HIGH RESOLUTION PHOTOABSORPTION SPECTROSCOPY OF CH_3Br, CH_3I AND THEIR ISOTOPOMERS.

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In the latest issue of the BESSY Jahresbericht [1] we reported on the investigation and testing of the newly commissioned 3m-NIM monochromator on the 3m-NIM-2 beamline at BESSY II. The aim of this preparative work was to find out the performance of this instrument which has to provide us high resolution photoabsorption spectra.

The present work has been achieved with the same experimental setup, i.e. (i) a 30 cm long absorption cell mounted on the monochromator equipped (ii) with a 2 400 l/mm Pt-grating. Most of the time, the entrance and exit slits were maintained at 25µm and 40 µm. The absorbance [$\log_{10}$ (I_0/I)] is obtained by scanning successively the absorption spectrum of the considered compound and the transmission spectrum of the monochromator.

First, the spectra of CH_3Br and CD_3Br have been measured between 5-25 eV photon energy, at a "coarse" level. A detailed Rydberg series analysis has been performed. Several series, corresponding to 2e→ns and np transitions, have been allocated. For the first time, two np-type transitions, i.e. transitions to npa_1 and npe orbitals have been assigned on the basis of characteristic quantum defects. Furthermore, fairly extended nd- and nf-type transitions account for many lines on the high energy side of the spectrum. All these Rydberg transitions are observed twice, converging to the two spin-orbit split ^2E ionic states.

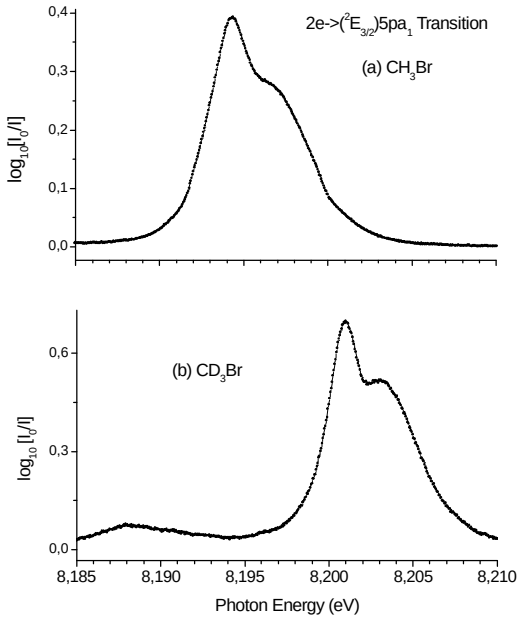

Fig. 1: 2e→($^2E_{3/2}$) $5pa_1$ line profiles in CH_3Br and CD_3Br

In the "coarse" photoabsorption spectrum several lines showed presumed structure on a meV scale. Therefore, short spectral regions of interest were scanned with 50 µeV intervals. Fig.1 shows a typical example of the observed line profile corresponding to the 2e→($^2E_{3/2}$) $5pa_1$ Rydberg transition in both CH_3Br and CD_3Br. Such a manifold of these lines is highlighted for the first time. Remarkably, the same type of manifold has been observed for the 2e→($^2E_{3/2}$) $5pa_1$ line in CD_3Br, whereas this feature is absent in CH_3Br. The structures are separated by 2.0-4.0 meV (16-32 cm^{-1}). The lines corresponding to 2e→ ($^2E_{3/2}$/$^2E_{1/2}$) npe Rydberg transitions don't show any of these structures at the same scale. On the other hand, in the same way, the nd- and nf-type

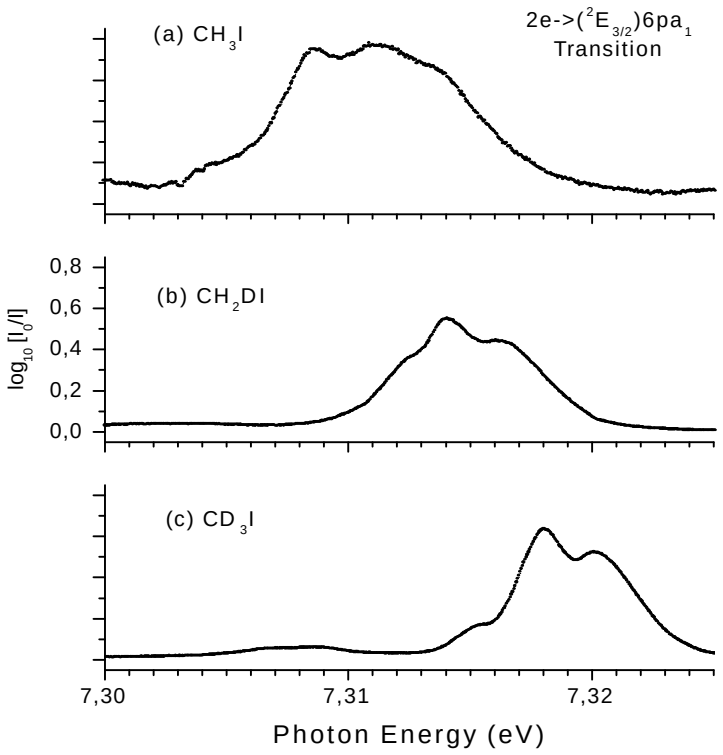

Fig. 2 : 2e→($^2E_{3/2}$) 6pa$_1$ line profiles in CH_3I, CH_2DI and CD_3I.

transitions show up fine structures with energy differences ranging from 4.0-12.0 meV (32-96 cm^{-1}).

The photoabsorption spectrum of CH_3I, and of its two isotopomers CH_2DI and CD_3I, has been recorded under the same experimental conditions between 5.0-10.5 eV photon energy in a "coarse" scan and several fine scans. This enabled us to resolve Rydberg transitions characterized by high principal quantum numbers, i.e. n≥30. Typical results of the fine scans are displayed in fig.2. where also, for the first time, the manifold of the 2e→($^2E_{3/2}$) 6pa$_1$ line is highlighted for the three isotopomers. Well resolved structures are observed at 1.6-3.2 meV (13-25 cm^{-1}) energy intervals. It has further to be noticed that the heaviest isotopomer exhibits the narrowest line profile and the line shape drastically changes with the number of isotopic substituants.

The magnitude of the splittings observed in the 2e→npa$_1$ lines is smaller by one order than those measured e.g. in the 2e→nd lines observed in the spectrum of CH_3I in this work. In this latter case the fine structure was ascribed to the perturbation of the Rydberg electron by the quadrupole moment of the ^2E ionic core [2]. The test of this hypothesis is in progress. On the other hand, through the symmetry lowering from C_{3v} to C_s upon excitation of a 2e electron to a npa$_1$ orbital degeneracies have to be removed.

Acknowledgment.

R.L. gratefully acknowledges the Bundes Ministerium für Forchung und Technologie for a grant. R.L. and B.L. wish to thank the Communauté Française de Belgique for the "Actions de Recherche Concertée" (A.R.C.) contract.

References.

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