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Gas phase UV absorption spectra for a series of alkyl sulfides

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Abstract

Absorption cross-sections have been measured for a series of alkyl sulfides between 209.0 and 235.0 nm. Measurements are reported for dimethylsulfide ($(CH_3)_2S$, h_6-DMS) and its deuterated isotopomer ($(CD_3)_2S$, d_6-DMS), methylethylsulfide ($CH_3SC_2H_5$, MES), diethylsulfide ($(C_2H_5)_2S$, DES), dipropylsulfide ($(C_3H_7)_2S$, DPS) and dibutylsulfide ($(C_4H_{10})_2S$, DBS).

Keywords: Absorption spectra; Alkyl sulfides

1. Introduction

As the largest natural source of reduced sulfur, dimethylsulfide (CH_3SCH_3, DMS) plays a critical role in atmospheric sulfur cycling and has been linked to changing climate [1]. For these reasons, the chemistry of reduced sulfur compounds, most notably DMS, has been a focus of intense laboratory study. The alkyl sulfides are also convenient photolytic precursors of both alkyl and alkylsulfenyl radicals for kinetic and spectroscopic studies; however, accurate absorption cross-sections and quantum yields are required for calculation of radical concentrations. The vacuum-ultra violet (VUV) absorption spectrum of DMS in the wavelength range 190–250 nm was first reported by Thompson et al. [2] and then by Scott et al. [3]. McDiarmid [4] reported observations of the spectra of both h_6-DMS and d_6-DMS between 125 and 250 nm and tabulated the isotope shifts associated with 24 transitions. More recent observations include, Tokue et al. [5], Hearn et al. [6] and a recent high-resolution spectrum from Limão-Vieira et al. [7]. Single, atomic line measurements have been reported in conjunction with kinetic measurements for both isotopomers [8,9].

Spectroscopic data on the larger alkyl sulfides is sparse. A measurement of the UV spectrum of methylethylsulfide ($C_2H_5SCH_3$, MES) between 200.0 and 235.0 nm with a resolution of 0.50 nm was reported by Tycholiz and Knight [10]. Hearn et al. [6] reported a spectrum of diethylsulfide ($(C_2H_5)_2S$, DES) between 200.0 and 280.0 nm with a resolution of 0.1 nm. The UV absorption cross-sections of dipropylsulfide ($(C_3H_7)_2S$, DPS) and dibutylsulfide ($(C_4H_9)_2S$, DBS) have not previously been reported. In addition to spectra, a limited number of absorption cross-section measurements are available at 228.8 and 213.9 nm for h_6-DMS, d_6-DMS, DES and MES [9,10]. These have been reported in conjunction with kinetic measurements, and correspond to the wavelengths of zinc and cadmium atomic lines that are particularly convenient for monitoring sulfide concentrations in kinetic studies. A recent experimental study by Martínez-Haya et al. [11] detail the photodissociation dynamics of both h_6-DMS and d_6-DMS. In this work we report absolute cross-sections for several alkyl sulfides in the wavelength range of 200.0–235.0 nm, including the first reported measurements for d_6-DMS, DPS and DBS.

2. Experimental

Absorption cross-sections were measured between 209.0 and 237.5 nm using a diode array spectrometer. A deuterium

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lamp (Hamamatsu L979-01) served as the light source for the array measurements. The light passed through an absorption cell with heated windows and an attached capacitance manometer for pressure measurements. Light was then dispersed by a 0.5 m spectrograph (Jobin–Ivon HR640), detected by a 1024-element photodiode array (EG&G M1421) and processed by an optical multichannel analyzer (OMA, EG&G M1463). The wavelength scale was calibrated using the atomic lines from Zn and Cd lamps (BHK Inc.). With a 3000 lines per mm spectrometer grating, we obtained a resolution of ∼0.05 nm, taken from the FWHM of isolated atomic lines. In addition, for h_6-DMS and d_6-DMS, the absorption cross-sections at the 213.9 nm atomic line of Zn and the 228.8 nm atomic line of Cd were measured. For the single line measurements, the attenuation of the atomic line was monitored using a photomultiplier masked by a narrowband dichroic filter of the appropriate wavelength. A 100.3 cm cell was used for all experiments.

Spectra for h_6-DMS, d_6-DMS and MES were measured using a static system. A known pressure of the standard, sulfide/N_2 bulb mixture was introduced into the absorption cell and the attenuation of the deuterium lamp or the atomic line, was monitored as a function of pressure. For DPS and DBS, initial measurements using the neat sulfide suggested significant artifacts due to difficulties in pressure measurement caused by the adherence of the sulfide to the walls. Instead, cross-section measurements were made using very dilute mixtures of DPS and DBS in argon in large pyrex storage bulbs. For DPS and DBS bulbs, known amounts of the liquid sulfide were introduced into pre-filled bulbs containing argon, which were then allowed to mix for 24 h. The concentration of the sulfide was monitored using gas chromatography in conjunction with flame ionization and mass spectrometric detection (GC/FID/MS). After an initial loss of sulfide to the walls, the gas phase concentration stabilized and this mixture was used for absorption measurements. Although, adherence to the cell walls was diminished somewhat with this technique, static measurements using these mixtures were irreproducible. Finally, measurements were made in a flowing system which apparently allowed the cell walls to "condition" and reach a steady state in which absorption and desorption were proceeding at equal rates. This was confirmed by taking 20 scans of optical density as a function of wavelength and ensuring that the wavelength-dependent optical density did not vary significantly over the course of the measurement. Each scan consisted of a 1 min average, ensuring that the concentration was stable over a period of at least 20 min. Spectra of DPS and DBS were obtained using the flowing, dilute mixtures only, while spectra of h_6-DMS and DES were obtained using both the static and flowing methods. Standard mixtures of h_6-DMS, d_6-DMS, MES and DES were made both manometrically and by liquid injection with GC/FID/MS determination of the concentration.

The GC/FID/MS measurements utilized a gas chromatograph (Hewlett-Packard 5890) fitted with a 60 m × 0.25 mm i.d. × 1.4 μm film HP-624 column and both flame ionization (FID) and mass spectrometric (MS) detection were employed. Samples ranging from 10 to 50 cm^3 were concentrated on a silanized glass bead filled, stainless steel loop immersed in liquid argon. Concentrated samples were injected for 2 min at 90 °C. Sample volumes were measured by pressure difference in a previously evacuated volume with a capacitance manometer. The oven temperature program was 35 °C for 6 min followed by a temperature ramp of 20 $°C\,min^{-1}$ to 190 °C, which was held for 5 min. Both the GC/FID and GC/MS systems were calibrated using single component and multi-component gravimetrically prepared standards that were prepared by NIST or referenced to NIST prepared standards and were cross-calibrated with permeation tubes and/or FTIR spectroscopy.

3. Results and discussion

Absorption cross-sections at each wavelength were calculated using the Beer–Lambert law:

$$\ln\left(\frac{I}{I_0}\right) = lc\sigma \qquad (1)$$

where I_0 and I are the measured light intensities through the

Table 1
UV absorption cross-sections for h_6-DMS, d_6-DMS, MES, DES, DPS and DBS. Comparison with previous measurements

Sulfide	$\sigma_{228.8\,nm} \times 10^{-19}\,cm^2$	$\sigma_{228.8\,nm} \times 10^{-19}\,cm^2$ (this work)	$\sigma_{213.9\,nm} \times 10^{-19}\,cm^2$	$\sigma_{213.9\,nm} \times 10^{-19}\,cm^2$ (this work)
h_6-DMS	11.6[a], 10.9[b], ∼9.6[c], 10.1[d]	10.9 ± 0.25	17.0[e], 16.97[b], ∼17.0[c], 14.0[d]	13.6 ± 0.31
d_6-DMS	5.16[a]	5.04 ± 0.01	12.3[e]	11.8 ± 0.08
MES	8.45[a], 7.6[f]	7.34 ± 0.22	19.0[f]	20.0 ± 0.09
DES	9.64[a], 9.15[b]	9.57 ± 0.39	32.6[b]	36.6 ± 0.17
DPS	None	7.50 ± 1.32	None	35.2 ± 3.58
DBS	None	8.47 ± 0.69	None	44.0 ± 2.51

[a] Hynes et al. [9]. Single line measurements reported only.
[b] Hearn et al. [6]. Spectra between 201 and 285 nm.
[c] Thompson et al. [2]. From plot.
[d] Limão-Vieira et al. [7]. High-resolution spectra between 110 and 250 nm.
[e] Barone et al. [8]. Single line measurements reported only.
[f] Tycholiz and Knight [10]. Spectra between 204 and 234 nm.

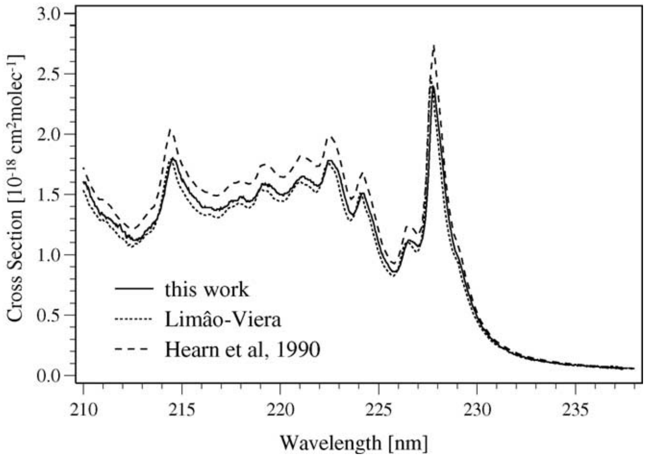

Fig. 1. h_6-DMS spectrum obtained in this work (solid line), together with the data of Hearn et al. (dashed line) and Limão-Vieira et al. (dotted line).

cell in the absence and presence of absorbing sulfide, *l* is the cell path length in cm, *c* the concentration of absorbing gas in molecules/cm^3, and σ the absorption cross-section in cm^2/molecule. Table 1 gives the measured absorption coefficients at 213.9 and 228.8 nm for all sulfides reported here and, where available, other literature data. The tabulated uncertainties associated with the work reported here are 1σ measures of precision only.

3.1. Spectra of h_6-DMS and d_6-DMS

The UV cross-section of h_6-DMS and d_6-DMS were determined in a static system using both the OMA and by monitoring the attenuation of the 228.8 nm Cd line with a PMT. Cell pressures of the dilute bulb mixtures (1–2%) were between 1 and 10 Torr. Although, there was no evidence of artifacts due to adherence to the cell walls and windows, additional flowing measurements were made for h_6-DMS to validate the experimental technique. The cross-sections for h_6-DMS and d_6-DMS are shown as a function of wavelength between 207.0 and 237.5 nm in Figs. 1 and 2 along with previous work. In each case, the optical density at 213.9 and 228.8 nm was plotted as a function of concentration using measurements taken with the OMA and at 228.8 nm using measurements taken with the PMT. Fig. 3 shows such a plot for d_6-DMS. The linearity of these plots was excellent suggesting a linear response of the detection systems to light attenuation in each case. The cross-sections were obtained by dividing the slope by the cell length. Measurements with the diode array system were slightly smaller than those obtained with the 228.8 nm atomic line of Cd. For h_6-DMS, we obtained $(1.10 \pm 0.03) \times 10^{-18}$ cm^2 using the Cd lamp/PMT and $(1.03 \pm 0.06) \times 10^{-18}$ cm^2 using the OMA, a difference of 6.4%. For d_6-DMS we obtained $(5.07 \pm 0.04) \times 10^{-19}$ cm^2 using the Cd lamp/PMT and $(4.87 \pm 0.03) \times 10^{-19}$ cm^2 using the OMA, a difference of 3.2%. In both cases, the measurements agree within their combined uncertainties. The Cd lamp/PMT measurements were not subject to any errors due to instrumental resolution or calibration uncertainties and therefore, the absolute cross-sections shown in the OMA spectra of both isotopomers were scaled to the independent, single line value at 228.8 nm.

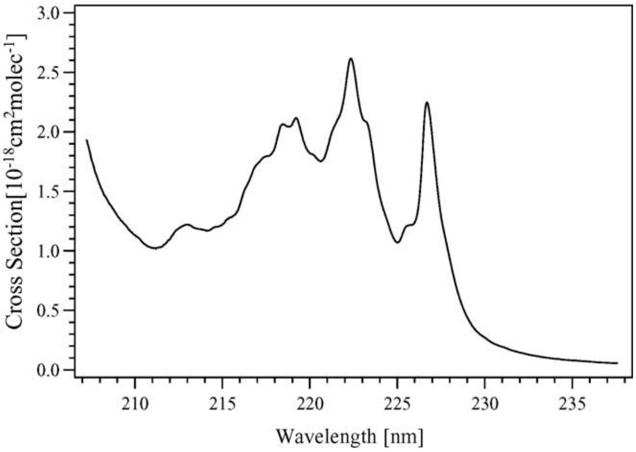

Fig. 2. d_6-DMS spectrum obtained in this work.

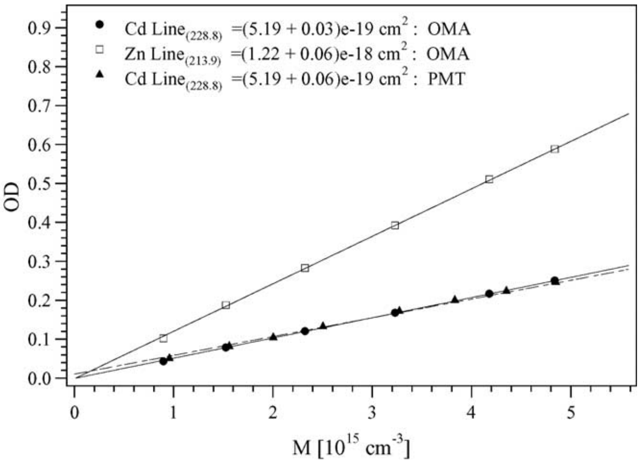

Fig. 3. Optical density as a function of d_6-DMS concentration at 213.9 and 228.8 nm. Solid lines show data obtained with the OMA at 213.9 and 228.8 nm. Data obtained with PMT/filter at 228.8 is shown as a dotted line.

Fig. 1 also shows the spectra reported by Hearn et al. [6] and Limão-Vieira et al. [7]. Good agreement is seen between the current work and the recent study of Limão-Vieira et al. Files containing the digitized spectra are included in supplementary material. The absorption cross-sections of Hearn et al. are slightly larger, with a value which is approximately 14% higher at 214.5 nm. This absorption band has been assigned as the 1^1B_1 ($9a_1 < -3b_1$)–X^1A_1 transition [11] with the strong feature at 228.8 nm being assigned to the (0–0) band. The diffuse band structure was assigned by Thompson et al. [2] and has been slightly revised by Limão-Vieira et al. [7] As noted in both Hearn et al. [6] and Limão-Vieira et al. [7], the positions of the diffuse band structure differ slightly from those reported by Thompson et al. [2] and, as can be seen in Fig. 1, our results are in excellent agreement with the more recent studies. Table 1 lists values of the absorption cross-sections measured in this work together with other literature values. The data at 228.8 nm is in good agreement with a somewhat larger variance in the data reported at 213.9 nm. There have been no prior reports of high-resolution spectra of d_6-DMS. McDiarmid [4] tabulated observations of isotopic shifts but did not publish a spectrum of d_6-DMS. More recently, Martínez-Haya et al. [11] reported a low-resolution spectrum but no cross-section data. Our results are consistent with these studies. The structure in our high-resolution spectrum is much more pronounced than the low-resolution spectrum of Martínez-Haya et al. [11] and the zero-point isotopic shift, 213 cm^{-1}, is in good agreement with the value reported by McDiarmid [4]. The absolute value of the absorption cross-sections for both isotopomers is identical within experimental error at the peak corresponding to the (0–0) band.

The studies on the photodissociation dynamics of h_6-DMS and d_6-DMS have been performed at several wavelengths between 220.0 and 231.0 nm and suggest that photodissociation is prompt with most of the available energy being disposed into photofragment translation and thus producing relatively cold methyl and methylsulfenyl radicals. This suggests that the quantum yield for photodissociation is one and that, in all probability, methyl and methylsulfenyl are produced with a quantum yield of one.

3.2. Spectrum of methylethylsulfide

The spectrum of MES was measured with the static system, deuterium lamp and OMA configuration described in Section 2. Cell pressures of the gas mixture (∼1%) were between 1 and 10 Torr. Optical density at 213.9 and 228.8 nm, when plotted as a function of pressure, was highly linear at both wavelengths and yields the cross-section values reported in Table 1. Separate single line measurements were not performed for MES. The value at 228.8 nm obtained in this work is 15% less than the value reported by Hynes et al. [9] and in good agreement with Tycholiz and Knight [10]. The spectrum obtained by Tycholiz and Knight is shown in Fig. 4 and agrees quite well with our measurement, despite the approximately 0.5 nm shift observed at 221.0 nm.

3.3. Spectrum of diethylsulfide

As noted in Section 2, spectra of DES were obtained using both static and flowing methods. Standard mixtures of DES were made both manometrically, with the partial pressure of DES being calculated from the pressure of DES introduced into the mixing bulb, and using liquid injection. For static measurements, the mixing ratio of DES was ∼1% and cell pressures were 1–10 Torr. This method gives the dotted line shown in Fig. 5. Identical results were obtained using both approaches for preparation of the standard mixture. The static measurement captures structure reported by Hearn et al. [6] but is 5% less in the peak magnitude. Measurements of DPS and DBS cross-sections, discussed in the following sections, revealed that adherence to vessel walls by the larger sulfur compounds was significant, and we concluded this behavior was possible for the lower sulfides. We therefore remeasured the DES cross-section using the same flowing gas method adopted for the measurement of DPS and DBS cross-sections. Mixing ratios were of the order of 35 ppm and were confirmed with GC–FID. Measurements were performed by flowing the gas at 800 Torr total pressure and taking 20 scans with the OMA system. Plots of optical density as a function of wavelength revealed no change in concentration over the duration of the 20 scans. The solid line in Fig. 5 is an average of the measurements using three separate bulb mixtures. It can be seen that agreement at 228.8 nm is good between the two methods we employed and the study of Hearn et al. [6]; however, a discrepancy of about 20% is apparent at the peak of absorption. We believe this is due in part to some

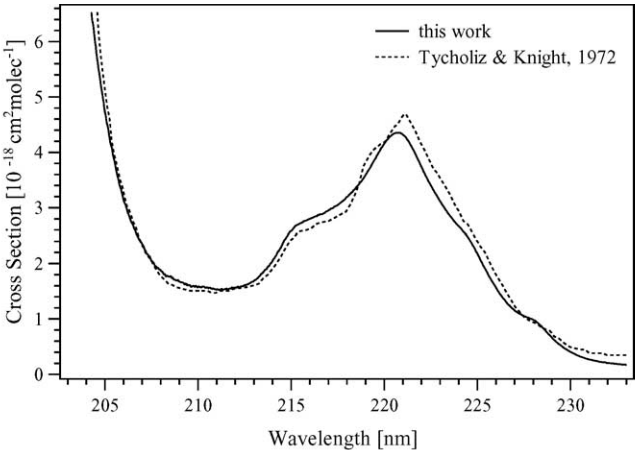

Fig. 4. Spectrum of methylethylsulfide obtained in this work shown with the spectrum of Tycholiz and Knight.

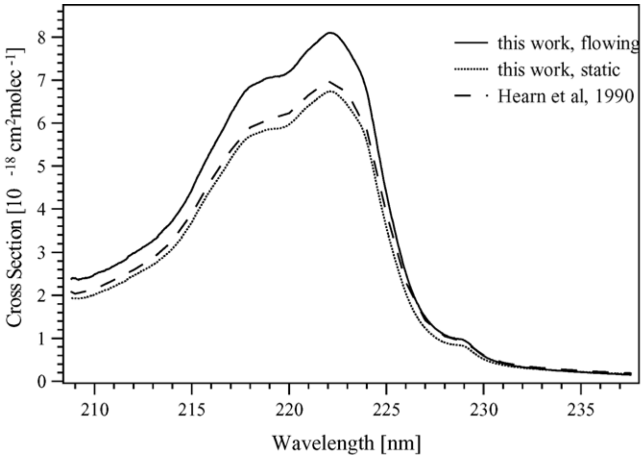

Fig. 5. Spectra of diethylsulfide obtained in this work using a static measurement (dotted line) and flowing measurement (solid line). Data from Hearn et al. (dashed line) is shown for comparison.

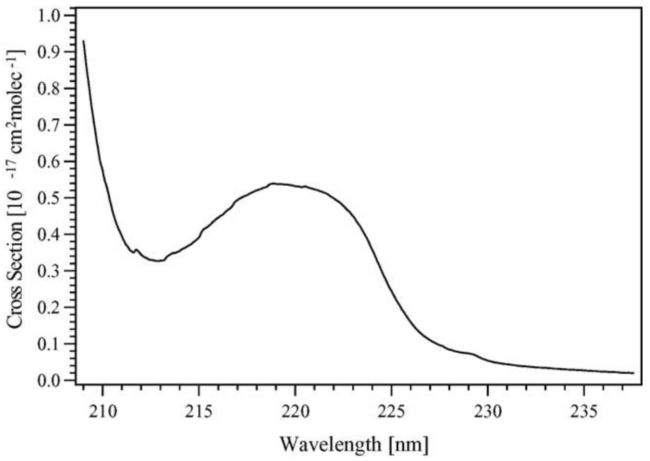

Fig. 6. Spectrum of dipropylsulfide obtained in this work.

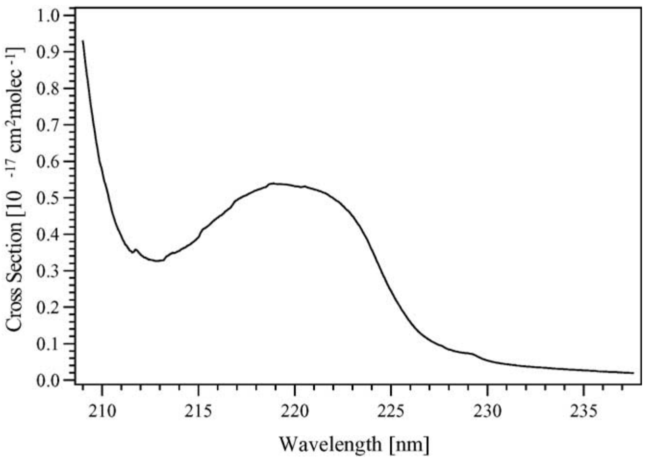

Fig. 7. Spectrum of dibutylsulfide obtained in this work.

loss of sulfide to the cell walls, cell windows, or bulbs, in our static measurement and possibly in the measurement of Hearn et al., resulting in an over-estimate of the concentration of sulfide in the cell and thus, an underestimate of the cross-section. The values given in Table 1 are based on the flowing measurements.

3.4. Spectra of dipropylsulfide and dibutylsulfide

Multiple attempts were made to measure the cross-section of DPS. The low vapor pressure of DPS precluded gas phase bulb mixtures of the order of 12,000 ppm (typical bulb mixing ratios in the laboratory for measurement of h_6-DMS, d_6-DMS, MES and DES). When the mixtures of DPS in Argon were let into the UV absorption cell, the pressure was observed to drop and then slowly rise, eventually stabilizing, suggesting the establishment of equilibrium between DPS on the walls and in the gas phase, similar to behavior previously observed for DMSO [12]. Due to the tendency of DPS to adhere to vessel walls, a flowing system with low sulfide concentration was employed with mixing ratios of the order of 35 ppm. The concentration in the bulb was measured by GC/FID. The concentration measurement in the bulb is made after, we believe, equilibration has been established. Hence, the partitioning between the wall and gas phase concentrations has reached a steady state, lessening error introduced by adherence to the bulb/cell/tube walls. Plots of optical density as a function of wavelength for all 20 scans in the measurement, showed very little variation, confirming a steady concentration over the 20 min course of the measurement. This method yields spectra with high reproducibility in the shape and moderate discrepancy in the absolute, peak magnitude. We believe this is due to our inability to completely suppress wall effects both in the system and in the bulb. Spectra were measured for three bulbs of DPS and the absorption cross-section shown in Fig. 6 is the average of the three individual determinations. The variance between the measurements is considerably larger than that observed for the smaller sulfides and this is reflected in the error we report for our single line cross-section values used in kinetic measurements. Spectra of DBS were obtained using an identical procedure to that used for DPS. The spectrum shown in Fig. 7 is the average of measurements on two different DBS bulbs. Cross-section values at 213.9 and 228.8 nm are listed in Table 1 and it can be seen that the cross-sections at 228.8 nm are significantly lower than those of the smaller sulfides making 213.9 nm the optimum wavelength for photometry.

3.5. Comparison of sulfide cross-sections

The alkyl sulfide absorption cross-sections reported in this work are shown in Fig. 8 and reveal a progression from h_6-DMS and d_6-DMS which have the lowest cross-sections and a clear, if somewhat diffuse vibrational structure, to larger cross-sections with less evidence of structure for MES and DES as the number of low frequency vibrations increases with the increased length of the carbon chains. For DBS and

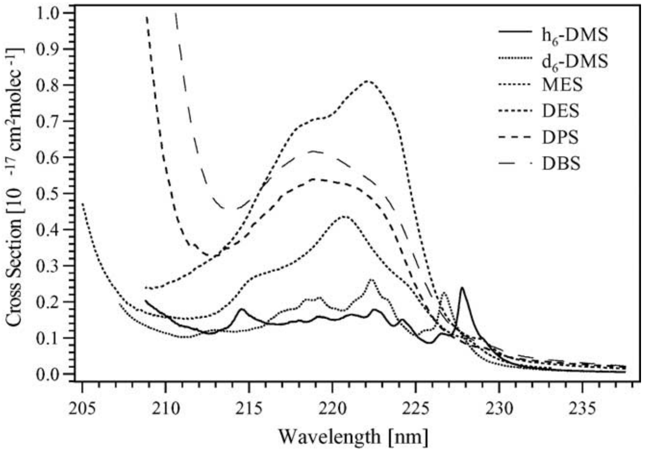

Fig. 8. Spectra of all alkyl sulfides measured in this work.

DPS, the trend in the cross-sections then reverses with values that are lower than observed for DES. The onset of absorption is also blue shifted as the chain length increases from one to four carbons.

4. Conclusions

High-resolution absorption cross-sections of a series of alkyl sulfides are presented, including the first reported absorption cross-sections for d_6-DMS, DPS and DBS. For h_6-DMS, our results are in excellent agreement with recent work of Limão-Vieira et al. both in the shape and absolute magnitude of the cross-sections. These results reduce the uncertainties in the absorption cross-sections of the lower sulfides and present values that should enable absolute concentrations of these sulfides to be reliably measured using photometry. In addition, they suggest these compounds are useful photolytic precursors for alkyl and alkylsulfenyl radicals using the fifth harmonic photolysis at 213.9 nm.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.photochem.2004.09.008.

References

[1] R.J. Charlson, J.E. Lovelock, M.O. Andreae, S.G. Warren, Nature 326 (1987) 655–661.
[2] S.D. Thompson, D.G. Carroll, F. Watson, F. O'Donnell, S.P. McGlynn, J. Chem. Phys. 45 (5) (1966) 1367–1379.
[3] J.D. Scott, G.C. Causley, B.R. Russell, J. Chem. Phys. 59 (12) (1973) 6577–6586.
[4] R. McDiarmid, J. Chem. Phys. 61 (1) (1974) 274–281.
[5] I. Tokue, A. Hiraya, K. Shobatake, Chem. Phys. 130 (1–3) (1989) 401–408.
[6] C.H. Hearn, E. Turcu, J.A. Joens, Atmos. Environ. 24A (7) (1990) 1939–1944.
[7] P. Limão-Vieira, S. Eden, P.A. Kendall, N.J. Mason, S.V. Hoffman, Chem. Phys. Lett. 366 (2002) 343–349.
[8] S.B. Barone, A.A. Tunipseed, A.R. Ravishankara, J. Phys. Chem. 100 (1996) 14694–14702.
[9] A.J. Hynes, P.H. Wine, D.H. Semmes, J. Phys. Chem. 90 (17) (1986) 4148–4156.
[10] D.R. Tycholiz, A.R. Knight, Can. J. Chem. 50 (11) (1972) 1734.
[11] B. Martínez-Haya, P. Quintana, L. Banares, P. Samartzis, D.J. Smith, T.N. Kitsopoulos, J. Chem. Phys. 114 (10) (2001) 4450–4456.
[12] A.J. Hynes, P.H. Wine, J. Atmos. Chem. 24 (1) (1996) 23–37.