

VUV spectroscopy of CH₃Cl and CH₃I

S. Eden^{a,*}, P. Limão-Vieira^{a,2}, S.V. Hoffmann^b, N.J. Mason^c

^a Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, UK

^b Institute of Storage Rings, University of Aarhus, Ny Munkegade, Aarhus, Denmark

^c Department of Physics and Astronomy, Open University, Walton Hall, Milton Keynes MK7 6AA, UK

Received 17 August 2006; accepted 24 October 2006

Available online 6 November 2006

Abstract

High-resolution photoabsorption spectra of CH₃Cl and CH₃I are reported in the energy range 3.9–10.8 eV (320–115 nm). Several features are observed for the first time in the CH₃Cl spectrum and a number of new assignments are proposed. For both molecules, the present work provides the most reliable absolute cross-sections yet reported at energies above the dissociative A band transition.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Photoabsorption; CH₃Cl; CH₃I; Electronic excitation; Vibrational excitation; Rydberg series

1. Introduction

CH₃Cl and CH₃I are important trace species in the terrestrial atmosphere. The principle sources of the species in the atmosphere are oceanic emissions and biomass burning [1,2], making them unusual among atmospheric halomethane gases whose major sources are anthropogenic [3]. CH₃Cl is the most abundant of the atmospheric halomethanes and accounts for 15% of the free chlorine radicals in the stratosphere [4,5]. Therefore, it plays a key role in the destruction of ozone. Conversely, CH₃I is believed to be relatively environmentally benign because of its short lifetime in the troposphere due to solar photolysis. Fahr et al. [6] and Rattigan et al. [7] estimated photolysis lifetimes of CH₃I in the troposphere to be 4 and *several* sunlit days, respectively, while its destruction rate due to reactions with OH radicals at low altitudes has been shown to be around

two orders of magnitude slower [8]. Monitoring the concentrations of CH₃Cl and CH₃I in the atmosphere requires a detailed spectral database to be assembled.

The VUV photoabsorption cross-section of CH₃Cl has been studied by several previous authors. Early spectra were reported by Price [9] and by Zobel and Duncan [10] from 6.2 to 12.4 and 24.8 eV, respectively. Absolute cross-sections were first measured by Tsubomura et al. [11] from 6.60 to 7.75 eV and subsequently by Russell et al. [12] in the energy range 6.20–11.16 eV. In each of these works, the authors do not specify their energy resolution. The spectrum of Russell et al. [12] was revisited by Raymonda et al. [13] who commented that the energy positions for sharp features observed in each spectrum are in agreement to within ±1 meV. Robin [14] reviewed the spectra of Price [9], Zobel and Duncan [10], and Russell et al. [12] in a broad discussion of the electronic excitation of alkyl halides. Hochmann et al. [15] measured photoabsorption by CH₃Cl using a McPherson Model 225 monochromator from 7.74 to 11.41 eV with an unspecified resolution. The result of Hochmann et al. [15] was analysed further by Felps et al. [16]. Truch et al. [17] reported the cross-section from 8.50 to 11.75 eV using a McPherson Model 231 monochromator. An indication of the resolution of the spectrum of Truch et al. [17] is given by that fact that they

* Corresponding author. Tel.: +33 4 72 43 12 59; fax: +33 4 72 44 80 04.
E-mail address: s.eden@ipnl.in2p3.fr (S. Eden).

¹ Also of Institut de Physique Nucléaire de Lyon, IN2P3-CNRS et Université Claude Bernard Lyon 1, 43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France.

² Also of Laboratório de Colisões Atômicas e Moleculares, CEFITEC, Departamento de Física, FCT, Universidade Nova de Lisboa, P-2829-516 Caparica, Portugal.

used a grating of 1200 lines per mm compared to 2000 at the ASTRID facility. Olney et al. [3] derived the photoabsorption cross-section in the range 6–50 eV with a resolution of 50 meV from electron energy loss spectroscopy (EELS) data taken using incident electrons of energy between 6 and 8 keV. The cross-section for the absorption of Lyman- α photons (10.120 eV) by CH₃Cl was measured by Vatsa and Volpp [18].

Recently Locht et al. [19] have published a detailed analysis of Rydberg structure observed in the photoabsorption spectrum of CH₃Cl from 6 to 25 eV. Their measurement was made with a wavelength resolution of 0.1 nm, only marginally less precise than the present result (0.075 nm). In a separate article the authors report the analysis of the vibrational structure in the energy range 7.5–10.5 eV [20]. Hitchcock and Brion [21] carried out EELS measurements on both CH₃Cl and CH₃I using incident electrons of 2.5 keV and analysing scattered electrons in the energy loss range 6–12 eV with a resolution of 80 meV. To our knowledge, the only low impact energy EEL spectra recorded for CH₃Cl are those of Nachtigallova et al. [22] measured with a resolution of 60–80 meV using incident electrons of 0.05, 0.25, 0.65, and 20.05 eV. Their experimental work was augmented with electronic structure calculations made using the single-excitation configuration interaction (CIS), complete-active-space self-consistent field (CASSCF), and multi-reference MP2 (CASPT2) methods [23].

The earliest measurement of the VUV photoabsorption spectrum of CH₃I was carried out by Price [9] between 6.2 and 12.4 eV with an unspecified resolution. However, the absolute cross-section was not reported until 1972 when Boschi and Salahub [24] published results using a McPherson Model 225 monochromator in the energy range 3.7–11.1 eV. Robin [14] cited the work of Price [9] and Boschi and Salahub [24] in a broad discussion of the electronic excitation of alkyl halides in which particular attention is devoted to the Rydberg states of CH₃I. Hochmann et al. [15] measured the photoabsorption spectrum from 6.05 to 10.33 eV, again using a McPherson Model 225 spectrometer with an unspecified energy resolution. The results of Hochmann et al. [15] were revisited by the same group in two subsequent papers focussing on the Rydberg series converging to the ionisation limits corresponding to the removal of an iodine lone pair electron [16,25]. The photoabsorption spectrum from 6.888 to 10.972 eV has been reported with a resolution of ± 0.003 Å ($\sim \pm 0.1$ meV at 9 eV) by Baig et al. [26]. This remarkable resolution was achieved using a grating of 5000 lines per mm at the Synchrotron Radiation Laboratory of the University of Bonn. The Rydberg transitions observed in the spectrum were discussed further by Dagata et al. [27,28]. However, the publications only show detailed plots and assignments for the structure observed from 9.3 to 10.3 eV. Furthermore, despite the exceptional precision of the measurement, the authors neither listed the energies of the assigned Rydberg peaks nor discussed the vibrational structure in detail. Waschewsky et al. [29] reported the photoabsorption

cross-section in the ranges 3.70–5.28 and 6.11–6.33 eV, claiming a maximum wavelength resolution of 0.1 nm (3 meV at 6 eV). Photoabsorption measurements of the diffuse A band (~ 4 –6 eV) have also been carried out by Jenkin et al. [30], Fahr et al. [6], and Rattigan et al. [7]. Olney et al. [31] derived the photoabsorption cross-section of CH₃I from 4 to 65 eV with a resolution of 50 meV from EELS data taken using incident electrons of 8 keV. As far as we are aware, no low impact energy electron energy loss data for scattering from CH₃I is available in the literature to clarify the assignment of optically forbidden transitions.

The valence shell molecular orbital configuration of CH₃Cl and CH₃I in the electronic ground state can be represented as $(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2(2e)^4$: 1A_1 [3,31]. Both molecules can be considered to be *pseudo-triatomic* molecules of C_{3v} symmetry, with the H atoms acting as H₃ groups positioned at the centre of mass of the three atoms. Accordingly, the vibrational modes listed in Table 1 include CH₃ stretching and deformation but no motion specific to the individual C–H σ bonds. Indeed only one symmetric CH₃ stretching vibration can be excited, the so-called “umbrella function” [34]. Comparison between the excitation energies of stretching modes indicates that the strongest bonds are those between the carbon atoms and hydrogen groups. The fact that the CH₃ bonds are apparently unaffected by the substitution of the iodine atom with chlorine is unsurprising as C–X (X = I, Br, Cl) σ orbitals tend to be localised close to the electronegative halogens and the larger halogens are situated relatively far from the carbon atom. Therefore, we can expect minimal overlap of CH₃ and C–I or C–Cl orbitals. Furthermore, it is worth noting that the C–X stretching excitation energies tend to be lower for the more electronegative halogen species.

In this paper, we report the results of detailed analysis of the photoabsorption spectra of CH₃Cl and CH₃I with emphasis on providing a systematic assignment of the spectral features and absolute cross-sections in the energy range 3.9–10.8 eV of the VUV region.

2. Experimental

The present photoabsorption measurements were made at the ASTRID facility, Aarhus University, Denmark. Due to the high performance of the monochromator and the stability of ASTRID synchrotron source, high-resolution spectra and low absolute cross-section errors can be measured with great efficiency. The tuneable energy range of the incident photons at the ISA photoabsorption facility (3.9–10.8 eV) coincides with the solar visible–UV spectrum which penetrates the stratosphere and troposphere (<6.89 eV) [35] making the facility highly suitable for probing the photolysis of aeronomic molecules.

The experimental apparatus has been described in detail elsewhere [36]. Synchrotron radiation is passed through a static gas sample. A photo-multiplier is used to measure the transmitted light intensity at 0.05 nm intervals and

Download English Version:

<https://daneshyari.com/en/article/5376561>

Download Persian Version:

<https://daneshyari.com/article/5376561>

[Daneshyari.com](https://daneshyari.com)