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POTENTIAL CURVES AND SPECTRA OF ClO⁻ AND HOCl SPECIES STUDIED BY AB INITIO METHODS

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Potential energy curves of the ground state and a number of excited states of the ClO⁻ and HOCl species along the photodissociation reaction channels are obtained on the basis of multireference configuration interaction, which correlate with the low-lying dissociation limits. The singlet-triplet nonadiabatic transition during the predissociation of the ground $X^1\Sigma^+$ state to the lowest limit $O(^3P)+Cl^-(^1S)$ is predicted on the basis of the calculations results. In order to predict the possible importance of the singlet-triplet absorption in the HOCl molecule spectrum, we have presented potential energy curves for the ground singlet X^1A' and the first excited triplet $1^3A''$ states. The results show that atmospheric photochemistry of heavy halogen-containing compounds substantially depends on the singlet−triplet transitions and the inclusion of relativistic effects. Thermochemical ab initio calculations of ClO⁻ as a possible product of HOCl molecule dissociation show that these compounds in the singlet ground state are stable enough. Our calculations based on multireference configuration interaction with regard to spin-orbit coupling indicate that the compounds are metastable.

Keywords: photodissociation, singlet−triplet transition, spin-orbit coupling, absorption

Introduction

The ClO radical plays an important role in the catalytic chain reaction leading to the depletion ozone cycle in the lower stratosphere [1]. A great number of experimental and theoretical investigations have been performed on the spectroscopic properties and photochemical reactions of the ClO radical in connection with the environmental importance of the ozone layer destruction problem [2−4]. The important electronic parameters of the ClO radical have been measured long time ago. Its electron affinity was determined to be greater than 1.6 ± 0.2 eV.

On the other hand, the hypochlorite ion (ClO⁻), which is familiar in solution chemistry, has been poorly characterized in the gas phase. Experimental appearance potentials of ClO⁻ were measured from electron impact studies on ClO_3F [5]. The photodestruction spectra of ClO⁻ were observed by Lee et al. in 1979, and they attributed a broad band near 5700 Å (2.17 eV) to the photodetachment of ClO⁻ and a narrow band peaked near 4300 Å (2.88 eV) to photodissociation of ClO⁻ to Cl⁻ $(^1S)+O(^1D)$ or $Cl^-(^1S)+O(^3P)$ [6].

Also the potential curves and dissociation energies for the ground states of ClO $(^2\Pi)$ and ClO⁻ $(^1\Sigma^+)$ and possible low lying excited states $(^1\Pi, ^3\Pi, ^3\Sigma^-, 3\Sigma^+, ^1\Delta)$ of ClO⁻ have been investigated using sophisticated ab initio quantum mechanical techniques with large basis sets including diffuse functions [2]. The equilibrium bond distance and vibrational frequency for the ground state $(^1\Sigma^+)$ of ClO⁻ are predicted to be 1.688 Å and 660 cm⁻¹ at the coupled-cluster single double (triple) [CCSD(T)]/ aug-cc-pVQZ level of theory [2]. The lowest excited singlet (S) state of ClO⁻ is predicted to be the open − shell $^1\Pi$ state, which is 2.43 eV higher in energy than the ground state, while the lowest triplet (T) state $(^3\Pi)$ of ClO⁻ has a potential with well depth of 0.32 eV [2].

A coupled cluster composite approach has been used to accurately determine the spectroscopic constants, bond dissociation energies, and heats of formation for the ground states of halogen oxides ClO, BrO and IO, as well as their negative ions ClO⁻, BrO⁻ and IO⁻ [7]. A few theoretical investigations of ClO⁻ have been reported on the electron affinity, vibrational frequency, bond distance

and spectroscopic properties [2].

Hypochlorous acid, HOCl, plays an important role in ozone depletion in the stratosphere [1]. The photodissociation of HOCl:

$$HOCl + h\nu \rightarrow HO(^2\Pi) + Cl(^2P) \qquad (1)$$
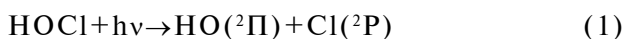
can lead to an effective ozone depletion process through the following chain [1]:

$$Cl + O_3 \rightarrow ClO + O_2; \qquad (2)$$

$$OH + O_3 \rightarrow HO_2 + O_2. \qquad (3)$$

Recombination of the products of reactions (2) and (3) produces hypochlorous acid again:

$$HO_2 + ClO \rightarrow HOCl + O_2. \qquad (4)$$
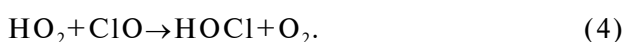
Thus, the net reaction $2O_3 \rightarrow 3O_2$ occurs. Since reaction (1) is the rate-determining step of the chain, an accurate determination of the UV absorption cross-section of hypochlorous acid is necessary for assessing the role of the HOCl molecule in the photochemical reaction cycles of ClO in the lower and middle stratosphere [1]. This is the reason that the UV absorption spectrum of HOCl has been the subject of so many experimental [8] and theoretical [1,9] studies.

In the present study, we report potential curves for the ground and few excited states of HOCl and ClO⁻ species during photodissociation reaction, which correlate with lowed dissociation limits based on the calculations results obtained by ab initio method. In this paper we also present the analysis of HOCl spectrum with particular attention to the role of the spin-orbit coupling (SOC) effects.

Method of calculations

The ground state $X^1\Sigma^+$ and the excited states of ClO⁻ were calculated by ab initio method using the GAMESS program and the TZV basis set [10]. 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 ClO⁻ may be represented as follows:

$$X^1\Sigma^+ = (core)^{16}(2\pi)^4(7\sigma)^2(3\pi)^4. \qquad (5)$$
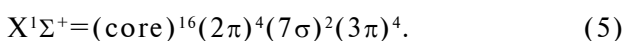
It should be noted that the core orbitals were

inactive in all CI calculations. The other three occupied (two π MO and one σ MO) and four unoccupied molecular orbitals (two σ-MO and two π-MO) were included in the complete active space (CAS) for CI calculations (10 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 $R_{O-Cl} = 1.6 - 5$ Å. The 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 ClO⁻ were carried out with CAS described above.

The calculations of spectral properties of the HOCl molecule have been performed with different basis sets and CAS accounting for linear and quadratic multi-configuration (MC) response functions. The choice of axes is given in Fig. 1.
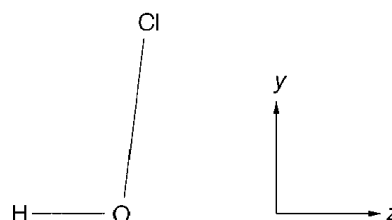

Fig. 1. Choice of axes for the HOCl molecule

The Dunning correlation-consistent polarized valence double − ζ(cc-pVDZ) basis set was used for all geometry dependent calculations [10]. Basis sets of Sadlej, Ahlrichs and the Dunning triple − ζ(cc-pVTZ) basis set are also used for comparison [10]. At the equilibrium ground state geometry the HF electronic configuration of HOCl is as follows:

$$1^1A' = (core)^{12}(6a')^2(7a')^2(2a'')^2(8a')^2(9a')^2(3a'')^2(10a')^2. \qquad (6)$$
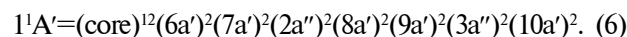
The core orbitals were inactive in all multi-configurational self-consistent field (MCSCF) calculations. All other occupied MOs (5,2) and three empty MOs (2,1) have been included in the MCSCF calculations (14 electrons in 10 orbitals). Exclusion of the lowest occupied valence orbital (6a' MO) with low energy (-1.4 au) hardly influences the results of spectral calculations. So almost all calculations were performed in a CAS with six MOs of the a' type and three MOs of the a'' type (12 electrons in 9 MOs).

Results and discussion

The cross-correlation diagram of the ground and few electronic-excited states of the ion ClO⁻ in the process of dissociation was calculated by ab initio
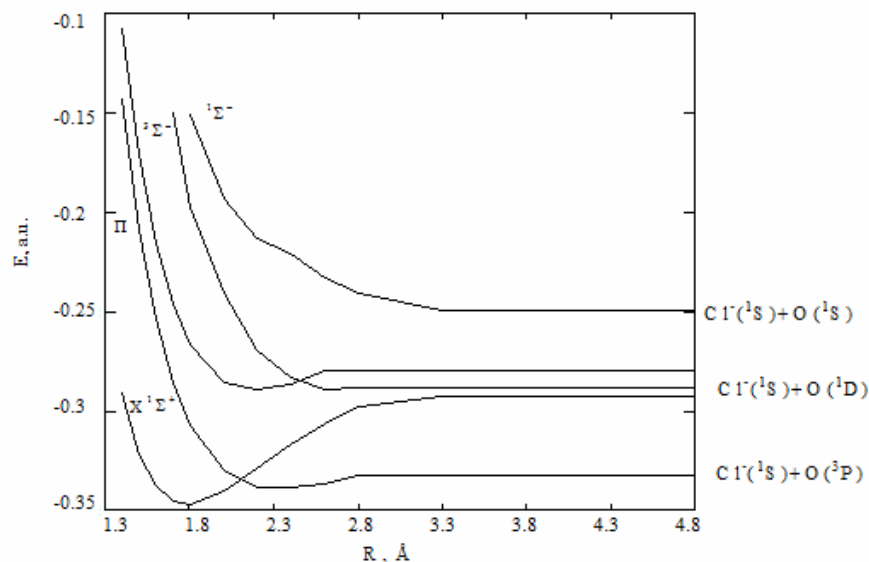
Fig. 2. The potential energy curves for the ground and few excited states of ClO⁻ anion along the dissociation reaction coordinate. The energy −534.00 a.u. has to be added

method in the TZV basis set, it is presented in Fig. 2. The results for the ground states of ClO⁻ and the asymptotic values of Cl+O fragments are in a reasonably good agreement with the tentative potential curves using experimental parameters observed and derived based on the iso-electronic and relatively well-investigated ArO potential curve [6].

The singlet $X^1\Sigma^+$ ground state of the anion is bonding and correlates with the limit $O(^1D)+Cl^-(^1S)$. The first excited singlet state ^1P also correlates with this dissociation limit.

The lowest excited $^3\Pi$ triplet and singlet $^1\Sigma^-$, $^1\Pi$ states and triplet $^3\Sigma^-$ correlating with $O(^3P)+Cl^-$ (^1S) and $O(^1D)+Cl^-(^1S)$, respectively, are strongly repulsive in the region that is close to the vertical excitation from the ground $X^1\Sigma^+$ state (Fig. 2).

Among the states which adiabatically dissociated to the limit of $Cl^-(^1S)+O(^1D)$, only $X^1\Sigma^+$ is bonding therm, which is in a good agreement with the experimental result [11]. Among the possible fragments of the dissociation process of ClO⁻, the $Cl^-(^1S)+O(^3P)$ fragments should be readily accessible from the triplet excited states, $^3\Pi$ or $^3\Sigma^-$ [2].

The mechanism of this photodissociation process is possible only under the condition of strong SOC between ground $X^1\Sigma^+$ and lowest excited triplet $^3\Pi$ states of ClO⁻.

For minor bond lengthening (r=2.0 Å), the lowest triplet state $^3\Pi$ potential energy curve (PEC) crosses the $X^1\Sigma^+$ curve (Fig. 2). A similar behavior has been observed for the BrO⁻ and IO⁻ anions [1,12]. The existence of this singlet−triplet (S−T) intersection in the course of ClO⁻ dissociation may lead to dissociation of the singlet ground state to the lowest

limit $O(^3P)+Cl^-(^1S)$ via the nonadiabatic S−T transition. The SOC matrix element between the $X^1\Sigma^+$ and $^3\Pi$ states of ClO⁻ is equal to 155 cm⁻¹. This is relatively large spin-orbit coupling. From our experience [1,9,12] we can predict a competitive T−S transition rate constant. Therefore it is suggested that the nonadiabatic $X^1\Sigma^+-^3\Pi$ transition has a rather high probability.

Thus ClO⁻ anion has been predissociative character and is metastable in excited vibrational levels because of the SOC integral between the $X^1\Sigma^+$ and $^3\Pi$ states at the crossing point is nonzero.

The results of the MCSCF geometry optimization in the ground and in the first excited triplet states of the HOCl molecule are presented in Table.

For the ground state all methods predict similar results which are quite close to the experimental data [13]. The basis sets of Ahlrichs et al. [10] slightly overestimate bond lengths and predict a wrong intensity ratio for the ν_1 (O−H stretch) and ν_2 (bend) vibrations.

MCSCF (cc-pVDZ) PECs for the $1^1A'$ and $1^3A''$ states along the dissociation reaction coordinate (prolongation of the O−Cl bond at the fixed O−H distance r_{O-H}=0.98 Å and angle $\angle HOCl$=100.8⁰) are shown in Fig. 3.

The lowest excited triplet state $1^3A''$ is repulsive in the Franck-Condon region in the vicinity of the vertical excitation from the ground $1^1A'$ state (Fig. 3). There is a very weak minimum on the lowest triplet state PEC at r_{O-Cl}=3.75 Å with a negligible dissociation energy D_e=0.06 kJ mol⁻¹.

It is interesting to note that the behavior of

MCSCF geometry optimization for the ground X^1A' and first triplet $1^3A''$ states of the HOCl molecule

method	r_{O-H}	r_{O-Cl}	$\angle HOCl^a$	$\nu_{1,O-H}$	$\nu_{2,bend}$	$\nu_{3,Cl-O}$	E_n
			ground state, X^1A'				
cc-pVDZ	0.9785	1.75175	100.652	3708(62.1)	1274.4(36.5)	668(0.02)	−534.97653
Sadlej	0.9784	1.7450	101.2	3718.9(60.5)	1284.5(38.5)	693(2.83)	−535.05558
AhlrichsVTZ	0.9941	1.8690	102.2	3467.8(21.9)	1206.6(41.8)	578(0.66)	−534.97047
expt^b	0.964	1.689	102.96	3609	1240	725	
			first excited triplet state, $1^3A''$				
cc-pVDZ	0.9829	3.9834^c	0	3655.7(19.2)	121.4(123.6)	52.9(0.12)	−534.90791
AhlrichsVTZ	0.9991	4.0954^d	0	−	−	−	−534.92144

Note: ^{a} − Degrees; ^{b} − Ref. [13]; ^{c} − This structure corresponds to ClHO complex with r_{Cl-H}=3.0005 Å; ^{d} − This structure corresponds to ClHO complex with r_{Cl-H}=3.0963 Å. r denotes the internuclear distance (Å); n is the vibrational harmonic frequency (cm^{-1}); IR intensities (km·mol^{-1}) are given in parentheses; E_n is the total energy (E_h) of the nth state.
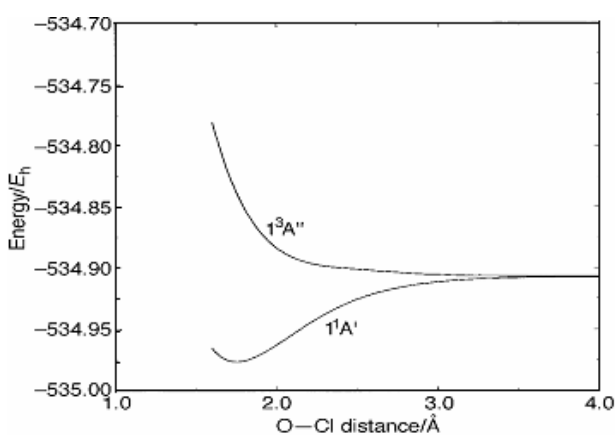

Fig. 3. O−Cl bond length dependence of the total energies for the ground and first excited triplet states in the HOCl molecule calculated by the MCSCF method in cc-pVDZ basis set

HOCl species near the dissociation limit is very peculiar. The above mentioned weakly bound HO···Cl associate is not a real minimum on the triplet state potential energy hypersurface; the angle was fixed ($\angle HOCl$=100.8^0) during its optimization. The complete geometry optimization at the same MCSCF level gives the new angle $\angle ClHO$=180^0; this means that the Cl atom migrates to the other side of the OH radical. Such isomerization can occur in the course of photolysis, or can be a final product of recombination of two OH and Cl radicals. This is a tightly bound radical pair Cl$^•$+HO$^•$ with a dissociation energy D_e=2.6 kJ mol^{-1}. The Cl−H distance in this triplet state molecule (radical pair) is about 3 Å. Such prediction is qualitatively correct, since the similar results have been obtained in all our MCSCF calculations with different basis sets and CAS.

One can believe that the predicted ClHO triplet species occurring near the dissociation limit is important for the real photodissociation process. Of course, the Cl and OH fragments pass through this region with high velocity after the photo-excitation. But this triplet state radical-pair-like structure could definitely be important for the recombination reaction. The earlier discussed disproportionation reaction (4) must proceed only on the triplet state PES since its products HOCl+O$_2$ are in the total triplet state (the HOCl molecule has the singlet ground state and dioxygen (O$_2$) has the triplet ground state). The separated pair of the two radicals HO$_2$+ClO could be either in the singlet or in the triplet state. The intermediate triplet state in the disproportionation reaction (4) which consists of two triplet molecules ClHO and O$_2$ is an important intermediate. It can play a role of a spin trap which finally passes through the T→S transition inside the ClHO moiety in order to produce separated products of reaction (4). Besides, the triplet ClHO species obtained during photolysis can react with dioxygen and produce singlet, triplet and quintet channels for the reversed disproportionation reaction (4). There are five quintet collisions, three triplets and one singlet during such process. Since the quintet collisions are non-reactive, the possibility of the reversed disproportionation reaction (4) is very limited.

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 dissociation processes, we conclude that the photochemistry of the triplet state must play an important part in the stratospheric ozone problem. The results show that atmospheric photochemistry of heavy halogen-containing compounds depends essentially on the S−T transitions and inclusion of relativistic effects. Thermochemical ab initio calculations for ClO$^-$ as possible dissociation products

of HOCl molecule show that these compounds in the singlet ground state are stable enough. Our MC SCF and CI calculations including SOC indicate that the compounds are metastable.

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ПОТЕНЦІЙНІ КРИВІ ТА СПЕКТРИ МОЛЕКУЛ ClO⁻ І HOCl, ДОСЛІДЖЕНІ МЕТОДАМИ АВ INITIO

О.М. Хоменко, Б.П. Мінаєв

На основі методу багатоконфігураційної взаємодії одержано криві потенційної енергії для основного та низки збуджених станів молекул ClO⁻ і HOCl вздовж каналів фотодисоціації, що корелюють з нижніми межами дисоціації. Результатами розрахунків передбачено неадіабатичні синглет-триплетні переходи під час переддисоціації основного $X^1\Sigma^+$ стану до нижчої межі $O(^3P)+Cl^-(^1S)$. Надано криві потенційної енергії для основного синглетного X^1A' та першого збудженого триплетного $1^3A''$ станів молекули HOCl з метою прогнозування важливого значення синглет-триплетного поглинання в спектрі цієї молекули. Результати показують, що атмосферна фотохімія важких галогенвмісних сполук значнлю мірою залежить від синглет-триплетних переходів і врахування релятивістських ефектів. Термохімічні ab initio розрахунки ClO⁻, як можливого продукту дисоціації молекули HOCl, показують, що ці сполуки є достатньо стабільними в їх основному синглетному стані. Наші розрахунки з використанням багатоконфігураційної взаємодії із врахуванням спін-орбітальної взаємодії вказують, що ці сполуки мають метастабільний характер.

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

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Potential energy curves of the ground state and a number of excited states of the ClO⁻ and HOCl species along the photodissociation reaction channels are obtained on the basis of multireference configuration interaction, which correlate with the low-lying dissociation limits. The singlet-triplet nonadiabatic transition during the predissociation of the ground $X^1\Sigma^+$ state to the lowest limit $O(^3P)+Cl^-(^1S)$ is predicted on the basis of the calculations results. In order to predict the possible importance of the singlet-triplet absorption in the HOCl molecule spectrum, we have presented potential energy curves for the ground singlet X^1A' and the first excited triplet $1^3A''$ states. The results show that atmospheric photochemistry

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Keywords: photodissociation; singlet−triplet transition; spin−orbit coupling; absorption bands; spectrum.

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