The Absorption Spectrum and the Threshold- and CIS-photoelectron spectra of CS_2.

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In the line with the investigation of the ionization and dissociation of small molecular systems, such as N_2O and CO_2 /1/, SO_2 and C_2H_2 /2/, the study of the ionization of CS_2 has been started.

The threshold- and CIS(Constant Ion State)-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-1 monochromator. The energy resolution of the electron analyser is 20-30 meV in the "threshold photoelectron spectroscopic"-mode whereas it is 50-100 meV in the "fixed-wavelength"-photoelectron spectroscopic-mode, depending on the experimental conditions of the monochromator and the electron analyser.

The absorption spectrum of CS_2, as observed between 9.9-17.9 eV photon energy, is displayed in fig.1. It exhibits an abundant autoionization fine structure. This observation is closely related to photoionization mass spectrometric work reported earlier /4/. This autoionization structure, already investigated /5/, is presently reexamined.

In the same figure the threshold photoelectron spectrum of CS_2 is shown between 9.9-17.9 eV photon energy. To a large extent this spectrum reproduces the absorption spectrum. Series of sharp resonances, as well as broad peaks exhibiting a slightly resolved fine structure, are present in this spectrum. Few of these structures are difficult to indentify in the absorption spectrum. For this purpose, a low resolution HeI-simulated photoelectron spectrum of CS_2 is shown in fig.1. Excepting the $A^2\Pi_u$ state at about 13 eV, showing an extended vibrational structure, the $X^2\Pi_g$, $B^2\Sigma_u$ and the $C^2\Sigma_g$ essentially show the transition to v=0, in agreement with previous measurements /6/. Both satellite peaks, at about 14.1 eV and 17.0 eV successively, are also observed in the present work.

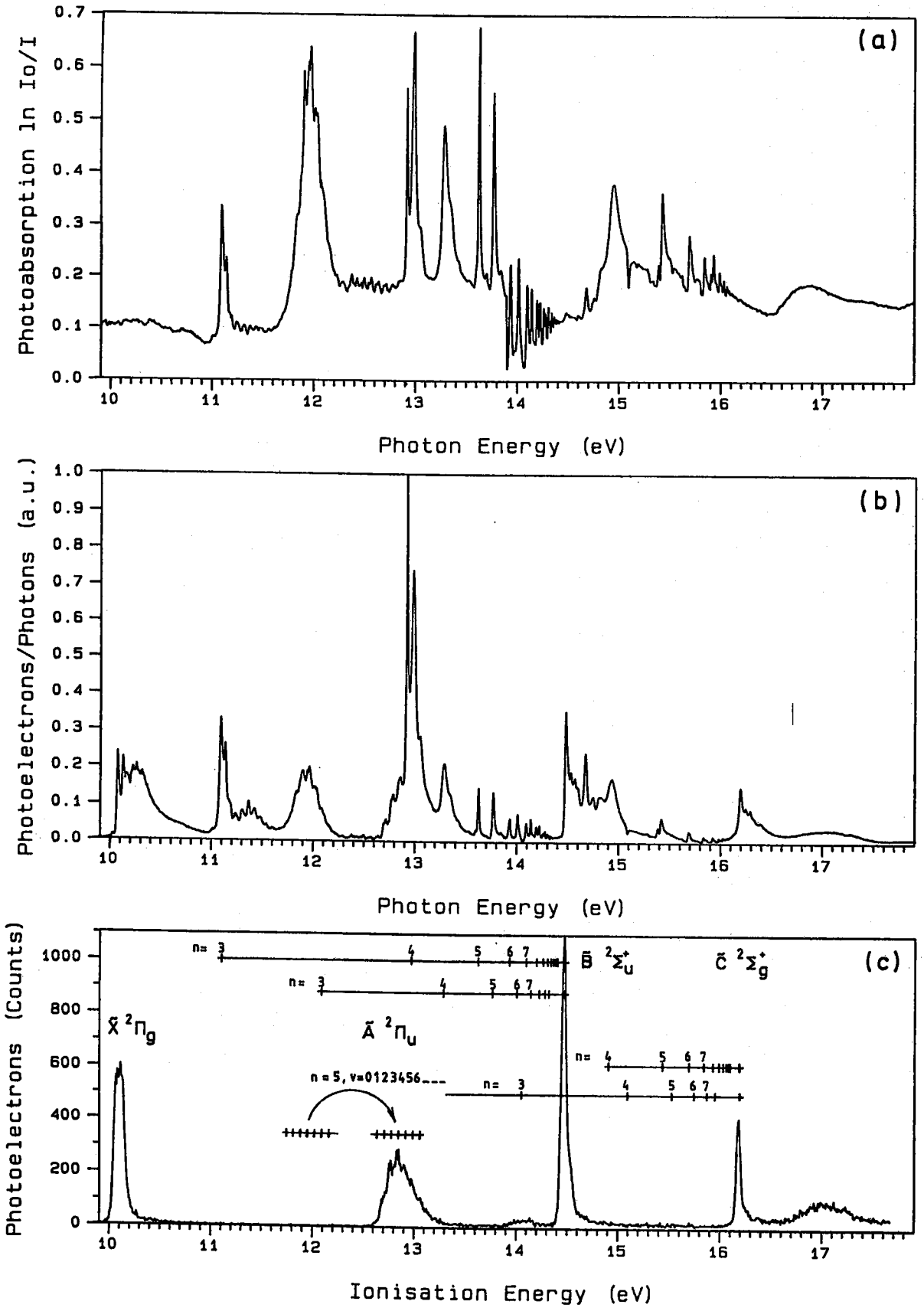

Fig.1. (a) Absorption spectrum, (b) Threshold-photoelectron spectrum and (c) Low resolution HeI-simulated photoelectron spectrum of CS_2. A tentative assignment of the Rydberg series observed in (a) and (b) is inserted in (c).

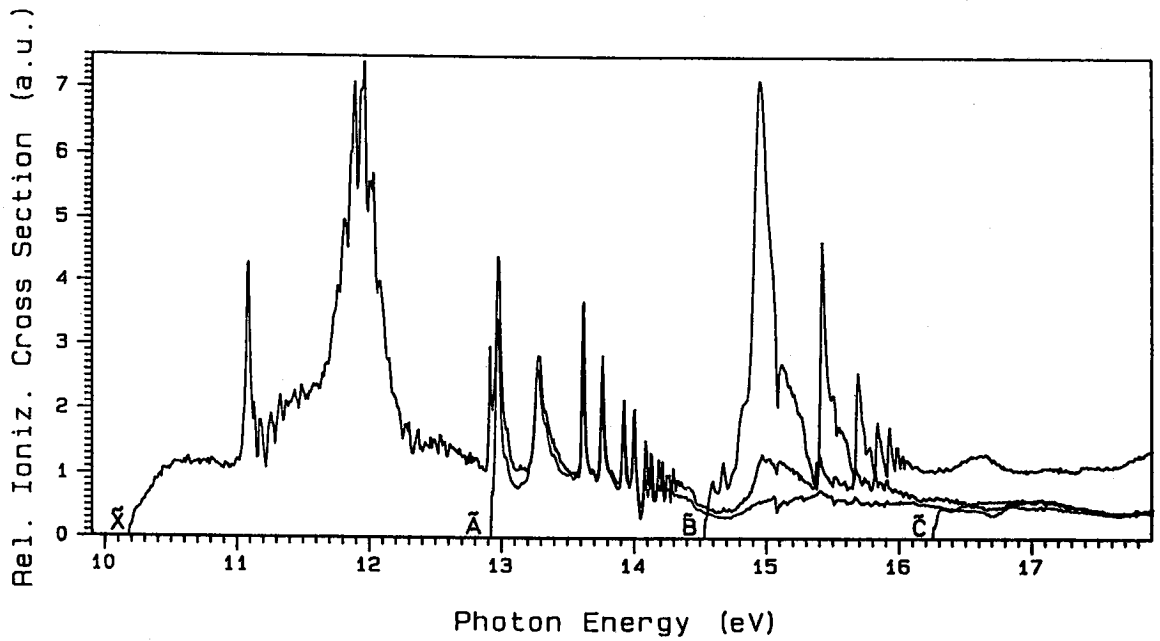

Fig.2. Typical CIS-photoelectron spectra corresponding to the most probable transition to $X\,^2\Pi_g$, $A\,^2\Pi_u$, $B\,^2\Sigma_u^+$ and the $C\,^2\Sigma_g^+$.

CIS-photoelectron spectra for about 70 vibronic states of CS_2^+ have been recorded between 10.080 and 20.5 eV photon energy. Typical CIS -photoelectron spectra are shown in fig.2. corresponding to the most probable transitions observed in the HeI-simulated photoelectron spectrum of the $X\,^2\Pi_g$, $A\,^2\Pi_u$, $B\,^2\Sigma_u^+$ and $C\,^2\Sigma_g^+$ states. The vibronic ground state mainly contains the contributions from autoionization of Rydberg states converging to $B\,^2\Sigma_u^+$. Smaler contributions from Rydberg series converging to the $C\,^2\Sigma_g^+$ are detected. At the vertical ionization energy of $CS_2^+(A\,^2\Pi_u)$ state almost the Rydberg states converging to the $C\,^2\Sigma_g^+$ state contribute significantly. Up from 14.5 eV to 20 eV, the $B\,^2\Sigma_u^+$, $C\,^2\Sigma_g^+$, ... states are involved in the dissociative ionization of CS_2 giving rise to the S^+, CS^+ and S_2^+ ions. The $B\,^2\Sigma_u^+$ state contains a major contribution of Rydberg states converging to the $C\,^2\Sigma_g^+$ state.

References.

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