

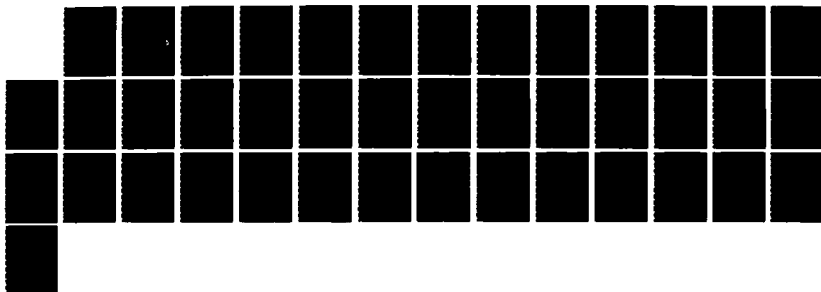
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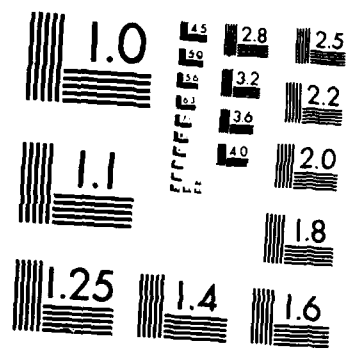
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The electron attachment rate constants of SO_2 , CS_2 , and SOCl_2 in buffer gases of Ar, N_2 , and CH_4 were measured at various E/N by a parallel-plate drift-tube electron-swarm technique. The initial electron-swarm was produced by irradiation of cathode with excimer laser. The electron attachment processes for the electronegative gases studied were investigated. The transient increase of electron conduction current by photoelectron-detachment of negative ions in the discharge medium of SOCl_2 in N_2 was observed. This switching is useful for the development of opening switches. Key words:		

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Annual Scientific Report for Grant No. AFOSR-82-0314
Covering the Period from 1 August 1985 to 31 July 1986

ELECTRON PRODUCTION, ELECTRON ATTACHMENT, AND CHARGE
RECOMBINATION PROCESS IN HIGH PRESSURE GAS DISCHARGES



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I. INTRODUCTION

This annual report covers the period from August 1, 1985 to July 31, 1986 for the research project under Grant No. AFOSR-82-0314. The processes for electron production, electron attachment, and charge recombination in high pressure gaseous mixtures were investigated in this research program. The information obtained from this program is currently needed for the development of various electrical switching devices as well as for the understanding of basic phenomena in plasma physics.

Electrical switching devices, for example, high repetition-rate discharge switches, opening switches, radiation or e-beam controlled switches, are needed for the development of high power lasers, fusion experiment, magnetic energy storage system, as well as particle beam experiment. High pressure gaseous discharges are often involved in these switching devices. Every discharge switch requires special characteristics pertinent to the pulse rise time, decay time, discharge stability, discharge uniformity, and current density. These characteristics are determined by the electron transport parameters of a gas mixture, such as electron drift velocity, electron attachment, detachment and ionization coefficients as well as charge recombination rates. Thus, for the design of various discharge switches, these electron transport parameters need to be well studied. This research program provides these basic data for the development of various discharge switches.

In addition to measuring fundamental data for practical applications, we also develop new techniques for laser-controlled electrical switching. It has been observed that the electron conduction current in a gaseous discharge medium can be enhanced by photoelectron-detachment of negative ions. The electron conduction current can also be reduced by the optically-enhanced electron-attachment process. The observed current switching can, in principle, be applied to develop diffuse-gaseous-discharge opening switches.

II. RESEARCH ACCOMPLISHMENTS

The electron transport parameters in high pressure buffer gases were measured with a parallel-plate drift-tube apparatus. Electrons were initially produced by irradiating the cathode with an intense excimer laser pulse. The electric field produced by applying a negative high voltage on the cathode was used to drift the electrons. The transient voltage pulse induced by electron motion between the electrodes was monitored by a digitizer and stored in an IBM XT microcomputer. The electron attachment rate was obtained from the ratio of the amplitudes of transient pulses with and without a gas attachers in the buffer gas. The electron drift velocity and the electron diffusion coefficient were obtained by analyzing the time profile of transient pulse.

In this period, the switching of electron conduction current by photoelectron-detachment and photodissociation processes was also observed in the discharge medium of SOCl_2 in N_2 , where a negative point-to-plane corona discharge was used. Results

accomplished in this period are described below:

1. Electron Attachment Coefficients of SO₂

The electron attachment rate constants of SO₂ in buffer gases of Ar, N₂, and CH₄ were measured as a function of E/N. The electron attachment rate constant of SO₂ in Ar increases with E/N, and it is independent of Ar pressure, indicating that the electron attachment is due to the dissociative attachment process. The characteristic that the electron attachment rate increased with E/N is desirable for the design of opening switches.

For the SO₂-N₂ and SO₂-CH₄ gas mixtures, the electron attachment rates decrease with increasing E/N and increase with increasing buffer gas pressure. The electron attachment to SO₂ in N₂ and CH₄ is attributed to the Bloch-Bradbury two-step three-body nondissociative attachment process. The mean electron energy in the N₂ or CH₄ buffer gas is lower than 1 eV, electrons do not have sufficient energy for the dissociative attachment process.

The results for the electron attachment of SO₂ in various buffer gases are reported in more detail in a paper attached as Appendix A, which has been published in the Journal of Chemical Physics.

2. Electron Attachment Coefficients of CS₂

The electron attachment coefficients of CS₂ in the buffer gases of N₂ and CH₄ were measured as a function of E/N. In both N₂ and CH₄ buffer gases, the electron attachment rates of CS₂

increase with increasing CS₂ and buffer gas pressures and decrease with increasing E/N. This attachment process is attributed to the Bloch-Bradbury two-step three-body nondissociative attachment process. The collisional-stabilized rate for the "temporary" negative compound ion of CS₂^{-*} by various gases (CS₂, N₂, and CH₄) were also investigated.

The results for the electron attachment of CS₂ in various buffer gases are reported in the paper attached as Appendix A.

3. Electron Attachment Coefficients of SOCl₂

It has been demonstrated that the conduction current in a corona discharge of SOCl₂-N₂ mixture can be switched (increased and decreased) when the gas medium is irradiated by ArF laser photons. This observation is, in principle, useful for the development of laser-controlled opening switches. The electron attachment rates for SOCl₂ in various buffer gases are needed for such application.

The electron attachment coefficients of SOCl₂ in buffer gases of Ar, N₂, and CH₄ were measured as a function of E/N. For SOCl₂ in Ar, the electron attachment rate constant is maximum at E/N = 4 Td. For SOCl₂ in N₂ and CH₄, the electron attachment rate constants decrease with increasing E/N (1-15 Td). For every gas mixture studied, the electron attachment rate constant is independent of buffer gas pressure, indicating that the electron attachment to SOCl₂ is due to a dissociative electron-attachment process. The electron attachment processes in various gas mixtures were investigated.

The results for the electron attachment of SOCl_2 in various buffer gases are reported in more detail in a paper attached as Appendix B, which has been accepted by the Journal of Chemical Physics for publication.

4. Switching of Conduction Current in the Discharge Medium of SOCl_2

The transient current in a negative point-to-plane corona discharge of $\text{SOCl}_2\text{-N}_2$ mixture produced by ArF laser pulse was investigated. The experimental apparatus is shown in Fig. 1. It has been observed that the transient current increases initially because of the increase of conduction electrons that are produced from the photoelectron-detachment of negative ions (SO^- , Cl^- , Cl_2 , SOCl^- , etc) in the discharge medium by laser photons; and the transient current decreases later because of the increase of electron attachment rate by the photofragments (e.g. Cl , Cl^* , SO , SO^*) produced from laser dissociation of SOCl_2 . As an example, the transient current pulses at various SOCl_2 pressure are shown in Fig. 2. Both of the amplitudes and duration of the transient current are being investigated as a function of $[\text{SOCl}_2]$, laser energy, and laser beam size.

The results for the current switching in the discharge medium of SOCl_2 in N_2 will be summarized in a paper and submitted to a scientific journal for publication. After this paper is prepared we will continue to pursue this type of experiment with different electronegative gases (e.g. SF_6) in the next funding period.

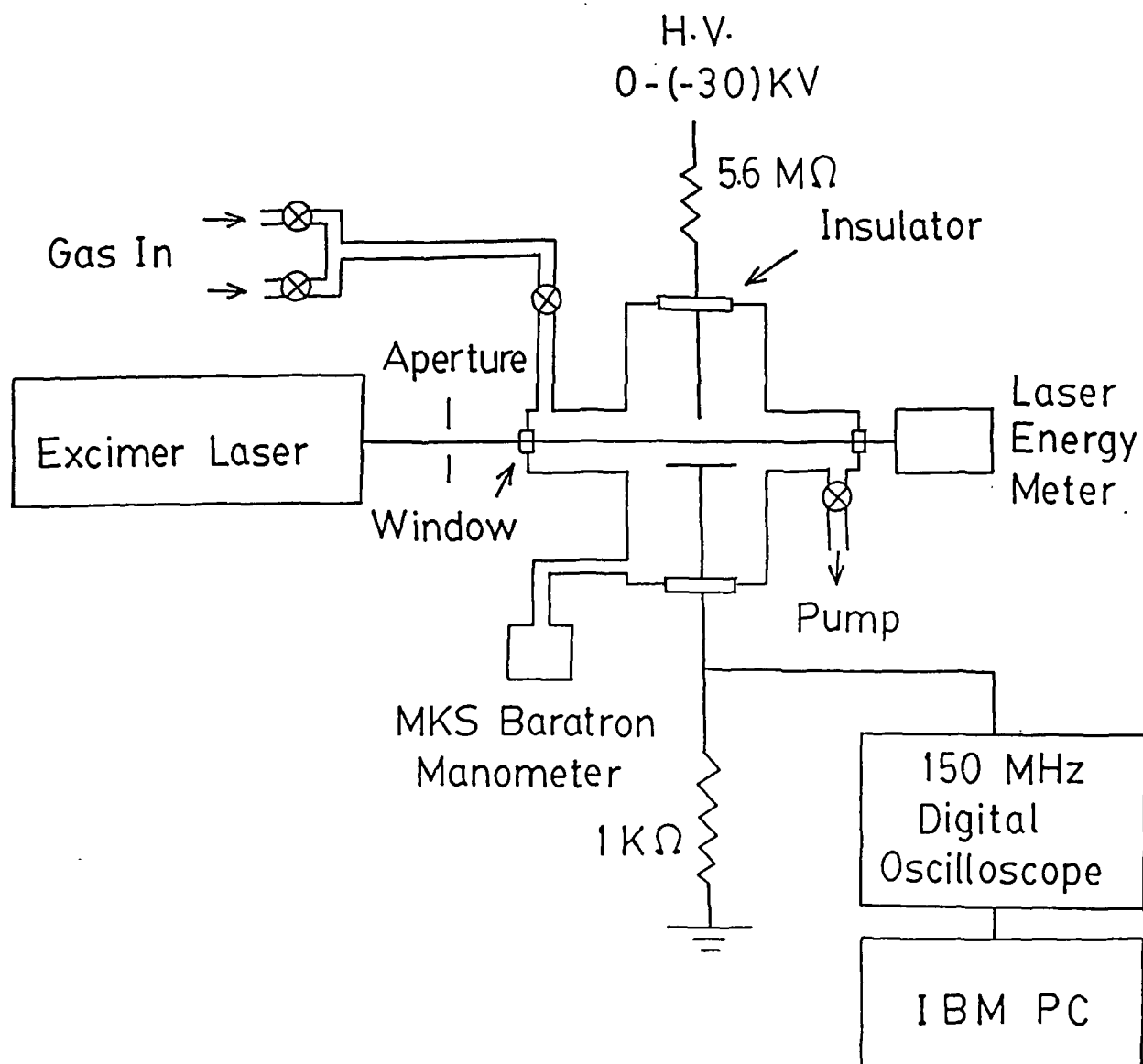


Fig. 1. Schematic diagram for experimental apparatus.

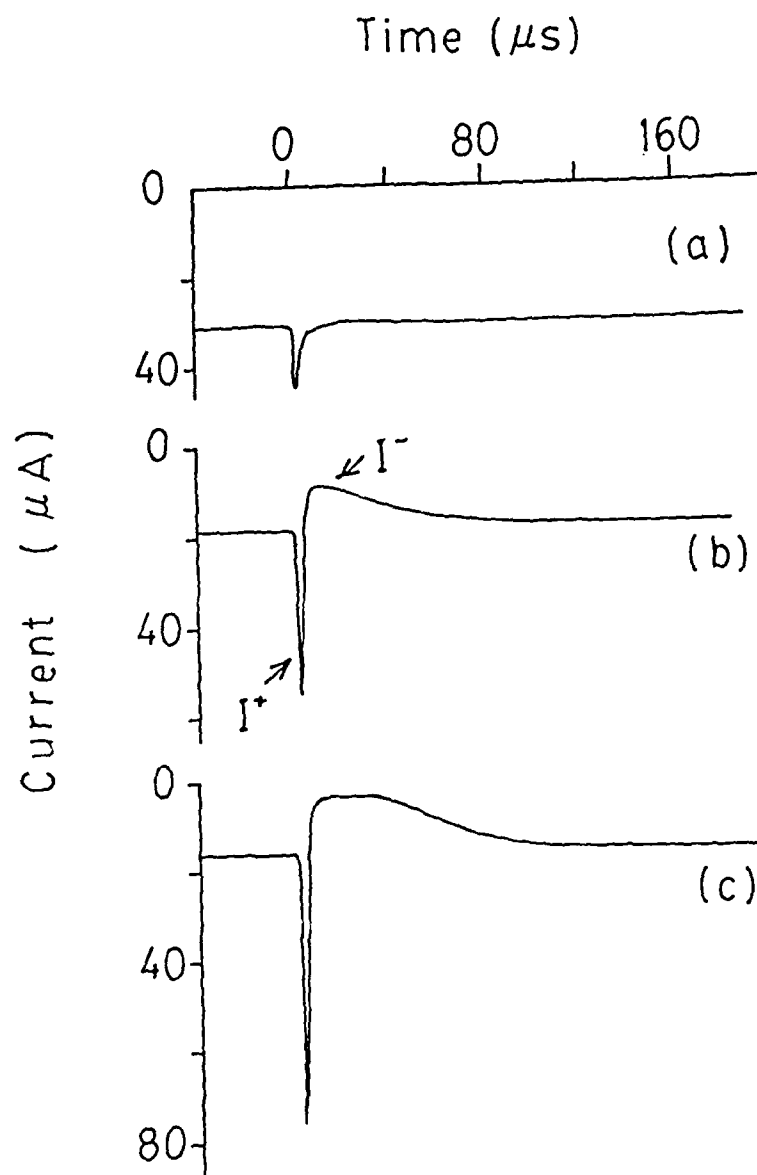


Fig. 2. The transient current waveforms after the discharge medium was irradiated by an ArF laser pulse. The partial pressures of SOCl_2 were (a) 0, (b) 0.8, and (c) 3.4 mtorr, the laser energy was 1.5 mJ/pulse, the laser beam diameter was 6 mm, the applied voltage was -0.75 kV, and the N_2 pressure was about 26 torr. I^+ and I^- indicate the current increase and decrease from the DC current level (about 18 μA), respectively.

III. CUMULATIVE PUBLICATIONS AND PRESENTATIONS

1. "Two-Photon-Ionization Coefficients of Propane, 1-Butene, Methylamines" L. C. Lee and W. K. Bischel, presented at the 12th International Conference on the Physics of Electronic and Atomic Collisions, Gatlinburg, TN, July 15-21, 1981.
2. "Electron Attachment and Charge Recombination Following Two-Photon-Ionization of Methylamines" L. C. Lee and W. K. Bischel, presented at the 34th Gaseous Electronics Conference, Boston, MA, October 20-23, 1981.
3. "Two-Photon-Ionization Coefficients of Propane, 1-Butene, and Methylamines" L. C. Lee and W. K. Bischel, J. Appl. Phys. 53, 203 (1982).
4. "Electron Ionization and Attachment Processes in Diffuse Discharges" L. C. Lee, presented to the Workshop on Optical Control of Diffuse Discharges, Eugene, OR, December 2-3, 1982.
5. "Diffusion of Electrons in Gases Under Electric Field" F. Li and L. C. Lee, presented at the 1983 Annual Meeting, APS Division of Electronic and Atomic Physics, Boulder, CO, May 23-25, 1983.
6. "Electron Longitudinal Diffusion Coefficients in Ar" F. Li and L. C. Lee, presented at the 36th Gaseous Electronics Conference, Albany, NY, October 10-14, 1983.
7. "Space Charge Effect on the Electron Kinetics Occurring in Atmospheric Gas Pressure" L. C. Lee and F. Li, presented at the 1984 IEEE International Conference on Plasma Science, St. Louis, MO, May 14-16, 1984.
8. "Shortening of Electron Conduction Pulses by Electron Attachers O₂, N₂O and CF₄" L. C. Lee and F. Li, J. Appl. Phys., 56, 3169 (1984).
9. "Electron Attachment to C₃F₈ in High Pressure Buffer Gases" W. C. Wang and L. C. Lee, presented at the DEAP Meeting, American Physical Society, Norman, OK, May 29-31, 1985.
10. "Electron Attachment to H₂O in Ar, N₂, and CH₄ in Electric Field" W. C. Wang and L. C. Lee, J. Appl. Phys. 57, 4360 (1985).
11. "Shortening of Electron Conduction Pulses by Electron Attacher C₃F₈ in Ar, N₂, and CH₄" W. C. Wang and L. C. Lee, J. Appl. Phys. 58, 184 (1985).

12. "Shortening of Electron Conduction Pulses by Electron Attachers" L. C. Lee and W. C. Wang, presented at the IEEE Pulsed Power Conference, Arlington, VA, June 10-12, 1985.
13. "Electron Attachment to H_2O , SO_2 , and C_3F_8 in Ar, N_2 , and CH_4 " W. C. Wang, M. A. Fineman and L. C. Lee, presented at the XIV International Conference on the Physics of Electronic and Atomic Collisions, Palo Alto, CA, July 24-30, 1985.
14. "Electron Production by Photoionization of CS_2 and SO_2 at 193 nm" L. C. Lee and W. C. Wang, presented at the Thirty-Eighth Annual Gaseous Electronics Conference, Monterey, CA, Oct. 15-18, 1985.
15. "Electron Attachment to SO_2 and CS_2 in Ar, N_2 and CH_4 " W. C. Wang and L. C. Lee, presented at the Thirty-Eighth Annual Gaseous Electronics Conference, Monterey, CA, Oct. 15-18, 1985.
16. "Two-Photon-Ionization Coefficients of CS_2 , SO_2 , and $(CH_3)_3N$ " W. C. Wang and L. C. Lee, J. Appl. Phys. 58, 3295 (1985).
17. "Electron Attachment Rate Constants of SO_2 and CS_2 in Ar, N_2 , and CH_4 at varied E/N " J. Chem. Phys. 84, 2675 (1986).
18. "Electron Attachment Rate Constants of $SOCl_2$ in Ar, N_2 and CH_4 " W. C. Wang and L. C. Lee, presented at the Joint Meeting of the DAMO and DCP of the American Physical Society, Eugene, OR, June 18-20, 1986.
19. "Switching of Conduction Current by Photodetachment and Photodissociation Processes Occurring in the $SOCl_2$ - N_2 Gas Mixture" W. C. Wang and L. C. Lee, accepted for presentation at the Thirty-Ninth Annual Gaseous Electronics Conference, Madison, WI, October 6-10, 1986.
20. "Electron Attachment to $SOCl_2$ in Ar, N_2 , and CH_4 " W. C. Wang and L. C. Lee, J. Chem. Phys. to be published Dec 15, 1986.
21. "Switching of Electron Conduction Current by Molecular Photoelectron Detachment and Photodissociation Process" submitted to SPIE, Optoelectronics and Laser Applications in Science and Engineering, Los Angeles, CA, Jan. 11-16, 1987.

IV. PERSONNEL INVOLVED IN THIS RESEARCH

1. Principal Investigator:
Dr. Long C. Lee, Professor of Electrical & Computer Engineering
2. Research Associates:

Dr. W. C. Wang
3. Students:

Mr. Dan Diehl
Mr. Robert Tahimic
Mr. F. Mehran
Ms. M. Waxman

V. INTERACTIONS

1. We have sent our papers to Dr. A. H. Guenther at the Air Force Weapons Laboratory, Dr. Alan Garscadden at the Air Force Wright Aeronautical Laboratory, Dr. M. Gundersen at the University of Southern California, Dr. J. T. Moseley at the University of Oregon, Dr. Bob Reinovsky at the Air Force Weapons Laboratory, and Dr. S. K. Srivastava at the Jet Propulsion Laboratory. We appreciate the useful comments and suggestions received from them.
2. The results obtained in the current funding period had been presented at (i) the Thirty-Eighth Annual Gaseous Electronics Conference, Monterey, CA, Oct. 15-18, 1985; (ii) the APS Joint Meeting of The Division of Atomic Molecular and Optics Physics and The Division of Chemical Physics, Eugene, OR, June 18-20, 1986.
3. To participate in the workshop on "Research Issues in Pulsed Power Conditioning" held at the University of Southern California, Los Angeles, December 3-4, 1985.

Appendix A

Electron Attachment Rate Constants of
SO₂ and CS₂ in Ar, N₂, and CH₄ at Varied E/N

Electron attachment rate constants of SO₂ and CS₂ in Ar, N₂, and CH₄ at varied E/N

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(Received 7 October 1985; accepted 19 November 1985)

The electron attachment rate constants of SO₂ and CS₂ in the buffer gases of Ar, N₂, and CH₄ (150 to 530 Torr) at various E/N (1–16 Td) were measured by a parallel-plate drift-tube electron-swarm technique. The electrons were produced by irradiating the cathode with KrF laser photons. For the SO₂-Ar mixture, the electron attachment rate constant of SO₂ increases with increasing E/N and is independent of Ar pressure. For SO₂ in N₂ and CH₄, the electron attachment rates decrease with increasing E/N and increase with increasing buffer gas pressure. For CS₂ in N₂ and CH₄, the electron attachment rates increase with increasing CS₂ and buffer gas pressures and decrease with increasing E/N . The electron attachment to SO₂ and CS₂ in the buffer gases of N₂ and CH₄ is a three-body process. The collisional-stabilized rates of "temporary" negative compound ions SO₂⁻* and CS₂⁻* by various gases are investigated.

I. INTRODUCTION

Recent advances in pulsed-power technology require¹ opening switches for developing a magnetic energy storage system whose energy density is much higher (10^2 – 10^3 times) than the capacitive system.² An opening switch requires a fast decay of the conduction current which may be achieved by attaching electrons to electronegative gases mixed in a buffer gas.¹ The electron attachment rates for various gas mixtures are thus of interest in practical applications as well as in basic understanding of electron attachment processes as indicated in recent electron-swarm experiments.³ In this paper, the electron attachment processes and rate constants for SO₂ and CS₂ in Ar, N₂, and CH₄ are reported.

Electron attachment to SO₂ was first studied by Bradbury and Tatel⁴ and later by several other authors^{5–10} either in pure SO₂ or in various SO₂ mixtures. In pure SO₂, Lakdawala and Moruzzi⁵ and Schlumbohm⁶ observed that the electron attachment rate constant of SO₂ had a pressure dependence and they attributed it to the three-body nondissociative attachment process. The attachment rates of SO₂ were observed to be dependent on buffer gas pressure by Bouby *et al.*⁷ for the buffer gases of N₂, CO₂, C₂H₄, and CH₃OH and by Rademacher *et al.*⁸ for N₂ and C₂H₄. The electron attachment to SO₂ in various gas mixtures was attributed to the three-body nondissociative attachment process. For the SO₂-Ar mixture, the dissociative attachment process is dominant.

There is very little information available for the electron attachment process of CS₂. To the best of our knowledge, the nondissociative electron attachment rate constant of CS₂ has not been reported. CS₂⁻ is known to be a stable negative ion, because CS₂ has a positive electron affinity.^{11,12} In fact, it has been observed in several charge-transfer reactions such as: (i) collisional ionization of alkali atoms¹³; (ii) charge transfer from highly excited Rydberg states of Kr atom¹²; (iii) charge transfer from negative ions¹⁴; and (iv) charge transfer from the dissociative negative ion fragments of CS₂.^{15,16}

However, there are no reports on the observation of direct electron attachment to CS₂. Due to a large nuclear deformation from CS₂ to CS₂⁻,¹² the probability for direct attachment of slow electrons to CS₂ may be small.

In this experiment, a parallel-plate drift-tube electron-swarm technique^{16–18} was applied to measure the electron attachment rates of SO₂ and CS₂ in Ar, N₂, and CH₄ at various E/N . The E/N can be converted to the mean electron energy using the known electron energy distribution function.³ The attachment processes in SO₂ and CS₂ are explainable by the Bloch-Bradbury two-step three-body attachment mechanism.¹⁹

II. EXPERIMENT

The experimental setup has been discussed in detail in previous papers.^{16–18} In brief, the gas cell is a 6 in. six-way aluminum cross. The electrodes are two parallel uncoated stainless steel plates of 5 cm in diameter and 3.6 cm apart. The electron swarm was produced by irradiation of the cathode with KrF (Lumonics model 861S) laser beam which has a pulse duration of about 10 ns. An ArF laser is not used here, because it can ionize CS₂ and SO₂ by two-photon process,²⁰ and the electrons produced in the gas phase will perturb the electron attachment measurements. The energy of the laser pulse was monitored by an energy meter (Scientech model 365). A negative high voltage was applied to the cathode. The conduction current induced by the electron motion between the electrodes was observed as a transient voltage pulse across a resistor (100–2000 Ω) connecting the anode to ground. The transient pulse was monitored and stored by a 275 MHz storage oscilloscope (HP model 1727A) and was photographed for permanent record.

The gas pressure in the gas cell was maintained constant in a slow flow system (flow rate about 20 cm³ STP/min). The gas pressure was measured by an MKS Baratron manometer. All measurements were done at room temperature. The Ar, N₂, and CH₄ gases (supplied by MG Scientific) have purities of 99.998%, 99.998%, and 99.99%, respective-

ly. SO_2 or CS_2 was diluted in Ar, N_2 , or CH_4 before being introduced into the gas cell. The SO_2 supplied by Matheson has a purity of 99.98%. The CS_2 liquid with 99.9% purity was supplied by MCB Manufacturing Chemists, Inc. The CS_2 liquid contained in a stainless steel cylinder was pumped several hours at dry ice temperature to remove dissolved impurities before its vapor was used in the experiment. The impurity level was believed to be very low, because the experimental results were reproducible before or after an additional pumping. The impurities that possibly accompanied CS_2 vapor should not be more than 0.1%.

III. RESULTS AND DISCUSSION

A. SO_2

The waveforms of electron transient voltages for the SO_2 -Ar mixture at $E/N = 2.5$ Td are shown in Fig. 1, where the pressure of Ar was 240 Torr, and the pressures of SO_2 were (a) 0, (b) 0.032, and (c) 0.082 Torr, respectively. The pulse was produced by a single shot, but it is a representative for the average of several sequential shots. From shot to shot, the pulse amplitudes varied within 10%. This variation was mainly caused by the fluctuation of laser energy. The curves shown in Fig. 1 were taken under the same experimental conditions.

As shown in Figs. 1(b) and 1(c), both the pulse durations and the amplitudes decreased when a small amount of SO_2 was admitted into the gas cell. The shortening of pulse duration is due to the increase of electron drift velocity, similar to the cases observed in the H_2O -Ar^{17,21} and C_3F_8 -Ar^{18,22} mixtures. The decrease of amplitudes is caused by electron attachment to SO_2 . This decrease of amplitude can be used to derive the electron attachment rate as described in previous papers.^{16,17} The method of analysis of our data is briefly described below.

The electron conduction current induced by electron motion between the electrodes can be expressed as follows²³:

$$i(t) = eN_e W / d, \quad (1)$$

where N_e is the number of electrons existing between the electrodes, W is the electron drift velocity, and d is the electrode spacing. When a small amount of SO_2 is added to the gas cell, the electron conduction current will decrease due to attachment, which becomes

$$i'(t) = eN_e' W' e^{-\nu_a t} / d, \quad (2)$$

where ν_a is the electron attachment rate (or frequency). N_e' and W' may vary slightly from the values of Eq. (1). The transient voltage in Fig. 1 is related to the electron conduction current by

$$V(t) = f(t)i(t)R, \quad (3)$$

where R is the resistor connecting the anode to ground, and $f(t)$ is the electronics response function that approaches a constant at $t > RC$ (about 60 ns).

The logarithm of the ratio of the voltages with and without SO_2 in buffer gas is thus

$$\ln(V'/V) = \ln(N_e' W' / N_e W) - \nu_a t. \quad (4)$$

At atmospheric pressure and relatively low values of E/N , electrons can reach an equilibrium state in a very short time.^{17,23} Thus, W and W' can be practically considered as constant except for those electrons near the electrodes. For $T < d/W$ (or d/W'), N_e (or N_e') is a constant except for the beginning of the pulse where some electrons diffuse back to the cathode.²³ Therefore, after a short period of time, the first term of Eq. (4) should be independent of time and the slope of $\ln(V'/V)$ vs time gives the electron attachment rate.

The electron attachment rate constant of the two-body process is determined by $\nu_a/[\text{SO}_2]$. In the SO_2 -Ar mixture, we find that the $\nu_a/[\text{SO}_2]$ value is independent of Ar pressure and decreases with increasing $[\text{SO}_2]/[\text{Ar}]$, similar to the results reported by Rademacher *et al.*⁸ This decrease is likely caused by the effect of SO_2 on the electron energy distribution in Ar, similar to the case of H_2O .¹⁷ The electron attachment rate constant, k_a , which is obtained from extrapolating the plot of $\nu_a/[\text{SO}_2]$ vs pressure at $[\text{SO}_2] = 0$, is associated with the electron energy distribution of pure Ar. The results of the k_a values at various E/N are shown in Fig. 2 for an Ar pressure of 240 Torr. The scale of the mean electron energy, $\langle \epsilon \rangle$, is shown in the top of Fig. 2, where the $\langle \epsilon \rangle$ value in Ar was given by Christophorou and Hunter.²⁴ For comparison, the results of Rademacher *et al.*⁸ are plotted as a solid line in Fig. 2, and the agreement between these two data is quite good.

The electron attachment in the SO_2 -Ar mixture is mainly due to the dissociative attachment process,⁸ for which SO_2 is dissociated into $\text{SO} + \text{O}^-$, $\text{SO}^- + \text{O}$, and $\text{S}^- + \text{O}_2$ whose threshold energies are 4.15, 4.52, and 3.6 eV,^{3,5,8} respectively. As shown in Fig. 2, the electron attachment rate constant increases with increasing E/N .

The attachment rates of low-energy electrons to SO_2 in N_2 were measured at various E/N (0.5–3 Td). The values of $\nu_a/[\text{SO}_2]$ vs E/N and $\langle \epsilon \rangle$ are shown in Fig. 3, where $[\text{N}_2] = 490$ Torr and $[\text{SO}_2] = 0.4$ –1.7 Torr. The values of $\langle \epsilon \rangle$ in N_2 as a function of E/N were given by Christophorou and Hunter.²⁴ In the SO_2 pressure range studied, the $\nu_a/[\text{SO}_2]$ values are not significantly affected by $[\text{SO}_2]$. As shown in Fig. 3, the $\nu_a/[\text{SO}_2]$ values decrease with increasing E/N . At E/N higher than 3 Td, the electron attachment rates are too small to be measured accurately.

The dependence of the $\nu_a/[\text{SO}_2]$ values on $[\text{N}_2]$ was investigated extensively by Rademacher *et al.*⁸ for the N_2

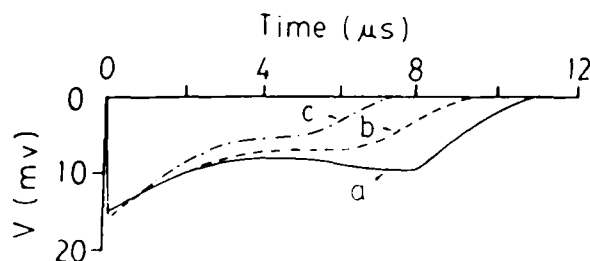


FIG. 1. The waveform of transient voltage pulses produced from electron motion in 240 Torr of Ar (a) without SO_2 , (b) with 0.032 Torr of SO_2 , and (c) with 0.082 Torr of SO_2 . The electrons were produced from irradiation of the cathode by KrF laser photons. The E/N was fixed at 2.5 Td, the electrode spacing was 3.6 cm, and the external resistor was 2 k Ω .

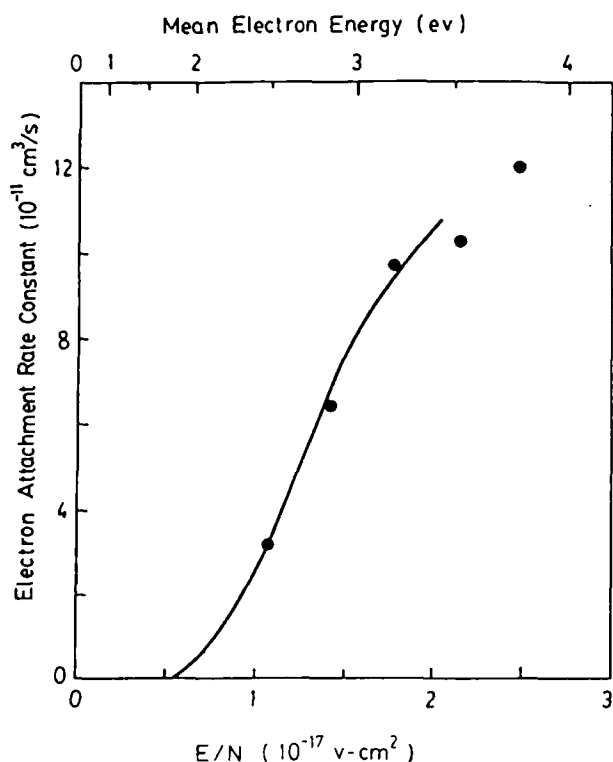
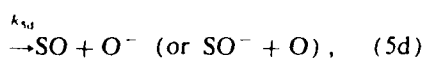
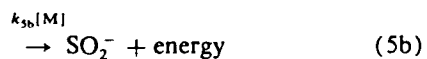
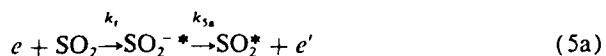


FIG. 2. Electron attachment rate constant as a function of E/N (bottom scale) and mean electron energy (top scale) for SO_2 in Ar. The data from Ref. 8 (—) are plotted for comparison.

pressure in the range of 300–23 000 Torr. The electron attachment rates (αW in Ref. 8) increase linearly with $[\text{N}_2]$ at pressures less than 4000 Torr, and they show saturation at higher pressures. The data with $[\text{N}_2] = 500$ Torr in Ref. 8 are plotted in Fig. 3 to compare with our data. As shown in Fig. 3, the agreement between these two data is again very good.

The values of $\nu_a/[\text{SO}_2]$ for the $\text{SO}_2\text{--CH}_4$ mixtures were measured as a function of E/N or $\langle\epsilon\rangle$ as shown in Fig. 4 for $[\text{CH}_4] = 257$ and 427 Torr. At each E/N , the $\langle\epsilon\rangle$ value is assumed to be equal to $3/2(eD_L/\mu)$, where D_L/μ is the ratio of lateral electron diffusion coefficient to electron mobility.²⁴ In this measurement, the SO_2 pressure was varied in the range of 0.4–1.7 Torr, and the observed $\nu_a/[\text{SO}_2]$ values did not depend on $[\text{SO}_2]$.

The electron attachment processes of SO_2 in various buffer gases have been explained⁸ by the following processes:



where k_t is the rate constant for the formation of the "temporary" compound negative ion SO_2^- , k_{sa} is the rate constant for autoionization, k_{sb} is the rate constant for the collisional

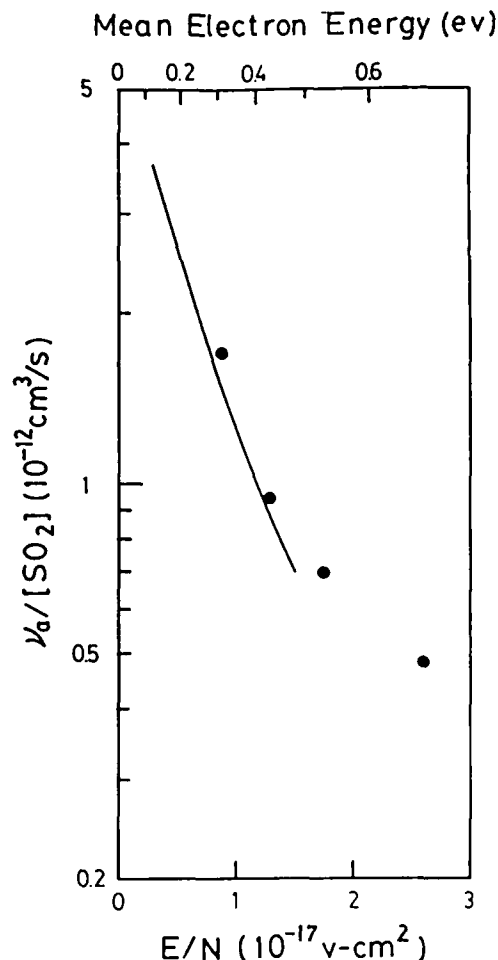


FIG. 3. The $\nu_a/[\text{SO}_2]$ values (●) as a function of E/N (bottom scale) and mean electron energy (top scale) for SO_2 (0.4–1.7 Torr) in 490 Torr of N_2 . The data from Ref. 8 (—) which were taken at 500 Torr of N_2 are plotted for comparison.

stabilization of SO_2^- by a third body M, k_{sc} is the rate constant for the radiative stabilization of SO_2^- , and k_{sd} is the dissociative electron attachment rate constant.

For $\langle\epsilon\rangle > 2$ eV, the dissociative electron attachment process (5d) will occur as observed in the Ar buffer gas (see

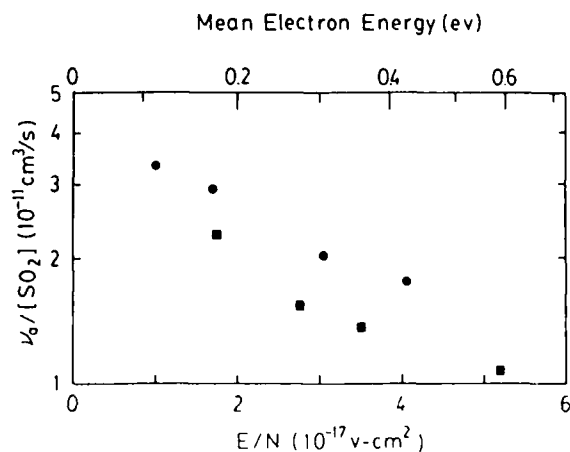


FIG. 4. The $\nu_a/[\text{SO}_2]$ as a function of E/N (bottom scale) and mean electron energy (top scale) for SO_2 (0.4–1.7 Torr) in 427 (●) and 257 (■) Torr of CH_4 .

Fig. 2). For lower $\langle\epsilon\rangle$, only the processes (5a)–(5c) are possible. The third body M here could be either N_2 , CH_4 (or C_2H_4 in Ref. 8), or even SO_2 . The $[SO_2]$ dependence of $\nu_a/[SO_2]$ had been observed^{5,6} before in pure SO_2 but not in this work and Refs. 7 and 8 whose SO_2 mixtures were used. Since the buffer gas pressures were about two orders of magnitude higher than $[SO_2]$ in this work, unless the k_{sb} with SO_2 as a third body is more than two orders of magnitude higher than those with the buffer gases, the collisional stabilization of SO_2^-* by SO_2 should be negligible here. The attachment rate derived from processes (5a)–(5c) is

$$\nu_a/[SO_2] = k_i(k_{sb}[M] + k_{sc})/(k_{sa} + k_{sb}[M] + k_{sc}). \quad (6)$$

For the case⁸ of C_2H_4 , k_{sc} is much smaller than $k_{sb}[M]$, because $\nu_a/[SO_2] \rightarrow 0$ as $[C_2H_4] \rightarrow 0$. This may be also the case in CH_4 . Thus, $\nu_a/[SO_2]$ can be approximated as

$$\nu_a/[SO_2] = k_i k_{sb}[M]/(k_{sa} + k_{sb}[M]). \quad (7)$$

The k_i value will depend on $\langle\epsilon\rangle$. However, at low $\langle\epsilon\rangle$, it may not vary largely with $\langle\epsilon\rangle$. The k_i values⁸ are 8.9×10^{-11} and 7.0×10^{-11} cm³/s for SO_2 – N_2 in $0.04 \leq \langle\epsilon\rangle \leq 0.13$ eV and for SO_2 – C_2H_4 in $0.041 \leq \langle\epsilon\rangle \leq 0.085$ eV, respectively. If we take the k_i value in SO_2 – CH_4 to be equal to the value in SO_2 – C_2H_4 , the $\nu_a/[SO_2]$ value of 3.3×10^{-11} cm³/s measured at 427 Torr of CH_4 and $E/N = 1.0$ Td ($\langle\epsilon\rangle = 0.11$ eV) gives the ratio of $k_{sb}/k_{sa} = 2.1 \times 10^{-3}$ Torr⁻¹ for CH_4 as a third body. This value is between the values⁸ of 6.7×10^{-5} and 6.3×10^{-3} Torr⁻¹ obtained from N_2 and C_2H_4 , respectively. These results show that CH_4 is more effective than N_2 in stabilizing SO_2^-* to SO_2^- , but it is less effective than C_2H_4 . This is consistent with the fact that large molecules have more degrees of freedom to take away the excess energy of SO_2^-* . This phenomenon is also observed in the electron attachment processes of CS_2 as described below.

B. CS_2

The transient waveforms of electron voltages with 0, 0.236, and 0.367 Torr of CS_2 in 250 Torr of N_2 are shown in Figs. 5(a), 5(b), and 5(c), respectively, where E/N is fixed at 5.1 Td. Again, the decrease in the electron voltages in Figs. 5(b) and 5(c) is due to the electron attachment to CS_2 . The attachment rate ν_a can be obtained from the ratio of the voltages with and without CS_2 in N_2 .

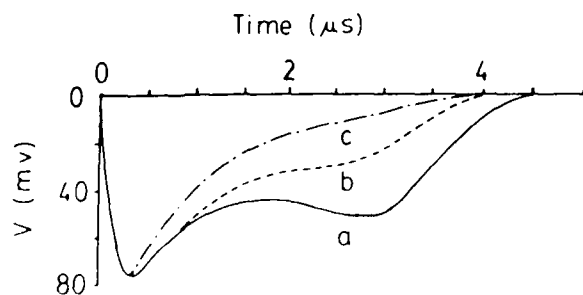


FIG. 5. The waveforms of transient voltage pulses produced from the electron motion in 255 Torr of N_2 : (a) without CS_2 , (b) with 0.236 Torr, and (c) with 0.367 Torr of CS_2 . The E/N was fixed at 5.1 Td. The electrode spacing was 3.6 cm, and the external pressure was 1 Torr.

The $\nu_a/[CS_2]$ value for the CS_2 – N_2 mixture is dependent on both $[CS_2]$ and $[N_2]$ in the gas cell, in contrast to the SO_2 – N_2 mixture whose $\nu_a/[SO_2]$ value is only dependent on $[N_2]$. At a fixed $[N_2]$, it increases linearly with increasing $[CS_2]$ as shown in Fig. 6, where E/N is 9.64 Td and $[N_2]$ are 256, 371, 440, and 515 Torr. At each $[CS_2]$, the $\nu_a/[CS_2]$ value increases with increasing $[N_2]$. The intercepts of Fig. 6 are linearly dependent on $[N_2]$ as shown in Fig. 7.

The above results suggest that the electron attachment to CS_2 is explainable by processes (5a)–(5c), where SO_2 is replaced by CS_2 . These processes are often used to explain the low-energy electron attachment to electronegative gases.²⁵ Since $\nu_a/[CS_2] \rightarrow 0$ as both $[CS_2] \rightarrow 0$ and $[N_2] \rightarrow 0$ as shown in Fig. 7, the k_{sc} in Eq. (6) is thus negligible when compared with $k_{sb}[M]$. Thus, only the processes (5a) and (5b), which are called the Bloch–Bradbury two-step three-body attachment processes,¹⁹ are needed to explain our work in CS_2 . In order to accommodate the results that $\nu_a/[CS_2]$ is linearly dependent on $[CS_2]$ and $[N_2]$, the k_{sa} in Eq. (6) (with $[SO_2]$ replaced by $[CS_2]$) must be larger than $k_{sb}[M]$. Taking these approximations into consideration, Eq. (6) (with $[SO_2]$ replaced by $[CS_2]$) simplifies to

$$\nu_a/[CS_2] = k_i k_{sb}[M]/k_{sa}. \quad (8)$$

It should be noted that for the case of CS_2 , $[M]$ includes both $[CS_2]$ and $[N_2]$, because the stabilization rate of CS_2^-* by CS_2 is comparable with N_2 in the gas cell, namely,

$$\nu_a/[CS_2] = k_0[CS_2] + k'_0[N_2]. \quad (9)$$

A plot of $\nu_a/[CS_2][N_2]$ vs $[CS_2]/[N_2]$ at each E/N will give k_0 as the slope and k'_0 as the intercept. The plots measured at various E/N (2.55–16.7 Td) are shown in Fig. 8, from which the values of k_0 and k'_0 are determined and are

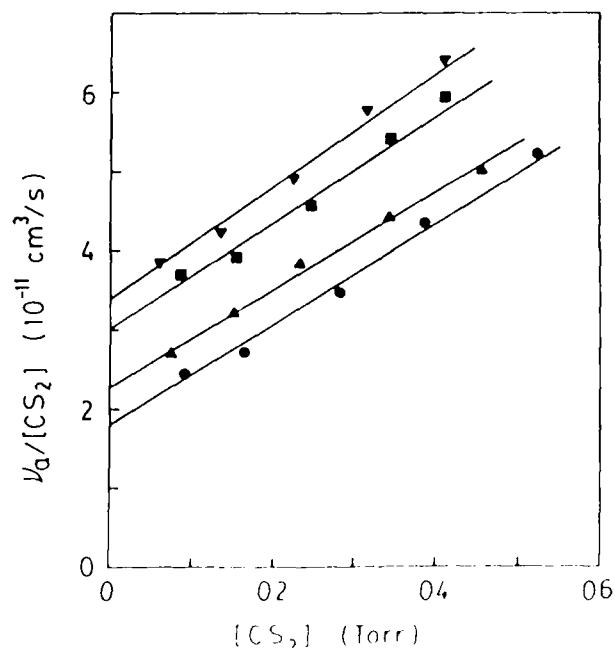


FIG. 6. The $\nu_a/[CS_2]$ vs $[CS_2]$ at fixed $[N_2]$: 256 (●), 371 (▲), 440 (■), and 515 (▼) Torr, respectively. The E/N was fixed at 9.64 Td. The $[N_2]$ data are from Ref. 26 (p. 1).

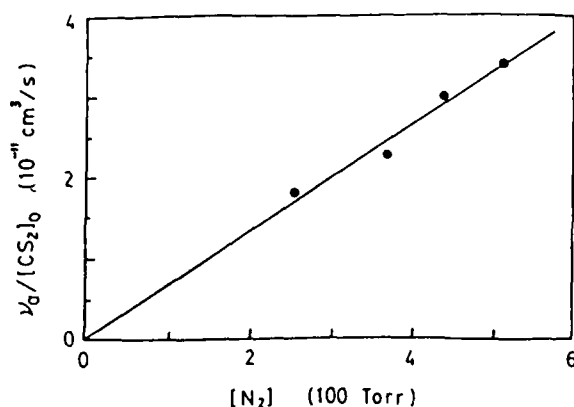


FIG. 7. The intercepts, $\nu_a/[\text{SO}_2]_0$, of the lines in Fig. 6 at $[\text{CS}_2] = 0$ as a function of N_2 pressure.

plotted as a function of E/N in Figs. 9(a) and 9(b), respectively. k_9 is about three orders of magnitude higher than k_{10} , indicating that CS_2 is much more effective than N_2 to stabilize CS_2^- .

The electron attachment to CS_2 in CH_4 was also studied in this experiment. Similar to the $\text{CS}_2\text{--N}_2$ mixture, at a fixed $[\text{CH}_4]$, the $\nu_a/[\text{CS}_2]$ values increase linearly with increasing $[\text{CS}_2]$ as shown in Fig. 10, where E/N was fixed at 10.1 Td and $[\text{CH}_4]$ were 146, 255, 390, and 525 Torr. The intercepts of the linear lines of $\nu_a/[\text{CS}_2]$ vs $[\text{CS}_2]$ in Fig. 10 increase linearly with increasing $[\text{CH}_4]$, similar to the case of N_2 (See Fig. 7).

Again, the $\nu_a/[\text{CS}_2]$ values for the $\text{CS}_2\text{--CH}_4$ mixture can be expressed by

$$\nu_a/[\text{CS}_2] = k_{10}[\text{CS}_2] + k'_{10}[\text{CH}_4]. \quad (10)$$

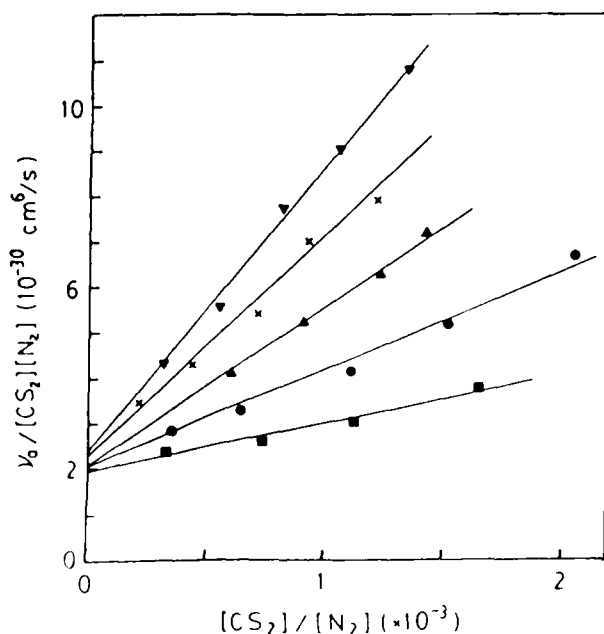


FIG. 8. Three-body attachment rate constant $\nu_a/[\text{CS}_2][\text{N}_2]$ as a function of $[\text{CS}_2]/[\text{N}_2]$, where $[\text{N}_2]$ was fixed at 255 Torr, and $E/N = 2.55$ ($\blacktriangledown$), 3.4 ($\times$), 5.1 ($\blacktriangle$), 9.64 ($\bullet$), and 16.7 ($\blacksquare$) Td, respectively.

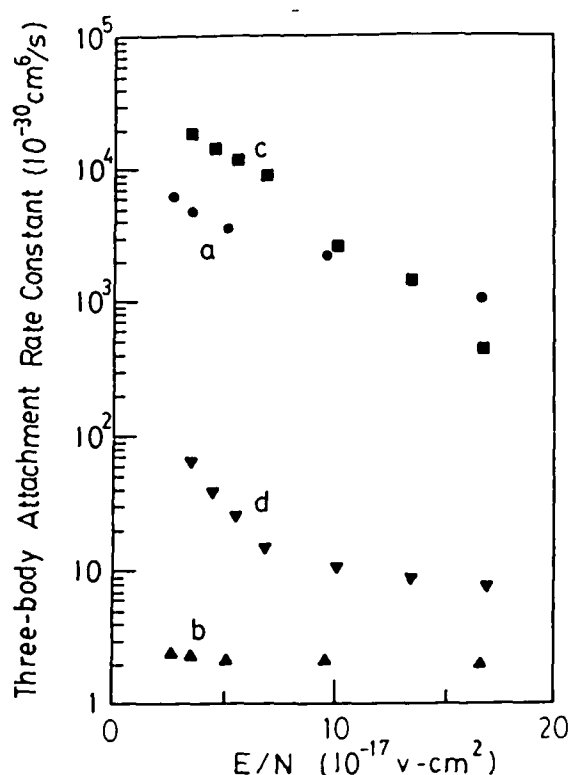


FIG. 9. Three-body attachment rate constants k_9 and k_{10} of CS_2 with CS_2 as a third body in N_2 (a) and CH_4 (c), and k'_9 with N_2 (b) and k'_{10} with CH_4 (d) as a third body as a function of E/N .

The plot of $\nu_a/[\text{CS}_2][\text{CH}_4]$ vs $[\text{CS}_2]/[\text{CH}_4]$ at each E/N will give k_{10} and k'_{10} . These plots for various E/N the range of 3.39 to 16.79 Td are shown in Fig. 11. These k_{10} and k'_{10} values derived from Fig. 11 are plotted in Figs. 9(c) and 9(d). At each E/N , k_{10} is about two orders of magnitude higher than k'_{10} . Similar to the $\text{CS}_2\text{--N}_2$ case, CS_2 is also much more effective than CH_4 as a third body in stabilizing CS_2^- .

CS_2^- is a stable molecule because of its positive electron affinity (about 0.5–1 eV^{11,12}). CS_2^- has been observed in several experiments, although a direct attachment of low-energy electron to CS_2 has not yet been reported. In the stud-

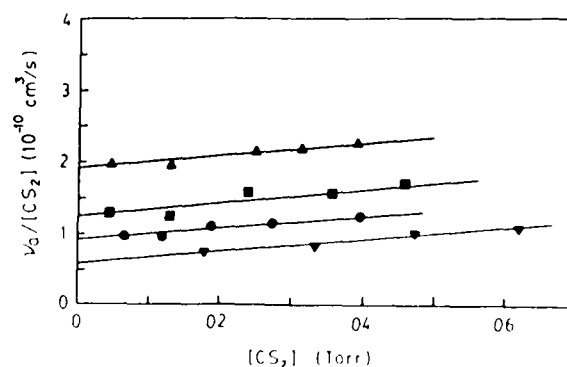


FIG. 10. The $\nu_a/[\text{CS}_2]$ values as a function of $[\text{CS}_2]$ at $E/N = 10.1$ Td, and $[\text{CH}_4] = 146$ ($\blacktriangledown$), 255 ($\bullet$), 390 ($\blacksquare$), and 525 ($\blacktriangle$) Torr.

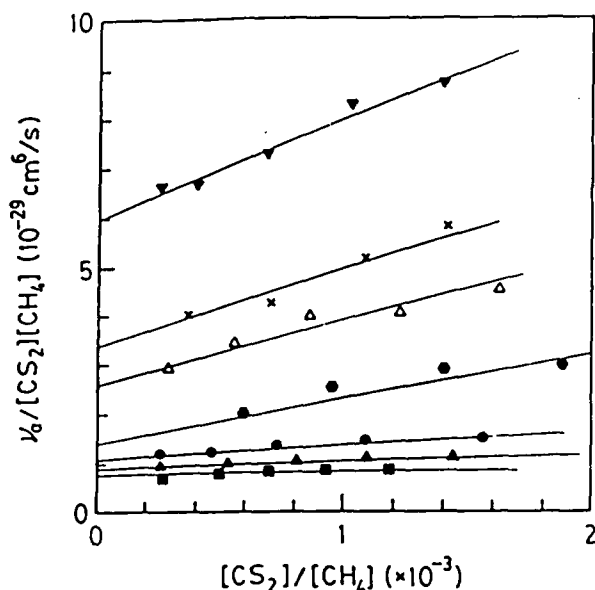


FIG. 11. Three-body attachment rate constant $k_0/[CS_2][CH_4]$ as a function of $[CS_2]/[CH_4]$ at $[N_2] = 255$ Torr and $E/N = 3.39$ (∇), 4.42 ($\times$), 5.43 (Δ), 6.77 ($\circ$), 10.1 ($\bullet$), 13.45 ($\blacktriangle$), and 16.79 ($\blacksquare$) Td.

ies of the dissociative electron attachment process of CS_2 (the energy threshold is about 3 eV)^{13,15,26}. CS_2^- as well as C^- , S^- , CS^- , and S_2^- have been observed.¹³⁻¹⁵ The observed CS_2^- ion was attributed to the secondary charge transfer process, possibly by $CS_2 + CS^- \rightarrow CS_2^- + CS$. CS has an electron affinity comparable with CS.^{15,26} The CS_2^- ion was also observed in the collisional ionization of Na, K, and Cs,¹² namely, $(Na, K, Cs) + CS_2 \rightarrow (Na^+, K^+, Cs^+) + CS_2^-$. CS_2^- was also observed in the reaction of CS_2 with Kr^{**} in highly excited Rydberg states. Such a highly excited Kr atom has a similar characteristic to a free slow electron,¹² i.e., $Kr^{**} + CS_2 \rightarrow Kr^+ + CS_2^-$. CS_2^- was also observed in the charge transfer from several negative ions¹¹ (O^- , Cl^- , and S^-).

The mean electron energy in N_2 or CH_4 is so low (< 1.5 eV) that the dissociative attachment process is not energetically possible. The electron attachment observed in this experiment must be due to the three-body process which is explained by the two-step processes. Our results show that the efficiencies of CS_2 , N_2 , and CH_4 in stabilizing the CS_2^-* ion are quite different as shown in Fig. 12. The three-body attachment rate constants k_0 and k_{10} for CS_2 as a third body, and k_0' and k_{10}' for N_2 and CH_4 as third bodies are plotted vs the mean electron energy $\langle \epsilon \rangle$ in Fig. 12. CS_2 is about two orders of magnitude more efficient than CH_4 for the stabilization of CS_2^-* . The efficiency of CH_4 in stabilizing CS_2^-* is about one order of magnitude higher than that of N_2 . This is similar to the SO_2 case where CH_4 is also about one order of magnitude more efficient than N_2 in stabilizing SO_2^-* . This may be due to the fact that CH_4 has more degrees of freedom than N_2 so that CH_4 is a better quencher in that it is able to carry away the excess energy of CS_2^-* more effectively.

It is surprising to see that CS_2 is so much more efficient to stabilize CS_2^-* than CH_4 . There may be an accidental resonance between the states of CS_2^-* and CS_2 such that the

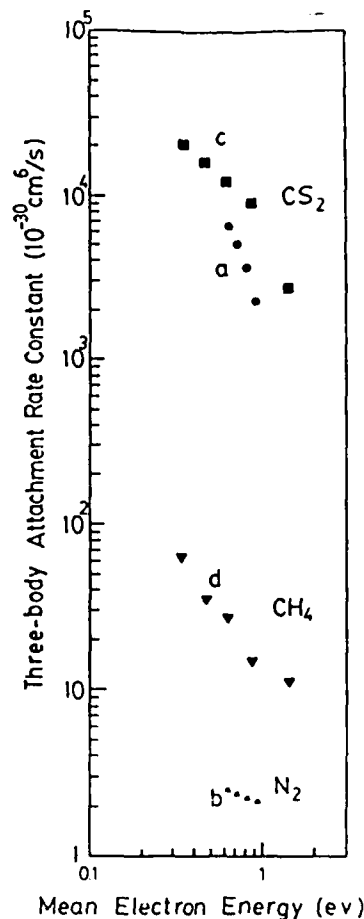
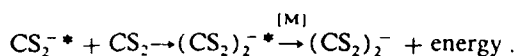


FIG. 12. Three-body attachment rate constants, k_0 and k_{10} of CS_2 with CS_2 as a third body in N_2 (a) and CH_4 (c), and k_0' with N_2 (b) and k_{10}' with CH_4 (d) as a third body as a function of mean electron energy.

energy transfer process occurs very fast. There is another possibility CS_2^-* may be from a charge transfer process such as $CS_2^-* + CS_2 \rightarrow CS_2^+ + CS_2^-$, instead of a collisional stabilization such as $CS_2^-* + CS_2 \rightarrow CS_2^- + CS_2 + \text{energy}$. At each $\langle \epsilon \rangle$, the values of k_0 and k_{10} should be the same, because these rate constants only associate with CS_2 . However, they show a discrepancy in Fig. 12. The discrepancy could be due to the fact that the $\langle \epsilon \rangle$ in CH_4 is not appropriately determined from E/N . The assumption of the Maxwell function for the electron energy distribution in CH_4 used to determine $\langle \epsilon \rangle = 3/2(eD_L/\mu)$ may not be quite appropriate.

The anomalous pressure dependence of the electron attachment had been observed in dense gases. For O_2 and N_2O , for instance, their high electron attachment rates at high buffer gas pressure were not consistent with the results predicted by the Bloch-Bradbury mechanism. Hatano and Shimomori²⁸ proposed that the electron attachment to van der Waals molecules plays an important role in those O_2 and N_2O cases. Recently, Hunter *et al.*²⁹ observed that electron attachment to 1- C_3F_6 was dependent on 1- C_3F_6 pressure. They attributed this to be the clusterization of the transient parent anion. The above electron attachment mechanism may also be one of the reasons that causes the unusual CS_2 pressure dependence observed in this work. That is, the electron attachment in CS_2 may be by the pre-existing dimer molecules of CS_2 or by the dimerization of the transient parent anion, i.e.,



The electron attachment rate for the CS_2 -Ar mixture was also studied in this experiment. However, at low $[\text{CS}_2]$, the attachment rates were too small to be measured within the experimental certainty. This is due to the fact that the dissociative attachment cross section of CS_2 is quite low²⁷ (one order of magnitude less than that of SO_2). It requires very high $[\text{CS}_2]$ in order to observe a sufficient attachment rate. In this case, the breakdown starts to occur and the transient voltage is disturbed by the noise associated with prebreakdown phenomena.

IV. CONCLUSION

A parallel-plate drift-tube electron-swarm technique is applied to measure the low-energy electron attachment rate constants of SO_2 and CS_2 in the buffer gases of Ar, N_2 , and CH_4 at various E/N . For SO_2 in Ar and N_2 , our results are consistent with the published data.⁸ New data are obtained for SO_2 in CH_4 and CS_2 in N_2 and CH_4 . Both the low-energy electron attachment to SO_2 and CS_2 in N_2 and CH_4 are attributed to the Bloch-Bradbury two-step three-body attachment process. The relative effectiveness of N_2 , CH_4 , CS_2 , and SO_2 as third bodies in the three-body attachment process are also determined from the measured attachment rate constants.

ACKNOWLEDGMENTS

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Appendix B

Electron Attachment Rate Constants of

SOCl_2 in Ar, N_2 , and CH_4

Electron Attachment Rate Constants of SOCl_2 in
Ar, N_2 , and CH_4

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ABSTRACT

The electron attachment rate constants of SOCl_2 in the buffer gases of Ar, N_2 , and CH_4 (150 to 500 Torr) at various E/N (1-15 Td) were measured by a parallel-plate drift-tube electron-swarm technique. Electrons were produced by irradiating the cathode with KrF laser photons. For the SOCl_2 -Ar mixture, the electron attachment rate constant has a maximum value of $1.2 \times 10^{-10} \text{ cm}^3/\text{s}$ at $E/N = 4 \text{ Td}$. For SOCl_2 in N_2 , the electron attachment rate constant is $2.5 \times 10^{-9} \text{ cm}^3/\text{s}$ at $E/N = 1.3 \text{ Td}$, and decreases with increasing E/N . For SOCl_2 in CH_4 , the electron attachment rate constant is $9.5 \times 10^{-9} \text{ cm}^3/\text{s}$ at $E/N = 1 \text{ Td}$, and decreases with increasing E/N . For every gas mixture studied, the electron attachment rate constant is independent of buffer gas pressure, indicating that the electron attachment to SOCl_2 is due to a dissociative process. The electron attachment processes in the three gas mixtures are discussed.

I. INTRODUCTION

Recently, we have observed that the conduction current in a glow discharge of the $\text{SOCl}_2\text{-N}_2$ mixture could be reduced when the gas medium was irradiated by ArF laser photons. The current reduction may be caused by the enhancement of electron attachment due to the Cl and SO radicals, where these radicals are produced from the photodissociation of SOCl_2 by ArF laser photons. This result indicates that SOCl_2 could be useful for the development of laser controlled opening switches. The electron attachment rates for SOCl_2 in various buffer gases are the basic information needed for such application. Such need motivates us to do this investigation.

A parallel-plate drift-tube electron-swarm technique has been used in our laboratory to measure the electron attachment rate constants of several molecules.¹⁻⁴ The electron attachment rate constants of SOCl_2 in Ar, N_2 , and CH_4 at varied E/N are reported in this paper. These data are not yet available in the literature. The electron attachment processes of SOCl_2 in various buffer gases are discussed based on the experimental data measured.

II. EXPERIMENT

The experimental set-up was described in previous papers.¹⁻⁴ In brief, the gas cell was a 6 in. six-way aluminum cross. The electrodes were two parallel uncoated stainless steel plates 5 cm in diameter and 3 cm apart. The electron swarm was produced by irradiation of the cathode with a KrF (Lumonics model 861S) laser

beam which had a pulse duration of about 10 ns. These photons, of wavelength 248 nm (~ 5.0 eV), are energetically capable of dissociating SOCl_2 .^{5,6} In order to minimize the interference of the SOCl_2 electron attachment measurement by photofragments such as SO, Cl, and Cl_2 , the size of the laser beam was reduced to 0.3 cm radius such that only a small fraction of SOCl_2 between the electrodes was irradiated by laser photons. (This arrangement confines the photofragments to a small region around the cathode.) In the data analysis (see next section), only electron motion in the region far away from the cathode was considered. This way of data analysis ensures that the electron attachment rate measured is due to SOCl_2 only.

A negative high voltage was applied to the cathode to maintain an electric field between the electrodes. The conduction current induced by the electron motion between the electrodes was observed as a transient voltage pulse across a resistor ($330\text{--}2000\ \Omega$) connecting the anode to ground. The trace of each transient pulse was monitored by a 150 MHz digital storage oscilloscope (Tektronix 2430) and was subsequently stored in an IBM XT microcomputer; data were analyzed by the computer.

Pressure in the gas cell was kept constant as monitored by an MKS Baratron manometer while a slow flow of gas, $20\text{ cm}^3/\text{min}$, was maintained. All measurements were at room temperature, C. All gases were supplied by MG Scientific and were used as received; purities of the Ar, N_2 , and CH_4 were better than 99.998%, 99.998%, and 99.99%, respectively. Thionyl chloride was supplied by Fisher Scientific and was of 99% purity.

The thionyl chloride liquid is stored in a glass bottle

inside a stainless steel container. The thionyl chloride vapor was carried from the container into the gas cell by the buffer gas, Ar, N₂, or CH₄. The concentration of SOCl₂ was determined from the ratio of SOCl₂ vapor pressure (110 Torr at 23°C) and carrier gas pressure (2 atm). The measurements were also done by pre-mixed SOCl₂ in various buffer gas. These mixtures had well defined concentrations of SOCl₂. Results obtained by using different methods of mixing gases did not differ. The major dissolved impurity in SOCl₂ has been reported to be SO₂,⁷ however, the attachment rate constant for SO₂ is much smaller than that for SOCl₂, so the effect of possible SO₂ impurity on these measurements should be negligible.

III. RESULTS

A. SOCl₂-Ar Mixture

The electron transient waveforms for the SOCl₂-Ar mixture at $E/N = 0.26$ Td ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$) are shown in Fig. 1, where the pressure of Ar was 390 Torr, and the pressures of SOCl₂ were (a) 0, (b) 23, and (c) 50 mtorr. Each waveform is the average of 64 pulses which were captured by the digital storage oscilloscope. As can be seen from Fig. 1 (a) (with only Ar in the gas cell), voltage decreased rapidly after the first peak. This is probably due to the loss of electrons by back diffusion to the cathode.⁸ After the peak, the voltage approached a nearly constant value until the electrons arrived at the anode, where the voltage dropped to zero. When small amounts of SOCl₂ were added to the gas cell, both pulse duration and amplitude decreased as shown in

Fig. 1 (b) and (c). This decrease is caused by the electron attachment to SOCl_2 .

The electron attachment rate v_a at a fixed SOCl_2 concentration is obtained from the ratio of transient voltages as a function of time with and without SOCl_2 . The method of data analysis has been described in detail elsewhere.^{1,2} In the data analysis, only the flat portion of the trace was used for the rate measurement (the first peak was avoided). For example, the ratios for the voltages in Fig. 1 were considered only from $t=2$ to 4 μs . At this later time, the conduction electrons are far away from the region irradiated by laser, so the possible interference by the Cl and SO radicals (which may be produced by photodissociation of KrF laser photons) is avoided. Thus, the measured electron attachment rates were caused by SOCl_2 only.

The electron attachment rate does not depend on the pressure. This shows that the electron attachment is a two-body dissociative process. The electron attachment rate constant k_a of the two-body process is determined by $v_a/[\text{SOCl}_2]$. Values of k_a measured at various E/N are shown in Fig. 2 for an Ar pressure of 390 Torr along with a scale of the mean electron energy, $9.10 \langle \epsilon \rangle$. The electron attachment rate constant reaches a maximum value of $1.2 \times 10^{-9} \text{ cm}^3/\text{s}$ at $E/N = 4 \text{ Td}$ ($\langle \epsilon \rangle = 4.5 \text{ eV}$). The electron attachment rate constants were also measured at different Ar pressures and the results are the same as that shown in Fig. 2.

B. $\text{SOCl}_2\text{-N}_2$ Mixture

The measured electron attachment rate does not depend on the N_2 pressures from 150-500 Torr. This shows that the electron

attachment is a two-body dissociative process. The measured values of k_a , in the $\text{SOCl}_2\text{-N}_2$ mixture for E/N from 1 to 8 Td, are shown in Fig. 3, where the N_2 pressure is about 475 Torr. A scale of mean electron energy⁹ in N_2 is also shown on the top axis of Fig. 3. The attachment rate constant is about $2.5 \times 10^{-9} \text{ cm}^3/\text{s}$ at $E/N = 1.3 \text{ Td}$ ($\langle \epsilon \rangle = 0.4 \text{ eV}$), and decreases with increasing E/N .

C. $\text{SOCl}_2\text{-CH}_4$ Mixture

Similar to results obtained in Ar and N_2 buffer gases, the electron attachment rate does not depend on the CH_4 buffer pressure (varied from 150-500 Torr), indicating that the electron attachment is a two-body dissociative process. The electron attachment rate constants for the $\text{SOCl}_2\text{-CH}_4$ mixture are shown in Fig. 4 for E/N from 1 to 15 Td and for two different pressures of CH_4 . The mean electron energies⁹ in CH_4 are shown on the top axis of Fig. 4. (The mean electron energy in CH_4 for E/N higher than 12 Td is not available). As shown in Fig. 4, the attachment rate constant is about $9.5 \times 10^{-9} \text{ cm}^3/\text{s}$ at $E/N = 1 \text{ Td}$ ($\langle \epsilon \rangle = 0.1 \text{ eV}$) and decreases with increasing E/N .

IV. DISCUSSION

The electron attachment rate constants of SOCl_2 for the $\text{SOCl}_2\text{-Ar}$ and $\text{SOCl}_2\text{-N}_2$ mixtures are replotted against the mean electron energy as shown in Fig. 5. The attachment rate constant has a peak at the thermal energy and a broad band with a maximum at 4.8 eV. This result indicates that the electron attachment is due to at least two different dissociative attachment processes. (Note that the attachment is attributed to

a dissociative process because the attachment rate is independent of the buffer gas pressure). The attachment process at the thermal energy has an attachment rate higher than other processes.

The electron attachment rate measured in the $\text{SOCl}_2\text{-CH}_4$ mixture is higher than that measured in the $\text{SOCl}_2\text{-N}_2$ mixture at the same value of $\langle \epsilon \rangle$ (see Figs. 3 and 4). This difference could be due to the fact that $\langle \epsilon \rangle$ in CH_4 is not appropriately converted from E/N . The assumption of the Maxwell function used to determine the electron energy distribution in CH_4 as $\langle \epsilon \rangle = 3(e D_L / \mu) / 2$ may not be correct. On the other hand, the electron energy distributions in Ar and N_2 have been well studied.^{9,11} The electron attachment rate constants in the $\text{SOCl}_2\text{-N}_2$ and $\text{SOCl}_2\text{-Ar}$ mixtures match very well, as shown in Fig. 5. A similar case was observed for CS_2 ,⁴ whose three-body electron attachment rate constant, measured in the $\text{CS}_2\text{-CH}_4$ mixture, was higher than that measured in the $\text{CS}_2\text{-N}_2$ mixture at same $\langle \epsilon \rangle$.

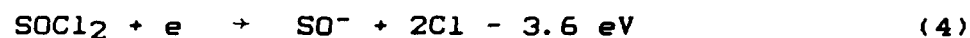
When SOCl_2 is excited by photons or electrons, it may be dissociated into the following products,



The thresholds for the above processes can be determined from their dissociation energies. The dissociation energy for $\text{D}(\text{Cl-SOCl})$ was calculated by Sanderson¹² to be 2.86 eV. The dissociation energy for $\text{D}(\text{SO-2Cl})$ is 4.70 eV.¹³ Using $\text{D}(\text{Cl-Cl}) = 2.52 \text{ eV}$,¹³ the dissociation energy for $\text{D}(\text{SO-Cl}_2)$ is 2.18 eV.

The thermochemical energies for the electron dissociative

attachment processes of SOCl_2 can be calculated from the dissociation energies as follows:



The electron affinities⁹ of Cl, SO, and Cl_2 used in the calculation are 3.67, 1.1, and 2.2 eV, respectively. The calculated energy thresholds for all these possible dissociation processes and dissociative attachment processes of SOCl_2 are shown in Fig. 6.

The energy threshold of $\text{SOCl} + \text{Cl}^-$ is about 0.8 eV below the ground state energy of SOCl_2 , indicating that the electron dissociative attachment could occur at thermal energy. This explains our observation that the electron attachment is a two-body dissociative process with a high attachment rate constant at low electron energy. The $\text{Cl}_2^- + \text{SO}$ process also requires no electron energy to occur, except for the possible potential barrier. Since process (8) has a high exothermic energy and the electron energy in the buffer gas CH_4 or N_2 is low, process (8) is probably the main electron attachment process occurring in the $\text{SOCl}_2\text{-CH}_4$ and $\text{SOCl}_2\text{-N}_2$ mixtures. A Similar case was observed in the $\text{Cl}_2\text{-N}_2$ mixture by McCorkle et al.¹⁴, where the electron dissociative attachment rate constant has a maximum at $\langle \epsilon \rangle \sim 0.07$ eV and decreases with increasing $\langle \epsilon \rangle$. The attachment rate constant for the $\text{SOCl}_2\text{-CH}_4$ mixture at $\langle \epsilon \rangle \sim 0.1$ eV measured in

this experiment is much higher than that in the $\text{Cl}_2\text{-N}_2$ mixture.¹⁴ This is expected from the fact that the molecular size of SOCl_2 is larger than Cl_2 . In fact it has been observed¹⁰ that the electron attachment rate constants of perfluoroalkane molecules increase with increasing size.

The electron attachment rate constants of SOCl_2 increase when $\langle \epsilon \rangle > 1$ eV as shown in Fig. 5. This increase is probably caused by the dissociative attachment processes (4)-(6). The processes (7) and (8) are responsible for the attachment at the thermal energy and they will be less important at high electron energy. This is evident by the fact that the thermal electron peak rapidly decreases with increasing electron energy. Because energy thresholds for the processes (5) and (6) are about 1 eV above the ground state of SOCl_2 , these processes are likely responsible for the electron attachment at electron energy higher than 1 eV. For electron energy higher than 3.6 eV, the process (4) will provide additional attachment channel to enhance the attachment rate. For electron energy higher than 4.8 eV, the attachment rate constant starts to decrease, which may be caused by the electron energy moving away from the energy range where the attachment processes are available. The next high energy process is $\text{Cl}_2^- + \text{S} + \text{O}$ whose energy threshold is 5.3 eV, where $D(\text{S-O}) = 5.34$ eV¹³ is used to determine the threshold.

V. CONCLUSION

Electron attachment rate constants of SOCl_2 in Ar, N_2 , and CH_4 were measured at various E/N (or mean electron energy). The electron attachment rate constant has a maximum at the thermal

energy and a second maximum peak around 4.5 eV. The dissociative attachment processes of $\text{Cl}^- + \text{SOCl}$ and $\text{Cl}_2^- + \text{SO}$ are likely to be the dominant processes for the low energy electrons. For the high energy electrons, the dissociative attachment processes of $\text{Cl}^- + \text{Cl} + \text{SO}$, $\text{SO}^- + \text{Cl}_2$ and $2\text{Cl} + \text{SO}^-$ become important.

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FIGURE CAPTIONS

- Fig. 1 The waveforms of transient voltage pulses produced from electron motion in 390 Torr of Ar with SOCl_2 (a) 0, (b) 23 mTorr, and (c) 50 mTorr. Electrons were produced from irradiation of the cathode by KrF laser photons. The E/N was fixed at 0.26 Td. The electrode spacing was 3 cm, and the external resistor was 1 K Ω .
- Fig. 2 Electron attachment rate constant as a function of E/N (bottom axis) and mean electron energy (top axis) for SOCl_2 in Ar. The Ar pressure was 325 Torr.
- Fig. 3 Electron attachment rate constant as a function of E/N (bottom axis) and mean electron energy (top axis) for SOCl_2 in N_2 . The N_2 pressure was 475 Torr.
- Fig. 4 Electron attachment rate constant as a function of E/N (bottom scale) and mean electron energy (top scale) for SOCl_2 in CH_4 . The CH_4 pressures were 340 Torr ($\bullet$) and 490 Torr ($\blacktriangle$).
- Fig. 5 Electron attachment rate constant as a function of mean electron energy for the SOCl_2 - N_2 ($\blacktriangle$) and SOCl_2 -Ar ($\bullet$) mixtures.
- Fig. 6 Energy thresholds for the dissociation processes (left) and the electron dissociative attachment processes (right) of SOCl_2 .

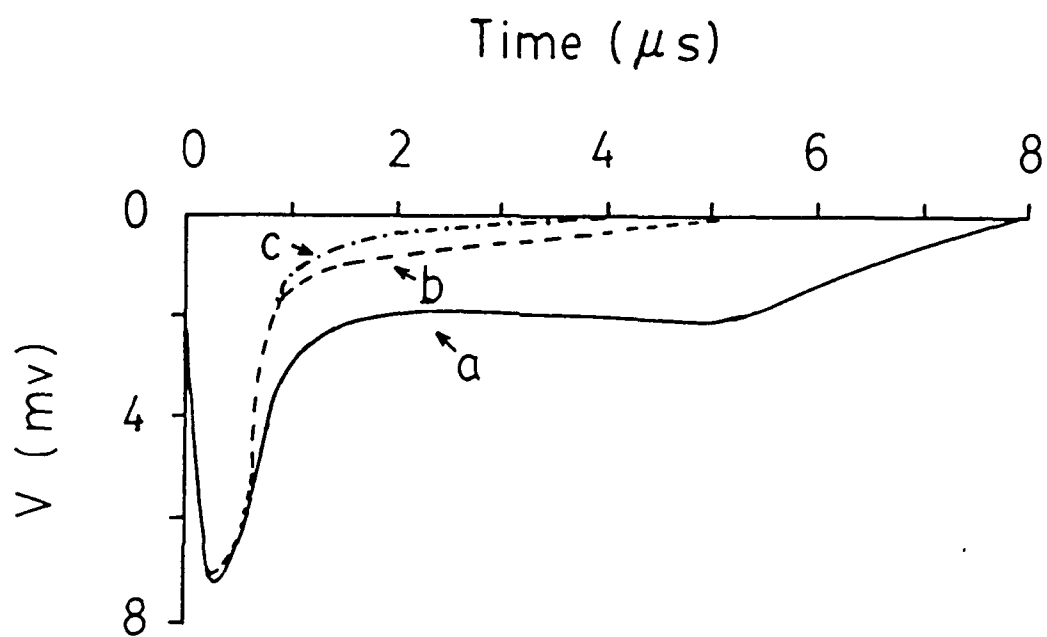


Fig. 1

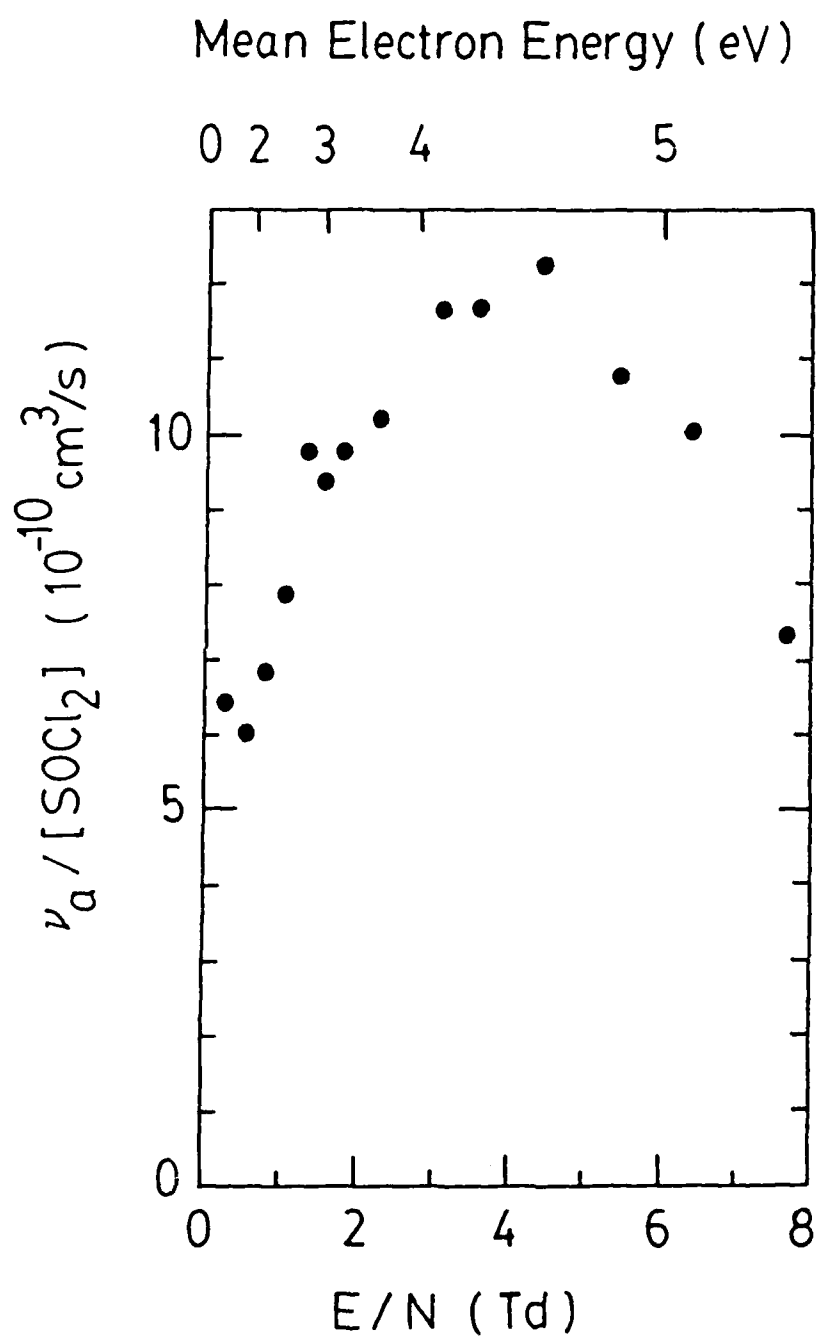


Fig. 2

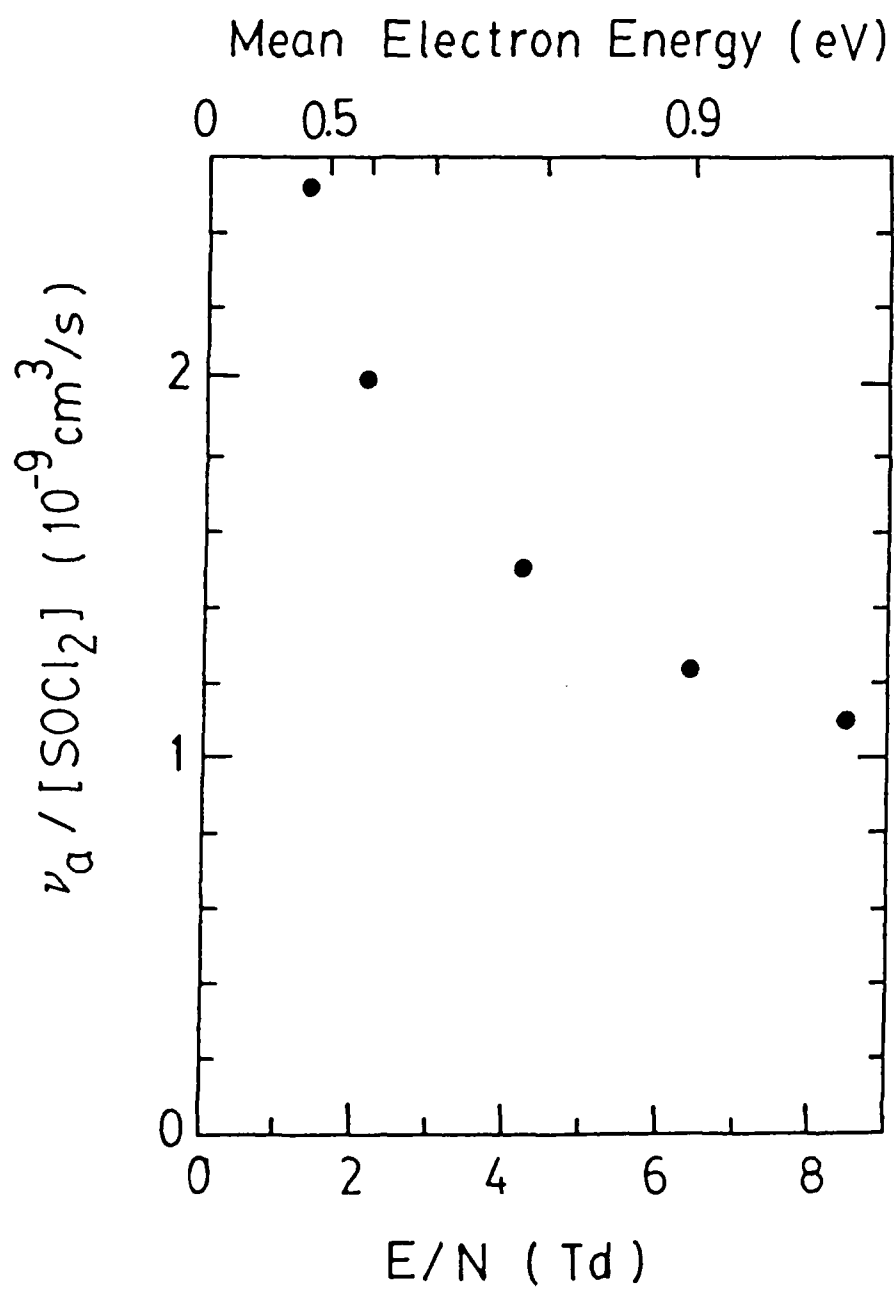


Fig. 3

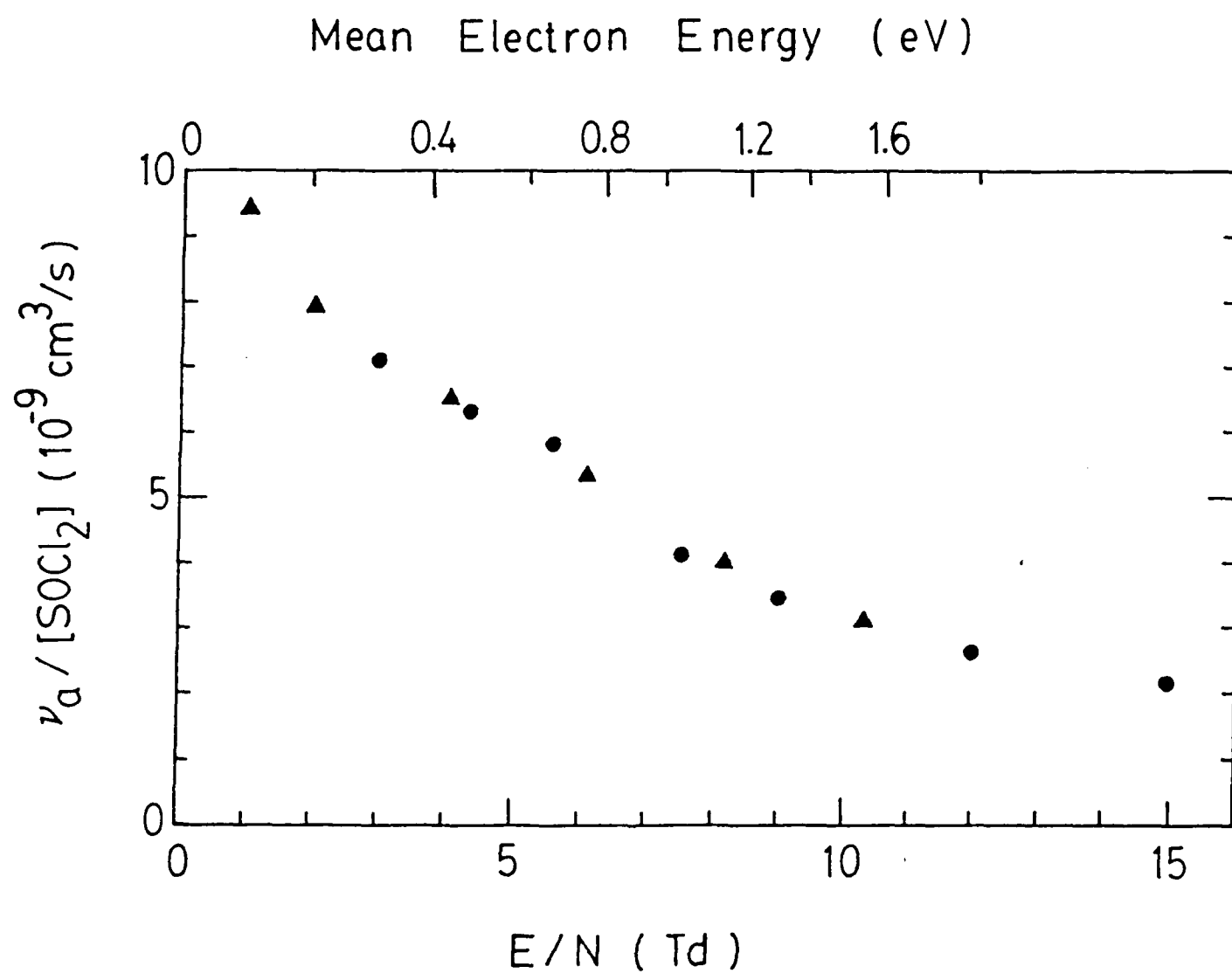


Fig. 4

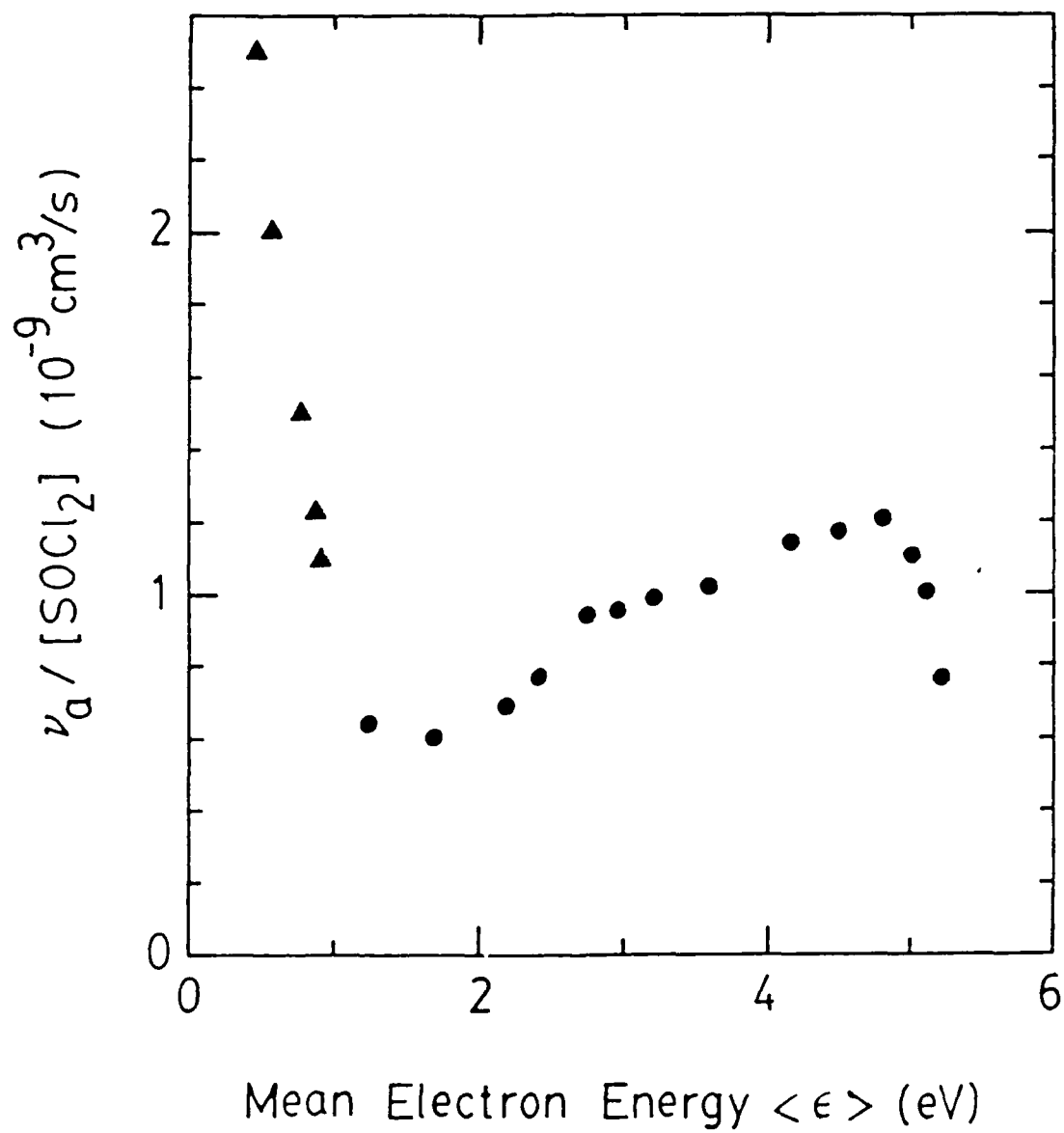


Fig. 5

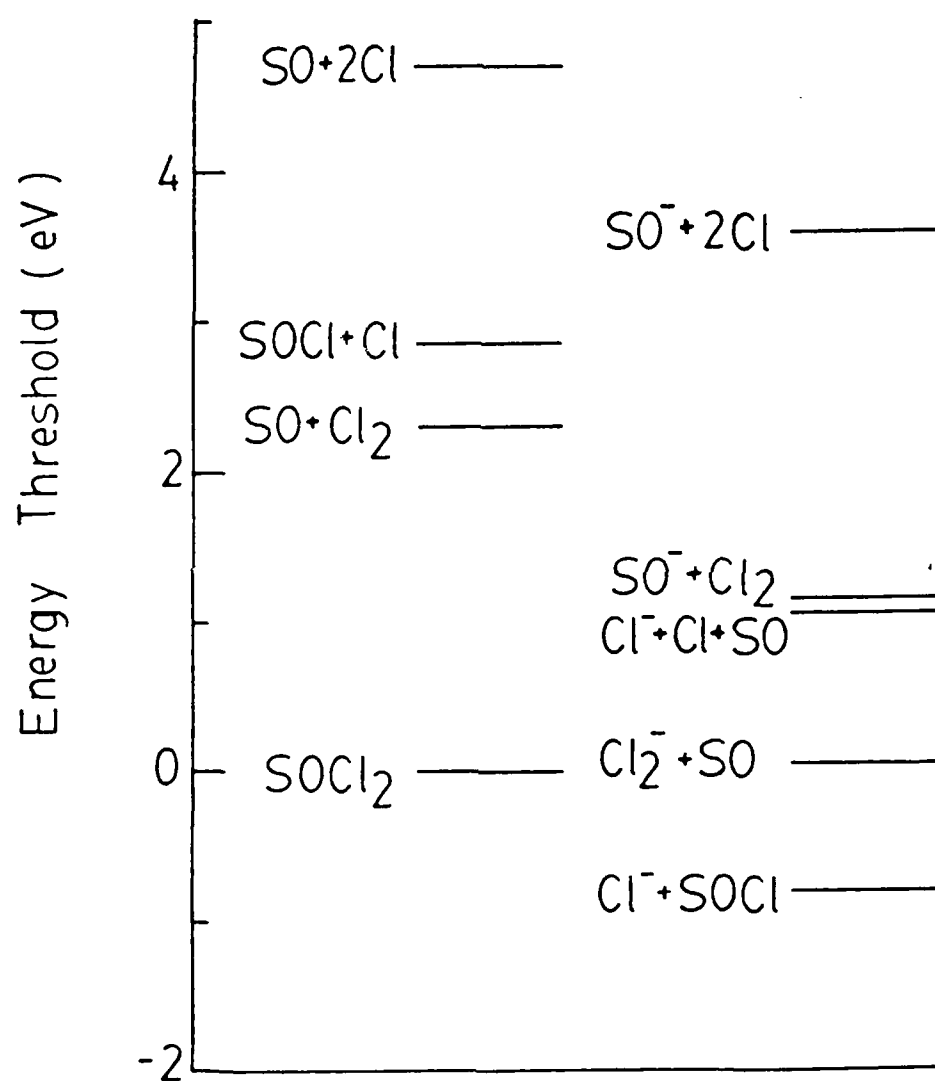


Fig. 6

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