Electron–bromine-molecule total ionisation and electron attachment cross sections†

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Abstract. Cross sections for absolute total ionisation between 10 and 100 eV, dissociative attachment between 0 and 10 eV, and negative ion-pair formation between 10 and 40 eV of the bromine molecule have been measured by electron collisions using a parallel-plate type interaction chamber. The maximum of the ionisation curve was found to be at 83 eV with a peak value of 10.25×10^{-20} m^2. Six dissociative attachment processes peaking at 0.00, 0.50, 1.45, 3.75, 5.30 and 8.50 eV with cross sections of 17.7, 1.50, 2.80, 4.94, 0.42 and 0.325 units of 10^{-22} m^2, respectively, were detected. Negative ion formation cross sections with a maximum at 18.0 eV and a value of 5.26×10^{-22} m^2 were measured. The relative error, except for the first attachment maximum close to the zero electron energy, is ± 0.05.

1. Introduction

In this paper we present an electron beam study of ionisation, ion-pair formation and dissociative attachment study of the bromine molecule. This is a continuation of our efforts to measure total absolute cross sections for electron–molecule collisions with the production of charged particles.

The knowledge of cross sections for ionisation and electron attachment processes in bromine contribute to the better understanding of energy dissipation mechanisms in some types of lasers. Donovan *et al* (1970), Petersen *et al* (1975, 1976) and Petersen and Smith (1978) have studied electronic to vibrational transfer lasers with bromine molecules and some bromine-atom containing molecules added to other gases. In these lasers besides the Br* ($^2P_{1/2}$) atoms formed by photodissociation of the bromine molecule, other species are also formed influencing the resulting laser action.

Data of this sort are also needed for the explanation of gas discharges involving bromine molecules, such as flowing afterglows, Townsend discharges, proportional and Geiger–Müller counters etc.

There have been three attempts so far to study the bromine molecule by electron impact. They have a common factor in that a mass spectrometer was used for the analysis of the ions formed. The advantage of a mass spectrometer is that it can yield more information on processes leading to the formation of a particular ion species, while its main disadvantage is that it cannot give accurate cross section values except after extremely careful calibration.

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Blewett (1936) was mainly interested in the isotope abundances and the determination of their masses. Nevertheless, he was able to give some values for threshold energies, both of positive and negative ions, and he obtained relative ion intensities against electron energy.

Frost and McDowell (1960) were interested in the threshold energy determination and relative ion currents against electron energy measurements. They studied in detail the curves for Br_2^+, Br^+ and Br^- ions and tried to obtain threshold energies for ionisation, ion-pair formation and electron attachment.

Tam and Wong (1978) focused their attention on the electron attachment processes for comparison with the behaviour of other halogen molecules, and on the determination of positions and relative intensities of dissociative attachment maxima.

None of these authors measured cross sections, for ionisation, ion-pair formation or electron attachment.

2. Experimental procedure

Full details of the apparatus used in this experiment are given elsewhere (Kurepa *et al* 1974), so only a brief description will be presented here, with hints to the changes introduced.

For the absolute cross section determination the equation

$$\sigma = \frac{I_i}{I_e} \frac{1}{nL}$$

was used, where I_i is the total positive or negative current formed by the passage of the electron beam of current I_e along a collector electrode of length L, inside the target-gas atmosphere of particle density n $(=p/kT)$.

The interaction chamber in our experiment was a parallel-plate condensor system introduced by Smith (1930) and Tate and Smith (1932) and used thereafter by many authors. The electron beam from an electron gun was energy selected by a trochoidal electron monochromator (Stamatović and Schulz 1968). In the present measurements the electron beam half width was 150 meV and its intensity was in the range of $0 \cdot 1$ μA.

The target-gas atmosphere at a pressure in the range from 10^{-3} to 10^{-1} Pa was measured by a capacitance manometer (Baratron type) with an error of $\pm 2\%$. The gas was introduced through a leak valve from a gas handling system and it flowed towards the pumping system so that an equilibrium pressure was maintained in the interaction chamber region.

3. Experimental results

With the parallel-plate type interaction chamber it is not possible to distinguish and measure separately the various ionic species formed in electron–molecule collisions. The measurements were done by separately collecting all positive or negative ions formed along the electron beam path.

The collection of positive ions gives absolute values for the total ionisation cross section. Positive ions can be formed in a great number of processes, the most important being molecular ionisation

$$e + Br_2 \rightarrow Br_2^+ + e + e$$
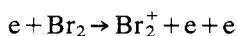
dissociative ionisation

$$e + Br_2 \rightarrow Br^+ + Br + e + e$$

and ion-pair formation

$$e + Br \rightarrow Br^+ + Br^- + e.$$
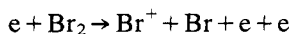
All other processes with the molecular ion, atom or ion in excited states are possible as well and contribute to the total positive ion signal.

Negative ions can be formed in processes of dissociative attachment
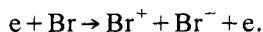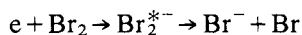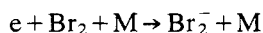
$$e + Br_2 \rightarrow Br_2^{*-} \rightarrow Br^- + Br$$

electron attachment in the three-body collisions

$$e + Br_2 + M \rightarrow Br_2^- + M$$

and ion-pair formation. The electron attachment is unlikely to occur under binary electron–molecule collision conditions. Thus, the collection of negative ions gives the cross section for total negative ion formation. Since the ion-pair formation process starts at electron energies higher than the lowest positive ion threshold energy, the negative ions collected for electron energies lower than that give a dissociative attachment cross section only.

3.1. Total ionisation

Total ionisation cross sections were measured in the energy interval between 10 and 100 eV. The energy scale was calibrated within 0·05 eV by linear extrapolation of the cross section curve to the $10·51 \pm 0·01$ eV value for the Br_2^- ion threshold energy obtained by photoionisation by Cornford *et al* (1971) and Watanabe (1957).

Although the cross section curve in the range of a few eV above the threshold shows breaks, we avoided analysing them because the linear extrapolation method cannot give reliable results for higher ionisation potentials. This type of determination was done by Frost and McDowell (1960) for Br_2^+ and Br^+ ions with a mass spectrometer analysis following electron collision with molecules. Cornford *et al* (1971) investigated photo-electron spectra and determined the lowest and higher ionisation potentials for the formation of the Br_2^+ ion and derived the spin–orbit splitting of the $^2\Pi_g$ and $^2\Pi_u$ molecular ion states.

For a more complete knowledge of processes leading to the formation of Br_2^+ and Br^+ ions further experiments are needed, the photoelectron mass spectrometer coincidence technique being the most appropriate.

The numerical values of the measured cross sections are listed in table 1. We are not aware of any other measurements of either total or partial ionisation cross sections of the bromine molecule by electron impact with which the present results could be compared.

3.2. Dissociative attachment

At energies lower than 10 eV only dissociative attachment processes lead to the formation of negative ions. The measured cross section curve is presented in figure 1. The energy scale was calibrated within 0·05 eV of the threshold energy of negative ions for the ion-pair formation process at 10·41 eV. This value was obtained using 11·80 eV

Table 1. Total ionisation cross section of the bromine molecule. Units of $10^{-20}\,\text{m}^2$. Relative error 0·05.

Electron energy (eV)	Cross section	Electron energy (eV)	Cross section	Electron energy (eV)	Cross section
10·6	0·04				
10·8	0·10				
11·0	0·20	17·0	2·99	40	8·17
11·2	0·30	17·2	3·07	42	8·35
11·4	0·40	17·4	3·20	44	8·56
11·6	0·47	17·6	3·27	46	8·71
11·8	0·57	17·8	3·37	48	8·84
12·0	0·67	18·0	3·44	50	8·97
12·2	0·74	18·2	3·54	52	9·17
12·4	0·84	18·4	3·61	54	9·33
12·6	0·94	18·6	3·71	56	9·46
12·8	1·04	18·8	3·77	58	9·69
13·0	1·11	19·0	3·84	60	9·84
13·2	1·21	19·2	3·94	62	9·94
13·4	1·34	19·4	4·01	64	10·05
13·6	1·41	19·6	4·04	66	10·12
13·8	1·48	19·8	4·16	68	10·20
14·0	1·61	20	4·21	70	10·22
14·2	1·68	21	4·54	72	10·23
14·4	1·81	22	4·87	74	10·24
14·6	1·92	23	5·16	76	10·24
14·8	2·02	24	5·43	78	10·25
15·0	2·08	25	5·73	80	10·25
15·2	2·19	26	5·96	82	10·25
15·4	2·32	27	6·20	84	10·24
15·6	2·38	28	6·37	86	10·29
15·8	2·49	29	6·57	88	10·29
16·0	2·59	30	6·74	90	10·20
16·2	2·66	32	7·18	92	10·23
16·4	2·76	34	7·48	94	10·21
16·6	2·83	36	7·74	96	10·22
16·8	2·90	38	7·99	98	10·17
				100	10·21

for the ionisation potential (Herzberg 1944) and 3·36 eV for the electron affinity (Berry and Reiman 1963) of the bromine atom, as well as 1·97 eV for the dissociation energy of the bromine molecule (Pritchard and Skinner 1955).

The attachment cross section curve shows four prominent maxima as already reported by Babić *et al* (1980). Nevertheless, detailed deconvolution of this experimental curve led us to the conclusion that altogether six attachment processes contribute to its formation, i.e. the following states of the intermediate excited Br_2^- molecular ion

$$^2\Sigma_u^+,\ ^2\Pi_{g3/2},\ ^2\Pi_{g1/2},\ ^2\Pi_{u3/2},\ ^2\Pi_{u1/2},\ ^2\Sigma_g^+.$$
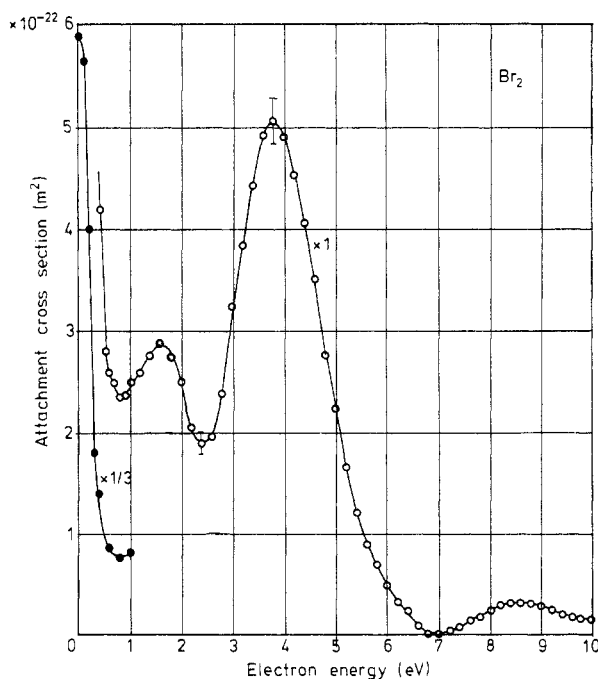
Figure 1. Total electron attachment cross section of the bromine molecule in the enegy range between 0 and 10 eV.

In our view, the first maximum at zero electron energy is due to two processes in which the electron is attached to the molecule and forms the $^2\Sigma_u^+$ ground and the $^2\Pi_{g3/2}$ excited state of the Br_2^- molecular ion. The existence of the attachment at a near zero electron energy was discovered by Frost and McDowell (1960) and confirmed by Tam and Wong (1978). In both these experiments the mass spectometer analysis shows that Br^- ions are formed in the attachement process. It is important to stress this point here, since at low electron energies a collection of electrons can occur in experiments without mass analysis such as ours.
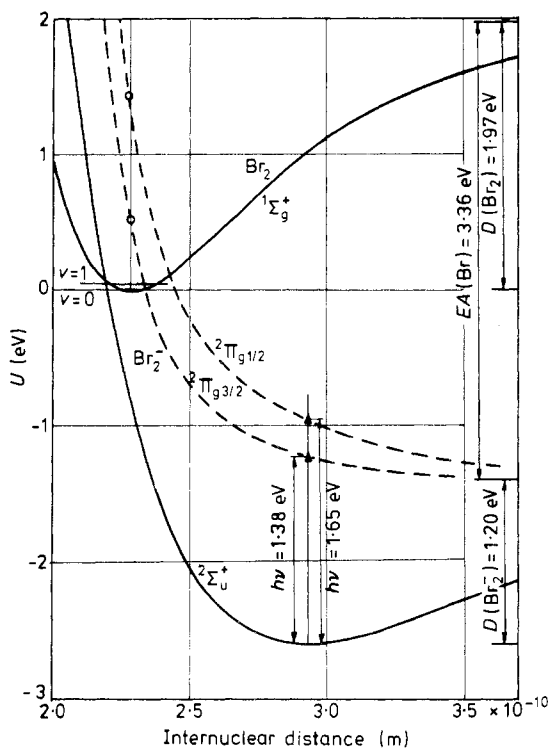
The cross section value at zero electron energy is only a factor of three higher than for the process peaking at 7·75 eV, and more than one order of magnitude smaller than the corresponding zero energy cross sections in fluorine (P Chantry 1978, private communication) and chlorine (Kurepa and Belić 1978). That the cross section for the low-energy attachment process in bromine is much smaller than in chlorine was suggested by Sides *et al* (1976) on the basis of data obtained in flowing afterglow experiments. Their values for the attachment rate coefficients at 350 K are $3·7 \times 10^{-9}$ in chlorine and $1·0 \times 10^{-11}$ in bromine (in units of $cm^3 \, mol^{-1} \, s^{-1}$).

This small attachment cross section value at zero electron energy indicates that the formation of the ground $^2\Sigma_u^+$ state of the Br_2^- ion does not start from the bromine molecule ground vibrational state ($v = 0$) of the ground electronic state $^1\Sigma_g^+$, as is the case in fluorine and chlorine. In order to corroborate this proposition we have constructed the Br_2 ground state, $^1\Sigma_g^+$, and the Br_2^- ground state, $^2\Sigma_u^+$, potential curves using the Morse equation and the parameters listed in table 2 (Herzberg 1950).

The position and crossing of these curves are shown in figure 2. They cross at an interatomic distance outside the Franck–Condon region of the Br_2 molecule, toward

Table 2. Molecular parameters used for constructing ground-state potential curves.

	Units	Br_2 value	Br_2^- value
D_e	(eV)	1·771	1·20
R_e	$\times 10^{-8}$ cm	2·28	2·90
ω_e	$\times 10^4$ cm^{-1}	3·232	1·60
μ_A		39·958	39·958
	$EA(\mathrm{Br}) = 3 \cdot 363$ eV		

Figure 2. Details of the bromine molecule ground state, $^1\Sigma_g^+$, and the Br_2^- ion ground, $^2\Sigma_u^+$, and excited, $^2\Pi_{g3/2}$, state potential curves.

lower R values. This supports the suggestion that the attachment to the vibrational ground state ($v = 0$) of the bromine $^1\Sigma_g^+$ molecular electronic state cannot lead to the zero-energy attachment process. The first vibrationally excited state ($v = 1$) of the bromine $^1\Sigma_g^+$ ground electronic state could, on the other hand, be responsible for this attachment process since the two potential curves cross at an interatomic distance value where the probability distribution density is still appreciable. With the position of the potential curves known, we calculated the possible partial attachment process curve shapes fitting them to the measured cross section values.

In figure 2 we have also shown the possible position of the $^2\Pi_{g3/2}$ state potential curve for the Br_2^- molecular ion. This position was located on the basis of two sources of information. Firstly, Delbecq *et al* (1961) have measured the absorption of light to the Br_2^- ground state, $^2\Sigma_u^+$, imbedded in a KBr crystal. Secondly, the difference of the measured attachment curve to the Br_2 and the partial attachment due to the $^1\Sigma_g^+$, $v = 1$ state, as interpreted by the fitting procedure, gave a curve peaking at 0·50 eV. Its shape closely follows a Gaussian distribution, indicating that the attachment to the ground state $^1\Sigma_g^+$, $v = 0$ of the Br_2 molecule occurs.

The process peaking at 1·45 eV has been assigned to the attachment to the bromine $^1\Sigma_g^+$ ground state with the formation of the $^2\Pi_{g1/2}$ state of the molecular ion. This again is in good agreement with the light absorption data of Delbecq *et al* (1961). They have clearly distinguished the two substates of the $^2\Pi_g$. The spin–orbit splitting in the light absorption experiment at the equilibrium interatomic distance of the Br_2^- $^2\Sigma_u^+$ ground state is 0·27 eV, and it is to be expected that it could be detected as a separate maximum in the attachment process, too. This process was measured by Tam and Wong (1978) with the peak at 1·40 eV.

We assign the process peaking at 3·75 eV to the formation of the $^2\Pi_{u3/2}$ state of the Br_2^- molecular ion. Tam and Wong (1978) have detected it, too, with the peak at 3·70 eV electron energy. The reason for attributing this process to the $^2\Pi_{u3/2}$ substate is that when fitting the measured values with a Gaussian distribution, the difference gives a maximum at an energy of 5·30 eV, possibly due to the formation of the $^2\Pi_{u1/2}$ substate.

Table 3. Attachment curve peak positions.

Authors	$^2\Sigma_u^+$	$^2\Pi_{g3/2}$	$^2\Pi_{g1/2}$	$^2\Pi_{u3/2}$	$^2\Pi_{u1/2}$	$^2\Sigma_g^+$
Blewett (1936)	—	—	—	2·80	—	—
Frost and McDowell (1960)	0·03	—	—	—	—	—
Tam and Wong (1978)	0·07	—	1·40	3·70	—	—
Present results (±0·05)	0·00	0·50	1·45	3·75	5·30	8·50

Table 4. Total and partial dissociative attachment cross sections of the bromine molecule. Units of 10^{-22} m^2. Relative error 0·05.

Electron energy (eV)	Total	Partial					
		$^2\Sigma_u^+$	$^2\Pi_{g3/2}$	$^2\Pi_{g1/2}$	$^2\Pi_{u3/2}$	$^2\Pi_{u1/2}$	$^2\Sigma_g^+$
0·0	17·74	17·50	0·254	0·039	—	—	—
0·1	17·00	14·55	—	—	—	—	—
0·2	12·0	9·55	0·89	0·128	—	—	—
0·3	5·40	4·95	—	—	—	—	—
0·4	4·20	2·74	1·25	0·313	—	—	—
0·5	2·80	1·33	—	—	—	—	—
0·6	2·60	0·51	1·50	0·593	—	—	—
0·7	2·50	0·25	—	—	—	—	—
0·8	2·35	—	1·23	1·02	—	—	—
0·9	2·38	—	—	—	—	—	—

Table 4. (continued)

Electron energy (eV)	Total	Partial					
		$^2\Sigma_u^+$	$^2\Pi_{g3/2}$	$^2\Pi_{g1/2}$	$^2\Pi_{u3/2}$	$^2\Pi_{u1/2}$	$^2\Sigma_g^+$
1·0	2·50	—	0.69	1·64	0.0034	—	—
1·2	2·60	—	0.254	2·25	0.025	—	—
1·4	2·78	—	0.064	2·69	0.051	—	—
1·6	2·90	—	0.011	2·80	0.099	—	—
1·8	2·75	—	—	2·51	0.206	—	—
2·0	2·50	—	—	1·95	0.372	—	—
2·2	2·05	—	—	1·32	0.629	—	—
2·4	1·90	—	—	0·794	1·00	—	—
2·6	1·95	—	—	0·400	1·52	—	—
2·8	2·42	—	—	0·202	2·16	—	—
3·0	3·23	—	—	0·0684	2·86	—	—
3·2	3·84	—	—	0·0256	3·59	—	—
3·4	4·43	—	—	0·0057	4·24	—	—
3·6	4·93	—	—	—	4·72	—	—
3·8	5·05	—	—	—	4·94	—	—
4·0	4·90	—	—	—	4·86	0·019	—
4·2	4·53	—	—	—	4·52	0·041	—
4·4	4·04	—	—	—	3·93	0·088	—
4·6	3·50	—	—	—	3·24	0·156	—
4·8	2·76	—	—	—	2·50	0·240	—
5·0	2·23	—	—	—	1·81	0·327	—
5·2	1·65	—	—	—	1·26	0·396	—
5·4	1·22	—	—	—	0·808	0·420	—
5·6	0·89	—	—	—	0·491	0·396	—
5·8	0·70	—	—	—	0·277	0·327	—
6·0	0·49	—	—	—	0·150	0·240	—
6·2	0·34	—	—	—	0·076	0·156	—
6·4	0·255	—	—	—	0·036	0·088	—
6·6	0·08	—	—	—	0·016	0·041	—
6·8	0·025	—	—	—	0·006	0·0196	—
7·0	0·038	—	—	—	0·002	—	0·043
7·2	0·072	—	—	—	—	—	0·070
7·4	0·108	—	—	—	—	—	0·105
7·6	0·152	—	—	—	—	—	0·147
7·8	0·196	—	—	—	—	—	0·197
8·0	0·250	—	—	—	—	—	0·245
8·2	0·300	—	—	—	—	—	0·286
8·4	0·320	—	—	—	—	—	0·314
8·6	0·330	—	—	—	—	—	0·325
8·8	0·320	—	—	—	—	—	0·314
9·0	0·280	—	—	—	—	—	0·286
9·2	0·250	—	—	—	—	—	0·245
9·4	0·200	—	—	—	—	—	0·197
9·6	0·190	—	—	—	—	—	0·147
9·8	0·180	—	—	—	—	—	0·105
10·0	0·180	—	—	—	—	—	0·070

And finally, the last peak in our measured curve is at an electron energy of 8·50 eV. To our knowledge, it has not previously been observed and we assign it to the formation of the $^2\Sigma_g^+$ excited state of the Br_2^- molecular ion.

All detected attachment processes are compared with existing data in table 3.

The total attachment cross section values at 0·2 eV energy intervals are listed in table 4, as well as the partial attachment cross sections as calculated by a deconvolution procedure of the experimentally measured values. The cross section values at energies lower than 0·3 eV could have a relative error as high as 0·5, decreasing with electron energy, and reaching a relative error value of 0·05 already at 1·0 eV.

3.3. Ion-pair formation

Cross sections for ion-pair formation are listed in table 5. They were measured by collecting negative ions in the electron energy range between 10 and 40 eV. The energy scale was calibrated by linear extrapolation of the measured cross section curve above the threshold to the value of 10·41 eV.

Table 5. Negative ion formation cross sections. Units of 10^{-22} m^2. Relative error 0·05.

Electron energy (eV)	Cross section	Electron energy (eV)	Cross section
		15·5	4·50
		16·0	4·70
		16·5	4·90
10·6	0·21	17·0	5·07
10·8	0·42	17·5	5·21
11·0	0·62	18·0	5·26
11·2	0·81	18·5	5·25
11·4	0·98	19·0	5·25
11·6	1·22	19·5	5·17
11·8	1·44	20	5·12
12·0	1·67	22	4·79
12·2	1·92	24	4·50
12·4	2·16	26	4·27
12·6	2·41	28	4·10
12·8	2·66	30	3·88
13·0	2·89	32	3·71
13·5	3·41	34	3·55
14·0	3·82	36	3·48
14·5	4·08	38	3·43
15·0	4·34	40	3·44

References

Babić D S, Belić D S and Kurepa M V 1980 *10th Summer School and Symposium on the Physics of Ionized Gases, Dubrovnik, Yugoslavia*
Berry R S and Reiman C W 1963 *J. Chem. Phys.* **18** 67
Blewett J B 1936 *Phys. Rev.* **49** 900
Cornford A B, Frost D C, McDowell C A, Ragle J L and Stenhouse I A 1971 *J. Chem. Phys.* **54** 2651
Delbecq C J, Hayes W and Yuster P H 1961 *Phys. Rev.* **121** 1043
Donovan R J, Husain D and Stephenson C D 1970 *J. Chem. Soc. Faraday Trans.* **66** 2148
Frost D C and McDowell C A 1960 *Can J. Chem.* **38** 407
Herzberg G 1944 *Atomic Spectra and Atomic Structure* (New York: Dover)
—— 1950 *Molecular Spectra ana Molecular Structure* (New York: Van Nostrand)
Kurepa M V and Belić D S 1978 *J. Phys. B: Atom. Molec. Phys.* **11** 3719
Kurepa M V, Čadež I M and Pejčev V M 1974 *Fizika* **6** 185
Petersen A B and Smith I W M 1978 *Chem. Phys.* **30** 407
Petersen A B, Wittig C and Leone S R 1975 *Appl. Phys. Lett.* **27** 305
—— 1976 *J. Appl. Phys.* **47** 1051
Pritchard H O and Skinner H A 1955 *Chem. Rev.* **55** 745
Sides G D, Tiernan T O and Hanrahan R J 1976 *J. Chem. Phys.* **65** 1966
Smith P T 1930 *Phys. Rev.* **36** 1293
Stamatović A S and Schulz G J 1968 *Rev. Sci. Instrum.* **39** 1752
Tam W C and Wong S F 1978 *J. Chem. Phys.* **68** 5626
Tate J T and Smith J P 1932 *Phys. Rev.* **39** 270
Watanabe K 1957 *J. Chem. Phys.* **26** 542