Evidences for a new Ultraviolet Absorption Band of the FSO₃ Radical

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An unpublished absorption band of the fluorosulphate radical, FSO₃, based on earlier experiments of Schumacher and co-workers (Z. Phys. Chem. NF **42** (1964) 174) and detailed calculations of the whole FSO₃ spectra based on the time-dependent (TD) generalization of the density functional theory (DFT), TD-DFT, are reported. Part of this band, that increases in intensity at wavelengths below 275 nm, has been extracted from an absorption spectrum taken from equilibrated mixtures of FSO₃ with the dimer FS(O₂)OO(O₂)SF at 403 K. A set of thirteen exchange-correlation hybrid functionals combined with the 6-311+G(3df) basis set predict an intense absorption band centred at 256 ± 10 nm in very good agreement with the experimental observations. Another significant band peaked at 184 ± 10 nm was also found. The calculations reproduce accurately the position of the maximum and the experimental oscillator strength of the well-known visible FSO₃ band system.

1. Introduction

The peroxydisulfuryl difluoride $FS(O_2)OO(O_2)SF$ ($F_2S_2O_6$) exists in equilibrium with the fluorosulphate radical, FSO_3 , $FS(O_2)OO(O_2)SF \leftrightarrow 2 FSO_3$. This equilibrium plays a relevant role in the organic synthesis of numerous substances realized with $F_2S_2O_6$, because FSO_3 exclusively accounts for the reactivity of the system [1]. The equilibrium constant was studied almost simultaneously by Dudley and Cady [2] and Schumacher and co-workers [3] employing manometric methods. From these studies quite similar values for the O–O bond dissociation enthalpy of 22.0 [2] and 21.8 kcal mol⁻¹ [3] were derived. More recently, the bond strength has been confirmed by electron spin resonance,

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22.4 kcal mol⁻¹ [4], and laser flash photolysis techniques, 22.1 kcal mol⁻¹ [5]. In addition to the equilibrium constant measurements, Dudley and Cady [1] and Schumacher and co-workers [2] determined the absorption spectra of equilibrated $F_2S_2O_6$ -FSO₃ mixtures as a function of the temperature. They demonstrated the existence of a strong FSO₃ absorption band located above about 300 nm.

The FSO₃ spectrum has been analyzed in detail by Warren and coworkers [6-13]. They assigned three absorption systems, two of them presenting weak diffuse absorption bands in the near infrared region of 2000-1000 nm and 1000-570 nm and the third system exhibiting a strong discrete band assigned, under C_{3v} molecular point group, to the electronic transition ${}^{2}E-X^{2}A_{2}$ [6]. The last band is strongly structured between its origin, situated at 516 nm, and the maximum lying about 470 nm. At larger wavelengths it is partially overlapped by a fairly strong continuum which decreases in intensity up to about 340 nm. The analysis of the vibronic structure of this band has been used to derive vibrational frequencies for the ground state [10-12]. More recently, FSO₃ absorption coefficients from about 340 to 470 nm have been determined by using spectrokinetic techniques [5, 14, 15] and conventional absorption methods [16]. Some of these studies have been recently compiled [17]. On the other hand, the monitoring of FSO₃ by time-resolved absorption spectrophotometry has been amply employed in the kinetic studies of a number of reactions involving this radical [18–27].

In the present work, the spectroscopic data recorded by Schumacher and co-workers [3] have been analyzed to derive absorption coefficients for a new FSO₃ ultraviolet band overlapped with the $F_2S_2O_6$ spectra. For this, $F_2S_2O_6$ absorption coefficients have been here determined. The study is complemented by a large number of TD-DFT calculations which support the experimental results.

2. Experiments

The temperature dependent absorption depicted in the Fig. 3 of the paper of Schumacher and co-workers is the experimental basis of our study [3]. The data were carefully determined with a spectrophotograph equipped with glass and quartz prisms. The original spectra of the paper recorded in a transmittance scale between 235 and 400 nm were here digitalized and transformed to an absorbance scale [28]. A set of data obtained from the experiments conducted at 403 and 473 K are shown in Fig. 1. Due to saturation effects (more evident in the measurements at 473 K) the spectra recorded at 403 K have been mostly considered. The $F_2S_2O_6$ absorption coefficients necessary for the extraction of the FSO₃ absorption from the equilibrated mixtures were measured in a Cary 14 spectrophotometer at 295 K. They were obtained from Beer–Lambert plots constructed at $F_2S_2O_6$ concentrations ranging from 3.6×10^{-4} M



Fig. 1. Digitalized absorbances of $F_2S_2O_6$ -FSO₃ mixtures [3, 28]. Δ : T = 403 K, $F_2S_2O_6 = 3.19 \times 10^{-3}$ M, FSO₃ = 1.09×10^{-4} M; \bigcirc : T = 473 K, $F_2S_2O_6 = 2.89 \times 10^{-3}$ M, [FSO₃] = 7.29×10^{-4} M.

to 4.0×10^{-3} M. We assumed that $\varepsilon(F_2S_2O_6)$ exhibits only small temperature dependence over the 295–400 K range, leading to a negligible vibrational broadening of the $F_2S_2O_6$ spectra. Consequently, these data can be employed in the analysis of the high temperature experiments.

The $F_2S_2O_6$ was prepared by photolyzing F_2 in the presence of SO_3 in a Pyrex reaction vessel with a Hanau Q700 mercury lamp. It was condensed at 195 K and small amounts of formed $FS(O_2)OF$ were eliminated by trap-to-trap distillations at 223 K [29]. The $F_2S_2O_6$ purity was verified by IR spectrophotometry.

3. Results and conclusions

3.1 Analysis of the experimental spectra

As Table 1 shows, the measured absorption coefficients for $F_2S_2O_6$ are in excellent agreement with those determined by Burley and Johnston [16]. Over the wavelength range relevant for the present study, 260-280 nm, they were accurately fitted with the equation $\varepsilon(F_2S_2O_6) = 23.9/[1+5.55 \times 10^{-2}(\lambda - 260) + 2.11 \times 10^{-3}(\lambda - 260)^2]$ (in M⁻¹ cm⁻¹) which was employed in the spectra analysis. The selected digitized absorbance data from Fig. 1, A_{exp} , containing

λ (nm)	$\epsilon(F_2S_2O_6) \ (M^{-1} cm^{-1})^a$	$\epsilon(F_2S_2O_6) \ (M^{-1} cm^{-1})^b$	λ (nm)	$\begin{array}{c} \epsilon(F_2S_2O_6) \\ (M^{-1}cm^{-1})^a \end{array}$	$\begin{array}{c} \epsilon(F_2S_2O_6) \\ (M^{-1}cm^{-1})^{b} \end{array}$
240 245	80.7	77.8 57.6	275 280	7.83	10.6 7.71
250	41.7	41.8	285	_	6.23
255	-	30.8	290	4.61	4.77
260	23.1	23.9	295	_	3.07
265	-	17.6	300	2.72	2.94
270	13.4	13.9	-	_	_

Table 1. Absorption coefficients for $F_2S_2O_6$.

^a T = 298 K, [16]; ^b T = 295 K, this work.

λ (nm)	\mathbf{A}_{exp}	$ \begin{aligned} & \varepsilon(\mathrm{F}_2\mathrm{S}_2\mathrm{O}_6) \\ & (\mathrm{M}^{-1}\mathrm{cm}^{-1}) \end{aligned} $	$\epsilon(FSO_3)$ $(M^{-1} \operatorname{cm}^{-1})^a$	$\begin{array}{c} \epsilon(FSO_3) \\ (M^{-1}cm^{-1})^b \end{array}$
260.0	1.97	23.9	1108	845
261.25	1.72	22.3	925	706
262.5	1.48	20.8	749	572
263.75	1.30	19.3	628	480
265.0	1.05	18.0	437	335
266.25	0.870	16.7	309	238
267.5	0.736	15.6	219	171
270.0	0.515	13.5	77	62
272.5	0.409	11.8	30	26
275.0	0.341	10.4	8	9

Table 2. Absorption coefficients for FSO₃ at 403 K.

^a $F_2S_2O_6 = 3.19 \times 10^{-3}$ M, $FSO_3 = 1.09 \times 10^{-4}$ M (calculated using the equilibrium constant of Ref. [3]); ^b $F_2S_2O_6 = 3.15 \times 10^{-3}$ M, $FSO_3 = 1.44 \times 10^{-4}$ M (calculated using the equilibrium constant of Ref. [5]).

information on both FSO₃ and F₂S₂O₆ spectra were employed to derive the absorption coefficients for FSO₃ in the UV region [3, 28]. At wavelengths larger than about 340 nm the third absorption band of FSO₃ is evident from the experiments conducted at 473 K. The absorption coefficients were calculated with the following formula ε (FSO₃) = { $A_{exp} - \varepsilon$ (F₂S₂O₆)/[F₂S₂O₆]}//[FSO₃]. Here, l = 10 cm is the path length of the cell [3]. The equilibrium concentrations for F₂S₂O₆ and FSO₃ were obtained from both the equilibrium constants of Ref. [3], and those measured by laser flash photolysis of F₂S₂O₆ at 293–381 K [5]. The results are listed in Table 2. The resulting ε (FSO₃) values indicate the presence of a new strong absorption band that increases in intensity below 275 nm. The values calculated with the equilibrium constant of Ref. [5] are about 20% smaller that those estimated with the equilibrium constant of



Fig. 2. Visible and UV absorption spectra of FSO₃. The spectra measured for $F_2S_2O_6 = 4.0 \times 10^{-3}$ M at 295 K is depicted in solid lines; \bigcirc : Experimental values from Ref. [14]; •: Experimental values from Ref. [15]; \blacktriangle : T = 403 K, this work; \Box : T = 473 K, this work. The dashed line was modeled using the functionals B3P86, B3PW91, B3LYP, B1B95, B98, B97-1, B97-2, O3LYP, MPW1B95 and MPWB1K (see text). The dotted line was modeled using the functionals B1LYP, mPW0, PBE0 (see text).

Schumacher and co-workers [3]. Unfortunately, as Fig. 1 shows, saturation effects only permit the deconvolution of part of the absorption band.

Absorption coefficients determined by 193-nm laser flash photolysis of FSO_3 precursors $FS(O_2)OF$ [14] and $F_2S_2O_6$ [15] nm are illustrated in Fig. 2. In addition, the vibronic structure of the third FSO₃ absorption system obtained from a sample of $F_2S_2O_6 = 4.0 \times 10^{-3}$ M at 295 K is also given. From the latter a value of $2200 \text{ M}^{-1} \text{ cm}^{-1}$ (not shown in Fig. 2) for ε (FSO₃) at the wavelength origin of 516 nm was determined. As Fig. 2 shows, the present absorption data constitute a significant part of a new fourth system of the spectra. A few and less precise data measured at 473 K, also illustrated in Fig. 2, follow a similar trend. Despite the $\varepsilon(FSO_3)$ values are much larger than those corresponding to $F_2S_2O_6$, at room temperature the $F_2S_2O_6 \leftrightarrow 2FSO_3$ equilibrium is almost totally displaced towards $F_2S_2O_6$ which covers totally the FSO₃ UV bands. In fact, the degree of dissociation of F₂S₂O₆ at 300 K varies between 1.5×10^{-4} and 5.4×10^{-5} for samples ranging between total concentrations of 5.4×10^{-3} M and 4.1×10^{-2} M. Therefore, the data of Table 1 exclusively belong to $\varepsilon(F_2S_2O_6)$. The derived experimental information was complemented with quantum chemical calculations of the FSO₃ spectra.

3.2 TD-DFT calculations for FSO₃

It has been shown that TD-DFT gives remarkable results in the calculation of the observed transition energies of the electronically excited states of a large number of molecules [30]. It is particularly well suited for valence excited states which can be described by combinations of single one electron transitions. In fact, due to the fact that the ground state wave function in DFT is represented well as a single Kohn–Sahm determinant, problems inherent to the multi-determinantal character and spin contamination are in general not frequent. In particular, the TD-DFT gives a well-balanced description of open-shell systems such as excited states of radicals [31]. Generally, this formalism provides results of quality similar to those obtained with more sophisticated and time-consuming post-Hartree–Fock high level methods.

The real exchange-correlation functional which incorporates the manybody and quantum effects in DFT is, according the Hohenberg-Kohn theorem, unknown [32]. Besides, the particular contributions that will give the best results are difficult to establish a priori. Therefore, as in recent publications from this laboratory, different models were employed [33-37]. In particular, the following set of traditional and last generation hybrid functionals: B3P86 [38, 39], B3PW91 [38, 40], B3LYP [38, 41], B1B95 [38, 42], B1LYP [38, 41, 43], mPW0 [40, 44], B98 [45], B97-1 [46], B97-2 [46, 47], PBE0 [48, 49], O3LYP [50], MPW1B95 [42, 44, 51] and MPWB1K [42, 44, 51] as implemented in the Gaussian 03 program package were employed [52]. In all calculations the large 6-311+G(3df) triple split valence basis set was employed [53]. The p, d and f-type polarization functions included in the basis confer angular flexibility to represent regions of high electron density among the bonded atoms, and the diffuse functions grant radial flexibility to represent electron density far from the nuclei (particularly relevant for systems containing lone pairs of electrons as the present). The 49 valence electrons of FSO_3 were accommodated in molecular orbitals which comprise 203 basis functions based on 304 primitive Gaussians.

Geometry optimizations without symmetry constraints were carried out using analytical gradient methods. The calculations predict two different molecular point groups for the minimum energy structures of FSO₃. In contrast to the B3P86, B3PW91, B3LYP, B1B95, B98, B97-1, B97-2, O3LYP, MPW1B95 and MPWB1K models which lead to structures with C_{3v} symmetry, the nonempirical functionals B1LYP, mPW0 and PBE0 predict C₂ structures with a S–O bond distance about 0.035 Å smaller that the other two. The computed average bond distances for the C_{3v} structure are $d(SF) = 1.548 \pm 0.012$ Å and $d(SO) = 1.437 \pm 0.007$ Å, while for the less symmetric structure the values are $d(SF) = 1.545 \pm 0.006$ Å, $d(SO) = 1.452 \pm 0.003$ Å and $d(SO) = 1.417 \pm$ 0.003 Å. In all the cases, real vibrational frequencies were obtained assuring that molecular structures correspond to energy minima. No direct experimental data for comparison are available. From estimations based on the rotational

Table 3. Vert states of FSC	ical excitatio 3 calculated	n energies using diffe	(in eV), w. rent hybrid	avelengths functionals	(in nm) an with the 6	d oscillator -311+G(36	ff) basis set	for the first t.	electronic
Level of theory	Property	State 1	State 2	State 3	State 4	State 5	State 6	State 7	State 8
B3P86	${ m E} { m \lambda_{max}}$	1.11 1118 0.0008	1.11 1118 0.0008	2.66 466 0.0232	2.66 466 0.0232	4.73 262 0.0181	4.73 262 0.0181	6.54 189 0.0129	6.54 189 0.0129
B3PW91	${\rm E}$ ${\cal F}_{\rm max}$	$\begin{array}{c} 1.11 & 1 \\ 1117 \\ 0.0009 \end{array}$	1.11 1117 0.0009	2.64 470 0.0232	2.64 470 0.0232	4.73 262 0.0177	4.73 262 0.0177	6.53 190 0.0129	6.53 190 0.0129
B3LYP	\mathcal{F}_{\max}	$1.10 \\ 1130 \\ 0.0008$	$1.10 \\ 1130 \\ 0.0008$	2.62 474 0.0233	2.62 474 0.0233	4.69 265 0.0170	4.69 265 0.0170	6.44 192 0.0127	6.44 192 0.0127
B1B95	${\rm E}_{{\cal F}_{\rm max}}$	1.07 1160 0.0009	1.07 1160 0.0009	2.59 478 0.0231	2.59 478 0.0231	4.85 256 0.0223	4.85 256 0.0223	6.83 182 0.0105	6.83 182 0.0105
B1LYP	${\rm E}$ ${\cal F}_{ m max}$	1.01 1223 0.0008	1.45 853 0.0011	2.62 474 0.0150	2.72 456 0.0348	4.91 252 0.0132	5.04 246 0.0253	6.85 181 0.0127	6.87 180 0.0074
mPW0	${\rm E}_{{\cal F}_{ m max}}$	1.03 1200 0.0009	1.50 827 0.0012	2.66 466 0.0144	2.76 449 0.0354	4.98 249 0.0131	5.11 243 0.0270	6.97 178 00.133	7.00 177 0.0073
B98	${\cal F}_{ m max}$	$1.10 \\ 1122 \\ 0.0009$	$1.10 \\ 1122 \\ 0.0009$	2.63 471 0.0238	2.63 471 0.0238	4.78 259 0.0191	4.78 259 0.0191	6.62 187 0.0120	6.62 187 0.0120

analysis of the 516 nm system, a C_{3v} structure with values of $d(SF) \cong 1.64$ Å and $d(SO) \cong 1.46$ Å was obtained [8]. However, the ground state symmetry of FSO₃ is still controversial. In fact, fluorescence experiments suggest that the radical may be distorted to a lower symmetry [12].

Calculated vertical excitation energies (E), the associated wavelengths of the band maxima (λ_{max}) and oscillator strengths (f) for the first electronic transitions of FSO_3 are listed in Table 3. The magnitude of f provides information on the intensity of the experimental band and depends on elec-

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Table 3. cont	inued.								
Level of theory	Property	State 1	State 2	State 3	State 4	State 5	State 6	State 7	State 8
B97-1	${ m E} { m {\cal F}}$	1.09 1138 0.0008	1.09 1138 0.0008	2.63 471 0.0232	2.63 471 0.0232	4.73 262 0.0180	4.73 262 0.0180	6.54 190 0.0126	6.54 190 0.0126
B97-2	${ m E} { m \lambda}_{ m max}$	$1.10 \\ 1129 \\ 0.0009$	$1.10 \\ 1129 \\ 0.0009$	2.64 470 0.0233	2.64 470 0.0233	4.77 260 0.0185	4.77 260 0.0185	6.60 188 0.0126	6.60 188 0.0126
PBE0	${ m E} { m \lambda}_{ m max}$	1.03 1209 0.0008	1.49 833 0.0011	2.66 465 0.0143	2.77 447 0.0350	4.97 250 0.0131	5.10 243 0.0268	6.96 178 0.0135	6.98 178 0.0074
03LYP	${ m E} { m \lambda}_{ m max}$	1.05 1185 0.0005	1.05 1185 0.0005	2.70 460 0.0207	2.70 460 0.0207	4.43 280 0.0129	4.43 280 0.0129	6.17 201 0.0162	6.17 201 0.0162
MPW195	$\mathrm{E}_{\mathcal{F}_{\mathrm{max}}}$	1.08 1144 0.0011	1.08 1144 0.0011	2.58 481 0.0240	2.58 481 0.0240	4.93 251 0.0240	4.93 251 0.0240	7.02 177 0.0094	$7.02 \\ 177 \\ 0.0094$
MPWB1K	$\mathop{\rm E}_{\lambda_{\max}}_{f}$	$1.13 \\ 1097 \\ 0.0022$	$1.13 \\ 1097 \\ 0.0022$	2.47 502 0.0277	2.47 502 0.0277	5.23 237 0.0295	5.23 237 0.0295	7.88 157 0.0061	7.88 157 0.0061

tronic, Frank–Condon and spin factors, which reduce the unity maximum value expected for a perfectly allowed transition. The electronic contribution accounts for the forbiddeness arisen from the spatial overlap of the orbitals and symmetry of the wavefunctions relevant in the electronic transition. As Table 3 shows, the ten functionals predicting C_{3v} molecular structures lead to four sets of doubly degenerate E^2 electronically excited states while A^2 type of states are obtained with the B1LYP, mPW0 and PBE0 models.

System	Property	C _{3v} symmetry ^a	C ₂ symmetry ^b	Experimental
1	$\begin{array}{c} {\rm E} \\ {\lambda_{\max }} \\ {f} \end{array}$	- - -	1.02 ± 0.01 1210 ± 12 $0.0008 \pm 0.0001^{\circ}$	0.95^{d} 1310 ^d 0.0005 ^d
2	$\begin{array}{c} \mathrm{E} \\ \lambda_{\mathrm{max}} \\ f \end{array}$	$\begin{array}{c} 1.09 \pm 0.02 \\ 1134 \pm 25 \\ 0.0020 \pm 0.0008^{\circ} \end{array}$	$\begin{array}{c} 1.48 \pm 0.024 \\ 838 \pm 14 \\ 0.0011 \pm 0.0001^{\circ} \end{array}$	$1.6^{\rm d}$ $770^{\rm d}$ $0.002^{\rm d}$
3	$\begin{array}{c} \mathrm{E} \\ \lambda_{\max} \\ f \end{array}$	$\begin{array}{c} 2.61 \pm 0.06 \\ 475 \pm 11 \\ 0.0472 \pm 0.0034^{\circ} \end{array}$	$\begin{array}{c} 2.70 \pm 0.03 \\ 460 \pm 5 \\ 0.0497 \pm 0.0004^{\circ} \end{array}$	2.6^{d} 470 ^d 0.05 ^d
4	$\begin{array}{c} \mathrm{E} \\ \lambda_{\mathrm{max}} \\ f \end{array}$	$\begin{array}{c} 4.79 \pm 0.20 \\ 259 \pm 11 \\ 0.0394 \pm 0.0044^{\circ} \end{array}$	$5.02 \pm 0.03 \\ 247 \pm 2 \\ 0.0395 \pm 0.0008^{\circ}$	$\geq 4.8^{\rm e}$ $\leq 260^{\rm e}$
5	$\begin{array}{c} \mathrm{E} \\ \lambda_{\max} \\ f \end{array}$	$\begin{array}{c} 6.72 \pm 0.45 \\ 185 \pm 12 \\ 0.0236 \pm 0.0026^{\circ} \end{array}$	6.93 ± 0.07 179 ± 2 $0.0206 \pm 0.0003^{\circ}$	

Table 4. Average values for the vertical excitation energies (in eV), wavelengths maxima (in nm) and oscillator strengths for the electronic absorption systems of FSO_3 .

^a Calculated with the functionals B3P86, B3PW91, B3LYP, B1B95, B98, B97-1, B97-2, O3LYP, MPW1B95 and MPWB1K; ^b calculated with the functionals B1LYP, mPW0 and PBE0; ^c obtained summing the pairs of f values listed in Table 3 of the states 1 and 2, 3 and 4, 5 and 6, and 7 and 8; ^d Ref. [6]; ^e this work.

Despite of the variety of different exchange and correlation functionals employed, the large difference in the fraction of the accurate Hartree–Fock energy included in each method (from 0.20 in B3LYP to 0.44 in MPWB1K), a quite similar trend is evident and, for the present case, none can be definitely claimed superior to the rest. Therefore, to confront with experiments, the results of Table 3 were averaged. The resulting values and the estimated standard deviations (ranging from 1% to 4% for λ_{max} and close to 7% for f) are given in Table 4. To compare the calculated oscillator strengths with those obtained from integrated absorption bands [6], the two f values of each FSO₃ absorption systems were summed. As Table 4 shows, by contrast with the experimentally observed band peaked near to 1300 nm and the broad band located at 770 ± 70 nm [6], the functionals that give C_{3v} structures predict a single band with maximum at 1134 nm and a f value of 0.002, close to the experimental which results of summing the first two systems of 0.0025. On the other hand, the B1LYP, mPW0 and PBE0 functionals predict two well-resolved bands assigned to the first two systems. The fist band is 100 nm blue-shifted and exhibits an f value comparable with the experimental. The second band is, within the combined experimental and theoretical uncertainties, in reasonable agreement with the measured in Ref. [6].

The third system of FSO_3 spectrum has been extensively studied [6–16]. Most of the spectrum lies between 340 and 550 nm and is the responsible of the brownish yellow color of the radical. The experimental f value is two orders of magnitude larger than the estimated for the first system and twenty five times larger than the corresponding to the second system [6]. An inspection of the individual results consigned in Table 3 and the experimental and calculated mean values given in Table 4 shows the quality of the computed results. The most notable finding is the remarkable accuracy of TD-DFT to match the experimental values. In fact, an excellent agreement between the predicted wavelength maximum of 470 ± 12 nm and oscillator strengths of 0.048 ± 0.003 and the experimental values of 470 nm and 0.05 were obtained. The calculated average values of E, λ_{max} and f obtained for the fourth FSO₃ system along the experimental estimations from the data of Table 3 are given in Table 4. The DF-TDF calculations lead to a band peaked at $256 \pm$ 10 nm supporting the experimental data. In addition, the existence of another system with a band, probably less intense, situated at 184 ± 10 is also predicted.

The DF-DFT levels of theory employed here were checked against the experimental spectra of the related SO₂ molecule. The resulting λ_{max} values of 292 ± 4 nm and 190 ± 3 nm compare also very well with the experimental lying close to 290 and 200 nm [17]. These findings support the accuracy of the methods employed for this type of molecules.

The reported experimental ε (FSO₃) values together with a simple modelling of the absorption spectra based on the theoretical λ_{max} and *f* values is shown in Fig. 2. To do this, we used the well-known formula [54]

$$f \cong 4.3 \times 10^{-9} \int_{E_1}^{E_2} \varepsilon(E) \mathrm{d}E \,. \tag{1}$$

This expression allows estimating the oscillator strength for an absorption band lying between energies E_1 and E_2 as a function of the decadic molar absorption coefficient $\varepsilon(E)$. Because the DF-DFT calculations do not account for vibrational broadening, the simulated spectra are obtained by representing each transition with suitable shape functions centered at the calculated λ_{max} . The overall shape of an electronic peak with vibronic progressions often resembles a Gaussian function [55–58]. We selected here for the electronic transitions the following expression

$$\varepsilon = \varepsilon_0 \beta \exp\left[-\left(\beta/\sigma^2\right) \left(E - E_{\max}\right)^2\right],\tag{2}$$

where $\varepsilon_{\text{max}} = \varepsilon_0 \beta$ is the value of the absorption coefficient at the maximum and σ the full width of the band at 1/e height. After replacing (2) in (1) and integrating, the following relationship

$$\varepsilon_0 \cong f / \left[4.3 \times 10^{-9} (\beta \pi)^{1/2} \sigma \right] \tag{3}$$

is obtained. Now replacing (3) in (2) and summing over all electronic transitions we obtain

$$\varepsilon \cong \sum_{i=1}^{\infty} 1.6 \times 10^4 \left(f_i / \beta^{1/2} \sigma_i \right) \exp\left[- \left(\beta / \sigma_i^2 \right) \left(E_i - E_{\max,i} \right)^2 \right],\tag{4}$$

which allows to represent the simulated spectra in M^{-1} cm⁻¹ units as a function of the computed *f* values. The third band of the FSO₃ spectra can be reasonable fitted using the values $\beta = 3/2$ and $\sigma = 0.55$ eV in (4). A less satisfactory fit is found employing β values of 1 and 2. In the absence of a theoretical basis, we have ascribed the same width for all transitions, which is equivalent to assuming a constant decay rate for all excited states involved in the third, fourth and fifth system of bands. The results of these calculations for both the symmetric and the asymmetric FSO₃ is in average about 0.15 eV redshifted, improving somewhat the fit of the left part of the bands. However, this study is not appropriate to discern between the two possible FSO₃ conformations.

According to the Thomas–Reiche–Kuhn rule that establishes an unity value for the sum of all oscillator strengths [59–62], and the estimated f values of Table 4, we infer that most FSO₃ transitions are outside of valence excitation energies and correspond to high-lying diffuse excited states and particularly Rydberg excited states. Due to the fact that exchange-correlation potentials generated by most conventional functionals decay too fast, a break down at high energies normally occurs. A promissory approach is provided by the PBE0 model which does not contain parameters fitted to experimental data and the fraction of the Hartree–Fock exchange is included self-consistently to the DFT contribution [48, 49, 63]. A TD-PBE0/6-311+G(3df) calculation involving fifty FSO₃ excited states leads to a cumulative f value of 0.60, larger than the obtained from the values of Tables 3 of 0.11 but yet lower than the theoretically expected.

In summary, the present work shows that a significant part of a new UV absorption band for the FSO₃ radical situated below 275 nm can be extracted from studies performed more than forty years ago by Schumacher and coworkers. An extensive set of TD-DFT calculations leads to $\lambda_{max} = 256 \pm 10$ nm supporting the experimental findings and, in addition, predicting another band situated at 184 ± 10 nm. Both of them are close to the wavelengths provided by the KrF and ArF excimer laser transitions of 248 and 193 nm. In this context, future photochemical studies and more detailed temperature dependent experiments of FSO₃ spectra are planned.

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