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Electronic spectroscopy of bromopentafluorobenzene by high-resolution vacuum ultraviolet photoabsorption, electron impact, and photoelectron spectroscopies

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ABSTRACT

The electronic transitions of bromopentafluorobenzene (C_6F_5Br) have been investigated by high-resolution photoabsorption spectroscopy in the energy range 4–10.8 eV. In addition, the electron energy loss spectrum (EELS) was recorded in non-strictly electric dipolar interaction conditions (40 eV incident energy, 10° scattering angle) over the range 4–13.0 eV. The present spectra provide the first experimental data on the electronic states of bromopentafluorobenzene. The characteristics of the electronic excited states are discussed and the terrestrial atmospheric photolysis rates have been derived from the absolute photoabsorption cross-sections. The ionisation energies of the occupied molecular orbitals have been measured by high-resolution He(I) photoelectron spectroscopy, allowing a precise value of 9.679 ± 0.002 eV to be derived for the ionic ground state.

1. Introduction

Bromopentafluorobenzene, C_6F_5Br, is a brominated compound which is used in the production of pesticides and the preparation of catalysts [1]. It has also been proposed as a potential source of active $CF_x^\bullet$ radicals and CF_x^+ ions for silicon etching in industrial plasma reactors [2].

As industrial use increases the probability of C_6F_5Br release into the terrestrial atmosphere, it is important to explore the behaviour of this molecule when subjected to solar radiation. C–Br bonds are much weaker than CF-bonds in perfluorinated molecules and can be photolysed by solar radiation relatively easily [3], releasing highly reactive bromine atoms which can increase stratospheric ozone depletion. Accordingly it is necessary to characterise the electronic states of C_6F_5Br since its photolysis rate will be determined by the excitation energy and symmetry of the lowest excited states. The formation of $CF_x^\bullet$ radical species needed in semiconductor plasma reactors for silicon etching will also be dependent upon the dissociation dynamics of these states. However, to date there is little data, either experimental or theoretical, on the excited states of neutral and ionic bromopentafluorobenzene. Indeed, to the authors' knowledge, the only spectroscopic data on C_6F_5Br are three He(I) photoelectron spectra [4–6] recorded at much lower resolution (200 meV) than the present work. There are no previous photoabsorption studies or electron impact investigations.

The present work aims to elucidate the neutral and ionic electronic excited states of C_6F_5Br on the basis of new high-resolution photoabsorption, electron impact and photoelectron spectroscopic data. Calculated atmospheric photolysis rates are also reported for the first time for this significant industrial molecule.

2. Experimental

The electronic states of C_6F_5Br have been studied using different experimental techniques including: VUV photoabsorption using a synchrotron source, which provides data on optically allowed transitions and allows absolute photoabsorption cross-sections to be measured; high-resolution electron energy loss spectroscopy (HREELS) performed under non strictly electric dipolar interaction conditions which allows the character (allowed vs. forbidden) of the transitions to be explored and He(I) photoelectron spectroscopy (PES) to determine the ionisation energies of the occupied molecular orbitals.

2.1. VUV photoabsorption

High-resolution VUV photoabsorption measurements were performed using the ASTRID–UV1 beam line at the Institute for Storage Ring Facilities (ISA), University of Århus, Denmark. A detailed

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description of the apparatus can be found elsewhere [7] so only a brief description will be given here. A toroidal dispersion grating is used to select the synchrotron radiation with a FWHM wavelength resolution of approximately 0.075 nm. The synchrotron radiation passes through the static gas sample at room temperature. A photomultiplier is used to detect the transmitted light. For wavelengths below 200 nm, He gas is flushed through the small gap between the photomultiplier and the exit window of the gas cell to prevent any absorption by oxygen from air contributing to the spectrum. An LiF entrance window acts as an edge filter for higher order radiation and restricts the photoabsorption measures to below 10.8 eV (115 nm), while the grating itself defines the maximum wavelength (lower energy limit) of 320 nm (3.9 eV). The sample pressure is measured by a Baratron capacitance gauge. To avoid any saturation effects, sample pressures were chosen to ensure that the transmitted flux was >10% of the incident flux.

Gas transmission results are compared to a background scan recorded with an evacuated cell. Absolute photoabsorption cross-sections may then be calculated using the Beer–Lambert law:

$$I_t = I_0 \exp(-n\sigma x),$$

where I_t is the intensity of the light transmitted through the gas sample, I_0 is that through the evacuated cell, n is the molecular number density of the sample gas, σ is the absolute photoabsorption cross-section and x is the absorption path length (25 cm). The accuracy of the absolute cross-section is estimated to be better than ±5%.

2.2. High-resolution electron energy loss spectroscopy (HREELS)

The instrument used at the Université de Liège, Belgium (VG-SEELS 400) has been described in detail elsewhere [8]. An electrostatic electron energy monochromator defines a narrow energy spread about the mean incident electron energy and a three-element lens focuses the electrons into the collision region. The electron beam intersects an effusive gas beam, which flows through a hypodermic needle, at 90°. The working pressure in the chamber with target gas is $\sim 1.0 \times 10^{-5}$ mbar. The analyser system is also an electrostatic energy analyser with the scattered electron signal detected by an electron multiplier of the continuous dynode type. Both electron energy selectors work in the constant pass-energy mode. Spectra were recorded for energy losses between 4.0 eV and 13.0 eV at step intervals of 10 meV. The electron energy loss scale was calibrated to the “elastic scattering peak”. The resolution, measured as the FWHM of the elastically scattered electron peak, was about 40 meV. The apparatus was used with medium incident electron energy (40 eV) and a small scattering angle ($\theta = 10°$), such that non-strictly electric dipolar interaction conditions apply.

2.3. Photoelectron spectroscopy (PES)

He(I) (21.22 eV) photoelectron spectra of C_6F_5Br were measured at the Université de Liège, Belgium. The apparatus has been described in detail previously [9]. Briefly, the spectrometer consists of a 180° hemispherical electrostatic analyser with a mean radius of 5 cm. The analyser is used in constant energy pass mode. The incident photons are produced by a DC discharge in a two-stage differentially pumped lamp. The energy scale was calibrated using xenon lines and the values ${}^2P_{3/2} = 12.123$ eV and ${}^2P_{1/2} = 13.436$ eV given in the NIST ChemWebbook [10]. The resolution of the present spectrum, in the presence of bromopentafluorobenzene, is measured from the full width half maximum of the Xe peaks to be 20 meV. The intensities in the spectrum were corrected for the transmission of the analyzing system. The accuracy of the energy scale is estimated to be ±2 meV. The photoelectron spectrum presented in this paper is the sum of individual spectra, a procedure that ensures a good signal-to-noise ratio while keeping the pressure in the spectrometer at a very low level ($<5 \times 10^{-6}$ mbar).

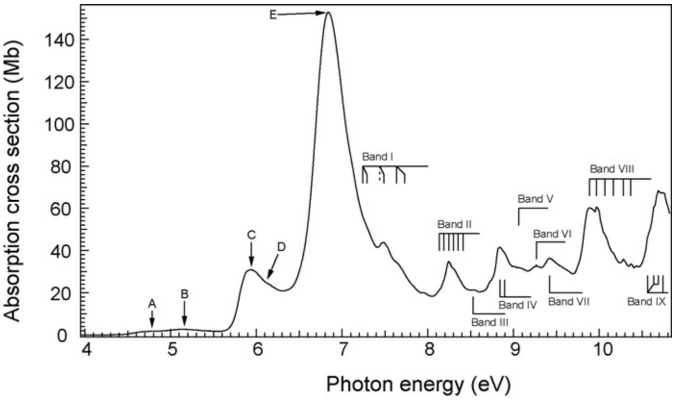

Fig. 1. The absolute photoabsorption cross-section of bromopentafluorobenzene in the 4.0–10.8 eV region.

2.4. The sample

The sample has been provided by Sigma–Aldrich with a stated purity better than 99%. It was used directly without further purification except for repetitive freeze–pump–thaw cycles in order to eliminate air and any other volatile impurities in the sample.

3. Properties of bromopentafluorobenzene

The structural constants for C_6F_5Br, determined experimentally for the gas-phase [11,12], are summarized as follows:

Experimental:

C–C = 1.394 Å
C–F = 1.327 Å
C–Br = 1.879 Å
Angle CCC = 120°
Angle CCF = 120°

The molecule belongs to the C_{2V} symmetry class in its gas-phase electronic ground state. This is in contrast with hexafluorobenzene (C_6F_6) that has been found to belong to the D_{6h} symmetry group. Despite the different symmetry classes, comparison with C_6F_6 helped in the assignment of the features observed in the spectra of C_6F_5Br.

The molecule has 30 normal vibrational modes of which there are 20 fundamental vibrations. Eleven of these modes available for a C_{2V} molecule belong to the a_1 species, 10 to the b_2, 3 modes to the a_2, and 6 to the b_1. The vibrational representation for the neutral ground state is $11a_1 + 3a_2 + 6b_1 + 10b_2$. The data from the literature are presented in Table 1.

4. Results and discussion

4.1. Valence and Rydberg states

The high-resolution absolute VUV photoabsorption spectrum of C_6F_5Br recorded between 4.0 eV and 10.8 eV is shown in Fig. 1. It can be split into two regions; the first between 4 eV and 7 eV is composed of broad bands and the second from 7 eV to 10.8 eV with several broad bands with superimposed fine structure. The shape

Table 1
Symmetries, indentification, energies, and wavenumbers of the normal vibrational modes of bromopentafluorobenzene in the neutral electronic ground state

Symmetries	Normal modes	Energies (meV)	Wavenumbers (cm^{-1})
a_1V	ν_1	203.1	1638
	ν_2	188.3	1519
	ν_3	177	1428
	ν_4	159.9	1290
	ν_5	136	1097
	ν_6	104.1	840
	ν_7	72.4	584
	ν_8	61.4	495
	ν_9	44.9	362
	ν_{10}	35	282
	ν_{11}	29.8	240
a_2	ν_{12}	80.8	652
	ν_{13}	46.9	378
	ν_{14}	17.4	140 (solid)
b_1	ν_{15}	89.1	719
	ν_{16}	76.9	620
	ν_{17}	43.1	348
	ν_{18}	25.7	207
	ν_{19}	21.7	175 (liquid)
	ν_{20}	11	89
b_2	ν_{21}	203.1	1638
	ν_{22}	187.6	1513
	ν_{23}	157.8	1273
	ν_{24}	143.7	1159
	ν_{25}	123.4	995
	ν_{26}	91.4	737
	ν_{27}	54.6	440
	ν_{28}	38.3	309
	ν_{29}	29.8	240
	ν_{30}	19.2	155

From Refs. [11,12].

of the absorption spectrum is confirmed by the high-resolution electron energy loss spectrum recorded between 4 eV and 13.0 eV and shown in Fig. 2. The HREELS result also shows the 10.8–13 eV region, not accessible in the photoabsorption experiment, to be characterised by a smooth spectrum without any distinct transition features.

The present tentative assignments for the neutral excited states and the ionic states of C_6F_5Br are based on comparisons with hexafluorobenzene [13] and the hypothesis that the order of the occupied and unoccupied orbitals is the same in the two molecules.

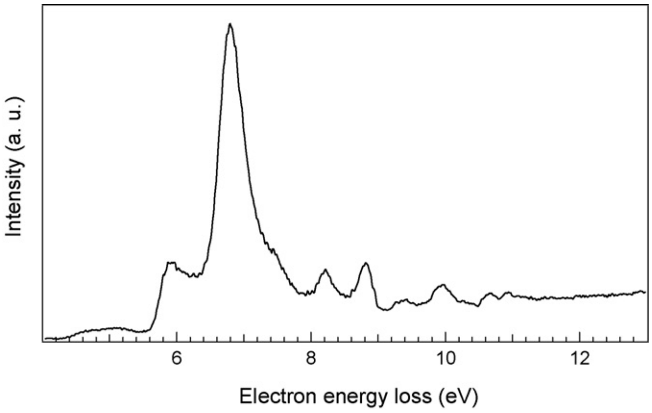

Fig. 2. Electron energy loss spectrum of bromopentafluorobenzene recorded at the University of Liège in the 4–13 eV energy loss region at 40 eV incident energy and ~10° scattering angle.

Table 2
Energies of the bands in the valence region of bromopentafluorobenzene measured by electron impact and photoabsorption spectroscopies and compared with analogous hexafluorobenzene transitions (photoabsorption)

Bands	Bromopentafluorobenzene		Hexafluorobenzene[a]	Assignments
	Electron impact	Photoabsorption		
A	4.78	4.785	4.86	$\pi-\pi^*\ 1^1B_{2u}$
B	5.11	5.161	5.38	$\pi-\sigma^*$
C	5.94	5.942	5.66	$\pi-\sigma^*$
D	6.10	6.114	6.39	$\pi-\pi^*1^1B_{1u}$
E	6.83	6.845	7.10	$\pi-\pi^*1^1E_{1u}$

All energies are in eV.
[a] See Ref. [13].

4.1.1. *Valence state region from 4 eV to 7 eV*

This region consists of five absorption bands, the energies and proposed assignments of which are given in Table 2. The bands are quite broad (Figs. 1 and 2), suggesting that the valence excited states lead to rapid dissociation into neutral radicals. All the observed bands are shifted to lower energies compared to the corresponding bands in hexafluorobenzene except the third one which is located at a very slightly higher energy.

The band with the largest absolute cross-section (150 Mb) is centred at 6.845 eV and may be due to an optically allowed transition. The corresponding band located at 7.10 eV in hexafluorobenzene has been assigned to the $\pi-\pi^*$ ($\tilde{X}^1A_{1g}-1^1E_{1u}$) excitation.

The low absolute photoabsorption cross-sections of the first four bands suggest that they are due to symmetry forbidden excitations. The lowest energy band, centred at 4.785 eV, is only partly resolved from the second band and corresponds to the symmetry forbidden transition $\pi-\pi^*$ ($\tilde{X}^1A_{1g}-1^1B_{2u}$) in hexafluorobenzene. The second band is centred at 5.161 eV and assigned to a $\pi-\sigma^*$ transition by analogy with hexafluorobenzene. Band C at 5.942 eV may be identified as a $\pi-\sigma^*$ transition, observed in the completely fluorinated molecule at 5.66 eV. A weak partially resolved absorption feature (D) at 6.11 eV (Fig. 1) is found to have greater relative intensity in the electron energy loss spectrum (Fig. 2). This feature is energetically close to the 6.39 eV band in hexafluorobenzene assigned to the symmetry forbidden excitation $\pi-\pi^*$ ($\tilde{X}^1A_{1g}-1^1B_u$).

4.1.2. *Rydberg state region from 7 eV to 10.8 eV*

The photoabsorption spectrum in the 7–10.8 eV region is shown in detail in Fig. 3. It is characterised by the presence of numerous, rather sharp, features with lower cross-sections than the 6.845 eV valence band. The absolute cross-section in this region is much higher than in the hexafluorobenzene spectrum [13].

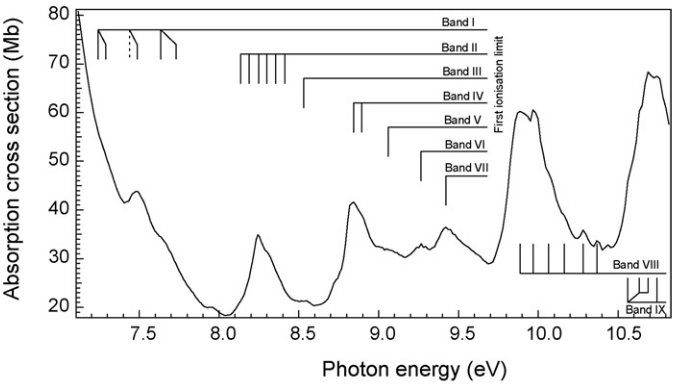

Fig. 3. The absolute photoabsorption cross-sections of bromopentafluorobenzene in the Rydberg state region.

Table 3
Bromopentafluorobenzene Rydberg states and associated vibrational features observed by photoabsorption

Bands	Energy (eV)	Delta (meV)	Assigments[a]
I	7.242	0	5p to the first ionisation limit
	7.290	48	1 νA (48 meV)
	7.487	245	1 νB + 1 νA (1 νB = 197 meV)
	7.635	393	2 νB
	7.938	696	2 νB + 2 νA
II	8.135	0	6s to the first ionisation limit
	8.189	54	1 νA (54 meV)
	8.248	113	2 νA
	8.299	154	3 νA
	8.355	220	4 νA
	8.412	277	5 νA
III	8.530	0	6p to the first ionisation limit
IV	8.843	0	5d to the first ionisation limit
	8.894	51	1 νA
V	9.060	0	6d
VI	9.266	0	7p
VII	9.421	0	9d to the first ionisation limit
VIII	9.887	0	6 s to the second ionisation limit
	9.983	96	1 νA
	10.064	177	2 νA
	10.163	276	3 νA
	10.281	394	4 νA
	10.367	480	5 νA
IX	10.561	0	6p to the third ionisation limit
	10.633	72	1 νA (1 νA = 72 meV)
	10.688	127	2 νA
	10.744	183	1 νB (183 meV)

[a] Notation: νA represents the lowest energy feature in a band, and νB the highest.

The features observed in this region are assigned to Rydberg series converging to the three lowest energy ionisation limits at 9.679, 11.485 eV and 11.904 eV (see Section 4.2). The peak positions of such features, E_n, must fit the Rydberg formula: $E_n = E_i - R/(n-\delta)^2$, where E_i is the ionisation energy, n is the principal quantum number of the Rydberg orbital of energy E_n, R is the Rydberg constant and δ is the quantum defect resulting from the penetration of the Rydberg orbital into the core. Quantum defects for compounds with bromine are between 2.9 and 3.2 for s series, between 2.3 and 2.7 for p series and between 1.0 and 1.2 for d series (see here after) [14]. Three Rydberg series are reported converging to the ground state ionisation limit. In addition, it is possible to identify the first members of an s and a p series converging to the first and second ionic excited states, respectively (Table 3).

Vibrational excitations associated with Rydberg states are presented in detail in Table 3. Two normal vibrational modes are observed for the 5p term with mean activation energies of 48 meV and 197 meV. For the $n = 6$ term of the s series, just one vibrational mode is excited with a mean value of 50 meV. These values are close to the equivalent activation energies for vibrational modes of the ion in the ground state (see Section 4.2).

For the first member of the s series converging to the first excited state of the ion, fine structure is observed with individual features separated by about 80 meV (Table 3, Fig. 3). This value is a little bit lower than observed in the corresponding ionic excited state. The band at 10.561 eV (Fig. 3) assigned to the six term of a p series converging to the third ionisation limit exhibits fine structure characterised by 72 meV and 183 meV activation energies. These values are slightly lower than those reported in the electronic ground state [11,12].

4.2. *Ionic states*

The He(I) photoelectron spectrum (PES) of C_6F_5Br is shown in Fig. 4. While the spectrum is similar to that reported by [6], several additional features are resolved in the present result. It exhibits seven bands whose energy positions are given in Table 4. Fine structure is observed within bands I, II, III, V, and VII.

The lowest energy ionic band (Fig. 4) begins at 9.679 eV and includes fine structure which is not completely resolved, despite the excellent spectral resolution. This fine structure has been interpreted in terms of excitation of two vibrational modes with energies of 76 meV and 178 meV, respectively (Table 4). These values are close to those observed for four normal modes in the neutral electronic ground state: ν_7 (72.4 meV), ν_8 (61.4 meV), ν_2 (188.3 meV), and ν_3 (177 meV) [11,12]. The shape and the broadness of this first ionic band suggest that the parent ion in the ground electronic state may have a short lifetime.

The second and third PES bands can be assigned to electron emission from the non-bonding lone pairs of the bromine atom. They are not present in the hexafluorobenzene photoelectron spectrum [13] but are observed in bromobenzene [15,16]. Band II, centred at 11.485 eV, is rather broad and corresponds to the out-of-plane lone pair of B_1 symmetry. Band III, centred at 11.9 eV, is sharper and attributed to the lone pair of B_2 symmetry in the plane of the aromatic ring. The energy separation of these two bands is mainly due to differences in the interactions of these pairs with the molecular orbitals of the aromatic ring.

It should be noted that the energetic order of bands II and III is the inverse of the order observed for bromobenzene. This is probably due to the *perfluoro* effect which increases ionisation energies for non-bonding orbitals out of the aromatic plane by up to 1 eV and, for non-bonding orbitals in the plane of the aromatic ring, by 1 eV or more [17]. This effect will tend to shift the ionisation energy of the molecular orbital b_1 to a lower energy than b_2 in C_6F_5Br.

The vibrational structure in band II (Table 4) is characterised by mean activation energies of 0.021 eV and 0.093 eV. By comparison with the neutral electronic ground state (Table 1), these series have been assigned to the modes (ν_{14}) and/or (ν_{30}), and to (ν_{15}) and/or (ν_{26}), respectively.

Band III, centred at 11.9 eV (Fig. 4), also shows evidence for the excitation of two vibrational modes (Table 4) with mean activation energies of 50 meV and 194 meV. These respective energies are close to the modes (ν_8) and/or (ν_{27}), and to (ν_2) and/or (ν_3) in the neutral electronic ground state.

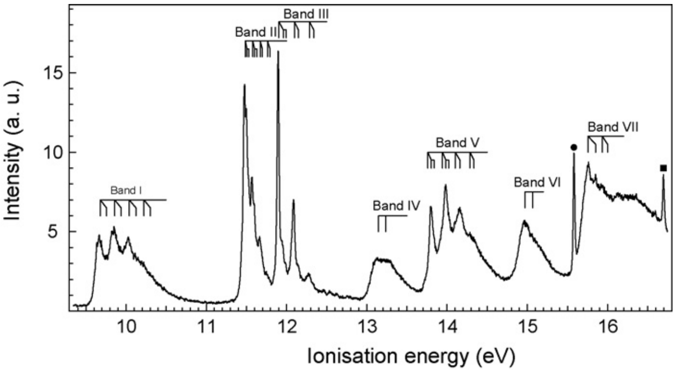

Fig. 4. He(I) photoelectron spectra of bromopentafluorobenzene recorded at the University of Liège in the 9.5–16.50 eV energy region (impurities: (●) indicates the nitrogen $X^2\Sigma_g^+ \nu' = 0$ state; (■) indicates the nitrogen $A\ ^2\prod_u \nu' = 0$).

Band IV at 13.144 eV (Fig. 4) is rather broad with only a single feature at 13.236 eV. The next band, centred at 14 eV (Fig. 4), exhibits several partially resolved features which are attributed to the excitation of vibrational modes with mean values 50 meV and 183 meV. By comparison with the neutral ground state, these modes may be assigned to (ν_8) and/or (ν_{27}), and to (ν_2) and/or (ν_3), respectively.

The maxima of the last two bands occur at 14.970 eV and 15.757 eV. Their fine structure are only partially resolved but may be assigned to vibrational excitation of the modes (ν_{15}) and/or (ν_{26}) for the 14.970 eV ionic state and, for the 15.757 eV ionic state, to the activation of (ν_{15}) and/or (ν_{26}), and of (ν_2) and/or (ν_3).

5. Absolute cross-sections and UV photolysis rates

The absolute cross-section values of C_6F_5Br have been used to model its atmospheric destruction by UV photolysis as a function of altitude. The photolysis rates of C_6F_5Br were calculated at a given wavelength as the product of the Solar Actinic Flux [18] and the molecular photoabsorption cross-section by 1 km altitude steps from the surface up to the stratopause (50 km). At each altitude, the total photolysis rate may be calculated by summing over the individual photolysis rates for that altitude. The reciprocal of the total photolysis rate for a given altitude gives the local photolysis lifetime at that altitude, i.e., the time taken for the molecule to photodissociate assuming that the solar flux remains constant. The local lifetimes and the photolysis rates are shown in Fig. 5, where for the former we assume that the quantum yield for dissociation is unity.

Table 4
Energies of the photoelectron bands for bromopentafluorobenzene

Bands	Energies (eV)	Deltas (meV)	Assigments[a]
I	9.679	0	
	9.755	76	$1\,\nu A \equiv (1\,\nu_7, 1\,\nu_8)$
	9.857	178	$1\,\nu B \equiv (1\,\nu_2, 1\,\nu_3)$
	9.938	259	$1\,\nu B + 1\,\nu A$
	10.039	360	$2\,\nu B$
	10.123	444	$2\,\nu B + 1\,\nu A$
	10.222	543	$3\,\nu B$
	10.302	623	$3\,\nu B + 1\,\nu A$
II	11.485	0	
	11.506	21	$1\,\nu A \equiv (1\,\nu_{14}, 1\,\nu_{30})$
	11.529	44	$2\,\nu A$
	11.578	93	$1\,\nu B \equiv (1\,\nu_{15}, 1\,\nu_{26})$
	11.602	117	$1\,\nu B + 1\,\nu A$
	11.631	146	$1\,\nu B + 2\,\nu A$
	11.672	$187 = 2 \times 93$	$2\,\nu B$
	11.696	211	$2\,\nu B + 2\,\nu A$
	11.762	$277 = 3 \times 93$	$3\,\nu B$
	11.793	308	$3\,\nu B + 1\,\nu A$
III	11.904	0	
	11.959	55	$1\,\nu A \equiv (1\,\nu_8, 1\,\nu_{27})$
	11.994	90	$2\,\nu A$
	12.098	194	$1\,\nu B \equiv (1\,\nu_2, 1\,\nu_3)$
	12.146	242	$1\,\nu B + 1\,\nu A$
	12.287	383	$2\,\nu B$
	12.338	434	$2\,\nu B + 1\,\nu A$
IV	13.144	0	
	13.236	92	$1\,\nu_{15}, 1\,\nu_{26}$
V	13.759	0	
	13.804	45	$1\,\nu A \equiv (1\,\nu_8, 1\,\nu_{27})$
	13.840	81	$2\,\nu A$
	13.942	183	$1\,\nu B \equiv (1\,\nu_2, 1\,\nu_3)$
	13.985	226	$1\,\nu B + 1\,\nu A$
	14.019	260	$1\,\nu B + 2\,\nu A$
	14.102	343	$2\,\nu B$
	14.160	401	$2\,\nu B + 1\,\nu A$
	14.285	526	$3\,\nu B$
	14.334	575	$3\,\nu B + 1\,\nu A$
VI	14.970	0	
	15.065	95	$1\,\nu_{15}, 1\,\nu_{26}$
N_2	15.583		$X^2\,\Sigma_g^+$
VII	15.757	0	
	15.850	93	$1\,\nu A \equiv (1\,\nu_{15}, 1\,\nu_{26})$
	15.934	177	$1\,\nu B \equiv (1\,\nu_2, 1\,\nu_3)$
	16.000	273	$1\,\nu B + 1\,\nu A$
N_2	16.969		$A^2\,\prod_u$

[a] Notation: νA represents the lowest energy feature in a band, and νB the highest.

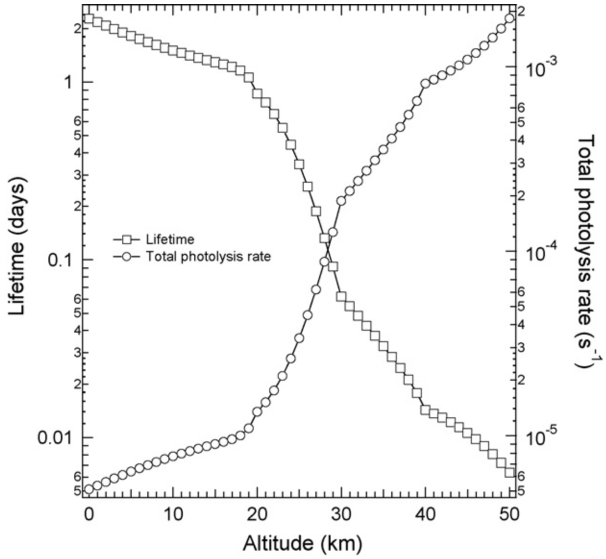

Fig. 5. Total photolysis and local lifetime of bromopentafluorobenzene between 0 and 50 km.

The results show that the local photolysis lifetime of C_6F_5Br is about 2 days at altitude of 15 km and diminishes rapidly at higher altitudes. The very short lifetime at 40 km altitude suggests that it can be quickly broken up releasing reactive bromine atoms into the stratosphere. Therefore the molecule might be expected to have significant Ozone Depletion Potential (ODP). The lifetime may also determined by competing pathways for the removal of the compound from the atmosphere i.e. the solubility and reactions with OH radicals if the corresponding removal times are low compared with transport times from the surface to high altitudes. The OH radicals are known to be the most abundant and the most reactive species present in the tropospshere [3]. However, reaction with other radicals cannot be excluded but they are much less abundant and much less reactive. As far as the authors know, the reactions of this compound with OH radicals have not already been investigated.

6. Conclusions

The present work provides the first experimental data on the electronic spectroscopy of C_6F_5Br in the 4.0–13.0 eV energy region. Most of the valence excited states are slightly shifted to lower energy compared to hexafluorobenzene, an effect ascribed to the presence of fluorine atoms in the molecule. The high-resolution of the measurements has enabled the present analysis to be extended to the fine structure associated with vibrational excitation in the Rydberg state region. In addition, precise energies for the ionic excited states located between 9 eV and 17 eV have been measured for the first time.

The absolute photoabsorption cross-sections measured in this work have been used to estimate the photolysis rates of this compound in the Earth's atmosphere (0–50 km) for the first time. The lifetime due to solar photolysis is shown to be rather short suggesting C_6F_5Br may be an ozone depleting compound. The "absolute" lifetime depends also upon rival processes for the removal of the molecule such as reaction with the OH radicals and solubility.

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