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ABSTRACT

A metastable state in CO_2^{++} dissociating into $CO^+ + O^+$ with a half-life of 2.3 ± 0.2 μsec has been observed. The corresponding metastable peaks are observed at $(M_1/q_1)^* = 35.6$ and $(M_2/q_2)^* = 11.6$, respectively. The widening of these peaks with accelerating voltage shows the repulsion energy to be 2.7 eV and the corresponding charge separation at fragmentation to be 5.3 $\overset{o}{A}$. The appearance potential of CO_2^{++} was found to be 38.0 ± 0.2 eV, and this value is discussed in terms of the various repulsion energies and energy balances. The data is consistent with the hypothesis of an immediate fragmentation into CO^+ ($^2\Sigma$) and O^+ and the metastable fragmentation into CO^+ ($^2\Pi_i$) and O^+. The fragmentation of CO_2^{++} enriched in ^{18}O has also been reinvestigated. It is shown that the unsymmetrical doubly charged molecule ion $(C^{16}O^{18}O^{++})$ has a lower yield than the corresponding symmetrical molecule ions containing ^{16}O and ^{18}O, respectively.

A METASTABLE STATE OF THE

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INTRODUCTION

In 1952 it was reported that the doubly charged ion of CO_2 containing
one ^{18}O atom was relatively less abundant than the doubly charged ion of nor-
mal CO_2.[1] This difference was attributed to an increased fragmentation of
the isotopically unsymmetrical molecule and it was suggested that the doubly
substituted $C^{18}O_2$ should show the same fragmentation pattern as normal CO_2.
Recently higher concentrations of oxygen-18 have become available and the prob-
lem has been reinvestigated. In the course of the work it was found that a
metastable state of CO_2^{++} exists and some studies have been made in regard to
this metastable transition.

EXPERIMENTAL

The mass spectrometer used in this work was a Consolidated Electro-
dynamics Corporation Model 21-103A. The normal operation of the instrument
is with an ionizing current at 37.5 µamps from a rhenium filament at a nominal
ionizing voltage of 70 V. Modifications described elsewhere were made for
reducing the repeller voltages and anode voltage during appearance potential
measurements.[2]

Isotopically enriched O_2 was prepared by the electrolysis of water
enriched in ^{18}O. The resulting O_2 was purified by passing it through a liquid

N_2 trap, condensing it in a liquid hydrogen trap with pumping to as low a pressure as possible. Only traces of N_2 were detectable as impurities in the O_2. Carbon dioxide was prepared from this O_2 by exploding an exactly 2 to 1 molar ratio of O_2 and C_2N_2 in a quartz vessel. The yield of CO_2 was almost quantitative and trace impurities of CO, NO, and NO_2 were removed by trap to trap distillation using -196° and -140° traps. The resulting enriched CO_2 had an ^{18}O content of 58.1% and was isotopically equilibrated.
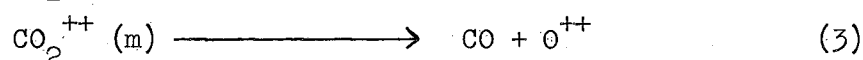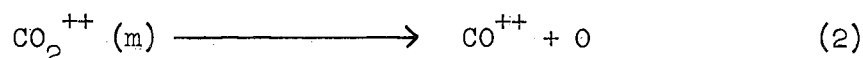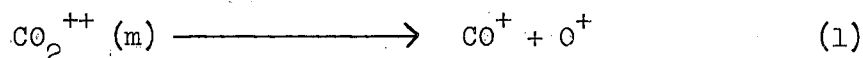
EXPERIMENTAL RESULTS

In a CEC-103 type mass spectrometer in normal operation, ion repellers in the ion source are run at a constant fraction of the accelerating voltage (V_a) in order to keep the ion collection efficiency constant. The actual ionizing voltage is, however, a function of repeller voltage and in an experimental determination of the effect of repeller voltage on the observed voltage shift of the Kr^{++} and Ne^+ appearance potentials, 45% of the average repeller voltage was found to be added to the nominal ionizing voltage. In addition, our mass spectrometer exhibits a 5% compression of the ionizing voltage scale, i.e., the true voltage scale is 1.05 times the nominal voltage scale as measured with the usual divider in the ionizing voltage control circuit. The compression value has been shown to be independent of the shield setting from 0 to 7.5% of V_i, and of the ionizing current from 10 to 37.5 μamps. The exact source of the discrepancy between the measured and actual voltage scales has not been determined. Thus, with a nominal ionizing voltage of 70 volts, in a voltage scan from 4000 to 400 volts, the effective ionizing voltage varies from 95 to about 76 volts using an average repeller voltage of 1.3% of V_a.

In Fig. 1, the calculated actual ionizing voltage at a nominal ion-
izing voltage of 70 volts is shown (solid curves A) while dotted curves B
show the nominal ionizing voltage at each accelerating voltage necessary to
keep the actual ionizing voltage at 80 volts. The importance of this change
in actual ionizing voltage with accelerating voltage in voltage discrimination
work is shown in Fig. 2 where the ionization efficiency curves of CO_2^{++} and
Ar^{++} show markedly different slopes in the region from 70 to 95 volts.

With a corrected actual ionizing voltage of 80 volts, the voltage
discrimination curves of CO_2^+ and Ar^+ are identical within reading error of
0.2% from 300 to 3800 volts, showing there is no mass discrimination over
this mass and accelerating voltage range. In Fig. 3 the voltage discrimina-
tion curves of CO_2^{++} and Ar^{++} show markedly different behavior, the Ar^{++} being
almost flat while the CO_2^{++} rises by almost 20% between 300 and 3800 volts.
Such behavior as exhibited by the CO_2^{++} is characteristic of 1) an ion of
high initial kinetic energy, or 2) a metastable ion decaying in flight.
Since there is no physical process by which a molecule ion of appreciable
initial kinetic energy can be formed by electron irradiation with 80 volt
electrons, it was concluded that process 2) was the cause and a metastable
form of CO_2^{++} exists. Subtraction of the curves in Fig. 3 after normalization
of the Ar^{++} peak heights by trial and error, yields a straight line semi-log
plot when the abscissa is converted from a voltage scale to a time scale from
time of formation to time of collection. The result. in Fig. 4 shows a half-
life of 2.3 ± 0.2 μsec for the metastable ion. This same value was obtained
whether CO_2^{++} are Ar^{++} were run separately or together. The probable error
of ±0.2 μsec placed on this value is an estimate of the maximum the curves
can be shifted by ignoring the low voltage points and the possible error on
the constancy of the actual ionizing voltage of 80 volts. In Figs. 3 and 4

all points were corrected for leak rate as each curve required about 15 minutes to run, the time being consumed in resetting the magnet and the nominal ionizing voltage for each point.

If CO_2^{++} exists in a metastable state, there are three possible ways it can decay.

$$CO_2^{++} \text{ (m)} \longrightarrow CO^+ + O^+ \qquad (1)$$

$$CO_2^{++} \text{ (m)} \longrightarrow CO^{++} + O \qquad (2)$$

$$CO_2^{++} \text{ (m)} \longrightarrow CO + O^{++} \qquad (3)$$

According to the generalized metastable transition equation, the apparent M/q of the product ions from the transition:

$$M_i^{q_i+} \text{ (m)} \longrightarrow M_f^{q_f+} + R^{q_r+} \qquad (4)$$
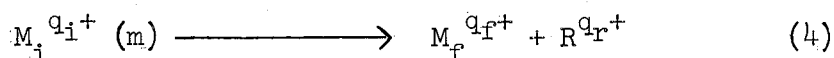
$$(M/q)^* = (M_f/q_f)^2 \div M_i/q_i \qquad (5)$$

Calculations on reactions 1, 2, and 3 show that in 1) the metastable ions should appear at apparent masses of 35.6 for CO^+ and 11.6 for O^+, in reaction 2) the apparent mass of CO^{++} should be 8.9 and in reaction 3) the O^{++} should appear at mass 2.9. A search for these metastable peaks showed broad peaks at about mass 11.6 and mass 35.6 as shown in scans A of Figs. 5 and 6 respectively. No other metastable peaks were seen at 400 μ pressure and 37.5 μamps ionizing current.

The kinetic energy of these ions, i.e., the metastable suppressor voltage (V_{mss}) required for cutoff of the peaks is readily shown to be given by equation (6) if the approximately 3% potential well in the metastable suppressor field is ignored.

$$V_{mss} = V_a (M/q)^* \div M_f/q_f = V_a\, M_f/q_f \div M_i/q_i \tag{6}$$

From Eq. (6) one calculates that the mass 11.6 peak should be cut

off at 72% of the accelerating voltage while 127% of the accelerating voltage

would be required to cut off the mass 35.6 peak. In Fig. 5 curve B at the

normal metastable suppressor setting of 1.6% above the accelerating voltage

mass 11.6 peak is eliminated. The dip at mass 11.3 in both A and B is caused

by negative ions created by mass 12. In Fig. 6 curves B and C show that even

at the maximum setting of the metastable suppressor, 4.8% above the accelerat-

ing voltage there is no effect on the mass 35.6 peak. Curve C shows every

normal peak eliminated and, in fact, reversed, owing to negative ion creation

when these normal ions are retarded back to the collector slit. The behavior

with metastable suppressor of these two metastable peaks is confirming evidence

of their creation from doubly charged ions by reaction (1) as a metastable

peak can only have a higher kinetic energy than its parent ion when the

fragment ion is of higher M/q than the parent ion.

Kupriyanov, Tikhomirov, Potapao and Karpova[3] have reported a number

of collision induced transitions in CO_2 giving rise to peaks at masses 3.27,

5.14, 5.82, 9.14 mass units. Under our operating conditions we see none of

these peaks. Table I shows the effect of pressure on the metastable peaks

at masses 11.6 and 35.6 showing their peak height to be linear with pressure

hence from a unimolecular process. The width of the metastable peaks is

caused by charge repulsion of the fragments on separation. From the change

in peak width with accelerating voltage, i.e., transit time, and assuming

the maximum width to be due to those ions with kinetic energies perpendicular

to the trajectory and decaying at the ion source accelerating slit, the

kinetic energy of each of these ions has been calculated as shown in Table

II. The calculated energy for each ion results in good agreement of total

Table I. Effect of Pressure on Metastable Peak Height

	PEAK HEIGHTS[a]	
$P(\mu)$	$(M/q)^* = 11.6$	$(M/q)^* = 35.6$
100	0.2	0.5
200	0.5	1.1
400	1.0	2.2

[a]The width of the peaks are independent of pressure.

kinetic energy and corresponds to a charge separation of 5.3 $\overset{O}{A}$ at separation.
This appears to be a reasonable value if the charges at fragmentation are

Table II. Fragmentation Energy and Charge
Separation in CO_2^{++} (m)

	MV	Peak width mass units	ΔW (m.u.)	Calculated K.E. eV
Mass 11.6	38000	1.8_6	1.6_4	1.7_2
	11310	3.5_0		
Mass 35.6	121600	4.1_0	2.5_0	1.0_0
	38400	6.6_0		
		Observer Total K.E.		$\overline{2.7_2}$ eV

Calculated Total K.E.
1) from O^+ ion = 2.70 eV

2) from CO^+ ion = 2.75 eV

Charge separation from K.E. of fragments = 5.3 $\overset{O}{A}$

located on the oxygen atoms, it being only slightly over twice the normal

distance between oxygen atoms in uncharged CO_2.

Appearance potential curves on CO_2^{++} have been run at various accelerating voltages from 1000 to 3000 volts, in each case comparing them to a Kr^{++} standard run at the same voltage, to see if the formation of the metastable state could be detected in the A. P. curves. The curves appear identical and an appearance potential of 38.0 ± 0.2 volts compared to Kr^{++} at 38.56 volts[4] found. One of these curves is shown in Fig. 7. The internal consistency was better than ± 0.1 volts. This compares with Dorman and Morrison's figure of 36.5 volts which appears to be low.[5] The downward break about 6 volts above the appearance potential was also observed by Dorman and Morrison. It appears not to be connected with the formation of the metastable state but this conclusion is only tentative. The upward break in the Kr^{++} curve has also been observed by Dorman and Morrison.[6]

Coming back to the original problem of the effect of isotopic substitution on the fragmentation probability of isotopically substituted CO_2^{++}, the results of determinations of the pattern factors of CO_2^{++}/CO_2^{+} in the various isotopically substituted molecules at 1000, 2000 and 3000 volts accelerating voltage are presented in Table III.

Table III. Ratios of CO_2^{++}/CO_2^{+} for Various Isotopic Compositions at Various Ion Accelerating Voltages

		PEAK PATTERN AT V_a		
Accelerating Voltage		1000	2000	3000
Isotopic comp.	Peak Ratio			
$C^{16}O^{16}O$	22/44	1.41_5	1.63_7	1.82_1
$C^{16}O^{18}O$	23/46	1.34_7	1.55_8	1.73_1
$C^{18}O^{18}O$	24/48	1.41_1	1.63_9	1.82_1

At each voltage the pattern of 22 with respect to 44 is equal to that of 24 with respect to 48. In the unsymmetrical molecule, however, the pattern of 23 with respect to 46 is below the value for the symmetrical molecules by about 5%. The level of the pattern factor for CO_2^{++} with respect to CO_2^+ rises with accelerating voltage because the actual ionizing voltage increases (nominal V_i = 70 volts) with increase in repeller voltage as the accelerating voltage is increased as shown in Figs. 1 and 2.

The ionization efficiency curves of all three isotopic species of CO_2^{++} extrapolate to the same value of the appearance potential (38.0 eV compared to Kr^{++} at 38.56 eV) and the curve for M/q = 23 shows no character-istics suggesting the increased dissociation of the unsymmetrical ion.

A study of the metastable behavior of CO_2^{++} of each isotopic composi-tion shows that within experimental error, they all have the approximately same half-life and initial yield (relative to the stable state of CO_2^{++}), values of 2.3, 2.5, and 2.4 µsec being observed for the half-lives of mass peaks at M/q values of 22, 23, and 24 respectively. Thus an increased rate of dissociation of the metastable state of CO_2^{++} in the isotopically unsym-metrical molecule $C^{16}O^{18}O$ cannot be invoked to explain the low yield of the unsymmetrical ion. The increased dissociation of this ion must be in that part of the ion which dissociates by a fast process ($t_{\frac{1}{2}} < 10^{-7}$ sec).
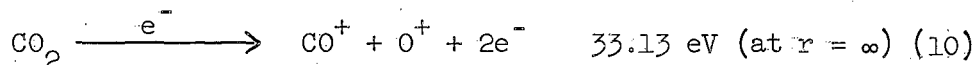
In Fig. 8 the ratios of peak heights of 23/22 and 24/22 have been plotted as a function of nominal ionizing voltage and it is seen that as the appearance potential of CO_2^{++} is approached, the ratio of 23/22 peak heights approaches that of 46/44, showing that at the appearance potential of CO_2^{++}, the molecules of all three isotopic compositions exhibit the same probability of formation as is assumed to be the case with the singly charged ions. As the data represent an extrapolation based upon progressively smaller peaks,

it is not possible to determine whether the increased instability of the
unsymmetrical molecule begins immediately at the appearance potential or a
few volts above it.

DISCUSSION

The occurrence of a metastable state of CO_2^{++} dissociating into two
singly charged ions is the first case of this type of metastable dissociation
which has been reported. Meyerson and Vander Haar[7] have reported metastable
states of several doubly charged ions of aromatic compounds each of which
dissociate into a doubly charged ion and a neutral molecule, but CO_2^{++} (m)
does not dissociate in this manner. The metastable peaks in CO_2 are diffuse
owing to coulombic repulsion of the charge species which explains why they
have not previously been recognized. The behavior of the $(M/q)^* = 35.6$
peak with voltage applied to the metastable suppressor demonstrates con-
clusively its origin from a doubly charged ion. This behavior further sug-
gests that a general survey of the spectrum of any molecule at high meta-
stable suppressor values will show the presence or absence of metastable
peaks where M/q of the final ion is greater than M/q of the initial ion,
i.e., a doubly charged ion breaking into heavier and lighter fragment ions.
The metastable peak observed will, of course, be due to the heavier ion.
This method is of limited utility at present owing to the reversal of all
normal peaks and the occurrence of dips several mass units before intense
singly charged peaks which result from negative ions produced when these
ion beams strike the collector slit. A modification of the metastable sup-
pressor will be required before the method can be generally applied to com-
plex molecules.

Hall[8] has reported an O^+ ion of 3.5 eV kinetic energy in the mass

spectrum of CO_2. If this O^+ ion arises from the immediate fragmentation of

CO_2^{++}, it represents a fragmentation energy of 5.0 eV. Our measured frag-

mentation energy of 2.7 eV for the metastable CO_2^{++} thus differs from this

by 2.3 eV. While the present authors realize the following discussion may

be a pure coincidence of numbers, we would like to call attention to the

existence of an excited state of CO^+ ($^2\Pi_i$ state) at 2.53 eV above the ground

state ($^2\Sigma^+$ state) of CO^+.[9] The following energy balance can be set up to

estimate the appearance potentials involved.

$$CO_2 \longrightarrow CO + O \qquad D = 5.51 \text{ eV} \qquad (7)$$

$$CO \xrightarrow{\ e^-\ } CO^+ + e^- \qquad 14.01 \text{ eV} \qquad (8)$$

$$O \xrightarrow{\ e^-\ } O^+ + e^- \qquad 13.61 \text{ eV} \qquad (9)$$

$$CO_2 \xrightarrow{\ e^-\ } CO^+ + O^+ + 2e^- \qquad 33.13 \text{ eV (at } r = \infty) \quad (10)$$

If one adds to this total energy in Eq. (10), the 5.0 eV repulsion energy

calculated from Hall's observed O^+ energy, the result, 38.13 eV, balances

our observed appearance potential quite well. The repulsion energy of the

metastable state can be brought into agreement with this formulation by

postulating the metastable state to dissociate into O^+ and the $^2\Pi_i$ state

CO^+, with the resultant total energy now being 38.3 eV. These numbers are

certainly within experimental error of each other, and imply a fairly

shallow well in the CO_2^{++} curve as well as an intersystem crossing between

the states dissociating into O^+ and the $^2\Sigma^+$ state of CO^+, and the state

dissociating into O^+ and the $^2\Pi_i$ state of CO^+. We would not attempt,

however, to draw potential energy surfaces for these two states from this

meager data. The above correspondence of energies may be fortuitous and

the actual situation more complicated than that suggested above. The

above formulation of the double ionization process does not agree with that proposed by Dorman and Morrison[5] who suggest the doubly charged ion of CO_2 is formed from the separated products $C^+ + O^+ + O$ rather than $CO^+ + O^+$.

We have not been able to experimentally isolate the high kinetic energy 3.5 eV O^+ ion observed by Hall. The high kinetic energy O^+ ions we observe in CO_2 at low accelerating voltage and high metastable suppressor settings cover a broad band in which peaks with 1.7 eV and 3.5 eV kinetic energies could be overlapping without resolution. Further, there is no conclusive proof that the observed high kinetic energy O^+ ions are all formed from the doubly charged state rather than at least partly from a high-lying repulsive state of CO_2^+.[2]

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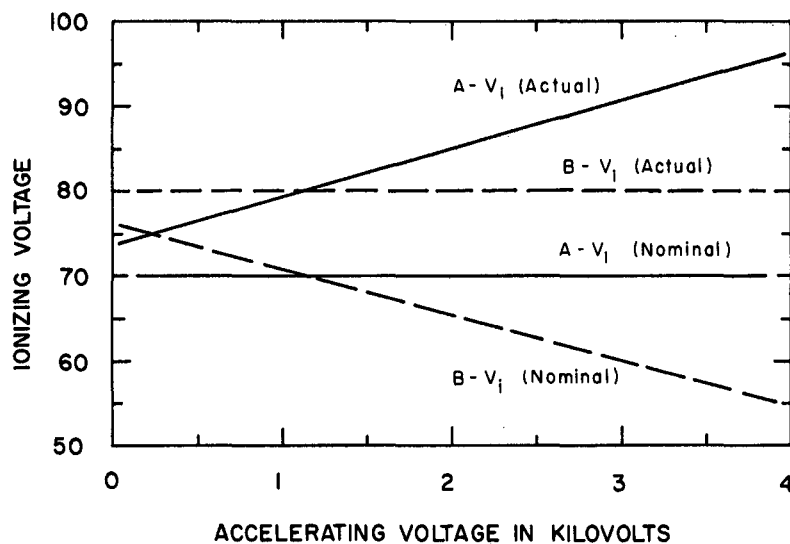
MU-30917

Fig. 1.   Nominal vs actual ionizing voltage as a function of
   accelerating voltage under normal operating conditions

   I.R.   = 1.50% V_a
A) Actual V_i for a nominal V_i of 70 V   O.R.   = 1.13% V_a
B) Nominal V_i for an actual V_i of 80 V   Shield = 7.4% V_i
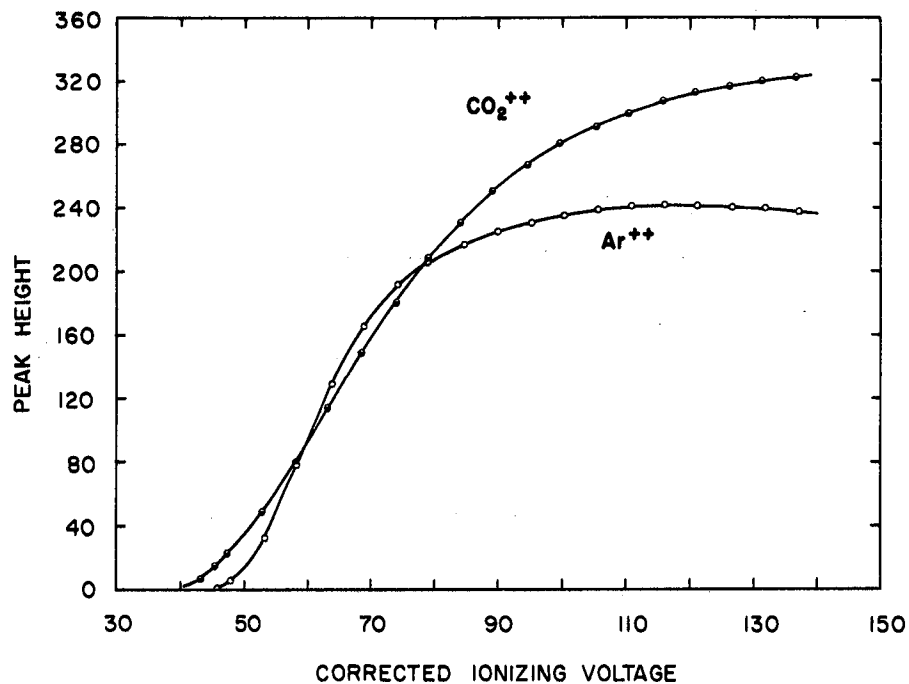
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Fig. 2.   Ionization efficiency curves for Ar^{++} and CO_2^{++} under
normal operating conditions.
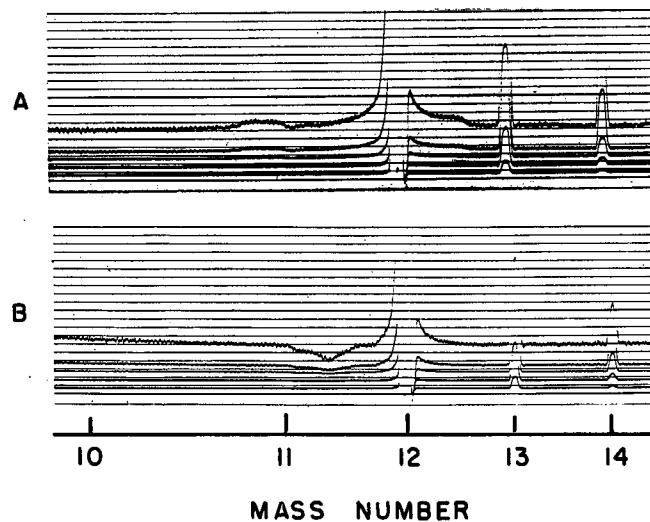
I.R. = 15.0 V   Shield = 7.4% V_i
O.R. = 11.3 V V_a = 1000 V
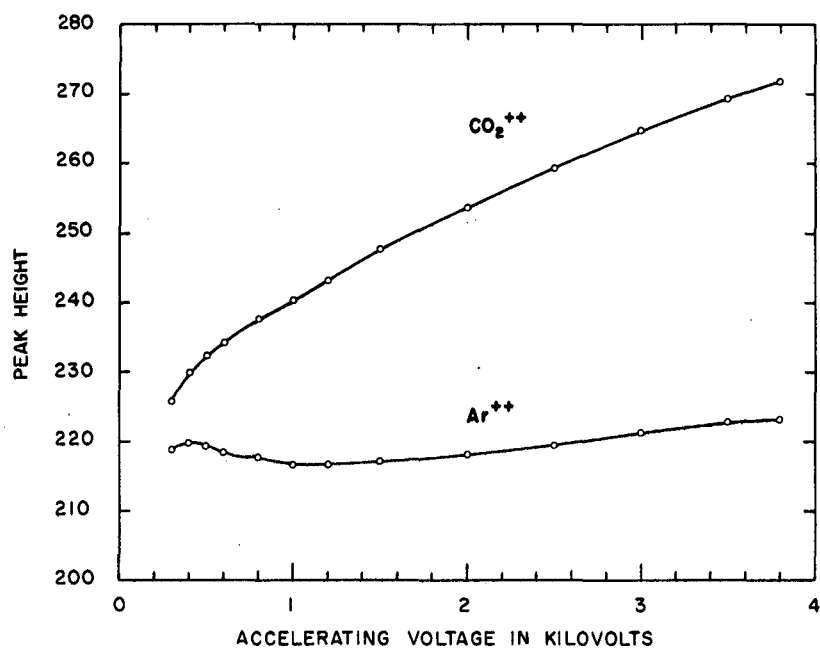
Fig. 3.   Accelerating voltage discrimination curves of Ar^{++}
    and CO_2^{++} at V_i (actual) = 80 V.
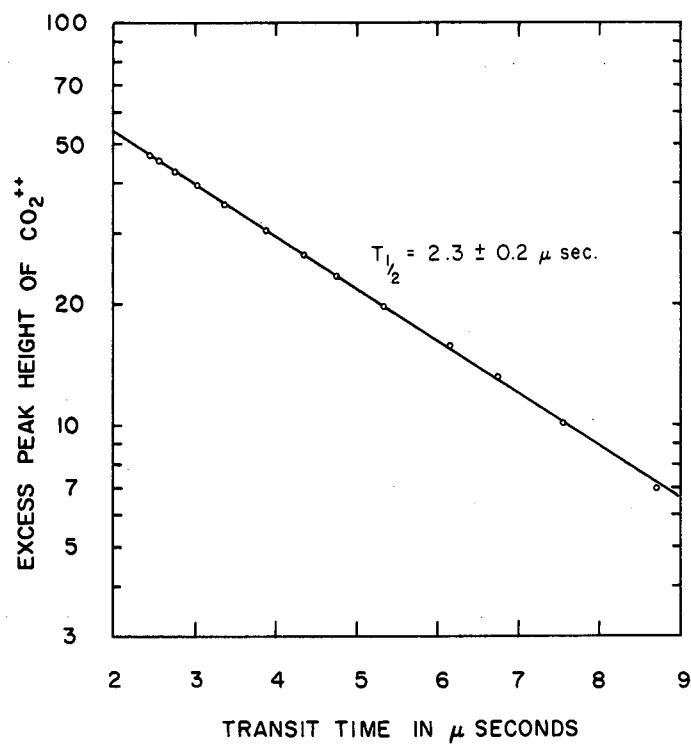
Fig. 4.   Decay of CO_2^{++} (m) in transit from formation in ion
    source to collector.

MASS NUMBER

MU-30921

Fig. 5.   Metastable peak from $CO_2^{++}(m)$ at $(M/q)^* = 11.6$.
        Scanned at $MV_a = 38,000$, 400μ CO_2, nominal $V_i = 70$ V.

                A - metastable suppressor grounded
                B - metastable suppressor at $1.016 \, V_a$
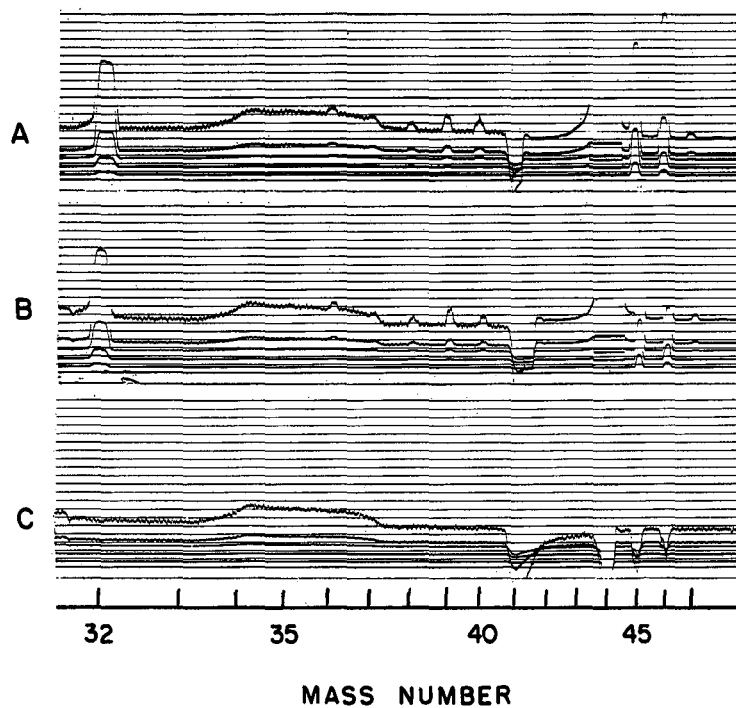
MU-30922

Fig. 6.   Metastable peak from CO_2^{++} (m) at $(M/q)^* = 35.6$.
    Scanned at $MV_a = 121,600$, 400μ CO_2, nominal $V_i = 70$ V.

        Galvanometers off at $M/q = 44$ in A and B

            A - metastable suppressor grounded
            B - metastable suppressor = 1.016 V_a
            C - metastable suppressor = 1.048 V_a

ELECTRON ENERGY (corrected) FOR CO_2^{++}
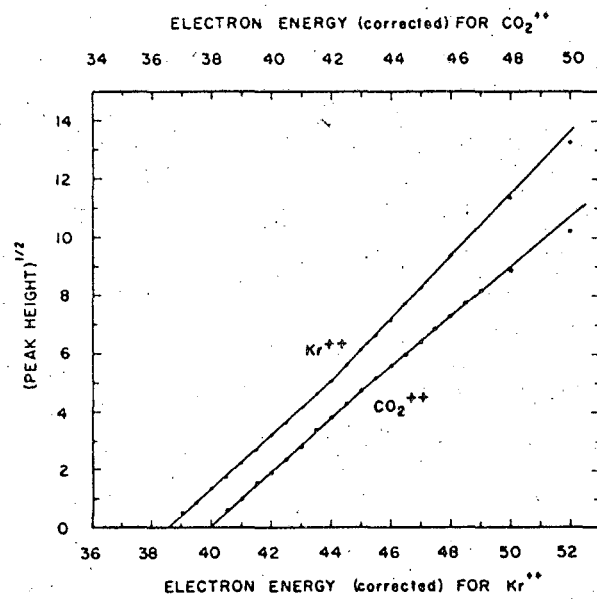
Fig. 7. Ionization efficiency curves for CO_2^{++} and Kr^{++}. $V_a = 1000$ V, Repellers $\sim$ I V, Shield = 0.
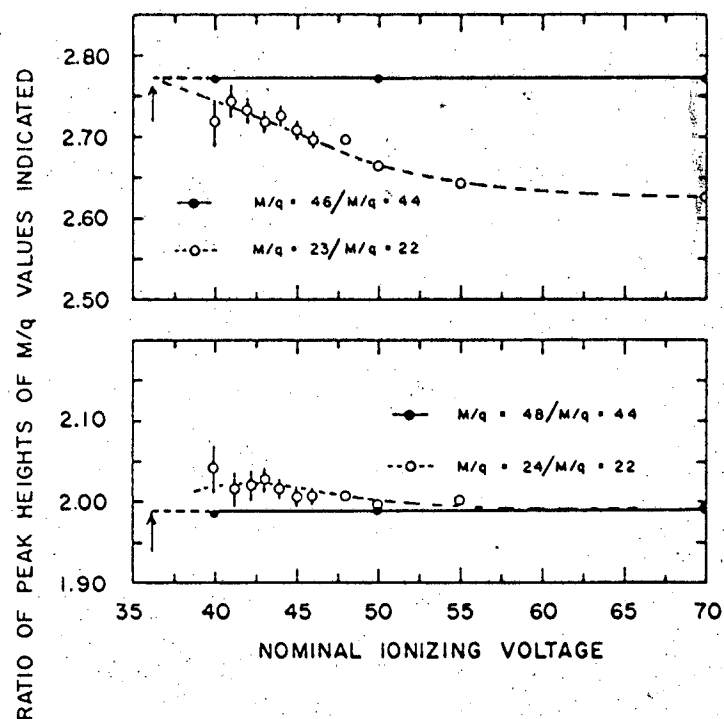
MU-30924

Fig. 8.   Ratio of peaks of masses 23/22 and 24/22 in
    isotopically substituted CO_2^{++} as a function of
    nominal ionizing voltage.
    Arrow points to CO_2^{++} A.P. on this voltage scale.