Photoelectron Spectroscopy of Transient Species:

A Case Study

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INTRODUCTION

Relating to a short-lived reaction intermediate. It can be defined only in relation to a time scale fixed by the experimental conditions and limitation of the technique employed in the detection of the intermediate

- Femtosecond, picosecond or nanosecond resolution
- Pump-probe configuration in which an ultrafast pump pulse initiates the reaction, creates a nonstationary state and is monitored by means of a probe pulse.
- Condensed phase- transient absorption
- Molecules and clusters in the gas phase- LIF and RMI

ALKOXY RADICALS

* CH_3O^-
* CD_3O^-
* $CH_3CH_2O^-$
* $CD_3CD_2O^-$

Methoxy Radical

Ground State electronic configuration:-

$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 1e^4\ 5a_1^2\ 2e^3$

First excited state:-

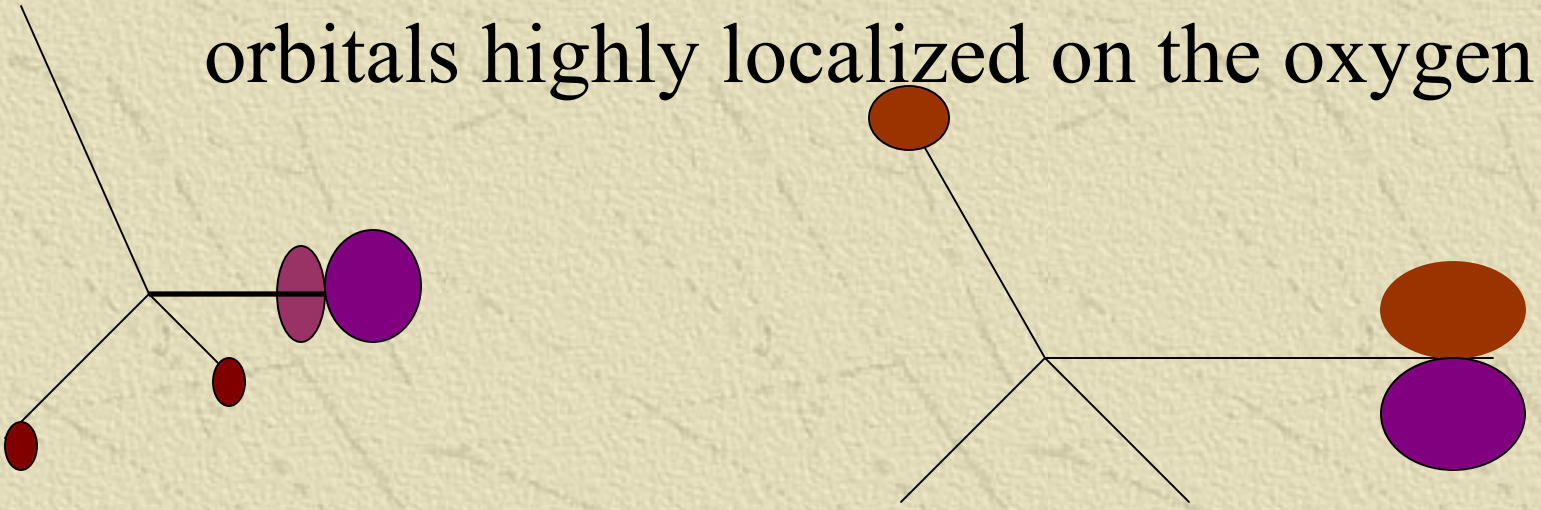
$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 1e^4\ 5a_1\ 2e^4$

Electronic configuration of CH_3O^-:-

$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 1e^4\ 5a_1^2\ 2e^4$

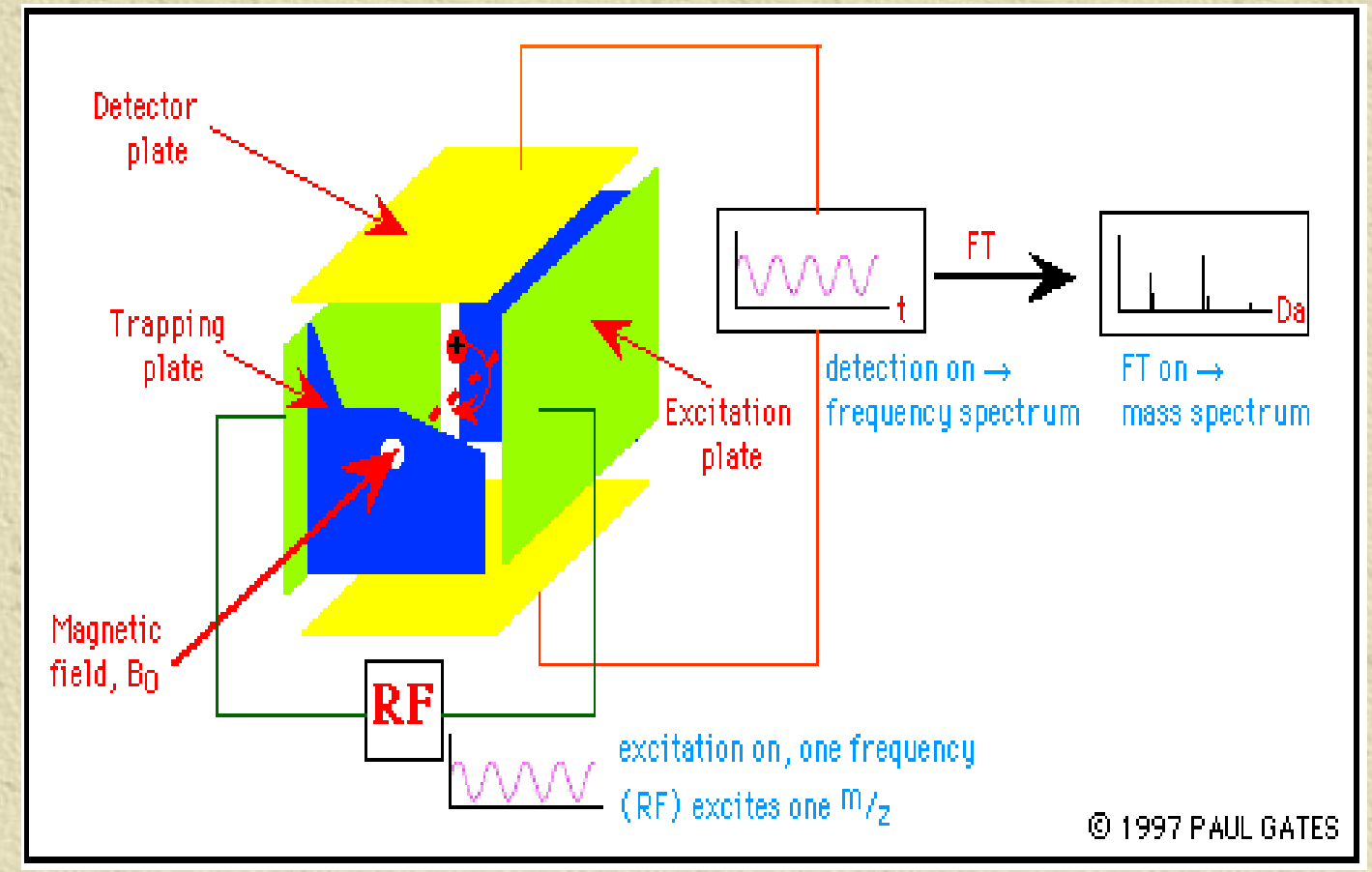
Anion with C_{3v} geometry

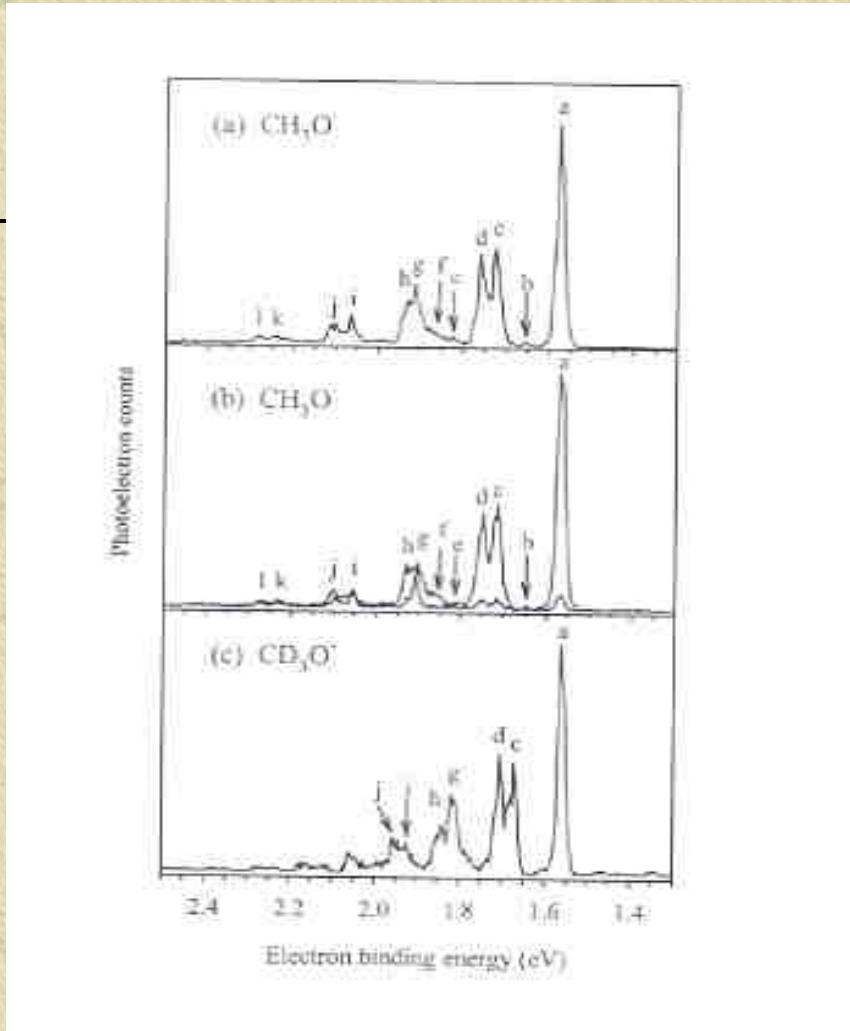
HOMO involve the 2 nonbonding atomic p orbitals highly localized on the oxygen atom



The 2 degenerate HOMO of CH_3O^-

Experimental Setup

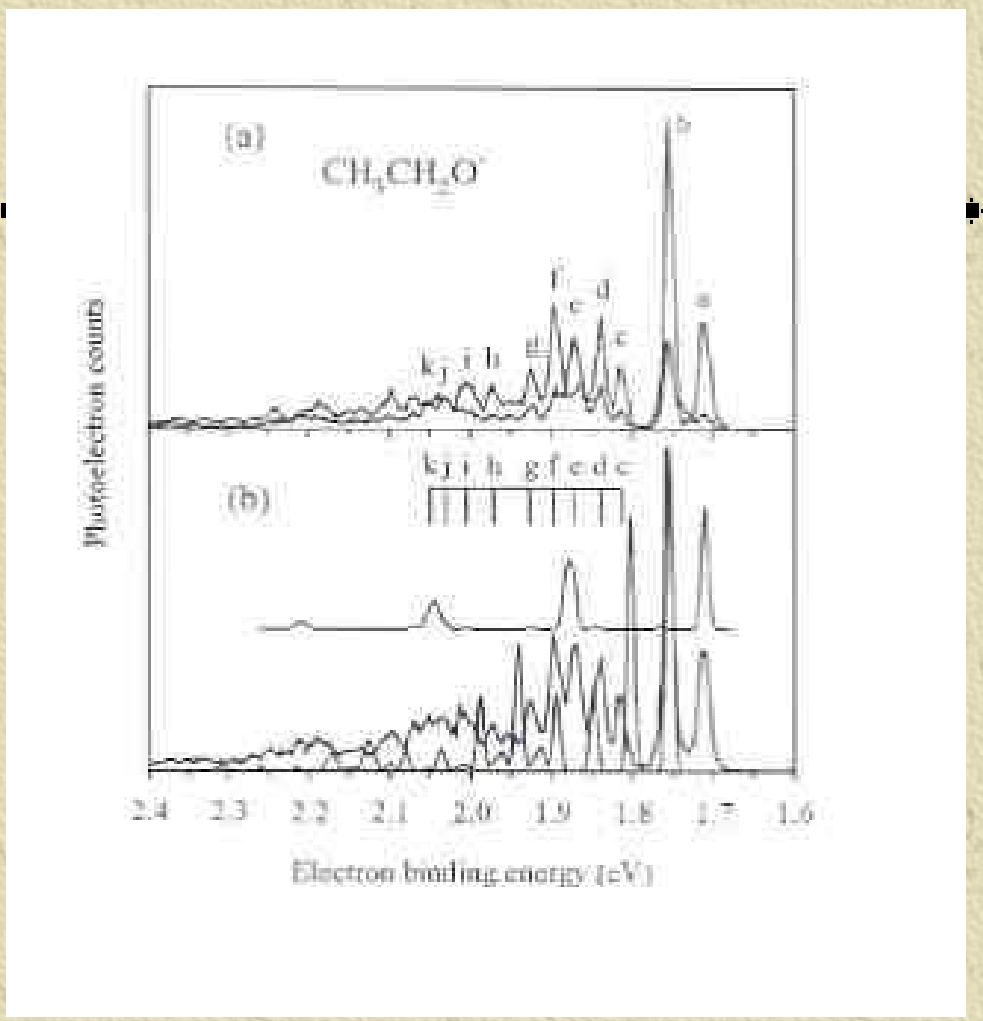




a) Magic angle photoelectron spectrum of CH_3O^- at 200K

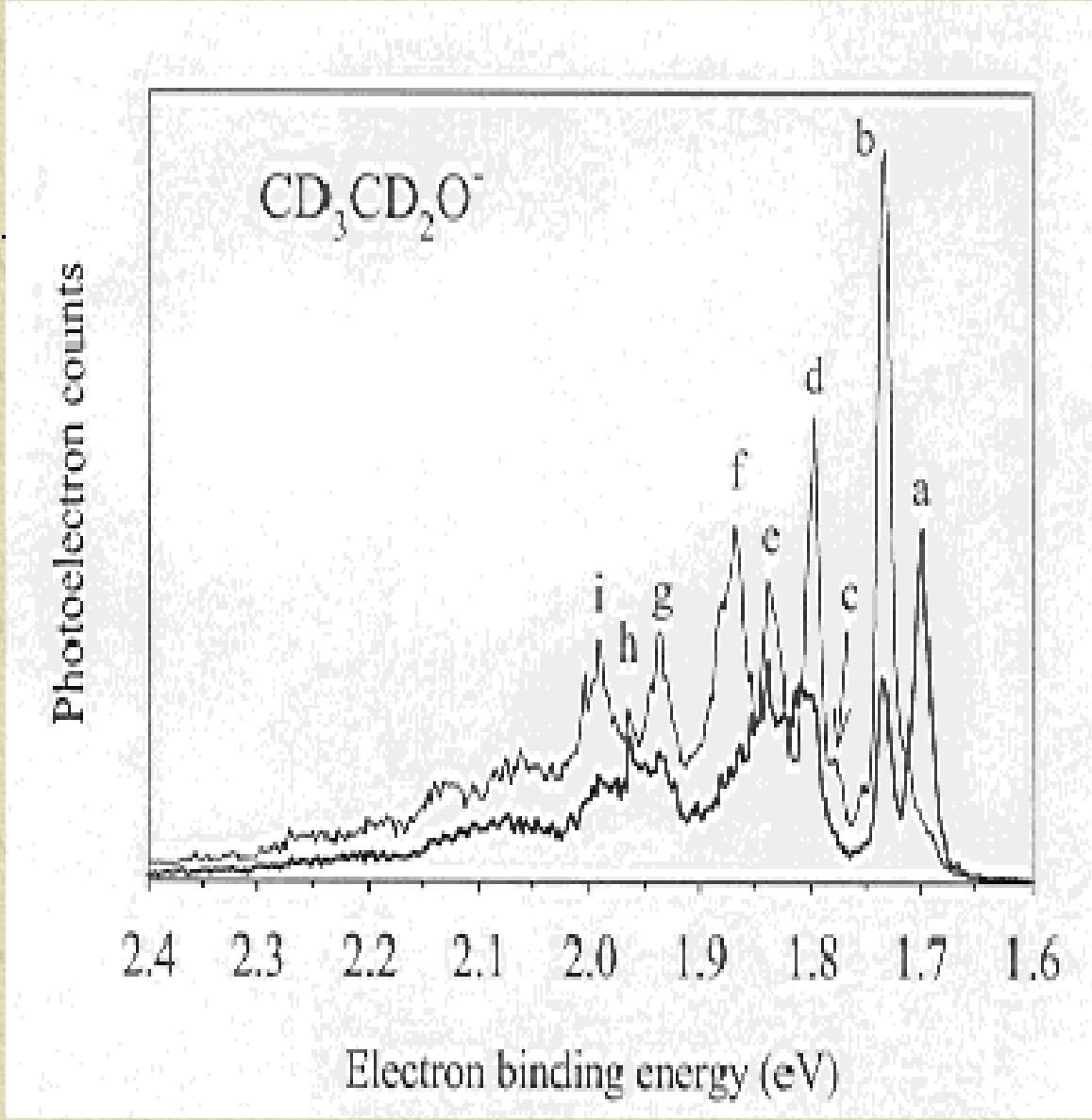
b) Photoelectron spectrum at 90 and 0 degrees of CH_3O^- at 200K

c) Magic angle photoelectron spectrum of CD_3O^- at 200K



a) 200K photoelectron spectrum taken at 90 and 0 degrees

b) 200K magic angle photoelectron spectrum



300K photoelectron spectrum taken at 90 and 0 degrees

Conclusions

- Photoelectron Spectra of alkoxides were presented and analysed.
- Jahn-Teller effects dominate the CH_3O^- and CD_3O^- spectra
- Spectra of $CH_3CH_2O^-$ and $CD_3CD_2O^-$ were also analysed

References

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