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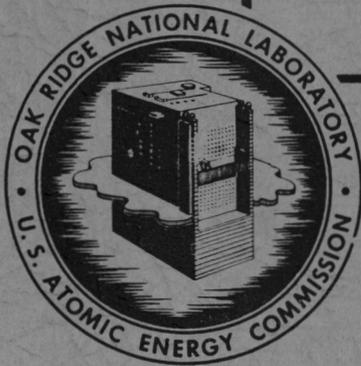


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MASS SPECTROMETER STUDY  
OF SILICON TETRAFLUORIDE

By

Robert E. Rummel  
John R. Sites  
Russell Baldock



OAK RIDGE NATIONAL LABORATORY

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John R. Sites  
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ABSTRACT

SiF<sub>4</sub> was analyzed in a sector type mass spectrometer and the cracking pattern determined along with appearance potential curves. Also uranium tetrafluoride was investigated at high temperatures and an intense SiF<sub>4</sub> pattern with several metastable masses were found.

## MASS SPECTROMETER STUDY OF SILICON TETRAFLUORIDE\*

Robert E. Rummel\*\*, John R. Sites, and Russell Baldock

During the study of some uranium fluorides, mass fragments of silicon tetrafluoride ( $\text{SiF}_4$ ) appeared on the scans. Also certain diffuse peaks were obtained at non-integral mass positions. When an explanation of these peaks was sought, it was found that the most prominent peak might be due to a metastable silicon trifluoride ( $\text{SiF}_3$ ) ion dissociating into a silicon difluoride ( $\text{SiF}_2$ ) ion. This led to the search for peaks at positions which would result from  $\text{SiF}_3^+$  ions losing one, two, and three fluorine atoms after acceleration of the  $\text{SiF}_3^+$  fragment. These peaks were found.

These metastable peaks are formed from an ion after it has been accelerated either through the entire accelerating potential or partially through it, disintegrating into a neutral particle and into a particle of lesser mass (see Figure 1).

Consider an ion of mass  $m_0$  at a point where the potential is zero. Allow this ion to be accelerated through a potential  $V_1$ . After acceleration through the potential  $V_1$  the ion dissociates into an ion of mass  $m$  and a neutral particle of mass  $m_0 - m$ . The new ion of mass  $m$  would continue on with little change in velocity, however, it will be accelerated by the electric field in going from  $V_1$  to the full accelerating potential  $V$ .

The kinetic energy just before dissociation is  $eV_1$ , but after dissociation the ion will have a kinetic energy of  $\frac{m}{m_0} eV_1$ . The remainder of the kinetic energy will be taken off by the neutral fragment. When the new ion finally has been accelerated through the entire field its kinetic energy will be

$$T_v = \left(\frac{m}{m_0}\right) eV_1 + e(V - V_1)$$

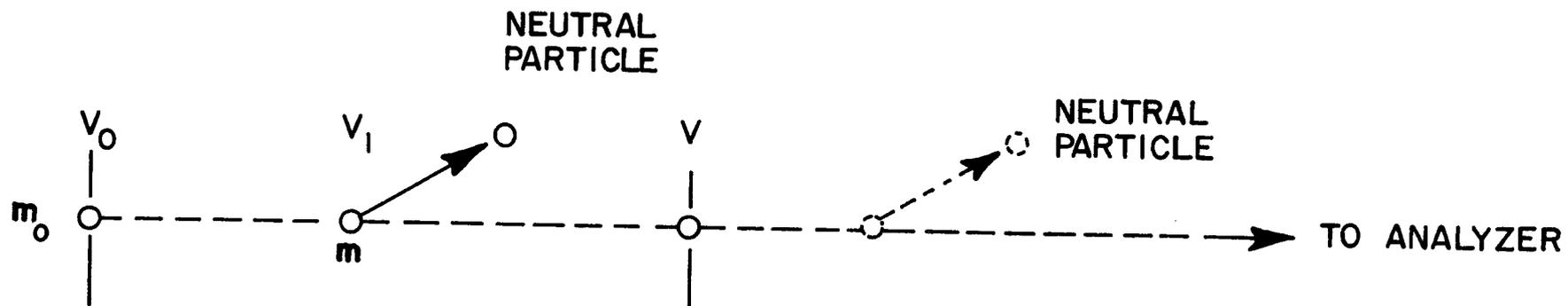
The radius in which these ions will move will be given by

$$R = \frac{c}{eH} (2mT)^{\frac{1}{2}} = \frac{c}{eH} (2m^*T^*)^{\frac{1}{2}}$$

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\* Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy at Pittsburgh, Pa., March 5, 6 and 7, 1952.

\*\* Research Participant, Vanderbilt University



$$T_{V_1} = eV_1$$

$$R = \frac{C}{eH} (2mT)^{\frac{1}{2}}$$

$$T_f = \left(\frac{m}{m_0}\right) eV_1$$

$$m^* = \frac{m^2}{m_0} \frac{V_1}{V} + m \left(1 - \frac{V_1}{V}\right)$$

$$T_V = \left(\frac{m}{m_0}\right) eV_1 + e(V - V_1)$$

$$m^* = \frac{m^2}{m_0}$$

FIGURE I. METASTABLE ION FORMATION

Therefore the ion will arrive at the collector for the same combination of  $V$  and  $H$  as would a normal ion of mass  $m^*$  where

$$m^* = \frac{m^2}{m_0} \left( \frac{V_1}{V} \right) + m \left( 1 - \frac{V_1}{V} \right)$$

If dissociation takes place before the ion is accelerated then its effective mass is  $m$ . If it takes place after complete acceleration but before entering the analyzer, then  $V_1 = V$  and

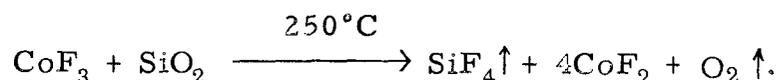
$$m^* = \frac{m^2}{m_0}$$

It is apparent that the dissociation might take place (1) during acceleration; (2) after acceleration but before entering the analyzer; (3) after entering the analyzer. This will cause the peaks to be diffuse rather than sharp.

The work described in this report was carried out on an all metal 60° mass spectrometer.<sup>1</sup>

The  $\text{SiF}_4$  first detected was the result of a reaction at elevated temperatures in the sample tube.

The  $\text{SiF}_4$  used when this study was undertaken was prepared<sup>2</sup> by the following reaction in a copper system:



The gas inlet system was so arranged that  $\text{SiF}_4$  or iron carbonyl ( $\text{Fe}(\text{CO})_5$ ) could be introduced separately or together. The purpose of the  $\text{Fe}(\text{CO})_5$  was to produce mass markers at the higher mass positions. The gases were introduced at room temperature (80°F).

In Figure 2 is shown the cracking pattern of  $\text{SiF}_4$ . The solid lines are for  $\text{SiF}_4$  introduced from outside the tube while the dashed lines are for  $\text{SiF}_4$  formed inside the tube. It will be noted that the graph is plotted on a 5 cycle semi-log scale. In general, the relative amounts of the fragments are the same. The  $\text{SiF}_4$  formed in the tube was produced at elevated temperatures and the absolute peak heights were approximately twice that of the externally introduced  $\text{SiF}_4$ . The pressure in the tube was approximately the same in each case. The absolute peak heights were temperature sensi-

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1. Baldock, Russell and John R. Sites, "A Versatile All-Metal 60° Mass Spectrometer," Document No. Y-755.
  2. Prepared by L. O. Gilpatrick of this department.

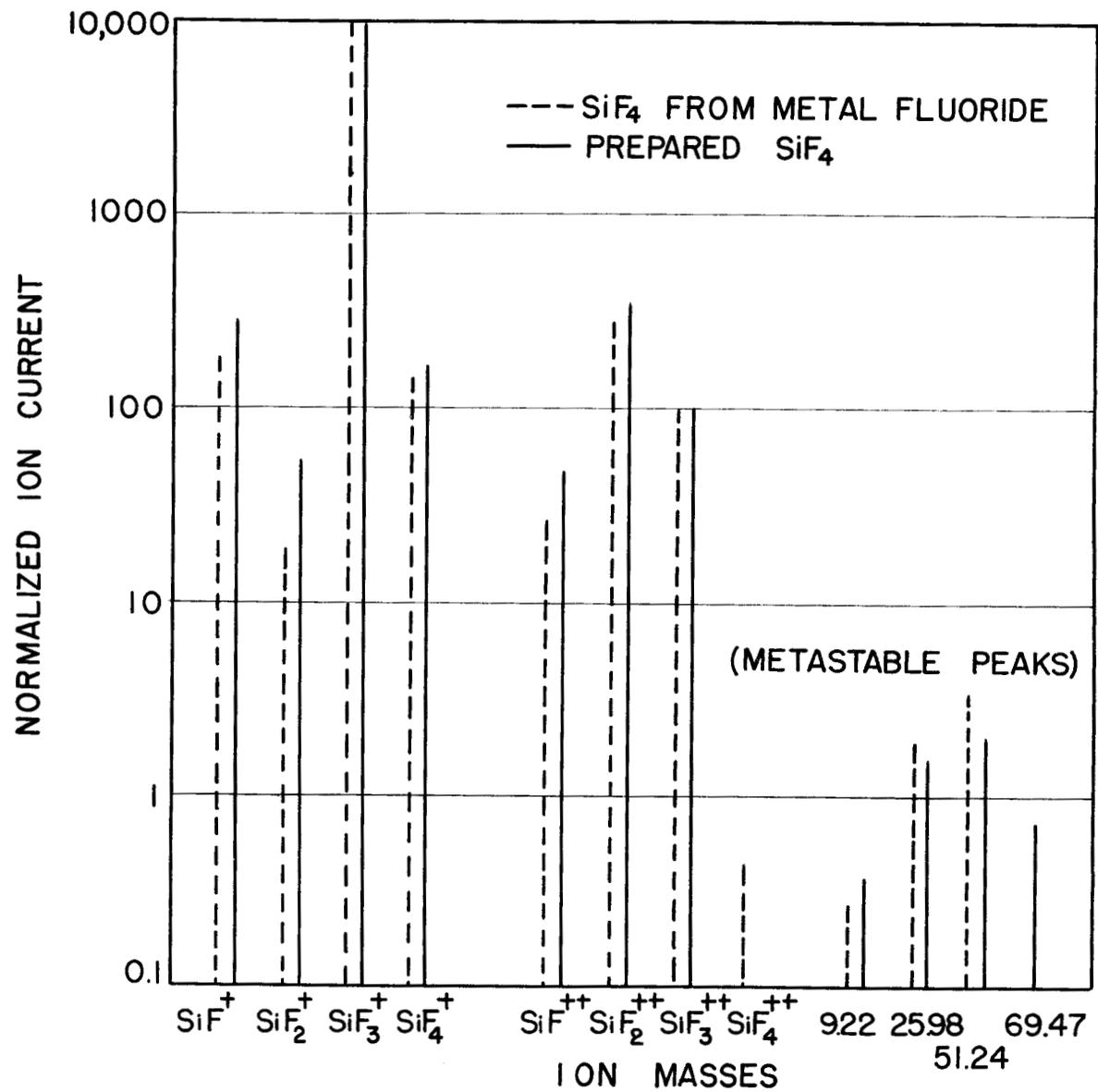


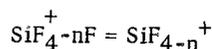
FIGURE 2. MASS CRACKING PATTERN  $\text{SiF}_4$

tive in the case of the internally formed  $\text{SiF}_4$ . During the observations on the internally formed  $\text{SiF}_4$  it was noted that the trap current increased ( $\sim 80 \mu\text{ a}$ ), whereas the emission current regulator was set for an emission of  $40 \mu\text{ a}$ . This would indicate certain dangers in using trap current to regulate the emission current.

The acceleration potential on the ionizing electron beam was 75 volts with an ion repeller voltage of 3 volts.

In Table I are given the mass numbers of the various products

TABLE I

METASTABLE PEAKS FROM  $\text{SiF}_4$ 

Ion	Mass	-F	-2F	-3F	-4F
$\text{SiF}_4^{+}$	104	(69.47)	41.24	21.24	7.54
$\text{SiF}_3^{+}$	85	(51.24)	(25.98)	(9.22)	
$\text{SiF}_2^{+}$	66	33.46	11.87		
$\text{SiF}^{+}$	47	(16.68)			

which might be formed from metastable  $\text{SiF}_4$ . These mass numbers are based on the silicon isotope of mass 28. The mass numbers which are bracketed are the ones detected in this study. The most abundant metastable ion was that due to  $\text{SiF}_3^{+}$  ion, losing a single F with a resultant apparent mass of 51.24. This peak amounted to 0.02 per cent of the  $\text{SiF}_3^{+}$  peak (see Figure 2).

In Figure 3 there is given a comparison of the cracking pattern of  $\text{SiF}_4$  and  $\text{SiCl}_4$ . The  $\text{SiCl}_4$  data is taken from Vought<sup>3</sup> and it is normalized using the  $\text{SiCl}_3^{+}$  ion as the basis of comparison. The relatively larger quantities of  $\text{SiCl}_4^{+}$  ion and its fragments are in keeping with the smaller bond energies involved as compared to the bond energies of the  $\text{SiF}_4$ .

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3. Vought, R. H., Phys. Rev. 71, 93 (1947).

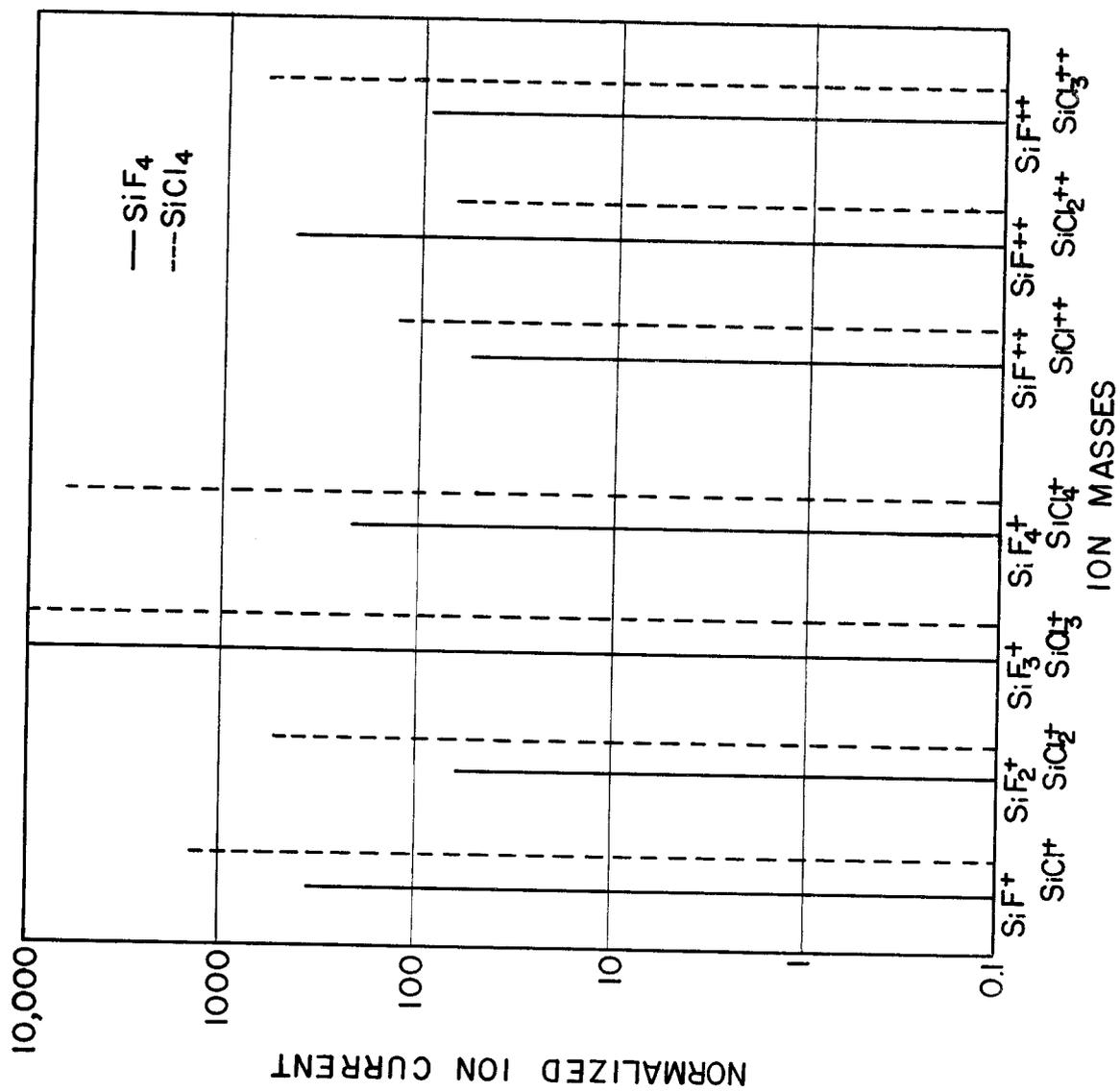


FIGURE 3. MASS CRACKINGS PATTERNS OF SiF<sub>4</sub> AND SiCl<sub>4</sub>