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The vacuum UV photoabsorption spectrum of methyl bromide (CH_3Br) and its perdeuterated isotopomer CD_3Br: a vibrational analysis

R. Locht [a,*], B. Leyh [a], D. Dehareng [b], H.W. Jochims [c], H. Baumgärtel [c]

[a] *Laboratoire de Dynamique Moléculaire, Département de Chimie, Institut de Chimie Bât.B6c, Université de Liège, Sart-Tilman par, B-4000 Liège 1, Belgium*

[b] *Centre d'Ingénierie des Protéines, Institut de Chimie, Bât.B6a, Université de Liège, Sart-Tilman par, B-4000 Liège 1, Belgium*

[c] *Institut für Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustraße 3, D-14195 Berlin, Germany*

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Abstract

The fine structure of the vacuum UV photoabsorption spectrum of CH_3Br and CD_3Br has been analyzed in the 6.9–10.2 eV photon energy range. A large number of lines have been observed, classified and assigned to the vibrational excitation accompanying a series of Rydberg transitions. The effects of the Jahn–Teller distortion and of the spin–orbit splitting of the ground electronic state of the ion have been considered. The former effect has been evaluated by ab initio calculations, showing that the ^2E state (in the C_{3v} symmetry group) splits into $^2A'$ and $^2A''$ states in the C_S symmetry group. Even though the energy difference of about 1 meV is extremely small, the $^2A'$ state is energetically the lowest component whereas the $^2A''$ is found to be a transition state. The Jahn–Teller stabilization energy and the wavenumbers associated with all vibrational modes have been calculated. Experimentally, the entire fine structure could be described in terms of three vibrational modes, i.e., $hc\omega_4 = 146 \pm 6$ meV (1178 ± 48 cm^{-1}), $hc\omega_5 = 107 \pm 6$ meV (863 ± 48 cm^{-1}) and $hc\omega_6 = 71 \pm 4$ meV (572 ± 32 cm^{-1}), respectively, as resulting from an average over all analyzed Rydberg states. In CD_3Br the corresponding energies are $hc\omega_4 = 104 \pm 3$ meV (839 ± 24 cm^{-1}), $hc\omega_5$=82 ± 4 meV (661 ± 32 cm^{-1}) and $hc\omega_6 = 62 \pm 4$ meV (500 ± 32 cm^{-1}). These values are in fairly good agreement with those predicted by the present ab initio calculations for the ionic ground state. The experimental isotopic ratio $\rho_i = [\omega/\omega_{\mathrm{isot}}]_i$ is 1.15 ± 0.14, 1.31 ± 0.14 and 1.39 ± 1.0 and is predicted to be 1.04, 1.34 and 1.36, respectively, for ω_6, ω_5 and ω_4. On the basis of the present study an alternative assignment of the $CH_3Br^+(\tilde{X}^2E)$ photoelectron band structure is proposed.

Keywords: Photoabsorption; Vacuum UV; Rydberg series; CH_3Br; Jahn–Teller effect; CD_3Br; Vibrational analysis; Ab initio calculations; Photoelectron spectrum

1. Introduction

In previous papers, we investigated in detail the photoabsorption and photoionization dynamics of fluoro and chloromethanes [1–3]. Their vacuum UV photoabsorption spectrum proved to be an essential piece of information for the puzzling interpretation of the threshold photoelectron spectrum (TPES), constant ion state spectra (CIS) and the fragment ion yields in photoionization mass spectrometry.

The previous paper is devoted to a detailed analysis of the pure electronic Rydberg excitations in CH_3Br and CD_3Br [4] between 6 and 12 eV photon energy. In these spectra, numerous weaker and generally broader features are identified. Previous studies of these

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[*] Corresponding author. Tel.: +32 4 366 35 20; fax: +32 4 366 34 13.
E-mail address: robert.locht@ulg.ac.be (R. Locht).

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structures are very scarce in the literature and are limited to a narrow low photon energy range.

Essentially, two papers contributed to the analysis of the vibrational fine structure of the Rydberg series in CH_3Br. First, Causley and Russell [5] examined the photoabsorption spectrum of CH_3Br and other bromomethanes in the 6–10 eV photon energy range. These authors proposed a vibrational analysis of the first *n*s- and *n*p-type Rydberg states converging to both spin–orbit ionization limits $\tilde{X}^2E_{3/2}$–$\tilde{X}^2E_{1/2}$. The spectrum of CD_3Br was not included in this work.

Felps et al. [6] restricted their investigation to the study of the vacuum UV photoabsorption spectrum of CH_3Br in the 54,000–64,000 cm^{-1} (6.69–7.93 eV) spectral region which corresponds to the $2e \rightarrow 5s$ Rydberg transition. An extensive vibrational analysis is presented. This study was extended to CD_3Br. The pressure dependence of the absorption spectrum has also been examined.

The aim of the present work is to identify and classify most of the weak features present in the vacuum UV absorption spectrum of both CH_3Br and CD_3Br over the 6.9–10.2 eV spectral region. Our assignments are supported by ab initio quantum mechanical calculation of the wavenumbers associated with the vibrational normal modes of CH_3Br^+ and CD_3Br^+. This will allow us to make a comparison between the experimental and predicted isotope effect on the vibrational wavenumbers.

2. Experimental

2.1. Experimental set-up

The experimental set-up used in this work has already been described in detail elsewhere [7]. Only the most salient features will be reported here.

Synchrotron radiation available from the BESSY I facility (Berlin, Germany) is dispersed with a modified vacuum UV normal incidence 225 McPherson monochromator with a focal length of 1.5 m, instead of 1 m in the commercial version (1m-NIM-2 beamline). A laminar Zeiss grating is used for the efficient reduction of the second spectral order. It is gold coated with 1200 l/mm and its transmission vanishes above 26 eV (210,000 cm^{-1} or 47 nm). The width of the entrance and exit slits of 100 μm provides a 0.1 nm resolution. The light passes through a 1 mm thick stainless steel microchannel plate necessary to maintain a differential pressure of 1:1000 before entering a 30 cm long stainless steel absorption cell. The vapor pressure in the cell is measured by a Balzers capacitor manometer. CH_3Br and CD_3Br vapors are introduced at a pressure of 20 μbar. The light is detected by a sodium salicylate sensitized photomultiplier located at the end of the absorption cell and in front of the monochromator exit slit. The recording of an absorption spectrum requires one scan with gas in the absorption cell and one with the empty cell. The stability of the synchrotron radiation and of the pressure in the cell ensures reliable absorption data. If required, the spectra presented in the following sections are corrected for any pressure drift. The commercially available CH_3Br, purchased from Praxair and of 99.5% purity, was used without further purification. The CD_3Br, purchased from Merck, Sharp and Dohme, is certified at 99 at.% purity. No noticeable impurity was observed by mass spectrometry at 21.2 eV photon energy. Therefore, the sample was used without further purification.

2.2. Data handling and error estimation

The wavelength calibration of the monochromator has been performed by using the Ar^+ absorption spectrum between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic states. The accuracy of this calibration was estimated to be 2 meV. In the photoabsorption spectra extending between 6 and 12 eV photon energy, an energy increment of 1.5 meV has been adopted. The precision on the energy position of a feature is estimated to be of the order of 2 meV. Therefore, in these cases the assigned total error would be 4 meV. This evaluation is confirmed by the reproducibility of energy positions measured in four different spectra recorded over a two year interval.

3. Experimental results

3.1. The CH_3Br photoabsorption spectrum

Fig. 1(a)–(c) reproduces the photoabsorption spectrum of CH_3Br on an expanded photon energy scale. The assignments of the observed fine structure to various vibrational progressions have been inserted in this figure as far as not overcrowded.

They will be discussed in Section 5.

3.2. The CD_3Br photoabsorption spectrum

The photoabsorption spectrum of CD_3Br has been recorded between 6 and 12 eV photon energy. The fine structures, assigned to excitation of vibrational progressions in the successive Rydberg states, are clearly identified in an expanded photon energy scale, as shown in Fig. 2(a)–(c).

4. Ab initio calculations: methods and results

Ab initio quantum mechanical calculation of the geometry and the vibrational wavenumbers of the cation proved to be very helpful for the interpretation of the vacuum UV spectroscopy of CH_3Cl and CD_3Cl [3]. A similar extensive ab initio calculation on the ground state of CH_3Br and CD_3Br and their cations has been performed.