

MODULATED EXCITED IR (MEIR) SPECTROSCOPY: DIACETYL IN ETHYLBENZENE

M. Forster and Hs. H Günthard

Laboratory for Physical Chemistry, Swiss Federal Institute of Technology,
 Universitätsstr. 22, CH-8092 Zürich (Switzerland)

MEIR spectroscopy consists in the use of modulated UV/VIS excitation and phase and amplitude analysis of the modulated components of the IR absorption spectrum. By the modulated excitation the concentration of all particles involved in the photoprocess are modulated. Phase sensitive detection allows the reconstruction of the chemical network. A typical example has been reported by Forster et al.¹

In this paper MEIR spectroscopy of diacetyl in ethylbenzene at ambient temperature with excitation in the 350 - 560 nm range will be reported². MEIR spectra in the range 4000 - 3000 cm^{-1} are shown in Fig. 1 together with the results of line shape analysis. Phase and amplitude analysis yielded the Bodediagrams of the type shown in Figs. 2 and 3.

Variations of light flux intensity and concentration showed that the transient MEIR signal at 3498 cm^{-1} (IV) exhibits 2nd order kinetics. The Bodediagrams

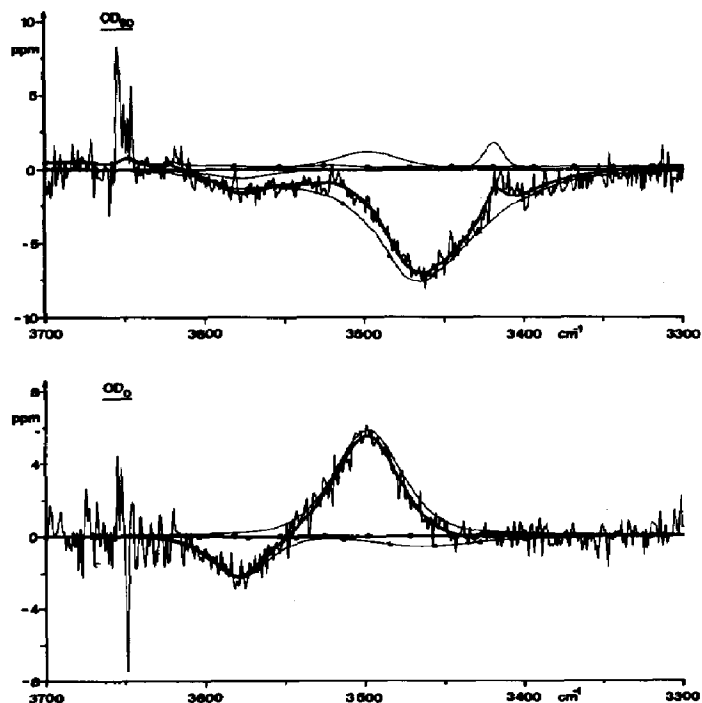


Fig. 1. MEIR spectra of diacetyl in ethylbenzene 10^{-2} mol/dm³, 8 Hz modulation frequency, 0°- and 90°-channel: noisy line, experiment; solid thick line, line shape analysis; thin lines, —○—○— solvent, —△—△— products; 3418 cm^{-1} , educt 2, $\nu(\text{C}=\text{O})$; 3498 cm^{-1} , acetoynradical.

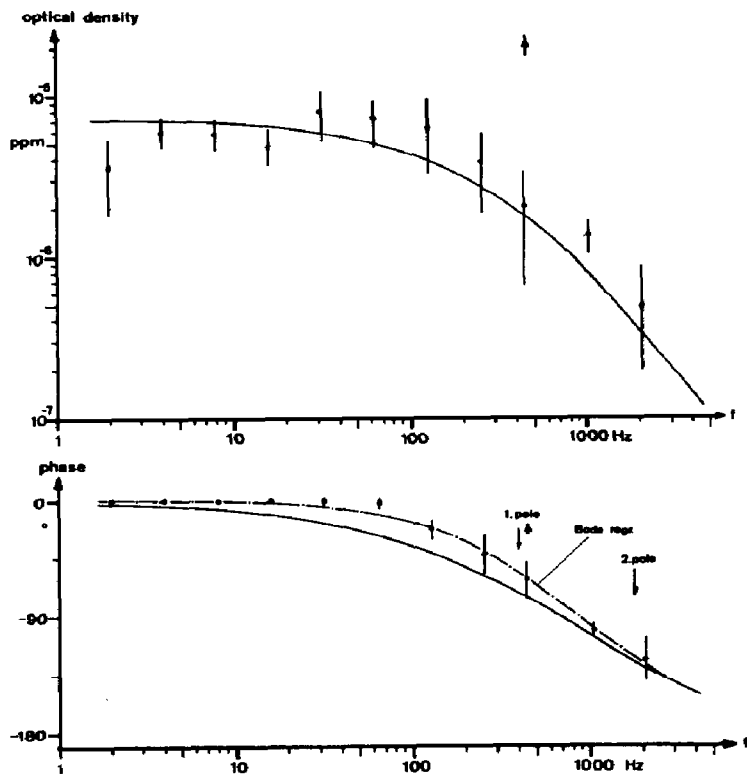


Fig. 2. Bodediagrams of the transientband at 3498 cm^{-1} .

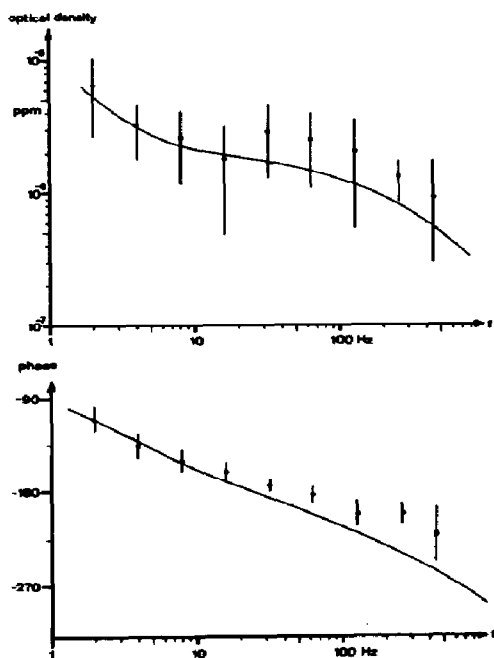


Fig. 3. Bodediagrams of the band at 3580 cm^{-1} , $\nu(\text{OH})_{\text{free}}$ of endproducts.

of the products indicate the transient (IV) ($\tau = 0.4$ ms) to be the precursor of these endproducts and the 2nd pole shown in Fig. 2 indicates that the transient (IV) itself is preceded by another transient (II) ($\tau = 80$ μ s). Since diacetyl yields acetoinradicals upon UV/VIS irradiation in solvents with abstractable H-atoms (via $S_0 \rightarrow S_1 \rightarrow T_1$) the transient (IV) can be assumed to be the acetoinradical (IV) which features an internal hydrogen bond. The precursor (II) of the transient (IV) is the diacetyl triplet T_1 (II).

The Bodediagrams in Fig. 3 are only compatible with the assumption that (IV) associates with the nonbonded OH-group of endproducts. Numerical calculations of the whole kinetic system yielded the solid curves in Figs. 2 and 3.

A mechanism will be discussed which is consistent with the MEIR data and ESR and MESR observations.

- 1 M. Forster, K. Loth, M. Andrist, U. P. Fringeli and Hs. H. Günthard, Chem. Phys., 17 (1976) 59.
- 2 M. Forster, Thesis No. 6180, Swiss Federal Institute of Technology, Zürich, Switzerland, 1978.

MULTIPHOTON PHOTODISSOCIATION OF NAPHTHALENE CATIONS

R. C. Dunbar and M. S. Kim

Case Western Reserve University, Cleveland, Ohio 44106 (U.S.A.)

Photodissociation of naphthalene [or methylnaphthalene] cations at visible wavelengths may proceed through one-, two- or four-photon processes, depending on the energetics of the dissociation. At moderate light intensities using continuous sources, the multiphoton dissociations follow a sequential photon-absorption sequence over a period of the order of a second, with energy storage in the photoexcited ion in internal (probably vibrational) degrees of freedom. All three of these orders of photodissociation processes have been observed in naphthalene cations, using trapped-ion photodissociation techniques in the ICR spectrometer, and the kinetics of the processes have been studied with respect to light intensity and neutral-gas pressure. Noteworthy is the finding that the four-photon dissociation of naphthalene cations is between second order and third order in light intensity, rather than being fourth order as might have been expected. Detailed modeling of the kinetics by analytical and numerical methods reproduces this behavior, and gives excellent agreement with experiment for one-, two- and four-photon processes. Sequential multiphoton dissociation processes will in general show deceptively low orders of light-intensity dependence.

Spectroscopic information for the naphthalene ions is available from the photodissociation spectra, and will be briefly described and compared with condensed-phase spectroscopy.