Algebraic Studies for Electronic Structures and Photodissociation of Bromine Molecule

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Abstract

I have theoretically studied the nonadiabatic transitions among the lower states with $\Omega=1_u$ symmetry ($1_u^{(1)}$ to $1_u^{(3)}$) in the photodissociation of Br_2 using the Comlete Active Space Self-Consistent Field (CASSCF) computations and the time-independent SchrÖdinger equations. The CASSCF wave function is formed from a complete distribution of a number of active electrons in a set of active orbitals, which in general constitute a subset of the total occupied space. From the configuration analysis of the CASSCF wavefunctions, we found that the nonadiabatic transition between $1u^{(2)}$ and $1u^{(1)}$ is a noncrossing type, while that between $1u^{(2)}$ and $B^3\Pi_{0+u}$ is a crossing type. The spectroscopic constants for the $X^1\Sigma_g^+$, $A^3\Pi_{1u}$ and $B^3\Pi_{0+u}$ states of Br_2 is calculated. The absorption cross-section for the ground and the lower excited states in the photodissociation of Br_2 molecule is presented as well as the numerical estimates of nonadiabatic transition probabilities. Also, the five highest occupied and the five lowest unoccupied orbitals of Br_2 have been calculated.

1. Introduction

Classical investigations of the discrete absorption spectrum of halogen molecules, specially Br_2 and I_2, have resulted in the accurate identification of transitions between specific vibrational and rotational levels of these diatomics[1]. Such analyses have permitted the precise characterization of the potential curves for the bound $X^1\Sigma_g^+$ ground and $B^3\Pi_{0+u}$ excited states. A drawback, common to the above methods, is that such techniques cannot, however, to be used for the study of repulsive states or those portions of bound excited states which lie above the thermochemical threshold for dissociation into open-shell atomic fragments in ground configuration with which they correlate.

Diatomic halogen and interhalogen molecules continue to serve as benchmark systems to study photodissociation dynamics. Recent experimental activity has been devoted to the study of the orientation and alignment, namely the m_j distributions, of the product angular momentum. Details of the nonadiabatic transition probabilities have been estimated from such analysis for Cl_2[2-5] and Br_2[4]. Also, recent advances in both experimental and theoretical studies of molecular photodissociation enable us to investigate quite detailed information on the dissociation dynamics.

Yukako Asano and Satoshi Yabushita[6] calculated the potential curves of I_2 by the spin-orbit configuration interaction (SOCI) method, and evaluate the radial derivative coupling elements among the five lower states with $\Omega=1_u$ symmetry ($1_u^{(1)}$ to $1_u^{(3)}$) to examine the nonadiabatic transition processes and to compare the results with those of Cl_2 and Br_2. Also, Yukako Asano and Satoshi Yabushita[5] evaluated the

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nonadiabatic transition probabilities of Cl_2 and Br_2 by solving the semiclassical time-dependent coupled SchrÖdinger equations.

Balasubramanian et al.[7] calculated the spectroscopic properties and potential curves of I_2 by the complete active space SCF method followed by the nonrelativistic first-order and second- order configuration interaction (CI), and rtecent relativistic many-body perturbation methods. Teichteil and Pelissier[8] calculated the potential curves of I_2 with an ab initio relativistic atomic pseudo- potential method and analyzed the available experimental data. Nieuwpoort et al.[9] employed an all-electron Dirac- Fock method followed by the CCSD(T) calculations. However, none of the previous workers has studied the nonadiabatic transitions in the photodissociation of I_2.

The ability to accurately describe complicated molecular wave functions with only few terms has often been claimed to be one of the major advantages of the MCSCF mrthod[10]. This simple picture is usually contrasted to the very long expansions encountered in conventional CI methods where the orbitals are not variationally optimized. In the CASSCF method, the philosophy is quite different from that of traditional MCSCF methods, in that it should involve complete sets of multiconfigurational wave functions although it tends to be rather time consuming, thus providing an ideal path for the systematic study of electron correlation effects in excitation processes involve not only one photon.

A potential energy surface is a mathematical relationship linking molecular structure and the resultant energy. For a diatomic molecule, it is a two-dimensional plot with the internuclear separation on the X-axis, and the energy at that bond distance on the Y-axis, producing a curve. For larger systems, the surface has as many dimensions as there are degree of freedom within the molecule.

Potential energy surfaces may be determined by ab initio electronic structure calculations. In this method one performs a large number of electronic structure calculations (which may be very expensive) and then fits the results using a least square procedure. The reliability of the PES depends on the basis set completeness and how well electron correlation is accounted for.

In the paper[10] the CASSCF method was presented in detail. In this study, we introduce the brief discussion of the method and presents some experience from an application to the bromine molecule, we calculate the ground and some excited states of Br_2 by the Comlete Active Space Self-Consistent Field (CASSCF) computations at 6-31+G(d,p) level and the semiclassical time-dependent coupled SchrÖdinger equations.

2. Computational Methods and Theory

The CASSCF program used is a part of the GAUSSIAN 03[11] suite of programs. A CASSCF calculation is a combination of SCF computation with a full configuration interaction calculation involving a subset of the orbitals. The orbitals involved in the CI are known as the active space. In this way, the CASSCF method optimizes the orbitals approprietly for the excited state.

All calculations have been performed using the implementation of the CASSCF procedure and the standard 6-31+G(d,p) basis set available in the Gaussian 03[11] Locations of excited-state minima and transition structures have been carried out by using the methods available in the same program package.

The numerical estimates of nonadiabatic transition probabilities are calculated by using the program of Yukako Asano and Satoshi Yabushita[6]. That program depends on the semiclassical theory, in which the total wavefunction $\psi_e(R(t),r)$ satisfies the following time – dependent Schrodinger equation

$$i\hbar \partial \Psi_e(R(t),r)/\partial t = [H_e(R(t),r)]\Psi_e(R(t),r)$$

where H_e is the electronic Hamiltonian, r is the electronic co-ordinate, and R(t) is the internuclear distance, and the molecular rotation is not considered here. If ψ_e is expand in terms of the adiabatic wavefunctions, $1_u^{(1)}$ through $1_u^{(5)}$, the expansion coefficients $C_n(t)$ satisfy a set of the first-order coupled equations,

$$i\hbar \, dC_k(t)/dt = \sum_n [E_k \delta_{kn} - i\hbar \upsilon g_{kn}]C_n(t)$$

where E_k are the eigenvalues of H_e, υ is the relative nuclear velocity, $g_{kn} = \langle 1_u^{(k)} | d / dR | 1_u^{(n)} \rangle$ are the radial derivative (nonadiabatic) coupling elements between $1_u^{(k)}$ and $1_u^{(n)}$ and $|C_n(t)|^2$ stands for the probability of finding the system in the adiabatic state $1_u^{(n)}$. The relative nuclear motion is described by the classical equation of motions.

$$\mu \, d^2R(t)/dt^2 = -\partial E_i / \partial R ,$$

where μ is the reduced mass and E_i is the adiabatic potential energy on which the photodissociation takes place.

3. Results and Discussion

The calculated adiabatic potential curves of Br_2 are shown in Figure 2. Spectroscopic constants of the $X^1\Sigma_g^+$, $A^3\Pi_{1u}$ and $B^3\Pi_{0+u}$ states of Br_2 are shown in Table 1, and are in reasonable agreement with the experimental results[15, 16]. We

thus expect that quantitative results can be obtained for the photodissociation processes with these ab initio potential energy curves.

Table 1. Our calculations in comparison with experimental spectroscopic constants[15, 16] for the $X^1\Sigma_g^+$, $A^3\Pi_{1u}$ and $B^3\Pi_{0+u}$ states of Br_2

		R_e(Å)	D_e(kJ/mol)	ω_e(cm^{-1})	$\omega_e\xi_e$(cm^{-1})
$X^1\Sigma_g^+$	This work	2.304	188.53	320.7	1.24
	Experiment	2.280	190.17	325.3	1.08
$A^3\Pi_{1u}$	This work	2.758	22.57	144.8	2.85
	Experiment	2.690	24.77	153	2.7
$B^3\Pi_{0+u}$	This work	2.760	43.51	163.1	1.91
	Experiment	2.677	44.96	167.6	1.64

R_e, D_e, ω_e, and $\omega_e\xi_e$ are the equilibrium bond length, the dissociation energy at equilibrium R for the corresponding state, vibrational frequency characterize, and the anharmonic spectroscopic constants, respectively. Our calculations for these characterestics is explored by performing a potential energy surface scan on the model chemistry CASSCF /aug-cc-pVTZ level, where the notation (10,8) defines the complete active space: 10 electrons distributed over 8 molecular orbitals (MOS) $\{\sigma_{Br-Br}^*, \pi_x(Br), \pi_x^*(Br), \pi_y(Br), \pi_y^*(Br), 2n_{Br}, \sigma_{Br-Br}\}$

The calculated potential curves of Br_2 are shown in Fig.1. Note that the $A^3\Pi_{1u}$ (1_u) and $^1\Pi_u$ (1_u) states correlate to the ground state Br+Br limit, whereas the $B^3\Pi_{0+u}$ (0_u^+) state correlates to the Br+Br* limit. The potential energy curve for another repulsive 1_u state, correlating to the Br+Br* limit, what it mean that potential is implicated in the propsed explanation for the non-limiting β values observed for the Br+Br* product recoil velocity distributions[17]
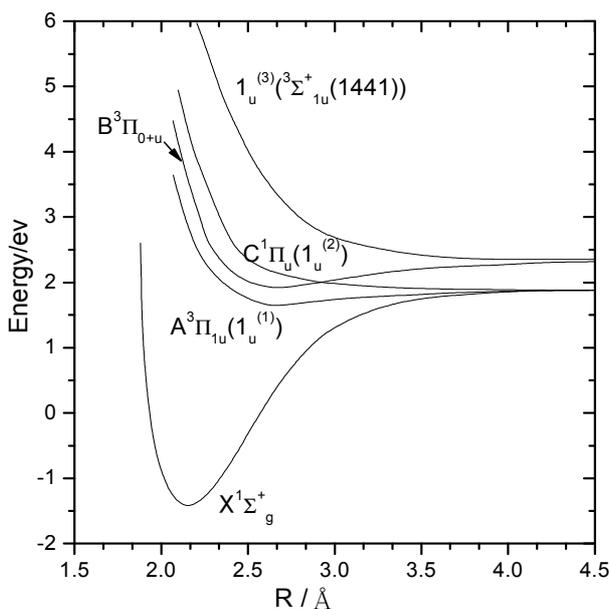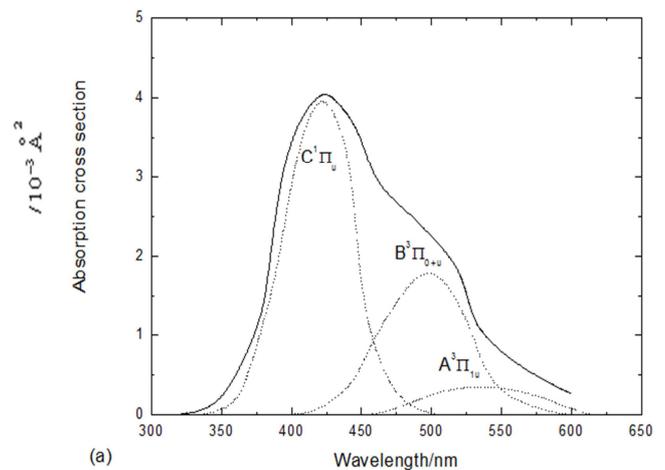
In the numerical calculation of the absorption cross-section for the photodissociation of Br_2 molecule, we used the program by Balint-Kurti et al.[18] employing the time-dependent quantum dynamical method. The mechanism is assumed to involve the absorption of a photon of ultraviolet radiation which causes an electronic transition in the molecule from a bound to a repulsive electronic state. The two atoms then fly apart under the influence of the forces on the repulsive electronic state causing the molecule to break up into its atomic fragments. This program permits the calculation of cross-sections for molecules in different initial vibrational states.

Our programmed calculations of the total absorption cross section to the A, B, and C states are shown in Fig.2a, also portrayed are the partial absorption coefficients from these discrete state, which corresponding to the schematic deconvolution of the total absorption spectrum and indicate that the A-X and, particulary, B-X transitions contribute to the continuous absorption at shorter wavelengths(λ<510 nm); the latter is deemed responsible for the inflexion in the absorption profile at λ ≈ 460 nm. Electronic absorption spectrum of Br_2 recorded over the wavelength range 300-600 nm (solid lone)，together with an illustrative decomposition into contributions associated with excitations to the $A^3\Pi_{1u}$ (1_u), $B^3\Pi_{0+u}$ (0_u^+) and $^1\Pi_u$ (1_u) states (dot lines).

It also apparent that the first absorption band has a peak at 421.4 nm due to the excitation to the $C^1\Pi_u$ ($1_u^{(2)}$) state and agrees well with both of ref [5] in which it has a peak at 419.6 nm and the experimental value of 420 nm[17,18]. The calculated absorption cross section to the $^3\Sigma_{1u}^+$ (1441) state in Fig.2b has a maximum at 235.3 nm, which is in reasonable agreement with both of ref[6] in which it has a peak at 234.8 nm and with the experiment, supporting the tentive assignment[19].
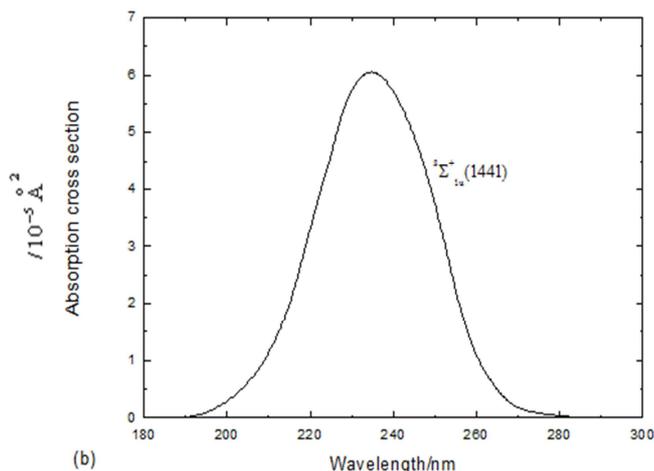

Fig. 1. Potential energy curves for ground state Br_2 and for the three excited states determined by CASSCF calculations

Fig. 2. (a) Absorption cross sections to the lower excited states of Br_2. (b) Absorption cross section to the $^3\Sigma_{1u}^+$ (1441) state of Br_2.

Fig.3a Show the probabilities after the photoexcitation to the $C^1\Pi_u(1_u^{(2)})$ state at 355 nm for Br_2 and the nonadiabatic transition from $1_u^{(2)}$ takes place only to $1_u^{(1)}$. Fig.3b show the probabilities after the vertical excitation to the $^3\Sigma_{1u}^+$ (1441) $(1_u^{(3)})$ state and the nonadiabatic transition takes place only to $1_u^{(4)}$.

Table 2 summarizes the low-lying excitations of the parent Br_2 molecule. According to the TD-DFT computations, in both states, the transition $\sigma_z(Br) \rightarrow \pi_z^*(Br\text{-}Br)$ calculated at 8.6373 eV (143.54 nm) and $n_x(Br) \rightarrow \pi_z^*(Br\text{-}Br)$, $n_y(Br) \rightarrow \pi_z^*(Br\text{-}Br)$ calculated at 2.6446 eV (468.81 nm) are found to dominate the absorption from the estimated oscillator strength f=0.8774 and f=0.0004 respectively. Because the excitation energies to the $\sigma_z(Br) \rightarrow \pi_z^*(Br\text{-}Br)$ transition lies very close to the Rydberg transition, the measured spectrum band can be ascribed mainly to the transitions $n_x(Br) \rightarrow \pi_z^*(Br\text{-}Br)$ and $n_y(Br) \rightarrow \pi_z^*(Br\text{-}Br)$. This indicates that experimental absorption profile will show a maximum cross-section nearby the wavelength of 460 nm.

In order to help better explore the photodissociation channels correlate to the low lying excited states of Br2, we have examined the relevant molecular orbitals. Fig.4 Shows the five highest occupied and the five lowest unoccupied orbitals calculated at the TD-DFT/6-311++G(3df,2pd) level of theory.

The five highest occupied orbitals 31-33 correspond to the lone-pair of nonbonding p electrons of the bromine atoms and 34-35 correspond to the bonding p electrons of the bromine atoms. The five lowest unoccupied orbitals 36, 39, 40 correspond to the excited nonbonding p electrons of the bromine atoms, but 39 and 40 are of higher order, the
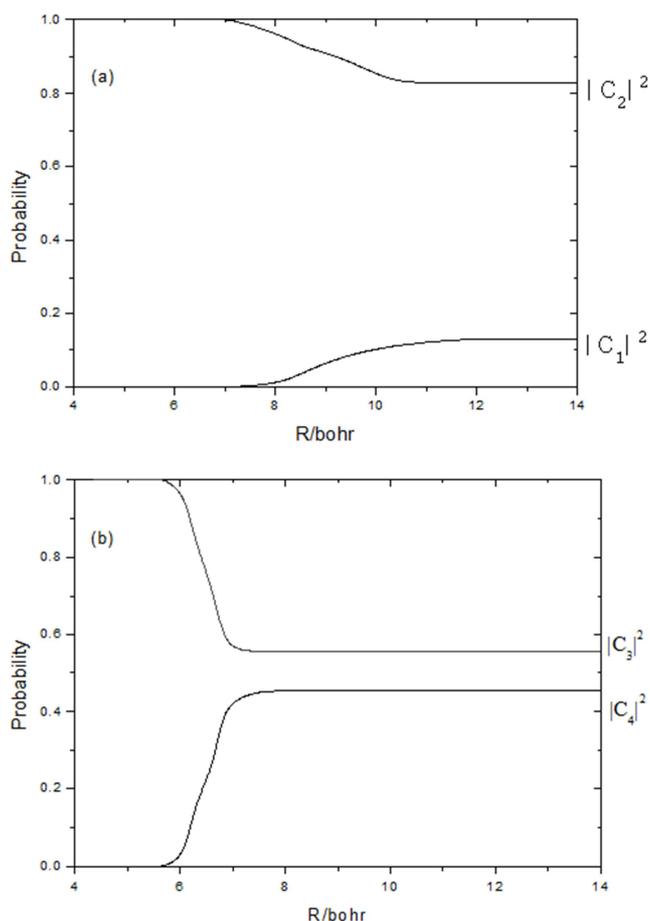
unoccupied orbitals 37,38 can be described as the $\sigma_{Br\text{-}Br}^*$.

Fig. 3. Semiclassical probabilities as a function of R with 355 nm photon of Br_2 from the initial excitation to the $1_u^{(2)}$ ($C^1\Pi_u$) state(Fig.3a) and from the initial excitation to the $1_u^{(3)}$ ($^3\Sigma_{1u}^+$ (1441)) state (Fig.3b).

Table 2. TD-DFT calculated excitation energies ΔE (in eV), corresponding main excitations and oscillator strengths f, for the Br_2 molecule in the equilibrium geometry.

| Br_2	Main excitation	Transition energies ΔE (eV)	Excitation wavelength/ nm	oscillator strengths
State				
$^1\Pi_x$	$n_x(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	2.6446	468.81	f=0.0004
$^1\Pi_y$	$n_y(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	2.6446	468.81	f=0.0004
$^1\Sigma^-$	$\sigma_y(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	4.6611	266.00	f=0.0000
$^1\Sigma^+$	$\sigma_x(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	4.6611	266.00	f=0.0000
$^1\Delta$	$\sigma_z(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	8.6373	143.54	f=0.8774
$^3\Pi_x$	$n_x(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	1.8508	669.90	f=0.0000
$^3\Pi_y$	$n_y(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	1.8508	669.90	f=0.0000
$^3\Sigma^-$	$\sigma_y(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	3.9168	316.55	f=0.0000
$^3\Sigma^+$	$\sigma_x(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	3.9168	316.55	f=0.0000
$^3\Delta$	$\sigma_z(Br) \rightarrow \pi_z^*(Br\text{-}Br)$	5.1270	241.83	f=0.0000
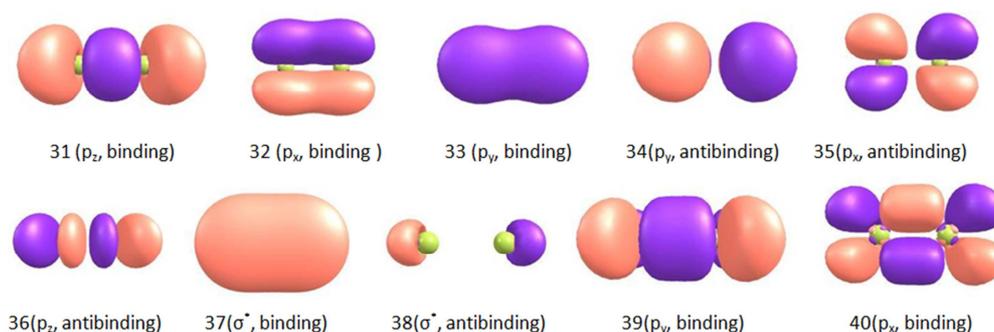
Fig. 4. The five highest occupied and the five lowest unoccupied orbitals of Br2 at TD//B3LYP/6-311++G(3df,2pd) level of theory.

4. Conclusion

We calculated the ground and low-lying excited states of Br_2 by using the Comlete Active Space Self-Consistent Field (CASSCF) computations, and examined the spectroscopic constants of the $X^1\Sigma_g^+$, $A^3\Pi_{1u}$ and $B^3\Pi_{0+u}$ states which are found in reasonable agreement with experimental results. Numerical calculations of the absorption cross-section to the A, B, and C states for the photodissociation of Br_2 molecule, have been done employing the time-dependent quantum dynamical approach, and agree well with experimental results. The nonadiabatic transition probabilities have been also evaluated in the frame of the semicalssical theory.

The five highest occupied and the five lowest unoccupied orbitals of Br_2 could to obtain to explore the photodissociation channels at TD//B3LYP/6-311++G(3df,2pd) level of theory. Finally, we can say that CASSCF is quite good method to investigate structures on the electronic excited states and photodissociation of bromine molecule and also, produce results of high accuracy.

Acknowledgment

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