Electron scattering from hexafluoride molecules: WF_6 and C_2F_6. Absolute total cross section measurements from 1 to 250 eV

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Abstract. Electron-scattering absolute total cross sections for tungsten hexafluoride (WF_6) and hexafluorethane (C_2F_6) molecules have been measured in a linear transmission electron-beam experiment within the impact energy range from about 1 to 250 eV. For electron scattering from WF_6 the cross section shows a prominent resonant-like peak centred at 3 eV and a very broad enhancement in the energy range between 20 and 70 eV overlaid with some much less pronounced features. The cross section for C_2F_6 has two resonant structures at 5 and 9 eV, respectively, and a very broad hump ranging from 20 to 60 eV with a distinct shoulder near 20 eV. Comparison of the e^-–C_2F_6 total cross section with available low-energy data from other experiments is made. The effect of fluorination is indicated.

1. Introduction

Considerable interest in the electron scattering properties of perfluorinated polyatomic compounds is related to their wide application as etching agents in semiconductor technology, as gaseous dielectrics in the electrical industry and the consequent pollution problems. Modelling operational conditions for a particular purpose requires knowledge of the basic interaction processes and access to comprehensive sets of reliable and accurate experimental cross sections.

Studies of electron scattering on a tungsten hexafluoride (WF_6) molecule have so far been rather incidental and have been mainly focused on the formation of negative ions (Thynne and Harland 1973, de Wall and Neuert 1977, Hildenbrand 1977). Rianda *et al* (1979) have studied the electron-impact excitation spectra in a crossed-beam experiment. Formation of WF_6^- and its dissociative products in electron transfer reactions was investigated by Dispert and Lackmann (1977). To our knowledge, no published e^-–WF_6 total cross section data are available.

Total cross sections for electron scattering from hexafluorethane (C_2F_6) at very low and low electron impact energies have been obtained quite recently in three various electron-transmission experiments. Sanabia *et al* (1998) determined absolute total cross sections from near-thermal energies up to 20 eV with the trochoidal spectrometer. Sueoka *et al* (1997) reported normalized data between 0.9 and 20 eV taken with the time-of-flight technique. Lunt *et al* (1998) obtained a backward scattering cross section below 1 eV, and using the modified effective-range fit for very low-energy data, they estimated the total cross section at

zero energy. A very extensive synthesis of available data concerning the various fundamental processes which result from electron collisions with the C_2F_6 molecule has been presented by Christophorou and Olthoff (1998). Very recently, Nishimura *et al* (1999) have measured and calculated the electron-impact total ionization cross section of C_2F_6.

This work represents a continuation of our efforts in measuring accurate absolute electron-scattering grand total cross sections for fully fluorinated polyatomic molecules (Szmytkowski *et al* 1992, 1998, Kasperski *et al* 1997, Karwasz *et al* 1998). In this paper, we report absolute total cross sections for electron scattering from WF_6 and C_2F_6 at energies from about 1 to 250 eV.

2. Experimental procedure

The apparatus and procedures used in the present experiments are as described by Szmytkowski *et al* (1998) and will be only briefly mentioned here. The electron spectrometer consists of a thermionic electron source, an electrostatic $127°$ cylindrical condenser for energy selection, electrostatic optics to form an electron beam of the desired energy, a reactive cell filled with the target molecules followed by a retarding field element and a Faraday cup as an electron detector. The spectrometer electron optics is immersed in the vacuum container at the background pressure of 10^{-5} Pa. The system of Helmholtz coils reduces the magnetic field along the electron-beam trajectory in the spectrometer to a value below 0.1 μT.

The incident energy scale was calibrated against an oscillatory structure around 2.3 eV observed in the transmitted current after the admixture of N_2. Electron current intensity in the presence of C_2F_6 ranged from 0.1 to 100 pA with an energy spread of 70 meV (FWHM). The WF_6 reduced greatly the electron current emission from the filament (the effect varies with the time of exposure) and it was necessary in the course of the experiment to increase the voltage drop across the filament and the current flowing through it to obtain adequate conditions for measurements. As a result, the accuracy of the energy scale in the e^-–WF_6 experiment worsened to about ± 0.1 eV (0.06 eV for C_2F_6).

The absolute total cross section $Q(E)$, at each given energy E, was evaluated using the Bouguer–de Beer–Lambert attenuation relationship

$$I(n, E) = I(0, E) \exp(-Q(E)nl),$$

where $I(n)$ and $I(0)$ are the intensities of the electron beam in the presence and absence of the target in the scattering volume, respectively, n is the target number density and l is the effective path length of electrons through the target.

The density number n was derived from its relation to the target pressure and the target temperature using the ideal gas law. The gas pressure was measured with a capacitance manometer and corrected for the thermal transpiration effect by applying the Knudsen (1910) formula. Effusion of target molecules through the entrance and exit orifices of the scattering cell disturbs the distribution of target density close to orifices. For the same reason, the path over which the scattering events take place is made longer than the geometrical distance between orifices. Calculations show, however, that for our experimental arrangement the effect of a density drop across the orifices is almost compensated (to within 0.5%) by extension of the electron path length in the target region. Exposure of the electron gun to the gas effusing from the collision cell might seriously change the intensity of the primary electron beam, $I(0)$, and in consequence affect the measured cross section. To keep the conditions in the electron optics region nearly constant the target gas was bypassed into the electron optics volume. As a result, the pressure in this volume was constant while the pressure in the scattering cell changed over three orders of magnitude, depending on whether the target was in or off the cell. The time

necessary for filling and emptying of the scattering cell with the WF_6 sample was twice that for C_2F_6. The stated purity of the C_2F_6 and WF_6 was better than 99% and 99.9%, respectively. Both samples were used without further purification.

Incomplete discrimination of the detection system against electrons scattered in the small-angle forward direction causes some fraction of the scattered electrons to be registered as unscattered current. The effect related to inelastic forward scattering was considerably reduced by the use of the discrimination-retarding field element beyond the scattering cell. To estimate the systematic lowering of the measured total cross section due to elastic forward scattering, experimental differential elastic e^-–C_2F_6 cross sections (Takagi *et al* 1994) have been used. For the applied geometry of the detection system in the present experiment (acceptance angle ~1 msr) the upper limit of an error associated with the elastic forward scattering is estimated to be about 2% at 100 eV, and it becomes smaller at lower energies. Estimation by rule of thumb gives an error value less than 3% at the highest energy applied, 250 eV. The reported data have not been corrected for the forward scattering effect.

Measurements at a given energy were carried out in 5–20 series typically consisting of 6–10 single runs. It was established that the total cross sections obtained in different series at the same energy were independent, within the statistical uncertainties, of the applied target pressure and electron beam intensities. The final total cross section values at particular energies are weighted means of the average from different series of individual runs. The statistical relative uncertainties (one standard deviation of weighted mean values) are: (i) for WF_6, about 2% below 1.5 eV and less than 1% above 2 eV; and (ii) for C_2F_6, 1.5% below 0.8 eV and less than 1% above 1 eV. The direct sum of all potential individual systematic errors for WF_6 and C_2F_6 was estimated to be 8% and 6% below 4 eV, respectively, and about 4% for other investigated energy ranges.

3. Results and discussion

Absolute results of the present total cross section measurements for WF_6 at energies from 1.2 to 250 eV and for C_2F_6 between 0.5 and 250 eV are listed in tables 1 and 2, respectively.

Table 1. Absolute total cross sections (TCSs) measured for electron impact on WF_6 molecules in units of 10^{-20} m².

E (eV)	TCS WF_6	E (eV)	TCS WF_6	E (eV)	TCS WF_6	E (eV)	TCS WF_6
1.2	21.7	4.5	25.0	14.0	28.9	80	34.4
1.3	22.0	5.0	22.9	16.0	32.8	90	33.7
1.4	21.6	5.5	22.8	18.0	36.3	100	32.5
1.5	21.8	6.0	22.9	20.0	36.5	110	31.8
1.6	21.7	6.5	22.9	22.5	36.7	120	30.9
1.7	22.1	7.0	22.8	25.0	36.6	140	28.6
1.8	22.5	7.5	23.3	27.5	36.8	160	27.6
1.9	22.6	8.0	24.2	30	37.1	180	26.1
2.0	22.6	8.5	24.0	35	37.8	200	25.3
2.3	26.9	9.0	24.4	40	37.8	220	24.4
2.7	30.1	9.5	25.6	45	37.7	250	23.2
3.0	31.4	10.0	26.8	50	36.8		
3.5	27.4	11.0	27.2	60	36.3		
4.0	25.9	12.0	28.2	70	35.0		

Table 2. TCSs measured for electron impact on C_2F_6 molecules in units of 10^{-20} m^2.

E (eV)	TCS C_2F_6	E (eV)	TCS C_2F_6	E (eV)	TCS C_2F_6	E (eV)	TCS C_2F_6
0.5	16.3	2.1	19.1	8.0	33.2	40	34.3
0.6	16.5	2.2	19.3	8.5	34.0	45	34.0
0.7	16.6	2.3	19.3	9.0	33.4	50	34.0
0.8	16.9	2.4	19.3	9.5	32.1	60	33.0
0.9	17.0	2.5	19.6	10.5	30.5	70	31.4
1.0	17.2	2.8	20.3	11.5	29.5	80	30.1
1.1	17.2	3.2	23.4	12.5	29.0	90	29.0
1.2	17.7	3.5	25.5	14.5	28.9	100	27.1
1.3	17.9	4.0	29.5	16.5	29.3	110	25.8
1.4	18.0	4.5	30.5	18.5	30.2	120	24.8
1.5	18.5	5.0	31.2	20.5	31.4	140	24.1
1.6	18.5	5.5	31.3	23.0	32.2	160	22.7
1.7	18.8	6.0	30.0	25.5	32.4	180	21.1
1.8	18.8	6.5	30.1	28.0	32.7	200	20.0
1.9	18.9	7.0	31.5	30.0	33.1	220	18.8
2.0	19.0	7.5	32.6	35.0	33.7	250	17.9

3.1. WF_6

Figure 1 illustrates variations of the e$^-$–WF$_6$ total cross section with the impact energy. No absolute data are available for comparison. The cross section function exhibits two distinct features: the first, very sharp resonant-like peak is centred around 3 eV where the total cross section reaches a value of 32×10^{-20} m^2, while the second, very broad, enhancement of the cross section appears between 20 and 70 eV. The maximum at 3 eV is most probably associated with a shape resonance arising from the temporary trapping of an extra electron into the lowest antibounding orbitals of WF$_6$ molecule. The evidence for the resonant character of the e$^-$–WF$_6$ scattering processes in the vicinity of 3 eV comes from the electron-attachment experiment of de Wall and Neuert (1977) in which they observed the creation of a parent negative ion, WF$_6^-$, around 3 eV. Thynne and Harland (1973) registered fragment F$^-$ ions around 2.8 eV but did not notice WF$_6^-$ near this energy. Resonant peaks in electron attachment spectra have been also observed by Stockdale *et al* (1970) and Compton (1977) for MoF$_6$ (around 1 eV) and UF$_6$ (at 2.15 eV) which are valence isoelectronic systems of WF$_6$. Another interesting feature, which may also be in part related to resonant processes, is visible near 10 eV as a shoulder on the low-energy edge of the very broad hump. Close to this energy, the ionization efficiency curve (Thynne and Harland 1973, de Wall and Neuert 1977, Hildenbrand 1977) shows maxima corresponding to the creation of fragment negative ions (F$^-$, WF$_4^-$ and WF$_5^-$) as a result of electron bombardment. The structure located in the 8–10 eV energy range is more or less visible in electron-scattering total cross sections of all fully fluorinated targets investigated so far (e.g. figure 2), as well as the majority of polyatomic compounds. Between 20 and 70 eV the cross section has values ranging from 35 to 38×10^{-20} m^2. This very broad hump is the most characteristic common behaviour of the total cross section function of perfluorinated complex targets (figure 2). Around 20 eV an additional weak but repetitive feature superimposed on the broad hump is noticeable. It might be related to the creation of high-energy resonances but could also be a result of the superposition of direct processes allowed in this energy range. Between 60 and 250 eV the energy dependence of the e$^-$–WF$_6$ total cross section can be approximated by $Q(E) \sim E^{-a}$ with the parameter $a = 0.3$, similar to that for another octahedral hexafluoride: SF$_6$ (figure 5).
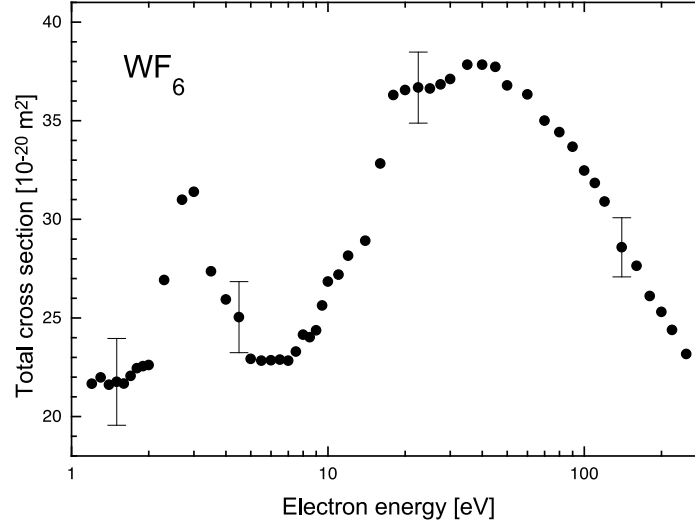
Figure 1. Absolute total electron–WF_6 scattering cross section: ●, present. The error bars at selected points represent the total (systematic plus statistical) experimental uncertainties.
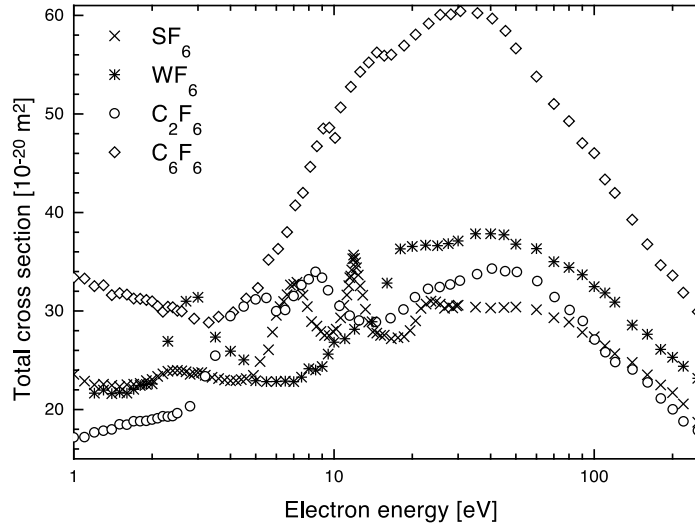

Figure 2. Total cross section for electron scattering from hexafluorides: ×, SF_6, Kasperski *et al* (1997); ∗, WF_6, present; ○, C_2F_6, present; ◇, C_6F_6, Kasperski *et al* (1997).

3.2. C_2F_6

In figure 3 we present our experimental results for C_2F_6 and compare them with the only available absolute low-energy total cross section measurements of Sanabia *et al* (1998). Normalized data of Sueoka *et al* (1997) are also included for completeness.

There is an excellent similarity in the shape of the total cross section energy dependence between the three sets of data in the common energy range. However, the present results are somewhat higher than the other data. The divergence occurs from about 10% near 1 eV up to 20% on the slope between 3 and 4 eV and increases to about 15% near cross section maxima.
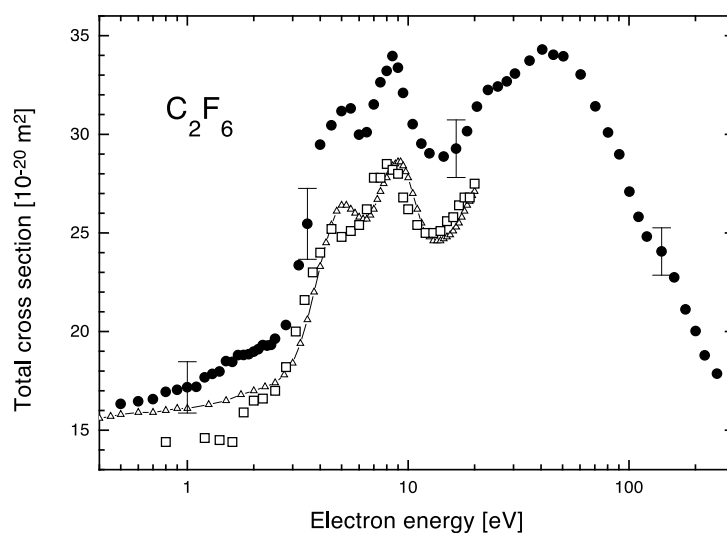
Figure 3. Total electron–C_2F_6 scattering cross section. Absolute: ●, present; –△–, Sanabia *et al* (1998). Normalized: □, Sueoka *et al* 1997. The error bars at selected points represent overall experimental uncertainties.

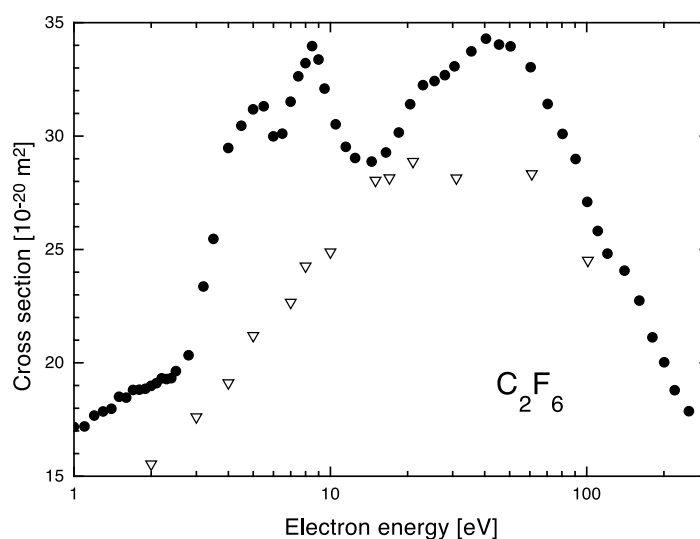**Figure 4.** Comparison of the present total cross section for e^-–C_2F_6 scattering, ●, with the sum of elastic (Takagi *et al* 1994) and ionization (Nishimura *et al* 1999) cross sections, ▽.

Similar differences between results of the afore-mentioned groups and measurements from our laboratory have been already observed for other targets (Szmytkowski *et al* 1997, Karwasz *et al* 1998) and were partly explained by the presence of a guiding magnetic field in the Sueoka *et al* and Sanabia *et al* spectrometers while such a field is absent in our experimental setup. According to Golden (1978), use of a magnetic field can lead to an underestimation of the measured total cross section which is difficult to estimate. It is worth noting, however, that the apparent discrepancies do not exceed the combined uncertainties of the experiments compared.
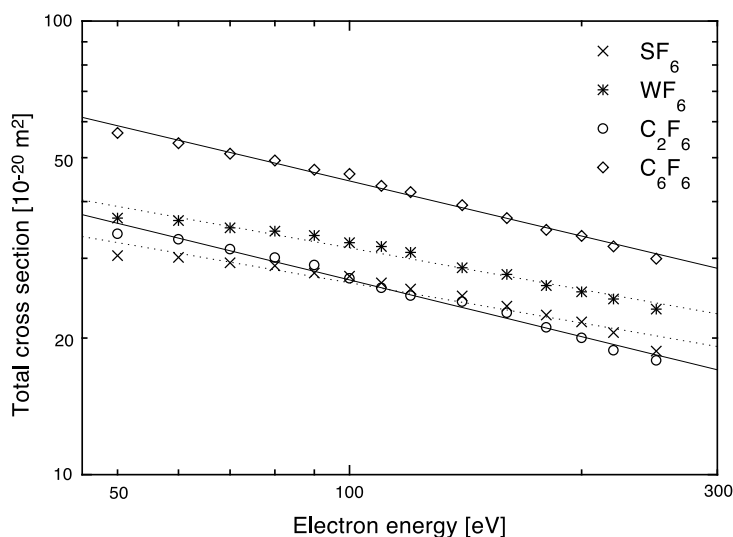
Figure 5. Energy dependence of the electron-scattering total cross section for hexafluorides (symbols are the same as in figure 2).

Moreover, total cross sections for electron scattering from other targets, especially those for noble gases and some diatomic molecules, measured in our laboratory (Szmytkowski *et al* 1996), are consistent with results obtained in other laboratories.

The e^-–C_2F_6 total cross section function exhibits, apart from two previously observed (Takagi *et al* 1994, Sueoka *et al* 1997, Sanabia *et al* 1998) well-marked resonant maxima located at 5 and 8 eV, a very broad enhancement spanning between 20 and 60 eV. Again, as in other perfluorides' total cross sections, a weak shoulder around 20 eV is visible.

The specific increase of the total cross section between 15 and 70 eV for perfluorinated molecules may be related to two facts: (i) the elastic cross section for electron scattering from those molecules has a broad enhancement spanning between 10 and 30 eV, while for other compounds it is much narrower and usually peaked below 10 eV; (ii) the gross ionization cross section, which for the majority of targets has a maximum below 100 eV (around 75 eV), in the case of perfluorinated compounds it has a maximum between 100 and 200 eV. Superposition of elastic and ionization cross sections reproduces reasonably well the general trend of the intermediate-energy total cross section dependence for fully fluorinated compounds studied so far. Figure 4 illustrates this effect for the C_2F_6 target. Some other fluorination effects in the elastic differential cross section and in the ionization cross section have already been indicated by Tanaka *et al* (1997) and Deutsch *et al* (1986), respectively.

Above 60 eV, the e^-–C_2F_6 total cross section gradually decreases with increasing impact energy and down to 250 eV it behaves like $Q(E) \sim E^{-0.4}$, which is very similar to that for C_6F_6 (figure 5).

4. Conclusion

In this paper we have presented the results of our absolute total cross section measurements for electron scattering from WF_6 and C_2F_6 at impact energies from 0.5 to 250 eV. The shape of the total cross section functions obtained depends strongly on scattering energy. Below 10 eV the cross sections indicate maxima which can be related to the formation of transient resonant

states. The enhancement observed between 20 and 70 eV seems to be a common feature of all perfluorinated compounds.

Acknowledgments

References

Christophorou L G and Olthoff J K 1998 *J. Phys. Chem. Ref. Data* **27** 1–29
Compton R N 1977 *J. Chem. Phys.* **66** 4478–85
Deutsch H, Scheier P and Märk T D 1986 *Int. J. Mass Spectrom. Ion Proc.* **74** 81–95
Dispert H and Lackmann K 1977 *Chem. Phys. Lett.* **45** 311–5
Golden D E 1978 *Adv. At. Mol. Phys.* **14** 1–85
Hildenbrand D L 1977 *Int. J. Mass Spectrom. Ion Phys.* **25** 121–8
Karwasz G P, Brusa R S, Piazza A, Zecca A, Możejko P, Kasperski G and Szmytkowski Cz 1998 *Chem. Phys. Lett.* **284** 128–34
Kasperski G, Możejko P and Szmytkowski Cz 1997 *Z. Phys.* D **42** 187–91
Knudsen M 1910 *Ann. Phys., Lpz.* **31** 205–29
Lunt S L, Randell J, Ziesel J-P, Mrotzek G and Field D 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 4225–41
Nishimura H, Huo W M, Ali M A and Kim Y-K 1999 *J. Chem. Phys.* **110** 3811–22
Rianda R, Frueholz R P and Kuppermann A 1979 *J. Chem. Phys.* **70** 1056–61
Sanabia J E, Cooper G D, Tossell J A and Moore J H 1998 *J. Chem. Phys.* **108** 389–91
Stockdale J A D, Compton R N and Schweinler H C 1970 *J. Chem. Phys.* **53** 1502–7
Sueoka O, Takaki H, Hamada A and Kimura M 1997 *20th Int. Conf. on Physics of Electronic and Atomic Collisions (Vienna 1997) (Abstracts of Contributed Papers vol 1)* ed F Aumayer, G Betz and H P Winter (Vienna) WE057
Szmytkowski Cz, Krzysztofowicz A M, Janicki P and Rosenthal L 1992 *Chem. Phys. Lett.* **199** 191–7
Szmytkowski Cz, Maciąg K and Karwasz G 1996 *Phys. Scr.* **54** 271–80
Szmytkowski Cz, Możejko P and Kasperski G 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 3917–28
Takagi T, Boesten L, Tanaka H and Dillon M A 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 5389–404
Tanaka H, Masai T, Kimura M, Nishimura T and Itikawa Y 1997 *Phys. Rev.* A **56** R3338–41
Thynne J C J and Harland P W 1973 *Int. J. Mass Spectrom. Ion Phys.* **11** 137–47
de Wall R and Neuert H 1977 *Z. Naturf.* a **23** 968–71