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Absorption cross-sections for vibrationally excited fluorosulphate radicals

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Abstract

The absorption cross-sections of vibrationally excited FSO_3 radicals have been measured over the 340–470 nm wavelength range at 295 K. The radicals are formed following the electronic quenching of the $FSO_3(B^2E)$ radicals initially generated in the photolysis of $F_2S_2O_6$ at 193 nm. Using previously obtained relaxation rate coefficients, a modelling of the double-exponential decay of the vibrationally excited FSO_3 with a consecutive first-order mechanism allows the determination of the absorption cross-sections for these species. Evidence is presented which suggests that these phenomenological cross-sections correspond to low-lying manifolds of vibrational states.

Keywords: Absorption cross-sections; Fluorosulphate radicals; Excited states; Laser flash photolysis

1. Introduction

Vibrationally excited molecules in the electronic ground state often present ultraviolet and visible absorption spectra quite different from those of the corresponding relaxed species. These molecules can be prepared in the dense manifold of rovibrational states at high energies by laser-induced excitation followed by fast internal conversion processes. Vibrationally excited radicals can be also generated by molecular photodissociation [1,2]. The nature and extent of the excitation depend on the details of that process and, in most cases, an unknown amount of vibrational energy remains in the excited radicals. The relaxation rate of the excited species by the colliding partners depends, amongst others, on the excitation energy [3].

In earlier work, convincing evidence for the formation of hot fluorosulphate radicals, FSO_3, following the 193 nm photodissociation of peroxydisulphuryl difluoride, $F_2S_2O_6$, was found [4,5]. This was based upon the observation of the perturbation of the $F_2S_2O_6 \rightleftarrows 22FSO_3$ equilibrium at 415–525 K due to a small temperature jump caused by collisional release of internal energy of the excited photoproducts. In subsequent laser flash photolysis experiments, a mechanism including electronically and vibrationally excited FSO_3 radicals was proposed to explain the pressure-dependent build-up and decay of the observed absorption signals [6]. In addition, phenomenological rate coefficients for the quenching of the excited FSO_3 by several colliders [6,7] and for that associated with the self-relaxation of the radicals [8] were determined. Moreover, absorption cross-sections for relaxed FSO_3 have been recently measured [9–12].

The present work is the continuation of a series of time-resolved studies devoted to explore the chemistry of FSO_3 radicals [4–8,10,12–15]. The aim of the experiments has been to investigate the transient absorption assigned to the vibrationally excited FSO_3 radicals formed during the 193 nm laser photolysis of $F_2S_2O_6$. Absorption cross-sections for a manifold of vibrational states of FSO_3 have been determined over the 340–470 nm spectral region.

2. Experimental details

The laser flash photolysis/absorption spectroscopy arrangement used in the present experiments has been described elsewhere [4–8,10,12–16]. The 193 nm output of an ArF excimer laser (Lambda Physik EMG 101 MSC) was used to irradiate mixtures of 1.3×10^{17} to 2.3×10^{17} molecule cm^{-3} of $F_2S_2O_6$ and about 6.5×10^{18} molecule cm^{-3} of He at 295 ± 2 K. The fast electronic quenching of the $FSO_3(B^2E)$ initially formed in the photolysis [6] was followed by the decrease of the initial-state populations of the vibrationally excited FSO_3 radicals [7,8]. The excited radicals were probed in real time by absorption spectroscopy using a 150 W Hanovia Xe arc lamp (901C-1) as the light source. A cylindrical quartz vessel was employed as the reaction cell

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and both beams were passed perpendicularly through it. Transient absorbance signals were recorded using a prism double-monochromator (Zeiss MM12), a photomultiplier tube (RCA 1P28) and a digital storage oscilloscope (Nicolet 2090). The determinations were made point-by-point at spectral resolutions within the 3.4–3.9 nm wavelength range. Further reduction of the spectral resolution by almost a factor of two had no observable effect on the measured absorption cross-sections. Normally five to 25 laser shots were averaged to improve the signal-to-noise ratios. The signals were subsequently transferred to a computer for storage and analysis. A pyroelectric detector (Gentec ED-500) was employed to determine laser pulse intensities incident on the reaction cell. The linearity of the detection system was checked at several wavelengths.

The gases were handled in a conventional vacuum system, and the pressures measured with a calibrated pressure transducer (MKS Baratron, type 310CA) and with a sensitive quartz spiral gauge. $F_2S_2O_6$ was synthesized by photolysis of F_2 in the presence of SO_3 in a Pyrex reactor, using a Hanau Q700 mercury lamp. The products were condensed at 195 K and small amounts of FSO_2OF were eliminated by trap-to-trap distillations at 223 K [14,17]. The purity of $F_2S_2O_6$ was verified by IR spectrophotometry. The helium (Union Carbide, 99.999%) was passed through a trap cooled at 153 K and stored in a Pyrex flask.

3. Results and discussion

FSO_3 presents two weak diffuse absorption systems in the 1300–1400 nm (A^2A_1–X^2A_2) and 720–840 nm (B^2E–X^2A^2) regions, and a stronger discrete band with an origin at 516 nm (C^2E–X^2A^2). The last system is partially overlapped by a fairly strong continuum which decreases in intensity from approximately 470 to 340 nm [18] and the present measurements have been performed precisely over this region. From ca. 470 nm up to 516 nm, the strongly structured spectrum makes the absorption cross-section determinations for the relaxed and excited radicals less precise under the present experimental conditions [10,18].

When $F_2S_2O_6$ is photolyzed, fluorosulphate radicals are generated exclusively. In fact, early conventional UV (photolysis light ranging from 250 nm to 600 nm) flash spectroscopy observations [9] agree with recent excimer laser flash photolysis experiments which lead to a quantum yield of two for fluorosulphate radical formation at 193 nm [14]. Moreover, the generated radicals are excited [4–8]. The assignment of the electronic state B^2E for the radical formed by prompt photodissociation of $F_2S_2O_6$ is based upon a comparison between the measured and the calculated (from the integrated oscillator strengths [18]) radiative lifetimes, for which the value 4.2±0.5 μs was obtained [6]. The $FSO_3(B^2E)$ radical is subsequently collisionally deactivated giving place to the formation of ground-state vibrationally excited radicals which, thereafter, on a longer timescale are relaxed by the colliders following a double-exponential decay law [7]. Finally, the resulting thermalized FSO_3 radicals recombine on a millisecond timescale [11]. The transient species responsible for the faster decay are denoted here by $FSO_3{}^*$ while the slower decay is attributed to the species $FSO_3{}^{**}$. Therefore, in the global scheme proposed, the excited radicals are related, via consecutive first-order decays, by collisional and radiative processes which drive their respective state populations

$$FSO_3(B^2E) + Q \longrightarrow FSO_3{}^* + Q \tag{1}$$

$$FSO_3{}^* + Q \longrightarrow FSO_3{}^{**} + Q \tag{2}$$

$$FSO_3{}^{**} + Q \longrightarrow FSO_3 + Q \tag{3}$$

$$FSO_3(B^2E) \longrightarrow FSO_3 + h\nu \tag{4}$$

$$FSO_3{}^* \longrightarrow FSO_3 + h\nu^* \tag{5}$$

$$FSO_3{}^{**} \text{——} FSO_3 + h\nu^{**} \tag{6}$$

where Q represents the collision partners and reactions (4)–(6) are spontaneous collision-free radiative processes. Figs. 1 and 2 show the variation of the absorbance with time at 350 nm and 450 nm, respectively. Similar traces were obtained at

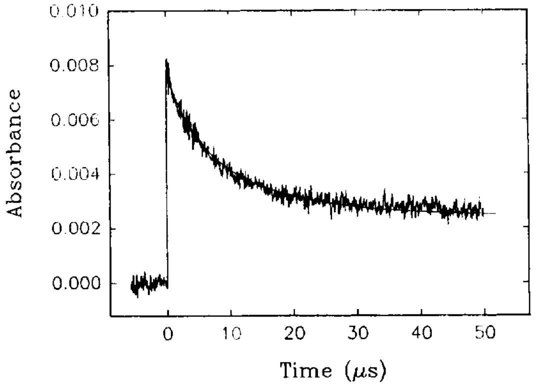

Fig. 1. Time-resolved absorbance monitored at 350 nm following the 193 nm photodissociation of 2.1×10^{17} molecule cm^{-3} of $F_2S_2O_6$ and 6.0×10^{18} molecule cm^{-3} of He. The solid line is the result of the modelling described in the text.

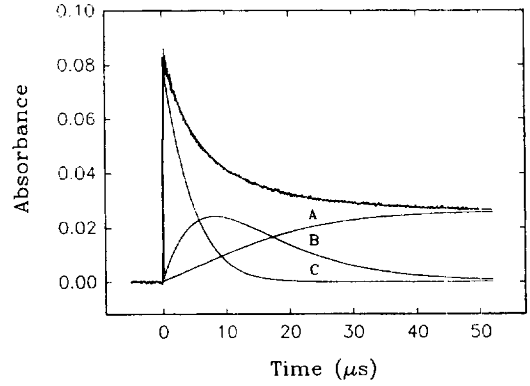

Fig. 2. Time-resolved absorbance monitored at 450 nm following the 193 nm photodissociation of 1.9×10^{17} molecule cm^{-3} of $F_2S_2O_6$ and 6.5×10^{18} molecule cm^{-3} of He. The solid line fitted through the data is a result of a modelling simulation. Curves A, B and C indicate the individual contributions of the FSO_3, $FSO_3{}^{**}$ and $FSO_3{}^*$ radicals to the signal.

Table 1
Measured cross-sections for the FSO_3, FSO_3** and FSO_3* radicals

λ (nm)	$\sigma(R_i)$ (cm^2 molecule^{-1})		
	R = FSO_3[a]	R = FSO_3**[b]	R = FSO_3*[b]
340	2.75 ± 10^{-19}	4.1×10^{-19}	8.6 ± 10^{-19}
350	3.28×10^{-19}	6.2×10^{-19}	1.0×10^{-18}
360	4.92×10^{-19}	8.8×10^{-19}	1.4×10^{-18}
370	6.79×10^{-19}	1.2×10^{-18}	1.8×10^{-18}
380	8.47×10^{-19}	1.5×10^{-18}	2.0×10^{-18}
390	1.24×10^{-18}	2.1×10^{-18}	3.1×10^{-18}
400	1.58×10^{-18}	2.7×10^{-18}	4.3×10^{-18}
410	1.87×10^{-18}	2.9×10^{-18}	4.8×10^{-18}
420	2.34×10^{-18}	3.6×10^{-18}	5.7×10^{-18}
430	2.63×10^{-18}	4.3×10^{-18}	6.6×10^{-18}
440	3.35×10^{-18}	5.3×10^{-18}	8.3×10^{-18}
450	3.64×10^{-18}	6.2×10^{-18}	1.2×10^{-17}
460	4.27×10^{-18}	6.8×10^{-18}	1.1×10^{-17}
470	4.43×10^{-18}	6.7×10^{-18}	1.1×10^{-17}

[a] Ref. [12].
[b] This work.

the other wavelengths investigated. The signals exhibit an identical kinetic behaviour. The marked difference in the magnitude of the absorbances is exclusively attributed to differences among the absorption cross-section of the excited species monitored. The decay of the profiles due to the depopulation of the vibrational levels indicates that, according to the proposed model, the species FSO_3* and FSO_3** are characterized by absorption cross-section greater than those corresponding to the thermalized FSO_3 radicals. Although not given here for the reasons mentioned above, a similar pattern was observed over the 470–516 nm wavelength range. After a sufficiently long time and before significant FSO_3 self-recombination occurs [14], an almost constant concentration of relaxed FSO_3 is approached. This fact indicates a practically quantitative conversion of hot radicals into relaxed radicals.

The present experiments show that the absorption spectrum of FSO_3 is sensitive to the distribution of energy among the internal modes of this radical. In order to extract the absorption cross-section $\sigma(FSO_3{*})$ and $\sigma(FSO_3{**})$ from the experimental profiles, as modelling of the system was carried out. For this, a fourth-order Runge–Kutta algorithm was used to integrate the rate expressions of the kinetic scheme formed by processes (1) to (6). From these calculations the temporal evolution of the concentrations of the species FSO_3, FSO_3* and FSO_3** were obtained. Afterwards, the experimental absorbances were fitted using the expression $A = l(\Sigma_i \sigma(R_i)[R_i])$, where $\sigma(R_i)$ and $[R_i]$ stand respectively for the absorption cross-sections and time-dependent concentrations of the relaxed and excited FSO_3 radicals, and $l = 2.4$ cm is the analysis path length. The $\sigma(FSO_3)$ values given in Table 1 were employed in the computations. The relaxation rate coefficients for collisionally-mediated, k_Q, and for spontaneous-free-collision processes, k_S, listed in Table 2 were used in the simulations. These phenomenological rate coefficients characterize the average behaviour of the ensemble of vibrationally excited FSO_3 radicals. From the absorbances determined at about 70 μs and the $\sigma(FSO_3)$ values, the initial concentrations of the $FSO_3(B^2E)$ radicals employed in the simulations were estimated. The best $\sigma(FSO_3{*})$ and $\sigma(FSO_3{**})$ values were obtained from a non-linear least-squares fit of the computed decay curves to the experimental profiles. In order to illustrate the contribution of each different radical, the respective simulated absorption profiles are also depicted in Fig. 2. The calculations show that at about 8 μs, FSO_3* has been mostly quenched while FSO_3** has reached its maximum concentration. On the other hand, at sufficient long times the absorption becomes almost exclusively due to the relaxed radicals. In fact, the contribution of the FSO_3 to the total absorption trace is of 90%, 94% and 97% at the delay times of 50, 60 and 70 μs, respectively. Similar values were observed at the other wavelengths investigated. The absorption cross-sections determined by this procedure are listed in Table 1. The estimated overall uncertainty is about 15% for the measurements carried out at the smaller wavelengths.

Photolysis at 193 nm provides initially an energy of 619.2 kJ mol^{-1} to the $F_2S_2O_6$. After accounting for the O–O bond dissociation energy, 92.5 kJ mol^{-1} [14], and the average thermal energy of $F_2S_2O_6$, 26.4 kJ mol^{-1}, a simple impulsive spectator model of energy partitioning [19] leads to a surplus

Table 2
Second-order quenching rate coefficients k_Q and radiative rate coefficients k_S employed in the modelling

Reaction	k_Q (cm^3 molecule^{-1} s^{-1})			k_S (s^{-1})
	Q = $F_2S_2O_6$	Q = FSO_3	Q = He	
1	3.3×10^{-11}[a]	–	3.2×10^{-12}[a]	–
2	6.8×10^{-13}[c]	2.6×10^{-11}[c]	5.8×10^{-15}[b]	–
3	1.6×10^{-13}[b]	7.0×10^{-12}[c]	1.5×10^{-15}[b]	–
4	–	–	–	2.8×10^{5}[a]
5	–	–	–	3.7×10^{4}[b]
6	–	–	–	4.8×10^{3}[b,c]

[a] Ref. [6].
[b] Ref. [7].
[c] Ref. [8].

of excitation energy of 230.1 kJ mol^{-1} for each fragment initially formed. This energy is mainly employed to populate the B^2E of the fluorosulphate radical, which is 155.2 kJ mol^{-1} over the ground state [18], and then is probably channelled during collision into several relaxation pathways.

The average amount of excess energy in the vibrational degrees of freedom of the radicals is uncertain. Nevertheless, the deactivation kinetic data measured previously [7,8] may be used to gain some insight on the region of excitation energy sampled in the experiments. Vibration-to-vibration (V–V) and vibration-to-translation (V–T) energy transfer, or a combination of both, would be expected to occur. This assumption is based on the large difference observed between the rate coefficients k_Q for the FSO_3 and $F_2S_2O_6$ quenchers and He. Particularly, in the first case, near-resonant intermolecular V–V energy transfer is probably dominant [8]. From the values of Table 2 it may be inferred that the average energy transferred per collision between FSO_3 and $F_2S_2O_6$ is much greater than between FSO_3 and He. These differences are much bigger than those derived from collisions between the most efficient colliders and He measured in the dense manifold of high excitation rovibrational levels [3]. Moreover, the maximum energy transferred in the present experiments, which can be crudely estimated as the maximum energy available for each fragment divided by the number of gas kinetic collisions, is very small compared with those measured in high vibrationally excited molecules [3]. Both facts suggest that a region of low excitation energies (where V–V energy transfer is the dominant mechanism and V–T/R processes are rather slower [20–22]) has been monitored here. Thus, the small k_Q values reflect the well-known slowing down of the vibrational relaxation processes as the molecules approach thermal equilibrium [20–22].

Therefore, owing to the unavoidable averaging over collision parameters, the measured absorption cross-sections should be considered as mean weighted (according to population) cross-sections corresponding to a probably relatively sparse manifold of vibrational states placed at low-lying levels of excitation energies. More direct experiments are planned to elucidate the identity of the FSO_3 excited species.

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