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Bibliography of Electron and Photon Cross Sections
with Atoms and Molecules
Published in the 20th Century
– Halogen Molecules –

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Bibliography of Electron and Photon Cross Sections with Atoms and Molecules Published in the 20th Century

—— Halogen Molecules ——*

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A bibliographies of original and review reports of experiments or theories of electron and photon cross sections and also electron swarm data are presented for atomic or molecular species with specified targets. These works covered 17 atoms and 51 molecules. The present bibliography is only for halogen molecules (F_2, Cl_2, Br_2, I_2). About 190 (F_2), 360 (Cl_2), 140 (Br_2) and 240 (I_2) papers were compiled respectively. A comprehensive author indexes for each molecule are included. The bibliography covers the period 1901 through 2000 for F_2-I_2. Finally, author's comments for F_2-I_2 electron collision cross sections are given.

Keywords : F_2, Cl_2, Br_2, I_2 molecules, collision cross sections, electron, elastic scattering, rotational, vibrational and electronic excitations, dissociation, ionization photon, photoabsorption, photodissociation, photoexcitation, photoionization, electron swarm, drift velocity, diffusion coefficient, ionization coefficient, excitation and ionization energies, transition probabilities, lifetimes of excited states

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Introduction

History

This bibliography is the result of a continuing literature survey which was begun around 1970 and originally encompassed only electron collision cross section and electron swarm data. The organization responsible for continuing this survey is Nagoya Institute of Technology, Nagoya. From 1994, the work continued to Gaseous Electronics Insititute, Nagoya. In 1997, the collection of photon cross section references was begun. The search for references in both cases was retrospective and included all papers reporting measurements, theoretical calculations or reviews and data compilations of such cross sections and electron swarm data.

Scope

This bibliography contains references to original research papers which report experiments or theoretical calculations of cross sections for electron and photon collisions with halogen molecules F_2, Cl_2, Br_2, and I_2. The review papers on this subject are also included. Some halogen molecule cluster papers are included. Some conference reports, company or agency reports and PhD thesis are included. Halogen molecules ion papers and positron collision papers are not included in principle.

Papers reporting the following data are included.

For electron collision cross section :

1) elastic scattering
2) rotational excitation
3) vibrational excitation
4) electronic excitation
5) dissociation
6) ionization
7) attachment
8) grand total scattering (sum of elastic and inelastic cross sections)
9) electron swarm parameters (drift velocity, diffusion coefficient)
10) excitation and ionization coefficients

For photon collision cross section :

1) photoabsorption
2) photoexcitation and fluorescence
3) photodissociation
4) photoionization

For some related data :

1) excitation and ionization energies
2) transition probabilities
3) lifetimes of excited states
4) others

The energy range for electron cross section data is usually 0 - 10 keV, but some higher electron energy papers are included. The wavelength range for photon cross section data is from microwave to X-ray. Most papers are concerned with infrared, visible and ultraviolet ray region.

The bibliography includes the papers published in the 20th century, from 1901 to 2000. Oldest paper in this list is given by E.R.Laird (1901) for Cl_2. Oldest papers for other halogen molecules are shown in each molecules. So for this bibliography, published papers from 1901 to 1999 are compiled by alphabetical order of the first author's surname of the paper. And the references published in 2000 and plus some old papers found very recently after compilation are added as "Addenda of References for each Halogen Molecule". In total, about 190 for F_2, 360 foe Cl_2, 140 for Br_2 and 240 for I_2 papers are compiled in the four halogen molecules bibliography.

Organization

This report consists of four parts : introduction, the bibliography and its addenda, author index, and some comments on electron collision cross sections.

Bibliography

In this section the complete citation for all references are given. At first following classifications are shown :

E : Elastic collision
R : Rotational excitation
V : Vibrational excitation
EX : electronic EXcitation
D : Dissociation
I : Ionization
A : Attachment
ME : MEtastable molecules
S : electron Swarm
O : Others (photon cross sections and the others)

All authors' initials and surname, journal name, volume, inclusive pages and year of publication are given as well as the title, and some additional information in the square bracket [ ]. E and T in the square bracket mean experiment and theory.

Bibliography for F_2, Cl_2, Br_2, and I_2 are divided into two parts :

F_2
Part 1. 1900 - 1999 p. 1 - 16
Part 2. Addenda of References some old papers p. 17

Cl_2
Part 1. 1900 - 1999 p. 1 - 29
Part 2. Addenda of References published in 2000, plus some old papers p. 30 - 32

Br_2
Part 1. 1900 - 1999 p. 1 - 14
Part 2. Addenda of References published in 2000, plus some old papers p. 14 - 14

I_2
Part 1. 1900 - 1999 p. 1 - 23
Part 2. Addenda of References published in 2000, plus some old papers p. 24 - 24

Author Index

In this section all authors are listed alphabetically by surname. After each author's name is a list of page numbers indicating which references he or she authored or coauthored.

F_2 p. 1 - 4
Cl_2 p. 1 - 7 Addenda p. 8
Br_2 p. 1 - 4
I_2 p. 1 - 4

Each author index of four halogen molecules follows each bibliography.

Some Comments on Electron Collision Cross Sections for F_2, Cl_2, Br_2 and I_2

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Fluorine Molecule F_2

References for F_2 (1900 - 1999)

(Fluorine)

[Halogen]

E	: Elastic collision,	R	: Rotational excitation,
V	: Vibrational excitation,	EX	: Electronic excitation,
D	: Dissociation,	I	: Ionization,
A	: Attachment,	QT	: Grand total cross section,
S	: Swarm,	α	: Ionization coefficient,
O	: The others,	[ ]	: Additional informations, E : Exp., T : Theory.

The oldest paper in this list is given by H. G. Gale (1924).

O J. Aars : Z. Phys. 79, 122-138 (1932)
Uber eine photometrische Untersuchung der starksten Emissionsbanden von Fluor. [E, $h\nu$, F_2]

S N. L. Aleksandrov, I. V. Kochetov, A. P. Napartovich, V. G. Pevgov and A. N. Starostin : Sov. J. Plasma Phys. 6, 748-751 (1980)・
Electron kinetic coefficients in a weakly ionized plasma with high attachment rates. [T, F_2 + He]

O W. D. Allen and A. G. Csaszar : J. Chem. Phys. 98, 2983-3015 (1993)
On the ab initio determination of higher-order force constants at nonstationally reference geometries. [T, F_2, N_2, N_2O, F_2O]

O D. Andrychuk : J. Chem. Phys. 18, 233-233 (1950)
Raman spectrum of fluorine. [E, $h\nu$, F_2; 892 cm^{-1}]

O D. Andrychuk : Can. J. Phys. 29, 151-158 (1951)
The Raman spectrum of fluorine. [E, F_2; B_0 = 0.8828 cm^{-1}, r_0 = 1.418 A]

A K. A. Ashtiani, J. L. Shohet and R. E. P. Harvey : J. Vac. Sci. Tech. A11, 1136-1141
D (1993)・
Computer calculation of neutral-radical densities in a CF_4 electron cyclotron resonance plasma processing system. [T, F_2, CF_4]

A J. A. Ayala, W. E. Wentworth and E. C. M. Chen : J. Phys. Chem. 85, 768-777 (1981)
Electron attachment to halogens.
[E, F_2 - I_2; thermal electron attachment]

O G. G. Balint-Kurti and M. Karplus : J. Chem. Phys. 50, 478-488 (1969)
Multistructure valence-bond and atoms-in-molecules calculations for LiF, F_2, and F_2^-. [T, F_2, F_2^-, LiF]

V J. N. Bardsley : in Electron-Molecule and Photon-Molecule Collisions, Plenum
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Molecular resonance phenomena. [review, F_2, Cl_2, I_2, H_2, N_2, O_2, NO, HCl]

A J. N. Bardsley and J. M. Wadehra : J. Chem. Phys. 78, 7227-7234 (1983)・
Dissociative attachment in HCl, DCl, and F_2. [T, F_2, HCl, DCl]

O R. F. Barrow and A. D. Caunt : Proc. Roy. Soc. London A219, 120-140 (1953)
The ultra-violet absorption spectra of some gaseous alkali-metal halides and the dissociation energy of fluorine. [E, $h\nu$, F_2, NaF, etc.]

O O. M. Batovskii and V. I. Gurev : Opt. Spectrosc. 41, 185-187 (1976)
Temperature dependence of the continuous ultraviolet absorption spectrum of molecular fluorine. [E and T, $h\nu$, F_2; 300 - 990 K]

A E. M. Belenov, V. A. Isakov, A. N. Oraevskii and V. I. Romanenko : Sov. J. Quantum Elect. 4, 758-760 (1974)
Dissociation of fluorine molecules by electron impact.
[T, F_2; $F_2 + e \rightarrow F^- + F$ or $F^+ + F^- + e$, 0 - 32 eV]

O J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway and R. Spohr : J. Chem. Phys. 54, 5165-5180 (1971)
Photoionization mass spectrometric study of F_2, HF, and DF.
[E, $h\nu$, F_2, HF, DF; V_i of F_2 15.686 eV]

O J. Blauer and W. Solomon : J. Chem. Phys. 57, 3587-3589 (1972)
Shock tube calorimeter for the dissociation energy of fluorine.
[E, F_2 + HF + Ar; 1400 - 3200 K]

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The heat of dissociation of N_2 and the appearance potentials of some ions formed in F_2 and HF by electron impact. [, F_2, HF, N_2; from F. I. Vilesov]

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Dissociative attachment of electrons to F_2. [E and T, F_2]

QT M. Breitenstein, A. Endesfelder, H. Meyer and A. Schweig : Chem. Phys. Lett. 108, 430-434 (1984)
CI calculations of electron-scattering cross sections for some linear molecules. [T, F_2, N_2, O_2, CO, C_2H_2, ; first Born approx.]

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Electron scattering at high and intermediate energies. — Quantitative measurements in molecular spectroscopy.
[review, F_2, HF, COS, CS_2, CO_2, N_2O, etc.]

E M. Capitelli, R. Celiberto and M. Cacciatore : in Advances in Atomic, Molecular
V and Optical Physics, Vol. 33, Academic 321-372 (1994)
EX Needs for cross sections in plasma chemistry.
I [review, F_2, Cl_2, HF, HCl, H_2, N_2, O_2, CO, CO_2, etc.]

O D. C. Cartwright and P. J. Hay : J. Chem. Phys. 70, 3191-3203 (1979)・
Theoretical studies of the valence electronic states and the $^1\Pi_u \leftarrow X^1\Sigma_g^+$ absorption spectrum of the F_2 molecules. [T, F_2]

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D Estimate of the integral cross section for dissociative excitation of F_2 by electron impact. [estimation, F_2; th. - 500 eV]

I R. E. Center and A. Mandl : J. Chem. Phys. 57, 4104-4105 (1972)
Ionization cross sections of F_2 and Cl_2 by electron impact.
[E, F_2, Cl_2; th. - 100 eV]

A P. J. Chantry : Westinghouse Rep. 78-9C6-ATACH-RI (1978)
Attachment measurements in halogen bearing molecules. [E, F_2,]

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Dissociative attachment cross section measurements in F_2 and NF_3.
[E, F_2, NF_3]

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Negative ion formation in gas lasers. [review, F_2, NF_3, HCl, $HgBr_2$, etc.]

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Dissociative attachment of electrons to F_2. [E, F_2]

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Dissociation of fluorine by electron impact.
[E, F_2; dissociative attach. rate const.]

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Diatomic interhalogens : Systematics and implications of spectroscopic interatomic potentials and curve crossings. [T, F_2 - I_2, IBr, etc.]

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Electron attachment detachement processes in electronegative gases.
[E, F_2, Cl_2, SF_6, perfluoroalkanes]

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Kinetic energy of ions produced by photoionization of HF and F_2.
[E, $h\nu$, F_2, HF; $D_0(F_2)$ 1.58 eV, EA(F) 3.400 eV]

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Electron affinities of halogen diatomic molecules as determined by endoergic charge transfer. [E, F_2 - I_2]

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Electron attachment in F_2 : Conclusive demonstration of nonresonant, s-wave coupling in the limit of zero electron energy.
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The electronic spectrum of F_2.
[E, F_2; 780 - 1020 A, v = 1, 893.90 cm^{-1}, v = 2, 1764.15 cm^{-1}]

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The vacuum ultraviolet spectrum of molecular fluorine. [E, $h\nu$, F_2]

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The Franck-Condon principle and the ionization of molecules.
[compilation, F_2 - I_2, HF - HI, H_2, N_2, O_2, CO, NO, CO_2]

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Photoelectron spectra of the halogens. [E, $h\nu$, F_2 - I_2]

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Extended Hartree-Fock wavefunctions : Optimized valence configurations for H_2 and Li_2, optimized double configurations for F_2. [T, F_2, H_2, Li_2]

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Theoretical study of the F_2 molecule using the method of optimized valence configurations. [T, F_2; potential energy curve]

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Vibrational relaxation of excimers. [review, F_2, Cl_2, HCl, He - Xe]

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Dissociation energy of F_2. [E, F_2; 0 - 32 eV]

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Expanded electronic states of the fluorine molecule. [T, F_2]

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Calculation of electron impact ionization cross-sections. The fluorine anomaly. [T, F_2, CF_4, CCl_2F_2, SF_6, UF_6, N_2]

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Photoionization study of the dissociation energy of fluorine and the heat of formation of hydrogen fluoride. [E, $h\nu$, F_2, HF]

O M. Diegelmann, K. Hohla, F. Rebentrost and K. L. Kompa : J. Chem. Phys. 76, 1233-1247 (1982)
Diatomic interhalogen laser molecules : Fluorescence spectroscopy and reaction kinetics. [E, $h\nu$, F_2, Cl_2, ClF, etc.]

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Negative ion mass spectrometry. [review, F_2 - I_2, CCl_4, CH_3Cl, etc.]

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Electronic spectra of HF and F_2. [E, $h\nu$, F_2, HF]

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Characterization of homonuclear diatomic ions by semiempirical Morse potential energy curves. 1. The halogen anions. [T, F_2 - I_2, At_2]

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A Theory of resonance and threshold effects in electron-molecule collisions : The projection-operator approach.
[review, F_2, HCl, N_2, H_2, CO_2]

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Calculation of dissociative attachment cross section to F_2, Cl_2, and I_2 molecules. [T, F_2, Cl_2, I_2; 3.2 - 5 eV for F_2]

O D. Edelson and D. L. Flamm : J. Appl. Phys. 56, 1522-1531 (1984)
Computer simulation of a CF_4 plasma etching silicon. [T, F_2, CF_4, C_2F_6]

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Pure rotational Raman spectrum of fluorine. [E, $h\nu$, F_2]

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Photodissociation and photorecombination emission of diatomic molecules. [T, $h\nu$, F_2 - I_2, etc.]

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Dissociative attachment of an electron to a molecule.
[review, F_2 - I_2, etc.]

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Extension of Koopmans' theorem. IV. Ionization potentials from correlated wavefunctions for molecular fluorine. [T, F_2]

O D. J. Ellis, K. E. Banyard, A. D. Tait and M. Dixon : J. Phys. B6, L233-L236 (1973)
Potential energy curves and spectroscopic constants for some diatomic systems. [T, F_2, F_2^+, F_2^-, NF, etc.]

EX M. Elyaakoubi and P. Ranson : J. Appl. Phys. 78, 4733-4739 (1995)
D Time resolved study of a reactive low pressure plasma : Determination of basic data on electron-fluorine collisions. [E, F_2 + Ar + He]

O M. G. Evans, E. Warhurst and E. Whittle : J. Chem. Soc. 1524-1534 (1950)
The dissociation energy of fluorine. [E, F_2]

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Structural predictions for open-shell systems : A comparative assessment of ab initio procedures.
[comparison, F_2^+, N_2^+, O_2, O_2^+, NO, CH, CH_2, CH_3, etc.]

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The design of plasma etchants. [review, F_2 - Br_2, CF_4, BCl_3, etc.]

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Dissociation of F_2 by electron impact excitation of the lowest $^3\Pi_u$ electronic state. [T, F_2; DCS, 5 - 30 eV]

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Electron excitation of optically-allowed transitions in CO_2, SF_6, CO, F_2, and SO_2. [T, F_2, CO_2, SF_6, CO, SO_2]

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Studies in molecular structure. Ⅶ. Limited configuration interaction for selected first-row diatomics. [T, F_2, N_2, CO, HF, BF, etc.]

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Photoelectron spectra of the halogens and the hydrogen halides.
[E, $h\nu$, F_2 - I_2, HF - HI]

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Vibrational excitation cross section for F_2 by electron impact.
[E, F_2]

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The spectrum of fluorine. [E, $h\nu$, F_2; 3400 - 7800 A]

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Band spectrum, continuous emission, and continuous absorption of fluorine gas. [E, $h\nu$, F_2; 5100 - 7200 A, 2600 - 2800 A, 4100 A]

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Band spectrum of fluorine. [E, $h\nu$, F_2]

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A compilation of electron swarm data in electro-negative gases.
[compilation, F_2 - I_2, NF_3, SF_6, etc.]

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The vacuum ultraviolet spectrum of molecular fluorine.
[E, $h\nu$, F_2; 709 - 1500 A]

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Theoretical studies of UV-preionized transverse discharge KrF and ArF lasers. [T, F_2, Kr, Ar]

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Threshold photoelectron spectra of HF, DF, and F_2.
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[T, F_2; Herzenberg's theory]

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Theoretical study of a vacuum ultraviolet F_2 excimer lamp (157 nm) excited by microwave discharge. [E, F_2]

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Erratum 42, 398-398 (1976)
Rydberg ionic and valence interactions in the excited state of F_2.
[T, F_2]

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Calculation of electron swarm parameters in fluorine.
[T, F_2; cross section set for F_2, 0 - 10^3 eV]

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S Calculation of electron attachment rate coefficients in fluorine.
[T, F_2]

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May we measure the exact values of electron collision cross sections for molecules by beam and swarm experiments ?
[general comment; F_2 is the mixtures of F_2(r) and F_2(v) molecules]

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Impact-parameter method for electronic excitation of molecules by electron impact. [T, F_2, H_2, N_2; $1^1\Sigma_u^+$ and $3^1\Pi_u$ states for F_2]

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Ab initio study of dissociative attachment of low-energy electrons to F_2.
[T, F_2; vibrational level dependence, 0 - 1.5 eV]

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Author Index for F_2 References

J. Aars 1
T. Ajiro 6
S. H. Alajajian 3
N. L. Aleksandrov 1
W. D. Allen 1
D. Andrychuk 1
K. A. Ashtiani 1
J. A. Ayala 1

D. S. Babic 9
G. G. Balint-Kurti 1
K. E. Banyard 5
J. N. Bardsley 2, 15
R. F. Barrow 2
R. J. Bartlett 16
O. M. Batovskii 2
E. C. Beaty 6
E. M. Belenov 2
D. S. Belic 9
C. F. Bender 13
J. Berkowitz 2, 3, 7
D. Bermejo 10
R. B. Bernstein 3
F. Biggs 13
T. H. J. Bisschops 17
J. Blauer 2
J. F. Borns 2
R. S. Bradford 10
C. A. Brau 2, 7, 14
M. Breitenstein 2
C. E. Brion 2, 8
D. Britton 9
H. L. Brooks 12
R. S. Brusa 16

M. Cacciatore 2
P. Cancio 10
M. Capitelli 2
D. C. Cartwright 3, 7, 12
A. D. Caunt 2
J. W. Cederberg 12
R. Celiberto 2
R. E. Center 3
P. J. Chantry 3
N. F. Chebotanev 12
E. C. M. Chen 1, 5
H. -L. Chen 3
Z. Chen 6
M. S. Child 3
A. A. Christodoulides 10
L. G. Christophorou 3, 10
W. A. Chupka 2, 3, 7
A. Chutjian 3
H. H. Claassen 17
E. A. Colbourn 4
J. L. Cole 4
J. E. Collin 4
A. B. Cornford 4
L. M. Crapo 12
A. G. Csaszar 1

M. Dagenais 4
A. R. Dale 15
G. Das 4
V. V. Datsyuk 4
O. W. Day 5
J. J. de Corpo 4
C. A. de Lange 15
D. DeMoulin 4
H. Deutsch 4
V. H. Dibeler 4
M. Diegelmann 4
J. G. Dillard 5
M. A. Dillon 14, 15
G. Di Lonardo 5
M. Dixon 5
J. G. Dojahn 5
W. Domcke 5
V. M. Donnelly 6
A. E. Douglas 4, 5
G. F. Drukarev 5
J. Dutton 6

D. Edelson 5
H. G. M. Edwards 5, 17
A. V. Eletskii 5
J. C. Ellenbogen 5
D. J. Ellis 5
P. J. Elving 17
M. Elyaakoubi 5

A. Endesfelder 2
M. G. Evans 5

L. Farnell 6
D. Feldman 12
Z. Felfli 11
D. L. Flamm 5, 6
J. Fletcher 12
A. W. Fliflet 6
S. R. Foltyn 12
I. W. Fomunung 6
S. Fraga 6
J. L. Franklin 4
D. C. Frost 4, 6
Y. Fujita 6
W. I. Fyfe 3

H. G. Gale 1, 6
J. W. Gallagher 6
P. W. Gilles 10
J. L. Gole 7
E. A. M. Good 5
M. Gordon 17
A. E. Greene 2, 7
V. I. Gurev 2
D. Gutman 3
P. M. Guyon 2
P. -M. Guyon 7

R. J. Hall 7
R. J. Hanrahan 14
F. E. Harris 7
R. E. P. Harvey 1
T. Hasama 16
T. Hatakeyama 7
P. J. Hay 3, 7, 13
M. Hayashi 7
A. K. Hays 13
A. U. Hazi 7, 8, 10
E. Heinicke 12
G. Herzberg 8
K. Hijikata 8
A. P. Hitchcock 8
I. G. Hochenbleicher 14
R. Hofland 10
W. Hogervorst 10
K. Hohla 4
J. H. Holloway 2
J. M. Horne 8
C. A. Horton 17
K. P. Huber 8
S. R. Hunter 12
W. H. Huo 8

R. P. Iczkowski 8
M. Inokuti 8, 9
V. A. Isakov 2
Y. Itikawa 9
H. Iwaki 13
I. A. Izmailov 4

J. H. Jacob 15
D. M. Jaffey 15
R. Janoschek 9
P. S. Jarrett 15
C. D. Johnson 9
M. Jungen 4

H. J. Kaiser 12
F. Kannari 7
S. S. Kano 6
M. Karplus 1, 9
G. P. Karwasz 16
E. Kasseckert 9
T. Kelly 15
C. W. Kern 9
D. Kligler 9
V. D. Klimov 16
L. E. Kline 9
V. A. Kochelap 4
I. V. Kochetov 1
H. J. Kolker 9
K. L. Kompa 4, 16
L. Krauss 14
M. V. Kurepa 9
M. J. Kushner 9

N. Lane 9
P. W. Langhoff 8
K. Lanik 14
J. G. Lauderdale 10
L. C. Lee 16
B. H. Lengsfield Ⅲ 10
P. F. Levelt 10
V. G. Levin 10
J. C. Light 16
M. N. Lipscomb 9
D. A. Long 5, 17
W. H. Long 10

R. Love 17

C. J. MacCallum 13
P. Mahadevan 10
A. Mandl 3, 10
J. L. Margrave 4, 7, 8
T. D. Mark 4
R. Z. Martinez 10
D. L. McCorkle 10
K. E. McCulloh 4
C. W. McCurdy 10, 13, 15
C. A. McDowell 4, 6
B. V. McKoy 13
V. McKoy 6, 13
H. Meyer 2
H. H. Michels 7
D. R. Miller 8
T. A. Milne 10
K. Miyazaki 16
G. S. Monk 6
J. Morgan 8
L. A. Morgan 10
W. L. Morgan 10, 11
M. A. Morrison 11
R. C. Morrison 5
A. Z. Msezane 6, 11
R. S. Mulliken 11
C. Mundel 17
A. Murakami 13

Y. Nakamura 7
H. Nakatsuji 11
A. P. Napartovich 1
M. W. Nathans 11
V. G. Neudatchin 10
W. L. Nighan 11
T. Nimura 7
H. Nishimura 12
C. J. Noble 10
K. J. Nygaard 12

M. Obara 7
A. N. Oraevskii 2
A. E. Orel 8
I. Ozier 12

A. V. Pavlitchenkov 10
N. Kh. Petrov 12
V. G. Pevgov 1
L. Pichiarella 10
L. C. Pitchford 6
R. M. Pitzer 15
J. A. Pople 6
T. L. Porter 12
A. W. Potts 12
S. A. Pozdneev 5
H. Preuss 9
W. C. Price 12
D. Proch 16
S. Ya. Pshezhetskii 12

R. Rackwitz 12
A. A. Radzig 12
J. L. Ragle 4
N. F. Ramsey 12
B. J. Ransil 6, 12
P. Ranson 5
M. V. V. S. Rao 12, 13
J. W. Raymonda 4
F. Rebentrost 4, 16
A. L. G. Rees 13
T. N. Rescigno 6, 8, 10, 13
J. K. Rice 13, 16
M. E. Riley 13
S. D. Rockwood 2
M. Rokni 9
V. I. Romanenko 2
Z. Rozenberg 9
R. R. Rue 13
K. Ruedenberg 13

T. Sakai 13
Y. Sakai 14
J. Santos 10
T. Sato 16
V. A. Savel'ev 16
H. F. Schaefer III 13
P. Scheier 4
B. I. Schneider 2, 13, 14
A. Schweig 2, 15
H. Selig 17
J. Shamir 17
W. Shao-Yin 16
G. V. Shlyapnikov 5
T. Shoda 13
J. L. Shohet 1
J. M. Sichel 14
G. D. Sides 14
B. M. Smirnov 5, 12, 14
Yu. F. Smirnov 10

D. W. Smith 5
W. Solomon 2
D. Spence 14, 15
R. Spohr 2, 7
S. K. Srivastava 12, 13
A. N. Starostin 1
R. P. Steiger 4
J. I. Steinfeld
I. A. Stenhouse 4
R. K. Steunenberg 14
F. A. Stevie 14
S. Stolte 10
W. Stricker 14
H. Sugawara 14
W. Sun 15
H. Suzuki 6
A. Szoke 10

H. Tagashira 14
A. D. Tait 5
T. Takayanagi 6
H. Takuma 6
W. C. Tam 15
H. Tanaka 14
K. Tanaka 13
H. Terashima 13
W. Thiel 15
R. Thorburn 15
T. O. Tiernan 14
D. W. Trainor 3, 15
S. Trajmar 3, 12
D. Truhlar 17
R. P. Tuckett 15
J. E. Turner 9

W. Ubachs 10

W. J. van der Meer 15
H. van Lonkhuyzen 15
M. J. Vasile 14
F. I. Vilesov 2, 15
R. C. Vogel 14
M. Volmer 15
D. A. Vroom 6, 15

J. M. Wadehra 2, 15
A. C. Wahl 4, 15
K. Wakiya 6
J. A. Walker 4
R. -G. Wang 15
W. C. Wang 16
Z. -W. Wang 15
E. Warhurst 5
J. D. Watts 16
H. Weber 16
W. E. Wentworth 1, 5
M. A. Whitehead 14
E. Whittle 5
H. H. Willard 17
G. R. J. Williams 8
B. Wirsam 9
C. F. Wong 16
S. F. Wong 15, 16
J. R. Woodworth 13, 16

S. Yagi 6
K. Yamada 16
A. S. Yatsenko 14

V. V. Zaitsev 16
A. Zecca 16
G. Zhi-Yu 16
E. Yu. Zvereouskaya 16

Chlorine Molecule Cl_2

References for Cl_2 (1900 - 1999)

(Chlorine)

[Halogen]

E : Elastic collision,	R : Rotational excitation,
V : Vibrational excitation,	EX : Electronic excitation,
D : Dissociation,	I : Ionization,
A : Attachment,	QT : Grand total cross section,
S : Swarm,	α : Ionization coefficient,
O : The others,	[ ]: Additional informations,
	E : Exp., T : Theory.

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Author Index for Cl_2 References

R. Abouaf 2
N. G. Adams 1, 24
S. E. Adler 8
R. G. Aickin 1
A. B. Alekseyev 29
A. J. Alexander 22
E. Alge 1, 24
M. S. N. Al-Kahali 1
K. D. Allen 22
L. Andrews 1
G. C. Angel 23
E. v. Angerer 1
P. Archirel 13
T. Arikawa 19
M. N. Armenise 8
B. S. Ault 1
L. Avaldi 19
J. A. Ayala 2
E. S. Aydil 2
R. Azria 2

D. Babic 2
D. S. Babic 17
A. P. M. Baede 2
V. A. Bailey 2
E. J. Bair 3, 15
B. L. G. Bakker 23
G. G. Balint-Kurti 26
H. Baltes 17
J. N. Bardsley 2
R. F. Barrow 22
J. E. Bartmess 18
N. L. Bassett 2
A. O. Bawagan 11
N. S. Bayliss 1, 11
E. C. Beaty 11
J. L. Beauchamp 25
A. D. Becke 2
D. S. Belic 16, 17
A. T. Bell 2
A. Benz 2
H. N. Berko 11
J. Berkowitz 5
H. J. Bernstein 13
R. B. Bernstein 5, 18
F. Biggs 22
N. Billy 3, 12
V. V. Boiko 3
R. Boivin 25
V. E. Bondybey 3
F. Bose 17
M. Bougeard 24
I. D. Boyd 10
S. E. Bozin 3
N. E. Bradbury 3
C. A. Brau 26
M. Braunstein 3
N. J. Bridge 3
A. G. Briggs 3
C. E. Brion 11
M. Brith 3
D. Britton 24
H. L. Brooks 21
R. S. Brusa 29
A. D. Buckingham 3
R. J. Buenker 12, 21, 29
J. B. Burkholder 3, 15
J. P. Burrows 19
G. E. Busch 3
R. H. Burton 12
R. J. Butselaar 27
M. A. Byrne 26

M. Cacciatore 4
W. H. B. Cameron 4, 10
M. Capitelli 4
R. A. Carabetta 4, 21
T. A. Carlson 4
M. C. Castex 3, 4, 17, 29
R. Celiberto 4
R. E. Center 4
V. Cermak 4
D. K. Chakraborty 26
H. Chang 4, 14
J. P. Chang 4
P. J. Chantry 4
E. C. M. Chen 2, 4, 9
C. C. Cheng 5
M. Chergui 17
A. I. Chichini 5
M. S. Child 5
A. Chouki 21

A. A. Christodoulides 5, 19, 24
L. G. Christophorou 5, 6, 19
W. A. Chupka 5, 18
N. A. Ciampa 18
M. J. Clouter 28
M. A. A. Clyne 5, 6
J. W. Coburn 6, 16
J. E. Collin 6
S. D. Colson 18
J. Comer 25
G. D. Cooper 6
H. Cordes 6
P. B. Corkum 29
C. Cornaggia 24
A. B. Cornford 7
P. C. Cosby 7, 17
T. L. Cottrell 7
J. A. Coxon 5, 7, 8
I. A. Coxon 5
F. Cramarossa 8
P. J. Crutzen 12
D. Cvejanovic 15
S. Cvejanovic 15
P. Czuprynski 8

R. d'Agostino 8
H. Date 8
V. V. Datsyuk 8
G. P. Davies 12
G. Dawber 19
S. De Benedictis 8
J. J. DeCorpo 8
C. A. de Lange 16, 27
G. Denifl 20
P. G. Deo 8
S. C. Deshmukh 8
R. W. Diesen 8
G. A. DiLabio 29
J. G. Dillard 8
M. A. Dillon 25
S. S. Dimov 28
R. N. Dixon 26
S. Dobosz 8, 24
J. G. Dojahn 9
M. Dolg 9
P. D'Oliveira 24
V. M. Donnelly 5, 9, 10, 12, 14, 18, 19
R. J. Donovan 1
H. Doshita 9
A. E. Douglas 9
K. E. Drabe 16
G. F. Drukarev 9
J. Dutton 11

D. J. Economou 2, 8, 15, 18, 21
H. G. M. Edwards 9
A. M. Efremov 9
H. Ehrhardt 12
J. H. D. Eland 9
A. V. Eletskii 9
Ch. Ellert 29
A. Elliott 4, 10
A. Ernesti 10

W. C. Fergusson 10
D. Field 12
T. A. Field 12
B. J. Finlayson-Pitts 11
D. S. Fischl 10
J. B. Fisk 10
D. L. Flamm 9, 10, 12, 14, 19
C. Fletcher 3
G. W. Flynn 21
G. I. Font 10
C. Fotakis 29
J. Fournier 10
J. Fournies 23
F. Fracassi 8
J. L. Franklin 8
B. S. Freiser 25
L. Frost 11
D. C. Frost 7, 10, 11
G. S. Fu 29
U. Fuhr 26
I. Fujiwara 14
K. Fukuda 19
M. Fukuda 16

J. W. Gallagher 11
J. A. Ganske 11
A. Garscadden 21
F. Ghandour 11
G. E. Gibson 11
R. R. Giedt 15
T. L. Gilbert 12
B. Girard 3, 12
R. Gobel 26
A. P. Golovitskii 12
E. A. M. Good 9
C. C. Goodyear 3
O. Goscinski 12
M. Gote 10, 12

R. A. Gottscho 12, 23
G. Gouedard 3, 12
T. E. Graedel 12
M. Grapperhaus 27
D. B. Graves 16, 23
A. E. Green 26
J. W. Green 14
F. Grein 12
F. A. Grimm 4
A. M. Grisogokno 11
J. A. Guest 17
K. V. Guinn 5
R. J. Gulley 12
G. Guo 26
P. Gurtler 12, 20
D. Gutman 5

D. Haaks 3, 4, 17, 20, 29
H. v. Halban 12
R. I. Hall 19
J. C. Han 13
R. J. Hanrahan 24
P. B. V. Haranath 13
J. A. Harrison 23, 25
P. J. Hay 27
M. Hayashi 13
A. K. Hays 13
R. H. Healey 2
M. C. Heaven 6
G. A. Hebner 13
H. Helm 7
P. J. Hendra 13
I. P. Herman 5
D. W. Hess 10
P. C. Hiberty 13
G. Hirsch 29
G. Hochenbleicher 13
J. L. Holmes 18
W. Holzer 13
E. Hontzopoulos 29
W. F. Howard 1
H. G. Howell 13
A. R. Hoy 9
K. P. Huber 14
F. P. Huberman 14
S. Hubinger 14
R. H. Huebner 25
B. M. Hughes 14
S. Humbel 13
J. L. Hunt 28
S. R. Hunter 21
W. M. Huo 14
M. D. Hurley 27
D. -M. Hwang 4, 14

D. E. Ibbotson 9, 14
R. P. Iczkowski 14
E. Illenberger 20
F. Illuzzi 8
T. Intrator 23
T. Ishikawa 24
M. Yu. Ivanov 29
V. S. Ivanov 15
I. A. Izmailov 8

J. H. Jacob 23
T. A. Jacobs 15
M. Jacon 11
J. B. Jeffries 23
P. Jiang 2, 15
J. A. Joens 15
G. H. Johannesson 15
P. M. Johnson 18
F. W. Jones 15
B. Jordan 3, 4, 17, 20
J. Jortner 15
O. Joubert 8
J. Jureta 15

S. Kampf 29
S. A. Kandel 22
G. P. Karwasz 29
T. Kasuya 26
V. Kaufman 22
M. Kawasaki 19
T. Kawashima 19
B. N. Khanna 27
L. J. Kieffer 15
Y. -K. Kim 14
Z. H. Kim 22
M. Kimura 16
G. C. King 19, 24
T. Kinugawa 19
L. D. B. Kiss 16
T. N. Kitsopoulos 23
L. E. Kline 16
V. A. Kochelap 8
S. M. Koeckhoven 16
B. G. Koenders 16
A. Kornblit 18
H. J. Korsch 10
G. P. Kota 16

J. M. Kramer 23
M. O. Krause 4
H. Kuhn 16
G. J. Kuik 16
A. C. Kummel 29
H. Kunz 12
Y. Kurematsu 26
M. Kurepa 15
M. V. Kurepa 16, 17
T. Kusayanagi 14, 15
M. J. Kushner 16, 17, 25, 27
H. Kutz 17
A. Kvaran 15

P. Laborie 17
E. R. Laird 1, 17
P. W. Langhoff 11
K. P. Lawley 1
J. Le Calve 3, 17, 20, 29
J. le Calve 4, 12
C. Lee 13, 17
J. Lee 17
J. C. Lee 13
L. C. Lee 17
Y. Lee 21
Y. T. Lee 17
R. J. LeRoy 10, 18
R. D. Levin 18
H. J. Levinstein 20
M. Lewenstein 8
M. Lezius 8, 24
L. Li 18
S. G. Lias 18
A. J. Lichtenberg 17
M. A. Lieberman 17
J. F. Liebman 18
C. Lifshitz 14
R. J. Lipert 18
R. H. Lipson 28
J. Lobue 18
D. A. Long 9
S. L. Lunt 12
D. P. Lymberopoulos 18

C. J. MacCallum 22
M. A. MacDonald 19
R. T. Mahoney 3
A. P. Mahorowala 4
W. G. Mallard 18
M. V. Malyshev 18, 19
A. Mandl 4, 23
J. A. Mangano 23
D. M. Manos 19
S. T. Manson 19
J. L. Margrave 14
D. Maric 19
E. Martinez 6
N. J. Mason 12, 20
Y. Matsumi 19
T. Matsuura 19
W. Matthies 19
D. R. Matusek 29
I. E. McCarthy 11
A. G. McConkey 19
D. L. McCorkle 5, 19
E. W. McDaniel 19
I. S. McDermid 6
C. A. McDowell 7, 10, 11
V. McKoy 3
R. G. McLoughlin 19
E. Meeks 20
R. Meller 19
H. -D. Meyer 17
P. Meynadier 24
M. Meyyappan 20
G. N. Mikhailov 12
V. P. Mikhalkin 9
N. Mikoshiba 19
Z. Min 1
A. Misi 26
J. Miyawaki 29
C. J. Mogab 20
A. G. Molchanov 27
T. Moller 20, 29
C. K. Møller 9
J. H. Moore 6
G. K. Moortgat 19
W. L. Morgan 20
H. Morgner 2
J. D. Morrison 19, 20
R. I. Morse 3
J. T. Moseley 17
J. Mottl 28
D. Muigg 20
P. K. Mukherjee 11
R. S. Mulliken 20
J. Murota 19
W. F. Murphy 13
J. R. Murray 20

R. Nagpal 21

M. S. Naidu 22
G. Nakamura 21
Y. Nakamura 13
T. Nakayama 28
A. Namiki 9
J. B. Nee 14
P. D. Netyagov 29
A. J. C. Nicholson 20
W. L. Nighan 21
A. Nobs 28
D. Normand 8, 24
R. G. W. Norrish 3
V. M. Novikov 29
K. J. Nygaard 21

K. Obi 14
J. Oddershede 11
T. Ohmi 19
H. Ohtake 29
K. Ohtani 9
H. Okabe 21
I. V. Okuda 28
J. K. Olthoff 5, 6, 28
K. Ono 21
T. Oomori 21
H. Ootera 21

S. -K. Pack 21
H. B. Palmer 4, 21
L. Parenteau 2
H. Park 18, 23
J. Park 21
D. H. Parker 23
R. Patrick 17
M. Perdrix 24
W. B. Person 21
S. D. Peyerimhoff 12, 21
R. B. Piejak 23
N. Pinhao 21
L. C. Pitchford 11
A. W. Potts 21
H. T. Powell 20
S. Pozdneev 22
S. A. Pozdneev 9
S. Price 28
W. C. Price 21

L. J. Radziemaki 22
J. L. Ragle 7
A. T. Rakhimov 3
T. P. Rakitzis 22, 23
P. T. Rao 22
V. V. Rao 22
Y. V. Rao 22
F. H. Read 24
J. A. Rees 17
T. N. Rescigno 22
O. K. Rice 11
A. D. Richards 22
W. G. Richards 22, 26
T. Ridley 1
M. E. Riley 22
A. V. Risbud 22
J. -M. Rocard 17
G. L. Rogoff 23
M. Rokni 23
M. Rosi 11
M. D. Rowe 3
C. Roxlo 23

F. Salama 10, 23
P. C. Samartzis 23
J. A. R. Samson 11, 23
S. Samukawa 19, 23, 29
J. E. Sanabia 6
L. Sanche 2
A. D. Sappey 23
T. Sato 19
H. H. Sawin 4, 16, 22
M. N. Sawmy 23
H. F. Schaefer Ⅲ 23
P. M. Schaible 24
R. Schanker 7
G. R. Scheller 23
R. N. Schindler 5, 24
M. Schmidt 8, 24
W. F. Schneider 27
O. Schnepp 3
H. W. Schrotter 13
G. J. Schulz
E. Schultes 24
R. Schumacher 5
G. C. Schwartz 24
A. Schweig 26
D. J. Seery 24
A. Sgamellotti 11
D. A. Shaw 24
V. Shcheglov 22
R. J. Sheppard 24
M. Shimozuma 8
T. Shinzawa 14, 24

J. W. Shon 20
J. Si 14
J.-H. Si 14
G. D. Sides 24
K. Siedentopf 12, 27
L. Slotin 10
B. M. Smirnov 9
D. Smith 1, 24
D. L. Smith 19
G. P. Smith 17
U. Sokolov 15
T. J. Sommerer 25
V. N. Soshnikov 25
V. B. Sovkov 15
P. Spanel 24
D. Spence 25
H. Sponer 6
W. Spooner 15
S. K. Srivastava 25
A. Stamatovic 20
J. Stapelfeldt 29
D. S. Stedman 5
W. A. Steer 12
J. I. Steinfeld 25
I. A. Stenhouse 7
P. J. Stephens 3
R. K. Steunenberg 25
F. A. Stevie 25
B. P. Stoicheff 9
T. J. Stone 29
R. J. Stubbs 25
D. W. G. Style 10
N. V. Suetin 3
S. A. Sullivan 25
P. Sulzer 25
M. Suto 13, 17
E. N. Svendsen 11
V. I. Svettsov 9
M. N. Swamy 25
R. C. Sze 26

H. Tagashira 8
W.-C. Tam 26
H. Tanaka 25
I. Tanaka 14, 15, 24
K. Y. Tang 17
P. W. Tasker 26
D. Teillet-Billy 2
J. Tellinghuisen 6, 26
J. B. Tellinghuisen 28
P. C. Tellinghuisen 26
W. Thiel 26
E. W. Thomas 19
B. E. Thompson 22
R. Thorburn 26
T. O. Tiernan 14, 24
H.-J. Tiller 26
P. Tiruvenganna Rao 13
J. A. C. Todd 26
A. Tokunaga 24
S. Tsuchiya 26, 29
T. Tsuchizawa 26, 29
M. Tsukakoshi 26
K. Tsukiyama 26
M. Tuda 21
G. S. Tyndall 27

H. Uetake 19

L. Vallier 8
R. J. Van Brunt 28
W. J. van der Meer 27
H. van Lonkhuyzen 27
M. J. Vasile 25
C. J. Vear 13
K. Venkateswarlu 27
P. Venkateswarlu 22
P. L. G. Ventzek 8, 27
J. Vigue 3, 12
R. C. Vogel 25
M. G. Voitik 27
H. von Halban 27
W. Von Niessen 11
D. A. Vroom 11, 27

W. R. Wadt 27
A. C. Wahl 12
H. B. Wahlin 27
J. C. Wahr 8
I. C. Walker 20
F. Wallart 28
T. J. Wallington 27
A. D. Walsh 17
H. Wang 15
P. Wang 28
R.-G. Wang 25
Y. Wang 28
K. Watanabe 28
E. Weigold 11
W. C. Wells 28

W. E. Wentworth 2, 4, 9
R. J. Wheatley 28
T. A. Whitley 4
K. Wieland 25, 28
D. M. Wieringa 16
S. M. Wieringa 16
R. L. Wilkins 28
K. R. Wilson 3
R. G. Winkel 28
B. Woernle 28
S. F. Wong 26, 28
J. Wormer 29
J. S. Wright 29
M. Wu 18

K. Yamanouchi 26, 29
Y. Yamashita 19
C. Yan 29
A. J. Yarwood 1
K. K. Yee 29
A. Yokozawa 29
T. A. York 25

V. Z. Zafiropulos 29
V. V. Zaitsev 29
A. A. Zakharyan 29
R. N. Zare 22
A. Zecca 29
J. -P. Ziesel 12
G. Zimmerer 3, 4, 17, 20, 29
E. C. Zipf 28
Ya. I. Zukher 29
E. Yu. Zverevskaya 29

Author Index for Cl_2 References. Addenda

S. Barsotti 30
U. Becker 32
D. Bermejo 31
N. Berrah 30
E. Boursey 31
J. D. Bozek 30
S. K. Bramble 30
J. C. D. Brand 31

P. Calandra 30
S. Canton-Rogan 30
M. C. Castex 31, 32
J. Choi 31
M. A. A. Clyne 31
D. Cubaynes 30

A. del Olmo 31
C. Domingo 31

I. I. Fabrikant 30
I. Fujiwara 31

F. X. Gadea 30
P. Gurtler 32

D. Haaks 32
P. A. Hamilton 30
J. Hardwick 31
M. -C. Heaven 31
H. Hotop 30
A. R. Hoy 31

K. K. Innes 31
A. Ishiguro 31
T. Ishiwata 31, 32

S. J. Jackling 31
B. Jordan 32

Y. Kasai 31
M. Kawasaki 30, 31
E. Kukk 30

B. Langer 30, 32
J. Le Calve 32
J. le Calve 31

Y. Le Duff 31
T. Leininger 30

Y. Matsumi 30, 31
A. Menzel 32
T. Moller 32
R. S. Mulliken 32

K. Nanbu 30
O. Nayandin 30

K. Obi 31, 32
C. S. S. O'Connor 30
J. M. Orza 31
Y. Ota 32

L. Peters 32
S. D. Price 30

M. -W. Ruf 30

P. M. Schaible 32
G. C. Schwartz 32
J. -H. Si 31, 32
B. M. Smirnov 32
A. Sugita 30
K. Suto 30

I. Tanaka 31
T. W. Tolbert 31
K. Tonokura 31

Y. Uchida 32

J. Viefhaus 32

S. B. Whitfield 32
M. Wiedenhoeft 30
A. A. Wills 30
J. Wormer 32

A. S. Yatsenko 32

G. Zimmerer 32
B. A. Zon 30

Bromine Molecule Br_2

References for Br_2 (1900 - 1999)

(Bromine)

[Halogen]

E : Elastic collision,	R : Rotational excitation,
V : Vibrational excitation,	EX : Electronic excitation,
D : Dissociation,	I : Ionization,
A : Attachment,	QT : Grand total cross section,
S : Swarm,	α : Ionization coefficient,
O : The others,	[ ]: Additional informations, E : Exp., T : Theory.

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Author Index for Br_2 References

A. P. Acton 1
R. G. Aickin 1
J. Albaladejo 9
L. Andrews 1
E. v. Angerer 1
F. L. Arnot 1
J. G. Ashmore 12
B. S. Ault 1
D. Austin 12
O. I. Austin 1
J. A. Ayala 1

D. S. Babic 8
A. P. M. Baede 2
P. Baierl 2
J. E. Bailey 2
V. A. Bailey 14
K. Balasubramanian 2
G. G. Balint-Kurti 12
R. F. Barrow 2, 6
F. J. Basterrechea 9
A. O. Bawagan 5
N. S. Bayliss 1, 2
S. S. Bearder 2
E. C. Beaty 5
K. Becker 14
D. S. Belic 8
J. Berkowitz 4
H. J. Bernstein 6
R. B. Bernstein 8
P. Berwanger 2, 12
F. Bien 12
F. Biggs 10
J. P. Blewett 2
K. Blum 11
V. E. Bondybey 2
M. J. W. Boness 12
J. C. D. Brand 3
R. G. Briggs 3
C. E. Brion 5, 10
M. Brith 3
D. Britton 11
H. P. Broida 3
H. A. Brown 5
W. G. Brown 3
D. F. Broyd 2
E. D. Bugrim 3
G. Burns 8
M. A. Byrne 12

G. E. Caledonia 3
M. N. Cann 10
G. Capelle 3
J. H. Carver 3
F. Castano 9
V. Cermak 3
E. C. M. Chen 1, 5
Y. Chun 3
W. A. Chupka 4
T. C. Clark 2
M. A. A. Clyne 4
G. Cooper 10
H. Cordes 4
A. B. Cornford 4
J. A. Coxon 2, 4
D. Cvejanovic 11

L. Dabrowski 4
P. J. Dagdigian 7
O. Darbyshire 4
C. A. de Lange 13
U. D. Deshpande 3
H. Deutsch 14
V. H. Dibeler 5
J. G. Dillard 5
R. N. Dixon 12
J. Dojahn 5
V. M. Donnelly 5, 7
R. J. Donovan 1, 8, 12
K. E. Drabe 8
J. Dutton 5

J. H. D. Eland 6
A. V. Eletskii 5
R. S. Eng 5
J. J. Ewing 5
D. Feldman 10
D. L. Flamm 5, 7
C. Fletcher 2
M. J. Flood 8

D. C. Frost 4, 5
L. Frost 5

J. W. Gallagher 5
J. L. Gardner 3
S. Gerstenkorn 6
D. B. Gibbs 6
C. C. Goodyear 10
O. Goscinski 6
A. -M. Grisogono 5
D. Gutman 4

R. J. Hanrahan 11
P. B. V. Haranath 6
T. Harris 6
P. J. Hay 13
M. Hayashi 6
R. H. Healey 14
M. C. Heaven 4
E. Heinicke 10
C. P. Hemenway 6
G. Herzberg 6
J. G. Hochenbleicher 2
W. Holzer 6
A. Hopkirk 1
J. A. Horsley 6
W. F. Howard 1
A. R. Hoy 3, 8
R. S. Hozack 9
K. P. Huber 6
S. Hubinger 7
H. Hurzeler 9
E. Hwang 7

D. E. Ibbotson 5
R. P. Ibbotson 7
T. Ichimura 8
M. G. Inghram 9
K. K. Innes 14
T. Ishiwata 7, 11
V. Ivanov 7

S. J. Jackling Ⅲ 14
J. H. Jacob 5
S. M. Jaywant 3
Y. -J. Jee 8
J. Jortner 8
K. -H. Jung 8
Y. -J. Jung 8

H. J. Kaiser 10
J. Karle 12
K. Kasatani 11
M. Kawasaki 11
W. Kiefer 2
Y. S. Kim 8
G. C. King 11
B. G. Koenders 8
H. Kuhn 8
G. J. Kuik 8
A. C. Kummel 14
M. V. Kurepa 8

K. P. Lawley 1, 8, 12
S. R. Leone 8
R. J. LeRoy 8
F. -m. Li 14
T. G. Lindeman 6
R. H. Lipson 8
P. Luc 6
R. M. Lum 9

C. J. MacCallum 10
M. MacDonald 12
R. E. B. Makinson 2
S. N. Makrenko 3
A. Mandl 10
J. A. Mangano 5
T. D. Mark 14
E. Martinez 4
F. Martinez 9

K. B. McAfee 9
K. E. McCulloh 5
C. A. McDowell 4, 5
J. C. McLauchlan 1
M. V. McLoughlin 9
C. B. Moore 8, 14
H. W. Moos 12
J. D. Morrision 9
R. S. Mulliken 9
W. F. Murphy 6
J. R. Murray 9

M. S. Naidu 10
G. Nakamura 9
O. Nakamura 7
Y. Nakamura 6
J. B. Nee 7
A. J. Nichlson 9

A. Nobs 13
N. S. Nogar 14
R. G. W. Norrish 3

K. Obi 7
E. A. Ogryzlo 6
H. Ohtoshi 7
R. J. Oldman 9
T. N. Olney 10
Y. Ota 13

M. S. Park 8
L. B. Pederson 2
S. S. Penner 12
W. B. Person 10
L. C. Pitchford 5
A. W. Potts 10
S. Pozdneev 10
W. C. Price 10
P. Puyuelo 9

R. Rackwitz 10
J. L. Ragle 4
Y. V. Rao 10
A. Raynal 6
S. A. A. Razzak 10
F. H. Read 11
A. L. G. Rees 10
W. G. Richards 12
T. Ridley 8
M. E. Riley 10
A. V. Risbud 10
M. D. Rowe 3
C. Roxlo 10

K. Sakurai 3
R. K. Sander 9
V. N. Sarma 13
H. Sato 11
A. L. Schawlow 12
O. Schnepp 3
D. J. Seery 11
C. H. Shaw 11
D. A. Shaw 11
V. Shcheglov 10
T. Shinzawa 7, 11
G. V. Shlyapnikov 5
G. D. Sides 11
J. Sinzelle 6
B. M. Smirnov 5, 11
D. L. Smith 9
I. M. Smith 11
T. M. Snyder 11
U. Sokolov 8
J. M. Somerville 2
V. N. Soshnikov 11
V. B. Sovkov 7
D. Spence 11
H. Sponer 4
H. E. Stanton 9
I. A. Stenhouse 4
P. J. Stephens 3
R. K. Steunenberg 11
T. J. Stone 14
J. V. Sullivan 2
P. Sulzer 11
K. G. P. Sulzmann 12
A. Sur 12
D. A. Swick 12
J. C. Swingle 9

W. -C. Tam 12
I. Tanaka 7, 11
P. W. Tasker 12
A. W. Taylor 3
J. Tellinghuisen 2, 4, 7, 12
J. B. Tellinghuisen 13
D. G. Thompson 11
T. O. Tiernan 11
W. B. Tiffany 12
P. Tiruvenganna Rao 6
J. A. C. Todd 12
A. Tokunaga 7, 11
D. W. Trainor 12
F. K. Truby 12
I. L. Tsikora 3
R. P. Tuckett 6
C. E. Turner 9

Y. Uchida 13

H. van Lonkhuyzen 13
K. Venkateswarlu 13
P. Venkateswarlu 13
R. D. Verma 13
K. S. Viswanathan 2, 12
R. C. Vogel 11
W. von Niessen 5
D. A. Vroom 5, 13

W. R. Wadt 13
J. A. Walker 5
P. -n. Wang 14
Y. -f. Wang 14
K. Watanabe 13
E. Weigold 5
W. E. Wentworth 1, 5
K. Wieland 11, 13
J. R. Wiesenfeld 6
K. R. Wilson 9, 14
S. F. Wong 12
A. R. Woon-Fat 4

L. Xu 14

C. Yan 3, 14
A. S. Yatsenko 11
K. K. Yee 2, 14
A. J. Yencha 1, 8

M. Zackrisson 14
F. Zaraga 14

Iodine Molecule I_2

References for I_2 (1900 - 1999)

(Iodine)

[Halogen]

E	: Elastic collision,	R	: Rotational excitation,
V	: Vibrational excitation,	EX	: Electronic excitation,
D	: Dissociation,	I	: Ionization,
A	: Attachment,	QT	: Grand total cross section,
S	: Swarm,	α	: Ionization coefficient,
O	: The others,	[ ]	: Additional informations, E : Exp., T : Theory.

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Author Index for I_2 References

R. Abouaf 1
H. Aksela 1
S. Aksela 1
C. Amiot 8
D. A. Andrews 12
L. Andrews 10
E. v. Angerer 1
F. L. Arnot 1
K. Asagoe 24
R. K. Asundi 1
E. R. Ault 2
J. A. Ayala 1
A. Azria 1

R. Bacis 4, 12, 14
A. P. M. Baede 2
K. Balasubramanian 14
J. N. Bardsley 2
P. N. Barnes 2
R. F. Barrow 2, 13, 23
R. Batino 22
N. S. Bayliss 2
E. C. Beaty 8
K. Becker 24
R. A. Berg 3
J. Berkowitz 5
H. J. Bernstein 10, 11
R. B. Bernstein 5, 13
D. Bertuccelli 2
S. S. Bhatnager 2
M. L. Bhaumik 2
F. Biggs 17
M. A. Biondi 2
D. T. Birtwistle 2
R. S. Bradford 2
J. C. D. Brand 2, 10
C. A. Brau 7
L. Brewer 3, 5
A. G. Briggs 3
M. Brith 3
H. P. Broida 4
H. L. Brooks 3, 16
J. D. Brown 3
R. L. Brown 3
D. F. Broyd 2
M. Broyer 3, 4, 8, 9, 11, 21
R. Buchdahl 4
E. D. Bugrim 4
P. R. Bunker 4, 5, 9
G. Burns 3
G. E. Busch 4
B. S. Butayev 16

G. E. Caledonia 4
A. B. Callear 4
J. D. Campbell 18
G. A. Capelle 4
G. Cario 4
K. H. Casleton 9
D. Cerny 4
P. J. Chantry 4
G. D. Chapman 5, 18
E. C. Chen 5
E. C. M. Chen 1, 6
M. S. Child 5
W. A. Chupka 5
S. Churassy 4, 14
A. Chutjian 5
R. D. Clear 5
F. J. Comes 5
R. N. Compton 15
H. Cordes 5
A. B. Cornford 5
W. E. Curtis 6

C. E. Dahlstrom 9
F. W. Dalby 6
M. D. Danyluk 6
E. O. Degenkolb 6, 10
R. D. Deslattes 17
H. Deutsch 24
V. H. Dibeler 24
J. G. Dillard 6
J. G. Dojahn 6
R. J. Donovan 6, 13, 23
Th. Dorfmuller 8
F. H. Dorman 6
G. F. Drukarev 6
F. Duschinsky 6, 7

J. Dutton 8
S. H. Dworetsky 16, 22

A. Elliott 7
P. Erman 4
S. F. Evans 6
J. J. Ewing 7
S. Ezekiel 9, 17, 23

W. E. Falconer 22
S. Fei 23
A. Fernandez 22
R. W. Field 12
W. Finkelnberg 7
Ya. A. Fofanov 8
R. E. Fox 2, 7
J. Franck 7
G. Friedheim 12
D. C. Frost 5, 7

J. W. Gallagher 8
M. Geilhaupt 8
A. G. Gershikov 16
S. Gerstenkorn 8, 11, 20
Ts. I. Glozman 8
E. V. Golikova 8
G. Gouedard 8, 9
R. A. Gutcheck 14
D. Gutman 5
A. L. Guy 9

L. A. Hackel 9, 17, 23
J. S. Ham
G. R. Hanes 4, 9
T. W. Hansch 9, 18
P. B. V. Haranath 9
A. K. Hays 9
R. H. Healey 9
M. C. Heaven 16, 23
G. Herzberg 10
B. R. Higginson 10
W. Hilgner 10
R. M. Hill 14
A. Hiraya 6
E. Hirschlaff 6, 10
J. M. Hoffman 9
W. Holzer 10
A. Hopkirk 13, 23
W. F. Howard 10
A. R. Hoy 10, 14
H. R. Hoy 2
R. S. Hozack 16
K. P. Huber 10
D. L. Huestis 14
B. M. Hughes 10
S. R. Hunter 3, 16
W. M. Huo 10
H. Hurzeler 15
J. M. Hutson 11

D. Inard 4
M. G. Inghram 15
K. K. Innes 11, 12
Y. Inuzuka 24
I. Ishiwata 11

S. J. Jackling 11
T. C. James 3, 5
S. M. Jaywant 10
L. Jones 18
J. Jortner 11
L. M. Julien 11

J. Keck 11
W. M. Keeffe 11
D. K. Kela 13
J. -C. Keller 11
E. G. Kessler 17
J. Kessler 10
W. Kiefer 11
G. W. King 6, 12
U. K. A. Klein 19
W. Klemperer 6, 18
J. B. Koffend 12
J. Koo 12
G. Kortum 12
K. Kroll 12
H. Kuhn 12, 13
S. G. Kukolich 9, 17
J. Kurepa 4
M. J. Kushner 2
A. Kvaran 13

M. Lamrini 4
B. M. Landsberg 9, 13
J. Lapierre 9
H. P. Layer 17
J. C. Lehmann 3, 8, 9, 11, 13, 21
J. -C. Lehmann 3, 4
R. J. LeRoy 3, 8, 13, 20, 21

M. Lesk 18
M. D. Levenson 9, 13, 18
D. H. Levy 18
J. Li 14
C. Lifshitz 10
J. K. Link 5
R. H. Lipson 10, 14
I. M. Littlewood 12
D. R. Lloyd 10, 14
D. C. Lorents 14
P. Luc 8, 11, 14, 20
W. Luck 14

C. J. MacCallum 17
R. T. Mahoney 4
T. D. Mark 24
F. Martin 14
S. M. Mason 14
J. Mastromarino 19
L. Mathieson 14
K. N. Mathur 2
K. E. McCulloh 24
M. V. McCusker 14
N. McDonald 14
C. A. McDowell 5, 7
M. R. McKeever 19
R. Mecke 14
N. A. Melnikov 8
J. C. Miller 15
A. V. Mironov 8
A. Modinos 2
R. G. W. Morrish ?
J. D. Morrison 14, 15
R. I. Morse 4
R. S. Mulliken 15
W. F. Murphy 10
J. A. Myer 15

H. H. Nakano 14
A. Ya. Nasarenko 16
H. Neujmin 20
G. Newton 12
A. J. C. Nicholson 6
U. Nielsen 5
A. Nobs 16, 22
D. Normand 16
M. Nota 4
M. N. Nowlin 16
K. T. Nygaard 16

B. V. O'Grady 6
O. Oldenberg 4, 16
R. J. Oldman 16

J. A. Paisner 16, 21
Y. -H. Pao 20
G. D. Patterson 16
L. B. Pederson 2
A. Perrin 8
W. B. Person 11, 16
G. Petty-Sil 6
L. C. Pitchford 8
A. W. Potts 17
S. A. Pozdneev 6
T. A. Prasada 9
W. C. Price 17
P. Pringsheim 6, 7, 17
V. E. Privalov 8
M. H. L. Pryce 6

J. L. Ragle 5
A. Recknagel ?
J. W. Reed 9
A. L. G. Rees 14
R. D. Deslattes 17
M. E. Riley 17
P. J. Roberts 10
J. R. Robins 12
B. Rosen 17
G. M. Rosenblatt 3
H. M. Rosenstock 24
D. L. Rousseau 17, 22
M. D. Rowe 3
D. J. Ruben 17

J. A. R. Samson 15
R. K. Sander 16
S. K. Savelev 8
A. L. Schawlow 9, 13, 18, 21
M. Schmidt 16
O. Schnepp 3
W. H. E. Schwarz 5
W. G. Schweitzer 17
J. E. Selwyn 17
R. K. Sharma 2
T. Shinzawa 11
K. Shobatake 6
K. C. Shotton 9, 18
D. L. Shrivastava 2
A. M. Sibai 12

S. M. Singh 18
J. Sinzelle 8, 11
E. Skorko 18
B. M. Smirnov 7, 18
K. F. Smith 12
U. Sokolov 11
R. Solarz 18
M. S. Sorem 18
V. P. Spiridonov 16
H. E. Stanton 15
J. I. Steinfeld 6, 17, 18
I. A. Stenhouse 5
P. J. Stephens 3
C. B. Suarez 2
J. V. Sullivan 2
A. Sur 9, 19
A. Suwaiyan 19

C. Tai 6
W. C. Tam 19
I. Tanaka 11
D. Teillet-Billy 1
J. Tellinghuisen 3, 9, 18, 19, 20, 22, 23
A. Terenin 20
M. Tesic 20
T. D. Thomas 1
T. O. Tiernan 10
P. Tiruvenganna Rao 9
G. C. Tisone 9
L. P. Tkachenko 8
A. Tokunaga 11
T. W. Tolbert 11
J. W. Tromp 6, 20
R. P. Tuckett 14
L. A. Turner 20

J. T. Vanderslice 22
J. H. Van Vleck 20
K. Venkateswarlu 20
P. Venkateswarlu 1, 20, 21
J. Verges 14
R. D. Verma 21
J. Vigue 3, 4, 8, 9, 21
K. S. Viswanathan 9
D. A. Vroom 7, 21

J. A. Walker 24
R. Wallenstein 16, 21
J. Waser 22
E. Wasserman 6, 22
J. Wei 22
N. A. Weiss 18
S. Weissman 22
W. E. Wentworth 1, 5, 6
J. R. Whetstone 17
K. Wieland 16, 19, 22
P. F. Williams 17, 22
K. R. Wilson 4, 5, 16
S. P. Wong 19

W. A. Yager 22
A. S. Yatsenko 18
K. K. Yee 2, 23
A. J. Yencha 13, 14, 23
D. G. Youmans 17, 23

Yu. G. Zakharenko 8
R. N. Zare 18, 23
I. A. Zayats 23
X. Zheng 23

Some Comments on Electron Collision Cross Sections for F_2, Cl_2, Br_2 and I_2

The pioneer work on electron collision cross section set for F_2 is given by authors, M.Hayashi and T.Nimura in 1983a. Almost no exact experimental data for F_2 cross sections, because experiments are extremely difficult. Our cross section set for F_2 is still tentative value. Now author cannot improve the cross section set, in spite of twenty years are passed.

Now I do not like this F_2 cross section set by another reason. All molecules have the component M(g), M(r), M(v) and M_n (n = 2), depend on the pressure and temperature condition of the experiment. In F_2, there are some concentration of F_2(g) component, and plus many F_2(r) and small F_2(v) components. On the other hand, in I_2 molecules, there are no concentration of I_2(g), almost I_2 are I_2(r) of large j values and plus I_2(v) components at usual experimental conditions.

Many scientists requested the cross section set for Cl_2 to the author during these twenty years or so. The cross section sets for Cl_2 are given by G.L.Rogoff (1986), W.L.Morgan (1991), (1992), (1999), E.S.Aydil (1992), N.Pinhao (1995), and G.I.Font (1997). Recently, L.G.Christophorou and J.K. Olthoff (1999) compiled the cross sections for Cl_2. The summary said that we need more experimental studies of cross sections and other processes in Cl_2. Temperature dependence of electron collisions and other processes are interesting subject for this molecules.

Almost theoretical results of electron collision cross sections for molecules are for M(g). Theoretical studies involving the M(r) and M(v) are urgently required for many molecules.

I would like to present our two papers on F_2 and recent report on all molecules at the end of this report.

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M.Hayashi : Jpn.J.Appl.Phys. 22, L565-L566 (1983b)

M.Hayashi and Y.Nakamura : EMS-99, Tokyo 175-176 (1999)

Calculation of electron swarm parameters in fluorine

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Swarm parameters of electrons have been calculated for fluorine by a Monte Carlo simulation and the Boltzmann equation method for the first time. Values of these parameters have been obtained for ratios of the electric field to the gas number density E/N from 100 to 3000 Td ($E/p_0 = 35 \sim 1000$ V/cm Torr). Available experimental and theoretical cross sections were used for the calculations.

PACS numbers: 51.50. + v, 52.80.Dy, 52.25.Fi, 52.20.Fs

I. INTRODUCTION

The role of negative ions in gas lasers is important.[1] Rare-gas fluoride lasers are being investigated extensively. Experimental values of electron transport parameters for fluorine are not available. The high chemical activity of F_2 makes it difficult to obtain reliable values of the electron cross sections and the electron swarm parameters in F_2. In this paper, values of the electron drift velocity W, the characteristic energy eD_T/μ, the mean electron energy $\langle\epsilon\rangle$, the Townsend's ionization coefficient α, the attachment coefficient η, and the energy distribution functions $f(\epsilon)$ calculated by the Boltzmann equation and a Monte Carlo simulation method are reported. The calculated range of the electric field to the gas number density E/N is from about 100 to 3000 Td.

II. COLLISION CROSS SECTIONS

The cross sections used in this paper are shown in Fig. 1.

The theoretical values for elastic total cross sections q_t were given by Schneider and Hay[2] and Rescigno *et al.*[3] for the electron energy from about 0.03 to 14 eV. In Ref. 2, there are two calculated results for the values of q_t, one has a resonance at 1.8 eV (F_2 core orbitals) and another one has no resonance (F_2^- core orbitals). The result of Ref. 3 has a resonance at about 2.2 eV. Here the values of q_t, which have a resonance, were chosen, and calculations using the values of q_t of nonresonance were not carried out. These values of q_t are almost the same as q_t in N_2.[4] It is quite a coincidence. The assumption was therefore made that the values for elastic momentum transfer cross section q_m were equal to the values for q_t for F_2, as is approximately the case with N_2. The values for q_m at energies greater than 14 eV were assumed to be equal to the values for q_m in N_2.[4]

There is one theoretical paper giving values for the vibrational excitation cross section q_v.[5] These values were used for these calculations. The threshold energy is 0.11 eV.

Values for electronic excitation cross sections q_e were calculated by Fliflet *et al.*[6] for the lowest excitation level $a^3\Pi_u$ (threshold 3.16 eV), and by Hazi[7] for the two levels $C\,^1\Sigma_u$ (threshold 11.57 eV) and $H\,^1\Pi_u$ (threshold 13.08 eV). The values for q_e of triplet level $a^3\Pi_u$ were connected smoothly and decreased rapidly with electron energy. The energy dependence of the values for q_e for the two singlet states are similar to those for q_e in H_2. The values for q_e for the $C\,^1\Sigma_u$ and $H\,^1\Pi_u$ levels were extrapolated for higher energies.

The other q_e values for dissociative level $A\,^1\Pi_u$ (threshold 4.34 eV) were assumed. There are no theoretical and experimental data for this energy level. There is no base for the determination of the peak value of q_e, so we chose about half peak value of q_e compared with the peak value of q_e for $a^3\Pi_u$ level. The level $A\,^1\Pi_u$ is a singlet state, so the electron energy dependence on q_e is spread widely, as it is at q_e for $C\,^1\Sigma_u$.

The values for the four q_e's are small compared with the values for q_m and ionization cross section q_i as shown in Fig. 1. Consequently, the influence of the values chosen for q_e on the swarm parameters is small. If the values for q_e are much larger than the values used, the effect would be important. However, the values for q_e are sensitive to the values for α at low E/N.[8] Consequently, there is a possibility that the values for α at low E/N are affected by the values of q_e. However, the values of η are much larger than the values of α at low E/N. Therefore, we believe that the reasonable values of $(\alpha - \eta)$ were obtained, without large influence by the values of q_e.

Values of q_e for other electronic excitaion levels were

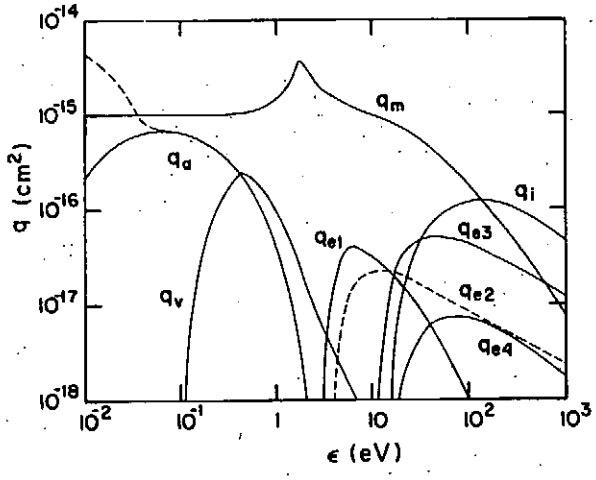

FIG. 1. Cross sections of electrons in F_2 used in this paper. The dotted curve for q_a is the low energy part of the attachment cross section obtained by Chantry. The solid curve for q_a was used for this calculation. The curves for q_{e1}, q_{e2}, q_{e3} and q_{e4} show the excitation cross sections of $a^3\Pi_u$, $A\,^1\Pi_u$, $C\,^1\Sigma_u^+$, and $H\,^1\Pi_u$ levels, respectively. The dotted curve for q_{e2} was assumed.

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neglected. More detailed information about q_e is needed.[9]

Recently measured values of ionization cross sections q_i were used in these calculations. The data were measured by Stevie and Vasile[10] and covered the energy range from threshold, 15.69 eV, to about 100 eV. The values for q_i above 100 eV were extrapolated smoothly using the usual energy dependence of q_i in many gases.

There are experimental values for attachment cross section q_a given by Chantry[1,11] at 365 K. Calculated values for q_a are given by Hazi *et al.*[11] The values of Hazi *et al.* were used below about 0.1 eV. There is little effect of the two values for q_a on swarm parameters for the range of E/N which is reported in this paper. For higher energies, Chantry's values were employed. There is a maximum value for q_a and the value is 7.0×10^{-19} cm^2 at 6.2 eV. These two values for q_a are shown in Fig. 1, however, a small peak at 6.2 eV is not shown in this figure.

III. PROCEDURES

The Monte Carlo simulation (MCS) method used in this paper has been discussed previously.[12]

The well-established two-term approximation was used to solve the Boltzmann equation.[13] The energy distribution functions of electrons $f^0(\epsilon)$ and $f^1(\epsilon)$ are described by the equations

$$\frac{(\alpha-\eta)\sqrt{\epsilon}}{3}f^1(\epsilon)+\frac{eE\sqrt{\epsilon}}{3}\frac{d}{d\epsilon}[\sqrt{\epsilon}f^1(\epsilon)]$$
$$=2\frac{m}{M}\frac{d}{d\epsilon}\left\{\epsilon\sqrt{\epsilon}Nq_m f^0(\epsilon)+kT\epsilon^2Nq_m\frac{d}{d\epsilon}\left[\frac{1}{\sqrt{\epsilon}}f^0(\epsilon)\right]\right\}$$
$$+\sum_j\left[\sqrt{\epsilon+\epsilon_e^j}\,Nq_{ex}^j(\epsilon+\epsilon_e^j)f^0(\epsilon+\epsilon_e^j)\right]$$
$$+2\int_\epsilon^\infty\frac{1}{\epsilon'}\sqrt{\epsilon'+\epsilon_i}\,Nq_i(\epsilon'+\epsilon_i)f^0(\epsilon'+\epsilon_i)\,d\epsilon'$$
$$-\sqrt{\epsilon}\left[\sum_j Nq_{ex}^j(\epsilon)+Nq_i(\epsilon)+Nq_a(\epsilon)\right]f^0(\epsilon),$$

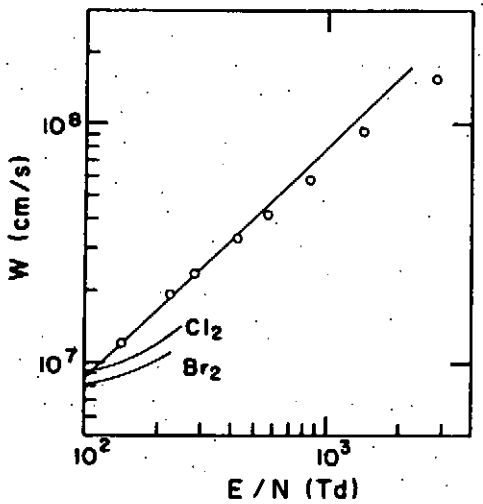


FIG. 2. Drift velocity of electrons W. Solid curve is the present calculation for F_2 by *B Eq* and the circles are the present calculated values for F_2 by MCS. Values for W in Cl_2 and Br_2, taken from references, are shown for comparison.

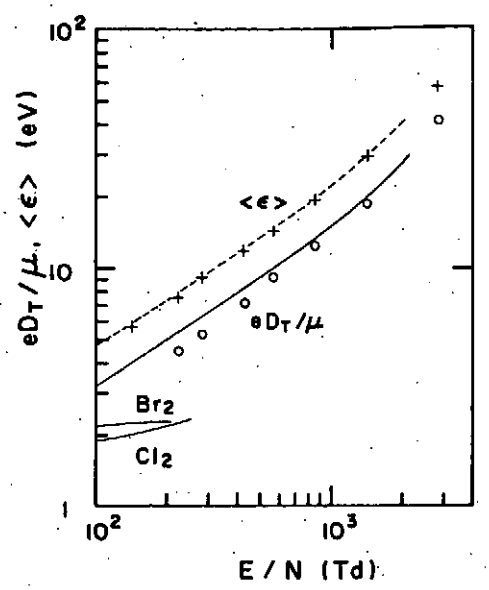


FIG. 3. Characteristic energy eD_T/μ and mean electron energy $\langle\epsilon\rangle$ in F_2. Solid and dotted curves are present calculated values for eD_T/μ and $\langle\epsilon\rangle$ by *B Eq* and circle and plus points are present calculated values of eD_T/μ and $\langle\epsilon\rangle$ by MCS, respectively. Values for eD_T/μ in Cl_2 and Br_2 taken from references are also shown.

and

$$f^1(\epsilon)=-\frac{1}{NQ(\epsilon)}\left\{(\alpha-\eta)f^0(\epsilon)+eE\sqrt{\epsilon}\frac{d}{d\epsilon}\left[\frac{1}{\sqrt{\epsilon}}f^0(\epsilon)\right]\right\},$$

where e and m are the electron charge and mass, M is the

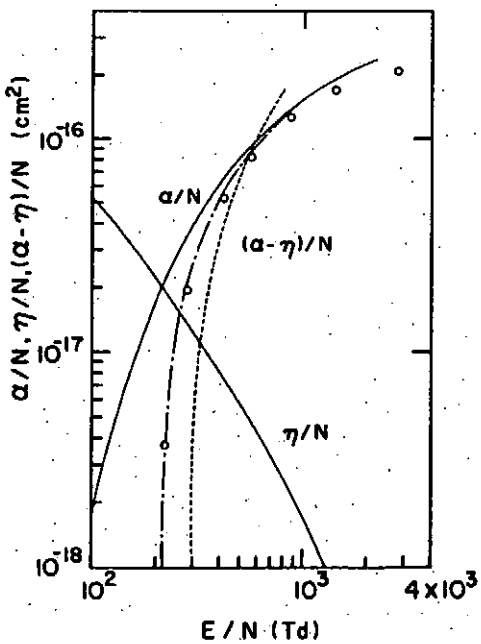


FIG. 4. Townsend's ionization coefficient α, attachment coefficient η, and effective ionization coefficient $(\alpha-\eta)$ in F_2. Solid curves are the present calculated values for α and η obtained by *B Eq*. Dot-dashed curve is the present calculated values for $(\alpha-\eta)$. Circles are present calculated values for $(\alpha-\eta)$ obtained by MCS. The dotted curve is the experimental values for $(\alpha-\eta)$ in Cl_2 and Br_2 for comparison. In Cl_2 and Br_2, values for $(\alpha-\eta)$ are almost the same.

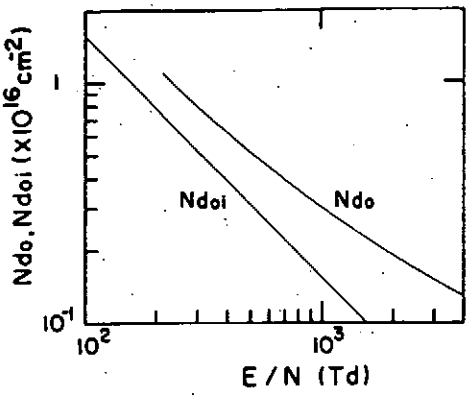


FIG. 5. Values of d_0 relating to the nonequilibrium distance in F_2 calculated by MCS. Straight line shows the values of $Nd_{0i} = V_i/(E/N)$.

mass of gas atom, ϵ is the energy of electrons, k is the Boltzmann constant, T is the gas temperature, and $\int_0^\infty f^0(\epsilon)\,d\epsilon = 1$. The total collision cross section Q is defined by

$$Q(\epsilon) = q_m(\epsilon) + \sum q_{\text{inel}}(\epsilon),$$

where the second term on the right side denotes the summation of all the inelastic collision cross sections. q_{ex} is the excitation cross section of all kinds, including $q_v, q_{e1}, \ldots, q_{e4}$, in this case. ϵ_e^j is the excitation energy loss for jth kind or state of species, and ϵ_i is the ionization energy loss.

The swarm parameters are given by

$$W = -\frac{1}{3}\sqrt{\frac{2}{m}}eE\int_0^\infty \frac{\epsilon}{NQ(\epsilon)}\frac{d}{d\epsilon}\left[\frac{1}{\sqrt{\epsilon}}f^0(\epsilon)\right]d\epsilon,$$

$$D = \frac{1}{3}\sqrt{\frac{2}{m}}\int_0^\infty \frac{\sqrt{\epsilon}}{NQ(\epsilon)}f^0(\epsilon)\,d\epsilon,$$

$$\langle\epsilon\rangle = \int_0^\infty \epsilon f^0(\epsilon)\,d\epsilon,$$

$$\nu_i = \sqrt{\frac{2}{m}}\int_0^\infty \sqrt{\epsilon} f^0(\epsilon) N q_i(\epsilon)\,d\epsilon,$$

$$\nu_a = \sqrt{\frac{2}{m}}\int_0^\infty \sqrt{\epsilon} f^0(\epsilon) N q_a(\epsilon)\,d\epsilon,$$

$$\alpha = \frac{\nu_i}{\frac{W}{2} + \sqrt{\left(\frac{W}{2}\right)^2 - (\nu_i - \nu_a)D}},$$

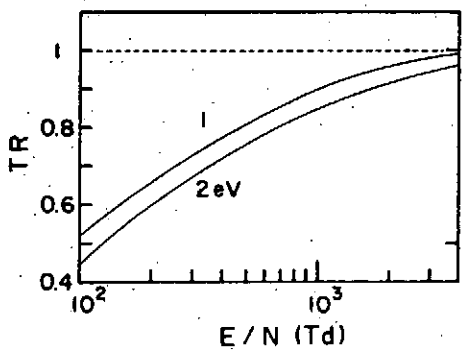
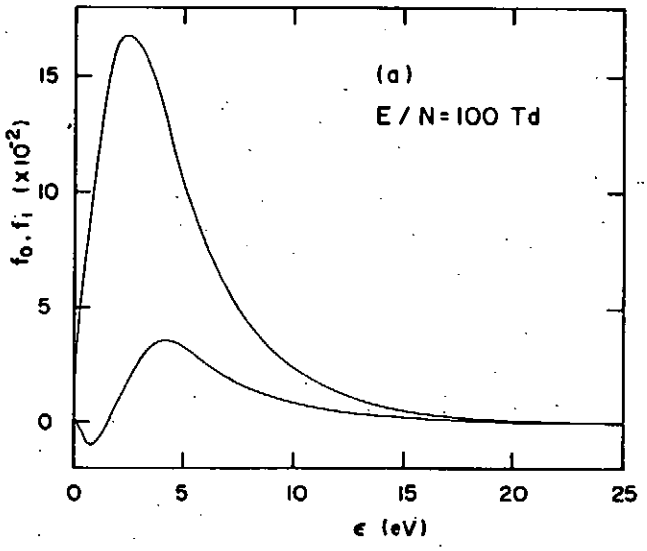
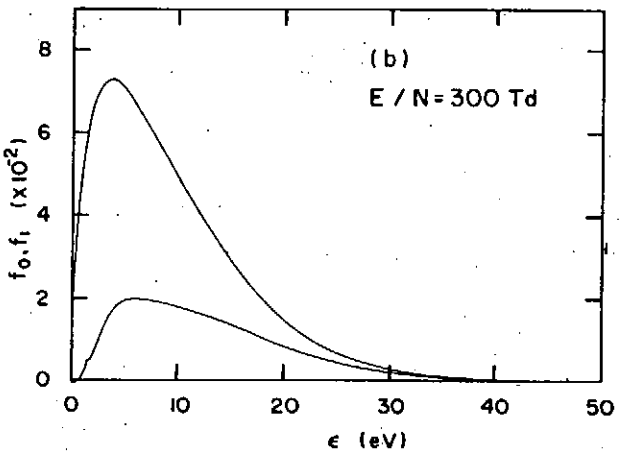


FIG. 6. Present calculated values for the transmission coefficient TR in F_2 by MCS for initial energy of electrons of 1 and 2 eV. The reflection coefficient of electrons at the cathode is assumed to be 0.5.





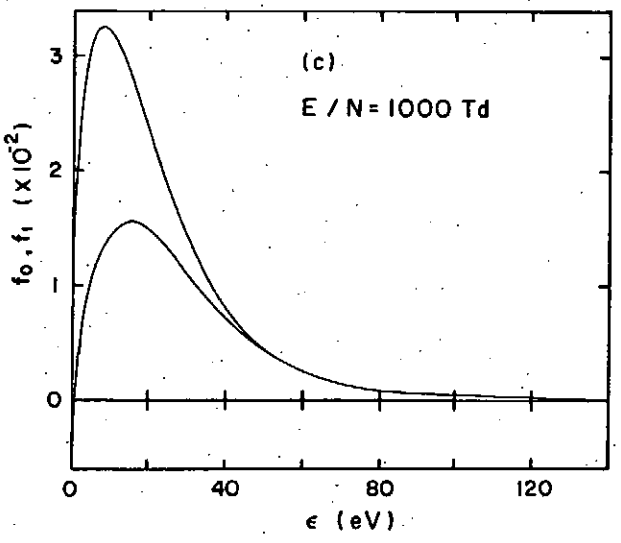


FIG. 7. Energy distribution function of electrons in F_2 calculated by B Eq at $E/N = 100$, 300, and 1000 Td, respectively.

and

$$\eta = \frac{\nu_a}{\frac{W}{2} + \sqrt{\left(\frac{W}{2}\right)^2 - (\nu_i - \nu_a) D}},$$

where ν_i and ν_a are ionization frequency and attachment frequency, respectively.

IV. RESULTS

Calculated values for W are shown in Fig. 2. There are no experimental data for W in F_2. However there are some old data for W in Cl_2 (Ref. 14) and Br_2.[15] These values are shown in Fig. 2 for comparison. The values for W at high E/N calculated by B Eq are higher than the values for W by MCS method.

The calculated values for eD_T/μ and $\langle\epsilon\rangle$ are shown in Fig. 3. Values for eD_T/μ in Cl_2 and Br_2 are also shown in Fig. 3. The values for eD_T/μ in Cl_2 and Br_2 were calculated from the equation $eD_T/\mu = 2.48\times10^{-2}\,K$, where K is the mean energy of agitation of an electron in terms of the mean energy of agitation of a molecule at 15 °C, given in Refs. 14 and 15.

The calculated values for α, η, and $(\alpha - \eta)$ are shown in Fig. 4. Experimental values for $(\alpha - \eta)$ in Cl_2 (Ref. 16) and Br_2 (Ref. 17) are also shown in Fig. 4 for comparison purposes. In Cl_2 and Br_2, values for $(\alpha - \eta)$ are almost the same.

The values d_0 relating to the nonequilibrium distance[18] were calculated by the MCS method. The values of Nd_0 as a function of E/N are shown in Fig. 5, along with the values of $Nd_{0i} = V_i/(E/N)$, where V_i is the voltage at which the electron runs to get the ionization energy of F_2.

The values for the transmission coefficient TR calculated by MCS are shown in Fig. 6 for the initial electron energies of 1 and 2 eV. In this case, the reflection coefficient of electrons at the cathode surface is assumed to be 0.5.

Some examples of the energy distribution functions of electrons at an equilibrium conditions are shown in Fig. 7.

It is difficult to estimate the errors of these swarm parameters. Determination of a more comprehensive set of cross sections or experimental swarm data will provide a basis for further analysis.

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Calculation of Electron Attachment Rate Coefficient in Fluorine

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Electron attachment rate coefficients have been calculated for fluorine by the Boltzmann equation. The range of E/N, ratio of the electric field to the gas number density, for which the coefficients were calculated ranged from 70 to 2000 Td.

§1. Introduction

Swarm parameters of electrons have been calculated for pure fluorine for the first time.[1] In these calculations, values of the electron drift velocity W and attachment coefficient η were obtained. From these values, electron attachment rate coefficients k_a have been determined and compared with available experimental data in dilute fluorine as well as with calculated data. It is concluded that the present calculated values of k_a are reasonable, in spite of the fact that values of cross sections used in the calculations are incomplete.

The methods of calculation and the cross sections used in this paper are given in detail in reference 1).

§2. Calculated Results

Calculated values of k_a are shown in Figs. 1 and 2.

Measurements of electron attachment rate coefficient studies for mixtures of gases including F_2 have been made by

Sides *et al.*[2],	0.065% F_2 in Ar,
Chen *et al.*[3],	0.25% F_2 in N_2,
Schneider and Brau[4],	0.01~0.03% F_2 in N_2 and Ar,
Trainor and Jacob[5],	0.13% F_2 in N_2, and
Nygaard *et al.*[6],	1% F_2 in He.

Calculated values of k_a for dilute F_2 have been given by

Hazi *et al.*[7],	F_2 in N_2 and Ar, and
Mitchell[8],	F_2 in He and N_2.

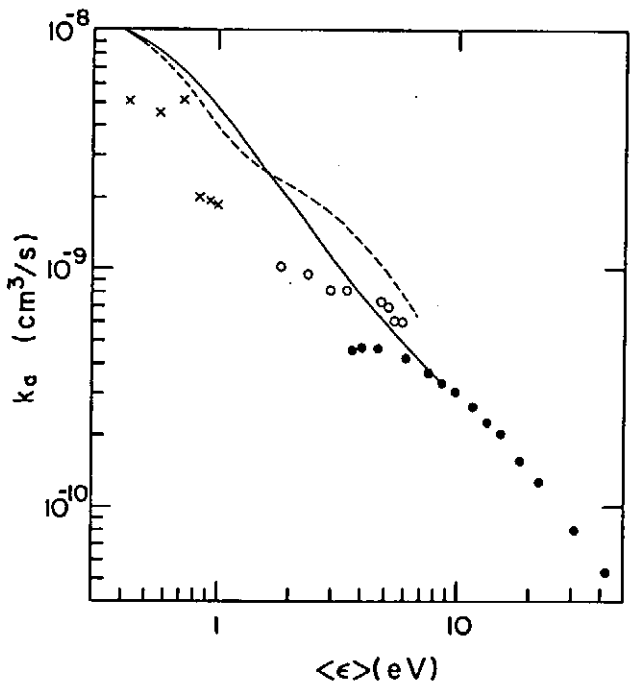

Fig. 1. Attachment rate coefficient k_a for F_2 as a function of electron mean energy. ● Values in pure F_2 calculated in the present work. ○ Experimental values obtained by Nygaard *et al.*[6] × Experimental values given by Chen *et al.*[3] ——, ---- Calculated values of Mitchell.[8]

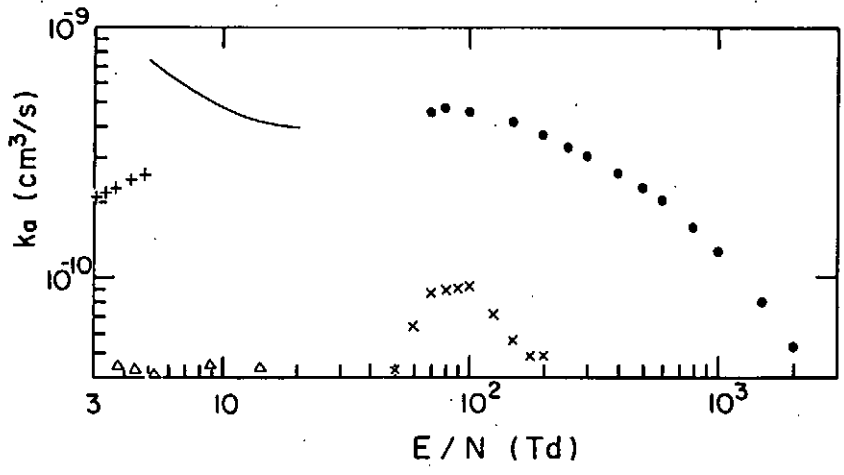

Fig. 2. Attachment rate coefficient k_a for F_2 as a function of E/N. ● Present calculated values. —— Nighan's experimental value. The symbols +, Δ and × are comparative experimental values for HCl: Christophorou *et al.*,[11] Sierra *et al.*[12] and Davies,[13] respectively.

These values have been summarized in a recent report.[9] Some examples of the values of k_a given in these references are also shown in Fig. 1 (k_a versus electron mean energy $<\varepsilon>$) for comparison.

Nighan has given the only experimental determination of k_a in dilute fluorine as a function of E/N[10]; the solid curve in Fig. 2 shows his results. Values of k_a for HCl measured by Christophorou *et al.*,[11] Sierra *et al.*[12] and Davies,[13] are also shown in Fig. 2 for comparison.

From these figures, it seems that the present calculated values of k_a are reasonable. We feel that some of the cross sections used in the present calculations are uncertain. In order to get more exact values of k_a, better experimental values of cross sections are needed.

Below $E/N=70$ Td, swarm parameters could not be calculated with our program code. It is of interest to determine whether or not electron swarms have equilibrium values of transport coefficients at low E/N in strong attaching gases.

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May We Measure the Exact Values of Electron Collision Cross Sections for Molecules by Beam and Swarm Experiments ?

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We cannot measure the exact values of DCS for molecules intrinsically. Of course, we can measure the approximate values of DCS for molecules, but can measure the exact values of DCS for atoms. The reason is very simple.

Target molecule M in both beam and swarm experiments consists of the mixture of different states :

$$M = M(g) + M(r_J) + M(v_1) + M_N$$

where $M(g)$, $M(r_J)$, $M(v_1)$ and M_N represent the completely ground state molecules, the rotationally excited molecules, the vibrationally excited molecules and the van der Waals clusters consisting of N molecules ($N \geqq 2$), respectively. Usually beam and swarm experiments are carried out at about 300 K. The concentration of $M(g)$ is small compared to $M(r_J)$ (except H_2 molecules) at 300 K. Then the molecule M is always mixture of $M(r_J)$ and $M(v_1)$, and the concentration of $M(r_J)$ and $M(v_1)$ changes with temperature. And electron collision cross section sets from elastic to inelastic collision processes for $M(r)$ and $M(v)$ are different each other. The target molecules M in the beam and swarm experiments are always mixtures of different molecules $M(r_J)$ and $M(v_1)$. In the case of H_2, the target gas consists of $M(g)$ and $M(r_J)$, especially $M(g)$ and $M(r_1)$ at 78 K.

Most clear change of cross sections of $M(r_J)$ and $M(v_1)$ will occur for triatomic molecules. CO_2, N_2O and so on. Triatomic molecules can change from linear to bend, or vice versa easily. The authors [1] have presented the different elastic momentum transfer cross sections q_{mr} and q_{mv} for $CO_2(r)$ and $CO_2(v)$, where they assumed that all other inelastic cross sections of $CO_2(r)$ and $CO_2(v)$ are practically the same. Then they have calculated the electron drift velocity W as a function of gas temperature T. When T increas, concentrations of $CO_2(v)$ increases, then W decreases with T at the same E/N, the electric field over the gas number density, around 50 Td.

We have a comment to the interesting and important paper of W. Johnstone, et al. [2]. They have measured the temperature dependence of elastic DCS for CO_2 at 4.0 eV. Unfortunitly, q_{mv} for $CO_2(v)$ at 4 eV is almost equal to q_{mr} for $CO_2(r)$ [1]. Then we propose the same experiments at about 3.4 eV for CO_2, because the temperature dependence of DCS seems to be very large there.

Winstead and McKoy [3] calculated the elastic DCS for $N_2O(g)$ at low electron energies and compare the experimental DCS data for $N_2O(r) + N_2O(v)$ mixture at 300 K. We can see large discrepancy between them at lower than about 10 eV. We urge Winstead and Mckoy to calculate the DCS

for N_2O(v) and also N_2O(r) for comparison. We can see the same discrepancy of DCS for CO_2 [4] [5] at low electron energies..

H_2 molecules have the famous long standing controversy in the vibrational excitation cross section [6]. A possible way to solve the problem may be as follows. At first, theoreticians calculate the q_{mg}, q_{mr}, q_{mv}, q_{rg}, q_{rr}, q_{rv}, q_{vg}, q_{vr}, and q_{vv} for H_2(g), H_2(r_1) and H_2(v_1), as a function of electron energies. Using these data, we calculate the electron swarm parameters. From beam experiments, we cannot determine the values of q_{mg}, q_{mr}, q_{rg}, q_{rr} for H_2(g) and H_2(r_1) at the same time. It is clear that the threshold energies of q_r and q_v for H_2(g) and H_2(r_1) are different. Bhattacharyya, et al. [7] have shown that elastic integral cross sections q_{tr} are larger than q_{tg} for 20 to 200 eV for H_2(g) and H_2(r_1). We want the elastic DCS values for H_2(g) and H_2(r_1) at low electron energies lower than 10 eV. Swarm experiments also carried out in the mixtures of H_2(g) and H_2(r_1), except for para-H_2(g) at 78 K (concentration of H_2(g) is 99.3 %). We compare the experimental and calculated swarm parameters at given conditions.

Usually, theoreticians calculate the DCS for M(g), not for M(r_J) and M(v_i), for most molecules. Theoretical studies involving the rotationally and vibrationally excited species are urgently required for many molecules. There is a interesting paper given by A. Jain [8].

If we have the cross section sets for excited inert gas clusters, we can calculate the electron swarm parameters of inert gases at high pressure and low temperature conditions. The concentration of the clusters for atoms and molecules are important at low temperature and high pressure conditions.

Most interesting temperature dependence occur for attachment cross sections q_a [9]-[13]. The values of non-dissociative q_{an} and dissociative q_{ad} are quite different for M(r) and M(v), and M(r) and M(v) have the definit and individual cross sections, independ on the temperature. Apparent temperature dependence of attachment cross section is caused through different concentration of the excited components M(r) and M(v) at different temperatures.

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Atoms (17)			Molecules (51)					
A + e,	A + hν		M + e,		M + hν,			
He 2	2170 *		2	H_2, D_2	2000		CH_4	780
Ne 10	1140 *			N_2	2240 ○			
Ar 18	1960 ○			O_2	1700		CF_4	390
Kr 36	1000			CO	1190		CCl_4	210
Xe 54	1180 ○			NO	880		CCl_2F_2	250
							CH_3Cl	90
Li 3	450			F_2	190 ○			
Na 11	800			Cl_2	360 ○		SiH_4	230
				Br_2	140 ○		SiF_4	140
K 19	370			I_2	240 ○		GeH_4	50
Rb 37	220							
Cs 55	370			HF	260	6	C_2H_4	370
				HCl	320		CH_3OH	350
O 8	390			HBr	200			
				HI	130	7	SF_6	920 ○
F 9	90							
Cl 17	130		3	CO_2	1240 ○			
						8	C_2H_6	260
Cu 29	180			H_2O	930		C_2F_6	150
Cd 48	210			H_2S	270		Si_2H_6	70
Ba 56	340			O_3	480			
				N_2O	450	9	C_3H_6	120
Hg 80	600			NO_2	300		C_2H_5OH	60
				SO_2	260			
				CS_2	260			
				OCS	280	11	C_3H_8	190
not final, but							C_3F_8	100
finished mostly			4	C_2H_2	390			
						12	C_4F_8	100
include electron				NH_3	500		C_6H_6	240
swarm papers				NF_3	110		C_6F_6	100
				BF_3	110			
include				BCl_3	90	60	C_{60}	300
review papers				PH_3	80			
				H_2CO	180		$M_r + M_v$	850

* He(Ne) + e only. Not include He(Ne) + hν papers.

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