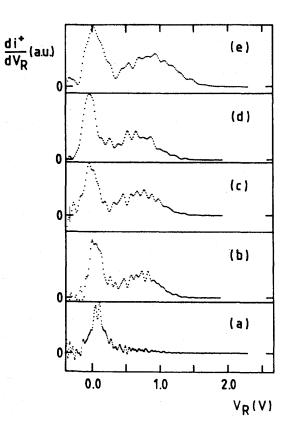
The Dissociative Photoionization of CH₃F.

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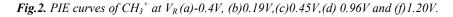
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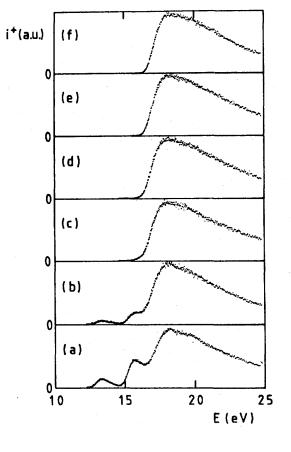
Using synchrotron radiation, dispersed by a 1m-NIM monochromator, the production of CH_2^+ , CH_3^+ and CH_2F^+ from CH_3F has been investigated over 10-25 eV photon energy range. The fragment ions are energy-analyzed by a retarding field and mass selected by a quadrupole filter. The photoabsorption curve of CH_3F has been recorded to enlighten the discussion. For the CH_3^+ ion kinetic energy spectra, as observed at different photon energies, are shown in fig.1. The ionization efficiency curves recorded at different retarding potential settings are displayed in fig.2. The resulting kinetic energy (KE)-vs-appearance energy (AE) diagram is shown in fig.3.

Fig.1. KE-spectra of CH_3^+ at (a)16.4eV,(b)17.3eV,(c)18.9eV(d)20.2eV and (e)21.2eV.



Several processes are observed, i.e. (1) $(12.45 \pm 0.06)eV$, (2) $(14.50 \pm 0.06)eV$ and (3) $(16.10 \pm 0.06)eV$ respectively. In agreement with earlier work /1-3/, process (1) and (3) are ascribed to dissociative autoionization





$$CH_{3}F \xrightarrow{h_{\nu}} CH_{3}F + e \rightarrow CH_{3}(X^{1}A'_{1}) + F(S)_{g}$$
(1)

and direct dissociative ionization

$$CH_{3+} \xrightarrow{h\nu} CH_{3} \xrightarrow{F} (\mathring{X} + \mathring{B}) + e \xrightarrow{F} CH_{3} \xrightarrow{F} (\mathring{X}^{1}A'_{1}, v) + F(\overset{2}{P}_{u})$$
(3)

where CH_3^+ carries vibrational and translational energy.

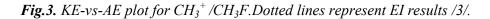
Process (2), not detected earlier by photoionization, is interpreted by dissociative autoionization, i.e.

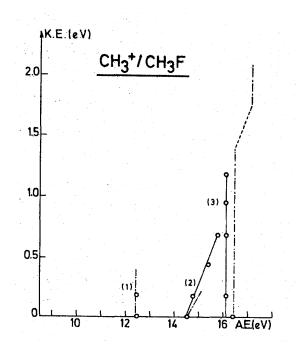
$$CH_{3}F \xrightarrow{h_{v}} CH_{3}F^{*} + e \rightarrow CH_{3}^{+}(\overset{\circ}{X}^{1}A'_{1}, v=0) + F(\overset{2}{P}_{u})$$

where the excess energy is entirely converted into kinetic energy.

The CH_2^+ ion, being of low intensity, has been recorded without ion energy analysis.

Three well defined onsets are measured at (13.90 ± 0.06) eV, (14.63 ± 0.04) eV and (22.36 ± 0.06) eV. As for CH₃⁺, dissociative autoionization is an important process. Beside direct ionization, the same applies to the formation of CH₂F⁺.





References

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