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THE DISSOCIATIVE IONIZATION OF CH_3F. A MASS SPECTROMETRIC PHOTOIONIZATION STUDY USING SYNCHROTRON RADIATION.

R.LOCHT* , E.RUHL[+] , J.MOMIGNY* , H.BAUMGARTEL[+]

**Département de Chimie Générale et de Chimie Physique , Institut de Chimie, Sart-Tilman par B-4000 Liège 1,Belgium.*

[+]*Institut fur Physikalische Chemie, Freie Universitat Berlin, Takustrasse 3, D-1000 Berlin 33, West Germany.*

The dissociative electroionization and fixed wavelength photoioriization of CH_3F has recently been investigated (1). New processes for the production of CH_2^+ and CH_3^+ , as well as the importance of autoionization were evidenced. This molecular system has been revisited by using mass spectrometric photoionisation.

The dissociative ionization work uses mono-chromatized synchrotron radiation from the Berlin storage ring BESSY. The quadrupole mass filter is equiped with a photoion source and an ion energy-analyzing retarding lens. This setup allowed to measure KE distributions at any desired wavelength and to record ionization efficiency curves for energy- selected photoions. The CH_3^+ producing dissociation channel has been examined upto 25 eV photon energy. The ionization efficiency curves, recorded at three different retarding potential settings, are shown in Fig.1. The KE-vs-AE diagram of CH_3^+ is shown in Fig.2. Three onsets are measured, i.e. at 12.45 eV corresponding to the ion pair process, and at 14.50 eV and 16.10 eV, both corresponding to dissociatve ionization processes.

The latter onset is produced by the decomposition of the CH_3F ($\tilde{A}^2 A_1 + \tilde{B}^2E$) state, confirming PIPECO measurements (2). The former onset missed by an earlier photoionization study (3) corresponds to the lowest dissociation limit:

$$CH_3F+h\nu \rightarrow CH_3^+ (\tilde{X}^1 A'_1)+F(^2P_u)+e^-$$

for which the thermodynamic onset is calculated at (14.6 ± 0.3) eV. This dissociation continuum is populated by dissociative autoionization, producing CH ions distributed from 0-0.7 eV translational energy (as shown by straight line 2 in Fig.2). This figure also shows that the excess energy with respect to the dissociation limit is entirely converted into KE of the fragments. For the CH_2^+ and CH_2F^+ ions, the ionization efficiency is only measured without retarding field. Several onsets are measured and interpreted. Dissociative autoionization has to plays an important role.

FIG.1: *CH_3^+ /CH_3F PI- efficiency curves at Retarding potential settings a) none, b) 0.2 V, and c) 1.2 V.*

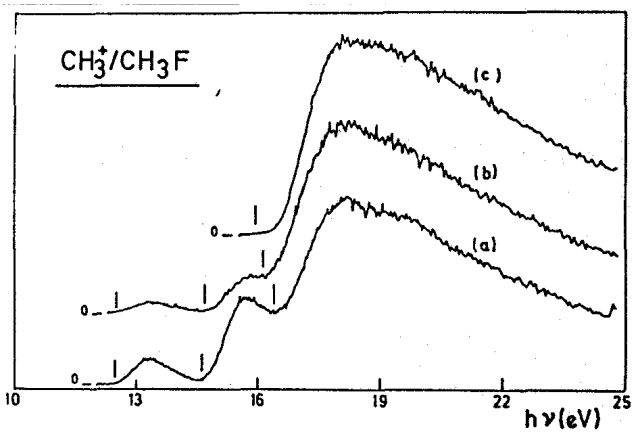

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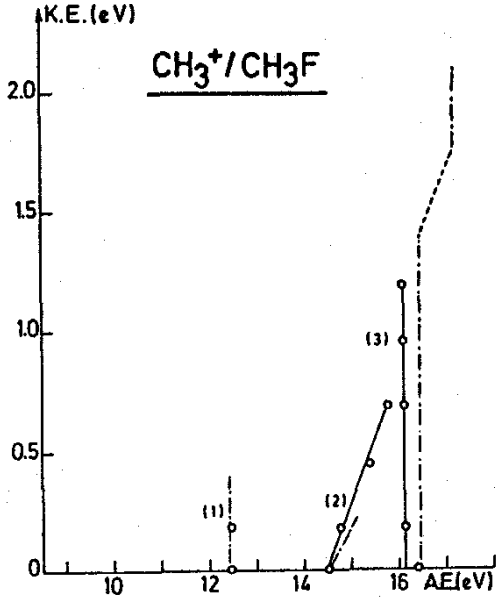
FIG.2: *KE-vs-Appearance Energy Diagram for CH_3^+/CH_3F*



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