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April 9, 1952

Berkeley, California

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SOME OBSERVATIONS ON THE MASS SPECTRUM OF CO_2

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In carefully checking the mass spectral pattern of CO_2 in some experiments in which traces of air impurities were undesirable, it was found that the most carefully purified CO_2 gave a small but definite mass 32 peak, apparently due to O_2^+. Since it is not obvious how an O_2^+ fragment can arise from a rearrangement of the linear CO_2 molecule during fragmentation, this has been investigated further.

A check of the variation of masses 32/44 ratio with pressure shows no change as illustrated in Table I. In this table the ratio of masses 22/32 and masses 32/44 are both calculated since mass 44 soon goes off scale on the mass spectrometer used (Consolidated Engineering Corporation Model 21-103). However, the constancy of ratio of masses 22/32 and masses 32/44 over a considerable pressure range shows the occurrence of O_2^+ to be independent of pressure hence a first order process. Since each figure represents a separate introduction of highly purified carbon dioxide which was further carefully frozen and degassed before introduction, it appears highly unlikely that this represents an oxygen impurity. The instrument used does have a mass 32 background of 0.22 divisions with no gas in the sample bottles due to a leak in the Isatron unit. This is quite

reproducible over long time periods and has been subtracted in all figures given since it is independent of pressure in the sample bottle, because it occurs on the high vacuum side of the leak. All measurements of the mass 32 peak were made at 5 times sensitivity (50 μa emission current compared to a normal of 10 μa) and calculated back to normal sensitivity.

The filament represents a possible source of oxygen from some such reaction as $CO_2 + MO \longrightarrow O_2 + CO$, which would give rise to a first

Table I

Effect of Pressure on 32/44 Ratio in Normal CO_2

Sample Pressure (Microns)	Pk ht $m/q = 32$	Pk ht $m/q = 22$	Pk ht $m/q = 44$	Ratios 22/32	32/44 x 100
33.7	0.215	22.9	1206	104.5±10	0.0198
39.1	0.255	26.6	1398	106.7±10	0.0203
58.8	0.402	40.2	2100	100.0±7	0.0190
142	0.941	97.5	>3000	103.6±5	0.0197*
215	1.49	146.9	>3000	98.6±3	0.0187*
251	1.70	170.6	>3000	100.6±2	0.0191*

* Calculated from 22/44 ratio of 0.0190

order dependence with pressure and not necessitate postulating a rearrangement. Treatment of the filament overnight with 100 microns of butene-1 in the sample bottle lowered the ratio of 22/32, i.e., raised the 32 peak as shown in Table II.

Table II

Time After Butene Treatment	Sample Pressure Microns	$m/q = 32$ Pk ht	$m/q = 22$ Pk ht	Ratio 22/32
5 min	135	1.31	92.0	81.5±4
30 min	121	0.99	82.4	83.2±4
60 min	118.6	0.92	80.8	87.6±4

This is in the opposite direction expected from interaction with the filament.

The following day the 22/32 ratio was back to its "normal" value of 100.

Through the kind cooperation of Prof. Richard Ogg of Stanford

University a sample of CO_2 enriched in oxygen 18 was obtained. This

contained 13.5% O^{18} and only a very small amount was available. While

larger samples and higher isotope content would be desirable for a completely

unambiguous answer, the results indicate that only half the oxygen of the

32 peak comes from CO_2, the other half arising from some source of normal

oxygen. The O^{18} in the sample as measured by the 46/44 ratio was 13.45%

while the ratio of oxygen content of the O_2^+ peak from the 34/32 ratio

was 6.9 ± 1%. A second run gave values of 13.45% and 7.7 ± 1% respectively.

It is not quite clear where the source of normal oxygen which gives rise

to the 32 peak can be, but it is certain that half of it arises from the

CO_2 molecule. If carbonization with butene removes oxygen from the filament,

this would suggest that the filament is not the source, since the 32 peak

actually increased with such treatment. This leaves the instrumental source

of oxygen unanswered at the present time.

One feature of the spectrum of $CO^{16}O^{18}$ noted was an apparent

discrepancy in the ratios 44/22, $(CO^{16}O^{16})^+/(CO^{16}O^{16})^{++}$ and 46/23, $(CO^{16}O^{18})^+/$

$(CO^{16}O^{18})^{++}$. In two runs values of 51.05 and 51.76 were found for the ratio

of 44/22 while the ratio of 46/23 in these runs were 54.93 and 56.35

respectively, the discrepancy being about 8% in each case. This is well outside

the experimental error, the pattern stability on normal CO_2 being about 2%

for the 22 peak over short time intervals, leading to the conclusion that

$(CO^{16}O^{18})^{++}$ has about 8% lower probability of formation than $(CO^{16}O^{16})^{++}$.

It is probable that this is due not to a difference in the ionization probability (loss of two electrons), but to the greater probability of fragmentation of the doubly ionized molecule containing O^{18} which is unsymmetrical in character, possesses a small dipole moment, and less resonance stability than the symmetrical molecule, thus reducing the effective yield of the 23 peak.

This postulate cannot be checked by the expected augmentation of the 28 or 30 and 16 or 18 peaks by the reaction:

$$CO_2^{++} \longrightarrow CO^+ + O^+$$

since the fragmentation of $(CO^{16}O^{18})^+$ is not identical with that of $(CO^{16}O^{16})^+$ nor is the pattern stability on normal CO_2 sufficient to observe the very small expected increase. The ratio of 48/24 which should be "normal" if the above explanation is correct could not be adequately checked using the above sample. The peaks were small and the reading errors greater than the difference.