

The Ionization of Sulphur Dioxide by Electron Impact

H. D. SMYTH AND D. W. MUELLER, *Palmer Physical Laboratory, Princeton University*

(Received December 8, 1932)

The mass-spectrograph previously described has been used to study ionization by electron impact in SO_2 . SO_2^+ ions appear at 13.1 ± 0.3 volts, SO^+ ions at 16.5 ± 0.5 and ions of mass 32, either S^+ or O_2^+ appear at 16.0 ± 0.7 and

increase sharply at 22.3 ± 1.0 . No O^+ ions are observed. The probable processes of formation of these ions are discussed.

THE study of H_2O reported in the previous paper left only two gases that had been on our original program for the study of the simple triatomic molecules. These were SO_2 and CS_2 . There was some doubt about the possibilities of getting good results with sulphur compounds in the apparatus and there was the further difficulty in SO_2 that S^+ and O_2^+ ions could not be distinguished. But one of the authors happened to be particularly interested in SO_2 at the time and therefore its study was undertaken.

Contrary to expectation the SO_2 caused no trouble at all. In fact the apparatus had never worked better. The procedure was unchanged, the ionization of argon being used as usual to calibrate the voltage scale. Runs in mixtures of argon and SO_2 and in the pure gases gave the same values for the I. P.'s of A^+ and SO_2^+ , respectively. This established the value of the SO_2 I. P. as 13.3 ± 0.3 volts and the appearance potentials of the other ions were referred to this value. Other ions were observed at masses 46 and 32 but none at 16. Current *vs.* voltage curves for these ions are shown in Fig. 1. Of the two breaks in the 32 curve one might naturally be attributed to S^+ and the other to O_2^+ but we shall see below that they are probably both S^+ .

This appears to be the first determination that has been made of the I. P.'s of SO_2 . Nor can we calculate that for SO_2^+ or SO^+ . But if we take¹ $\text{SO}_2 + 5.8$ volts \rightarrow $\text{SO} + \text{O}$, $\text{SO}_2 + 5.8 \rightarrow \text{S} + \text{O}_2$, and $\text{SO} + 5.1 \rightarrow \text{S} + \text{O}$, and the I. P.'s for S and O_2 as 10.3 and 13.0 volts,² respectively, we can calculate the minimum energies required for the

formation of S^+ , O_2^+ and O^+ . The theoretical and experimental results are combined in the following table:

TABLE I. *Theoretical and experimental critical energies in SO_2 .*

Ion observed	Appearance potential	Probable process	Calculated minimum energy required
SO_2^+	13.3 ± 0.3	(a) $\text{SO}_2 \rightarrow \text{SO}_2^+$	—
SO^+	16.5 ± 0.5	(b) $\text{SO}_2 \rightarrow \text{SO}^+ + \text{O}$	—
Mass 32	16.0 ± 0.7	(c) $\text{SO}_2 \rightarrow \text{S}^+ + \text{O}_2$	16.1
Mass 32	22.3 ± 1.0	(d) $\text{SO}_2 \rightarrow \text{S} + \text{O}_2^+$	18.8
		(e) $\text{SO}_2 \rightarrow \text{S}^+ + \text{O} + \text{O}$	21.2
O^+	Not observed	(f) $\text{SO}_2 \rightarrow \text{SO} + \text{O}^+$	19.3

The comparison of observed and calculated values raise several points of interest. First it is clear that the process (c) is certainly the one requiring the least energy to produce a mass 32 ion. But the calculated value is still a tenth of a volt above that observed. The calculated value is a minimum and previous experiments with the same or similar apparatus usually have given appearance potentials at least half a volt above the calculated value. It seems likely, therefore, that the heats of dissociation of SO_2 given by Franck, Sponer and Teller may be a few tenths of a volt high. The second point of interest is that the second break in the mass 32 curve corresponds better with process (e) than (d) suggesting that there may be no O_2^+ ions formed. This would be little more surprising than the absence of O^+ ions. Finally we may use the observed appearance potential of the SO^+ ion to calculate its ionization potential. It is $16.5 - 5.8 = 10.7$ volts. There are at present no spectroscopic data to be compared with these results.

¹ Franck, Sponer and Teller, *Zeits. f. physik. Chemie* **B18**, 97 (1932).

² Smyth, *Rev. Mod. Phys.* **3**, 290 (1931).

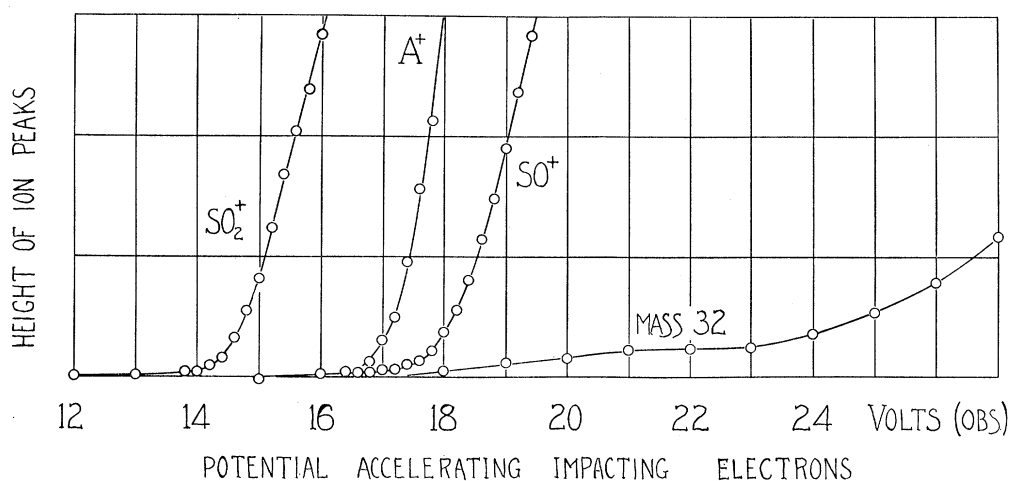


FIG. 1. Relative abundance of various ions formed by electron impact in SO_2 -argon mixture.

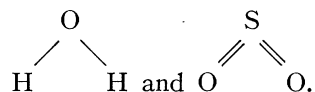
Some more general questions are raised by one process of ionization which occurs in both sulphur dioxide and water vapor and which suggests the value of summarizing the whole work done to date on triatomic molecules. This is done in Table II below where XY_2 is the generalized formula for the type of molecule studied.

TABLE II. Ionization processes in triatomic molecules of the type XY_2 .

Possible process	Occurrence in various gases					
	CO_2	NO_2	N_2O	H_2O	H_2S	SO_2
(a) $XY_2 \rightarrow XY_2^+$	Yes	Yes	Yes	Yes	Yes	Yes
(b) $XY_2 \rightarrow XY^+ + Y$	Yes	?	Yes	Yes	Yes	Yes
(c) $XY_2 \rightarrow XY + Y^+$	Yes	Yes	Yes	Yes	No	No
(d) $XY_2 \rightarrow X + Y_2^+$	No	Yes?	?	No	No	?
(e) $XY_2 \rightarrow X^+ + Y_2$	No	Yes?	Yes	Yes	Yes?	Yes
(f) $XY_2 \rightarrow X + Y + Y^+$?	?	?	?	No	No
(g) $XY_2 \rightarrow X^+ + Y + Y$	Yes	?	?	?	?	Yes?
(h) $XY_2 \rightarrow X_2^+ + Y^+$	—	—	—	Yes	—	—

Although the compositions of all these gases may be represented by the same formula, XY_2 , their molecular structure differs. Thus CO_2 is linear with the C atom in the middle, N_2O is probably linear but with the O on one end. The

others are all triangular to a greater or less extent, the structural formulas for water and sulphur dioxide being



Consider the processes (d) and (e). One might expect them to be quite possible in N_2O , almost impossible in CO_2 and highly improbable in H_2O and SO_2 where there is no bond between the two Y atoms to start with. Our expectation is confirmed in CO_2 entirely, and in N_2O so far as the evidence goes. But in the four other gases the process (d) apparently does not occur but (e) does. Furthermore the process (e) in SO_2 and H_2O where it has been best observed occurs at so low a potential that there can be little energy carried off in vibrational energy of the Y_2 molecule or in kinetic energy. Unfortunately our knowledge of the structure of these molecules is still too incomplete to offer an interpretation of these observations.