

ABSORPTION AND IONIZATION SPECTROSCOPY OF METHYL HALIDES AND DEUTERATED METHYL HALIDES BETWEEN 6 AND 12 eV.

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The autoionization of Rydberg series in the valence shell range has been shown to be involved in the dissociative photoionization of CH₃F, CH₃Cl, CH₃Br and CH₃I. To investigate such processes in more detail, we recorded the absorption spectra and some mass-resolved photoionization curves for CH₃Cl, CH₃Br and CH₃I as well as for their perdeuterated analogues in the 6-12 eV range. This study is in the line with a previous investigation performed at higher energy [1].

This work was performed on the 1.5m-NIM-1 beamline at the synchrotron radiation facility BESSY. A modified McPherson 1m normal incidence monochromator was used [2]. The light is dispersed by a 1200 l/mm Platinum grating. For the photoabsorption experiments, the sample was expanded in an absorption cell at controlled pressure. The entrance and exit slits were adjusted at 100µm. For the photoionization studies, the absorption cell was replaced by an ionization chamber followed by a quadrupole mass spectrometer.

As an example, the cases of CH₃Cl and CD₃Cl will be discussed now in more detail. The photoabsorption curves of CH₃Cl and CD₃Cl in the 6-12 photon energy range are displayed in Figures 1 and 2, respectively. Figure 3 shows the CH₃⁺ photoionization curve at low energy corresponding to the ion pair formation process:

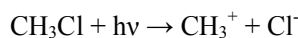
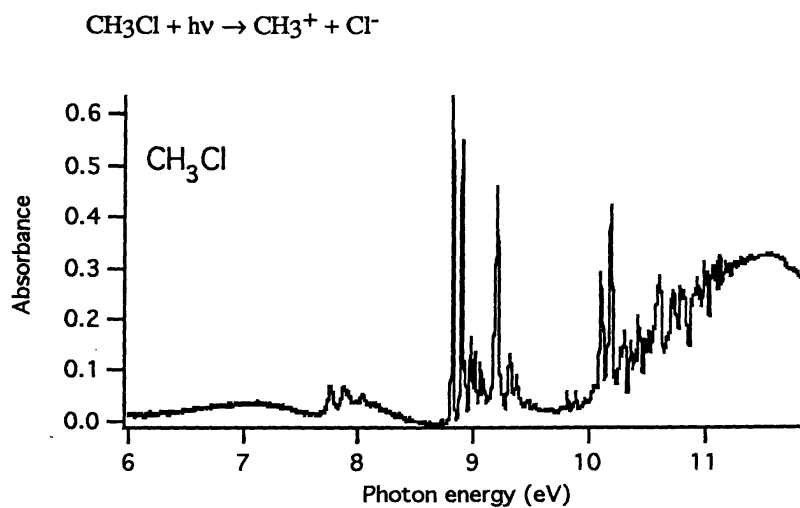


Figure 1. Absorption spectrum of CH₃Cl in the 6-12 eV range



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Figure 2. Absorption spectrum of CD_3Cl in the 6-12 eV range

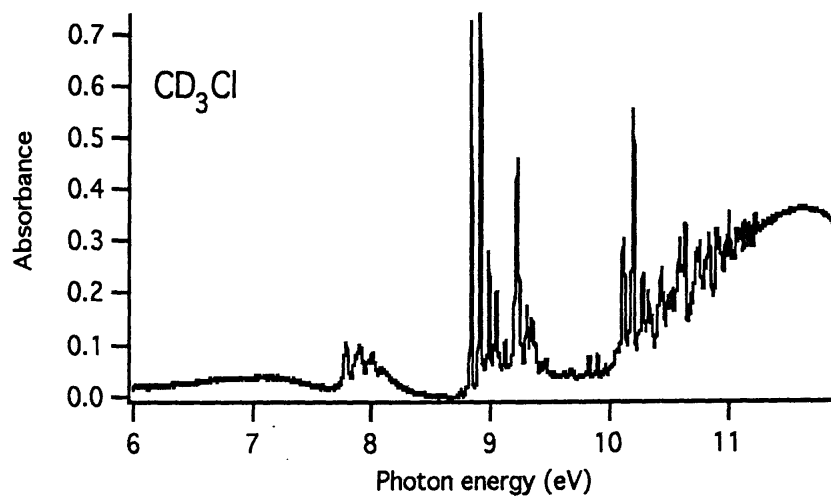
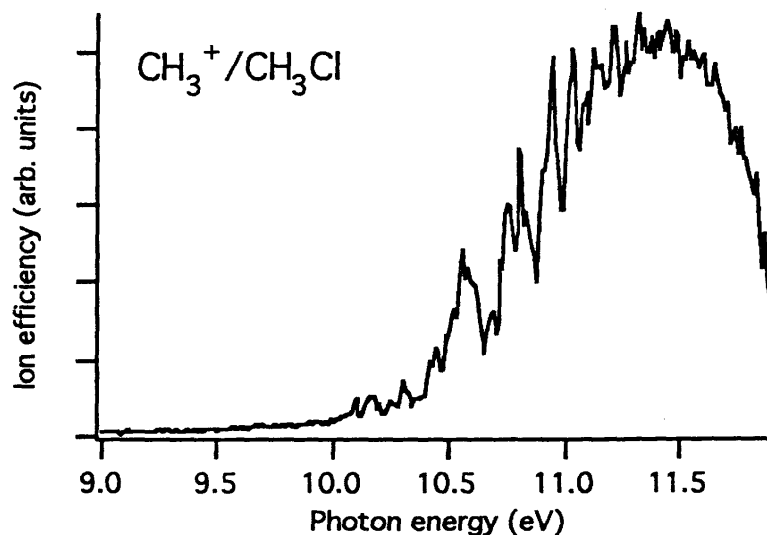


Figure 3. Low-energy part of the photoionization curve of CH_3^+ from CH_3Cl measured with a lithium fluoride window.



In the photon energy range investigated, the Rydberg series converging to the spin-orbit doublet ($^2E_{3/2}$ and $^2E_{1/2}$) of CH_3Cl^+ [3] corresponding to the $1e^43a_1^2e^3$ configuration are observed. The $n=3$ to $n \geq 10$ members of the $n's'a_1$, $n'p'a_1$ and $n'p'e$ series have been identified (Table 1) and their vibrational frequencies have been deduced. The isotope ratios observed for these frequencies are very close to those of the neutral molecule.

Table 1. Summary of the Rydberg series observed in the absorption spectra of CH_3Cl and CD_3Cl in the 6-12 eV range.

Series	ionic state	n range observed	quantum defect	n range observed	quantum defect
			CH_3Cl		CD_3Cl
's' a ₁	$^2\text{E}_{3/2}$	3-13	1.04	3-13	1.04
's' a ₁	$^2\text{E}_{1/2}$	3-11	1.02	3-13	1.01
'p' a ₁	$^2\text{E}_{3/2}$	3-7	0.44	3-8	0.45
'p' a ₁	$^2\text{E}_{1/2}$	3-8	0.40	3-11	0.42
'p' e	$^2\text{E}_{3/2}$	3-12	0.66	3-15	0.66
'p' e	$^2\text{E}_{1/2}$	3-9	0.63	3-17	0.64

Acknowledgements

R.L. and B.L. gratefully acknowledge the financial support of the European Community under Contract N°:ERBFMGECT 952031

References

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