

four alternatives are analyzed in terms of their convenience, experimental limitations and the statistical and interpretative confidence which one requires in the decay parameters obtained from the deconvolution of the experimental data.

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W8

Surface Spectroscopy and Photochemistry of Adsorbed Molecules

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From many experiments there is evidence that both spectroscopy and photochemistry can undergo drastic changes when the molecules under investigation are adsorbed on the surface of a solid [1]. For instance, the irradiation of carbon monoxide, adsorbed on a tungsten surface, by the light of a mercury resonance lamp leads to the formation of photoproducts like C_2O , CO_2 , C_2O_2 and C_3O_2 . Since these reactions, according to the law of Einstein, only can proceed if photons are absorbed the absorption threshold for carbon monoxide which in the gas phase is at about 1600 Å has been shifted to longer wavelengths by the interaction with the surface. There is evidence from our previous experiments that the primary step in these photoreactions is the dissociation of CO.

Extending the pathway for chemical reactions by co-adsorption of other gases beside carbon monoxide leads to the formation of more complex compounds. In the case of carbon monoxide and methane formaldehyde has been found to be one of the major products. To ensure the formation at the surface and not in the desorbed gas we developed an absorption spectrometer in which the for-

mation can be followed *in situ*. Another advantage of the spectrometer is the capability of obtaining spectra of adsorbed molecules at coverages down to less than a monolayer. The experimental details have been described elsewhere [2].

To study the formation of formaldehyde CO and CH_4 were adsorbed in equal amounts on a nickel film at 70 K. One half of the surface was irradiated by a Hg-resonance lamp and the spectrum of the photoproduct was measured as the difference in absorption between the irradiated and non-irradiated part of the surface. For identification this spectrum was compared to that of gaseous HCHO and to the spectrum of HCHO on LiF at 68 K. A very good correlation is obtained if the spectrum of the photoproduct is shifted to lower energies by $\Delta\tilde{\nu} = 770 \text{ cm}^{-1}$.

This bathochromic shift is explained in terms of an electric field perpendicular to the surface. The value for this field is estimated to be $1.25 \times 10^7 \text{ V cm}^{-1}$. In a model calculation the field strength above a surface of 5×5 Ni-atoms is presented.

Making use of this surface field it seems to be possible to perform Stark-spectroscopy measurements on adsorbed molecules without applying an external electric field.

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W9

The Condensed Phase Photochemistry of the Fluoroethylenes

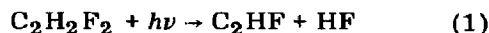
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Recently, attention has been drawn to the use of the matrix-isolation technique in an effort to gain a better understanding of primary photophysical and photochemical processes [1 - 4]. In particular, the roles played by specific electronic states in the generation of specific reaction products. The application of condensed phase photolysis with monochromatic light sources has proven to be an extremely useful technique in characterizing the relative importance of atom

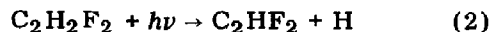
versus molecular elimination processes [1, 3], as well as providing valuable information concerning photophysical processes, *i.e.* intersystem crossing (ISC) and internal conversion (IC).

The vacuum-ultraviolet (VUV) photochemistry of the various isomeric difluoroethylenes and fluoroethylene has been performed in Ar, N₂, Kr, CO, and CO-doped argon matrices between 8 and 24 K. Selective excitation at various frequencies of the broad $\pi^* \leftarrow \pi$ absorptions was performed with N and Br resonance line sources and $\sigma^* \leftarrow \sigma$ and/or Rydberg absorptions were excited with the 1216 Å H-resonance line.

As major processes, all three difluoroethylenes photodissociate into HF and fluoroacetylene,

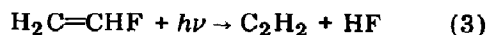


via molecular elimination, and all give rise to the same difluorovinyl free radical,

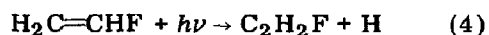


presumably via atomic detachment. No acetylene or difluoroacetylene was observed. Isomerization of the three difluoroacetylenes into each other was observed as minor processes. The results of experiments conducted in CO matrices, wherein almost total quenching of the atomic detachment process and normal occurrence of molecular elimination were observed, strongly suggest that the former occurs via intersystem crossing (ISC) and the latter via internal conversion (IC).

In the case of fluoroethylene, the major elementary processes which occur as a result of photoexcitation are:



and



where again (3) is molecular elimination and (4) a radical producing process. Photoexcitation with the Br and H resonance sources also produces fluoroacetylene via $\text{H}_2\text{C}=\text{CHF} + h\nu \rightarrow \text{C}_2\text{HF} + (\text{HH})$ (5) to a very small extent. Based on relative infrared intensities (3) \cong (4) \gg (5) at all the exciting frequencies. The results of the concurrent studies involving the difluoroethylenes suggest that (3) and (4) probably

occur via internal conversion and intersystem crossing, respectively.

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W10

Wavelength Dependence of Alkyl Iodide Photolysis: Secondary Photolysis of Alkyl Radicals

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The products of the photolysis of alkyl iodides in rare gas matrices at liquid helium temperature, as revealed by electron spin resonance (ESR) spectroscopy, are often too numerous to be explained by simple dissociation of the carbon-iodine bond. The most frequently observed additional products are H atoms and CH₃ radicals. Studies of alkyl iodide photolysis as a function of photon energy have shown that for $\gamma > 2800$ Å only the C-I bond dissociation product is observed, but for $\gamma < 2500$ Å H atoms and CH₃ radicals are also formed.

The results for the photolysis of n-butyl iodide at 2460 Å including the relative growth of the various products as a function of photolysis time are shown in Fig. 1. The n-butyl signal increases linearly and the H atom signal increases quadratically with photolysis time. The weak sharp-line CH₃ spectrum, which is superimposed on the four central lines of the n-butyl spectrum also increases supralinearly with photolysis time. These results are consistent with the photolysis mechanism involving secondary photolysis of n-butyl, as shown below,

