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The OCS Molecule. The Photoabsorption Spectrum. The Threshold Photoelectron and CIS-photoelectron spectra.

R. Locht

Département de Chimie Générale et de Chimie Physique, Université de Liege, Institut de Chimie, Bât. B6, Sart-Tilman par B-4000 Liège 1, Belgium.

K. Hottmann and H. Baumgärtel.

Institut für Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustrasse 3, 14195 Berlin, Germany.

The present work is in keeping with our thorough and systematic study of the dissociative ionization of simple molecules. Photoabsorption, photoelectron and threshold photoelectron spectra of these systems are investigated to help and sustain the interpretation of dissociative ionization results. With this aim CIS(Constant Ion State)-photoelectron spectra are also used. In line with this work we started to investigate the OCS molecule. Preliminary results on SO_2 and C_2H_2 /1/ and on CS_2 /2/ have already been presented in previous reports.

The threshold- and CIS-photoelectron spectra specially show (i) how autoionization populates ionic states outside the Franck-Condon region and (ii) the ionization cross section of the different vibronic states as a function of the excitation energy. This latter information could give a deeper insight in the dissociation dynamics when (pre)dissociative ionic states are involved.

The photoelectron spectra presented in this report were obtained by using a double hemispherical electron energy analyzer /3/ mounted on the 3m-NIM-l monochromator. The entrance and exit slits were adjusted between 50 μ and 100 μ. The energy resolution of the electron energy analyzer is 6.5 meV in the threshold photoelectron spectroscopic mode. This resolution is 16 meV in the He-I photoelectron spectrum as measured on the $^2P_{3/2}$ peak of Ar^+ The photon and electron energy scale calibration is provided by the Ar photoabsorption spectrum and the Ar, Kr and Xe ionization energies respectively.

The photoabsorption spectrum, measured with 100μ slits, observed below and above the ionization and dissociation energy range of OCS, is shown in fig. 1a between 11-19 eV photon energy. It exhibits an abundant fine structure below the first ionization limit and above this energy the fine structure is closely related to the photoionization yield curve of OCS^+ reported earlier /4/. Though already investigated earlier /4/, this autoionization structure being better resolved in this work, is presently reexamined.

In fig. 1b and 1C the threshold photoelectron spectrum and the He(I)- photoelectron spectrum of OCS are shown between 11-19 eV photon energy. The latter spectrum is in good agreement with that reported by Wang et al. /5/, though better resolution is obtained in this work. To a large extent the former spectrum reproduces the absorption spectrum.

CIS-photoelectron spectra for about 100 vibronic states of OCS^+ have been recorded between 11-19 eV photon energy. Typical CIS-photoelectron spectra are shown in fig.2 corresponding to the most probable transitions observed in the HeI-photoelectron spectrum of the $X^2\Pi$, $A^2\Pi$, $B^2\Sigma^+$ and $C^2\Sigma^+$ states. The vibronic ground state mainly contains the contributions from autoionization of Rydberg states converging to the $A^2\Pi$ and the $B^2\Sigma^+$. At the vertical ionization energy of $OCS^+(A^2\Pi)$ state almost the Rydberg states converging to the $B^2\Sigma^+$ state contribute significantly. Up from 13.5 eV to 19 eV, the $X^2\Pi$, $A^2\Pi$, $B^2\Sigma^+$, and $C^2\Sigma^+$ states are involved in the dissociative ionization of OCS giving rise to the S^+, CS^+ and CO^+ fragment ions.

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Fig. 1: *(a) The Photoabsorption spectrum, (b) the Threshold photoelectron spectrum and the He(I)-photoelectron spectrum of OCS.*

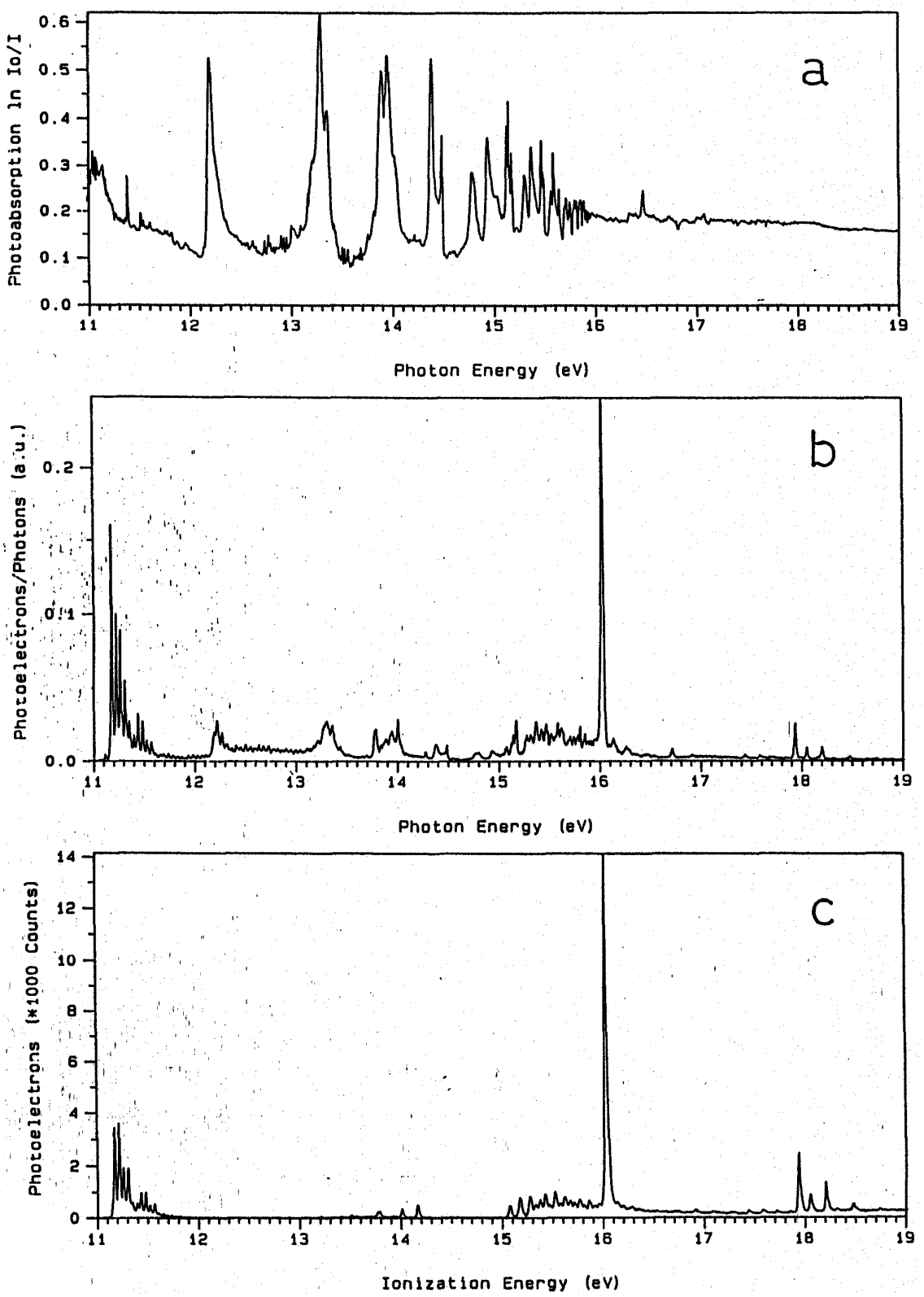

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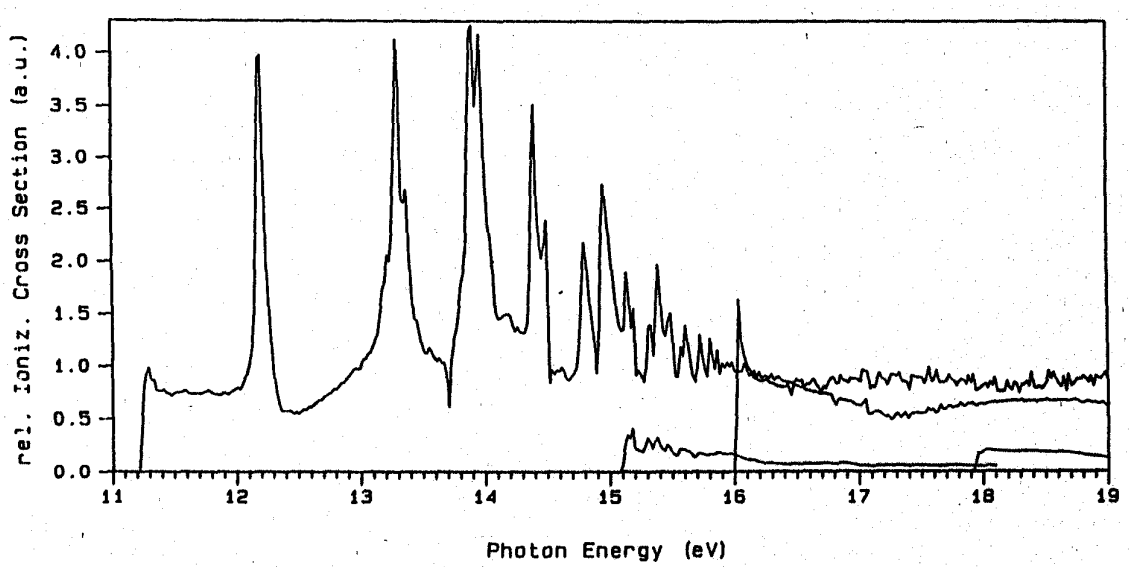
Fig.2. *Typical CIS-photoelectron spectra corresponding to the most probable transition to $X^2\Pi$, $A^2\Pi$, $B^2\Sigma^+$ and the $C^2\Sigma^+$ in OCS.*



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