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SPIN-ORBIT COUPLING EFFECTS IN BRO⁻ AND HOBr PHOTODISSOCIATION REACTIONS

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Abstract. Potential energy curves of the ground and a few excited states of the BrO⁻ and HOBr along the photodissociation reactions, which correlate with lower dissociation limits are obtained on the base of calculations results by *ab initio* method. The singlet-triplet nonadiabatic transition with dissociation of the ground $X^1\Sigma^+$ state to lower limit O(^3P) + Br⁻(^1S) is predicted on the basis of calculations results. The ground singlet $X^1\Sigma^+$ state of the BrO⁻ has predissociative and metastable character for the upper vibrational levels. It is shown that the singlet-triplet transition to the lower triplet state $a^3A'' \leftarrow X^1A'$ is responsible for a weak HOBr absorption in the visible region (440–650 nm).

Keywords: photodissociation, singlet-triplet transition, spin-orbit coupling, absorption bands, spectrum.

1. Introduction

Halogen-oxides and hypohalous acids have a great influence on the stratospheric ozone concentration [1, 2]. The radicals, $XO^.$ (X = Cl, Br, I), are central to the chemistry of ozone and its catalytic depletion cycle that occurs in lower stratosphere [3]. Several publications are devoted to spectroscopic studies of these compounds. For example, potential curves and spectroscopic data for the ground state of ClO⁻ and for the ground and various excited states of ClO⁻ are obtained [4]. The potential curves of the ground and first excited states of FO⁻ were calculated by the *ab initio* method using the 6-31+G^* basis [5].

For BrO⁻, calculations were performed only for the ground singlet state $X^1\Sigma^+$ [6, 7]. According to our knowledge, no calculations were carried out for the electronically excited states of BrO⁻, and the role of singlet–triplet (S–T) transitions in the photodissociation spectrum of this ion was not investigated.

Therefore here we attempt to calculate the potential curves of the electronically excited states of BrO⁻ and to establish the correlation diagram of the states forming in the course of O–Br bond cleavage. Our primary goal in this study is to examine the role of the lowest triplet $^3\Pi$ state of BrO⁻ during ion photodissociation.

Hypobromous acid, HOBr, plays an important role in stratospheric ozone depletion processes [8, 9]. It is produced in the atmosphere by the following reactions: by gas-phase disproportionation of two radicals

$$HO_2^. + BrO^. \rightarrow HOBr + O_2 \qquad (1)$$

and by heterogeneous reactions involving the hydrolysis of bromine nitrate, $BrONO_2$, on aerosol particles in the night time stratosphere [10]

$$H_2O + BrONO_2 \rightarrow HOBr + HNO_3. \qquad (2)$$

The role of the HOBr molecule in photochemistry of ozone depletion is highly dependent on its photolysis in the long wavelength region ($l \geq 300$ nm). The photodissociation of HOBr molecule

$$HOBr + hn \rightarrow HO^.(^2\Pi) + Br^.(^2P) \qquad (3)$$
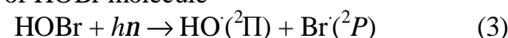
can lead to an effective ozone depletion processes through the chain [11]

$$^.OH + O_3 \rightarrow HO_2^. + O_2 \qquad (4)$$
$$Br^. + O_3 \rightarrow BrO^. + O_2. \qquad (5)$$

Recombination of the products reproduces hypobromous acid again. Thus the net process $2O_3 \rightarrow 3O_2$ occurs, which determines the role of hypobromous acid in the catalytic cycle for ozone destruction [11]. Since reaction (3) is the rate-determining steps of the chain, an accurate determination of the ultra-violet-visible (UV-vis) absorption cross section of the HOBr molecule is necessary for assessing the role of the HOBr molecule in the photochemical reaction cycles (1-5) in the atmosphere. That is why the UV-vis absorption spectrum of HOBr molecule has been the subject of many experimental [3, 12, 13] and theoretical [9, 14-16] studies. Spectroscopic data on hypobromous acid are sparse, although studies by Orlando and Burkholder [17] and by Barnes *et al*. [8] have provided accurate measurements of its absorption in the near-UV and visible regions.

The model of sudden ozone depletion in the Arctic troposphere [10] includes uncertainties in the HOBr photolysis rates; this hampers the assessment of the bromine containing compounds contribution to Artic ozone loss. An additional important contribution of the singlet-triplet long wavelength absorption to HOBr photolysis rate may have serious implications for the ozone depletion model [8, 13]. Ingham *et al.* [18] have shown that the *S–T* absorption in HOBr is responsible for up to 50 % of the total photolysis rate at high zenith angles. The influence of the *S–T* absorption on the photochemical lifetime of hypobromous acid is great due to proximity of the 440 nm region to the peak of the solar actinic flux [8].

A new absorption band ($l \approx 400$–650 nm) of hypobromous acid centered at 440 nm was detected by photofragment method and tentatively assigned to a triplet state of HOBr [8]. We have recently attempted [15, 19] to support this hypothesis by *ab initio* calculations of the HOBr spectra with an account of spin–orbit coupling (SOC) in the framework of a response theory approach. In this paper we present analysis of HOBr and BrO⁻ spectra photodissociation with particular attention to the role of the SOC effects.

2. Method of Calculations

The ground state $X^1\Sigma^+$ and the excited states of BrO⁻ were calculated by the *ab initio* method using the GAMESS program [20] and the pVDZ basis set [21]. At first, the singlet ground state $X^1\Sigma^+$ of the anion was calculated by the closed-shell Hartree-Fock (HF) method. The obtained molecular orbitals (MO) of the ground state were used in the calculation of the configuration interaction (CI) for the singlet and triplet excited states. In the HF method, in the case of the equilibrium geometry of the ground state, the electronic configuration of BrO⁻ may be represented as

$$X^1\Sigma^+ = (core)^{32}(10s)^2(4p)^4(5p)^4(11s)^2 \qquad (6)$$

Note that the core orbitals were inactive in all CI calculations. The other six occupied (two *s*-MO and four *p*-MO) and three unoccupied molecular orbitals (one *s*-MO and two *p*-MO) were included in the active space (AS) for CI calculations (12 electrons on 9 orbitals). The calculation took into account all single, double, triple, and quadruple excitations between these occupied and vacant orbitals. The CI calculations were fulfilled with different interatomic distances in the range $R_{O–Br} = 1.7$-6 Å. Exclusion of the lower-energy occupied valence orbitals from the calculation has little or no effect on the results of spectral data calculations; therefore the calculations of the

excited states of BrO⁻ were carried out with AS described above.

The matrix elements of SOC operator for the interaction between the $X^1\Sigma^+$ and $^3\Pi$ states were calculated in a multiconfigurational self-consistent field (MCSCF) approximation including the linear response functions [22] with the DALTON program. The MCSCF calculation used Sadlej extended basis set [23], which included the set of orbitals [10s6p4d/5s3p2d] for oxygen and [15s12p9d/9s7p4d] for bromine. The *z* axis was chosen as an internuclear axis.

In this work calculations of spectral properties of HOBr molecule have been performed by the MCSCF with function quadratic response (QR) method using the basis set of Sadlej [23]. This contains [15s12p9d–9s7p4d] functions for bromine with a total number of contracted orbitals in MO expansion of 83. The choice of axes for HOBr molecule in the ground state (a) and in the first excited triplet state with optimized geometry (b) is given in Fig. 1.
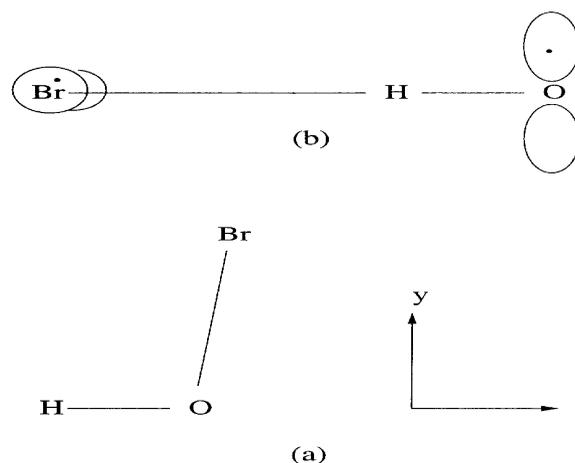
Fig. 1. Choice of axes for the HOBr molecule (a) and the biradical structure of the equilibrium lowest triple state (b)

At the equilibrium ground state geometry the HF electronic configuration of the HOBr molecule is

$$1^1A' = (core)^{30}(12a')^2(13a')^2(14a')^2(5a'')^2$$
$$(15a')^2(16a')^2(6a'')^2 \qquad (7)$$

The core orbitals plus the lowest occupied valence orbital, $12a'$ MO with low energy (-1.39 a.u.), which describes mostly the 2*s*-AO of oxygen, were inactive in the MCSCF AS calculations. All other occupied MOs (4, 2) and three empty MOs (2, 1) have been included in the MCSCF active space (12 electrons in 9 orbitals) which corresponds to 3560 determinants of the $^1A'$ symmetry for the reference ground state.

3. Results and Discussion

The calculated in basis set pVDZ [21] O–Br ($R_{Br–O} = 1.821$ Å) bond length for the ground singlet $X^1\Sigma^+$ state of the BrO⁻ ion agrees well with the experimental data ($R_{Br–O} = 1.814$ Å) of [24].

Results of geometry optimization of the HOBr molecule in the ground state and in the first excited triplet state by the MCSCF method with few different basis sets are presented in Table 1. The calculated ground state geometry and the infra-red (IR) spectrum are in reasonable agreement with the experimental data [9].

Fig. 2 shows the potential energy curves for the $X^1\Sigma^+$ state and for a number of the lowest excited states of BrO⁻. At first, the reaction coordinate is O–Br bond lengthening at the step of ~0.2 Å. The singlet ground state of the anion is bonding and correlates with the limit $O(^1D)+Br^-(^1S)$. The first excited singlet state $^1\Pi$ also correlates with this dissociation limit. As can be seen in

Fig. 2, the lowest excited triplet states $^3\Pi$ and $^3\Sigma^-$ correlating with $O(^3P)+Br^-(^1S)$ and $O^-(^2P)+Br(^2P)$, respectively, are strongly repulsive in the region that is close to the vertical excitation from the ground $X^1\Sigma^+$ state. For the $^3\Pi$ state, the potential curve is shallow with a long O–Br interatomic distance ($R_{O–Br} \geq 3$ Å), and is characterized by a shallow minimum at $R_{O–Br}=3.34$ Å.

For minor bond lengthening ($r = 2.31$ Å), the potential curves of the $X^1\Sigma^+$ and $^3\Pi$ states intersect at point 1 in the ground state (Fig. 2). The existence of this *S–T* intersection in the course of BrO⁻ dissociation may lead to dissociation of the singlet ground state to the lowest limit $O(^3P)+Br^-(^1S)$ *via* the nonadiabatic *S–T* transition. To analyze this process, we calculated the matrix element of the SOC operator between the $X^1\Sigma^+$ and $^3\Pi_0$ states at the intersection point of their potential curves. An *ab initio* calculation of SOC including the full Breit-Pauli operator in Sadlej's basis [23] gave a matrix element of 205.6 cm⁻¹ for the intermolecular distance of 2.16 Å.

Table 1

Geometry optimization for the ground singlet and lowest triplet states of the HOBr molecule

Method	$r_{O\text{-}H}$	$r_{O\text{-}Br}$	$\angle HOBr$	$v_{1, O\text{-}H}$	$v_{2, bend}$	$v_{3, Br\text{-}O}$	E_n
Ground state, $1^1 A'$							
Sadlej	0.964	1.849	102.82	3918.0 (59.1)	1181.5 (31.5)	603 (2.3)	-2647.88932
Exp.*	0.961	1.834	102.3	3614.9	1162.6	620.2	-
First excited triplet state, $1^3 A''$							
Sadlej	0.9852	4.0059	0	3358.2	138.2	52.3	-2647.80453

Note: *r* denotes the internuclear distances, Å; *n* the vibrational harmonic frequency, cm⁻¹; IR intensities are given in parentheses, km/mol; E_n is the total energy (hartree) of the *n*th state; *experimental data [9].
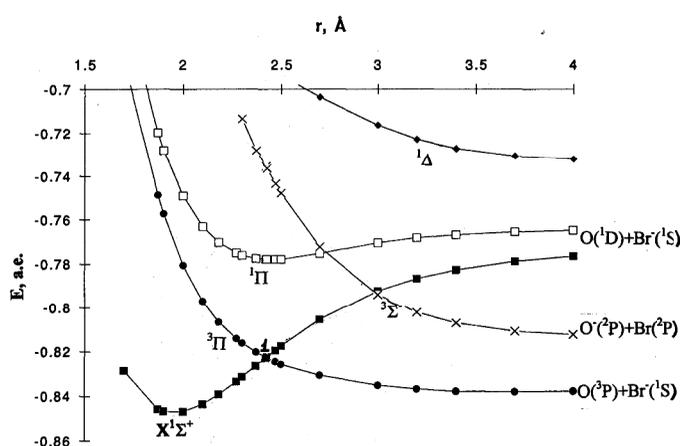
Fig. 2. Potential energy curves for the ground and some lowest excited states of BrO⁻ along the axis of the dissociation reaction. The total energy is $E_{tot} = -(2647.0 + E)$ au
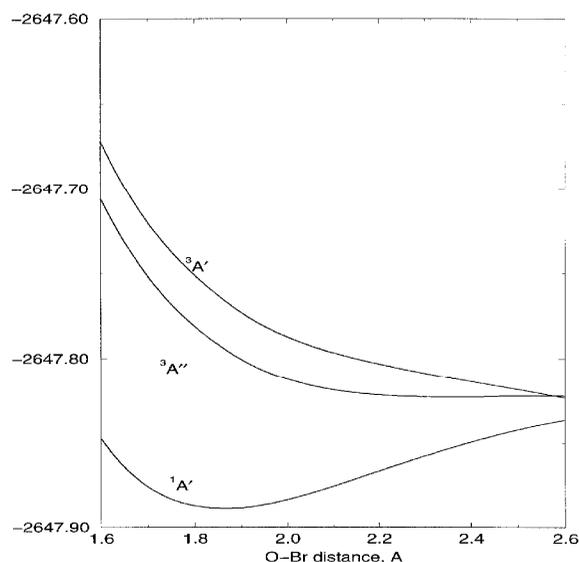
Fig. 3. Dissociation potential (the O–Br bond length dependence of the total energies) for the ground and few lowest excited states in the HOBr molecule calculated by the MCSCF method

Table 2

The $T_1 \leftarrow S_0$ transition HOBr molecule. MCSCF QR calculations of the vertical transition moment
$$M_a(T^b) = \left\langle 1^1A' \mid e\sum_i a_i \mid 1^3A''(T^b) \right\rangle \text{ near the experimental ground state geometry}$$

Basis	$M_a(T^b)$					$\Delta E_{S,T}$	f_a			
	M_x (T^x)	M_y (T^y)	M_z (T^y)	M_y (T^z)	M_z (T^z)		f_x	f_y	f_z	f_{total}
Sadlej*	64	2952	1977	31354	10089	2.72	$2.73\cdot10^{-10}$	$6.61\cdot10^{-5}$	$7.04\cdot10^{-6}$	$7.32\cdot10^{-5}$
Sadlej**	53	2904	1690	31813	10099	2.64	$1.82\cdot10^{-10}$	$6.6\cdot10^{-5}$	$6.78\cdot10^{-6}$	$7.28\cdot10^{-5}$

Note. * the experimental ground state geometry: r_{O-Br}=1.834 Å, r_{O-H}=0.964 Å, ∠HOBr=102.3°; ** the fixed ground state geometry: r_{O-Br}=1.85 Å, r_{O-H}=0.96 Å, ∠HOBr=102.3°; $M_a(T^b)$ is the transition moment, 10^{-6} a.u.; $\Delta E_{S,T}$ is the transition energy, eV; f_a is the oscillator strength for the $T_1 \leftarrow S_0$ absorption polarized along the a axis.

This point is close to the region of S–T intersection (Fig.2). Therefore, it is suggested that the nonadiabatic S–T transition at point 1 in the Fig. 2 has a rather high probability. The probability of this nonadiabatic $X^1\Sigma^+$–^3P transition estimated by the Landau-Zener formula is 0.014. Based on the estimated probability of the S–T transition, one can conclude that the majority of gas phase molecules behave adiabatically with small vibrations and remain in the bound $X^1\Sigma^+$ state. For several vibrationally excited levels, the minority of molecules dissociate *via* the nonadiabatic S–T transition to the $O(^3P)+Br^-(^1S)$ products.

Fig. 3 shows the dissociation potentials of the ground singlet and of the two triplet states at fixed O–H bond length (0.964 Å) and angle ∠HOBr=102.968°. The two lowest excited triplet states $1^3A''$ and $1^3A'$ of hypobromous acid are strongly repulsive in the vicinity of the vertical excitation from the ground $1^1A'$ state. The lowest triplet $1^3A''$ state potential gets flat at long O–Br distances ($r_{O-Br} \geq 2.2$ Å) in contrast to the second triplet ($1^3A'$) state, which is still a descending function in this region (Fig. 3). The flat part of the $1^3A''$ state potential has a weak minimum at r_{O-Br}=2.34 Å with a dissociation energy D_e. =1.31 kJ/mol.

The MCSCF QR results of the $1^3A'' \leftarrow 1^1A'$ vertical transition moment calculations in HOBr molecule are presented in Table 2. The T–S transitions to the three spin sublevels of the triplet state T^b have different intensities and polarizations, which follow simple selection rules. Each spin sublevel T^b has a zero spin projection on the b axis.

The transition to the z spin sublevel is the most intensive one and vector $M(T^z)$ is mostly oriented along the O–Br axis (Table 2). The transition to the y spin sublevel is much weaker (Table 2). The orientation of the $M(T^y)$ vector changes a few times as the system moves along the dissociation coordinate.

The $T^b_1 \leftarrow S_0$ excitations to both y and z spin sublevels can borrow intensity from spin-allowed n^1A'–$1^1A'$ transitions because of the SOC mixing.

$$\left\langle n^1A' \mid H^b_{SO} \mid 1^3A''(T^b) \right\rangle \qquad (8)$$

In Eq. (8) $b \in y, z$. The SOC integral (8) is large for the $b = z$ component.

This simple analysis explains some qualitative features of the $T^b_1 \leftarrow S_0$ transition intensity in HOBr molecule. This result determines a comparative importance of the $T^b_1 \leftarrow S_0$ absorption in the visible-near UV region for HOBr photolysis. Accounting for the overlap of the ground state vibrational wave function and the T_1 state nuclear continuum we can qualitatively predict a long tail of the $T_1 \leftarrow S_0$ absorption of HOBr; the value $|M_y(T^z)|^2$ is large enough even at large O–Br distances (2–2.6 Å) where the S–T transition energy is small and nuclear wave functions still have non-zero overlap. The spectrum of hypobromous acid recorded by Barnes *et al*. [8] exhibits a very long weak tail of the $T_1 \leftarrow S_0$ absorption in the visible region until 650 nm. Our results support the tentative assignment [8] and make it clear that the recent models of bromine chemistry in the Arctic troposphere [10] should be reconsidered with account of the $T_1 \leftarrow S_0$ absorption of hypobromous acid in visible region.

4. Conclusions

In view of the importance of the S–T transitions for the spectrum and reactivity of ozone and considering possible participation of the triplet states in HOCl and HOBr dissociation processes [14-16, 19], we conclude that the triplet state of halogen-containing compounds must play an important role in the photocatalytic ozone depletion in stratosphere. The results show that photodissociation processes of halogen-containing compounds depend essentially on the singlet-triplet transitions and account of spin-orbit coupling effects. Thermochemical *ab initio* calculations for BrO$^-$ ion [6, 7] as possible dissociation product of HOBr molecule show that these compounds in the singlet ground state are stable

enough. Our MCSCF and CI calculations with account of SOC indicate that the compounds are metastable. The calculated oscillator strength for the first $T_1 \leftarrow S_0$ transition ($1^3A'' \leftarrow 1^1A'$) of HOBr molecule is about $8 \cdot 10^{-5}$, so it is easily observed in the absorption spectrum at 440 nm [8].

Acknowledgements

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ЕФЕКТ СПІН-ОРБІТАЛЬНОЇ ВЗАЄМОДІЇ В РЕАКЦІЯХ ФОТОДИСОЦІАЦІЇ BrO⁻ і HOBr

Анотація. На основі результатів розрахунку методом ab initio одержано криві потенціальної енергії для основного та ряду збуджених станів BrO⁻ і HOBr в ході реакції фотодисоціації, що корелюють з нижніми межами дисоціації. За результатами розрахунку передбачено синглет-триплетний неадіабатичний перехід з дисоціацією основного X^1S^+ стану до нижньої межі $O(^3P) + Br^-(^1S)$. Основний синглетний стан йону X^1S^+ BrO⁻ є переддисоціативним і метастабільним для верхніх коливальних рівнів. Показано, що синглет-триплетний перехід до нижчого триплетного стану $a^3A'' \leftarrow X^1A'$ в молекулі HOBr відповідає за слабке поглинання у видимій області (440–650 нм).

Ключові слова: фотодисоціація, синглет-триплетний перехід, спін-орбітальна взаємодія, смуги поглинання, спектр.