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UV absorption cross-sections of a series of vinyl ethers

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ABSTRACT

UV absorption cross-sections of six vinyl ethers (ethyl vinyl ether, 1,4-butanediol divinyl ether, isobutyl vinyl ether, cyclohexyl vinyl ether, 4-hydroxybutylvinyl ether and diethyleneglycol divinyl ether) have been determined in the gas phase between 190 and 230 nm at 303 ± 2 K and pressures up to the corresponding saturation vapor pressures. The main band maxima of the vinyl ethers are below 200 nm with values under 8×10^{-17} cm^2 molecule^{-1}. The absorption vanishes above 225 nm with values of σ smaller than 1×10^{-21} cm^2 molecule^{-1}. Weak, overlaying vibrational progressions with spacings of 1400 cm^{-1} are observed for the alkyl vinyl ethers and are less pronounced for vinyl ethers with an extra O atom. Shifts of the positions and intensities are discussed on the basis of the differences in the chemical structure of this series.

1. Introduction

Replacement of the traditional non-polar solvents by oxygenated compounds has changed the composition of anthropogenic emissions quite recently. Vinyl ethers are such an upcoming group of oxygenated solvents, used in industry for synthetic polymers and manufacturing of paints. These atmospheric contaminants [1–3] motivated studies on their degradation pathways in the troposphere [1,4–6].

UV spectra provide invaluable information about the electronic structure and spectroscopic characteristics of organic molecules. Spectroscopic parameters, such as absorption cross-section, are useful for identifying and quantifying these species in the atmosphere. In this context, the characterization of spectroscopic properties is of considerable interest.

Based on the knowledge of the UV spectrum of methyl vinyl ether (MVE) [7], and on the rapid tropospheric degradation of vinyl ethers and olefinic compounds [1–6] it can be expected that the most important transformation processes of these series of molecules will involve ozone and hydroxyl radicals. However, the precise determination of the UV absorption cross-section of vinyl ethers will reveal a clearer picture of their fate in the atmosphere.

Furthermore, determination of the UV absorption cross-sections is essential to assess the contribution of the photolysis pathway to environmental transformation, degradation and final fate [8,9]. Direct photolysis in the atmosphere becomes a significant degradation pathway only for compounds that absorb light in the range above 290 nm, the edge of the solar actinic spectrum. Therefore, for the organic compounds which do not possess a chromophore able to absorb light above 290 nm, degradation is assumed to proceed mainly by reaction with OH and ozone [8,9].

To the best of our knowledge, no systematic studies of the UV spectra of vinyl ethers exist so far. Spectroscopic characteristics of selected vinyl ethers in the gas phase at 303 ± 2 K and pressures up to the saturation vapor pressures are presented in this work.

2. Materials and methods

All chemicals were provided by BASF AG, Ludwigshafen, Germany, and had the following minimum stated purities: ethyl vinyl ether (EVE, 99.0%), diethyleneglycol divinyl ether (DVE-2, 99.5%, stabilized with 0.01% KOH), 1,4-butanediol divinyl ether (BDDVE, 98.0%), isobutyl vinyl ether (iBVE, 99.0%), cyclohexyl vinyl ether (CVE, 99.0%), 4-hydroxybutylvinyl ether (HBVE, 99.0%, stabilized with 0.01% KOH). The chemicals were purified by bubbling N_2 through the liquids before use in order to evaporate more volatile contaminants. Acetonitrile (HPLC Gradient Grade, Carl Roth, Karl-

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sruhe, Germany) was used as solvent for calibration purposes.

Two spectrophotometers were used for the determination of the UV absorption spectra: Uvikon 860 (Kontron Analytical, Germany) and Cary 2300 (Varian Techtron, Germany). Both are double beam spectrometers equipped with quartz-halogen lamp and deuterium lamp. The Uvikon 860 is equipped with a Seya-Namioka monochromator and the Cary 2300 with a modified Czerny-Turner monochromator, where the beam passes twice to decrease the stray light and increase the photometric range. For both instruments, wavelength precisions were estimated to be better than ±0.02 nm, accuracies to be ±0.5 nm (checked by a holmium filter) and photometric precisions to be ±0.002 AU at 1.0 absorbance. Absorbance precisions were verified by the molar extinction coefficient of various $K_2Cr_2O_7$ solutions. The average deviation between measured values and expected ones was below $\pm 0.02\,M^{-1}\,cm^{-1}$ in the range 230–350 nm, confirming the manufacturer's specifications. Photometric linearities were determined by measuring the absorbance of $K_2Cr_2O_7$ solutions in 0.05 N NaOH at $\lambda = 373$ nm. The linear regression coefficients were $r^2 > 0.997$. Both spectrophotometers were purged with N_2.

Gas phase concentrations were generated in a saturator [10], the vapor pressures of EVE and iBVE were calculated from Antoine equation parameters [11]. For BDDVE and DVE-2, the gas phase concentrations were determined by freezing a known volume of the flow coming from the saturator in two cold traps in series (in order to check for breakthrough). The collected samples were then dissolved in a well-known volume of acetonitrile, and their concentrations were determined by UV spectroscopy. Concentrations were calculated from the respective calibration curves, and the results for BDDVE and DVE-2 were found to agree with the manufacturers' vapor pressure data. The dependencies of the absorbance on partial pressure observed by the two different methods have shown good linear relations according to Beer–Lambert's law. The error in the concentration measurements was estimated to be smaller than 10% where the main source of uncertainty resulted from temperature fluctuations of the absorption cells in the spectrophotometers. Only for CVE the pressure was measured directly using a membrane capacitance manometer (MKS Baratron, type 222BHS, 0–10 Torr, accuracy 0.5%).

UV absorption spectra of the series of vinyl ethers were measured in the gas phase in the wavelength range $\lambda = 200–300$ nm at $T = (303 \pm 2)$ K. They were registered at 1 nm resolution in gas-tight quartz cuvettes (Suprasil, $l = 100.0 \pm 1.0$ mm), using N_2 as reference gas.

3. Calculation of absorption cross-sections and oscillator strengths

The absorbance $A(\lambda)$ of a sample is defined by the equation:

$$A(\lambda) = -\log_{10}\left(\frac{I(\lambda)}{I_0(\lambda)}\right) \tag{1}$$

where $I_0(\lambda)$ and $I(\lambda)$ are the intensities of the reference and sample beams respectively. Converting to the natural logarithm, absorption cross-sections are obtained according to Beer's law (Eq. (2)):

$$A(\lambda) = \sigma(\lambda) C \frac{l}{2.303} \tag{2}$$

with $\sigma(\lambda)$, absorption cross-section (cm^2 molecule^{-1}); C, concentration (molecules cm^{-3}) and l, optical path length (cm).

Table 1
Observed gas phase UV absorption cross-sections of the vinyl ethers at $T = 303$ K (absorption band maxima and shoulders are marked in bold).

λ (nm)	σ (10^{-20} cm^2 molecule^{-1})					
	EVE	CVE	iBVE	BDDVE	DVE-2	HBVE
190	300	283	343	536	216	230
191	337	311	442	759	327	257
192	305	318	375	569	298	242
193	311	335	416	641	415	238
194	295	340	435	592	381	234
195	269	343	380	540	372	209
196	249	347	381	508	347	197
197	231	339	344	475	326	184
198	217	325	331	452	297	174
199	208	310	313	416	284	161
200	194	291	284	364	263	147
201	169	267	248	325	245	131
202	148	241	222	296	**226**	119
203	138	215	205	286	205	111
204	136	186	**208**	**280**	179	**108**
205	**142**	162	206	248	151	99
206	129	142	169	198	129	83
207	96	123	129	158	120	67
208	75	**111**	107	140	**112**	58
209	69	94	96	136	95	53
210	67	75	99	**141**	77	52
211	**75**	61	**112**	121	58	**48**
212	71	53	82	79	40	36
213	39	51	46	45	28	23
214	21	**49**	25	28	21	14
215	14	45	17	20	15	10
216	11	32	13	16	12	7.8
217	**9.0**	23	**12**	**13**	**9.6**	**6.0**
218	7.0	17	9.9	8.9	6.5	4.2
219	4.1	14	6.8	5.3	3.4	2.9
220	2.0	13	3.2	3.0	2.1	1.8
221	0.6	**11**	1.3	1.7		1.0
222	0.2	7.3	0.4	0.8		0.5
223	0.1	2.8	**0.2**			
224		1.5	0.1			
225		0.3				
226		0.2				
227		0.1				

The oscillator strength, f, of a molecular electronic transition is defined as the ratio of an atomic or molecular transition strength to the theoretical transition strength of a single electron using a harmonic-oscillator model. It is described by the integral of intensity over the whole width of the band according to Mulliken [12]:

$$f = 1.13 \times 10^{12} \int \sigma(\nu)\,d\nu \tag{3}$$

where ν is the wavenumber in cm^{-1}. This quantity corresponds to the probability for the transition that can approach unity for an allowed, strong transition. Typical values of oscillator strength for the $\pi^* \leftarrow \pi$ transitions in olefins are around 0.3 [13], and in the particular case of MVE we determined a value of $f = 0.29$ from the vacuum ultraviolet spectrum of Planckaert et al. [7].

Knowing $\sigma(\lambda)$, the solar actinic flux for average latitudes $F(\lambda)$ (photons $cm^{-2}\,s^{-1}$) and the number of transformed molecules per number of absorbed photons $\Phi(\lambda)$ (quantum yield) the photolytic rate constants (k_{phot}, s^{-1}) of atmospheric contaminants can be calculated [8]:

$$k_{phot} = \int_{\lambda} \sigma(\lambda)\,\Phi(\lambda)\,F(\lambda)\,d\lambda \tag{4}$$

4. Results and discussion

4.1. UV absorption cross-sections

The averaged UV absorption cross-sections are listed in Table 1 and presented in Fig. 1.

The standard deviation of the absorption cross-section values, calculated from 7 to 20 measurements, was between 2% and 20%

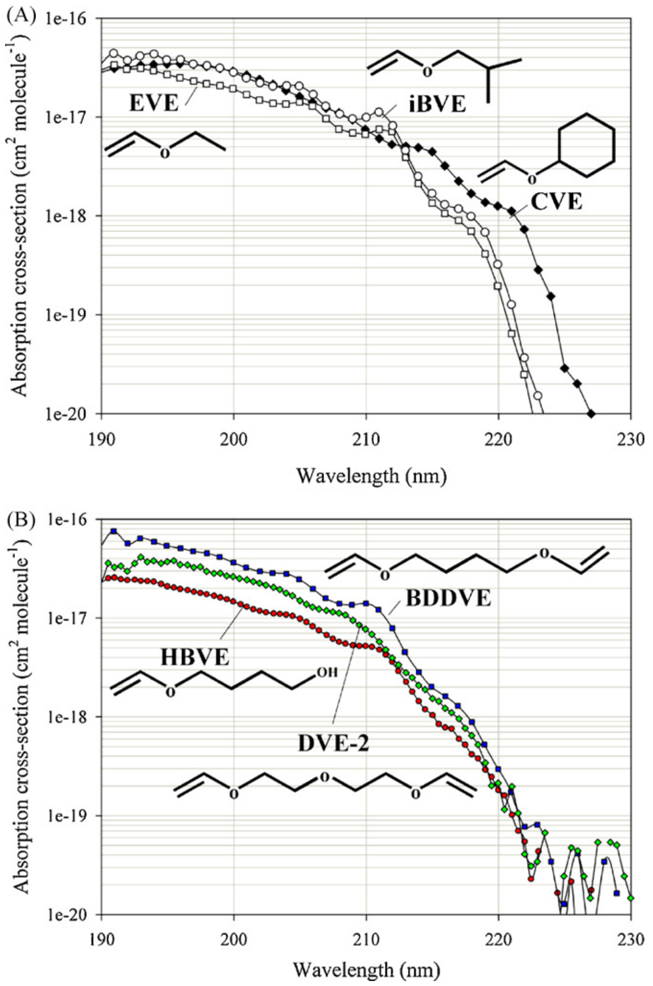

Fig. 1. UV absorption cross-sections of a series of vinyl ethers in the gas phase at 1 nm resolution. Bathochromic shifts of the band position can be observed for alkyl substituted vinyl ethers (A, recorded in 1 nm steps) and the less volatile vinyl ethers with an extra O atom in the substituent (B, HBVE and DVE-2 recorded in 0.5 nm steps), becoming uncertain above 220 nm due to low absorbance.

for all compounds in the 200–220 nm region. Other sources of error such as optical path, temperature and wavelength precision were estimated to be less than 1% each.

Under these experimental conditions, the spectra of the substituted ethenes show smooth profiles. However, it is possible to distinguish the predicted spectroscopic behaviour (red shift) with the different substituents as explained in Section 4.2. In general feature, the UV absorption bands fall rapidly in intensity toward longer wavelengths, around 220–230 nm (see Fig. 1).

The UV absorption spectra present broad, moderately intense bands with vibrational progressions, corresponding to 1450 ± 60 cm^{-1} (Table 2). The numbers and positions of the bands vary with the different substituents: R = $-CH_2-CH_3$, 205 and 211 nm; R = $-(CH_2)_4-O-CH{=}CH_2$, 204 and 211 nm; R = $-CH_2-CH(CH_3)-CH_3$, 205 and 211 nm; R = $-C_6H_{11}$, 208 nm (an almost imperceptible, broadened feature) and 214.5 nm (shoulder). Spectra of oxygen-substituted vinyl ethers with R = $-(CH_2)-O-(CH_2)_2-O-CH{=}CH_2$ and R = $-(CH_2)_4-OH$ show less pronounced features (though one may suggest 204.5 and 210.5 nm for HBVE and about 202 and 208 nm for DVE-2).

Vibrational progression is a typical feature in the 3s ← π transition band in olefins [7,13,14]. The C=C stretching vibration is activated by the electronic transition since this transition affects an electron which belongs to C=C and almost removes it from the double bond. In ethene, the vibrational progression is evident with a spacing of $\nu = 1290 \pm 30\,\text{cm}^{-1}$ [15]. The UV spectrum of MVE also exhibits the typical $\pi^* \leftarrow \pi$ band at $\lambda = 188.8$ nm [7]. Similar to this work, three bands at 199.1 nm (50,230 cm^{-1}), 204.6 nm (48,880 cm^{-1}) and 211.2 nm (47,340 cm^{-1}) were reported for MVE. They were assigned to the 3s ← π transition, and because they form a progression series (frequency 1450 ± 50 cm^{-1}), they were associated to the C=C stretching frequency of the excited state. Weak bands were observed at 210 nm (47,610 cm^{-1}), 209 nm (47,900 cm^{-1}) and 208 nm (48,150 cm^{-1}), which can be assigned to C–O–C bending vibration ($\nu_{16}(\delta_{\text{C–O–C}})$).

According to Robin [13], the 3s ← π transition band has been identified in ethene (57,340 cm^{-1}, term value 27,410 cm^{-1}), and the same R(3 s) ← π band in alkyl ethenes can be recognized in spite of its overlap with the strong $\pi^* \leftarrow \pi$ transition band. The author concludes that the R(3 s) ← π band position in olefins (as well as the 3p ← π and 3d ← π positions) can be estimated according to its term values between 27,000 and 22,000 cm^{-1} (and 22,000–18,000 cm^{-1} and 14,000–12,000 cm^{-1}, respectively).

4.2. Discussion

In order to describe the UV absorption spectra of the vinyl ethers, the group responsible for the electronic transition (C=C–OR) was considered as an ethene molecule where a hydrogen atom is substituted by an alkoxy group (–OR). In the ground state of ethene there are the two π electrons assigned to the same orbital Ψ_1 and due to the Pauli's exclusion principle, they must be paired. Theoretically, the UV absorption spectrum of ethene should present only one very intense transition band ($\pi_g^* \leftarrow \pi_u$ at 165 nm). Contrary to this, a very weak transition has been observed around $\lambda = 200$ nm and was attributed to a two-electron transition [16]. Because it is a forbidden transition, it is expected to be weak. An extremely weak band, which corresponds to the one electron triplet ← singlet transition, has been reported in the liquid phase UV absorption spectrum of ethene in the presence of high pressures of oxygen [15]. The allowed $\pi^* \leftarrow \pi$ band dominates the UV spectrum of olefins below 200 nm. For other classes of unsaturated compounds it is not that simple to determine the position of $\pi^* \leftarrow \pi$ transition [13].

The substitution of an atom or group with a lone pair of electrons (auxochromic group) for a hydrogen atom in the molecule of ethene causes a bathocromic shift of both bands. This phenomenon had been explained in terms of inductive and resonance effects. The resonance effect explains the increase of the strength of the C–C double bond due to the presence of a lone pair on an atom attached to the vinyl group. The interaction of the lone pair orbital, n, with the two π (π_u and π_g^*) orbitals in ethene results in three new molecular energy levels designated as π_1, π_2 (HOMO) and π_3 (LUMO). The energy level π_1 is much lower relative to the lone pair orbital n, than π_2 relative π_u in ethene due to an interaction of π_2 with the antibonding orbital π_g^*. Consequently, this interaction generates net resonance stabilization of the system. The lone pair of the substituent interacts also with π_2 (HOMO) and π_3 (LUMO) but this interaction is stronger with π_2 than with π_3. As a result it causes a red shift in the UV spectrum relative to unsubstituted ethene. At the same time, the raising of π_2 decreases the ionization potential, so it becomes easier to remove an electron from the substituted ethene than from ethene itself. The inductive effect lowers both π levels (π_u and π_g^*) in ethene but at the same time it rises the energy of the n orbital of the substituent. As a consequence, the molecular energy levels π_2 and π_3 in substituted ethene will be slightly affected. Consequently, the inductive effect has a small influence on the UV spectrum of these molecules.

The opposite effect has been reported by Orkin et al. [17] on electron-withdrawing substituted propenes, such as fluorinated propenes. The authors have reported a smooth, bell-shaped band

Table 2

Oscillator strengths, *f*, progression band positions and vibrational spacings of the overlying 3s ← π transition, observed in the UV absorption spectra of vinyl ethers in gas phase. The oscillator strengths are estimated by taking twice the area from the lowest energy to the maxima of the π* ← π transition. Only for MVE and CVE the absorption maxima are available.

Vinyl ether	π* ← π intensity *f*	Progression band position (nm)	Frequency (ν_6 c = c) (cm^{-1})	Frequency progression (cm^{-1})
MVE	0.29	199.1[a]	50230[a]	
				1350[a]
		204.6[a]	48880[a]	
				1540[a]
		211.2[a]	47340[a]	
EVE	>0.22	205	48780	
				1390
		211	47390	
				1310
		217s	46080	
iBVE	>0.31	205	48780	
				1390
		211	47390	
				1410
		217.5s	45980	
CVE	0.21	208	48080	
				1460
		214.5s	46620	
				1370
		221	45250	
BDDVE	>0.35	204	49020	
				1510
	(>0.18)[b]	210.5	47510	
				1430
		217s	46080	
DVE-2	>0.28	202	49500	
				1420
	(>0.14)[b]	208	48080	
HBVE	>0.18	204.5	48900	
				1390
		210.5	47510	

s: shoulder.

[a] Ref. [7].

[b] Per choromophore group.

below 190 nm (maximum absorption between 170 and 176 nm) in propene, while in fluorinated propenes it occurs below 170 nm. The maximum absorption cross-sections values for these fluorinated propenes are higher than 2×10^{-17} cm^2 molecule^{-1}.

Merer and Mulliken [14] have reviewed the gas phase UV absorption spectra of alkyl-substituted ethenes and have correlated the red shift in the strongest bands of these molecules in the region 160–240 nm with the number of substituents. They have observed that the ($\pi_g^* \leftarrow \pi_u$) transition falls rapidly in intensity towards longer wavelengths and it moves slightly to the red with increasing number of substituents on the ethylenic carbons. They have reported the presence of moderately intense R (Rydberg)–N transition bands at longer wavelengths. The R–N bands move much more rapidly to the red with increasing number of substituents. As a result, the R–N bands, which in ethene occur fairly close to the ($\pi_g^* \leftarrow \pi_u$) transition peak, appear clearly beyond the red end of the ($\pi_g^* \leftarrow \pi_u$) transition in tetramethylethene. Typically, the ($\pi^* \leftarrow \pi$) transition maximum is shifted by about 2000 cm^{-1} towards lower wavenumbers per alkyl group, attached to the olefin choromophore. The extent of π-system onto the substituent (hyperconjugation) has been established as the main cause of the observed shift [13].

In a very recent study [18], the gas phase UV absorption spectra of a series of styrene-like compounds have been investigated, and their absorption characteristics clearly correspond to the π system of ethene. The behaviour of the series is a typical effect of the substituents on the ethene group due to a net hyperconjugation. Consequently, the UV spectra of the compounds with substituents on the ring (2-methylstyrene and β-methylstyrene) show the expected bathochromic shift respect to styrene. In contrary, in the compounds with substituents attached directly to the ethene group (α-methylstyrene and indene) a hypsochromic effect is observed. This observation can be explained by an inhibition of the hyperconjugation effect due to the presence of a α-substituent on the ethene group.

For other kinds of substituents, chemically more complex than an alkyl group, the spectra of the resulting compounds show approximately the same general features, but some modifications in the details often occur. Specifically, in vinyl ethers the direct linkage between an O atom and the C=C bond leads, under favourable sterical orientation, to effective p–π conjugation in the vinyloxy system: $-\mathrm{O}-\mathrm{C}=\mathrm{C} \leftrightarrow -\overset{+}{\mathrm{O}}=\mathrm{C}-\overset{-}{\mathrm{C}}$. The strength of this conjugation will depend also on the nature, number and position of substituents attached to the –O–C=C. According to previous work of Taskinen and Hellman [19,20], substituent's bulkiness plays an important role in the spatial orientation of the –O–C=C system and therefore, in its polarization degree. In summary, the strength of p–π conjugation in vinyl ethers depends on several structural factors, such as the stereochemistry of the C–O–C=C fragment and the electronic nature of substituents attached to the β-carbon of the vinyl group.

Fig. 2 compares the UV spectra of CVE and EVE with the spectrum of MVE obtained by Planckaert et al. [7] and those of ethene and propene [17], acrylonitrile [21], the allyl radical [22], trifluoromethyl-ethene [17], vinyl chloride [23], vinyl bromide [24],

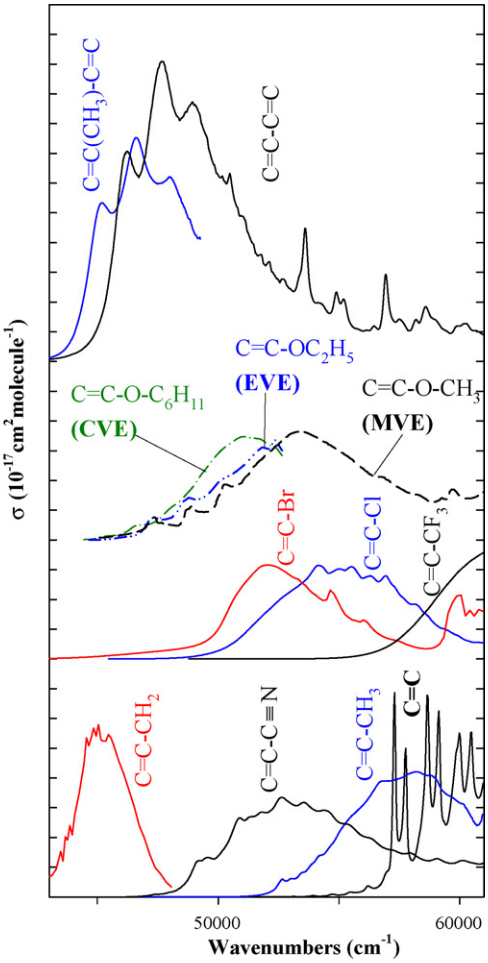

Fig. 2. Comparison of the UV spectra of the vinyl ethers (dashed) of the present study with those of MVE by Planckaert et al. [7] and of ethene and selected substituted ethenes in the region of the $\pi^* \leftarrow \pi$ transition, taken from the UV spectral database of Keller-Rudek and Moortgat [27] (spectra are vertically displaced for clarity, see text for individual references).

butadiene [25] and isoprene [26] (taken from the MPI-Mainz-UV-VIS Spectral Atlas [27]). Although the spectra were recorded at different resolutions, the broad V ← N and overlapped R ← N transitions can be distinguished throughout the series. Furthermore, the shift of the absorption maxima is consistent with the nature of substituent as explained above, and the spectra from this study fit within the series.

As explained in Section 3, oscillator strengths can be estimated from the integral of intensity over the whole band width. This condition could be an impediment because instrumental restrictions prevented the recording of the entire absorption band of the vinyl ether series in the present study. Nevertheless, one can expect the $\pi^* \leftarrow \pi$ transition band in vinyl ethers to have a similar highly symmetric feature in comparison with the spectrum of methyl vinyl ether [7]. Considering the band maxima at $\lambda = 190$ nm according to other substituted ethenes [14], the oscillator strength values were estimated to be twice the integral of intensity of the measured spectra (Table 2, Eq. (3)). Note that the molecules of BDDVE and DVE-2 have two chromophore groups, which must be considered when analyzing the relative intensity of the transition. CVE ($R = -C_6H_{11}$) has shown the most intense bathochromic shift in the series of vinyl ethers thus, p–π conjugation in the vinyloxy system of this molecule is more efficient. From the position of the bands in the UV absorption spectra, it is possible to assess the degree of p–π conjugation in the vinyloxy system of these vinyl ethers in the series: $R = -C_6H_{11}$ (CVE), $R = -CH_2-CH(CH_3)-CH_3$ (iBVE), $R = -CH_2-CH_3$ (EVE), $R = -(CH_2)_4-$(BDDVE), $R = -(CH_2)_4-OH$ (HBVE), $R = -(CH_2)-O-(CH_2)_2-$(DVE-2). A similar bathochromic shift exists for the weak band shoulders of CVE (221 nm), iBVE (218 nm) and EVE (217 nm) and BDDVE (218 nm), almost imperceptible for HBVE and DVE-2 (217 nm). A comparison of the UV absorption cross-sections, grouped by the nature of substituents and by vapor pressures values, is shown in Fig. 1 and presented in Table 1. In Fig. 1(A) are depicted the more volatile alkylsubstituted vinyl ethers (CVE, iBVE and EVE) whereas in Fig. 1(B), the less volatile oxygenated substituted vinyl ethers (BDDVE, HBVE and DVE-2). The presence of an extra O atom in HBVE and DVE-2 diminishes the bathochromic effect to a hypsochromic effect in the electronic transition by decreasing the inductive effect and thus, decreasing the p–π conjugation in the vinyloxy system (Table 2). Based on *f* values, iBVE exhibited the strongest hyperchromic effect ($f = 0.31$), followed by CVE and EVE with similar transition intensities ($f = 0.22$ and 0.21, respectively). The oxygenated substituted vinyl ethers have displayed lower *f* values in agreement with relative hypsochromic effect.

Photolytic rate constants of the organic compounds in the atmosphere are defined by Eq. (4). Since photolytic quantum yields, $\Phi(\lambda)$, are not available for the vinyl ethers, one may consider them to be equal to 1 for an estimate of the maximum photolytic rate coefficients. Actinic flux intensity $F(\lambda)$ depends on daytime, latitude, altitude, cloud cover and ozone (mainly stratospheric) and aerosol concentrations [9]. Due to the strong absorption of ozone in the continuous Hartley band between 210 and 290 nm and the additional absorption in the Huggins bands (extending to above 290 nm), the values of $F(\lambda)$ are close to zero for wavelengths inferior to $\lambda = 290$ nm ($<10^{12}$ photons cm^{-2} nm^{-1} s^{-1} at $\lambda = 295$ nm and below at 15 km altitude and 0° solar zenith angle). Because vinyl ethers measured in this work do not absorb above 290 nm, the photolytic rate constants in the atmosphere are negligible (similar to chlorofluorocarbons and carbon tetrachloride, which are photolytically inert in the troposphere). For the vinyl ethers, the atmospheric lifetimes are governed mainly by reaction with OH radicals and ozone. The rate coefficients for the reactions of EVE with OH radicals and ozone have been reported to be 6.8×10^{-11} cm^3 molecule^{-1} s^{-1} and 2×10^{-16} cm^3 molecule^{-1} s^{-1} [3], and for the reaction of iBVE with OH radicals even larger than for EVE, 11×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K [6]. Both reactions, with tropospheric OH radicals ($\sim 10^6$ molecules cm^{-3}) and ozone ($\sim 10^{12}$ molecules cm^{-3}) thus limit the lifetime of the vinyl ethers to a few hours, impeding a significant long-range transport in the troposphere or above the tropopause.

5. Conclusions

This work provides the first measurements of the UV absorption cross-sections of this series of vinyl ethers. The vapor spectra have been clearly interpreted based on the electronic transitions involved and the chemical structure. The good fit of the spectra obtained in the present study within the series of the already published ones corroborates our assumption on oscillator strength calculations which allows us to undoubtedly discard photolysis as a degradation pathway for these compounds in the troposphere.

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