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# EXPLORATORY DEVELOPMENT TO STUDY GRAPHITE VAPORIZATION KINETICS AND THERMODYNAMICS USING THE MODULATED BEAM MASS SPECTROMETER

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13 ABSTRACT

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## ABSTRACT

Progress is reported in a program of mass spectrometric studies of graphite vaporization kinetics. Emphasis has been placed on measurement of reflection coefficients for the three major constituents of carbon vapor impinging on a heated graphite surface. Use of modulation techniques has been employed to detect a reflected beam interacting with the graphite surface to $T_s \lesssim 2600^{\circ}K$. Development of a vapor source for an isotopically enriched carbon beam using graphite powder is described.


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## I. INTRODUCTION

As a prime candidate material for advanced re-entry vehicle applications, graphite appears particularly attractive for use when severe re-entry trajectories require survival under extreme conditions. In order to make the required calculations of recession rate, designers of graphitic components of such systems require a knowledge of the vaporization kinetics and thermochemistry of graphite. Experimental data on this subject has been limited, being confined mainly to studies of equilibrium vaporization below the temperature of 2800°K. Although other aspects of graphite vaporization have received some attention, design data must still be obtained in part by extrapolation, estimation and theoretical calculation. The present program was designed to provide experimental answers in several of the outstanding problem areas. These include measurement of condensation and reflection coefficients for carbon vapor at graphite surfaces and determination of the polymeric composition of carbon vapor produced by free evaporation from a graphite surface.

In response to the need for better, more advanced methods for the study of gas-surface interactions, Avco developed for the Air Force Materials Laboratory, a modulated beam mass spectrometer apparatus.[1] This unique apparatus allows reactions between a heated solid material and discrete pulses of the gas. Vaporizing reaction products are analyzed individually by the mass spectrometer. By synchronizing the spectrometer detection system to the vapor beam modulator, the periodic time-intensity waveform of the gaseous reaction products can be constructed, providing important information on the kinetics of the reaction under observation.

This apparatus is now being applied to studies of graphite-carbon vapor interactions, an induction heated graphite cylinder providing a carbon vapor beam which impinges on a resistively heated graphite target.

During this quarterly reporting period emphasis has been placed on the study of the condensation/reflection reactions using the beam modulation techniques. In the following sections progress is reported in extending reflection measurements to higher target temperatures. By using beam modulation we have succeeded in operating at target temperatures at which target vaporization obscures the reflected beam from observation in steady-state operation. Development of a new beam source capable of sustained operation using graphite powder has been achieved, paving the way to experimental use of isotopically enriched $C^{13}$ graphite powder and plans for a rotatable target holder are described.

## II. MODULATED BEAM EXPERIMENTS

Direct observation of carbon vapor reflection by graphite surfaces is limited to the single study by Chupka, Berkowitz, Meschi and Tasman.[2] In 1962 they reported the results on an experiment in which a mass spectrometer was used to detect carbon vapor reflected from a graphite filament. Two parallel 0.020 inch graphite filaments were suspended under the ion source of a mass spectrometer in such a way that only one filament was "visible" via a line-of-sight path to the ionizer. A portion of the atoms or molecules vaporized or reflected from this filament could be analyzed and detected by the mass spectrometer. Measurements were made to compare ion intensities of each species produced by direct evaporation from the visible filament with those produced by evaporation from the other filament and reflection from the surface of the visible filament. Values for a reflection coefficient $\alpha_r$ (number reflected/number impinging) were calculated assuming a random distribution for the reflected beam. Results were reported for $C_1$ and $C_3$ only, and for only two values of the temperature of the reflecting surface. These interesting observations gave: for $C_1$, $\alpha_r = 0.3$ ($T = 800^oK$) and $\alpha_r = 0.6$ ($T = 2300^oK$); for $C_3$, $\alpha_r = 1.1$ ($T = 800^oK$) and $\alpha_r = 0.9$ ($T = 2300^oK$).

Recently we have adopted our modulated beam mass spectrometer to a study of carbon vapor reflection.[3] Operating primarily without beam chopping we have verified qualitatively the results of Chupka, et al, and have greatly extended their study by including $C_2$ and by providing a continuous record of reflection as a function of target temperatures in the region $300^oK < T_s < 2100^oK$. These results are depicted in Figure 2.

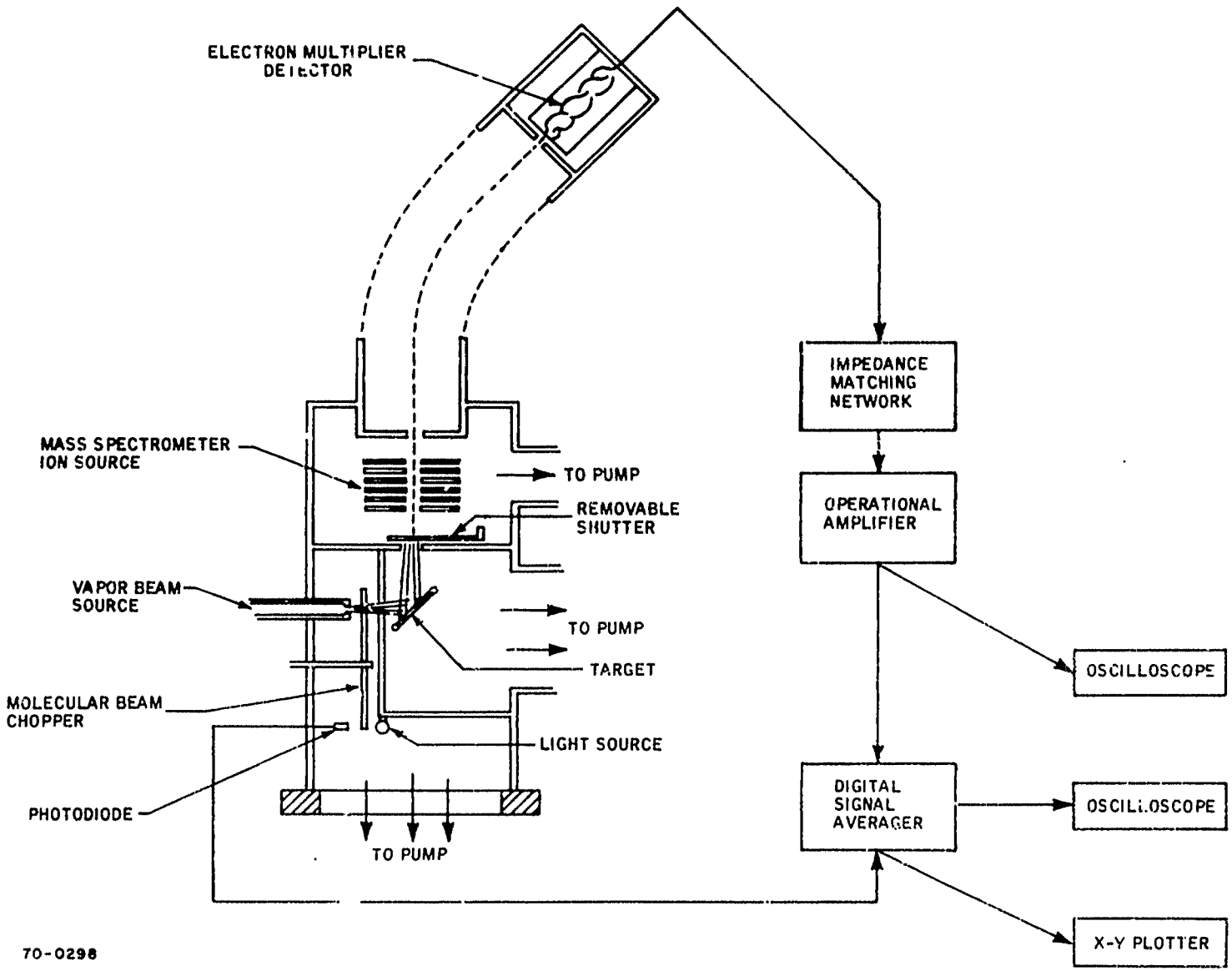


Figure 1. SCHEMATIC DIAGRAM OF AVCO'S PULSED MOLECULAR BEAM MASS SPECTROMETER

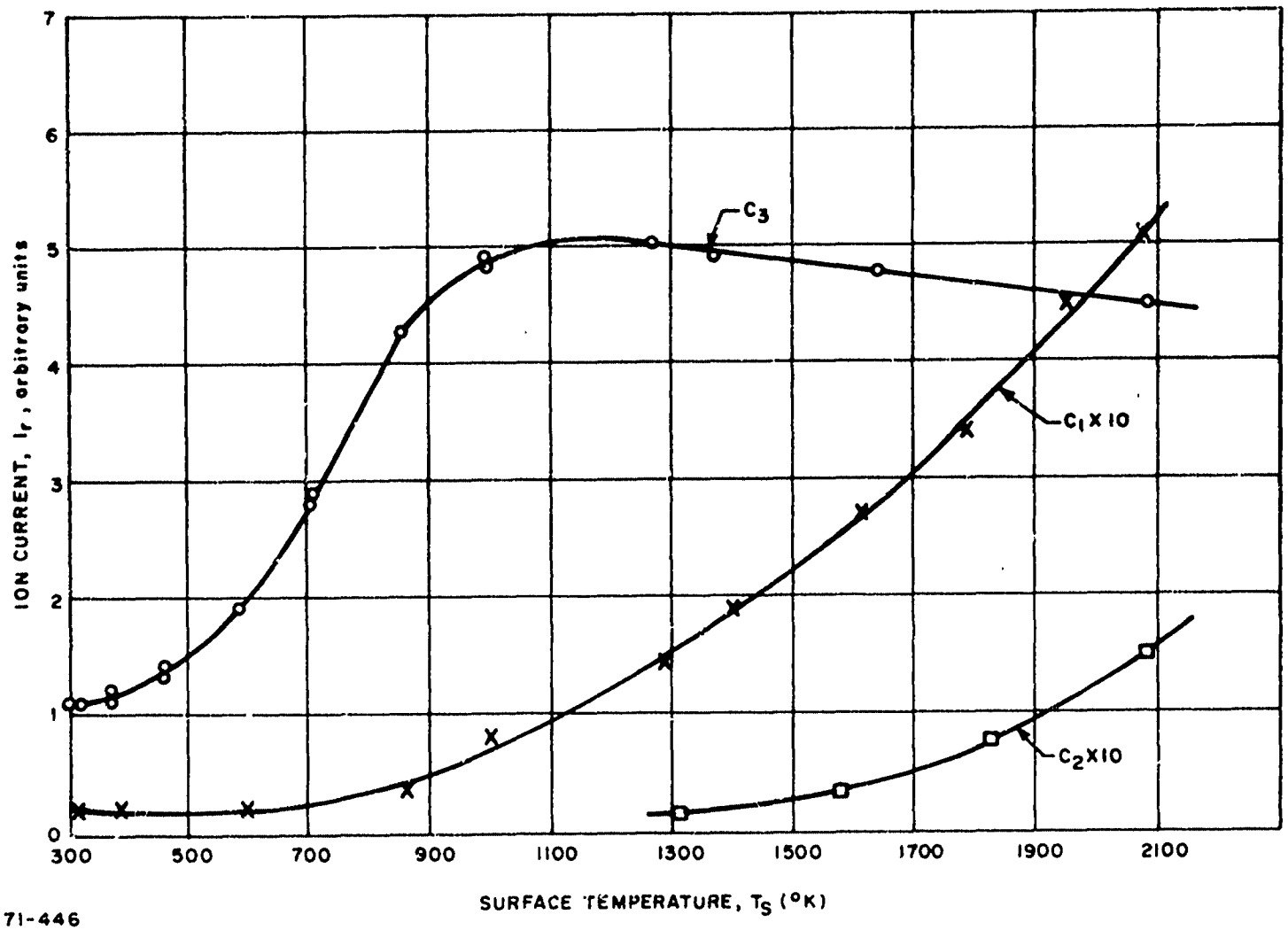


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Figure 2. $C_3$ REFLECTION FROM POLYCRYSTALLINE GRAPHITE

The upper temperature limit of 2100°K was imposed by target vaporization which obscured the reflected beam above this point. However, the region above 2100°K is of particular interest since here the surface temperature approaches the beam temperature and chemical interaction between beam molecules and surface atoms is most likely to occur.

In order to extend our measurements to $T_s > 2100°K$, we have used beam modulation to provide discrimination between the reflected beam (modulated) and the vaporizing surface (non-modulated). The apparatus is then used as depicted in Figure 1 and also with a Princeton Applied Research Corp lock-in amplifier (Model JB-5) replacing the digital signal averager. We have chosen to operate at a chopping frequency of about 40 cycles per second with the beam source operated at near 2700°K. Typical results are shown in Figures 3 and 4.

Intensity of the reflected $C_3$ beam is seen to continue to decrease slightly with increasing surface temperature to 2600°K. The intensity of the reflected carbon atom beam increases as $T_s$ increases to 2600°K. Pulse shapes as obtained on the digital signal averager continue to faithfully reproduce the chopper profile, showing no observable surface residence time for the vapor beam. These results show a continuation of the trends previously observed at lower temperatures.[3]

Above 2600°K ($T_s$) the situation changes dramatically. The lock-in amplifier output becomes wildly erratic and the digital signal averager is no longer able to construct a satisfactory waveform. The reason for this behavior is not clear. As this upper temperature limit is approached the signal to noise ratio approaches $10^{-3}$, a level which should not incapacitate our signal extracting system. The effect is reproducible

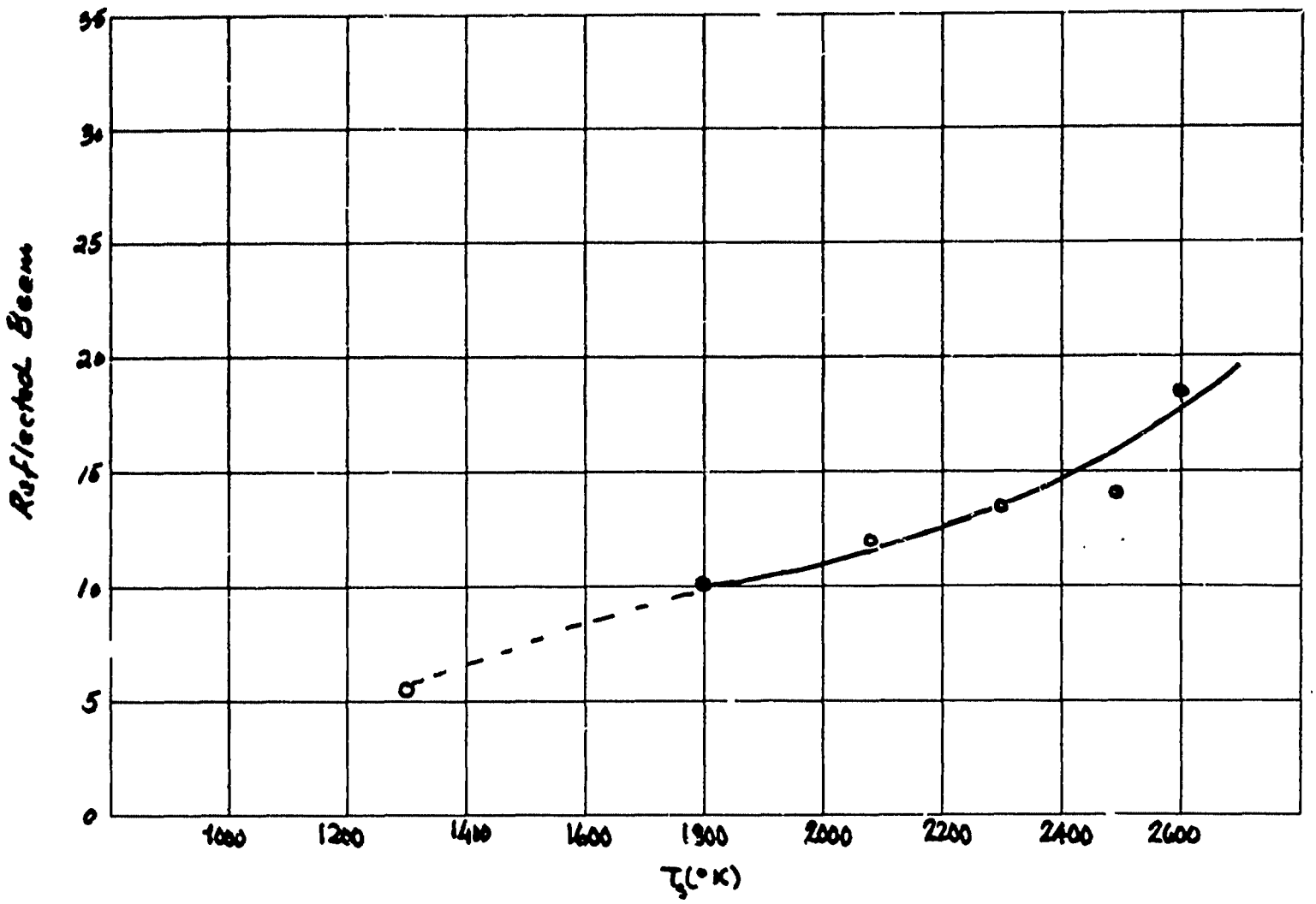


Figure 3. Carbon Atom Reflection

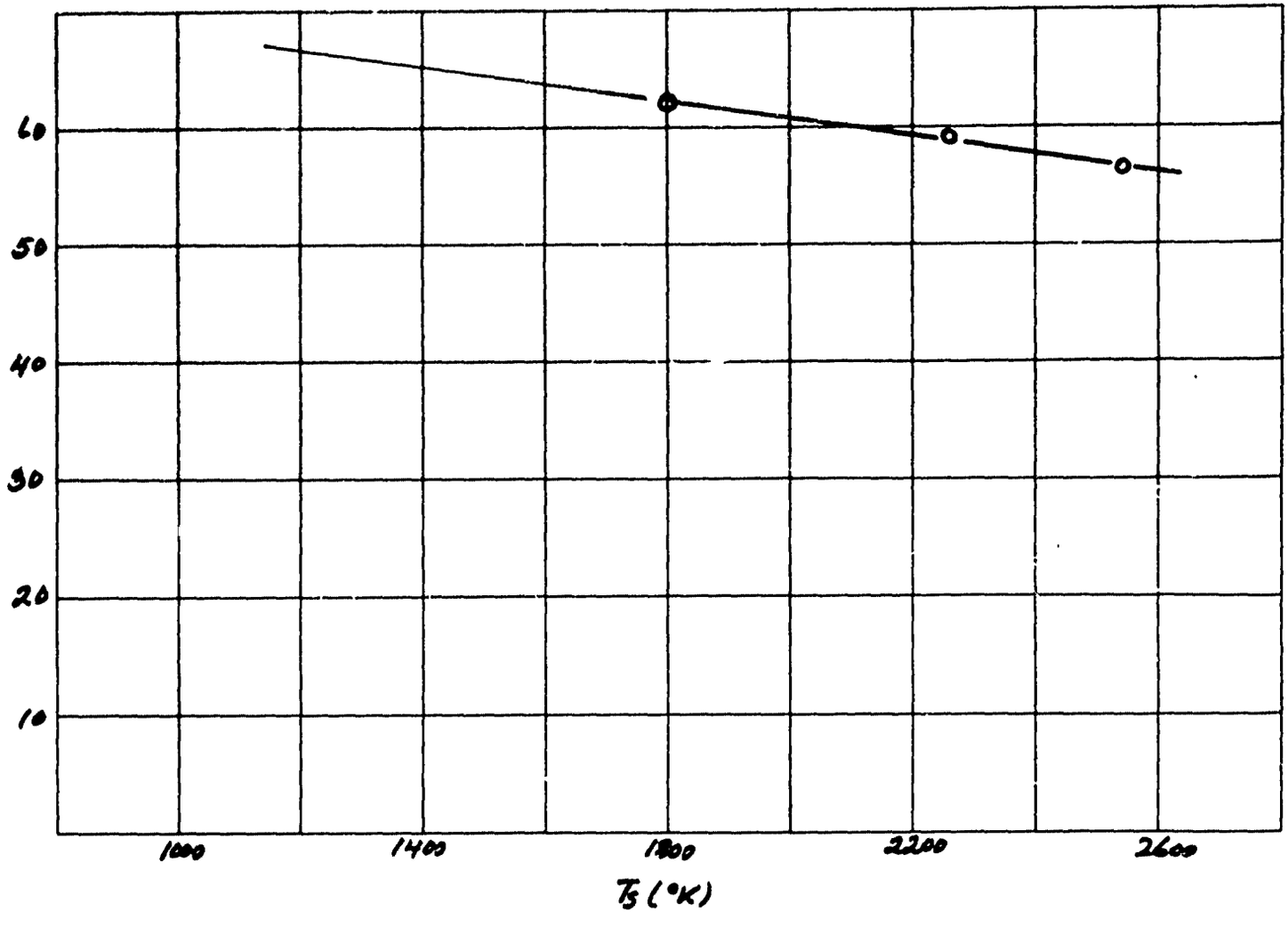


Figure 4. $C_3$ Reflection

and does not seem to be dependent on the absolute level of ion current reaching the mass spectrometer detector. If the explanation lies elsewhere, then one can speculate that an interaction between gas and surface may become increasingly important for high $T_s$. In order to further investigate this possibility, we are preparing for experiments using an isotopically labeled vapor beam to help separate the reflected beam from surface vaporization and to identify any reaction products of a chemical combination or exchange reaction.

## III. THE MASS SPECTRUM OF $C_3$

The selective reflection of $C_3$ (vs. $C_2$ and $C_1$) by graphite surfaces heated to about 1000°K (see Figure 2), affords an unusual opportunity to observe this species in relative isolation. The mass spectrum of $C_3$ is of special interest to the high temperature chemist interested in the composition of carbon vapor over hot graphite, since electron impact fragmentation of $C_3$ may affect the measured ion current due to $C_2^+$ and $C_1^+$ if the ionizing voltage is too high. Therefore, we have performed a simple experiment in which the ion currents at masses 12, 24 and 36 were recorded at 100 eV for the reflected carbon vapor beam at constant beam intensity and reflecting surface temperature ($T_s$ = 1000°K). Results are then corrected for contributions from atomic or diatomic vapor species by estimating the maximum possible contribution from the measurements performed at 17 eV and their known appearance potential curves.[3] The resulting net spectrum of $C_3$ is shown in Table I.

TABLE I

MASS SPECTRUM OF $C_3$

| m/e | ion | rel. int. |
|---|---|---|
| 36 | $C_3^+$ | 100. |
| 24 | $C_2^+$ | 2.1 |
| 12 | $C^+$ | 2.9 |

The effect of electron impact fragmentation is readily observable in our reflection measurements (Figure 2). At 20 eV the $C_1$ (atom) curve follows the course outlined while at 25 eV a large fragmentation contribution causes the $C_1^+$ (mass 12) curve to behave in the manner of $C_3$.

## IV. INSTRUMENTAL DEVELOPMENTS

A. Several improvements or developments in our experimental technique are necessary as preparation for future experiments aimed at extending our knowledge of the carbon vapor-graphite interaction. The first of these involves development of a vapor source to provide a beam of carbon vapor enriched in the $^{13}C$ isotope. Previous vapor sources providing our normal isotopic beam were fashioned from solid graphite rod encased in a tantalum sleeve. This provides a 0.1 inch diameter graphite surface from which a beam of carbon vapor of sufficient intensity is obtained by heating to 2700°K. The isotopically enriched graphite is available only as a fine-grained powder, and our experience has been that it is not possible to compact this powder into a useful rod without the addition of a binder material.

Inclusion of a foreign material would be most undesirable, so we have sought a different solution. Our first attempts to construct a carbon vapor source from tantalum foil and graphite powder failed. This resistively heated tube furnace regularly "burned out" in the high temperature regions of interest to us. This led to our efforts to compact a rod from the graphite powder, but the rods were also of insufficient quality to withstand the high temperatures.

The final solution consists of using the same tantalum tube used as the sleeve in our other sources. One end of this tube is crimped to produce a very narrow slit 0.15 inches high. The tube is filled with graphite powder and set on a base of graphite rod. This source is heated by RF induction with the graphite rod base slightly below the RF coil. An intense carbon vapor beam is produced by heating to the 2700°K region,

with the intensity and useful lifetime perhaps even surpassing that of the original source made of rod only. We are now testing this with $C^{13}$ powder.

B. A second development concerns the assembly of a rotatable target holder. Our calculation of the reflection coefficient from experimental determinations of reflected beam intensity must include some assumption of the angular distribution of the reflected beam. We have made the simple assumption of a cosine distribution, but specular reflection cannot be ruled out. Therefore, it is very desirable that a direct measurement of the angular distribution be made. The most complete measurement of this quantity would require an apparatus in which the angle of beam incidence to the target and the angle of detection of the reflected beam could be varied independently through a wide range of angles. As presently constituted, our apparatus has both angles fixed (at $45^{\circ}$), and modification to permit independent variation of both angles would be an undertaking much larger than can be justified for present purposes. A much simpler solution lies in using only a rotatable target holder. With source and detector in fixed positions (Figure 1) a rotation of the target through an angle of $\theta$ to produce an angle of incidence of $45^{\circ}-\theta$ will permit detection only at the angle $45^{\circ} + \theta$. Even with this restriction a satisfactory estimation of the angular reflection distribution can be obtained. A rotatable target holder is now being assembled.

A rotary vacuum feed-through similar to that used by Varian in their rotary sample manipulator is available. Special problems of high electrical heating currents (up to 150 amps) and water-cooled electrodes

as sample holders are being met through the use of flexible stainless steel bellows to carry both the heating current and the cooling water. Another bellows will be used to permit motion along the z-axis as well. We expect to complete assembly of this device during the next quarter.

## V. CONCLUSIONS AND FUTURE PLANS

During this quarter we have successfully extended our measurement of carbon vapor reflection by graphite to higher target surface temperatures. Earlier reflectance measurements using a constant vapor beam were limited to target temperatures below that which produces significant target vaporization ($T_S < 2100^{\circ}K$). In order to extend this measurement to the vaporizing region which is typical of the practical situation ($T_S \approx T_B$), beam modulation techniques have been adopted. Use of this method has resulted in extension of the maximum target surface temperature several hundred degrees higher, but fails as $T_S$ approaches $T_B$. In the newly explored regions for $T_S$, the modulated beam measurements have shown $C_3$ to be completely reflected, as is the case for all values of $T_S$ above $1100^{\circ}K$. The reflected beam intensity for monatomic carbon continues to increase with increasing surface temperature to the maximum value of $T_S$ attained.

In the preceding sections we have also described development of a carbon vapor beam source utilizing graphite powder as a carbon vapor source. This new source is suitable for use with our isotopically enriched graphite powder. In the next quarter we plan to initiate experiments with the $C^{13}$ source. This will permit us to study the reflection of $C_3$ at $T_S \geqslant T_B$ with a minimum of interference from directly vaporized $C_3$. Careful attention to the isotopic composition of all vaporized and/or reflected species will provide direct evidence on the chemical nature of the reflection/condensation interaction of carbon vapor and solid graphite. Further attention will be given to completion of the rotating target holder. Knowledge of the angular distribution

of reflected molecular beams is crucial to calculation of the reflection coefficient.

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