Absolute photoabsorption cross-sections (oscillator strengths) for valence and inner shell excitations in hydrogen chloride, hydrogen bromide and hydrogen iodide

C.E. Brion a,*, M. Dyck a, G. Cooper b

a Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1
b Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ont., Canada L8S 4M1

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Abstract

Absolute photoabsorption cross-sections (oscillator strengths) have been measured for the valence shell and selected (Cl 2p, Br 3d and I 4d) inner shell excitations in HCl, HBr and HI, respectively at photon energies up to 280 eV using dipole (e,e) spectroscopy. Absolute scales are established using the $S(0)$ and $S(−2)$ sum rules.

Keywords: Photoabsorption; Absolute cross-sections; Hydrogen halides; Electron impact

1. Introduction

The hydrogen halide diatomic gases are important in a number of practical applications, including etching and plasma processing [1], interstellar and atmospheric chemistry [2–4] and in gas discharges and chemical laser systems [5]. In addition, these are also important prototypical polar diatomic molecules for the testing and development of theoretical methods for calculation of physical properties such as absolute photoabsorption cross-sections and dipole polarizabilities. To date, only limited absolute photoabsorption data have been reported for HCl, HBr and HI. In the case of HCl absolute valence shell data has been reported in the 170–230 nm (5.4–7.3 eV) range [6,7], in the 1050–2150 Å (5.8–11.8 eV) region [8], from 106 to 185 nm (6.7–11.7 eV) [2] and in the 980–720 Å (12.65–17.22 eV) range using synchrotron radiation [9]. Cl 2p inner shell of HCl has also been investigated by Hayes and Brown [10], who used synchrotron radiation in the region from 196 to 210 eV to obtain absolute cross-sections. In other synchrotron radiation work Ninomiya et al. [11] measured absolute cross-sections of HCl in the range 198–280 eV. For HBr and HI extremely limited absolute data is available in the valence shells while there are no absolute measurements available for the inner shells. In the case of HBr valence shell data has been reported by Nee et al. [3] in the 105–235 nm (5.3–11.8 eV) region, using synchrotron radiation. Earlier works by Roxlo and Mandl [6], Huebert and Martin [12], Romand [7], and by Goodeve and Taylor [13] reported absolute photoabsorption cross-sections in the pre-edge region below 8 eV. For HI absolute studies have been reported in the 5.4–7.3 eV region by Roxlo and Mandl [6], and also by Romand [7] and Goodeve and Taylor [14]. Absolute measurements have also been published by Wang et al. [15] for HI in the very limited energy range 10.4–11.1 eV.

We now report high-resolution dipole (e,e) measurements of the absolute photoabsorption cross-sections of HCl, HBr and HI over wide energy ranges of the valence shell and selected inner shells. Measurements for HF have been published much earlier [16,17] using less accurate low-resolution dipole (e,e) techniques.

2. Experimental method

Dipole (e,e) spectroscopy [18–22] is now a well-established and proven method for the accurate determina-
tion of absolute photoabsorption cross-sections over wide energy ranges at resolutions as good as 0.05 eV FWHM. The dipole (e,e) method is not affected by line saturation effects (i.e., linewidth-bandwidth interactions), which can complicate direct photoabsorption methods using the Beer–Lambert law [18,19,21]. The dipole (e,e) method is also not subject to the effects of higher order radiation. In the dipole (e,e) method, relative inelastic electron scattering intensities obtained in fast (3 keV, 0.05 eV FWHM (high resolution)) or 8 keV, 1 eV FWHM (low resolution)) forward scattered electron energy loss spectra are converted to relative dipole oscillator strengths (i.e., photoabsorption spectra) using the known Bethe–Born factors [18,20] for the instrument as a function of photon energy (i.e., energy loss). The target pressure is constant at $\sim 10^{-5}$ Torr, but it is not necessary to know the absolute target density. The absolute energy scales are calibrated using the well-known He $2s$ $1S$ excitation [18] at 21.218 eV. Full details of the experimental method and the processing of the data can be found elsewhere [18–22]. The absolute oscillator strength scale for HCl is determined from Bethe–Born converted, wide range, low resolution (1 eV FWHM) dipole (e,e) spectra using the Thomas–Reiche–Kuhn (TRK), i.e., $S(0)$ Sum Rule [18,20–22] which, in the valence shell formulation (VTRK), can be written [22] as:

$$S_{\text{val}}(0) = \int_{E=0}^{E=\infty} \frac{d\sigma}{dE} dE = N_{\text{val}} + N_{\text{PE}}$$

(1)

where $N_{\text{val}}$ is equal to the number of valence electrons and $N_{\text{PE}}$ is a correction for Pauli-excluded transitions from the inner shells to already occupied valence orbitals [18–22]. The VTRK Sum Rule cannot be used to establish the absolute scales for HBr and HI because the respective low-lying Br 3d and I 4d inner shell excitations prevent fitting and extrapolation of the respective valence shell continua (see discussion elsewhere [21]). Therefore, for HBr and HI the absolute oscillator strength scales for the Bethe–Born converted, wide range, low resolution (1 eV FWHM) relative spectra have been established using the $S(-2)$ Sum Rule and incorporating known values [21] of the static dipole polarizability $\alpha_\infty$ according to Eq. (2).

$$S(-2) = \int_{E=0}^{E=\infty} \frac{1}{E^2} \frac{d\sigma}{dE} dE = \alpha_\infty$$

(2)

Very accurate values of the dipole polarizability are known from measurements of the refractive index or dielectric constant [21]. Dipole polarizabilities can also be used to check the accuracy of absolute photoabsorption cross-section measurements obtained using $S(0)$ or conventional absolute scale methods, as has recently been demonstrated for a large compilation [21] of absolute photoabsorption data obtained for 5 atoms and ~60 molecules using the dipole (e,e) method. The high-resolution (0.05 or 0.1 eV FWHM) spectra have been normalized on the low-resolution spectra in the respective smooth continuum regions.

3. Results and discussion

Absolute photoabsorption (oscillator strength) spectra for discrete and low energy continuum regions of the valence shells of HCl, HBr and HI are shown in Figs. 1–3, respectively and the assignments are from Ref. [23] for HCl, [24,25] for HBr and [26] for HI. In almost all cases, previous direct optical studies [3,6–8,12–15] show significantly lower cross-sections than the present work in the region of the sharp Rydberg structures while generally better agreement exists in the smooth continuum regions and also for the much broader valence excitations at lower energies. From these observations it is clear that the cross-sections for the sharp Rydberg states in the direct optical studies are strongly affected by line saturation (bandwidth/linewidth) errors, which result from...
in severe attenuation of the intensities. In many cases (e.g., see Ref. [19]) the direct optical intensities are several orders of magnitude lower than the presently reported dipole (e,e) values. With regard to this it should be noted that the dipole (e,e) method is not subject to line saturation errors [18,19,21], and in addition that the absolute scales for the dipole (e,e) data are subject to the stringent conditions of the $S(0)$ and/or $S(−2)$ sum rules. In the case of HCl, the dipole polarizability derived from the $S(0)$ normalized dipole (e,e) spectrum is within 2% of the published value determined from refractive index measurements (these are typically considered to be accurate within 1%—see Ref. [21] for details). The absolute synchrotron radiation data of Frohlich and Glass-Maujean [9] for HCl are 3–50% higher than the present work. Detailed Sum Rule analysis [21] of oscillator strength measurements for 5 atoms and ~60 molecules indicates that the dipole (e,e) method gives absolute cross-sections with an accuracy of better than ±5% in both the discrete and continuum regions over the complete energy range of the spectra.

The Cl 2p/HCl, Br 3d/HBr and I 4d/HI high-resolution (0.1 eV FWHM) inner shell absolute photoabsorption (oscillator strength) spectra are shown in Figs. 4–6, respectively. The direct optical studies of Cl 2p/HCl by Hayes and Brown [10] and by Ninomiya et al. [11] give absolute cross-sections typically 35% and 22–50% higher, respectively, than those of the present work shown in Fig. 4. There are significant differences in the reported energy scales of all three studies. However, it should be noted that the energy scale for the dipole (e,e) spectrum (Fig. 4) is based on the very accurate valence shell calibration relative to the He 2$^1\text{P}$ excitation [18]. The assignments shown on Figs. 5 and 6 are from Refs. [27,28], respectively.
Digital values of the experimental data obtained using dipole (e,e) spectroscopy over the complete energy ranges covered at both low (1.0 eV FWHM) and high (0.05 eV FWHM) resolution for HCl, HBr and HI (together with the values for all other atoms and molecules studied in our laboratory) can be found at: ftp://ftp.chem.ubc.ca/pub/cooper.

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References