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On the absolute absorption cross-section of SF_5CF_3

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Abstract

The absolute absorption cross-sections of a recently discovered atmospheric gas, SF_5CF_3, have been measured at He I (21.22 eV) and Ne I (16.64 and 16.82 eV) photon energies using a VUV discharge lamp and a double ion chamber method. Absorption cross-sections of $(9.52 \pm 0.95) \times 10^{-17}$ cm^2 (He I) and $(8.79 \pm 0.88) \times 10^{-17}$ cm^2 (Ne I) were obtained and compared with data from other studies. The consequences for the cross-section at the hydrogen Lyman-α energy (10.20 eV) are discussed.

1. Introduction

The polyatomic molecule trifluoromethyl sulphur pentafluoride (SF_5CF_3) has recently been reported in the atmosphere at a level of 0.12 parts per trillion, with an annual growth rate of 6% [1] and is believed to be of anthropogenic origin. Although the concentration of this compound is currently very small, it is notable that it has the highest global warming effect per molecule, as measured by its radiative forcing constant (0.57 W m^{-1} ppb^{-1}) of any known atmospheric gas [1]. This effect, coupled with an estimated atmospheric lifetime of the order of 1000 years [1–5], makes its study particularly timely.

One parameter of relevance to atmospheric studies is the photoabsorption cross-section of SF_5CF_3 at the hydrogen Lyman-α photon energy of 10.20 eV (121.6 nm) since this is the dominant VUV energy from solar radiation in the upper atmosphere. Such a measurement allows the contribution of photodissociation to the atmospheric lifetime of this molecule to be deduced, and compared with other removal mechanisms such as ion–molecule reactions [6,7] and electron dissociative attachment [4,5,8].

In this Letter, we report recent measurements of the absolute photoabsorption cross-sections of SF_5CF_3 at He I (21.22 eV) and Ne I (16.64 and 16.82 eV) photon energies. Although we do not measure the Lyman-α cross-section itself, our measurements are compared at the appropriate energies with recent measurements by Chim et al. [2] made over a wide energy range (6–26 eV). Hence we can compare the cross-section scales of

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Chim et al. [2] and Takahashi et al. [9], which we note differ by a factor of 70%.

2. Experimental

The experiments were performed using a commercial vacuum ultraviolet source (Thermo VG Scientific UPS helium discharge lamp) in combination with a modified double ion chamber [10] (Fig. 1). The lamp was operated with either CP grade (99.999% purity) helium (BOC) or 99.99% pure neon (Aldrich Chemicals) under conditions optimised for maximum flux as monitored by the ion currents. The photon flux was not directly measured, as it is not required for cross-section measurements using the double ion chamber method. A background pressure of about 2×10^{-6} mbar was maintained in the vacuum chamber via a Balzers 330 l/s turbomolecular pump. During measurements, the chamber was isolated from the pumping system and sample gas admitted via a leak valve to static pressures of typically 10–100 μbar, as measured by a MKS baratron. A potential of +15 V was applied to both the lower repeller plate and the terminator plate adjacent to the rear collector ensuring 100% ion collection within the absorption region. The ion currents i_1 and i_2 were measured using Keithley 617 and 614 electrometers. Under typical experimental conditions, ion currents of the order of 20 nA were achieved.

The double ion chamber method eliminates the need for photon flux measurement, since the cross-section simply depends on the ratio of the two currents and the lengths of the collector plates according to

$$\sigma = \frac{1}{nL} \ln\left(\frac{i_1}{i_2}\right), \tag{1}$$

where i_1 and i_2 are the ion currents as discussed above, L is the length of the collector plates and n is the atom or molecule number density of the sample gas given in terms of the pressure P (μbar) and temperature T (K) by

$$n = \frac{7.25 \times 10^{15} P}{T} \mathrm{cm}^{-3}. \tag{2}$$

Cross-sections were determined by measuring the ion currents over a range of pressures for a given sample, and producing a Beer–Lambert plot, shown in Fig. 2a for SF_5CF_3. We note that care is required in the analysis as the measured cross-section is constant only over a limited pressure range, as illustrated in Fig. 2b, for reasons discussed in detail in [11]. Briefly, at low pressures, (i_1/i_2) tends to unity, hence any systematic errors or offsets become highly significant. In the case of our experiment, these effects depress the apparent

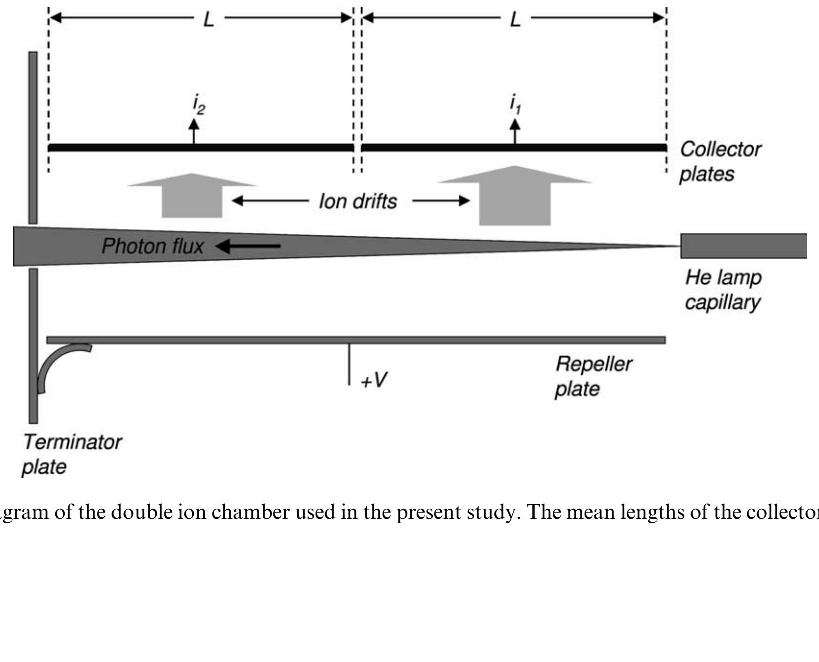

Fig. 1. Schematic diagram of the double ion chamber used in the present study. The mean lengths of the collector plates are 97 ± 1 mm.

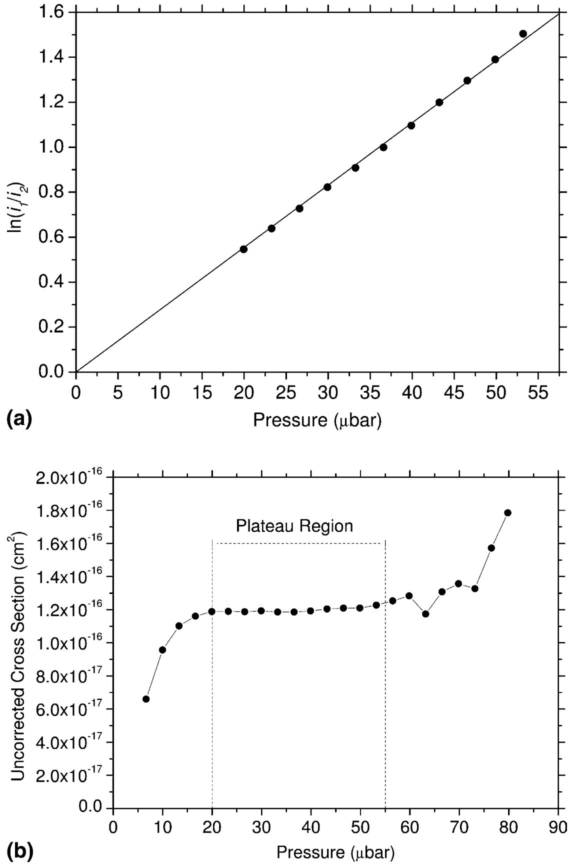

Fig. 2. (a) Beer–Lambert plot for SF_5CF_3 absorption at 21.22 eV (He I). (b) Absorption cross-section of SF_5CF_3 vs. sample pressure, illustrating the presence of a 'plateau' region from which (a) was derived. Note that the data in these figures are uncorrected for any calibration factors.

cross-section. At high pressures, saturation of the absorption leads to i_2 being essentially zero, yielding an erroneously high cross-section. The Beer–Lambert plot is therefore only produced from data in the 'plateau' region. It should be noted that the data shown in Figs. 2a,b are uncorrected for any systematic calibration effects.

The cross-section measurements were calibrated at both the He I and Ne I energies by measuring values for rare gases (Ar, Kr, Xe) and a number of small molecules (N_2, SF_6, CF_4, CH_4, N_2O), and comparing with recent measurements using similar methods [2,11–13]. In all cases, we systematically measure the cross-sections to be high by a factor of 1.24 ± 0.08, with the error reflecting the standard deviation of the individual factors obtained. This value was used as a calibration factor in the data analysis. Taking into account all sources of error, such as systematic errors in the electrometers, temperature measurement and uncertainties in the lengths of the collector plates, we conclude that the primary source of the calibration factor is a systematic error in the pressure measurement. In our final analysis of the cross-sections of SF_5CF_3, we have taken into account this calibration factor and, considering all other sources of error, we quote an overall uncertainty to one standard deviation of ±10%.

3. Results

Comparisons of the cross-sections for SF_5CF_3 at He I and Ne I energies from this study and from the data of Chim et al. [2] are shown in Fig. 3 and Table 1. For reference, the results from this study for CF_4 and SF_6 at He I and Ne I are also given in Table 1, and compared with previous work [2,13]. It should be noted that the Ne I result is an average of the cross-sections for the two Ne I lines at 16.62 and 16.84 eV. However, Fig. 3 shows that the cross-section for SF_5CF_3 does not change significantly over 0.2 eV in this

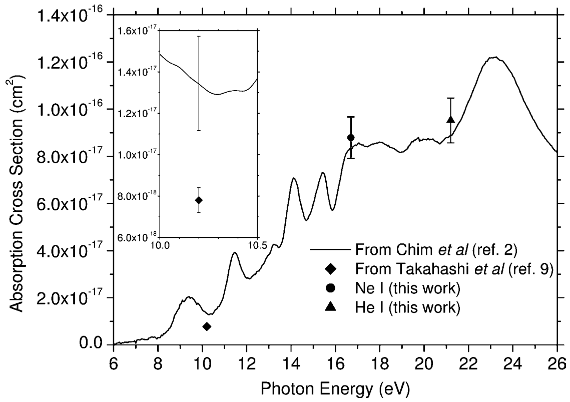

Fig. 3. Absolute absorption cross-sections for SF_5CF_3 from 6 to 26 eV from [2], showing the data from the present study at Ne I and He I energies. Inset – expansion of the region around 10.20 eV (H Lyman-α), showing the data from [2,9] and associated error bars. The axes on the inset have the same units as the main figure.

Table 1
Absolute absorption cross-sections for SF_5CF_3, SF_6 and CF_4

Energy (eV)	Molecule	Absolute cross-section ($\times 10^{-17}$ cm^2)	
		This work	Previous data
16.62, 16.84 (Ne I)	SF_5CF_3	8.79 ± 0.88	8.29 ± 1.41[a]
	SF_6	7.50 ± 0.75	7.67 ± 0.18[b]
	CF_4	4.40 ± 0.44	4.14 ± 0.70[a]
21.22 (He I)	SF_5CF_3	9.52 ± 0.95	8.88 ± 1.51[a]
	SF_6	5.73 ± 0.57	6.51 ± 0.15[b]
	CF_4	6.59 ± 0.66	6.90 ± 1.17[a]

[a] From [2] and R.P. Tuckett *Private Communication.*
[b] From [13] and D.M.P. Holland *Private Communication.*

region, hence we judge our Ne I result to be valid. The data show excellent agreement within the joint error bars (10% for this work, $\sim$17% for [2]) between the cross-sections for SF_5CF_3 in this work and at the relevant photon energies from Chim et al. [2].

With regard to the cross-section at H Lyman-α, the discrepancy is clear in the inset on Fig. 3 between the results of Chim et al. [2] ($(1.34 \pm 0.23) \times 10^{-17}$ cm^2) and Takahashi et al. [9] ($(7.8 \pm 0.6) \times 10^{-18}$ cm^2). Clearly, these two results lie outside their joint error bars and cannot therefore be reconciled. Our results support the overall cross-section scale of Chim et al. [2] in the photon energy region we have studied, and may therefore support their value at H Lyman-α. However we note that since the work of Chim et al. [2] utilised synchrotron radiation, the possibility of a small second-order radiation contribution in their work cannot be ignored. Whilst this contribution will not be of great significance at the Ne I and He I energies where there is a substantial cross-section, the effect at H Lyman-α where the cross-section is small (with a large cross-section at the second order energy of 20.4 eV) would be to give an erroneously large result.

4. Conclusions

We report data on the absolute absorption cross-sections for the recently discovered atmospheric gas SF_5CF_3 at Ne I and He I photon energies. Using our data, we have supported the absolute cross-sections of Chim et al. [2] in the Ne I and He I photon energy range. Such results may support their value for the cross-section of SF_5CF_3 at H Lyman-α and its consequences for the removal mechanisms of this gas from the atmosphere. However, we note that possible second order radiation contributions in [2] may increase the apparent H Lyman-α cross-section above the true value.

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