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Gas-phase ultraviolet absorption cross-sections and atmospheric lifetimes of several C_2–C_5 alkyl nitrates

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Abstract

Gas-phase ultraviolet absorption cross-sections of ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate have been measured over the wavelength range 220–340 nm using a dual-beam, diode array spectrometer. Each alkyl nitrate spectrum appears to be the sum of at least two Gaussian-shaped absorptions with an intense π–π^* band extending from 190–240 nm having a shoulder between 250–340 nm due to a n–π^* system. The absorption cross-sections recorded for ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate and 1-butyl nitrate are within 10% of previous data: those of 2-methyl, 1-propyl nitrate and 1-pentyl nitrate have been measured for the first time. For ethyl nitrate, absorption cross-sections between 280–340 nm in the tail of the near-ultraviolet band declined with decreasing temperature from 298–233 K. A two-dimensional numerical model of tropospheric chemistry was used to calculate atmospheric lifetimes with respect to photodissociation and OH radical reaction that are markedly dependent on season, latitude and altitude. Relatively long, surface level atmospheric lifetimes of several days to weeks confirm that the C_2–C_5 alkyl nitrates may act as temporary reservoirs for NO_x and suggest that they may also constitute a significant fraction of total reactive odd-nitrogen, NO_y, particularly during winter at northern hemisphere high latitudes.

Keywords: Absorption cross-sections; Atmospheric lifetimes; Alkyl nitrates; NO_x reservoir species; NO_y component

1. Introduction

Alkyl nitrates, $RONO_2$, are minor products of the OH radical initiated oxidation of alkane hydrocarbons, but play an important role in tropospheric chemistry by coupling the carbon and nitrogen cycles. They are formed in a minor channel of the reaction of alkyl peroxy radicals, RO_2, with NO via a mechanism that occurs most efficiently for secondary RO_2 with increasing C-number at low temperature and high pressure [1]:

$$RO_2 + NO \rightarrow RO + NO_2 \quad (1a)$$

$$\rightarrow [ROONO]^* \rightarrow RONO_2 \quad (1b)$$

Alkyl nitrates have relatively long atmospheric lifetimes that are of the order of several days or weeks [1]. They may therefore behave as reservoirs for reactive nitrogen and promote tropospheric ozone production in a similar manner to PAN (peroxyacetyl nitrate, $CH_3C(O)_2ONO_2$) [2], by undergoing long-range transport in the free-troposphere before decomposing to release NO_x ($NO+NO_2$) in regions remote from their formation [3]. Indeed C_2–C_5 alkyl nitrates are widespread throughout the troposphere and typically account for about 1–2% of the measured total reactive odd-nitrogen species, NO_y [4–10].

Thermal decomposition to $CH_3C(O)O_2$ and NO_2 is the major atmospheric loss process for PAN, which has a lifetime of between about 80 min and 80 h at altitudes up to 5 km [11]. Many C_2–C_5 alkyl nitrates, however, are thermally stable [1,12]. They possess a low aqueous solubility [13] and react slowly with OH radicals [14–17], which apparently occurs by both H-atom abstraction and OH radical addition [16]. Based upon gas-phase ultraviolet absorption cross-sections determined with relatively short optical pathlengths of 10 cm at room temperature [18,19] and direct measurements

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of their photolysis rate coefficients [20,21], the dominant decomposition pathway for the C_1–C_5 alkyl nitrates throughout the atmosphere is believed to be photodissociation to produce NO_2 with a quantum-yield of unity :

$$RONO_2 + h\nu \rightarrow RO + NO_2 \quad (\lambda = 220\text{–}340\ \mathrm{nm}) \qquad (2)$$

Reported here are measurements of gas-phase ultraviolet absorption cross-sections of several primary and secondary C_2–C_5 alkyl nitrates: ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate. The measurements were made at 294 K with an optical pathlength of 1 m in the wavelength region 220–340 nm, and for ethyl nitrate, over the temperature range 233–298 K. This study was carried out in an attempt to provide more accurate measurements in the spectral region of the weak, near-ultraviolet absorption tail important for atmospheric photodissociation, and to extend the previous data [18,19] to temperatures characteristic of the free-troposphere and lower stratosphere. A two-dimensional numerical model [22] has been used to calculate atmospheric lifetimes of the alkyl nitrates with respect to photodissociation and OH radical reaction as a function of season, latitude and altitude using the absorption cross-sections determined in this work and previously published kinetics data [14,15,17].

2. Experimental details

Absorption cross-section measurements of several C_2–C_5 alkyl nitrates were made between 220–340 nm at 294 K, and for ethyl nitrate over the temperature range 233–298 K, using a 1 m long, jacketed quartz cell coupled to a dual-beam, diode array spectrometer which has been described in detail previously [23]. The temperature of the cell was lowered by circulating cooled ethanol through the jacket from a circulator/cooler unit (Statim). Evacuated, double end-window assemblies prevented condensation on the optical faces. The alkyl nitrates were introduced into the sample cell from a mercury-free, Pyrex glass vacuum-line fitted with greaseless taps (Young and Co.). Gas pressures were measured with calibrated capacitance manometers (MKS Baratron, 0–100 Torr, model 222 A; 0–1000 Torr, model 122 AA).

A well-collimated beam from a 30 W deuterium lamp (Hamamatsu, model L1636) passed through a beam splitter (Oriel Scientific, model 78150) and the resultant dual beams were collected in fibre-optic couplers, either directly (reference beam), or after passage through the cell (sample beam). Both beams were directed, one above the other, into the 100 μm wide inlet slit of a 275 mm Czerney–Turner spectrograph (ARC, "Spectropro") using a fibre-optic adapter (Princeton Instrument Co., model OFA X1S). The spectrometer detector comprised a 600 groove mm^{-1} indexable holograph grating dispersed over two 512 channel, unintensified silicon diode arrays (Reticon). Each diode array had a range of about 75 nm and was mounted at the focal plane of the spectrograph in an evacuated housing cooled to 233 K. Measurements were made at a spectral resolution of approximately 0.6 nm (full width at half maximum) from 200–275 nm and 269–344 nm. Absorbances were normalised in the region of overlap and the data averaged to produce a complete spectrum which was used in the modelling calculations described below. For measurements at wavelengths greater than 300 nm, a Pyrex glass filter was mounted in the monitoring beam to prevent higher order radiation from reaching the detector. The detector function was controlled with a Spectroscopy Instruments model SI-180 O-SMA detector controller, which incorporated a 14-bit analogue to digital converter and was coupled to a Dell 316 SX desktop computer.

Spectroscopy Instruments POSMA software was used for wavelength calibration and linearisation, background subtraction and averaging of the data, and for calculations of absorbance using reference spectra to correct for changes in the deuterium source lamp intensity. Wavelength calibrations were carried out to within 0.15 nm using Hg, Zn and Cd emission lines from a Philips 93145 Spectral lamp with a spectrograph entrance slit width of 10 μm. The major limitation on the accuracy of absorption cross-section measurements for the continuous, broad-band spectra of the C_2–C_5 alkyl nitrates was baseline drift which affected measurements at the 0.0005 absorbance level, corresponding to cross-sections of approximately $1\text{–}3 \times 10^{-23}\ \mathrm{cm^2\ molecule^{-1}}$.

2-methyl, 1-propyl nitrate (Fluka, stated purity > 98%) and 2-propyl nitrate (Aldrich, stated purity 99%) were thoroughly degassed at 273 K following confirmation of their structure and purity by ^1H nuclear magnetic resonance (Jeol PMX60SI, 60 MHz) and Fourier transform infrared spectroscopy (Mattson Polaris, 1 cm^{-1} resolution). Ethyl nitrate, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate were synthesised by low-temperature (273–278 K) nitration of ethanol (Aldrich, stated purity 95%), propan-1-ol (Aldrich, stated purity 99%), butan-1-ol, (Aldrich, stated purity 99%) and pentan-1-ol, (Aldrich, stated purity 99%), respectively, using a procedure based on that of Boschan et al. [24]. Nitrogen (BOC, stated purity 99.99%) was bubbled through a stirred 50:50 v/v mixture of nitric acid (BDH, Analar, stated purity 95%) and sulphuric acid (BDH, Aristar, stated purity 98%) at 273 K, before and during the slow dropwise addition of the alcohol. The alkyl nitrate products were separated, thoroughly washed with deionised, distilled water at 273 K to remove unreacted acids, dried with anhydrous magnesium sulphate (Aldrich, stated purity 99%), filtered through BDH 5 μm filter paper and stored in the dark at 263 K. Gas-phase ultraviolet absorption cross-sections were recorded after structural and purity confirmation and degassing as above: NO_2 and HNO_3 were not observable in any spectra.

3. Results and discussion

3.1. Ultraviolet absorption spectra

Ultraviolet absorption spectra of 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate and 1-butyl nitrate were

Table 1
Absorption cross-sections between 220 and 340 nm for ethyl nitrate at 298 K and for 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate at 294 K

Wavelength/nm	Absorption cross-section, $\sigma/10^{-20}$ cm^2 molecule^{-1}					
	Ethyl nitrate	1-Propyl nitrate	2-Propyl nitrate	2-Methyl, 1-propyl nitrate	1-Butyl nitrate	1-Pentyl nitrate
220		95.0	132.1	103.3	97.2	
225		43.7	64.9	54.9	52.9	
230		25.5	37.4	30.7	28.7	
235	10.87	14.4	17.8	16.2	15.4	
240	6.98	8.68	10.0	9.65	8.69	
245	4.96	5.59	6.74	6.67	5.74	
250	4.12	4.39	4.90	5.17	4.46	
255	3.78	3.89	4.47	4.17	4.09	
260	3.54	3.51	4.17	4.07	3.86	
265	3.25	3.16	3.90	3.69	3.57	
270	2.89	2.88	3.41	3.22	3.17	3.28
275	2.48	2.48	2.94	2.77	2.71	2.76
280	2.02	2.03	2.38	2.26	2.20	2.30
285	1.58	1.57	1.88	1.76	1.71	1.80
290	1.16	1.13	1.42	1.28	1.25	1.31
295	0.829	0.800	1.02	0.903	0.862	0.911
300	0.548	0.545	0.685	0.592	0.563	0.611
305	0.336	0.317	0.436	0.360	0.343	0.388
310	0.192	0.184	0.259	0.211	0.200	0.232
315	0.106	0.102	0.149	0.120	0.109	0.129
320	0.0526	0.0536	0.0784	0.0667	0.0571	0.0676
325	0.0241	0.0306	0.0422	0.0362	0.0313	0.0390
330	0.0117	0.0221	0.0238	0.0234	0.0212	0.0250
335	0.0046	0.0176	0.0126	0.0157	0.0156	0.0174
340	0.0030	0.0159	0.0065	0.0113	0.0127	0.0131

measured at 294 K between 200–275 nm and 269–344 nm: those of ethyl nitrate were recorded above 220 nm between 233–298 K, while data for 1-pentyl nitrate was measured above 269 nm. At least 5 spectra were recorded for a range of sample pressures in each region, with the data averaged to produce absorption cross-sections at 0.15 nm intervals. In the shorter wavelength region, the accuracy of the absorption cross-sections was limited by difficulties in measuring the low partial pressures required because of the very large optical absorbances of the samples. Conversely, measurements in the longer wavelength, lower absorbance region were limited by the maximum vapour pressure exerted by the samples which prevented temperature-dependent measurements for the $C>3$ nitrates. The two spectral regions were combined by normalisation relative to the shorter wavelength section in which more accurate pressure measurements were made. Absorption cross-section measurements are reported between 220–340 nm because in the region below 220 nm poor transmission of the optical fibres limited their accuracy, and at wavelengths greater than 340 nm, residual absorbances were not significantly greater than the baseline drift of ± 0.0005 absorption units. Provided that absorbances were below unity, all measured spectra showed excellent agreement with the Beer–Lambert Law. The standard deviation (1σ) of the cross-section measurements for ethyl nitrate was approximately $\pm 5\%$ for 220–300 nm, increasing to $\pm 50\%$ at 340 nm.

Each alkyl nitrate spectrum appears to be the sum of at least 2 Gaussian-shaped absorptions attributed to π–π^* and n–π^* electronic transitions [25,26]. The maximum of the high-energy π–π^* absorption appears between 190–220 nm, while that of the low-energy n–π^* absorption lies between 250–270 nm in each case. Results obtained at 298 K for ethyl nitrate ($CH_3CH_2ONO_2$) and at 294 K for 1-propyl nitrate ($CH_3CH_2CH_2ONO_2$), 2-propyl nitrate ($CH_3CH_2(ONO_2)$-CH_3), 2-methyl, 1-propyl nitrate ($CH_3CH_2(CH_3)$-CH_2ONO_2), 1-butyl nitrate ($CH_3CH_2CH_2CH_2ONO_2$) and 1-pentyl nitrate ($CH_3CH_2CH_2CH_2CH_2ONO_2$) are listed at 5 nm intervals in Table 1. Comparisons with previous data are made in Figs. 1–4. Table 1 shows that in the region of the n–π^* absorption band at 260 nm the cross-sections are within 10% of each other, and in fact for 2-methyl, 1-propyl nitrate and 1-pentyl nitrate are almost identical. However, in general, an increase in the absorption cross-sections listed in Table 1 is observed with increasing C-chain length and degree of substitution. These effects are non-linear and have been attributed to a combination of stereochemical and electronic influences of the staggered alkyl group on the planar $-ONO_2$ chromophore [25]. The size and structure of the alkyl group changes the O–N–O bond angles while the $-ONO_2$ moiety withdraws electrons and exerts an inductive effect that is most effective over a short range of 2 to 3 C-atoms.

Figs. 1–4 show that the absorption cross-sections reported here for ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate and 1-butyl nitrate, respectively, are within 10% of previous data [18,19,27], although consistently lower than the measurements of Turberg et al. [19], particularly in the near ultraviolet region between 300–340 nm that is most important for

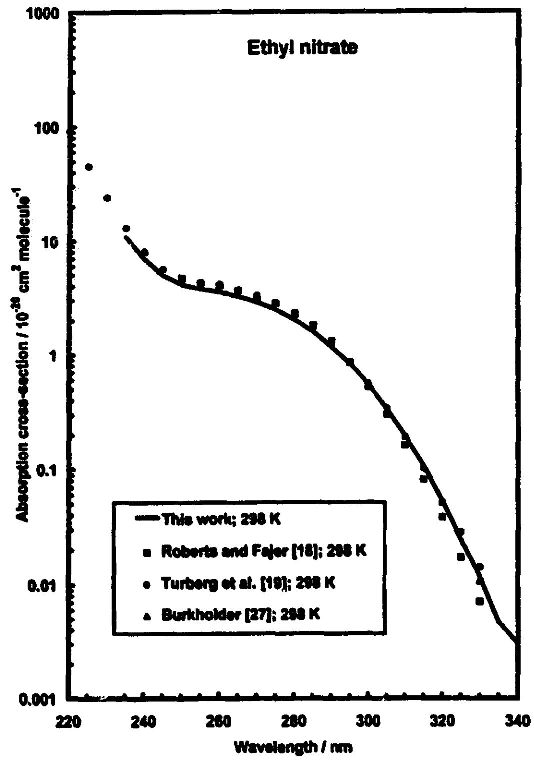

Fig. 1. Comparison of gas-phase, ultraviolet absorption cross-sections of ethyl nitrate recorded in this work between 220–340 nm at 298 K (line) and by Roberts and Fajer [18] (squares), Turberg et al. [19] (circles), and Burkholder [27] (triangles).

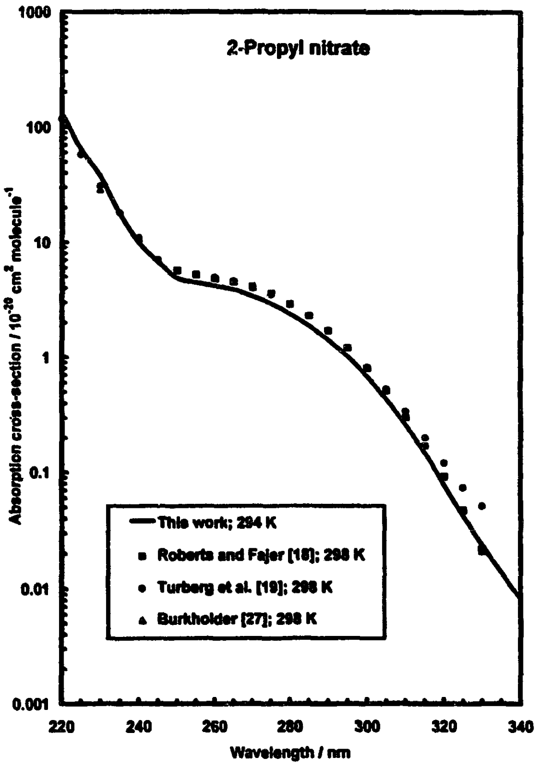

Fig. 3. Comparison of gas-phase, ultraviolet absorption cross-sections of 2-propyl nitrate recorded in this work between 220–340 nm at 294 K (line) and at 298 K by Roberts and Fajer [18] (squares), Turberg et al. [19] (circles) and Burkholder [27] (triangles).

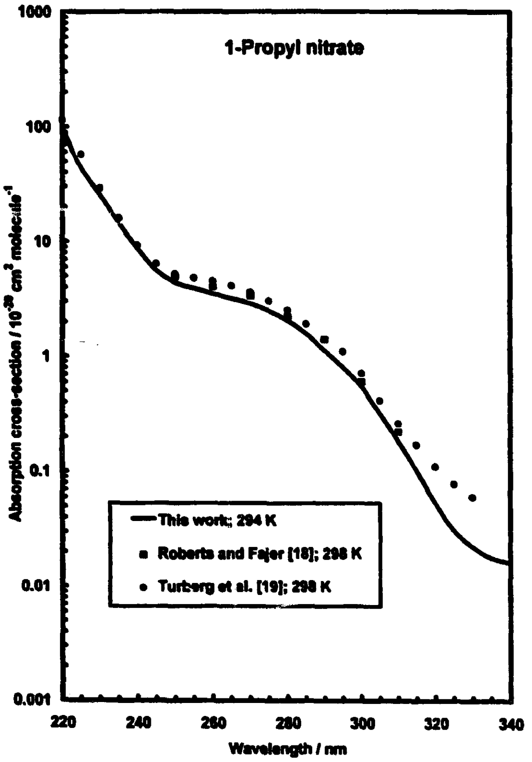

Fig. 2. Comparison of gas-phase, ultraviolet absorption cross-sections of 1-propyl nitrate recorded in this work between 220–340 nm at 294 K (line) and at 298 K by Roberts and Fajer [18] (squares) and Turberg et al. [19] (circles).

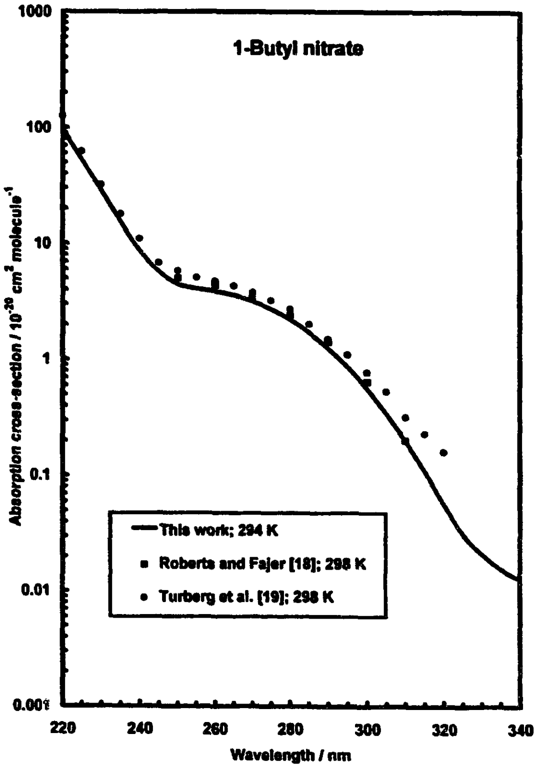

Fig. 4. Comparison of gas-phase, ultraviolet absorption cross-sections of 1-butyl nitrate recorded in this work between 220–340 nm at 294 K (line) and at 298 K by Roberts and Fajer [18] (squares) and Turberg et al. [19] (circles).

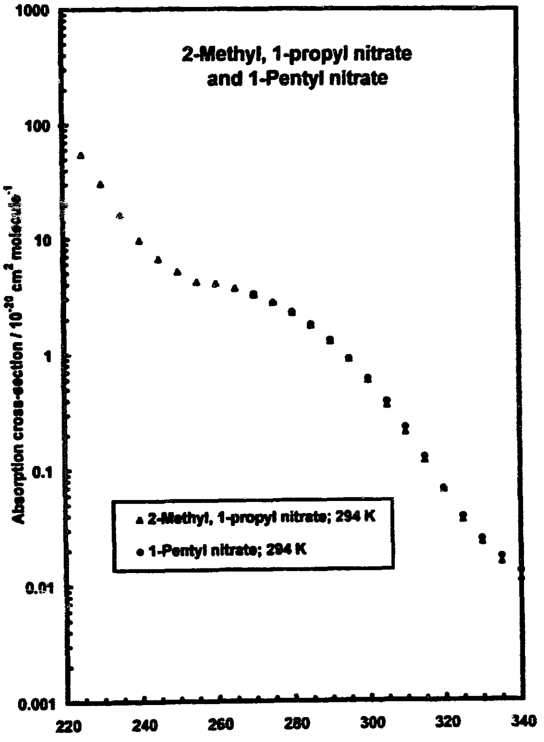

Fig. 5. Comparison of gas-phase, ultraviolet absorption cross-sections of 2-methyl, 1-propyl nitrate recorded in this work between 220–340 nm at 294 K (triangles) with those of 1-pentyl nitrate (circles).

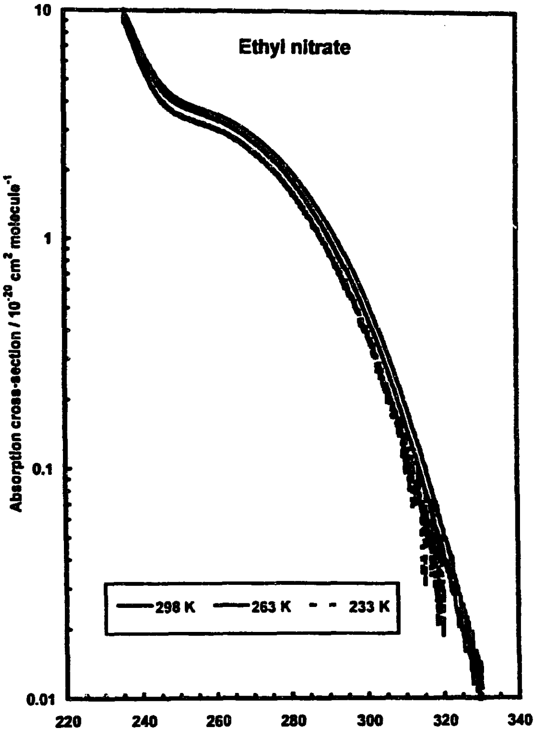

Fig. 6. Gas-phase, ultraviolet absorption cross-sections of ethyl nitrate recorded in this work between 220–340 nm at 298 K (black line), 263 K (grey line) and 233 K (dashed black line).

atmospheric photodissociation. The discrepancy with the data of Turberg et al. worsens with increasing wavelength which is consistent with absorption due to NO_2 [28], and therefore probably reflects the higher purity samples and longer optical pathlength employed in this work. There are no previously reported gas-phase absorption cross-section measurements either for 2-methyl, 1-propyl nitrate or 1-pentyl nitrate with which to compare the data of Table 1 and Fig. 5.

Absorption cross-sections were determined for ethyl nitrate at 298, 273, 263, 253, 243 and 233 K. At 233 K, the relatively low vapour pressure of less than 1 Torr exerted by ethyl nitrate coupled with the small cross-sections limited measurements to 320 nm. Fig. 6 illustrates that the cross-sections decline with decreasing temperature particularly at wavelengths greater than 300 nm where values at 233 K are a factor of 2 less than at 298 K. This behaviour is most apparent in the tail of the near ultraviolet n–π* band and is consistent with a variation with temperature of the population of the vibrational levels of the ground electronic state. According to the Franck–Condon Principle, absorption coefficients are largest when internuclear distances remain unchanged during electronic transitions. Absorption coefficients arising from vertical transitions from high vibrational levels of the ground electronic state to repulsive upper electronic states maximise towards longer wavelengths. Higher ground state vibrational levels become populated with elevated temperatures and therefore the absorption cross-sections of ethyl nitrate increase in the long wavelength tail of the absorption band. Similar temperature-dependent effects have been observed recently for methyl nitrate [23,29] and for several carbonyl compounds [30].

Fig. 7 shows that the temperature dependence of the logarithm of the absorption cross-sections of ethyl nitrate at several wavelengths above 280 nm in the tail of the absorption band is linear. As reported previously for methyl nitrate [23,29], such temperature dependent absorption cross-sections may be parameterised by an equation of the form:

$$\log_{10} \sigma_T = \log_{10} \sigma_{298} + B(T-298) \qquad \text{(i)}$$

where σ_T and σ_{298} are absorption cross-sections at a wavelength λ and at temperatures T and 298 K, respectively, and B is the temperature coefficient or gradient. Eq. (i) was applied to the data of Fig. 7. Table 2 lists B values obtained from linear regression analyses which have been used to extrapolate absorption cross-sections for ethyl nitrate beyond the experimental range of 233–298 K in the calculations of atmospheric lifetimes with respect to photodissociation described below. Table 2 shows that the absorption cross-sections of ethyl nitrate are generally 20% higher than methyl nitrate although, as illustrated in Fig. 8 also, the B values for methyl nitrate are greater than those of ethyl nitrate by approximately 15%. These relatively small differences are not unexpected considering the structural similarities between methyl and ethyl nitrate and the common $-ONO_2$ chromophore responsible for absorption.

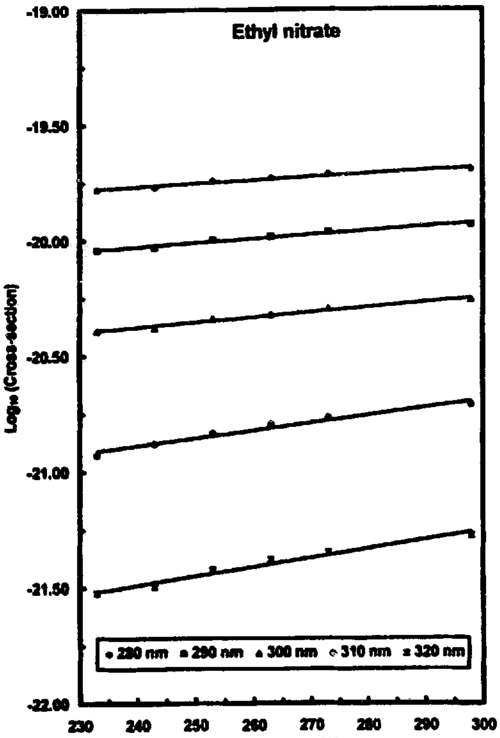

Fig. 7. Temperature dependence of the logarithm of the gas-phase, ultraviolet absorption cross-sections of ethyl nitrate over the temperature range 233–298 K at 280 nm (diamonds), 290 nm (squares), 300 nm (triangles), 310 nm (circles) and 320 nm (stars). The lines represent least squares fits to the data.

3.2. Atmospheric lifetimes with respect to photodissociation and OH radical reaction

Atmospheric photodissociation rate coefficients (J values) for ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate were calculated as a function of season, latitude and altitude using a two-dimensional numerical model [22]. The model employed a two-stream photolysis scheme which included the effects of solar radiation absorption by molecular O_2 and O_3, Rayleigh and aerosol scattering, surface albedo and 3 layers of cloud [22]. Total ozone mapping spectrometer (TOMS) data from 1990 was used for stratospheric O_3 concentrations. J values were calculated by integrating the product of the absorption cross-section, σ, and the solar flux intensity, F, over the absorbing wavelength range, λ:

$$J=\int \sigma(\lambda)F(\lambda)\,\mathrm{d}\lambda \qquad \text{(ii)}$$

As for previous studies [18–21,23,29], a quantum-yield of unity was assumed for the photodissociation process (reaction (2)):

$$\mathrm{RONO_2}+h\nu \rightarrow \mathrm{RO}+\mathrm{NO_2} \qquad (\lambda=220-340\ \mathrm{nm})$$

and the noon-time J values presented in Table 3 therefore represent upper limits.

The 1 January, 65°N data of Table 3 indicate that, at the Earth's surface during winter at northern hemisphere high-latitudes, atmospheric lifetimes with respect to photodisso-

Table 2
Temperature dependence of gas-phase absorption cross-sections of ethyl nitrate and methyl nitrate: 235–340 nm

Wavelength/nm	Ethyl nitrate		Methyl nitrate (Refs. [23,29])	
	$\sigma_{298}/10^{-20}$ cm^2 molecule^{-1} (a)	$B/10^3$ K^{-1} (b)	$\sigma_{294}/10^{-20}$ cm^2 molecule^{-1} (a)	$B/10^3$ K^{-1} (b)
235	10.87	0.60	9.00	
240	6.98	1.00	5.57	
245	4.96	1.13		
250	4.12	1.10	3.68	
255	3.78	1.04		
260	3.54	1.03	3.08	
265	3.25	1.08		
270	2.89	1.18	2.31	1.41
275	2.48	1.27		
280	2.02	1.39	1.55	1.70
285	1.58	1.55		
290	1.16	1.74	0.842	2.00
295	0.829	2.02		
300	0.548	2.10	0.357	2.58
305	0.336	2.61		
310	0.192	3.27	0.155	3.23
315	0.106	3.90		
320	0.0526	3.91	0.0279	6.56
325	0.0241	5.10		
330	0.0117	6.77	0.0052	7.38
335	0.0046	6.94		
340	0.0030			

Intercept (a) and gradient (b) of a plot of $\log_{10}\sigma_T=\log_{10}\sigma_{298}+B(T-298)$.

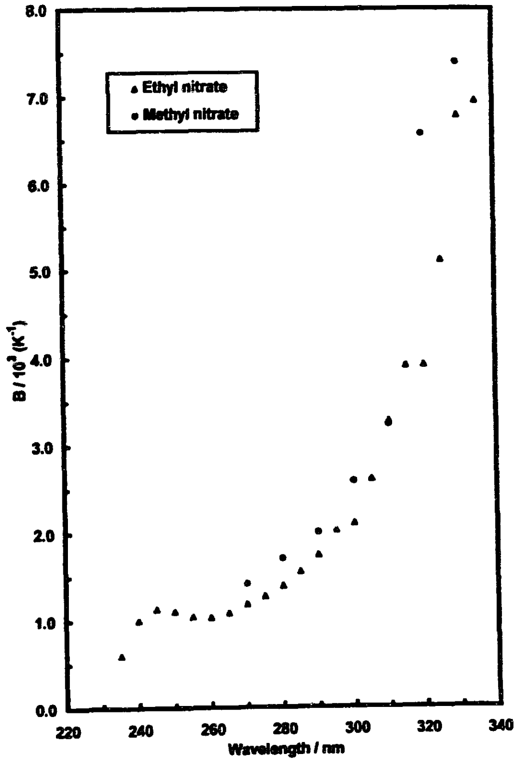

Fig. 8. Wavelength dependence of the temperature coefficients (B values) listed in Table 2 for ethyl nitrate (triangles) and methyl nitrate (circles).

ciation for the C_2–C_5 $RONO_2$ range from 2.4 years for ethyl nitrate to 1.1 years for 2-propyl nitrate, and decrease by 2 orders of magnitude to 17 and 11 days, respectively in summer (1 July). At mid-latitudes (40°N), surface level lifetimes of ethyl nitrate and 2-propyl nitrate are 36 and 20 days, respectively, in winter which reduce to 8 and 5 days in summer. At the equator, surface level $RONO_2$ lifetimes vary little throughout the year with a maximum of 7 days for ethyl nitrate in winter and minimum of 4 days for 2-propyl nitrate in spring (1 April). Table 2 also indicates that at northern hemisphere mid-latitudes in winter, the lifetimes of each alkyl nitrate decreases by a factor of almost 3 and 4 at altitudes of 10 and 20 km, respectively, with values ranging from 12 to 6 days. In summer, lifetimes calculated at 10 and 20 km are approximately 50% of those at ground level, whereas in spring and autumn (1 October) they are reduced by a factor of about 2.4 and 3, respectively. Throughout the year at the equator, lifetimes of 2 to 3 days at 10 and 20 km are approximately half of those at the surface.

Atmospheric loss rates due to reaction with OH radicals were calculated using the Cambridge two-dimensional tropospheric OH field [31,32] as k[OH], where k is the appropriate bimolecular rate coefficient [14,15,17] for reaction (3), as listed in Table 4 and [OH] is the average day-time OH concentration:

$$OH + RONO_2 \rightarrow \text{products} \qquad (3)$$

Table 5 shows that during winter at northern hemisphere high-latitudes, atmospheric lifetimes at the Earth's surface with respect to OH radical reaction range from approximately 53 years for 2-propyl nitrate to 6 years for 1-pentyl nitrate, which decrease to 53 days and 7 days, respectively in summer. At mid-latitudes, winter surface level lifetimes range from 159 to 20 days for 2-propyl nitrate and 1-pentyl nitrate, respectively, which reduce to approximately 14 and 2 days in summer and autumn. At the equator, the lifetimes are

Table 3
Summary of photodissociation rate coefficients for ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate calculated as a function of season, latitude and altitude in units of 10^{-7} s^{-1}

Compound	Altitude/km	1 January (Winter)			1 April (Spring)			1 July (Summer)			1 October (Autumn)		
		65°N	40°N	0°	65°N	40°N	0°	65°N	40°N	0°	65°N	40°N	0°
Ethyl nitrate	0	0.13	3.25	16.6	6.12	9.35	18.8	6.77	14.5	16.5	6.67	10.2	18.5
	10	0.21	9.61	33.3	8.74	21.9	38.4	15.2	29.1	33.1	9.74	24.4	38.1
	20	0.23	14.6	33.9	9.78	25.9	38.9	17.4	30.2	33.8	10.6	28.1	38.7
1-Propyl nitrate	0	0.21	4.27	17.5	7.75	10.5	19.6	7.69	15.6	17.3	8.27	11.2	19.4
	10	0.35	12.1	34.5	10.9	24.1	39.7	17.1	30.5	33.9	11.9	26.3	39.4
	20	0.39	15.6	36.9	12.1	27.7	40.2	19.5	32.1	36.5	12.9	29.6	39.9
2-Propyl nitrate	0	0.28	5.83	24.1	10.5	14.4	27.0	10.6	22.1	23.9	11.2	15.4	26.7
	10	0.46	16.7	47.3	14.8	33.2	53.7	23.5	43.7	47.1	16.1	36.2	53.3
	20	0.50	22.4	47.9	16.5	38.0	54.4	26.9	44.5	47.7	17.7	40.8	54.2
2-Methyl propyl nitrate	0	0.24	4.98	20.3	9.61	12.1	22.7	9.72	18.2	20.1	10.3	12.7	22.9
	10	0.41	14.5	39.8	13.4	27.9	45.2	20.3	35.8	39.6	14.6	30.5	44.7
	20	0.44	20.5	40.3	14.9	32.0	45.9	23.9	36.6	39.9	16.0	33.4	45.3
1-Butyl nitrate	0	0.24	4.46	18.5	9.02	11.0	20.7	9.05	16.3	18.2	9.3	11.3	20.3
	10	0.41	13.1	37.0	12.7	26.0	42.0	19.9	32.4	36.8	13.1	26.8	41.5
	20	0.44	19.7	37.4	14.1	29.7	42.6	22.7	34.0	37.1	14.7	31.1	31.2
1-Pentyl nitrate	0	0.25	5.30	21.7	10.0	13.0	24.4	10.0	19.6	21.5	10.7	13.5	24.0
	10	0.42	15.0	42.6	13.9	29.9	48.4	21.1	38.3	42.4	15.0	31.7	47.8
	20	0.45	20.9	42.9	15.6	34.0	48.7	24.6	39.5	42.8	16.4	36.2	48.5

Table 4

Summary of rate coefficients used to calculate atmospheric lifetimes with respect to reaction with OH radicals for ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate. Values are at 298 K unless a temperature dependence is specified

Compound	OH radical rate coefficient k/cm^3 molecule s^{-1}	Reference
Ethyl nitrate	$4.69\times10^{-14}\exp(716/T)$	Nielsen et al. [15]
1-Propyl nitrate	$5.03\times10^{-13}\exp(140/T)$	Nielsen et al. [15]
2-Propyl nitrate	4.10×10^{-13}	Atkinson et al. [17]
2-Methyl, 1-propyl nitrate	1.63×10^{-12}	Becker and Wirtz [14]
1-Butyl nitrate	1.74×10^{-12}	Nielsen et al. [15]
1-Pentyl nitrate	3.32×10^{-12}	Nielsen et al. [15]

Table 5

Summary of rates of reaction with OH radicals for ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate calculated as a function of season, latitude and altitude in units of 10^{-7} s^{-1}

Compound	Altitude/km	1 January (Winter)			1 April (Spring)			1 July (Summer)			1 October (Autumn)		
		65°N	40°N	0°	65°N	40°N	0°	65°N	40°N	0°	65°N	40°N	0°
Ethyl nitrate	0	0.01	1.06	6.42	0.23	4.15	7.63	3.19	11.4	9.12	1.57	11.0	8.27
	10	0.06	1.76	8.26	0.39	3.90	9.24	2.05	4.59	6.33	0.70	2.27	7.54
	20	0.07	1.01	9.08	0.56	2.17	10.7	3.14	4.60	8.45	1.49	4.20	8.91
1-Propyl nitrate	0	0.01	1.47	10.1	0.29	5.74	12.0	4.40	16.9	14.4	2.04	16.4	13.0
	10	0.05	1.41	7.91	0.31	3.10	8.88	1.76	4.10	6.09	0.55	2.06	7.21
	20	0.05	0.74	5.89	0.45	1.62	6.81	2.70	3.47	5.63	1.13	3.13	6.07
2-Propyl nitrate	0	0.006	0.73	5.17	0.14	2.85	6.11	2.18	8.53	7.34	1.00	8.28	6.64
	10	0.020	0.62	3.59	0.14	1.34	4.03	0.75	1.83	2.76	0.24	0.92	3.27
	20	0.024	0.31	2.43	0.19	0.89	2.80	1.19	1.48	2.33	0.48	1.33	2.53
2-Methyl, 1-propyl nitrate	0	0.026	2.86	20.5	0.56	11.3	24.3	8.67	33.9	29.2	3.96	32.9	26.4
	10	0.082	2.45	14.3	0.54	5.35	16.0	3.08	7.25	11.0	0.95	3.65	13.0
	20	0.089	1.25	9.67	0.77	2.74	11.1	4.73	5.90	9.28	1.93	5.30	10.0
1-Butyl nitrate	0	0.028	3.08	21.9	0.60	12.1	25.9	9.25	36.2	31.1	4.23	35.1	28.2
	10	0.088	2.61	15.2	0.58	5.71	17.1	3.29	7.74	11.7	1.02	3.90	13.9
	20	0.095	1.33	10.3	0.82	2.92	11.9	5.05	6.30	9.90	2.05	5.66	10.8
1-Pentyl nitrate	0	0.05	5.88	41.8	1.14	23.0	49.5	17.6	69.1	59.4	8.07	67.1	53.8
	10	0.17	4.98	29.1	1.10	10.9	32.6	6.27	14.8	22.4	1.94	7.44	26.5
	20	0.18	2.54	19.7	1.57	5.58	22.6	9.63	12.0	18.9	3.92	10.8	20.5

similar throughout the year with a maximum of 22 days for 2-propyl nitrate in winter and a minimum of 2 days for 1-pentyl nitrate in summer. Table 5 also shows that at northern hemisphere mid-latitudes in winter, the lifetimes of each alkyl nitrate except ethyl nitrate, increase by factors of between 2 and 3 at 20 km, with values ranging from 1 year for 2-propyl nitrate to 46 days for 1-pentyl nitrate. In summer, lifetimes calculated at 10 and 20 km are approximately 5 to 6 times longer than those at ground level, whereas in spring and autumn they are increased by a factor of almost 4 and 6, respectively. Throughout the year at the equator, lifetimes that range from 50 to 4 days at 10 and 20 km are approximately 2 and 3 times greater than those at the surface.

Fig. 9 compares the calculated winter and summer lifetimes of the C_2–C_5 alkyl nitrates with respect to photodissociation and OH radical reaction as a function of altitude and latitude. Fig. 9 shows that at altitudes of 10 and 20 km for each alkyl nitrate studied, atmospheric removal by photodissociation dominates that by reaction with OH radicals. However, for some of the larger alkyl nitrates in summer, surface loss rates due to reaction with OH are comparable to, and even exceed loss rates due to photodissociation. At northern mid-latitudes in winter, surface level lifetimes of the C_2–C_5 alkyl nitrates vary from 36 days for ethyl nitrate to 20 days for 2-propyl nitrate and 1-pentyl nitrate, which decrease to 8 days and 5 and 2 days, respectively, in summer. These relatively long lifetimes suggest that the C_2–C_5 alkyl nitrates will undergo extensive long-range transport in the northern hemisphere free-troposphere, and may therefore comprise a significant proportion of the budget of reactive odd-nitrogen, NO_y, particularly during winter at high-latitudes.

Evidence that confirms the long-range transport of C_3–C_5 alkyl nitrates and quantifies their contribution to the NO_y budget as less than 2% is provided by Atlas et al. [7]. Observations of a significant correlation between 2-propyl nitrate and propane, and branched-chain alkyl nitrates in excess of their straight chain isomers support their formation in the atmosphere via reaction (1b) which favours secondary RO_2

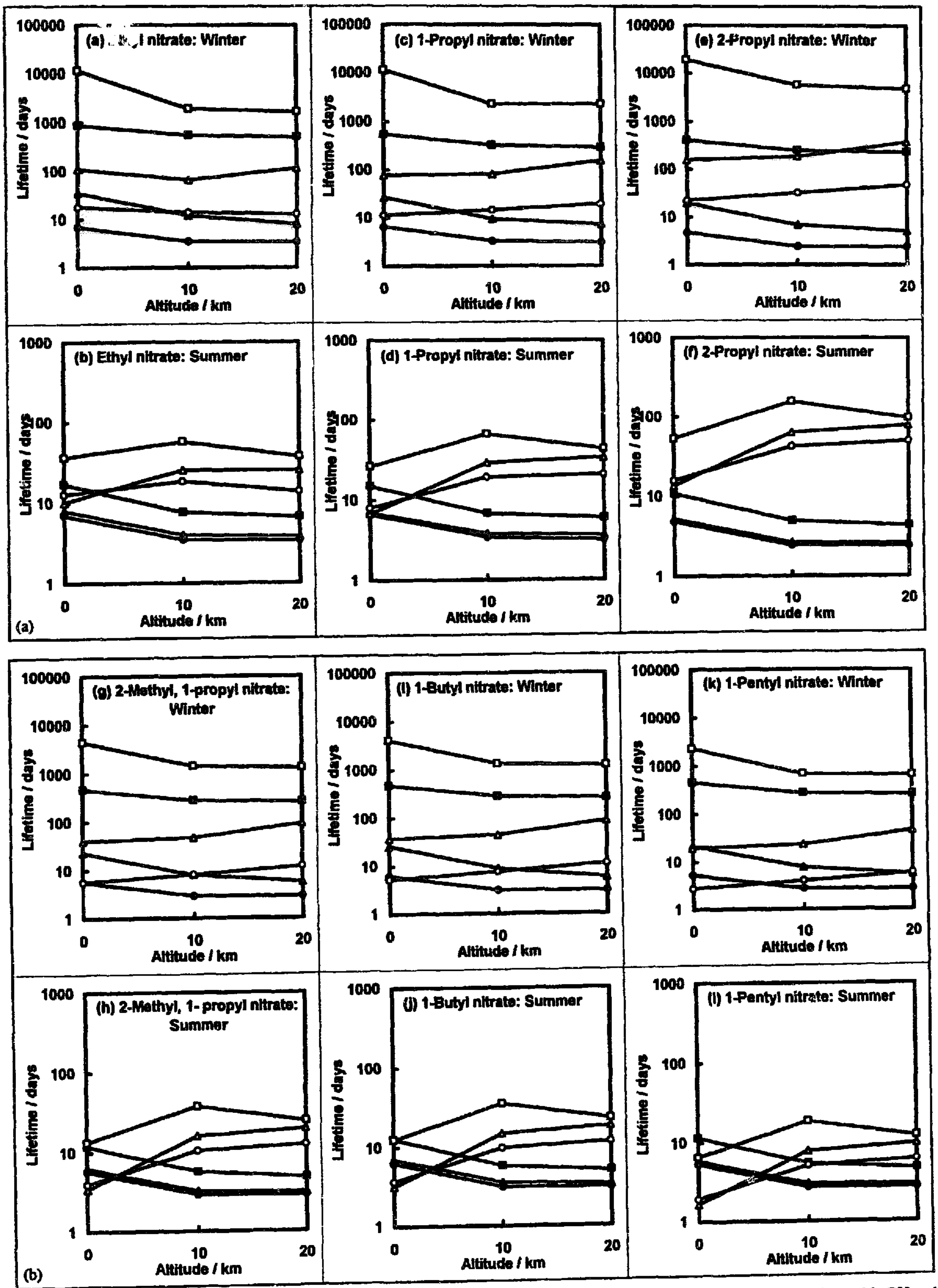

Fig. 9. Calculated atmospheric lifetimes for C_2–C_5 alkyl nitrates with respect to photodissociation (black symbols) and reaction with OH radicals (white symbols) as a function of season, altitude and latitude: 65°N (squares), 40°N (triangles) and 0°N (circles).

with increasing C-number [1]. Several other studies confirm that the C_3–C_5 alkyl nitrates typically comprise approximately 1–2% of NO_y but do not account fully for the deficit between NO_y and the sum of the major individual components of NO_y, ie NO, NO_2, HNO_3, NO_3^- and PAN [4–8]. Arctic air masses provide an important exception in which alkyl nitrates may comprise up to about 20% of NO_y [9]. Although higher branched-chain alkyl nitrates may be formed in increasing fractional yield via reaction (1b), Tables 1 and 4 predict increases in both their ultraviolet absorption cross-sections and rate coefficients for reaction with OH radicals. Consequently higher branched-chain alkyl nitrates are expected to possess atmospheric lifetimes relatively shorter than the C_1–C_5 alkyl nitrates. However, multi-functional organic nitrates produced upon the oxidation of alkenes by OH and NO_3 radicals [33] may contribute significantly to the NO_y deficit, particularly isoprene nitrates [8,10].

4. Conclusions

Gas-phase ultraviolet absorption cross-sections of ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate, 2-methyl, 1-propyl nitrate, 1-butyl nitrate and 1-pentyl nitrate have been measured over the wavelength range 220–340 nm. Each spectrum exhibits a π–π^* absorption with a maximum between 190–220 nm and a n–π^* band appearing as a shoulder at 250–270 nm. Absorption cross-sections recorded for ethyl nitrate, 1-propyl nitrate, 2-propyl nitrate and 1-butyl nitrate are within 10% of previous data: those of 2-methyl, 1-propyl nitrate and 1-pentyl nitrate have been measured for the first time. For ethyl nitrate, cross-sections in the tail of the near ultraviolet band declined with decreasing temperature according to an equation of the form: $\log_{10}\sigma_T = \log_{10}\sigma_{298} + B(T-298)$. A two-dimensional numerical model of tropospheric chemistry was used to calculate atmospheric lifetimes with respect to photodissociation and OH radical reaction that are markedly dependent on season, latitude and altitude. Relatively long atmospheric lifetimes of several days to weeks confirm that the C_2–C_5 alkyl nitrates may act as temporary reservoirs for NO_x and suggest that they may also constitute a significant fraction of NO_y, particularly during winter at northern hemisphere high-latitudes.

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