	632.393	-0.004	704.943	0.003	1337.336	-0.001
48	630.916	0.006	706.576	0.001	1337.492	0.007
50	629.442	-0.000	708.212	0.002	1337.654	0.002
52	627.973	0.000	709.850	0.001	1337.823	0.001
54	626.507	-0.003	711.491	-0.007	1337.998	-0.010
56	625.045		713.134	0.001	1338.179	-0.006
58	623.587	0.000	714.780	0.003	1338.366	0.004
60	622.132	0.001	716.428	0.003	1338.560	0.004
62	620.682	0.006	718.078	-0.006	1338.760	0.000
64	619.235	0.006	719.730		1338.965	
66	617.792		721.385	-0.004	1339.177	
68	616.353		723.042	-0.003	1339.395	-0.006
70	614.918		724.700	-0.005	1339.619	-0.008
72	613.487	-0.009	726.361	-0.002	1339.848	-0.011
74	612.060	0.004	728.024	0.006	1340.084	0.010
76	610.637	0.000	729.689	0.003	1340.325	0.004
78	609.217	0.000	731.356		1340.573	

RMS O-C = 0.0030 WAVENUMBERS

Table 1b Rotational constants and wavenumbers of lines in the Q branch of the  $^{12}\text{C}^{16}\text{O}_2$  fundamental (0100:0)-(000:0).

BAND CENTER= 667.381  
 BL= 0.3902180 BU= 0.3912529 BU-BL= 0.0010349  
 DL= 13.310-08 DU= 13.540-08 DU-DL= 22.590-10

J	Q CALC	O-C
32	668.471	-0.001
34	668.609	0.002
36	668.755	-0.000
38	668.910	-0.002
40	669.072	-0.005
42	669.243	-0.004
44	669.421	0.001
46	669.608	0.004
50	670.005	0.004
52	670.216	0.001
54	670.435	0.001
56	670.661	-0.001
60	671.138	-0.000
68	672.187	-0.001

RMS O-C = 0.0025 WAVENUMBERS



Table 2a Band center, rotational constants and wavenumber of lines in the P and R branches of the  $^{12}\text{C}^{16}\text{O}_2$  (020:2)-(010:1) band (c-c).

BAND CENTER= 667.751  
 BL= 0.3906375 BU= 0.3916697 BU-BL= 0.0010322  
 DL= 13.48D-08 DU= 13.94D-08 DU-DL= 45.64D-10

J	P CALC	O-C	R CALC	O-C	P+R CALC	O-C
3	665.413	-0.003	670.897		1336.310	-0.002
5	663.865	0.001	672.482	-0.004	1336.347	-0.003
7	662.325	0.001	674.075	-0.002	1336.401	-0.002
9	660.794	0.005	675.677	-0.001	1336.471	0.004
11	659.271	-0.000	677.286	-0.003	1336.557	-0.003
13	657.756	0.002	678.904	-0.003	1336.660	-0.001
15	656.250	0.002	680.529	0.001	1336.780	0.002
17	654.752	-0.002	682.163	-0.000	1336.915	-0.002
19	653.263	-0.004	683.805	0.003	1337.068	-0.001
21	651.782	0.004	685.454		1337.236	
29	645.942		692.130	-0.001	1338.073	
31	644.503	0.001	693.819	-0.004	1338.322	-0.003
33	643.073	0.004	695.515	0.000	1338.588	0.004
39	638.833	-0.003	700.648	0.000	1339.481	-0.003
41	637.436	0.003	702.374	0.001	1339.810	0.004
43	636.048		704.107	0.003	1340.155	0.005
47	633.297	-0.006	707.595	-0.002	1340.892	-0.008
49	631.934	0.005	709.350	-0.001	1341.284	0.004
51	630.580	-0.004	711.111	0.002	1341.691	-0.002
53	629.234	0.000	712.880	0.001	1342.114	0.001

RMS O-C = 0.0027 WAVENUMBERS

Table 2b Band center, rotational constants and wavenumbers of lines in the P and R branches of the  $^{12}\text{C}^{16}\text{O}_2$  (030:2)-(010:1) band of (d-d).

BAND CENTER= 667.751  
 BL= 0.3912529 BU= 0.3916621 BU-BL= 0.0004092  
 DL= 13.540-08 DU= 13.600-08 DU-DL= 57.400-11

J	P CALC	O-C	R CALC	O-C	P+R CALC	O-C
2	666.187		670.103	0.001	1336.290	
4	664.626	0.002	671.676	-0.004	1336.301	-0.001
6	663.068	-0.000	673.251	0.001	1336.319	0.001
8	661.514	0.005	674.830	-0.001	1336.344	0.004
10	659.963	0.005	676.412	-0.003	1336.375	0.002
12	658.416	-0.001	677.997	0.000	1336.412	-0.000
14	656.872	0.001	679.585	-0.002	1336.456	-0.000
16	655.331	0.004	681.176	0.000	1336.507	0.004
18	653.794	-0.000	682.770	0.001	1336.564	0.001
20	652.260	0.001	684.367	-0.000	1336.628	0.000
22	650.730	0.001	685.968	-0.003	1336.698	-0.002
24	649.204	-0.003	687.571	-0.002	1336.775	-0.005
26	647.681	-0.002	689.177	-0.002	1336.858	-0.004
28	646.162	0.001	690.786	0.000	1336.947	0.002
30	644.646	0.002	692.398	0.002	1337.044	0.004
32	643.134	0.000	694.012	0.001	1337.146	0.001
34	641.625		695.630	0.001	1337.255	0.002
38	638.620	0.004	698.873		1337.493	0.001
40	637.122	-0.003	700.499	0.001	1337.621	-0.002
42	635.629	-0.001	702.128	0.001	1337.756	0.001
44	634.139	0.002	703.759	-0.003	1337.898	-0.001
46	632.653	0.004	705.393	-0.003	1338.045	0.002
48	631.171	-0.006	707.029	0.003	1338.200	-0.003
50	629.692	0.001	708.668	0.000	1338.360	0.001
52	628.218	0.000	710.309	0.001	1338.527	0.001

RMS. O-C = 0.0023 WAVENUMBERS

Table 3a Band center, rotational constants and wavenumbers of lines in the P and R branches of the  $^{12}\text{C}^{16}\text{O}_2$  (030:3)-(020:2) band (c-c).

BAND CENTER= 668.105

BL= 0.3916621 BU= 0.3923806 BU-BL= 0.0007185

DL= 13.60D-08 DU= 13.91D-08 DU-DL= 30.90D-10

J	P CALC	O-C	R CALC	O-C
23	650.458		687.327	-0.002
25	648.961		688.965	0.012
27	647.469		690.608	0.000
29	645.983		692.256	0.004
31	644.504		693.909	-0.011
39	638.646	-0.020	700.573	
41	637.196	-0.003	702.252	0.005
43	635.753		703.936	0.005
45	634.316		705.624	0.007
51	630.040		710.718	-0.004
53	628.627		712.426	0.014
55	627.220		714.138	0.007
57	625.818		715.854	-0.015

RMS O-C = 0.0097 WAVENUMBERS

STOP 0  
EXECUTION TERMINATED

Table 3b Band center, rotational constants and wavenumbers of lines in the P and R branches of the  $^{12}\text{C}^{16}\text{O}_2$  (030:3)-(020:2) band (d-d).

BAND CENTER= 668.105  
 BL= 0.3916697 BU= 0.3923889 BU-BL= 0.0007192  
 DL= 13.94D-08 DU= 13.98D-08 DU-DL= 40.97D-11

J	P CALC	O-C	R CALC	O-C
4	664.980		672.043	-0.009
6	663.427		673.629	0.005
8	661.879		675.220	0.002
10	660.337		676.816	0.002
12	658.801		678.418	0.003
14	657.271	-0.009	680.026	0.004
16	655.747		681.639	0.001
18	654.228	-0.008	683.258	0.010
20	652.716	0.003	684.882	-0.009
22	651.210	0.012	686.512	
28	646.727	-0.012	691.434	0.000
30	645.245	-0.003	693.085	0.006
32	643.770		694.742	0.012
34	642.300		696.404	0.007
36	640.836		698.071	-0.007
38	639.379	-0.006	699.743	0.002
40	637.928		701.421	-0.004
42	636.483		703.104	-0.006
44	635.045		704.792	0.004
58	625.153		716.748	0.001

RMS O-C = 0.0068 WAVENUMBERS

Table 4 Band center, rotational constants and wavenumbers of lines in the P and R branches of the  $^{13}\text{C}^{16}\text{O}_2$  fundamental (010:1)-(000:0).

BAND CENTER= 648.481  
 BL= 0.3902350 BU= 0.3906002 BU-BL= 0.0003652  
 DL= 13.100-08 DU= 12.940-08 DU-DL=-16.270-10

J	P CALC	O-C	R CALC	O-C	P+R CALC	O-C
2	646.921	-0.005	650.827	0.001	1297.748	-0.004
4	645.364	-0.003	652.394	-0.001	1297.758	-0.004
6	643.809	0.002	653.965	0.001	1297.774	0.003
8	642.258	0.003	655.538		1297.796	0.003
10	640.710	0.000	657.114	0.002	1297.823	0.003
12	639.164	-0.000	658.692	0.002	1297.857	0.001
14	637.622	-0.000	660.274	0.001	1297.896	0.001
16	636.083		661.858	0.003	1297.942	0.004
18	634.547	-0.000	663.445	-0.000	1297.993	-0.001
20	633.015		665.035	-0.004	1298.050	-0.004
22	631.485		666.628	0.002	1298.113	-0.002
24	629.959	-0.000	668.223		1298.182	
30	625.400		673.024	-0.001	1298.424	
50	610.428	0.003	689.195		1299.623	0.002
52	608.950	-0.001	690.826		1299.777	-0.002
54	607.477	-0.001	692.460		1299.937	

RMS O-C = 0.0021 WAVENUMBERS

Table 5 Band center, rotational constants and wavenumbers of lines in the P and R branches of the  $^{12}\text{C}^{16}\text{O}^{18}\text{O}_2$  fundamental (010:1)-(000:0).

BAND CENTER= 662.367  
 BL= 0.3681640 BU= 0.3686018 BU-BL= 0.0004378  
 DL= 11.10D-08 DU= 12.45D-08 DU-DL= 13.46D-09

J'	P CALC	O-C	R CALC	O-C
3	660.161	0.019	665.321	
4	659.427		666.062	0.003
5	658.694		666.803	0.009
9	655.772	-0.013	669.778	
11	654.316	-0.012	671.270	
12	653.589	-0.008	672.018	
13	652.864	0.003	672.766	
14	652.139	-0.009	673.515	-0.001
15	651.415		674.264	0.011
16	650.692		675.015	-0.003
17	649.970		675.766	-0.004
18	649.248		676.519	0.004
21	647.090		678.780	0.009
22	646.372	0.004	679.535	
23	645.655	-0.010	680.291	-0.006
24	644.939	-0.004	681.047	
25	644.224	0.013	681.804	0.009
26	643.509	-0.003	682.562	-0.007
28	642.083	0.003	684.080	
31	639.950	-0.004	686.362	-0.009
33	638.531	-0.008	687.887	-0.009
34	637.824	0.012	688.650	
36	636.410	-0.001	690.178	
38	635.000	0.005	691.708	
39	634.296	0.000	692.474	
41	632.890	0.002	694.007	
42	632.188	-0.003	694.774	
45	630.087	0.001	697.079	
51	625.902	0.007	701.698	
65	616.216		712.510	-0.002

RMS O-C = 0.0077 WAVENUMBERS

A change of voltage from 400 to 520 volts changed the output by a factor of 7.75. This amounted to 30% change in voltage and a 675% change in output. The high voltage meter on the power supply had a full scale of 2000 volts. The span of 400-520 volts covered only 6 small divisions on the meter. To make the high voltage setting reproducible, a test point for an external digital voltmeter was installed on the power supply. The reading of 520 volts was made to show as 5.200 volts on the digital meter with a resolution of  $\pm 1$  digit or .02%. This addition drastically improved the resettability of the high voltage.

The UV spectrum of the mercury vapor lamp was recorded on a Brush recorder (fig. 1). All 6 lines mentioned in McCaa and Shaw (1967) were recorded with low background and good resolution. The very strong line at 3121.5 Å on p. 30 of McCaa and Shaw was adequately resolved into 2 peaks.

A chart (see fig. 2) showing the amount of ozone in atm-cm in the 3200 cm absorption cell vs  $(I/I_0) \times 100$  was prepared, based upon absorption coefficients given in McCaa and Shaw (1967) reproduced below for reference. This table shows 2 series of coefficients, one from Hearn (1961) and the other Walshaw (1957). The differences between them were not insignificant! The data of Hearn were used, except for the 3131.5 Å line. The net accuracy of these determinations of O<sub>3</sub> has yet to be determined.

The chart records of the infrared output of the Perkin Elmer Model 221 are not corrected for random variations in 0% and 100% transmittance. Because of the large amount of data that will be taken and the corrections needed, digital computer processing of the absorption data is desirable. The computer not only will make the 0% and 100% correction but also will provide the data

in a form suitable for further computer processing. After considering various possible ways of doing this, it was decided to use the laboratory's PDP-8 to record the raw data, to make the corrections, and to store the data for future use. The work is carried out as follows:

#### 1. Wavelength Data

The wavelength signal is generated in the form of pulses by a pentagon actuated microswitch plus power supply and logic circuits. The pentagon is mounted on a gear, rotated synchronously with the shaft of the wavelength counter. The shaft rotates at  $0.1 \mu\text{m}$  per revolution, corresponding to 5 actuations of the microswitch, or  $0.02 \mu\text{m}$  per actuation.

#### 2. Spectrum Data

The signal is an analog voltage corresponding to the pen deflection on the recorder of the spectrophotometer. The voltage swing is limited to  $\pm 5$  volts to conform to the requirement of the A to D converter of the computer.

Each data channel is sent from the spectrometer to the computer through a direct wire line. Each spectrum is started and ended between 2 selected wavelength limits, running 50 data points per  $\mu\text{m}$ . The 0% and 100% lines are sampled in the same way.

A purge solenoid valve for the McIntire air drying system was purchased and installed. This valve will save the air during the idling period.

A survey of room temperature was made at 2 locations in the spectrometer room. At each location, a thermistor was used, and its signal monitored with a Brush recorder.



Table 6  
 OZONE ABSORPTION COEFFICIENTS IN THE  
 ULTRAVIOLET FOR SIX Hg LINES  
 (after McCaa and Shaw)

Line No.	Wavelength (Å)	Absorption Coefficient $k(\lambda)$ (cmNTP) <sup>-1</sup>	
		Hearn	Walshaw (adopted)
6	2536.5	133.9 ± 1.9	115.7
5	2893.6	17.2 ± 0.3	16.0
4	2967.3	6.969 ± 0.030	
3	3021.5	3.340 ± 0.014	3.29
2	3131.5		0.76
1	3341.5	0.0498 ± 0.0007	0.0504

## B. Computer Processing of the Infrared Data (P. A. Titus)

Computer programs and interface hardware were developed during this work period for the PDP-8 data processing system. The data is processed in 3 steps.

- a) accept the voltage analog of transmissivity from the ozone system
- b) reduce it to transmissivity vs wavelength data
- c) punch the data on tapes for permanent storage and for further processing, plotting and analysis on an IBM 360/67 system

Analog voltages representing the transmissivities of 0 %, 100 % and of the gas sample (E) are generated by a precision potentiometer which is coupled to the optical attenuator of the spectrophotometer. Since the reference beam is attenuated to become equal to the intensity of the sample, the attenuator's position at null is a direct measure of the transmissivity. These voltages are connected by cable to the multiplexer on the computer.

The wavelength range of the prism is represented by a set of voltage pulses generated by a cam-switch unit. This unit is coupled to the wavelength cam of the monochromator scan motor. At each switch closure, the pulse is sent by cable to the computer where it is conditioned by the interface to the proper polarity, amplitude and duration, and connected to the computer interrupt line.

The data processing system consists of a PDP-8 computer, a multiplexer, an analog-to-digital converter and a time code generator. When the computer detects an interrupt pulse, the transmissivity analog voltage is

channeled through the multiplexer, measured and digitized by the analog-to-digital converter, and stored in the computer for processing.

The general procedure for the determination of the transmissivity of an ozone sample as a function of wavelength is as follows:

1. The 40 m cells are evacuated to better than 1.0 mm of Hg and the spectrophotometer is turned on and allowed at least an hour to stabilize.
2. Three sets of data are taken for steps 3 to 7, as follows.
  - a. A black painted card is inserted between the source of illumination and the light source optics.
  - b. The black painted card is removed.
  - c. An ozone sample is pumped into the sample cell.
3. The wavelength drive is set to the minimum wavelength.
4. The computer is turned on and sits in an idler loop waiting for the first interrupt pulse.
5. The spectrophotometer is started and the analog of transmittance is sent to the computer together with its corresponding set of wavelength pulses.
6. Each time the data processing system detects a pulse, the analog voltage is measured, binarized and stored for further processing.
7. When the wavelength range of the prism has been scanned, the computer stops; a few seconds later the spectrophotometer stops and then automatically recycles itself.

When the three successive runs of steps 2a-7, 2b-7, and 2c-7 have been completed, voltage level data for 0 %, 100 % and the gas sample

transmissivity will be stored in the computer.

8. The computer calculates, rounds and stores a transmissivity value of

$$T(\lambda) = \frac{1000(E - 0)}{100 - 0}$$

for each set of 0, 100 E levels for each wavelength increment (0.02  $\mu\text{m}$ ) in the prism wavelength range;  $T(\lambda)$  is a binary representation of a decimal integer. The set of  $T(\lambda)$  data is punched on a paper tape which is marked for identification and stored as a permanent record.

9. A second tape is punched on which the  $T(\lambda)$  data appear in binary-coded decimal form. These data are formatted for entry into the IBM 360/67 system for further processing.

In the equation above, the numerator (E-0) is multiplied by 1000 to insure the greatest accuracy in  $T(\lambda)$ . The resulting double-precision product, when divided by a single-precision number, yields a single-precision quotient and a remainder which is tested for rounding. And, since the rounded result is a binary integer, it can be converted exactly to its decimal equivalent.

A cam-switch combination driven by a constant-speed motor usually produces pulses which vary in time between successive pulses. The error in wavelength produced by the pulses will be checked during the next work period. The spectrophotometer will be run through its wavelength range and, each time the computer detects a pulse, the seconds-milliseconds register of a time code generator will be read and printed. The time information will be analyzed and converted to probable error in incremented wavelength.

Preliminary operation of the spectrophotometer has shown that the 0 % and 100 % voltage levels not only vary over the wavelength range but also that the levels are not repeatable for successive runs. This rules out the use of a single pair of 0 %, 100 % values for the reduction of a set of gas sample voltages; it also suggests that the use of one set of 0 %, 100 % values for the reduction of several successive sets of gas sample data could produce transmissivity data which will have appreciable error. A considerable effort will be made during the next work period to improve the stability of the ozone generating and handling system; and a number of runs using a polystyrene sample will be made. Analysis of the results should suggest methods for reducing the error in the transmissivity calculations.

#### V. Report Writing

The review paper "Radiation Processes and the Distribution of Radiative Sources and Sinks", by W. R. Kuhn, which was presented at the Symposium on the Dynamics of the Mesosphere and Lower Thermosphere of the AMS, June 15-18, 1970, Boulder, Colorado, by Prof. W. R. Kuhn is being written as a project report. It should be completed in May 1971.

#### VI. References

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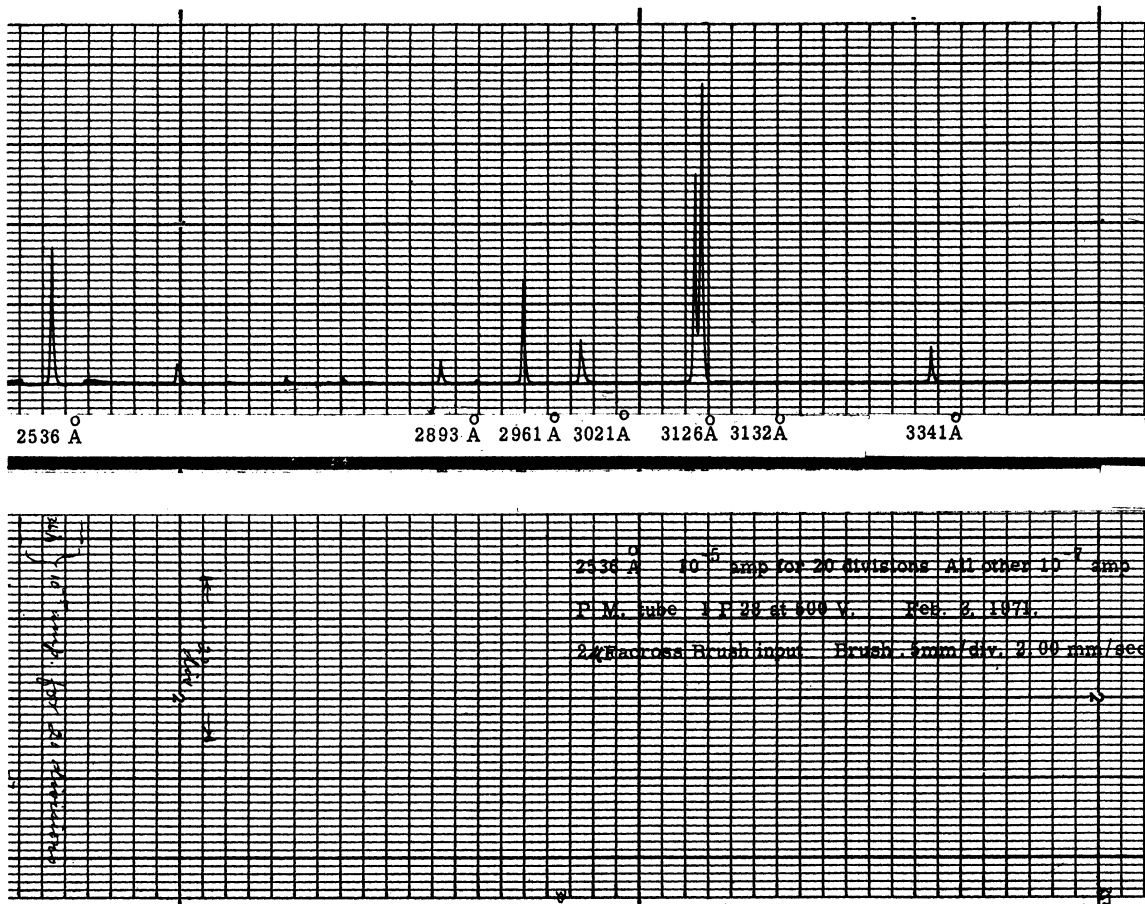


Figure 1. Spectrum of mercury vapor lamp showing six lines that will be used for determination of  $O_3$  amounts.

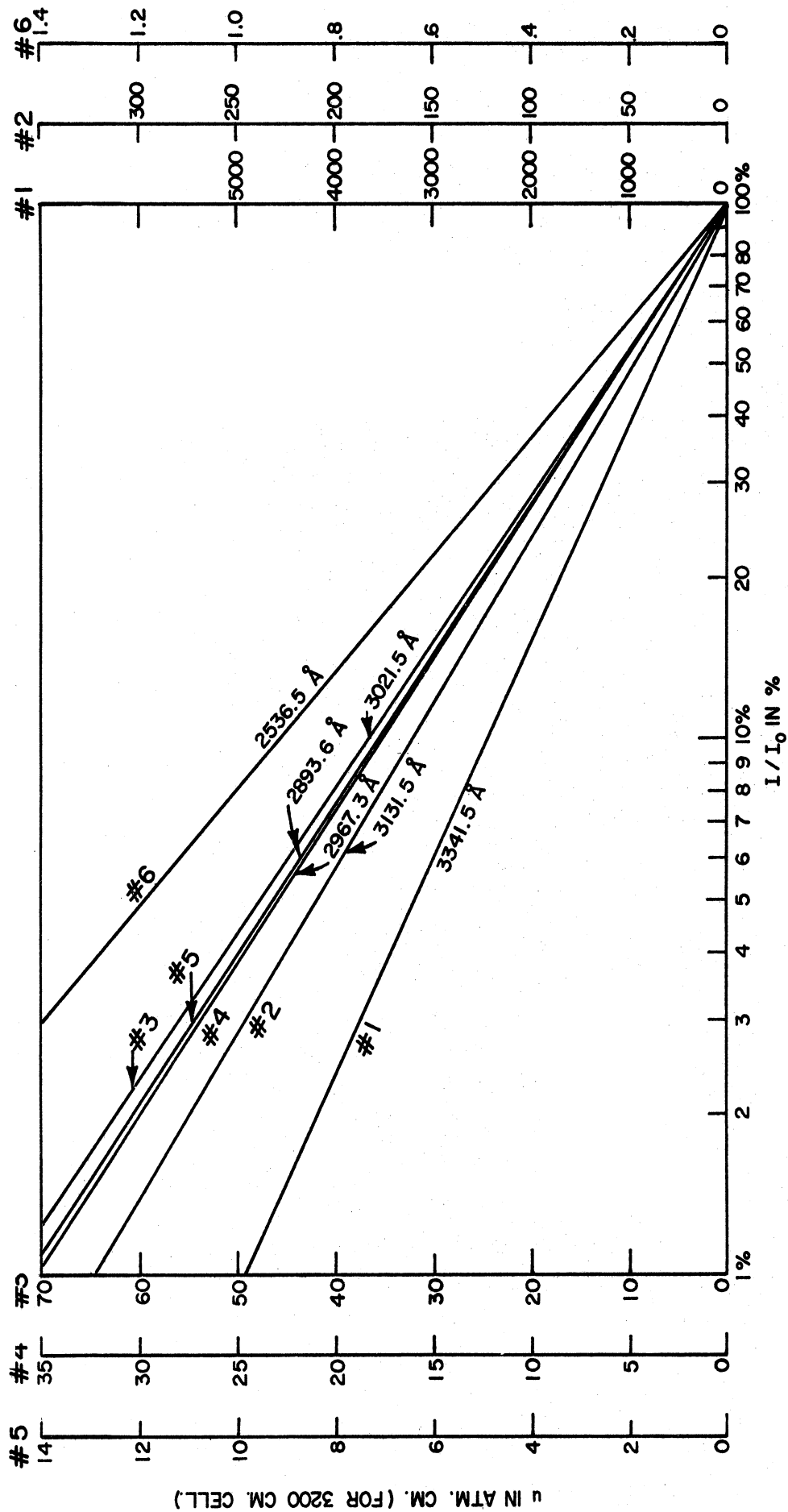


Figure 2. Amount of  $O_3$  (in atm-cm) in 3200 cm. absorption cell vs.  $I/I_0$  (%) for six Hg lines.

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