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1996 J. Phys. B: At. Mol. Opt. Phys. 29 1841

(http://iopscience.iop.org/0953-4075/29/9/026)

J. Phys. B: At. Mol. Opt. Phys. **29** (1996) 1841–1848. Printed in the UK

Cross sections for the production of positive ions by electron impact on F_2

M V V S Rao† and S K Srivastava

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA

Received 22 January 1996

Abstract. First measurements on the ionization cross sections for the production of F_2^+ and ($F^+ + F_2^{2+}$) ions from F_2 by electron impact are reported for an electron impact energy range of threshold energies to 1 keV and for F^{2+} at 100 eV. These measurements were carried out in a crossed-beams apparatus using the pulsed technique and the partial pressure method to determine the absolute cross sections. Total ionization cross sections at each electron impact energy were obtained by numerical summation of the respective partial ionization cross sections.

1. Introduction

Recently, there has been a considerable interest in the electron impact ionization of molecular fluorine, largely for electron-beam energized rare gas fluoride excimer lasers (e.g. ArF and KrF) where the rate of consumption of F_2 to form upper molecular states for lasing transitions is required. In addition, the ionization cross sections and rate coefficients of halogens are of practical importance in the plasma processing techniques employed for the etching of semiconductors and metals in the microelectronics industry. Besides the use of fluorine in applied research, an understanding of electron collisions with F_2 is important from the point of view of fundamental physics because the atomic fluorine is known for its high electron affinity.

However, there are only two experimental reports on the total ionization cross sections of F_2 reported by Center and Mandl (1972) and Stevie and Vasile (1981). The dearth of data for halogen molecules is due to several serious difficulties associated with handling them. For instance, they react with the material of an apparatus and give rise to unwanted impurity products which can impair the cross section measurements. In order to circumvent such problems, a small amount of these gases are usually mixed with the noble gases for collision studies. As a result, an accurate determination of the percentage concentration of them in a gas-mixture becomes important when measuring the absolute cross sections. In section 2.2 we describe the partial pressure method used in the present measurements to estimate the F_2 concentration in a gas-mixture of He and F_2.

The two previous measurements (Center and Mandl 1972 and Stevie and Vasile 1981), which are confined to total ionization cross sections up to electron impact energies of 100 eV, differ considerably from each other. In addition, no previous cross section measurements have been reported for the formation of F^+ from F_2. In view of this, we have carried out

† Present address: Building 220/B344, Electrical Systems Group, Electronics and Electrical Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-0001, USA.

0953-4075/96/091841+08$19.50

the measurements of partial ionization cross sections for the production of F_2^+ and (F^+ + F_2^{2+}) ions from F_2 at electron impact energies ranging from the ionization threshold to 1 keV and for the F^{2+} ion at 100 eV.

2. Experimental procedure

2.1. Apparatus and measurements

A detailed description of the apparatus used in the present measurements has been given in previous publications by Krishankumar and Srivastava (1988) and Rao and Srivastava (1993). A schematic diagram of the experimental arrangement for electron-molecular crossed-beams collision geometry is shown in figure 1. Briefly, the main components are an electron-beam source, a pair of ion-extraction grids, a quadrupole mass spectrometer (QMS), a time-of-flight mass spectrometer (TOFMS) and a conventional ion-detection system. The QMS and the TOFMS, which are 180 degrees apart and have a mass resolution of better than 1 amu, are mounted perpendicular to both the electron and molecular beams as shown in figure 1. A well defined electron beam with an FWHM energy spread of $\sim$ 300 meV is achieved by a combination of electric and magnetic fields which are set along the electron-beam axis. The electron-beam energy is continuously variable from 0 to 1 keV ramp generated by a multi-channel analyser (MCA). A pair of ion-extraction grids, made of high transmission molybdenum wire mesh, are mounted parallel to each other and also to the axes of both electron and molecular beams. A pulsed electric field of about 100 V cm^{-1} is set up between the grids to ensure complete collection of the ions regardless of their kinetic energies.

In the present crossed-beams arrangement, the production and collection of ions was performed by a pulsed technique in which a pulse of the electron beam was followed by a pulse of ion-extraction field in succession at a preset repetition cycle. The frequencies of the two pulses were adjusted according to the desired ion count rates. A detailed description of the pulsing scheme has been given by Krishnakumar and Srivastava (1988). In this method a narrow pulse ($\sim$100–200 ns) of electron beam was made to collide with the molecular beam orthogonally. The ions produced in the interaction volume, which was defined by the intersection of electron and molecular beams, were extracted by a wider pulse ($\sim$10–50 μsec) applied to the ion-extraction grids. The extracted ions were then focused at the entrance aperture of a mass analyser. The voltages on the ion transporting lenses were adjusted in such a way that all ions were well focussed into the entrance cone of the channeltron of one of the mass spectrometers (QMS or TOFMS) depending on which one was pre-selected for the cross section measurements. In practice, we used both of them alternately to cross check the cross section values. Identification of ions was done either by the QMS in accordance to their mass–charge ratio or by the TOFMS with respect to their time-of-flight to the charged particle detector. The detected ion-signals were subsequently processed by a set of conventional electronic circuits and the yield of ions as a function of electron impact energy was stored in the MCA. Several scans were made to improve the signal to noise ratio in the data. The accumulated data were then transferred to an on-line computer for data analysis.

2.2. Determination of fluorine density in a gas mixture

Because fluorine is highly reactive, it requires special handling to avoid the formation of gas phase impurity products due to the reaction of fluorine with the walls of the gas line, the

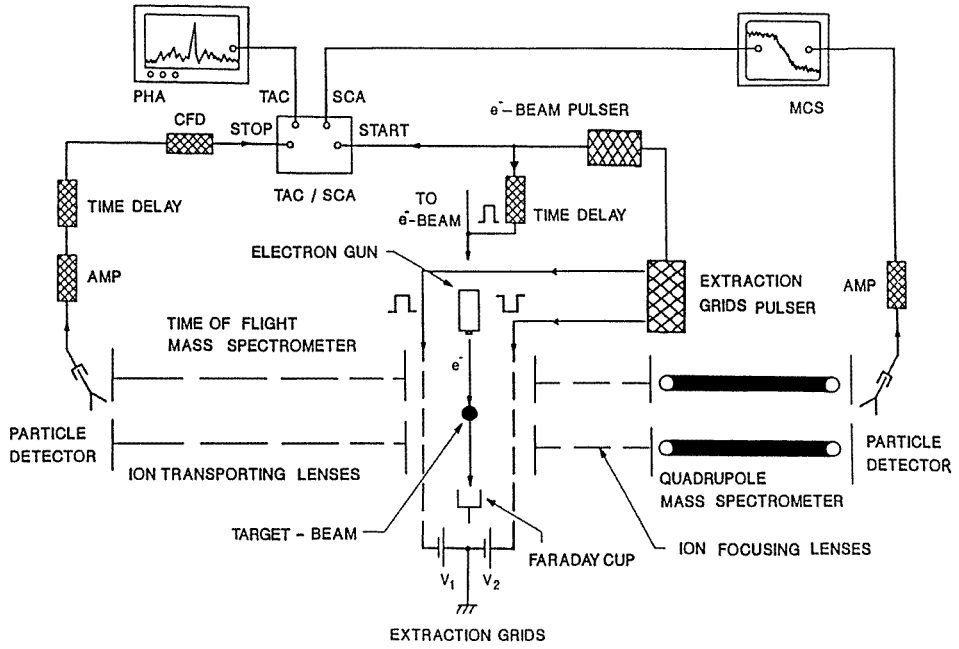

Figure 1. A schematic diagram of the experimental arrangement for crossed electron-molecular beams collision geometry.

vacuum chamber and the various components inside the chamber. Otherwise, this can lead to a loss of fluorine gas and an eventual rise of unwanted impurities in the interaction region during the experiment. In order to overcome this difficulty, inert gases are usually employed as buffer gases to the halogens. In the present measurements, a gas-mixture containing F_2 ($\sim$10%) and He ($\sim$90%) was used. The advantage of using He is that it is lighter than F_2 and He^+ does not interfere with the positions of singly-, doubly- and multiply-charged product ions of F_2 in the mass spectrum. However, the most probable impurity by-product contained in F_2 gas is HF. Fluorine gas contaminated with HF can give rise F^+ production by electron impact, which is undesirable in the present experiment. In order to remove the HF content from the gas mixture , the fluorine gas was passed through a commercially available HF-trap. Prior to admitting the fluorine into the collision region, the HF-trap was activated by heating it to about 300 °C for more than five hours and then purged several times with dry nitrogen gas to pump out the residual gases. By controlling the gas-flow with a variable leak valve, the gas mixture was slowly introduced into the interaction region through a capillary array. The necessary precautions, such as using stainless steel tubing for the gas line, viton and stainless steel gaskets in the joints, heating of the gas line to remove the water vapour etc, were taken to minimize the loss of fluorine during the measurements. However, due to the initial passivation there was an eventual loss of fluorine density in the interaction region. The loss was monitored by observing the $F_2{}^+$ signal over a longer period. The ion signal decreased initially but increased as time progressed and ultimately reached a constant value after a few hours. The mass spectrum of the gas mixture showed no sign of HF. After a steady state ion signal was attained, the percentage concentration of F_2 in the mixture (He + F_2) was determined carefully by the following procedure.

The pressure of the gas mixture behind the capillary array was measured as $P_1 = P_{\mathrm{He}} + P_{F_2}$ by a capacitance nanometer, where P_{He} and P_{F_2} are the partial pressures of He and F_2, respectively. The He^+ signal, $I_{\mathrm{He}}(E_0)$ and the $F_2{}^+$ signal, $I_{\mathrm{F}_2}(E_0)$, at an electron impact energy E_0 are related to their respective cross sections and pressures by the following equations:

$$I_{\mathrm{He}}(E_0) = \sigma_{\mathrm{He}}(E_0) K_{\mathrm{He}} P_{\mathrm{He}} I_e(E_0) \tag{1}$$

$$I_{\mathrm{F}_2}(E_0) = \sigma_{\mathrm{F}_2}(E_0) K_{\mathrm{F}_2} P_{\mathrm{F}_2} I_e(E_0) \tag{2}$$

where $\sigma_{\mathrm{He}}(E_0)$ and $\sigma_{\mathrm{F}_2}(E_0)$ are the respective ionization cross sections of He and F_2 at an electron impact energy E_0, K_{He} and K_{F_2} are the mass transmission efficiencies of the apparatus for He^+ and $F_2{}^+$, respectively and $I_e(E_0)$ is the incident electron beam current. After the $I_{\mathrm{He}}(E_0)$ and $I_{\mathrm{F}_2}(E_0)$ signals became steady, a small amount of He, of 99.999% purity, was added to the gas mixture behind the capillary array, through a seperate gas line. This increased the gas pressure behind the capillary array to $P_2 = (P_{\mathrm{He}} + P_{\mathrm{F}_2} + P'_{\mathrm{He}})$, where P'_{He} is the partial pressure of the newly introduced helium gas. During this process the $I_{\mathrm{F}_2}(E_0)$ remained the same but the $I_{\mathrm{He}}(E_0)$ signal increased in proportion to P'_{He} to a value of $I'_{\mathrm{He}}(E_0)$. $I'_{\mathrm{He}}(E_0)$ is related to various quantities through the following relation:

$$I'_{\mathrm{He}}(E_0) = \sigma_{\mathrm{He}}(E_0) K_{\mathrm{He}} (P_{\mathrm{He}} + P'_{\mathrm{He}}) I_e(E_0). \tag{3}$$

From the ratio of equations (1) and (3), the partial pressure of He in the gas mixture was obtained:

$$P_{\mathrm{He}} = \frac{P'_{\mathrm{He}}}{\left(I'_{\mathrm{He}}(E_0)/I_{\mathrm{He}}(E_0)\right) - 1} \tag{4}$$

where $P'_{\mathrm{He}} = P_2 - P_1$. Since $P_{\mathrm{F}_2} = P_2 - P_{\mathrm{He}} - P'_{\mathrm{He}}$, a substitution of experimentally determined values for P_2, P_{He} and P'_{He} yields the value of P_{F_2}. The self-consistency of this procedure was checked by varying the pressures of pure He and the gas mixture. We estimate that the partial pressures for the two gases in the mixture calculated by this method is accurate to within 5%.

2.3. Normalization procedure

Since the shape of the ionization efficiency curve of He to He^+ for electron impact energies from its threshold to 1 keV is well known (Krishnakumar and Srivastava (1988) and references therein), the He^+ signal from He in the gas mixture used in the present experiment was recorded to observe any possible variations in its shape due to fluctuations in the electron-beam current and in the overlap of electron beam and gas mixture stream as a function of electron impact energy. The recorded curve of He^+ was corrected with its known curve at all electron impact energies. The correction factors obtained from this method at various electron impact energies were in turn used in correcting the measured shapes of the ionization efficiency curves for $F_2{}^+$ and (F^+ + $F_2{}^{2+}$) ions under the same experimental conditions. The absolute values of ionization cross sections for the production of $F_2{}^+$, (F^+ + $F_2{}^{2+}$) and F^{2+} from F_2 by electron impact at E_0=100 eV, at which the electron impact energy dependence of the cross section is weak and only a small error would then be expected from the uncertainty in the electron-beam energy, have been obtained by normalizing their measured relative values to the known absolute cross sections of noble gases (Krishnakumar and Srivastava 1988) at the same electron energy as

$$\sigma_{\mathrm{F}}(E_0) = \sigma_{\mathrm{S}}(E_0) \frac{I_{\mathrm{F}}(E_0)}{I_{\mathrm{S}}(E_0)} \frac{K_{\mathrm{S}}}{K_{\mathrm{F}}} \frac{P_{\mathrm{S}}}{P_{\mathrm{F}}}. \tag{5}$$

The subscripts 'S' and 'F' in the above equation represent standard gas (e.g. He, Ne or Ar) and F_2^+, ($F^+ + F_2^{2+}$) or F^{2+} of F_2, respectively. The mass transmission efficiency of the apparatus, K, was determined for F_2^+, ($F^+ + F_2^{2+}$) and F^{2+} using the well known ionization cross sections for singly- and doubly-charged ions of noble gases (He, Ne, Ar, Kr and Xe). With respect to the absolute cross sections obtained at 100 eV from the above equation for ${F_2}^+$ or ($F^+ + {F_2}^{2+}$), the rest of their relative values, except for F^{2+}, were scaled to absolute cross sections for energies from thresholds to 1 keV. The determined cross section value for F^{2+} at 100 eV of 5.9×10^{-21} cm^2 is three orders of magnitude smaller than those for F_2^+ and ($F^+ + F_2^{2+}$) ions (see table 1). The F^{2+} ion intensity was very weak, therefore no attempt was made to record its intensity for the entire electron impact energy range. In order to reduce the possible error in the normalization procedure due to mass transmission efficiency of the apparatus, the ionization cross sections for noble gases, whose masses are nearer to their respective product ions of F_2, were chosen. In other words, the cross sections of Ar^+, Ne^+ and He^+ for F_2^+, ($F^+ + {F_2}^{2+}$) and F^{2+}, respectively, were used in equation (5) for normalization. Since F^+ and ${F_2}^{2+}$ are indistinguishable by mass spectroscopy, no serious efforts were made to estimate the contribution of each one to the combined, ($F^+ + {F_2}^{2+}$), cross section value.

2.4. Total ionization cross sections

The total ionization cross sections were deduced at each electron impact energy, E_0, by summation of the respective partial ionization cross sections, $\sigma_1(E_0)$ for F_2^+ and $\sigma_2(E_0)$ for ($F^+ + F_2^{2+}$), by the relation

$$\sigma_T(E_i) = \sigma_1(E_i) + \sigma_2(E_i) \tag{6}$$

where i varies from ionization energy thresholds to 1 keV. The contribution of F^{2+} and any other multiply-ionized species was ignored when obtaining the values of $\sigma_T(E_i)$ as their contribution was found to be much less than the estimated error in our measurements of σ_1 and σ_2. The cross section values at several electron impact energies for partial and total ionization are given in table 1.

2.5. Error analysis

The possible errors in the present cross section values are discussed in the following:

(i) The variation in the measured relative shape of the ionization efficiency curve over the entire electron impact energy range was about 5%.
(ii) The statistical fluctuation in the ion count rate was minimized to as little as 2% using the averaging techniques with an improved signal-to-noise ratio.
(iii) Observed change in the target gas pressure behind the capillary array during the experiment was less than 2%.
(iv) The estimated error in determining the percentage concentration of F_2 in the gas mixture was less than 5%.
(v) The uncertainty in the cross sections of noble gases employed in the normalization procedure was 10%.
(vi) Finally, the error associated with the mass transmission efficiency of the apparatus was less than 8%.

Thus, the total uncertainty in each value of the absolute cross section as measured by us is obtained by combining the systematic and statistical errors in quadrature. The resulting error in the present cross section values is estimated to be within $\pm 15\%$.

Table 1. Partial and total ionization cross sections of F_2 by electron impact (in units of 10^{-18} cm^2).

Energy E_0 (eV)	F_2^+	$F^+ + F_2^{2+}$	F_2 (total)
20	4.31	0.39	4.70
25	9.58	1.41	10.99
30	17.28	3.32	20.60
35	27.14	4.64	31.77
40	40.15	6.01	46.16
45	55.63	7.52	63.15
50	65.52	8.70	74.22
55	73.81	9.74	83.55
60	79.31	10.68	89.99
65	81.52	11.55	93.07
70	82.66	12.37	95.03
75	83.58	12.89	96.47
80	84.08	13.24	97.32
85	84.60	13.50	98.10
90	84.88	13.66	98.55
95	85.06	13.83	98.89
100	84.90	13.99	98.89
105	84.82	14.06	98.88
110	84.55	14.13	98.69
115	84.13	14.21	98.35
120	83.68	14.25	97.93
125	83.05	14.29	97.34
150	80.29	14.31	94.60
175	77.58	14.00	91.58
200	74.53	13.62	88.15
250	68.53	12.83	81.36
300	62.85	12.07	74.92
400	53.14	10.61	63.75
500	45.25	9.23	54.48
600	39.57	8.27	47.84
700	35.38	7.45	42.83
800	32.08	6.85	38.93
900	29.37	6.40	35.77
1000	27.23	6.05	33.28

3. Results and discussion

The ionization thresholds for $F_2{}^+$ and F^+ have been determined by calibrating the electron-beam energy with the accurately known ionization potentials (IP) of He (24.587 eV), Ne (21.565 eV) and Ar (15.760 eV). The IP for F_2^+ production and the appearance potential (AP) for F^+ production were 15.7 eV and 15.5 eV, respectively, with an accuracy of better than 0.25 eV. It is clear from these results that the F^+ ions are generated at a lower energy than $F_2{}^+$ ions. This is due to the fact that F^+ at 15.5 eV is produced by the process of polar dissociation (Dibler *et al* 1969 and Berkowitz *et al* 1971) i.e. $F_2 \rightarrow F^+ + F^-$, through repulsive states lying below the ionization continuum of F_2^+. This has also been confirmed from the measurements made in our laboratory in an experiment to produce negative ions from F_2 by electron impact (Rao and Srivastava 1993). The onset for negative ion continuum of polar dissociation (ion-pair formation) was observed to be 15.6 eV which agrees well with the measured AP for F^+ (15.5 eV). Although the onsets of $F_2{}^+$ and F^+ lie within the

uncertainty in the electron-beam energy, it was consistently observed that the appearance of F^+ was earlier than $F_2{}^+$. We have not made any attempts to determine AP for F_2^{2+} and F^{2+} and have assumed that the contribution of $F_2{}^{2+}$ to the F^+ ion would start at an electron impact energy higher than 15.5 eV.

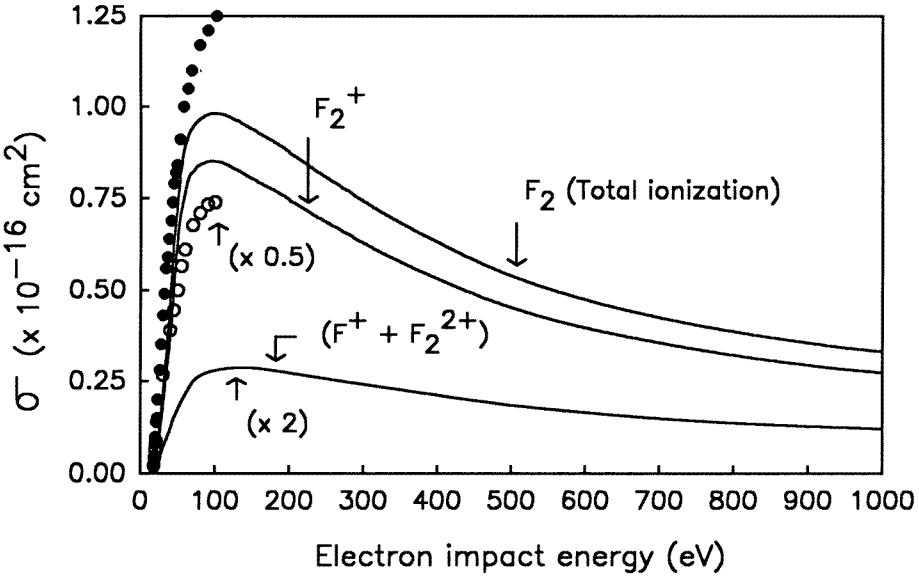

Figure 2. The total and partial ionization cross sections of F_2 as a function of electron impact energy. Solid lines represent our results; open circles, total ionization cross sections by Center and Mandle (1972); filled circles, total ionization cross sections by Stevie and Vasile (1981).

The cross section values as a function of electron impact energy for total ionization are shown in figure 2. We compare our total ionization cross sections with the earlier data reported by Center and Mandl (1972) and Stevie and Vasile (1981). In figure 2 the data of Center and Mandl (1972) (open circles; multiplied by a factor of 0.5) and Stevie and Vasile (1981) (filled circles) are shown along with the present results. The cross section value at 100 eV reported by Center and Mandle (1972) of 1.5×10^{-16} cm^2 is larger than the present value of 1.0×10^{-16} cm^2. Whereas the cross section value of 1.25×10^{-16} cm^2 at the same electron impact energy as measured by Stevie and Vasile (1981) lies between the two. The disagreement among various results could be due to different methods employed for the determination of absolute cross sections. For instance, Center and Mandle (1972) used a commercial gas analyser incorporating a quadrupole mass filter and an electron gun with an unknown energy spread and energy uncertainty of several volts. Moreover, they made the measurements with target gas presures as high as 1 Torr and high electron-beam currents, for which one would expect possible multiple collisions giving rise to a high ion-signal. In the case of Stevie and Vasile (1981), the total ionization cross sections were measured using a magnetic mass spectrometer in a crossed-beams apparatus in which the electron-beam currents are of the order of 100 μA or so and using a modulated molecular-beam at gas presures more than 2 Torr. Moreover, both groups did not follow any method for determing the concentration of F_2 accurately in the Ar-F_2 gas mixture used in their measurements. Besides this, the higher gas pressures and electron-beam currents could be one of the reasons for their higher cross sections. In comparison, we have carried out our

measurements using gas pressures of as low as 0.2–0.3 Torr behind the capillary array and electron-beam currents of 5–10 nA to make sure that only single collsions could occur.

The cross section data for the production of F_2^+ and ($F^+ + F_2^{2+}$) are also shown in figure 2. In the absence of any previous theoretical and experimental results no comparison can be made.

In summary, the first partial ionization cross sections for electron impact on F_2 are reported at electron impact energies from ionization thresholds to 1 keV. Although relative shapes of the ionization cross section curves of present and previous data are in reasonably good agreement with each other up to electron impact energies of 100 eV, the absolute values of ionization cross sections differ considerably at all electron impact energies.

Acknowledgments

This research was sponsored by NASA, Wright Research Laboratories and Los Alamos Scientific Laboratory. MVVS would like to thank the National Research Council of the USA for an associateship.

References

Berkowitz J, Chupka W A, Guyon P M, Holloway J and Spohr R 1971 *J. Chem. Phys.* **54** 5165
Center R E and Mandl A 1972 *J. Chem. Phys.* **57** 4104
Dibeler V H, Walker J A and McCulloh K E 1969 *J. Chem. Phys.* **50** 4592
——1969 *J. Chem. Phys.* **51** 4230
Krishnakumar E and Srivastava S K 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 1055
Rao M V V S and Srivastava S K 1993a *J. Geophys. Res.* **97**/**E7** 13137
——1993b *XVIII Int. Conf. on the Physics of Electronic and Atomic Collisions (ICPEAC)* ed T Anderson, B Fastrup, F Folkmann and H Knudsen (Aärhus: Aärhus University Press) p 294
Stevie F A and Vasile M J 1981 *J. Chem. Phys.* **74** 5106