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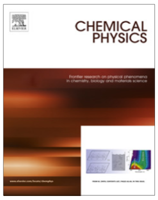

Tracing dissociation dynamics of CH_3Br in the $^3Q_0$ state with femtosecond extreme ultraviolet ionization

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ABSTRACT

The ultrafast photodissociation dynamics of gas phase CH_3Br molecules in the red wing of the A-band, i.e. the first molecular adsorption continuum, is investigated by pump–probe spectroscopy. The experiment employs femtosecond laser pulses at 266 nm in the ultraviolet to dissociate the molecule and high order harmonic extreme ultraviolet pulses in conjunction with time-of-flight mass spectrometry to ionize and detect the fragments. A dissociation time of 116 ± 25 fs is obtained from the pump–probe risetime of the Br^+ ion signal, which originates from formation of either or both $Br(^2P_{3/2})$ or $Br^*(^2P_{1/2})$. The timescale is in a good agreement with the previously calculated A-band dissociation time of CH_3Br using the anisotropy parameter β deduced from angular photodissociation experiments. Based on classical molecular dynamics simulations and previous spectroscopic information, the most likely pathway is dissociation of the CH_3Br molecule via the $^3Q_0$ state of the A-band, which correlates with the formation of the spin–orbit excited bromine fragment.

1. Introduction

The formation of reactive species, i.e. radicals, is of fundamental importance in various branches of chemical sciences and engineering. Particularly, the fate of complex chemical transformations is drastically influenced by the formation timescale of free radical fragments. Therefore, it is of considerable interest to probe the chemical bond breaking timescale, especially the distance over which the molecular fragments are fully formed and the bond completely dissolved.

In this paper femtosecond (fs) extreme ultraviolet (XUV) pulses are used to trace when the Br atom (and the corresponding CH_3 radical) appears as a free species after the photoexcitation of the CH_3Br molecule in the red wing of the A-band. The experimental procedure employed here is able to distinguish between the fragments produced via A-band dissociation and dissociative photoionization.

The A-band of CH_3Br can be accessed in the 170–270 nm spectral range with an absorption maximum around 200 nm [1–4]. The photodissociation of the methyl bromide molecule via A-band excitation was investigated in the gas phase by means of time-of-flight mass spectrometry and velocity map imaging by excitation at several wavelengths: 193 nm and 222 nm [5], 205 nm [6], 215.9 nm [7], 213–235 nm [8], 218–245 nm [9], and 240–280 nm [10]. In principle, two dissociation channels can be accessed by means of A-band excitation: (i) the Br-channel giving rise to the formation of a methyl radical and a ground state $Br(^2P_{3/2})$, and (ii) the Br^*-channel giving rise to methyl and a bromine atom in the spin–orbit excited state $Br(^2P_{1/2})$. The $^1Q_1$ state that correlates with the formation of Br is the main contributor to the absorption cross section of the A-band. However, in the red wing of the A-band (240–280 nm) the $^3Q_0$ and $^3Q_1$ states have significant absorption (see Ref. [11] and references therein). The $^3Q_0$ state correlates with the formation of Br^* while the $^3Q_1$ state correlates with the formation of Br. Experimentally it has been observed that the majority of Br^* fragments are produced by direct absorption to the $^3Q_0$ state [6]. However, Br fragments can be produced directly via excitation of the $^1Q_1$ and $^3Q_1$ states and also by a surface crossing mechanism via $^3Q_0$ state excitation [6].

The direct time-resolved dissociation dynamics of the gas phase CH_3Br molecule via A-band excitation has not been investigated so far. It was considered that CH_3Br may photodissociate faster than CH_3I (about 70 fs for CH_3I [12,13]) via the respective A-band excitations, because the CH_3Br A-band absorption is slightly higher in energy and lies on an even steeper region of the excited state potential than the CH_3I A-band [6]. However, investigations

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employing photofragment anisotropy measurements provide an estimate of the dissociation time through the rotational period. Those investigations estimated the dissociation time of the gas phase CH_3Br molecules to be between 111 fs and 120 fs for the Br^* dissociation channel and considerably longer, 188 fs for the Br dissociation channel [9,10]. The Br^* is formed in a shorter time than Br, because the CH_3 is born 'hotter', i.e. has higher vibrational energy, when it is formed together with the Br-channel. Although the CH_3Br A-band absorption is energetically higher and steeper than the CH_3I A-band, the CH_3Br should dissociate slower than CH_3I because a larger amount of the energy available for the dissociation is released into the CH_3 fragment as internal energy, making CH_3 vibrationally hotter when it is produced from CH_3Br than CH_3I photodissociation [14].

The only time-resolved experiment has been performed on CH_3Br molecules physisorbed on insulating ultrathin magnesia films [15,16]. The CH_3Br molecules adsorbed on the magnesia surface were found to dissociate in about 150 fs after a two-photon excitation at a central wavelength of 266 nm. However, the dissociation time of the CH_3Br molecule adsorbed on the surface is influenced by the molecular adsorption geometry and the changes in electronic states due to the interaction between the molecule and the surface [16–18] and the result does not necessarily reveal the dissociation time of the free molecule.

Here femtosecond pump–probe spectroscopy in conjunction with high-harmonic ionization, time-of-flight mass spectrometry is employed to quantitatively characterize the dissociation time of the CH_3Br molecule in the gas phase. After excitation at the central wavelength of 266 nm, the bromine fragments are detected via ionization by a single photon XUV high harmonic laser pulse. Various scenarios for the CH_3Br dissociation at 266 nm are discussed and compared with a classical molecular dynamics simulation.

2. Experimental

The experimental setup employed in the present investigation consists of three main parts: (i) a commercial amplified femtosecond laser system with a central wavelength of 800 nm, (ii) a pump–probe setup in conjunction with a monochromatic fs extreme ultraviolet high harmonic source and (iii) an investigation chamber equipped with an effusive molecular beam and a time-of-flight mass spectrometer (TOF-MS). Fig. 1 shows a schematic representation of the fs XUV source together with the investigation chamber.

The fs-laser light is produced by a Ti:Sapphire mode locked oscillator continuously pumped by a 5 W Spectra Physics Millennia Nd:YVO laser. Pulse amplification is carried out by a Nd:YLF laser pumped Ti:Sapphire amplifier to yield 90 fs pulses, with an energy of 2.2 mJ at a repetition rate of 1 kHz. The amplified near infrared laser beam (800 nm) is divided into two arms to produce the pump and the probe laser beams. One arm (30% of the total power) is used to generate the pump beam at 266 nm by frequency tripling of the fundamental wavelength in a homebuilt crystal-based third harmonic generator. The pump beam is focused by a 100 cm lens into the investigation chamber.

The second arm (70% of the total power) is used to generate the probe pulse consisting of fs XUV light, which is produced by means of high harmonic generation [19–22].For the high harmonic generation the 800 nm light is focused by a 40 cm lens into a 3 mm long Ar gas cell. The generated harmonics that co-propagate with the residual fundamental laser light are separated by means of a plane grating. Subsequently, the harmonics are focused into the investigation chamber by a cylindrical mirror and a toroidal mirror. A 2 mm slit positioned inside the investigation chamber allows a single harmonic to pass into the interaction region; all the other harmonics are blocked. The pressure in the gas cell as well as the 800 nm light intensity and focus position are tuned to maximize the flux of the 15th harmonic (0.15 nm spectral width), which is the only harmonic used. The pump beam, 266 nm, is reflected into the interaction region by an aluminum mirror mounted in the vacuum apparatus a few millimeters above the XUV beam (cf. insert in Fig. 1). The pump and the probe beams are overlapped in the interaction region at a 1.5° angle.

In the investigation chamber a skimmed effusive molecular beam crosses the laser beam at a right angle. The ions formed in the interaction region are analyzed by a 130 cm long Wiley–McLaren TOF-MS positioned with the longitudinal axis perpendicular to the plane formed by the laser beam and the molecular beam. The molecular beam intersects the laser beams and the longitudinal axis of the TOF-MS at the same point between the repeller electrode and the extraction electrode of the TOF-MS.

The zero time delay between the pump and the probe pulse as well as the instrumental time response function is measured in situ by time-resolved spectroscopy using ionization of He following excitation of the He($1s^2$-1s3p) transition. The 1s3p state in He atom has a lifetime of about 1.76 ns [23] and is resonantly excited with a pump pulse tuned to the 15th harmonic. Subsequently, a probe pulse at 266 nm, which is delayed with respect to the pump pulse, ionizes the excited He atoms and the ions are detected by the TOF-MS. The resonantly excited He(1s3p) state is an instantaneous transition that results in a step function response when the excited He atom is ionized by the probe pulse at variable time

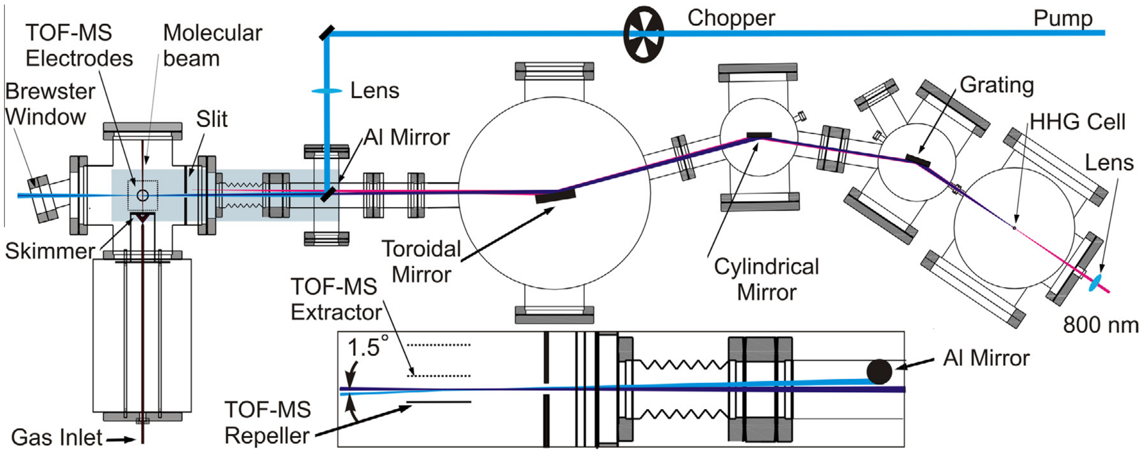

Fig. 1. Schematic layout of the fs-soft X-ray source together with the investigation chamber. Insert: detail illustrating the overlap between the pump and the probe beams into the interaction region.