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Absorption spectra of Cl_2, Br_2 and BrCl between 190 and 600 nm

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Abstract

Absolute photoabsorption cross sections at room temperature are reported for Cl_2 (190–500 nm), Br_2 (190–600 nm), and BrCl (190–560 nm). In addition, cross sectional data for BrCl were deconvoluted using a semi-logarithmic gaussian distribution function into a UV band centered at 228.3 nm, a C $^1\Pi_1$ band centered at 376.4 nm, a B $^3\Pi_0{}^+$ band centered at 454.9 nm, and an A $^3\Pi_1$ band centered at 533.1 nm. The BrCl band maximum at approximately 228 nm of 6.0×10^{-20} cm^2 molecule^{-1} was assigned to a transition from the X $^1\Sigma_0{}^+$ ground state to a repulsive 0^+ electronic state by analogy with similar UV bands present in ICl and IBr. Finally, an absorbance maximum was also detected for Br_2 at 227 nm of 0.96×10^{-20} cm^2 molecule^{-1}.

Keywords: Absorption spectra; Cl_2; Br_2; BrCl

1. Introduction

The visible and ultraviolet absorption spectra and associated electronic states of halogen (X_2) and interhalogen (XY) molecules have attracted scientific interest for three separate reasons. First, halogenated hydrocarbons are rapidly being added to the atmosphere due to their essential use as aerosol propellants, refrigerants, and fire retardants [1,2]. The discovery by Farman et al. [3] that a major decrease in ozone concentration occurs over Antarctica every spring [4–6] showed that the chemistry of the Antarctic stratosphere was greatly perturbed with large abundances of ozone-destroying halogen radicals ClO and BrO [7] which provide an efficient catalytic pathway for destroying ozone [8,9].

$$ClO + BrO \longrightarrow OClO + Br \quad (1a)$$

$$\longrightarrow ClOO + Br \quad (1b)$$

$$\longrightarrow BrCl + O_2 \quad (1c)$$

Since the formation of OClO is thought to be neutral in terms of the overall ozone cycle (photolysis of OClO yields primarily ClO + O and thus regenerates odd oxygen), any divergence of reaction (1) to yield BrCl, whose photolysis yields two halogen radicals and no odd oxygen, would have a significant albeit minor effect on atmospheric ozone levels.

Second, since the demonstration of Byer et al. [10] of an optically pumped molecular iodine (I_2) electronic transition laser, diatomic halogens and interhalogens have been extensively investigated as possible laser media with potential for high gain and high energy output [11,12]. High power visible CW lasers based on radiative binary halogen atom recombination and non-radiative ternary recombination leading to radiant excited electronic states are being developed [13–15]. The interhalogen molecule BrCl, operating on the B $^3\Pi_0{}^+$ to X $^1\Sigma_0{}^+$ electronic transition, is thought to be particularly promising as a chemically driven visible laser [16].

Third, the interhalogen molecules (e.g. BrCl) are an interesting class of molecules which display overlapping discrete, diffuse, and continuous absorption bands. Transitions from the X $^1\Sigma_0{}^+$ ground state to low lying A $^3\Pi_1$, B $^3\Pi_0{}^+$, and C $^1\Pi_1$ electronic states are strongly overlapped and display such interesting properties as predissociation and potential energy curve crossings [17–21]. Analysis of their spectra provides an opportunity to test theoretical models such as long range potential theory [22] and Mulliken's classic treatment of diatomic molecular energies and spectra [23].

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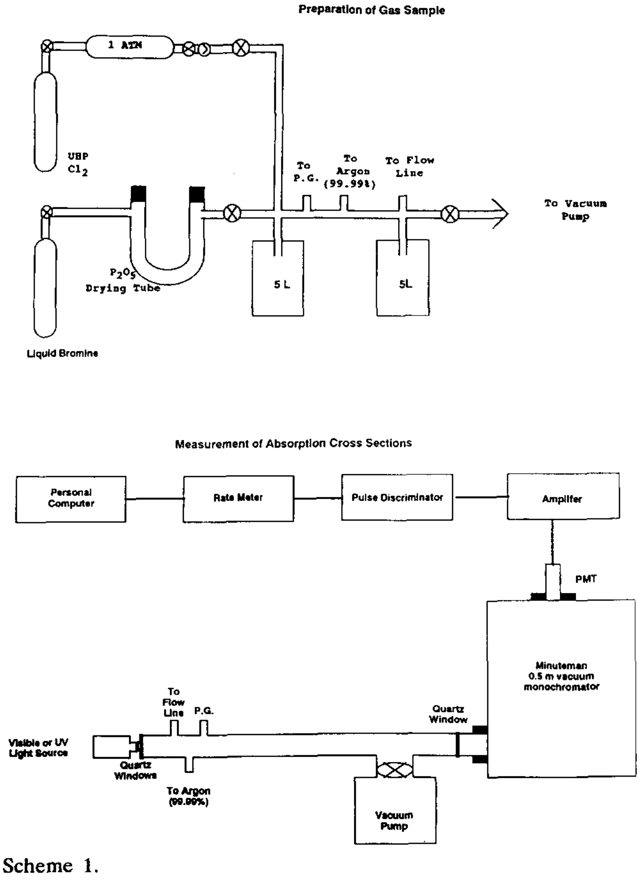
2. Experimental details

Halogen gas samples were prepared by partially filling an evacuated 10 liter Pyrex tank system (see Scheme 1) with either ca. 27 kPa Cl_2 (Matheson, UHP), or ca. 13 kPa Br_2 (made by heating $CuBr_2$ (Ferak Berlin) or taken directly from the pure liquid (Nippon Shiyaku Kogyo)) or ca. 27 kPa Cl_2 and 13 kPa Br_2. The Br_2 was further purified by passing it through a U-tube filled with P_2O_5 in order to remove water. For most experiments, the sample gases were diluted with argon up to a total pressure of approximately 67 kPa in order to insure a stable gas flow. The equilibrium tank concentration of BrCl was determined using an equilibrium coefficient $K_{eq} = [BrCl]^2/[Cl_2][Br_2]$ of 6.4 [24] for the reaction $Cl_2 + Br_2 \rightarrow 2\,BrCl$. Uncertainty in K_{eq} has only a minor impact on σ_{BrCl} ($K_{eq} = 8.01$ from Ref. [25] would change σ_{BrCl} by approximately 3% while $K_{eq} = 9.6$ from Ref. [11] would change σ_{BrCl} by approximately 5%).

The optical system used consisted of a Minuteman 0.5 m Vacuum Monochrometer with a dispersion of 1.67 nm mm^{-1} driven electronically by an IBM PC computer, a 200 cm Pyrex flow tube sealed on both ends with quartz windows, either a 1 watt car lamp filament (visible) or a Hamamatsu (L1626) deuterium lamp (UV) light source and a Hamamatsu photomultiplier tube (1P28). Signals from the PMT were detected with a pulse discriminator and amplifier system and then recorded by an IBM PC computer using an analog-to-digital converter. Wavelength data along with the signal from the PMT were recorded to disk simultaneously by an in-house C program. Recorded wavelengths were calibrated against a mercury (Hg) lamp at 10 different wavelengths between 253.652 and 579.0 nm (±0.10 nm) [26].



Scheme 1.

Halogen absorbances were determined at room temperature (295 ± 2 K) by first measuring the background (ca. 0.67 kPa Ar) light intensity as a function of wavelength and then repeating the same measurement with approximately 0.13 kPa of sample gas added to the flow tube. Cl_2 and Br_2 photoabsorption cross sections (σ) were determined directly from the flow tube pressure as measured by a 10 torr Baratron capacitance manometer. BrCl photoabsorption cross sections in units of cm^2 $molecule^{-1}$ were determined using Eq. (2) and previously recorded values for σ_{Cl2} and σ_{Br2}.

$$\sigma_{BrCl} = \frac{kT \times ABS}{200\ cm \times p_{BrCl}} - \sigma_{Cl_2} \times \frac{p_{Cl2}}{p_{BrCl}} - \sigma_{Br_2} \times \frac{p_{Br2}}{p_{BrCl}} \qquad (2)$$

3. Results

Absolute photoabsorption cross sections are hereby reported for Cl_2, Br_2, and BrCl at room temperature (see Fig. 1 and Table 1). A graphical comparison between our results for Cl_2 and those reported by Maric et al. [27] and by Ganske et al. [28] shows a near perfect correspondence with significant differences only in those wavelength regions where reported Cl_2 cross sections are below 10^{-21} (i.e. between 200 and 250 nm and after 500 nm). Since Cl_2 cross sections after 500 nm are effectively below our limit of detection, values are presented in Table 1 only between 190 and 500 nm. Furthermore, values given for Cl_2 between 200 and 250 nm must be regarded as upper limits only.

A similar graphical comparison between our results for Br_2 and those reported by Maric et al. [29], Passchier et al. [30], and by Wen and Noyes [31] also shows an excellent correspondence. Only when reported Br_2 cross sections fall below 10^{-21} (i.e. between 260 and 340 nm) do significant differences appear. Values are thus tabulated for Br_2 in Table 1 between 190 and 600 nm with those between 260 and 340 nm being upper limits only.

We also detected a UV continuum with a maximum at 227 nm. Although absorbance in this region has been detected previously (Gray and Style [32], Evans [33], Ogryzlo and Sanctuary [34], Passchier [30], Wen and Noyes [31]), to some extent it has been attributed to absorption caused by the formation of a collisional dimer (Br_2–Br_2). However, the former investigations

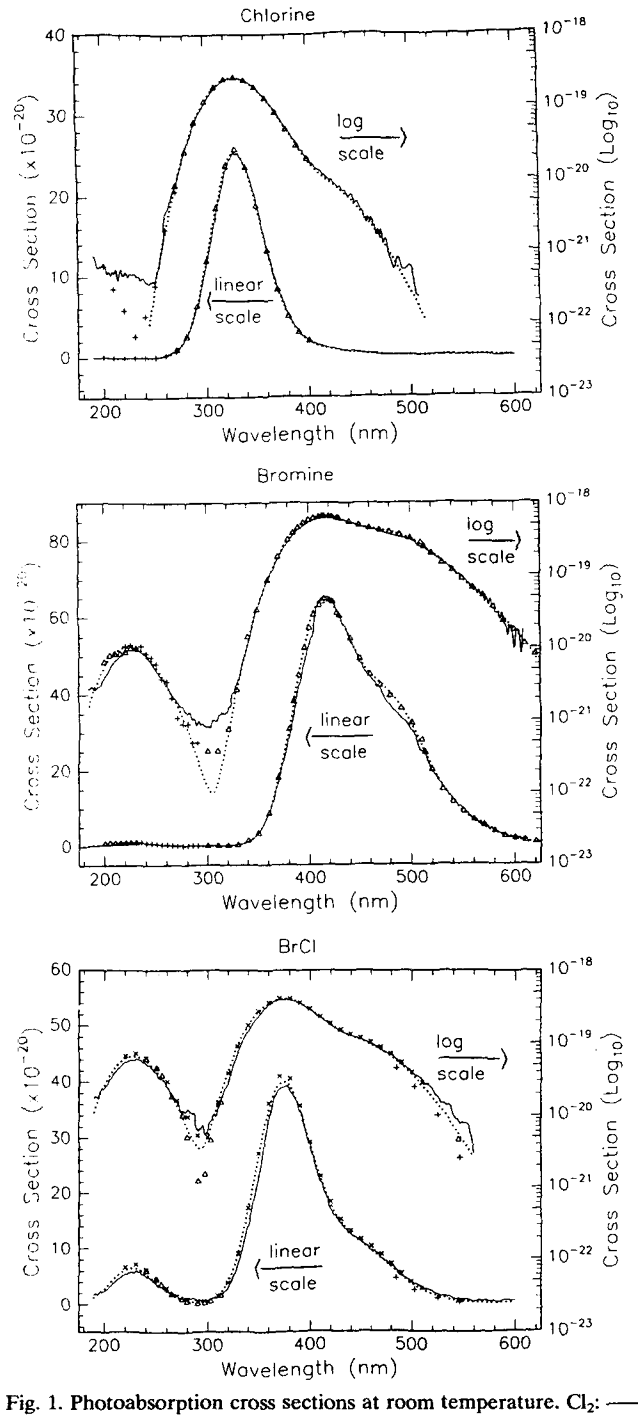


Fig. 1. Photoabsorption cross sections at room temperature. Cl_2: ——, present work; △, Ganske [28]; +, Maric [27]; – – –, Maric [27]. $\sigma=2.55\times10^{-19}\ \exp\{-86.6[\ln(329.5/\lambda)]^2\}+8.72\times10^{-21}\ \exp\{-80.0[\ln(406.5/\lambda)]^2\}$. Br_2: ——, present work; △, Passchier [30]; +, Wen and Noyes [31]; – – –, Maric [29]. $\sigma=1.06\times10^{-20}\ \exp\{-52.3[\ln(223.3/\lambda)]^2\}+6.19\times10^{-19}\ \exp\{-108.5[\ln(411.9/\lambda)]^2\}+3.49\times10^{-19}\ \exp\{-106.8[\ln(480.2/\lambda)]^2\}+3.78\times10^{-20}\ \exp\{-112.0[\ln(549.3/\lambda)]^2\}$. BrCl: ——, present work; △, Gray and Style [32]; +, Jost [35]; symbol, Seery and Britton [25]; ——, Maric [29]. $\sigma=6.52\times10^{-20}\ \exp\{-54.1[\ln(227.6/\lambda)]^2\}+3.86\times10^{-19}\ \exp\{-97.6[\ln(372.5/\lambda)]^2\}+9.99\times10^{-20}\ \exp\{-66.9[\ln(442.4/\lambda)]^2\}$.

Table 1
Absorption cross sections for Cl_2, Br_2, and BrCl

Wavelength (nm)	Chlorine (Cl_2)	Bromine (Br_2)	BrCl
	Cross section ($\times10^{-20}$)	Cross section ($\times10^{-20}$)	Cross section ($\times10^{-20}$)
190	0.09	0.28	1.8
200	0.07	0.40	2.4
210	0.05	0.67	4.0
220	0.05	0.91	5.4
230	0.05	0.95	6.0
240	0.04	0.77	5.1
250	0.04	0.49	3.7
260	0.37	0.31	2.5
270	0.89	0.19	1.5
280	2.5	0.13	1.2
290	6.0	0.10	0.63
300	11.3	0.09	0.61
310	17.5	0.12	1.2
320	23.2	0.15	2.8
330	25.2	0.35	7.4
340	23.7	1.1	14.2
350	19.3	3.4	22.9
360	13.1	8.4	33.3
370	8.4	16.8	38.7
380	5.2	28.7	38.5
390	3.1	42.1	34.7
400	1.9	53.0	28.2
410	1.4	64.1	21.9
420	1.0	64.8	16.9
430	0.76	60.5	14.2
440	0.58	53.4	12.4
450	0.45	48.1	11.1
460	0.29	44.3	9.6
470	0.17	41.5	8.0
480	0.09	36.6	6.8
490	0.07	33.5	5.0
500	0.05	30.2	3.8
510		24.7	3.1
520		19.5	2.3
530		15.4	1.5
540		12.1	0.96
550		9.5	0.76
560		7.0	0.31
570		5.3	
580		3.6	
590		2.5	
600		1.1	

were all performed at higher pressures which were at least a factor of 10 larger than the present experiment. The low pressures used in the present study (0.02 to 1.20 kPa) enabled us to measure cross sections in this region with reduced probability for dimer formation. As shown in Fig. 2, linear Beer–Lambert Law behavior was observed for Br_2 at 227 nm from 0.02 to 1.20 kPa. We find no evidence of non-linear absorbance due to the collisional dimer (Br_2–Br_2).

Finally, a graphical comparison between our results for BrCl and those reported by Maric et al. [29], by Jost [35], by Gray and Style [32], and by Seery and Britton [25] shows only minor differences even when examined on a logarithmic scale. Deviations between 260 and 320 nm (as seen on logarithmic scale) may

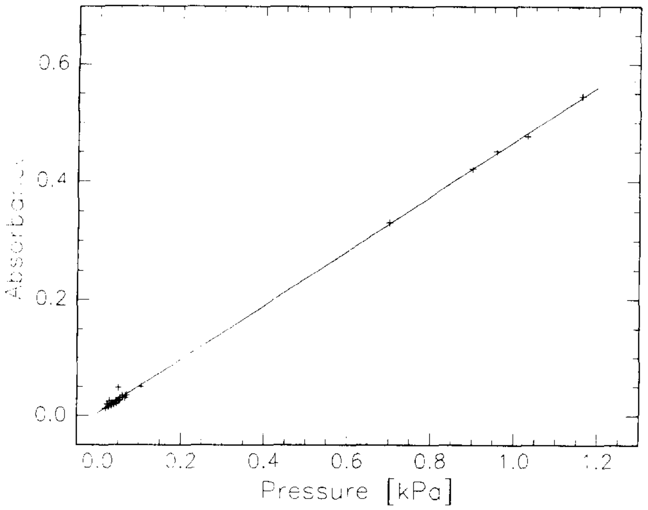


Fig. 2. Pressure dependence of Br_2 band centered at 227 nm.

result from unresolved BrCl structure. Because the observed BrCl spectrum became increasingly noisy as the wavelength was increased beyond 500 nm, values are presented in Table 1 for BrCl only between 190 and 560 nm. It should also be noted that in all three cases (Cl_2, Br_2, BrCl), cross sections do not go to zero at wavelengths below 190 nm. Although Cl_2, Br_2, and BrCl spectra have been studied in the vacuum UV region, absolute cross sections are not well established between the vacuum UV region and 200 nm. Although this region was not investigated in the present work, it is believed that Cl_2, Br_2, and BrCl cross sections are either unchanged or increase gradually between 190 nm and the vacuum UV region.

Like Br_2, BrCl is also found to have an absorbance maximum in the UV (ca. 228 nm). This peak must correspond to the UV continuum found for BrCl at 215 nm by Cordes and Sponer [36]. Its assignment, like the corresponding Br_2 UV maximum, has significant theoretical implications as will be discussed later.

The cross sectional data for BrCl between 190 and 560 nm were deconvoluted [27,37] according to an empirical equation (Eq. (3)) into 4 separate absorbing states: UV band; C $^1\Pi_1$, B $^3\Pi_0{}^+$; and A $^3\Pi_1$ (see Fig. 3 and Table 2). Temperature dependent absorbance cross section maxima ($\sigma_{max}(T)$), peak wavelengths (λmax), and empirical coefficients (a(T)) were determined for each absorbing state by calculating individual state absorbances ($\sigma(T)$) and then minimizing the difference between observed cross sections (σ(total)) and the sum of calculated cross sections for each absorbing state ($\sigma_{UV}+\sigma_C+\sigma_B+\sigma_A$).

$$\sigma(T)=\sigma_{max}(T)\times\exp(-a(T)\times(\ln(\lambda_{max}/\lambda))^2) \qquad (3)$$

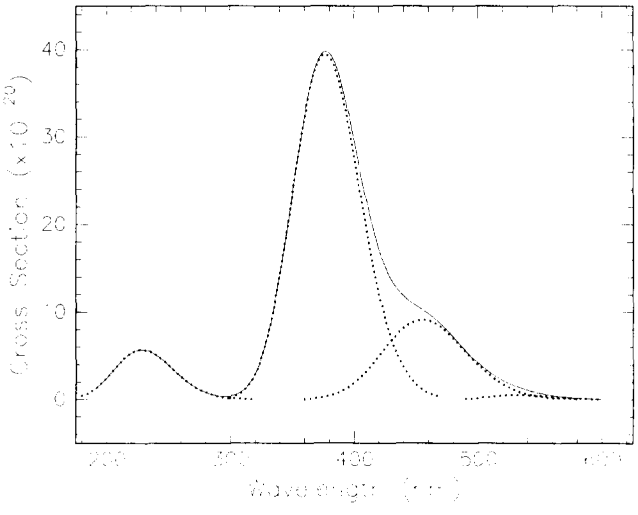


Fig. 3. Deconvolution of BrCl absorbance spectrum according $\sigma(T)=\sigma_{max}(T)\times\exp(-a(T)(\lambda_{max}/\lambda))^{2)}$.

Table 2
De-convolution coefficients for BrCl absorbance $\sigma(T)=\sigma_{max}(T)\times\exp(-a(T)\times(\ln(\lambda_{max}/\lambda))^2)$

	$\sigma_{max}(T)$	$a(T)$	λ_{max}
UV Band	5.71×10^{-20}	46.65	228.33
C ($^1\Pi_1$)	39.5×10^{-20}	98.2	376.39
B ($^3\Pi_0{}^+$)	9.14×10^{-20}	93.70	454.92
A ($^3\Pi_1$)	0.515×10^{-20}	250.99	533.05

Table 3
De-convolution coefficients for BrCl absorbance $\sigma=K\cdot\nu\cdot\exp-[(\nu-\nu_0)^2/(\Delta\nu)^2]$

	K (cm^2/molecule)	ν_0 (cm^{-1})	$\Delta\nu$ (cm^{-1})
UV Band	1.31×10^{-24}	43622.9	6352.7
C ($^1\Pi_1$)	14.75×10^{-24}	26435.8	2628.2
B ($^3\Pi_0{}^+$)	3.55×10^{-24}	21625.8	2088.9
A ($^3\Pi_1$)	0.185×10^{-24}	18670.0	1185.4

A comparison between our fitting parameters for BrCl and those of Maric et al. [29] (see Fig. 1) reveals nearly identical fitting parameters with only minor differences reflecting the underlying data. However, in the present study, the A $^3\Pi_1$ electronic state was also included in the deconvolution. Although clearly of minor importance (see Table 2) and barely significant, this state is well known spectroscopically and was included in order to provide at least an approximate measure of absorbance due to the A $^3\Pi_1$ electronic state as compared to other states.

It is also possible to deconvolute the BrCl data according to a gaussian function [48] (Eq. (4), Table 3). However, as found by Maric et al. [27] for Cl_2, it results in significant deviations (mostly between 300 and 500 nm) between predicted and experimental BrCl cross sections.

$$\sigma=K\cdot\nu\cdot\exp-[(\nu-\nu_0)^2/(\Delta\nu)^2] \qquad (4)$$

4. Discussion

The chlorine absorbance maximum at approximately 330 nm of 25.3×10^{-20} cm^2 molecule^{-1} is due to a transition from the X $^1\Sigma_{0g}{}^+$ ground state to a repulsive C $^1\Pi_{1u}$ excited state [27,38]. This assignment is based on the photofragment spectra [39] of Cl_2 by Wilson and his associates [40,41] which showed that photodissociated chlorine atoms recoiled at an angle perpendicular to the electronic vector (i.e. $\Delta\Omega = 1$) and that the dissociation products were both ground state chlorine atoms ($^2P_{3/2}$).

The visible spectrum of bromine is made more complicated and asymmetric by the presence of additional transitions to the B $^3\Pi_0{}^+{}_u$ and A $^3\Pi_{1u}$ electronic states (the Cl_2 B $^3\Pi_0{}^+{}_u$ absorbance band is very weak). Transitions to the C $^1\Pi_{1u}$ state dominate at wavelengths shorter than 460 nm while transitions to the B $^3\Pi_0{}^+$ electronic state become progressively more important from 420 to 580 nm [12,42]. A very weak transition to the A $^3\Pi_{1u}$ electronic state has also been detected and analyzed at wavelengths longer than 480 nm [43–47]. Photofragment spectroscopy of Br_2 has shown that transitions to the A $^3\Pi_{1u}$ and C $^1\Pi_{1u}$ electronic states produce two ground state ($^2P_{3/2}$) bromine atoms while transitions to the B $^3\Pi_0{}^+{}_u$ electronic state produces one ground state ($^2P_{3/2}$) atom and one metastable excited state ($^2P_{1/2}$) atom [38,48,49].

The BrCl visible absorption band at 376 nm can be assigned in analogy to the absorption bands for Cl_2 and Br_2 just discussed. For wavelengths shorter than 435 nm, the absorption band is dominated by transitions to a $\Omega = 1$ C $^1\Pi_1$ electronic state. Between 400 and 550 nm, transitions to the B $^3\Pi_0{}^+$ electronic state become increasingly important. Discovered by Clyne and Coxon [50] from the chemiluminescent reaction of bromine atoms with chlorine atoms, the BrCl B $^3\Pi_0{}^+$ electronic state is predissociated for vibrational states above 6 because of an avoided crossing with a repulsive 0^+ electronic state [51]. Although transitions to discrete levels of the BrCl (B $^3\Pi_0{}^+$) electronic state are very weak [52] at room temperature, absorbances become much more intense at higher temperature [53] and the state has been fully characterized spectroscopically [21,54].

Although absorbance near 228 nm has been reported for BrCl by both Cordes and Sponer [36] and by Seery and Britton [25], this transition has not received as much attention as the well characterized B $^3\Pi_0{}^+$ state and the fairly well understood vacuum UV states [55]. However, the corresponding UV bands for ICl at 240 nm [23,56] and, to a lesser extent, IBr at 270 nm [56] have been studied extensively using photofragment spectroscopy [57] and time resolved laser magnetic resonance detection of the $^2P_{1/2} \leftarrow {}^2P_{3/2}$ transition between Zeeman sublevels [20]. The 240 nm ICl absorbance was originally assigned by Cordes and Sponer to a transition from the X $^1\Sigma_0{}^+$ electronic state to a high point on the repulsive part of the 0^+ electronic state potential curve (i.e. the same state which has an avoided crossing with and hence perturbs the lower lying B $^3\Pi_0{}^+$ electronic state). Mulliken also assigned these UV absorbance bands (BrCl, ICl, IBr) to the 0^+ electronic state [23]. More recent work on the ICl UV band [20,57] has shown that excited state chlorine atoms ($^2P_{1/2}$) are produced from a parallel type transition (i.e. $\Delta\Omega = 0$). Of the two possible BrCl $\Omega = 0$ upper states, the 0^+ electronic state is correlated with excited state chlorine atoms ($^2P_{1/2}$) while the B $^3\Pi_0{}^+$ electronic state is correlated with ground state chlorine atoms ($^2P_{3/2}$) [21,51,58]. Thus, the BrCl UV absorbance maximum at 228 nm can be assigned to a transition from the X $^1\Sigma_0{}^+$ ground electronic state to the 0^+ excited electronic state.

Finally, Mulliken has suggested that the UV bands of the interhalogens BrCl, ICl, and IBr observed by Cordes and Sponer [36] are due to the promotion of an electron from the lighter atom's π orbital (i.e. Cl in BrCl and ICl, Br in IBr) to an excited σ^* orbital.

$$\sigma^2\pi_x{}^4\pi_y{}^4 \longrightarrow \sigma^2\pi_x{}^4\pi_y{}^3\sigma^*$$

Visible bands A $^3\Pi_1$, B $^3\Pi_0{}^+$, C $^1\Pi_1$

$$\sigma^2\pi_x{}^4\pi_y{}^4 \longrightarrow \sigma^2\pi_x{}^3\pi_y{}^4\sigma^*$$

UV band

where π_x represents the lighter atom and π_y represents the heavier atom.

However, UV absorbance by the homohalogen Br_2 has been known since 1940 [23b] while that by iodine (I_2) at 270 nm has been known since the 1930s [23a]. While undoubtedly the previous measurements for Br_2 and I_2 in the UV included substantial dimeric contributions, our low pressure measurements for Br_2 and BrCl greatly reduced the probability of dimer formation and yielded cross sections for pure Br_2 and BrCl.

The absorption process for the interhalogens (BrCl, IBr, ICl) has been consistently assigned as a transition from the ground state to an upper excited 0^+ state since the 1930s. By comparing the UV absorption spectra for both Br_2 and BrCl, it is quite reasonable to suspect that both molecules have similar upper states for the UV bands which lie next to the C $^1\Pi_1$ state for Br_2 and BrCl. However, identification of the exact electronic orbitals used in the Br_2 and I_2 UV transitions is more ambiguous. Mulliken assigned $\sigma_g{}^2\pi_u{}^3\pi_g{}^3\sigma_u{}^2$ ($^1\Sigma_u{}^+$) as the major candidate for the Br_2 transition with $\sigma_g{}^2\pi_u{}^4\pi_g{}^3\sigma_u{}^1$ ($0_u{}^+/1_u$) and $\sigma_g{}^1\pi_u{}^4\pi_g{}^4\sigma_u{}^1$ ($^3\Sigma_u{}^+$) as possible alternatives in his 1940 paper. Likewise, the UV band for I_2 at 270 nm was assigned to the $\sigma_g{}^1\pi_u{}^4\pi_g{}^4\sigma_u{}^1$ (1_u) state in Mulliken's 1971 paper [59]. Since the UV bands for Br_2 and BrCl are likely to be caused by similar excited states and since the $\sigma_g{}^2\pi_u{}^3\pi_g{}^4\sigma_u{}^1$ (0^+) state for the BrCl UV transition was firmly assigned since the 1930s, there is no reason to reject this 2341 state for Br_2. Previously, Mulliken ignored this state probably because his estimate of the vertical energy of this state was too low and because it is forbidden by the parity and spin selection rules (the 2341 state is a triplet g state). Case c coupling (Ω–ω) the selection rule in heavier atoms relaxes. This may explain why the UV absorbance of chlorine is extremely weak compared to that of bromine and iodine.

5. Conclusion

In the present work we have reported absolute photoabsorption cross sections for Cl_2, Br_2, and BrCl at room temperature from 190 to 600 nm. In addition, the cross sectional data for BrCl was deconvoluted according to the equation $\sigma(T)=\sigma_{max}(T)\times\exp(-a(T)\times(\ln(\lambda_{max}/\lambda))^2)$. The BrCl band maximum at 228 nm was assigned to a transition from the X $^1\Sigma_0{}^+$ ground state to a repulsive 0^+ electronic state by analogy with similar UV bands present in ICl and IBr. Finally, an absorbance maximum was also detected for Br_2 at 227 nm.

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