

Total Cross Sections for Ionization and Attachment in Gases by Electron Impact.

II. Negative-Ion Formation

DONALD RAPP AND DONALD D. BRIGLIA

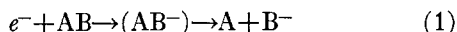
Lockheed Missiles and Space Company, Palo Alto, California

(Received 21 April 1965)

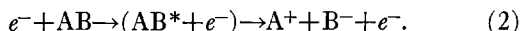
Absolute total cross sections for negative-ion formation in several gases (CO, NO, O₂, CO₂, N₂O, SF₆, and H₂) by electron impact have been measured in a total ionization tube. Both dissociative attachment and ion-pair formation have been measured, with careful attention paid to complete collection of the negative ions. Possible errors due to scattered electrons and energy spread are discussed.

I. INTRODUCTION

NEGATIVE ions may be formed in collisions of electrons with molecules in two-body collisions at low pressures by two primary mechanisms,¹ dissociative attachment:



and ion-pair formation:



These processes have been studied in a number of substances by several investigators.² However, as in the case of positive ionization, not all the measurements have been subjected to careful analysis for possible error, and except for a paper by Schulz,³ discussions of saturation curves and consistency checks are usually not given.

In the present work, we have carefully studied the ion-saturation characteristics and found conditions necessary for complete collection of ions. We have thus determined absolute cross sections for negative-ion formation in several gases (CO, NO, O₂, CO₂, N₂O, H₂, D₂, HD, and SF₆). It is believed that the cross sections are as accurate as have ever been determined, but among the errors still persisting, the largest is expected to be due to energy spread in the electron beam.

The method is essentially the same as that used for positive ions,⁴ except that the ion drawout field is reversed so as to collect negative particles. Comparison of the negative ion current with the positive ion current obtained in the usual way,⁴ leads to absolute normalization of the negative-ion cross section.

II. THEORY OF DISSOCIATIVE ATTACHMENT

Before presenting the experimental results on negative-ion formation, a brief discussion of the theoretical energy dependence of dissociative attachment is given. This serves to emphasize the effects of electron energy spread on the cross sections. Energy spread plays a major role in the accuracy of these cross sections, as opposed to positive ionization where energy spread is generally unimportant. The reason for this difference lies in the narrow resonance-peak dependence of the cross section on electron energy.

We may picture the dissociative-attachment process as occurring by attachment of an electron to a molecule X₂, to form X₂⁻ in a repulsive electronic state. It is presumed that this occurs in a time short compared to the characteristic time for nuclear kernel motion. Subsequently, the X₂⁻ dissociates into X + X⁻, this second step requiring ~10⁻¹⁸ sec. Some hypothetical potential curves for X₂ and X₂⁻ are shown in Fig. 1. If the initial molecules are almost entirely in the ground vibrational state, the statistical distribution of internuclear distances in X₂ will be as shown. Since the incoming electron must have precisely the correct energy to produce X₂⁻ on a particular potential curve, only a single-bond distance is effective in producing X₂⁻ at a particular electron energy.⁵ Thus, the cross section for dissociative attachment should be a projection of the initial distribution on a repulsive curve of X₂⁻, as shown in Fig. 2. For curve (X₂⁻)', a roughly symmetrical resonance peak is obtained. For curves (X₂⁻)' and X₂⁻, a vertical onset at energy E₁ is obtained. There is no meaningful onset energy for Curve (X₂⁻)'', only an exponential decrease in cross section below E₆. In general, the resonance peaks are found to be about 1 to 4 eV wide at half-height. Thus, energy spreads of several tenths of an electron volt can

¹ E. W. McDaniel, *Collision Phenomena in Ionized Gases* (John Wiley & Sons, Inc., New York, 1964) p. 382.

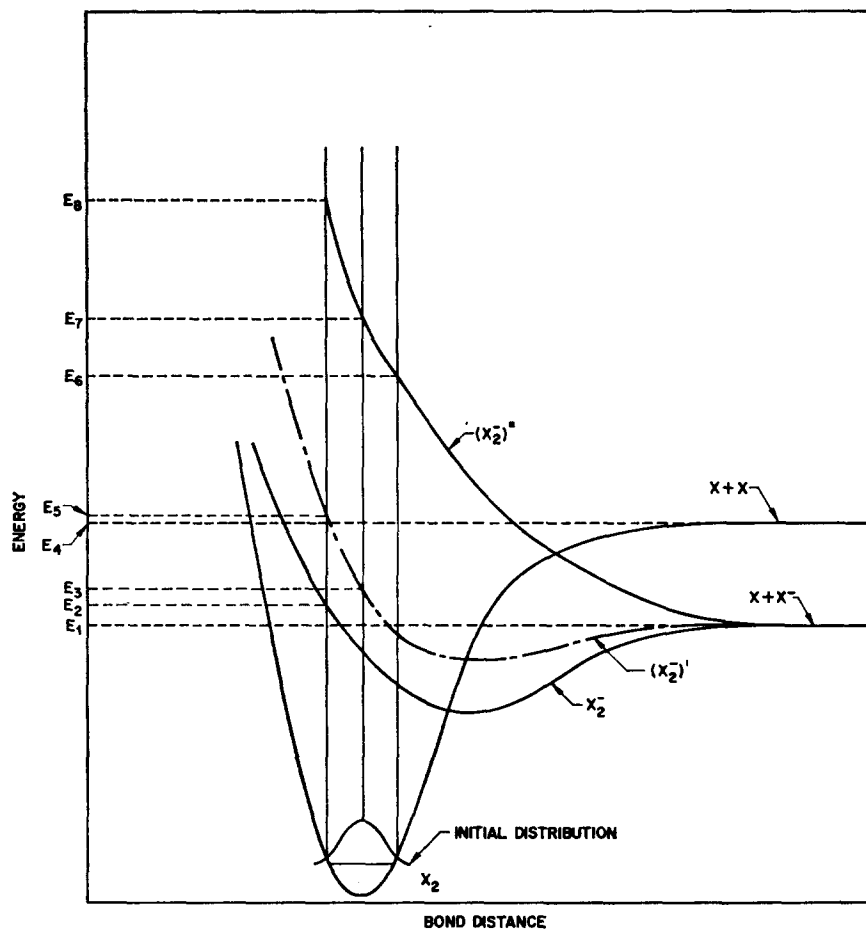
² L. J. Kieffer, "A Bibliography of Low Energy Electron Collision Cross Section Data," Joint Institute for Laboratory Astrophysics, Report No. 4 (NBS Report 7993), Boulder, Colorado, January 1964.

³ G. J. Schulz, *Phys. Rev.* **128**, 178 (1962).

⁴ D. Rapp and P. E. Golden, *J. Chem. Phys.* **43**, 1464 (1965), preceding paper.

⁵ This description is oversimplified and violates certain aspects of the uncertainty principle. If one more properly described the process in terms of an "overlap integral" between the initial state and the unbound final state, a similar result would follow. [See the discussion on pp. 391-392 of: G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).]

FIG. 1. Hypothetical potential curves for the ground state of a diatomic molecule X_2 and various states of negative ion X_2^- . The initial vibrational distribution function for the ground state in X_2 is pictured at the zero of energy. Vertical lines are drawn at the center of the distribution and at the classical turning points. These delimit the Franck-Condon region. The pertinent energies at which the potential curves intersect the Franck-Condon region are denoted. The electron affinity of X is $E_4 - E_1$.



seriously alter the observed cross sections for the narrower resonance peaks, and can extend the "tailing" in all resonance peaks. In the limiting case of molecules that are highly electronegative, such as halogens⁶ or SF_6 ,⁷ the true resonance peak is very narrow (perhaps ~ 0.1 eV), and the empirically observed width is generally the width of the electron energy distribution, instead of the true width.

The negative ions formed by dissociative attachment have initial kinetic energy by virtue of the dissociation from a repulsive negative molecule-ion state. Use of high ion drawout fields to collect these ions will result in an energy spread across the electron beam that can affect the measured cross sections.

III. EXPERIMENTAL METHOD

The experimental apparatus and method was essentially the same as that used for positive ions in the accompanying paper,⁴ except that the ion-collection field is reserved. There are several problems encountered, however, in the study of negative ions that are not encountered with positive ions.

⁶ R. E. Fox, Phys. Rev. **109**, 2008 (1958).

⁷ R. E. Fox, J. Chem. Phys. **26**, 1281 (1957).

First, there is the possibility of positive ions formed in front of the electron-collector plate being shot back into the ionization region due to the positive potential on the electron collector. The low absolute cross sections for attachment compared to ionization make this more of a problem here. By reducing the potential on the electron collector to the lowest value that would still maintain complete collection of the electron current, this problem was reduced to negligible proportions.

Second, scattered electrons that lose all their axial velocity can eventually reach the collector plate for negative ions, through multiple-scattering events. In collecting positive ions, the collector plate is negative, and this cannot occur. It was found that this effect could generally be kept very small, except when large ion drawout fields were used. In studying negative-ion formation at electron energies above the ionization potential for dissociative ionization ($e^- + X_2 \rightarrow X + X^+ + 2e^-$) it turns out that the energetic X^+ ions vastly outnumber the negative ions due to ion-pair formation. The measured ion current is actually positive unless high ion drawout fields are used to prevent the energetic X^+ ions from reaching the collector plate

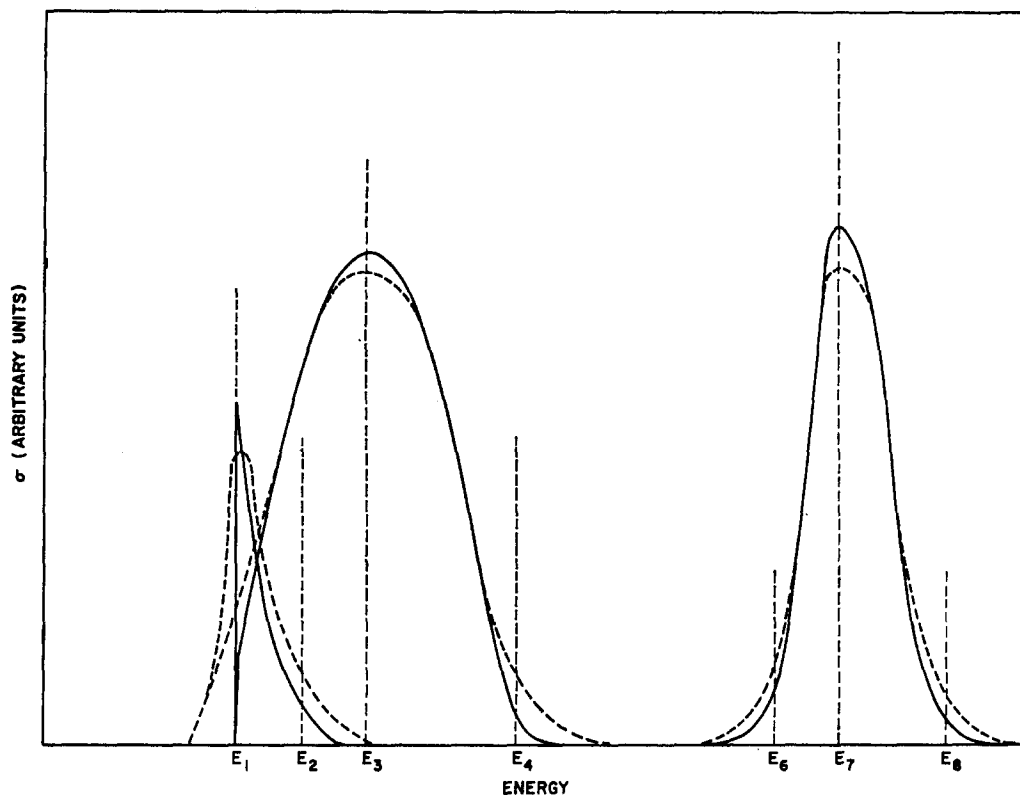


FIG. 2. Theoretical cross sections for dissociative electron attachment of electrons to molecules for the hypothetical potential curves in Fig. 1. No dissociative attachment is possible below E_1 . These curves are obtained by projecting the initial distribution in Fig. 1 on the potential curves in the Franck-Condon region. — Monoenergetic electrons, ---- finite energy spread.

for negative ions. At moderate electron energies (up to ~ 60 eV) one can usually adjust the field to saturate negative ions without collecting any positive ions. However, at higher electron energies, the ion drawout field required to prevent energetic positive ions from reaching the ion-collector plate is so large (> 35 V/cm) that scattered electrons are collected, and negative ion current saturation cannot be reached.

Third, the energy spread in the electron beam, due to thermal, space-charge, and ion-drawout-field effects, causes errors in the measured cross section for dissociative attachment as described in a previous section.

Fourth, the relatively small absolute cross sections for negative-ion formation in some substances make small amounts of impurities more of a problem, especially if the negative-ion cross section in the impurity is large.⁸ In H_2 , for example, small amounts of water vapor can produce relatively large amounts of H^- .^{8,9}

In the work reported herein, we pay particular at-

tention to these points as limiting factors on the reliability of the cross sections. Absolute cross sections were obtained by reversing the ion drawout field and comparing the positive ion current at some moderate electron energy, with the negative ion current at the highest resonance peak. The absolute cross sections for positive ionization were taken from Ref. 4. Denoting $\sigma_A(E_1)$ as the total cross section for attachment at energy E_1 , we have

$$\sigma_A(E_1)/\sigma_T(E_2) = i_-(E_1)/i_+(E_2),$$

where $\sigma_T(E_2)$ is the total ionization cross section at E_2 , i_+ is the saturated positive ion current at E_2 , and $i_-(E_1)$ is the saturated negative ion current at E_1 , corresponding to the same electron current.

The saturation curves for collection of negative ions were basically similar to those for positive ions, with the exceptions pointed out above. Figure 3 shows the saturation curve obtained in CO_2 for 8.1-eV electrons at the top of the resonance peak. It is seen that the negative ion current is saturated with an ion drawout field of ~ 3 V/cm. As the field is raised further, the energy spread across the finite width of the electron beam (0.005 in.) causes the apparent cross section to decrease. With 10-V/cm field, for example, the energy

⁸ G. J. Schulz, Phys. Rev. **113**, 816 (1959).

⁹ The absolute cross section for dissociative attachment in H_2O has been measured to be $\sim 5 \times 10^{-18}$ at the peak, whereas the peak cross section in H_2 is $\sim 2 \times 10^{-20}$ [I. S. Buchelnikova, Soviet Phys.—JETP **8**, 783 (1959); Zh. Eksperim i Tior **35**, 1119 (1959); and D. Rapp, D. D. Briglia, and T. E. Sharp, Phys. Rev. Letters, **14**, 533 (1965)]. Thus, 0.1% H_2O will have a $\sim 25\%$ effect on the cross section at low energies.

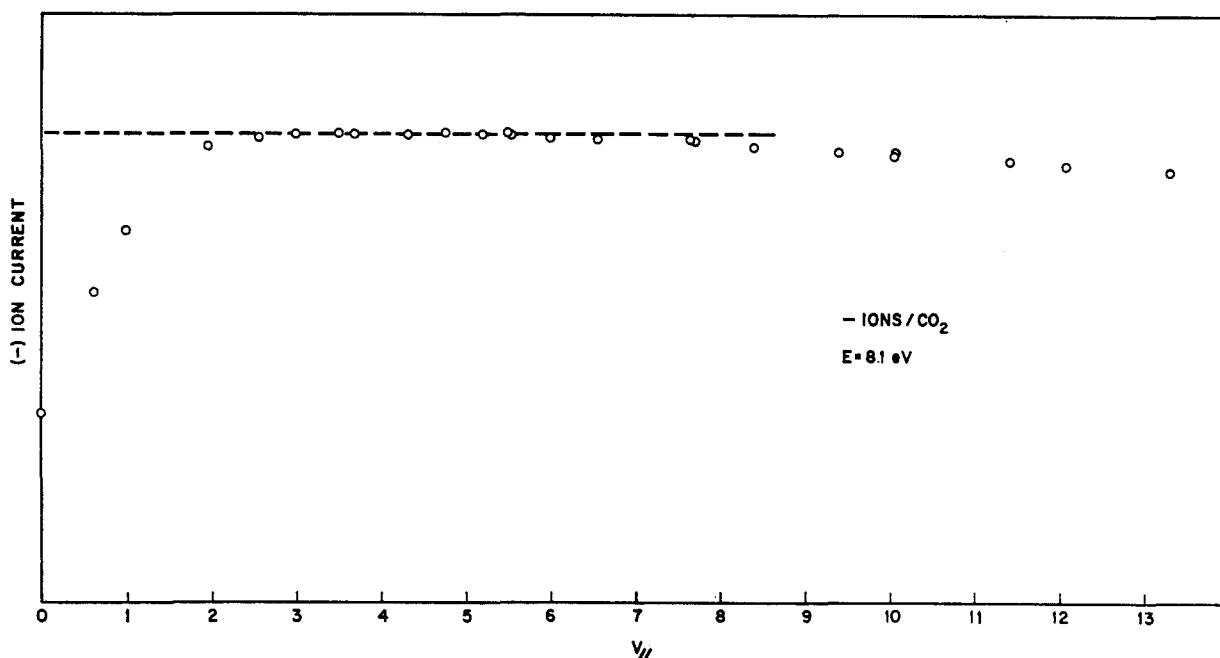


FIG. 3. Negative-ion saturation curve in CO_2 at 8.1 eV. As the ion-collection field is raised one gradually attains total collection (between 3 and 5.5 V). At higher fields, energy spread caused by the ion drawout field gradually reduces the measured ion current. The cross sections shown in Fig. 8 were taken for $V_{//}=4$ V.

spread due to the ion-collection field is ~ 0.12 V. This saturation curve is typical of saturation curves for negative ions produced by dissociative attachment in other gases. The cross section for dissociative attachment in CO_2 was taken with an ion-collection field of 4 V/cm. Figure 4 shows saturation curves for negative ions at several electron energies in CO. For 9.9-eV electrons, a saturation curve is obtained due to dissociative attachment, similar to that shown in Fig. 3 for CO_2 . At higher energies, where ion-pair formation is responsible for negative-ion formation, the effect of energy spread in the electron beam is small, and when saturation of the ion current is reached, the apparent cross section remains flat out to relatively high ion drawout fields. However, the energetic fragment ions from dissociative ionization must be prevented from reaching the ion-collector plate by increasing the ion drawout field. At low ion drawout fields, the current collected at the negative-ion collector is actually positive. Unfortunately, when the field is raised above ~ 35 V/cm, the negative current increases due to collection of multiply scattered electrons. It was therefore not possible to achieve negative-ion saturation at electron energies greater than ~ 60 eV. The negative ions from ion-pair formation in CO were studied with an ion drawout field of 26 V/cm. Table I shows the ion drawout fields used for saturation in the various gases.

The absolute energy scale was determined by plotting the electron current vs electron energy, and extrapolating to zero current, for the "contact potential."

It was found that this procedure gave good agreement (within ~ 0.1 eV) with spectroscopic appearance potentials for positive ions. The typical potential difference between the oxide-coated cathode and the metal plates of the ionization tube was ~ 1.5 V. The procedure used is illustrated in Fig. 5. It may be crudely rationalized by assuming there is a "turn-on" characteristic that is essentially a straight line above the contact potential, and that the thermal energy spread rounds the corners of this curve. The main justification of the procedure, however, is that it works for positive ions. Use of mass analysis¹⁰ in rare-gas- H_2 mixtures confirms the validity of this procedure.

The energy spread of the electron beam used in the experiments was ~ 0.2 eV full width at half-height as measured by retarding techniques. The width at $\frac{1}{10}$ height was ~ 0.4 eV.¹¹ These distributions are for zero ion drawout field. As mentioned before, there is an additional ~ 0.12 eV for each 10 V/cm of ion drawout field.

IV. EXPERIMENTAL RESULTS

The absolute cross sections for negative-ion formation were obtained by comparison with the positive-ion cross sections as shown in Table II. The magnitude

¹⁰ D. D. Briglia and D. Rapp, J. Chem. Phys. **42**, 3201 (1965).

¹¹ The distribution mentioned here is for an "R" distribution as discussed in Ref. 10, modified for higher absolute current at a slight sacrifice in resolution.

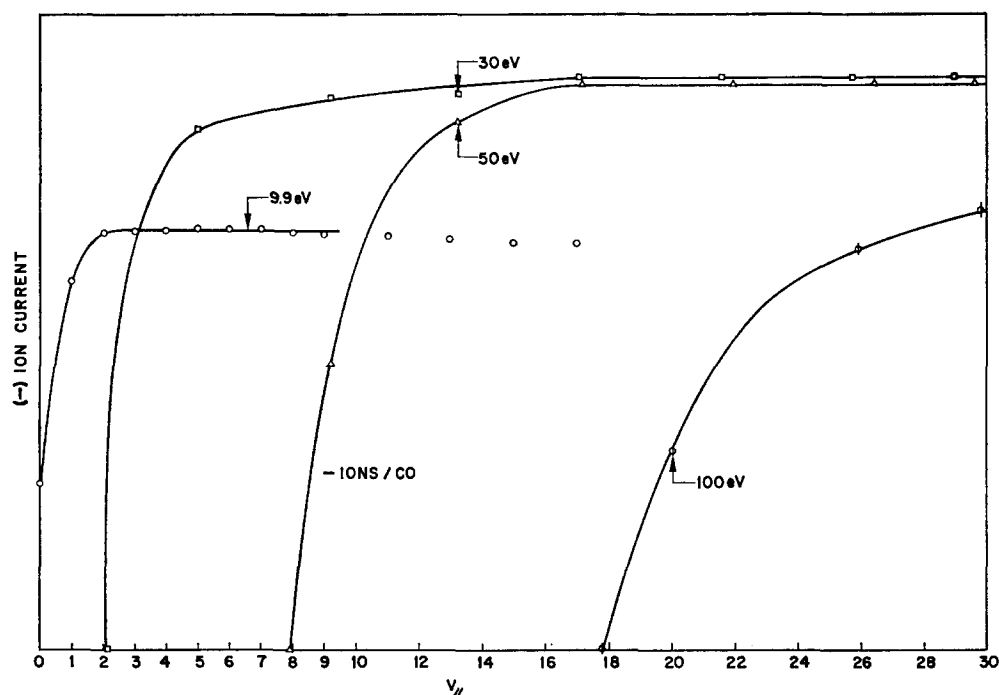


FIG. 4. Negative-ion saturation curves in CO for electron energies of 9.9, 30, 50, and 100 eV. At 9.9 eV, the typical curve for dissociative attachment is obtained. At higher energies, the negative ions are formed by ion-pair formation and are not affected by the energy spread induced in the electron beam by the ion drawout field. However, energetic positive ions formed by dissociative ionization greatly outnumber the negative ions at high energies, and it is difficult to reach saturation.

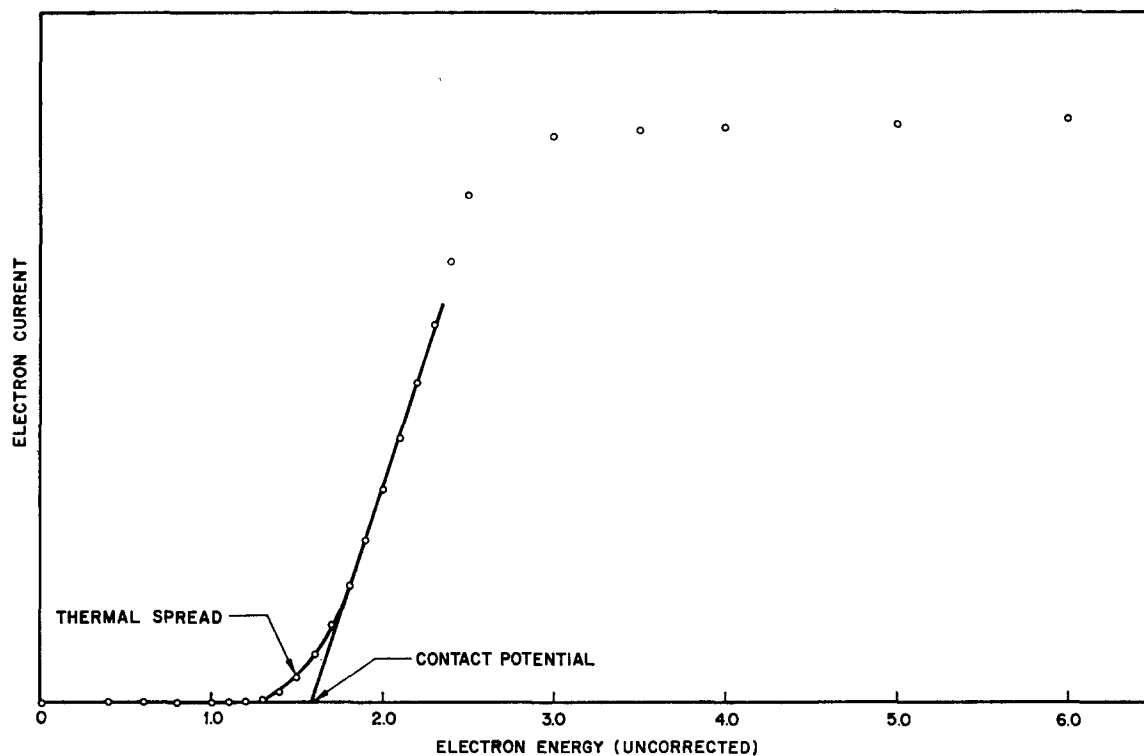


FIG. 5. Electron current as a function of electron energy. The 1.55-V contact potential is readily seen from the low-energy plot. At high energies the electron current varies slowly.

TABLE I. Ion drawout fields for saturation of negative ion currents in gases.

Gas	Electron energy range (eV)	Ion drawout field (V/cm)
CO ₂	0-12	4
	12-60	25
CO	0-15	5
	15-60	26
O ₂	0-12	5
	12-60	26
N ₂ O	0-6	3
	6-60	30
NO	0-14	4
H ₂ , D ₂ , HD	0-12.8	24
	12.8-18	10
SF ₆	0-10	2

for SF₆ is surely a severe underestimate due to electron energy spread, and the results in H₂ and CO may suffer slightly from energy spread. The energy dependences of the cross sections in H₂, HD, and D₂ were presented previously,¹² and are not given here. The cross sections in the gases, O₂, CO, CO₂, N₂O, and NO are given in Figs. 6-10. The low-energy data on dissociative attachment are tabulated in Table III. A plot of negative ion current and electron current vs electron energy near zero energy is shown in Fig. 11 for SF₆. The peak in the negative-ion-formation cross section occurs in the sharply rising portion of the electron "turn-on" curve, and it is readily apparent that the electron

TABLE II. Comparison of total ionization cross section at energy E_T , $\sigma_T(E_T)$, with resonance-peak attachment cross sections at E_A , $\sigma_A(E_A)$.

Gas	E_T (eV)	E_A (eV)	$\sigma_A(E_A)/\sigma_T(E_T)$	$\sigma_A(E_A)^a$ (πa_0^2)
O ₂	118	6.5	5.16×10^{-3}	0.0160
CO	99	9.9	7.64×10^{-4}	0.00230
NO	118.5	8.15	3.54×10^{-3}	0.0127
CO ₂	118	8.1	1.205×10^{-3}	0.00487
N ₂ O	109	2.2	2.29×10^{-2}	0.0978
SF ₆	110	~ 0.1	0.32 ^b	2.44 ^b
H ₂ ^c	69	13.9	2.01×10^{-4}	2.22×10^{-4}
HD ^c	69	13.95	1.41×10^{-4}	1.56×10^{-4}
D ₂ ^c	69	14.0	0.96×10^{-4}	1.07×10^{-4}

^a $\sigma_T(E_T)$ is taken from the adjoining paper on positive ionization.

^b May be a considerable underestimate due to actual energy spread and narrow resonance peak.

^c Data reported in Ref. 12.

¹² D. Rapp, D. D. Briglia, and T. E. Sharp, Ref. 9.

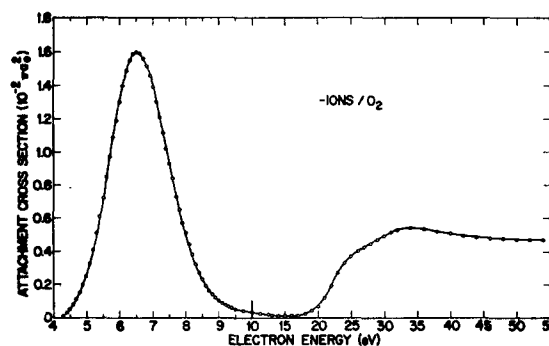
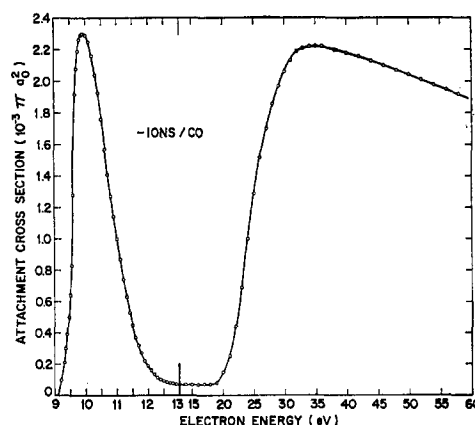
FIG. 6. Total cross section for negative-ion formation in O₂ by electron impact.

FIG. 7. Total cross section for negative-ion formation in CO by electron impact.

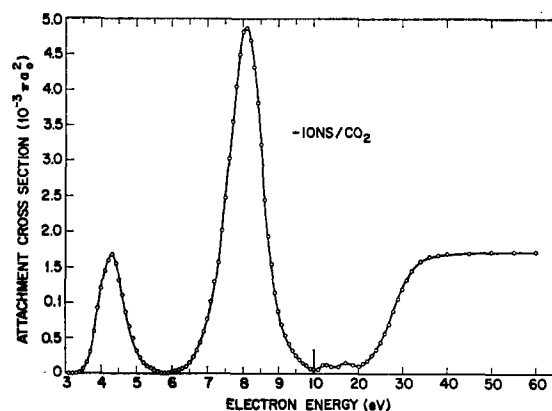
FIG. 8. Total cross section for negative-ion formation in CO₂ by electron impact.

TABLE III. Total cross sections for negative-ion formation as functions of electron energy. The cross sections were normalized as indicated in Table II.

O ₂		CO		NO		CO ₂		N ₂ O	
<i>E</i>	σ	<i>E</i>	σ	<i>E</i>	σ	<i>E</i>	σ	<i>E</i>	σ
(eV)	(10 ⁻² πa_0^2)	(eV)	(10 ⁻³ πa_0^2)	(eV)	(10 ⁻² πa_0^2)	(eV)	(10 ⁻³ πa_0^2)	(eV)	(10 ⁻² πa_0^2)
4.2	0.00	9.2	0.10	6.5	0.00	3.3	0.00	0.4	0.52
4.3	0.01	9.3	0.21	6.6	0.00	3.4	0.02	0.5	1.51
4.4	0.03	9.35	0.30	6.7	0.01	3.5	0.07	0.6	1.97
4.5	0.05	9.4	0.39	6.8	0.02	3.6	0.16	0.7	2.19
4.6	0.08	9.45	0.83	6.9	0.05	3.7	0.31	0.8	2.32
4.7	0.11	9.6	1.28	7.0	0.09	3.8	0.60	0.9	2.37
4.8	0.15	9.65	1.92	7.1	0.17	3.9	0.93	1.0	2.45
4.9	0.20	9.7	2.08	7.2	0.38	4.0	1.21	1.1	2.54
5.0	0.25	9.75	2.19	7.3	0.61	4.1	1.45	1.2	2.65
5.1	0.33	9.8	2.26	7.4	0.81	4.2	1.60	1.3	2.83
5.2	0.41	9.85	2.27	7.5	0.98	4.3	1.68	1.4	3.17
5.3	0.51	9.9	2.30	7.6	1.09	4.4	1.55	1.5	3.74
5.4	0.61	10.0	2.29	7.7	1.18	4.5	1.37	1.6	4.46
5.5	0.72	10.1	2.25	7.8	1.223	4.6	1.11	1.7	5.61
5.6	0.85	10.2	2.16	7.9	1.254	4.7	0.88	1.8	6.76
5.7	0.97	10.3	2.04	8.0	1.267	4.8	0.68	1.9	7.54
5.8	1.09	10.4	1.93	8.1	1.270	4.9	0.50	2.0	8.62
5.9	1.19	10.5	1.76	8.2	1.269	5.0	0.32	2.1	9.41
6.0	1.30	10.6	1.57	8.3	1.261	5.1	0.22	2.2	9.78
6.1	1.40	10.7	1.41	9.4	1.250	5.2	0.15	2.3	9.74
6.2	1.49	10.8	1.27	8.5	1.254	5.3	1.10	2.4	9.14
6.3	1.55	10.9	1.14	8.6	1.257	5.4	0.07	2.5	8.07
6.4	1.49	11.0	1.00	8.7	1.250	5.5	0.03	2.6	6.80
6.5	1.60	11.1	0.87	8.8	1.237	5.6	0.02	2.7	5.50
6.6	1.59	11.2	0.74	8.9	1.215	5.7	0.01	2.8	4.06
6.7	1.56	11.3	0.63	9.0	1.18	5.8	0.00	2.9	2.96
6.8	1.52	11.4	0.53	9.1	1.14	5.9	0.01	3.0	2.18
6.9	1.46	11.5	0.45	9.2	1.08	6.0	0.02	3.1	1.58
7.0	1.39	11.6	0.37	9.3	1.01	6.1	0.03	3.2	1.10
7.1	1.30	11.7	0.32	9.4	0.94	6.2	0.05	3.3	0.72
7.2	1.21	11.8	0.27	9.5	0.85	6.3	0.07	3.4	0.53
7.3	1.12	11.9	0.22	9.6	0.74	6.4	0.12	3.5	0.40
7.4	1.02	12.0	0.19	9.7	0.66	6.5	0.16	3.6	0.32
7.5	0.93	12.1	0.16	9.8	0.58	6.6	0.23	3.7	0.26
7.6	0.84	12.2	0.13	9.9	0.50	6.7	0.33	3.8	0.22
7.7	0.73	12.3	0.11	10.0	0.43	6.8	0.44	3.9	0.19
7.8	0.65	12.4	0.10	10.1	0.36	6.9	0.60	4.0	0.15
7.9	0.57	12.5	0.09	10.2	0.30	7.0	0.78	4.1	0.14
8.0	0.51	12.6	0.08	10.3	0.25	7.1	1.02	4.2	0.12
8.1	0.44	12.8	0.07	10.4	0.20	7.2	1.30	4.3	0.11
8.2	0.38	13.0	0.07	10.5	0.16	7.3	1.65	4.5	0.11
8.3	0.32			10.6	0.13	7.4	2.02	5.0	0.11
8.4	0.27			10.7	0.105	7.5	2.46		
8.5	0.23			10.8	0.09	7.6	3.03		
8.6	0.19			10.9	0.08	7.7	3.55		
8.7	0.16			11.0	0.07	7.8	4.06		
8.8	0.14			11.5	0.05	7.9	4.50		
8.9	0.12			12.0	0.05	8.0	4.82		
9.0	0.10			12.5	0.04	8.1	4.87		
9.1	0.08			13.0	0.04	8.2	4.70		
9.2	0.08					8.3	4.32		
9.3	0.07					8.4	3.82		
9.4	0.06					8.5	3.22		
9.5	0.05					8.6	2.44		
9.6	0.05					8.7	1.96		
9.8	0.04					8.8	1.55		
9.9	0.04					8.9	1.16		
						9.0	0.89		
						9.1	0.70		
						9.2	0.55		
						9.3	0.42		
						9.4	0.33		
						9.5	0.26		
						9.6	0.20		
						9.7	0.15		
						9.8	0.12		
						9.9	0.09		
						10.0	0.07		

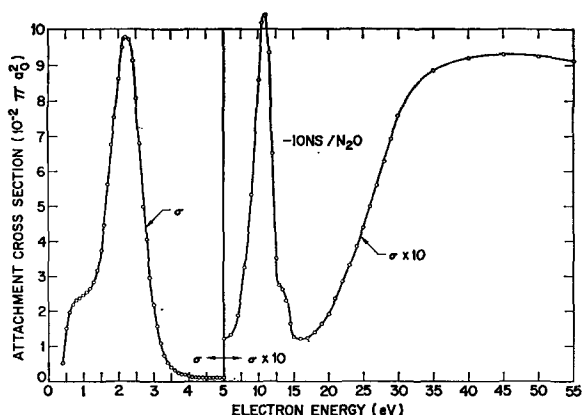


FIG. 9. Total cross section for negative-ion formation in N_2O by electron impact.

energy spread, not the width of the resonance peak, is being measured.⁷

V. DISCUSSION OF RESULTS

The cross-section peaks for dissociative attachment in O_2 , CO_2 , and NO are sufficiently broad that only

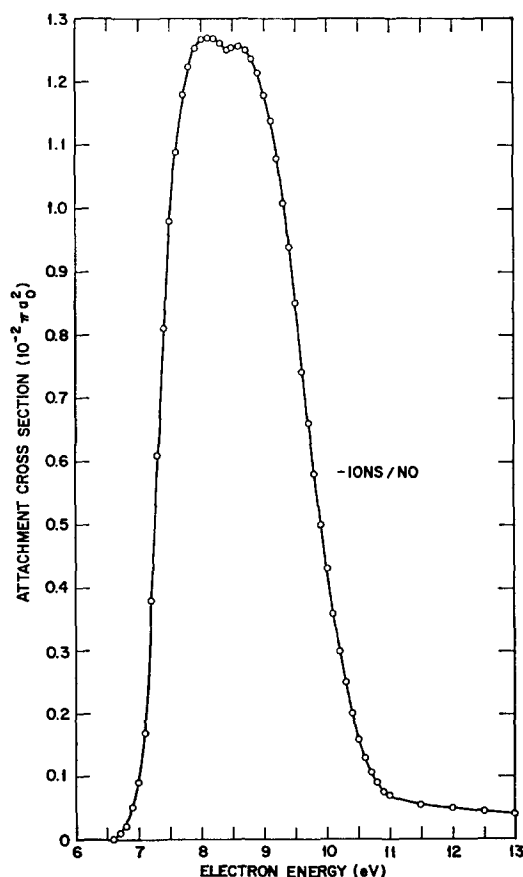


FIG. 10. Total cross section for negative-ion formation in NO by electron impact.

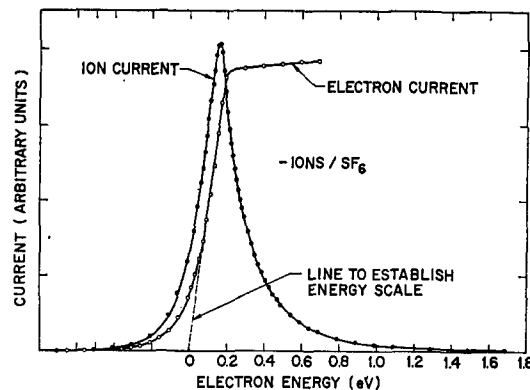


FIG. 11. Negative ion current and electron current in SF_6 as a function of electron energy.

slight errors should result from the energy spread in the electron beam. The mass-analyzed data of Hagstrum and Tate¹³ in O_2 , CO , and NO , show that O^- is the ion formed in the dissociation process. In CO , there is a difficulty that is discussed in a succeeding paragraph.

In Table IV, the absolute cross sections for dissociative attachment in CO , CO_2 , and O_2 measured by various investigators are compared. It can be seen that the general form of the energy dependences of the cross sections are the same for all investigators, but there are slight differences in absolute normalization, and energy scale. The cross sections in SF_6 are just rough approximations in either case. It is impossible to say exactly how high and how narrow the resonance peak is in SF_6 .

In CO , a special difficulty is encountered. The mini-

TABLE IV. Comparison of peak dissociative attachment cross sections in gases as measured by various investigators.

Gas	Investigator	Energy at peak (eV)	Peak cross section πa_0^2	Peak width at $\frac{1}{2}$ -height (eV)
O_2	R	6.5	0.0160	2.1
	S	6.7	0.015	2.2
	ACK (rel)	6.9	0.015	2.0
	ACK (abs)	6.5	0.015	2.0
	B	~ 6.3	0.015	1.9
CO	R	9.9	0.00230	1.3
	S	10.1	~ 0.0018	~ 1.4
	ACK (rel)	10.0	0.0024	1.3
	ACK (abs)	10.1	0.0027	1.3
$CO_2(1)$	R	8.1	0.0049	1.1
	S	8.2	0.0051	1.1
	ACK (rel)	8.3	0.0052	1.3
	ACK (abs)	8.0	0.0049	1.3
$CO_2(2)$	R	4.3	0.0017	0.9
	S	4.5	0.0017	0.9
	ACK (rel)	4.3	0.0015	0.9
	ACK (abs)	4.55	0.0017	1.0
SF_6	R	0.1	2.4	0.2
	B	0.0	5.7	0.5

¹³ H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

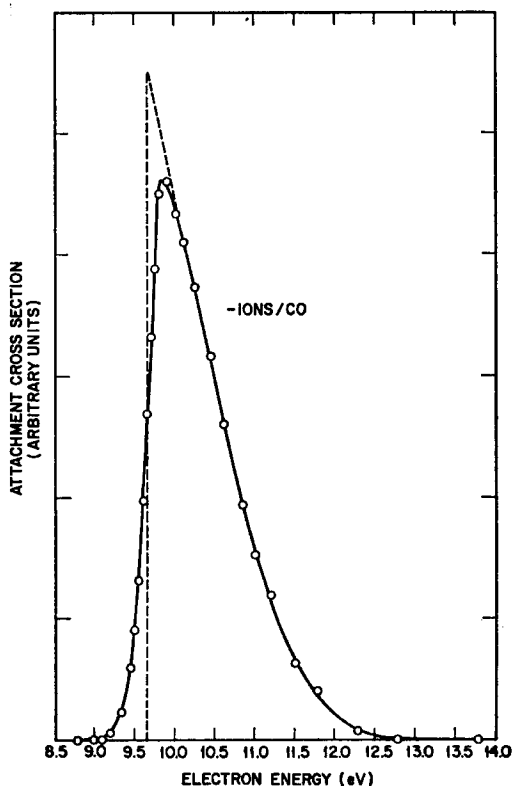


FIG. 12. Measured cross section for negative-ion formation in CO by the RPD method¹⁶ with a retarding potential difference of 0.1 eV and high electron current. The dotted line is hypothetical to indicate what the cross section may actually be with a mono-energetic electron beam.

imum energy required to produce $C+O^-$ from CO in the ground state is 9.65 eV.¹⁴ It therefore appears that the CO^- potential curve crosses the Franck-Condon region in the manner suggested by Curve X_2^- or $(X_2^-)'$ in Fig. 1. If a vertical threshold does occur in CO, the distortion of the apparent cross section due to energy spread can be considerable. An attempt to reduce the energy spread slightly by use of a retarding potential difference technique¹⁵ led to the apparent cross-section data points shown in Fig. 12. A suggested possible shape for the true cross section is given by the dotted line. This hypothetical cross section is commensurate with the observed cross section if the energy spread is taken into account.

¹⁴ The dissociation energy of CO is 11.11 eV and the electron affinity of O is 1.46 eV.

¹⁵ Unfortunately, the absolute electron current used in this work was too high to reduce the energy spread decisively. It has been found [D. D. Briglia and D. Rapp, *Bull. Am. Phys. Soc.* **10**, 181 (1965), Paper C3(d)] that the electron current must be reduced to $\sim 10^{-8}$ A to approach an energy spread corresponding to the retarding potential difference. At the higher currents (5×10^{-7} A) used here, the energy spread is larger than the retarding potential difference. The larger current was used because the cross section for dissociative attachment is very small, and the ion current would be too noisy at lower electron currents. With the retarding potential difference set at 0.1 eV and the high absolute current, it is found that the actual energy distribution is ~ 0.15 eV wide at half-height, and ~ 0.4 eV wide at one-tenth height.

The factors that determine the accuracy of the cross section are:

- (1) The energy spread in the electron beam must be small compared to the resonance-peak width or the peak height will be underestimated.
- (2) The energy zero must be determined by onset of a positive ion or by electron-current-vs-energy measurements. It is usually impossible to assess this to better than ± 0.1 eV, despite superior claims by some investigators.
- (3) Complete collection of the negative ions must be achieved with an ion drawout field small enough so that no substantial energy spread is put into the electron beam.
- (4) The absolute ionization cross section in the gas must be known for use as the ultimate absolute standard.
- (5) One must be sure that trapped electrons do not contribute to the "negative ion current." Such trapped electrons could be produced in electronic excitation processes near threshold.
- (6) The effect of impurities must be small.

The effects of energy spread have been discussed in preceding paragraphs. It is believed that only in SF_6 and CO is this a serious problem. The effects of energy spread appear to be roughly the same in this work as in measurements by various investigators.^{3,16} The determination of the absolute zero of energy also appears to be about as accurate in the previous work as in the present work. We have emphasized complete collection of the ion current at the cost of slight energy spread, and believe this to be the main contribution here. The absolute cross sections for positive ionization were taken from the accompanying paper.⁴ The effect of impurities was reduced to a minimum by using a completely bakable vacuum system so that the gases could be studied at pressures 10^4 above the background.

A problem that is difficult to evaluate is possible collection of trapped electrons at the ion-collector plate. It was found that when the ion drawout field was raised to very high values (> 35 V/cm) the collected negative current increased, presumably due to this effect. One can never be absolutely assured that the collected current is entirely due to negative ions, except by mass analysis. However, it is impossible to obtain absolute cross sections, or even relative cross sections, in a mass spectrometer,³ due to discrimination effects. One point in question is the small, but nonzero, negative current found between the main resonance peak and the onset of ion-pair formation (see Figs. 6-10). Hagstrum and Tate,¹³ using mass analysis, find the cross sections for negative-ion formation in this region to be essentially zero. It is difficult to assess whether this may have been due to discrimination effects and the ultimate sensitivity in their mass

¹⁶ R. K. Asundi, J. D. Craggs, and M. V. Kurepa, *Proc. Phys. Soc. (London)* **82**, 967 (1963).

spectrometer. On the other hand, the nonzero cross section found in total-collection devices may be due to instrumental errors (cf. the discussion of O_2 in Ref. 3).

The onsets for ion-pair formation need not be a measure of the minimum energy to produce the ion pair if the potential curve for the ion pair is repulsive in the Franck-Condon region.

VI. CONCLUSIONS

Absolute total cross sections for negative-ion formation in several gases have been measured in a total

ionization tube. Particular emphasis has been placed on total collection of the ions. Errors due to energy spread and scattered electrons are discussed. Good agreement is found with previous work on those cross sections that have been measured by other investigators.

ACKNOWLEDGMENTS

The authors would like to acknowledge the capable assistance of Mr. Raymond D. Rempt. They would also like to thank the Lockheed Independent Research Program for support.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 43, NUMBER 5

1 SEPTEMBER 1965

Reaction of Atomic Oxygen with Acetylene. II. Chemi-Ionization and Chemiluminescence

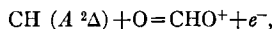
C. A. ARRINGTON, W. BRENNEN, G. P. GLASS, J. V. MICHAEL, AND H. NIKI

Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts

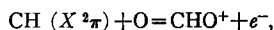
(Received 20 May 1965)

The chemiluminescence and chemi-ionization resulting from the room-temperature reaction of atomic oxygen with acetylene have been investigated. The absolute intensity of chemiluminescent radiation and the over-all rate of chemi-ion formation have been measured and the relative concentrations of various individual chemi-ions have been observed with a T.O.F. mass spectrometer.

It has been shown conclusively from these measurements that chemi-ionization does not arise primarily from the reactions:



It has been shown also that if ionization arises from the reaction



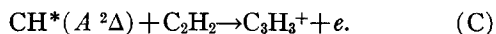
a mechanism that has also received wide support, then the ground state $CH(X^2\pi)$ molecule must be produced by some mechanism other than that producing $CH(A^2\Delta)$.

The $CH(A^2\Delta-X^2\pi)$ system was found to be the most intense feature of the chemiluminescent spectrum. Weak emission from the C_2 Swan bands and from the CN violet system was also observed. The intensity of the weak OH emission was found to be consistent with it being produced by reactions with molecular oxygen. The CH emission was shown to arise from a complex series of reactions involving the participation of three molecules of acetylene and two atoms of oxygen. Two possible mechanisms for its production are discussed.

INTRODUCTION

THE room-temperature reaction of atomic oxygen with acetylene exhibits intense chemi-ionization and chemiluminescence. The chemiluminescence spectrum has been described by Broida and Krishnamachari.¹ The most intense emission is produced by the $CH(A^2\Delta-X^2\pi)$ system. Weaker emission from $CH(B^2\Sigma-X^2\pi)$, C_2 , CN, and OH are also observed. Chemi-ionization in this reaction was first observed by Fontijn and Baughman.² Later, Fontijn, Hogan,

and Miller³ listed the most abundant ions in the system and noted the effect of carbon dioxide and several free-radical scavengers on both the chemi-ion spectra and on the intensity of chemiluminescence. They proposed the following mechanism of chemi-ionization:



Reactions (B) and (C) were thought to be dominant. Chemi-ionization in acetylene-oxygen systems has

¹ S. L. N. G. Krishnamachari and H. P. Broida, *J. Chem. Phys.* **34**, 1709 (1961).

² A. Fontijn and G. L. Baughman, *J. Chem. Phys.* **38**, 1784 (1963).

³ A. Fontijn, W. J. Miller, and J. M. Hogan, *Symp. Combust.* 10th, Cambridge, England, 1964, 545 (1965).