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Chemical Physics 314 (2005) 173–178
Chemical Physics
www.elsevier.com/locate/chemphys

Studies on photodissociation of dibromoalkane in UV region

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Received 3 September 2004; accepted 2 March 2005
Available online 7 April 2005

Abstract

The photodissociation of CH_2Br_2, 1,2-$C_2H_4Br_2$ and 1,4-$C_4H_8Br_2$ near 234 and 267 nm has been studied using resonance-enhanced multiphoton ionization with time-of-flight mass spectrometry. The wavelength dependence of the relative quantum yields Φ_{Br} and Φ_{Br^*} for both $Br(^2P^0_{3/2})$ and $Br^*(^2P^0_{1/2})$ channels was measured. The results indicated that the yields Φ_{Br} of $C_2H_4Br_2$ is larger than that of CH_2Br_2. And the quantum yields wavelength dependent of $C_4H_8Br_2$ shows a different tendency compared to CH_2Br_2 and $C_2H_4Br_2$. A likely explanation for the different quantum yields relies on the non-adiabatic transitions and avoided curve crossing mechanism. Additionally, ab initio calculations were performed to get potential energy surface curves of CH_2Br_2 to elucidate the photodissociation channels in UV region.

Keywords: Photodissociation; Branching ratio; Resonance-enhanced multiphoton ionization

1. Introduction

The photodissociation of dihaloalkane (CX_2Y_2; X = H, F; Y = Br, I) in the UV region has played an important role as a simple model system in the investigation of the photodissociation dynamics of polyatomic molecules [1–5]. The diffuse absorption bands observed in UV spectrum of alkyl halides are denoted as A-bands, and the photon absorption that gives rise to these bands stems from the promotion of a lone-pair p electron on the Y atom into the antibonding σ^* orbital localized on the C–Y bond [6]. Like the methyl halides, photoexcitation of CX_2Y_2 in the A-bands results in prompt fission of the C–Y bond due to the repulsive nature of the excited states, producing a electronically ground state alkyl radical CX_2Y radical and either a spin–orbit excited state $Y^*(^2P^0_{1/2})$ or a ground state $Y(^2P^0_{3/2})$ atom. According to Mulliken's notation [7,8], the A-band arises from the superposition of three electronic transitions leading from the ground state to the excited state denoted by $^3Q_1$, $^3Q_0$, and $^1Q_1$ in ascending order of electronic energy. Of these three states, only the $^3Q_0$ state is correlated with the spin–orbit excited state Y*, and the other states are correlated with the spin–orbit ground state Y.

In alkyl bromides photolysis, two possible dissociation channels exist in the UV wavelength region. Take CH_2Br_2 as example

$$CH_2Br_2 + hv \rightarrow CH_2Br + Br(^2P^0_{3/2}) \quad \Delta H = 247\ \mathrm{kJ/mol} \tag{1}$$

$$\rightarrow CH_2Br + Br^*(^2P^0_{1/2}) \quad \Delta H = 291\ \mathrm{kJ/mol} \tag{2}$$

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0301-0104/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2005.03.002

The bond dissociation energy, D_0 (CH_2Br–Br), is 247 kJ/mol [9] and the spin–orbit energy of bromine, E_{so} is 44 kJ/mol.

The photodissociation dynamics of methyl halides such as CH_3I [10–14], CH_3Br [15], CCl_3Br [16] and CF_3Br [17] have been extensively studied by both experiment and theory. The characteristic behavior of them is often used as a starting point to describe the photodissociation of other alkyl halides, including dihaloalkane compounds. A noteworthy conclusion drawn in these studies is that non-adiabatic dynamics plays an important role in the photodissociation process. The studies of CCl_3Br [16] and CF_3Br [17] using ion imaging technique have provided strong evidence for the importance of non-adiabatic transitions in the photodissociation dynamics. The photodissociation dynamics of methyl halides and dihaloalkane in A-band resemble each other [1], therefore, the property of the former can be used to deduce that of the latter. Furthermore, the reduction of the molecular symmetry during the photodissociation process can induce level splitting of the excited states, the coupling of these states can causes avoided crossing region. The investigation of CH_2BrCl [18] shows that the avoided crossing plays a very important role in the photo dissociation dynamics.

In comparison with the alkyl bromide, the photodissociation dynamics of dibromoalkane has received less attention. We investigate the wavelength-dependent photodissociation dynamics of CH_2Br_2, 1,2-$C_2H_4Br_2$ and 1,4-$C_4H_8Br_2$ using state-selected ion time-of-fight (TOF) mass spectrometry near 234 and 267 nm, respectively. The $[2+1]$ resonance-enhanced multiphoton ionization (REMPI) scheme was used to ionize Br and Br* state selectively. The relative quantum yields of Br and Br* of these molecules were measured. The wavelength dependence of the relative quantum yields provides an insight into the nature of the electronic excited states which contribute to the absorption spectrum in the A-band, and the role of non-adiabatic curve crossing and avoided crossing in the dissociation process. The results qualitatively suggest some important differences between the photodissociation dynamics of CH_2Br_2 and other dibromoalkane series. In the present study, we performed density functional (DFT) theory calculation to investigate the ultraviolet electronic transitions of CH_2Br_2. Furthermore, the molecular orbitals and potential energy curves (PESs) of CH_2Br_2 were also calculated using ab initio methods to illustrate the photodissociation process clearly.

2. Experiments and calculations

The details of the experimental setup used in this study have been described elsewhere [19]. In brief, the time-of-flight mass spectrometer composed a molecular beam source and a main chamber. The main chamber consists of electrode plates, a flight tube, and a detection system. The background pressure in the chamber was about 5×10^{-4} Pa. The samples were purchased commercially with 99.9% purity and used without further purification. The samples (CH_2Br_2, 1,2-$C_2H_4Br_2$ or 1,4-$C_4H_8Br_2$) seeded in He at 1.5 atm were expanded into the vacuum. A pulsed molecular beam was generated using a pulsed valve (General Valve, IOTA ONE) with a 0.2 mm nozzle. In order to minimize cluster formation, photolysis was performed on the rising edge of the pulsed molecular beam.

The 355 nm output of an Nd:YAG laser (YG981E10, Quantel) was used to pump a dye laser (ScanMate 2E, Lambda Physik), and then the visible light was frequency doubled by a BBO crystal (typically 0.5 mJ/pulse). The resulting laser beam was then focused onto the molecular beam by a lens with a focal length of 180 mm and perpendicularly intersected the supersonic molecular beam. Sample was photolyzed and the state selectively ionizations of photodissociated bromine atoms are followed via the $[2+1]$ REMPI. In the 267-nm region two wavelengths 266.580 and 266.643 nm are used to ionize bromine atoms in the Br ($5p^4P^0_{3/2}$) and Br* ($5p^4S^0_{3/2}$), respectively. In the 234-nm region the Br and Br* atoms are also ionized via $6p^2S^0_{1/2}$ and $6p^4P^0_{3/2}$ states at 233.634 and 233.974 nm.

The ions were detected by a pair of microchannel plates (MCP, Institute of the Peking electronics), which was positioned at the end of the drift tube (60 cm). The output signal was digitalized by a 100 MHz digital oscilloscope (TDS 2012, Tektronix). The TOF mass spectra were averaged over 128 shots on the oscilloscope and every result was accumulated up to 1280 shots. All the time delays were provided by a pulse generator (DG535, Stanford Research Systems).

Calculations were performed using the GAUSSIAN **98** program package [20]. The complete geometry optimization of CH_2Br_2 was done analytically at the B3LYP/6-31+G (2d, 2p) level of theory for the ground state, and those of the excited states were computed using UCIS/6-311++G (2d, 2p) level of theory under constraint of C_s symmetry where the plane of symmetry contained the carbon atom and the two bromine atoms. The potential energy curves along the C–Br bond distance were scanned, that means the potential energy were calculated point by point. The complete geometry optimization of CH_2I_2 was done at the B3LYP/3-21G** level of theory for the ground state. The vertical excitation energies were computed using TD/DFT methods. Note that calculations do not take spin–orbit coupling into account.