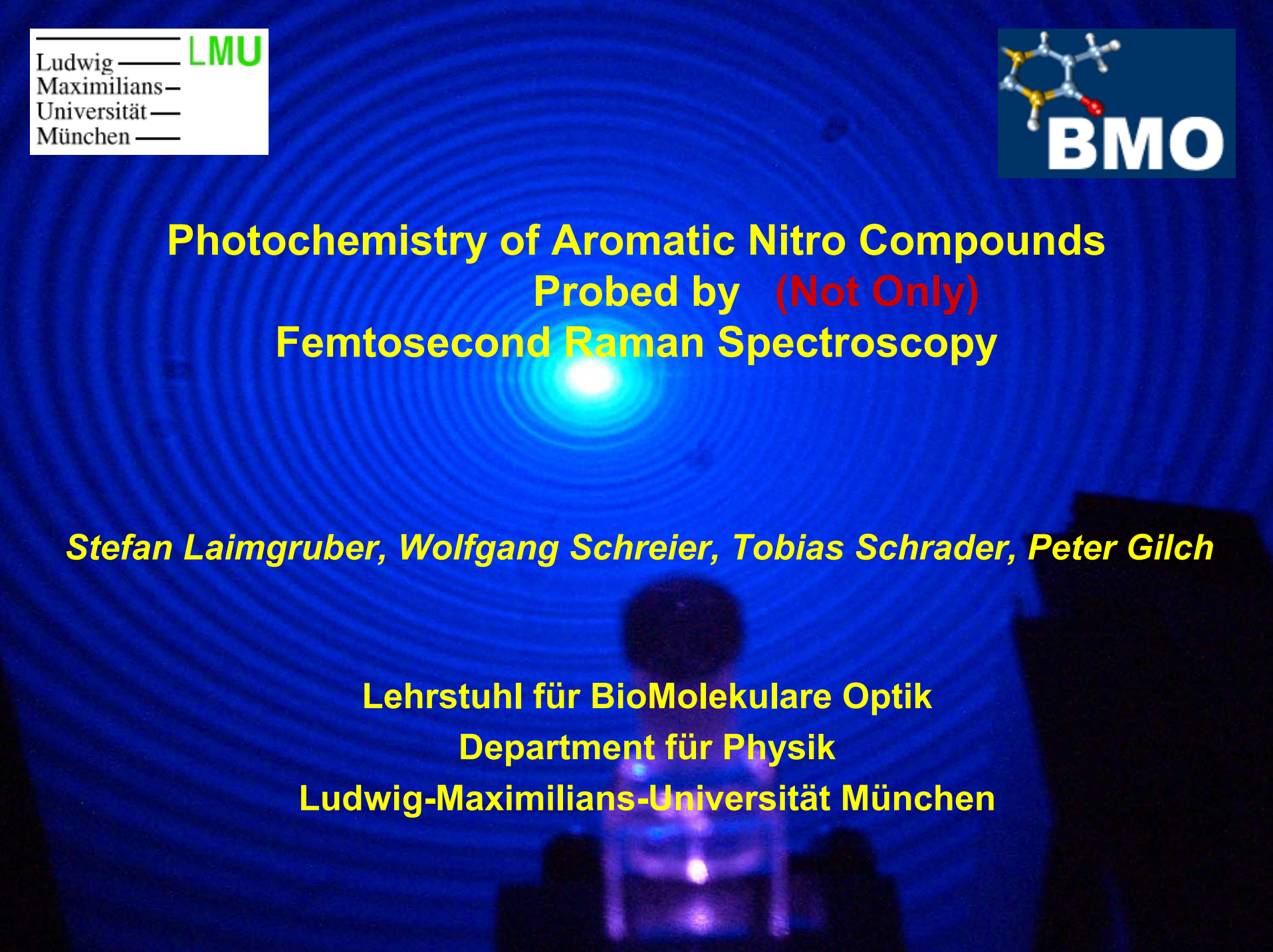
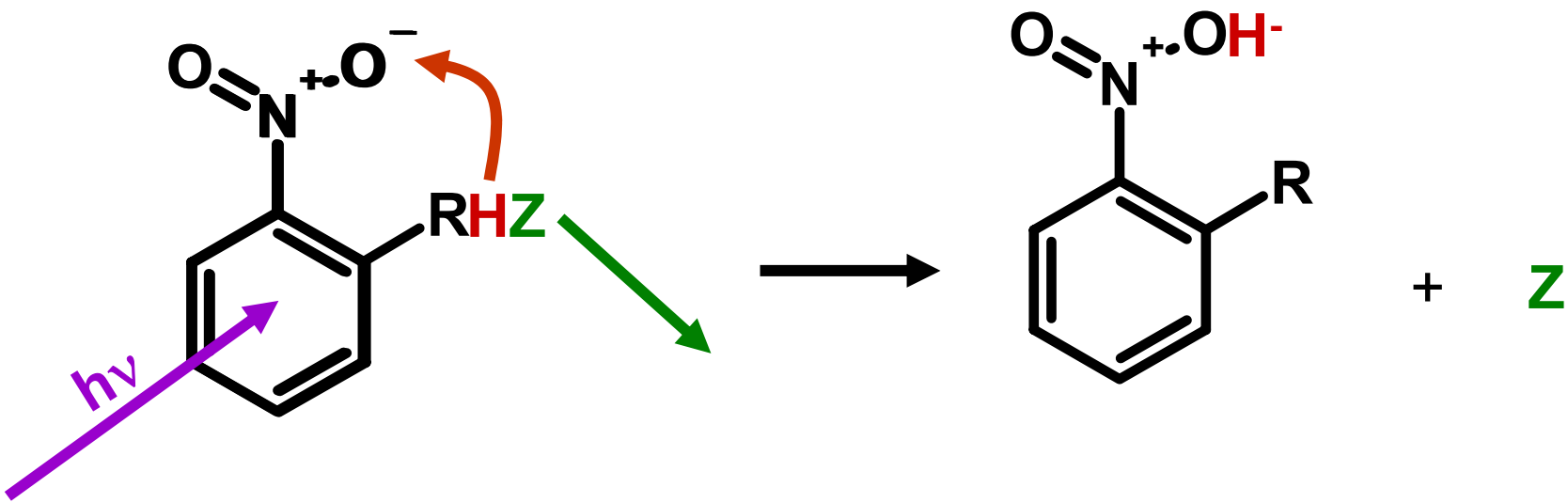


Photochemistry of Aromatic Nitro Compounds Probed by (Not Only) Femtosecond Raman Spectroscopy

Stefan Laimgruber, Wolfgang Schreier, Tobias Schrader, Peter Gilch

Lehrstuhl für BioMolekulare Optik
Department für Physik
Ludwig-Maximilians-Universität München

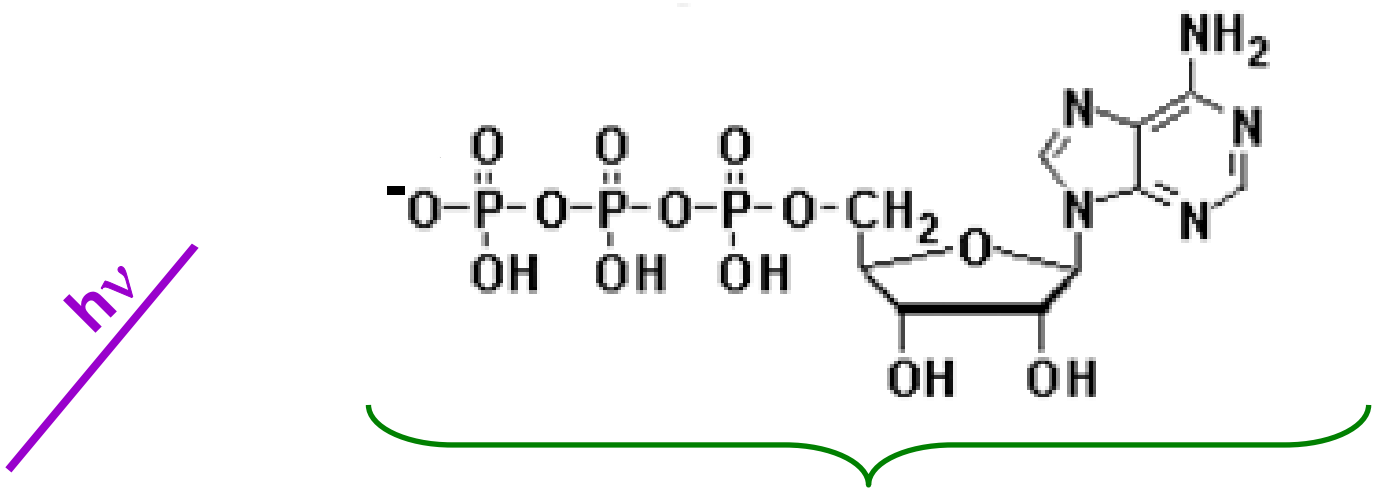
Photochemistry of Aromatic Nitro Compounds



Hydrogen Atom **H** transferred
Leaving Group **Z** released

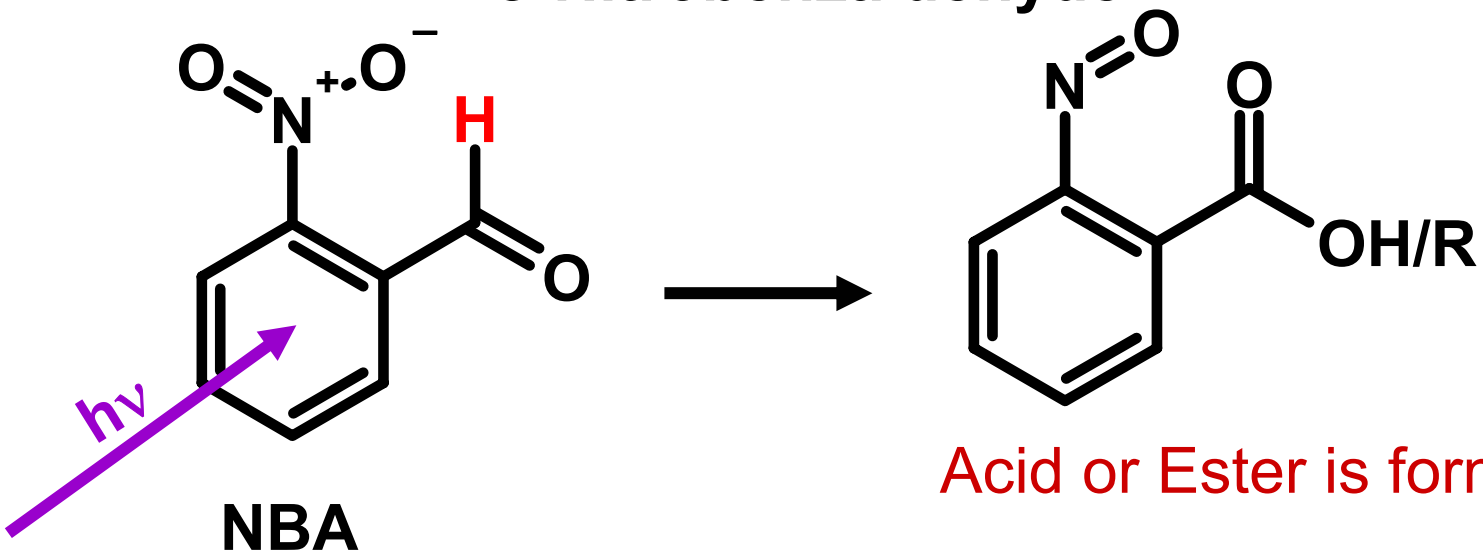
One Application: Caged Compounds

Example: Caged ATP (J. H. Kaplan et al. 1978)

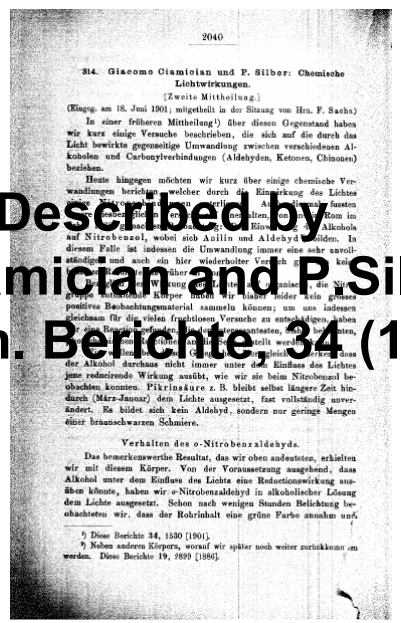


Directed Release of Biological Active Substances!

„Our“ Reaction: Photochemistry of *o*-Nitrobenzaldehyde



Acid or Ester is formed


2040

314. Giacomo Ciamician und P. Silber: Chemische Lichtwirkungen.

[Zweite Mittheilung.]

(Eingeg. am 18. Juni 1901; mitgetheilt in der Sitzung von Hrn. F. Sachs)

In einer früheren Mittheilung[1]) über diesen Gegenstand haben wir kurz einige Versuche beschrieben, die sich auf die durch das Licht bewirkte gegenseitige Umwandlung zwischen verschiedenen Alkoholen und Carbonylverbindungen (Aldehyden, Ketonen, Chinonen) beziehen.

Heute hingegen möchten wir kurz über einige chemische Verwandlungen berichten, welcher durch die Einwirkung des Lichtes

auf Nitrobenzol, wobei sich Anilin und Aldehyd bilden. In diesem Falle ist indessen die Umwandlung immer eine sehr unvollständige und auch ein hier wiederholter Versuch

der Alkohol durchaus nicht immer unter dem Einfluss des Lichtes jene reducirende Wirkung ausübt, wie wir sie beim Nitrobenzol beobachten konnten. Pikrinsäure z. B. bleibt selbst längere Zeit hindurch (März-Januar) dem Lichte ausgesetzt, fast vollständig unverändert. Es bildet sich kein Aldehyd, sondern nur geringe Mengen einer braunschwarzen Schmiere.

Verhalten des *o*-Nitrobenzaldehyds.

Das bemerkenswerthe Resultat, das wir oben andeuteten, erhielten wir mit diesem Körper. Von der Voraussetzung ausgehend, dass Alkohol unter dem Einfluss des Lichts eine Reductionswirkung ausüben könnte, haben wir *o*-Nitrobenzaldehyd in alkoholischer Lösung dem Lichte ausgesetzt. Schon nach wenigen Stunden Belichtung beobachteten wir, dass der Rohrinhalt eine grüne Farbe annahm und

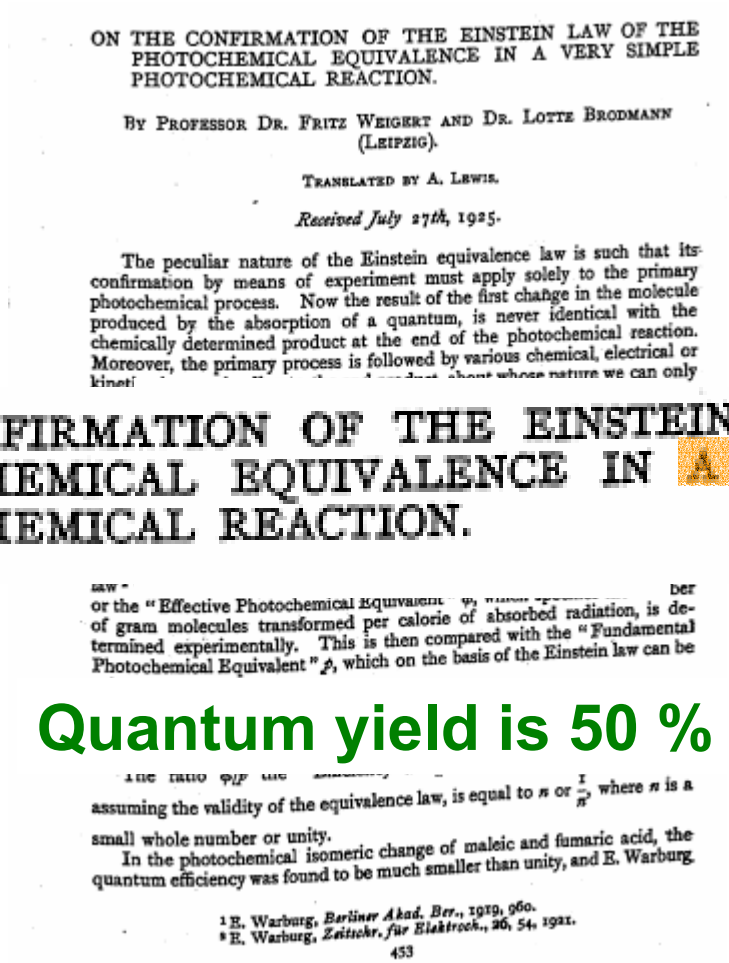
[1]) Diese Berichte 34, 1530 [1901].

[2]) Neben anderen Körpern, worauf wir später noch weiter zurückkommen werden. Diese Berichte 19, 2899 [1886].

First Described by G.Ciamician and P.Silber, Chem. Berichte, 34 (1901) 2040


EIN
STEIN
JAHR
2005
Eine gemeinsame Initiative
von Bundesregierung, Wissenschaft,
Wirtschaft und Kultur

o-Nitrobenzaldehyde and the Photochemical Equivalent



ON THE CONFIRMATION OF THE EINSTEIN LAW OF THE PHOTOCHEMICAL EQUIVALENCE IN A VERY SIMPLE PHOTOCHEMICAL REACTION.

By Professor Dr. Fritz Weigert and Dr. Lotte Brodmann (Leipzig).

Translated by A. Lewis.

Received July 27th, 1925.

The peculiar nature of the Einstein equivalence law is such that its confirmation by means of experiment must apply solely to the primary photochemical process. Now the result of the first change in the molecule produced by the absorption of a quantum, is never identical with the chemically determined product at the end of the photochemical reaction. Moreover, the primary process is followed by various chemical, electrical or

ON THE CONFIRMATION OF THE EINSTEIN LAW OF THE PHOTOCHEMICAL EQUIVALENCE IN A VERY SIMPLE PHOTOCHEMICAL REACTION.

or the "Effective Photochemical Equivalent" Φ, which on the basis of the Einstein law can be of gram molecules transformed per calorie of absorbed radiation, is determined experimentally. This is then compared with the "Fundamental Photochemical Equivalent" ϕ,

Quantum yield is 50 %

assuming the validity of the equivalence law, is equal to n or $\frac{1}{n}$, where n is a small whole number or unity.

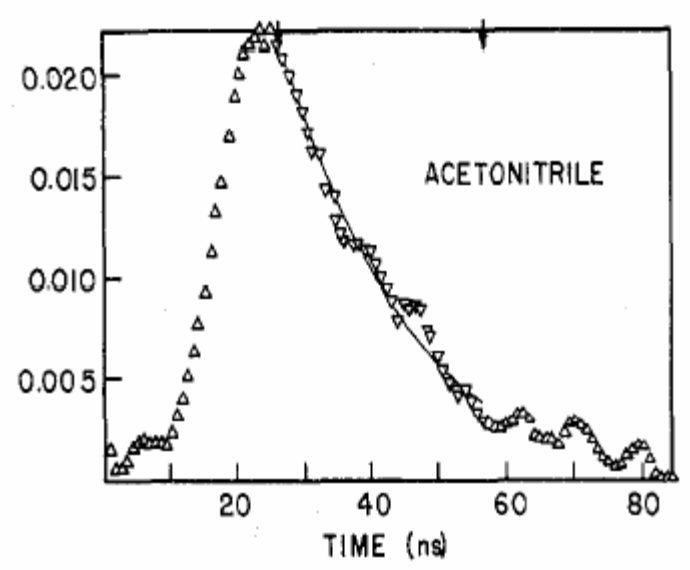
In the photochemical isomeric change of maleic and fumaric acid, the quantum efficiency was found to be much smaller than unity, and E. Warburg

[1] E. Warburg, *Berliner Akad. Ber.*, 1919, 960.
[2] E. Warburg, *Zeitschr. für Elektroch.*, 26, 54, 1921.

453

F. Weigert and L. Brodmann, Transaction of the Faraday Society 21 (1925) 453

Reaction Mechanism – What Others Did



- George and Scaiano saw nanosecond transients in aprotic solvents
- assigned to triplet state

M.V. George and J.C. Scaiano,
J. Phys. Chem. 84 (1980) 492

Lifetimes of the transient[a] from *o*-nitrobenzaldehyde in solution

Solvent	Lifetime
acetonit	24 ± 8 ns
THF	2.4 ± 0.3 ns
THF (3.0 M *cis*-1,3-pentadiene)	2.6 ± 0.2 ns
tert-butyl alcohol	163 ± 59 ps
acet	± 12 ps
acet	± 65 ps
acet (50% water)	74 ± 25 ps

[a] Monitored at 440 nm.

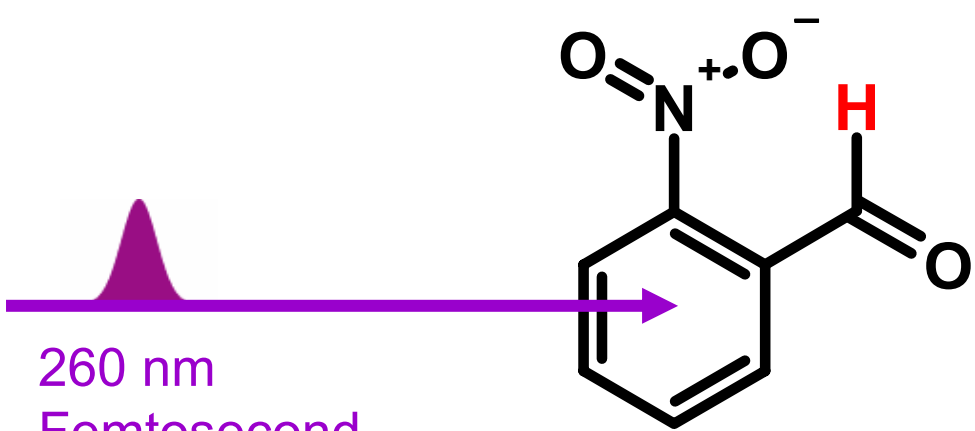
MeCN: 24 ns

50 % Water: 75 ps

- Yip and Sharma detected ps (ns) transients protic (aprotic) solvents
- assigned to a ketene intermediate

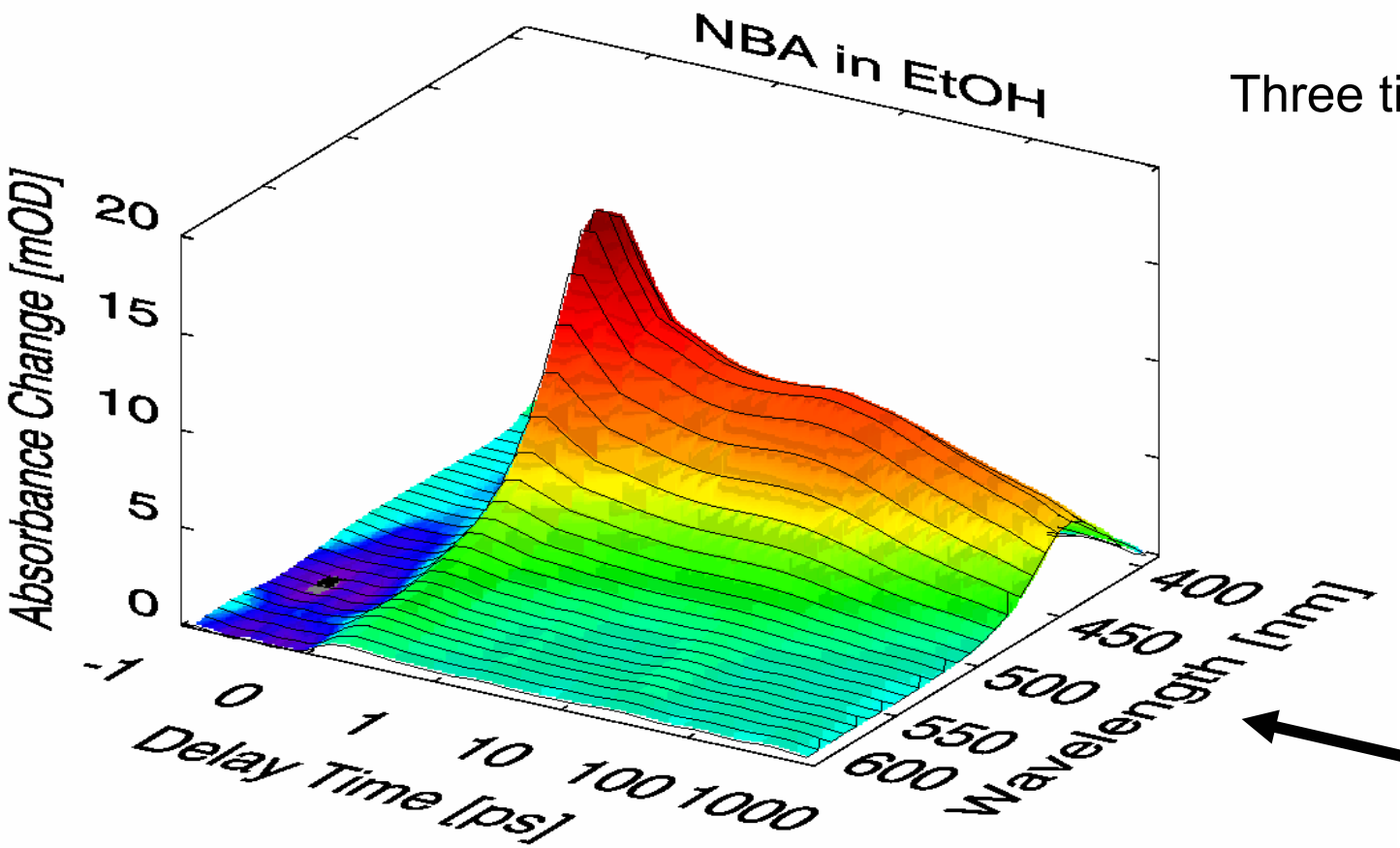
R.W.Yip and D.K.Sharma,
Research on Chem. Intermediates
11 (1989) 109

Our Experiments: Femtosecond Excitation, Probing by ...



260 nm
Femtosecond
Excitation

... UV/Vis Spectroscopy (I)



Three time constants:

0.4 ps

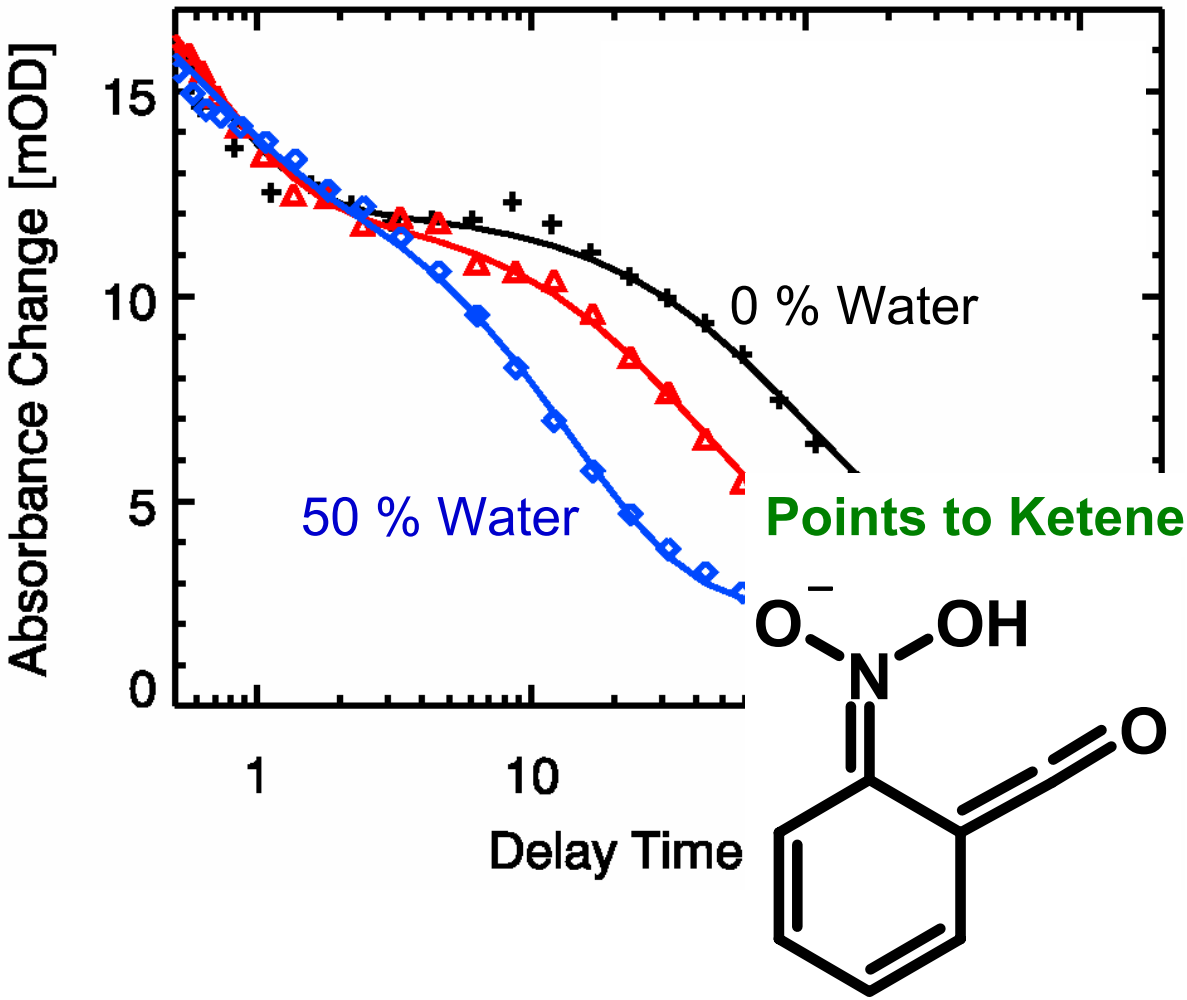
90 ps

3 ns

Assignment?

Solvent: Ethanol

... UV/Vis Spectroscopy (II)



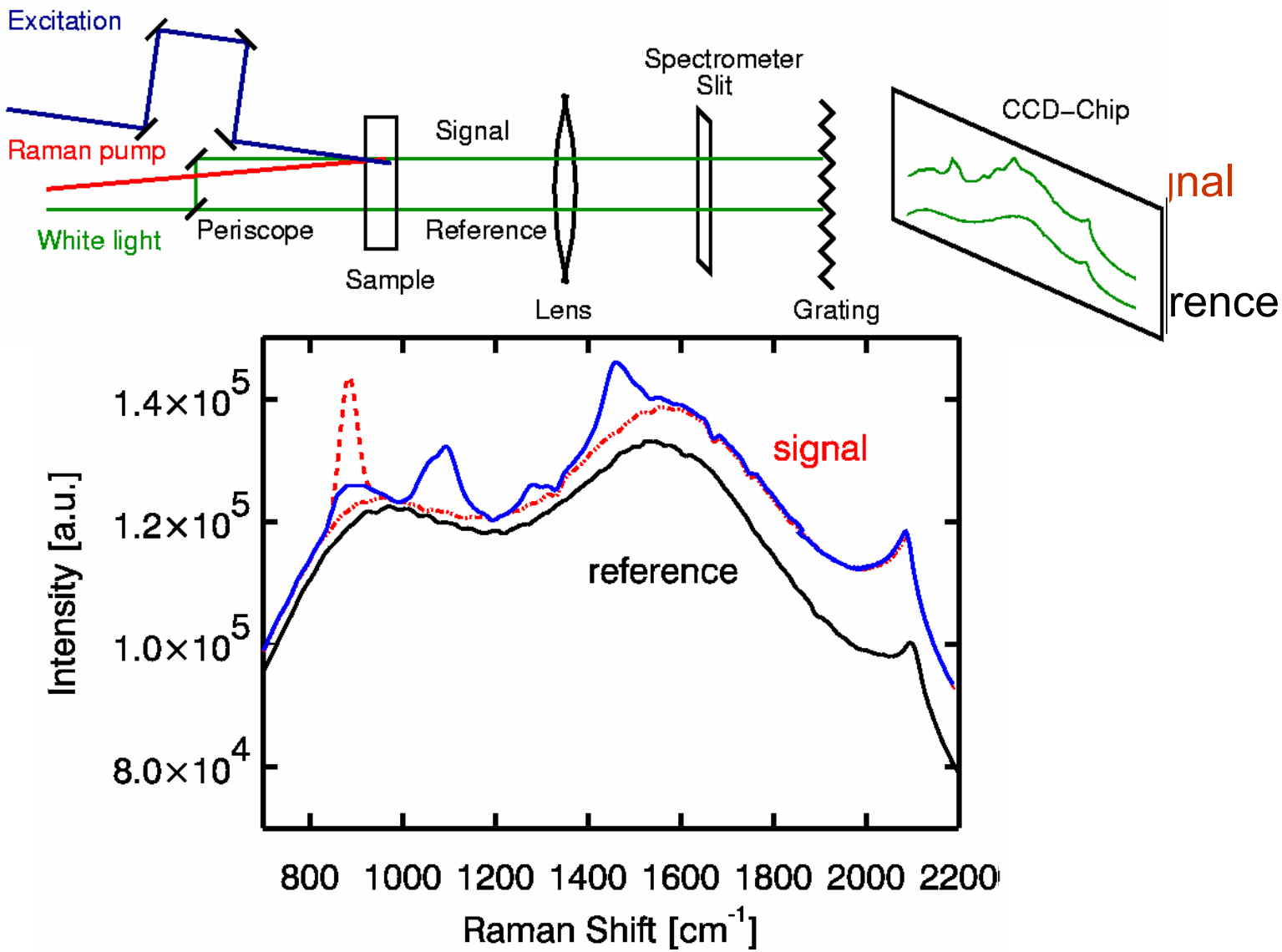
0.4 ps

90 ps →13 ps

3 ns

Spectroscopic Evidence?

... Stimulated Raman Scattering (Technique)



M.Yoshizawa and M. Kurosawa, Phys. Rev. A, 61 (2000) 013808

D.W.McCamant, P.Kukura, R.A. Mathis, J.Phys.Chem. A 107 (2003) 8208

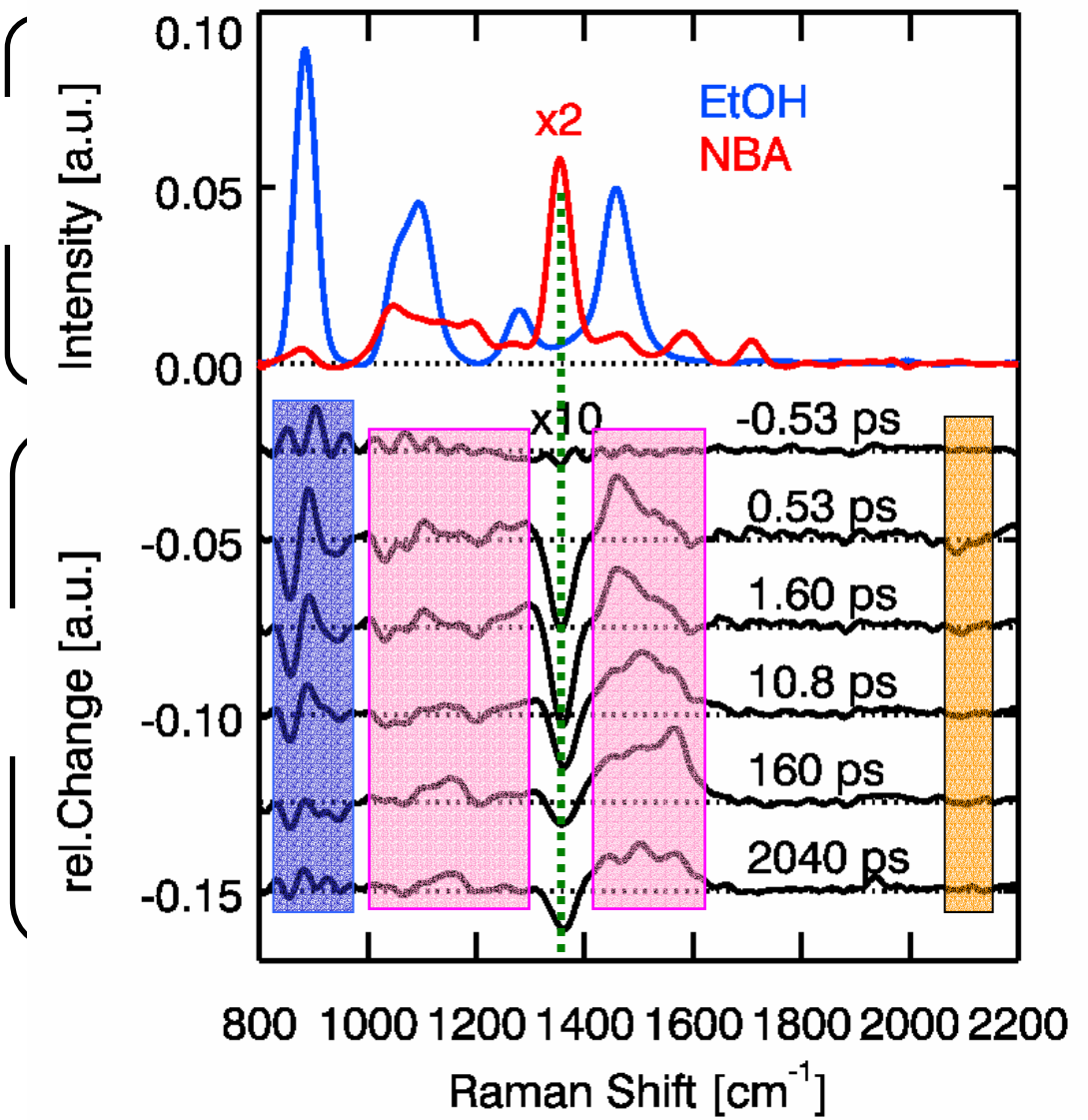
... Stimulated Raman Scattering (Results)

Bleach of NO_2 Band at 1360 cm^{-1}

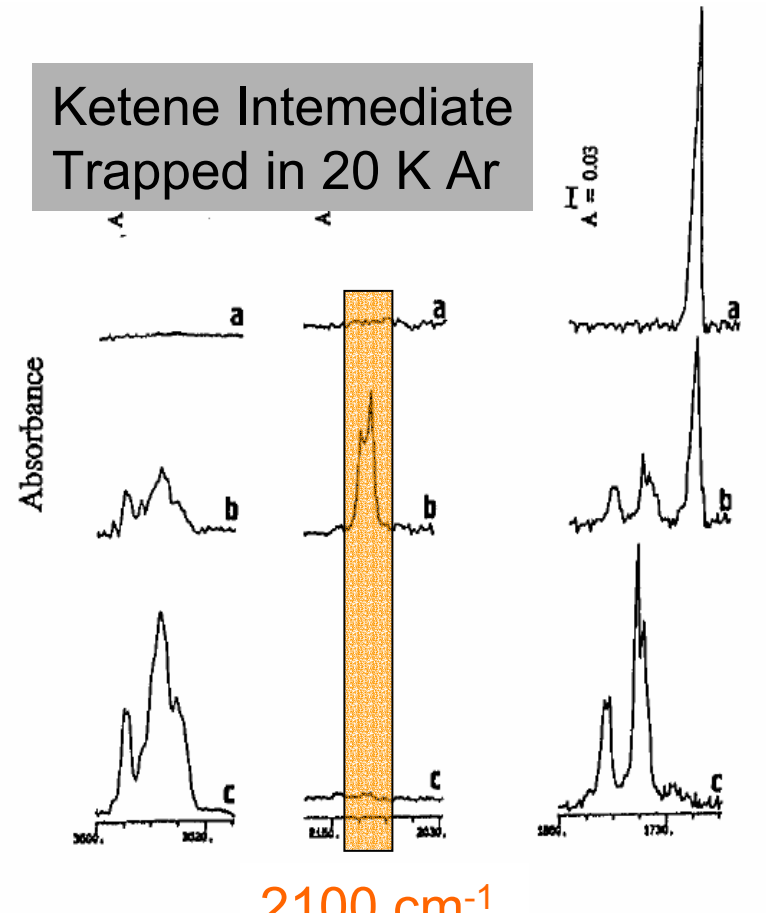
Emerging Bands of Intermediates

Solvent „Senses“ the Reaction

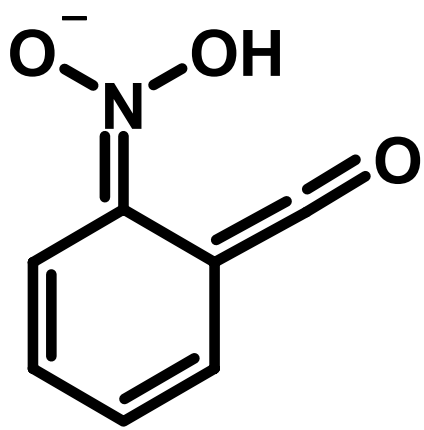
Something is missing!



Matrix Isolation Spectrum of Ketene Intermediate



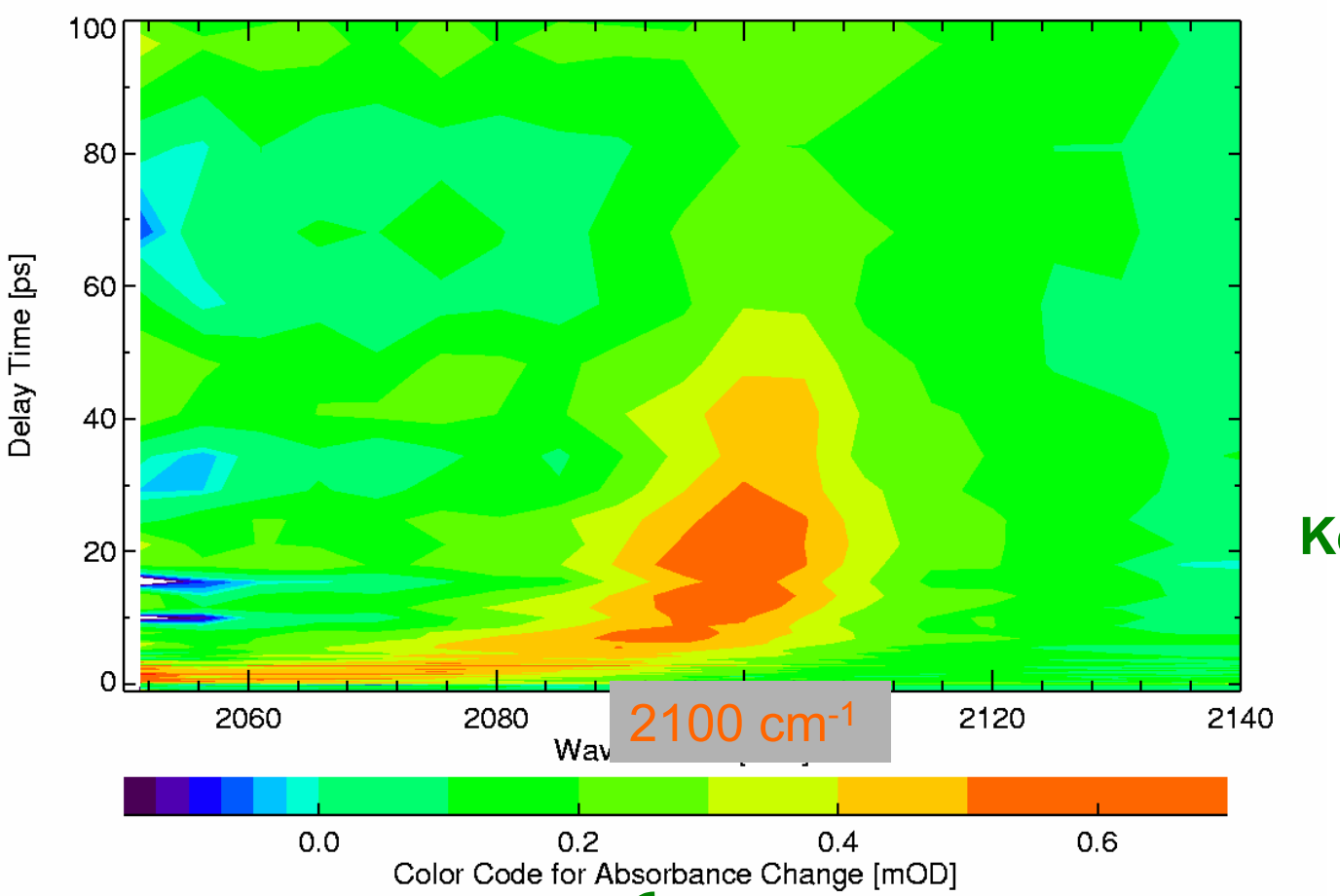
VERY Distinct
Resonance of Ketene

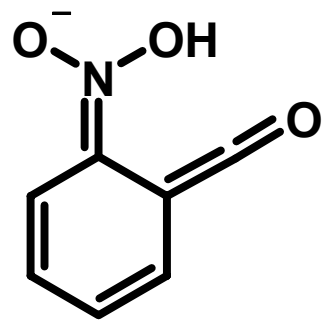


Maybe we see it in the IR?

S. Kuberski and J. Gebicki, J. Molecular Structure, 275 (1992) 105

... Probed by IR Spectroscopy





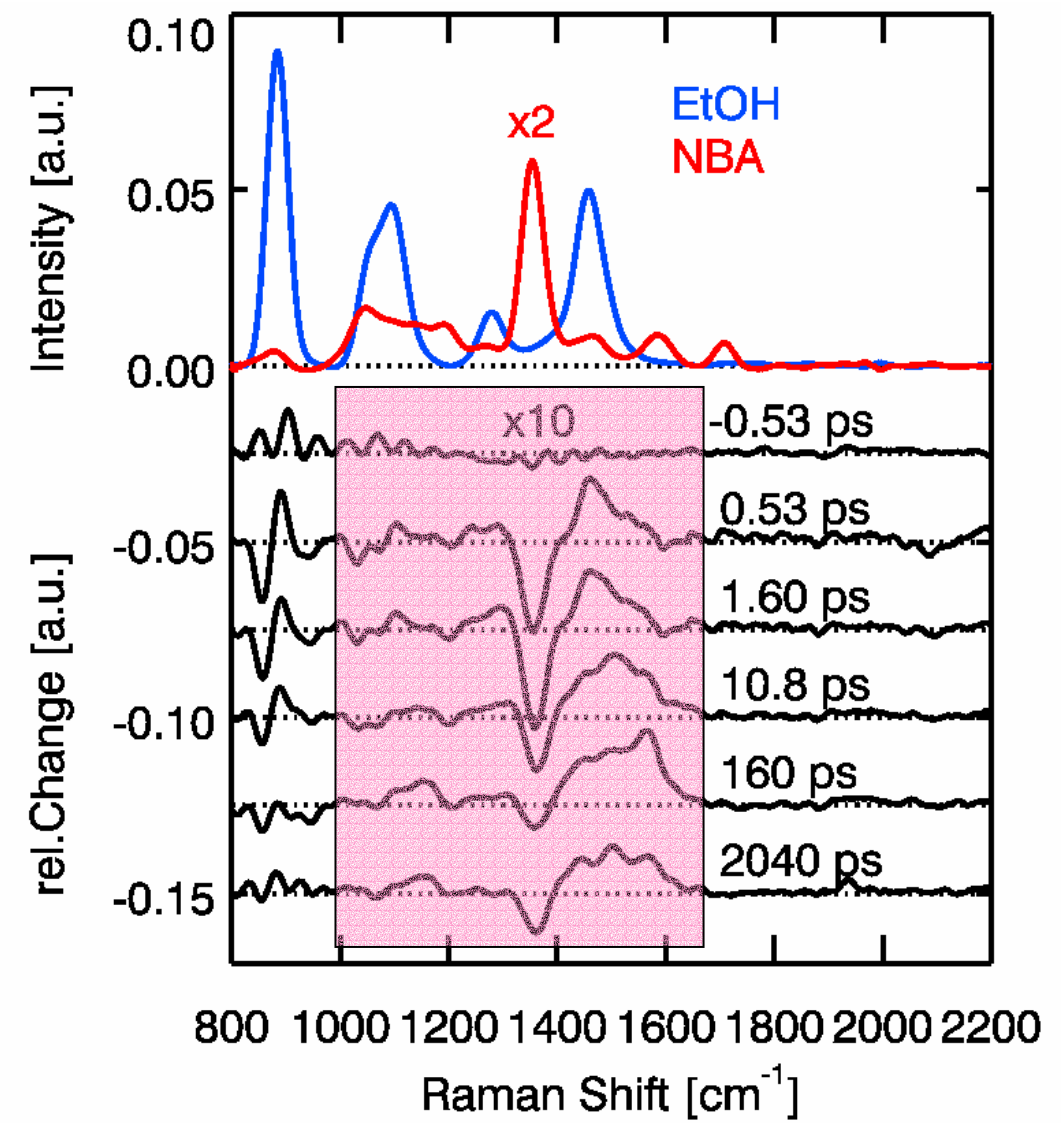
Ketene is Present!

Formed in some 100 fs ✓

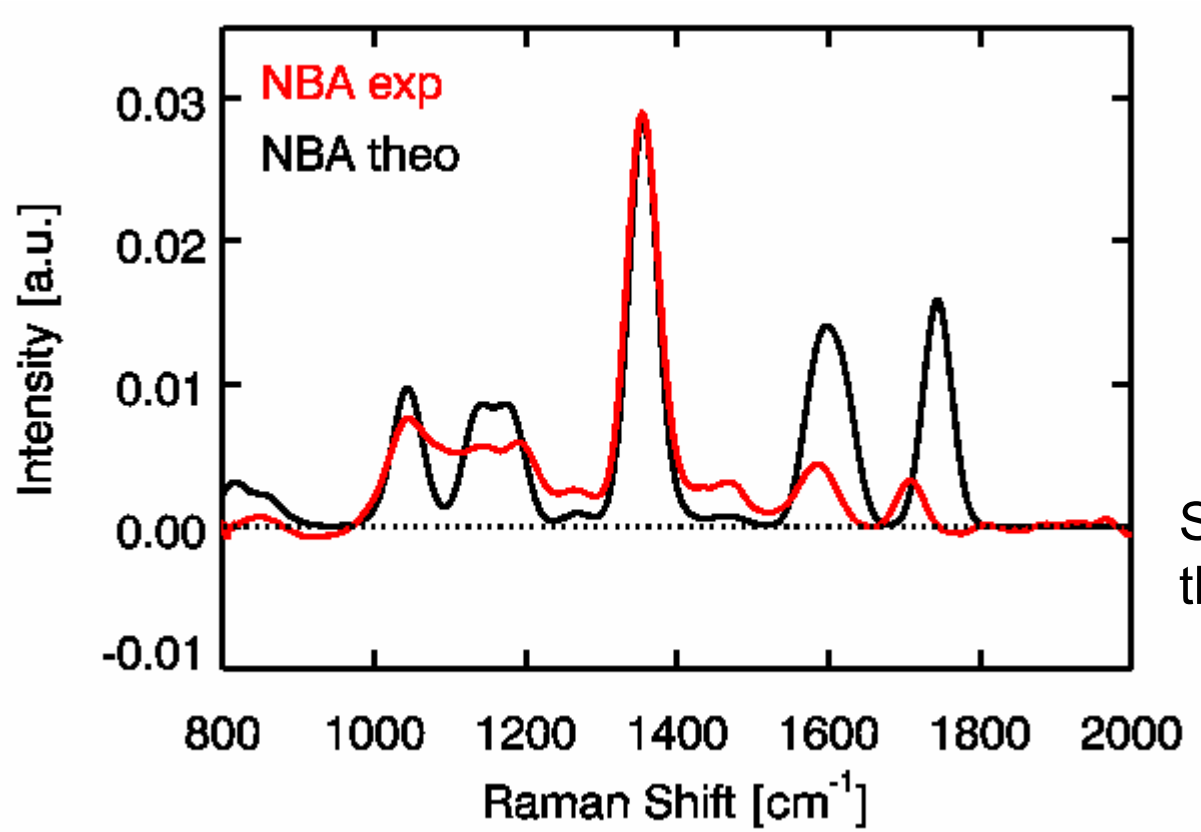
Decays in ~ 60 ps ✓

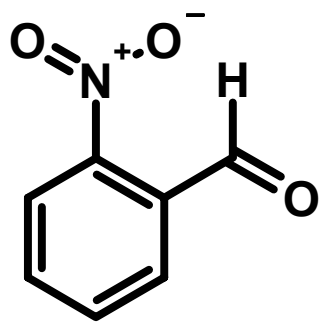
Shift due to Vibrational Relaxation!

Analysis of Raman Spectra



DFT Calculations



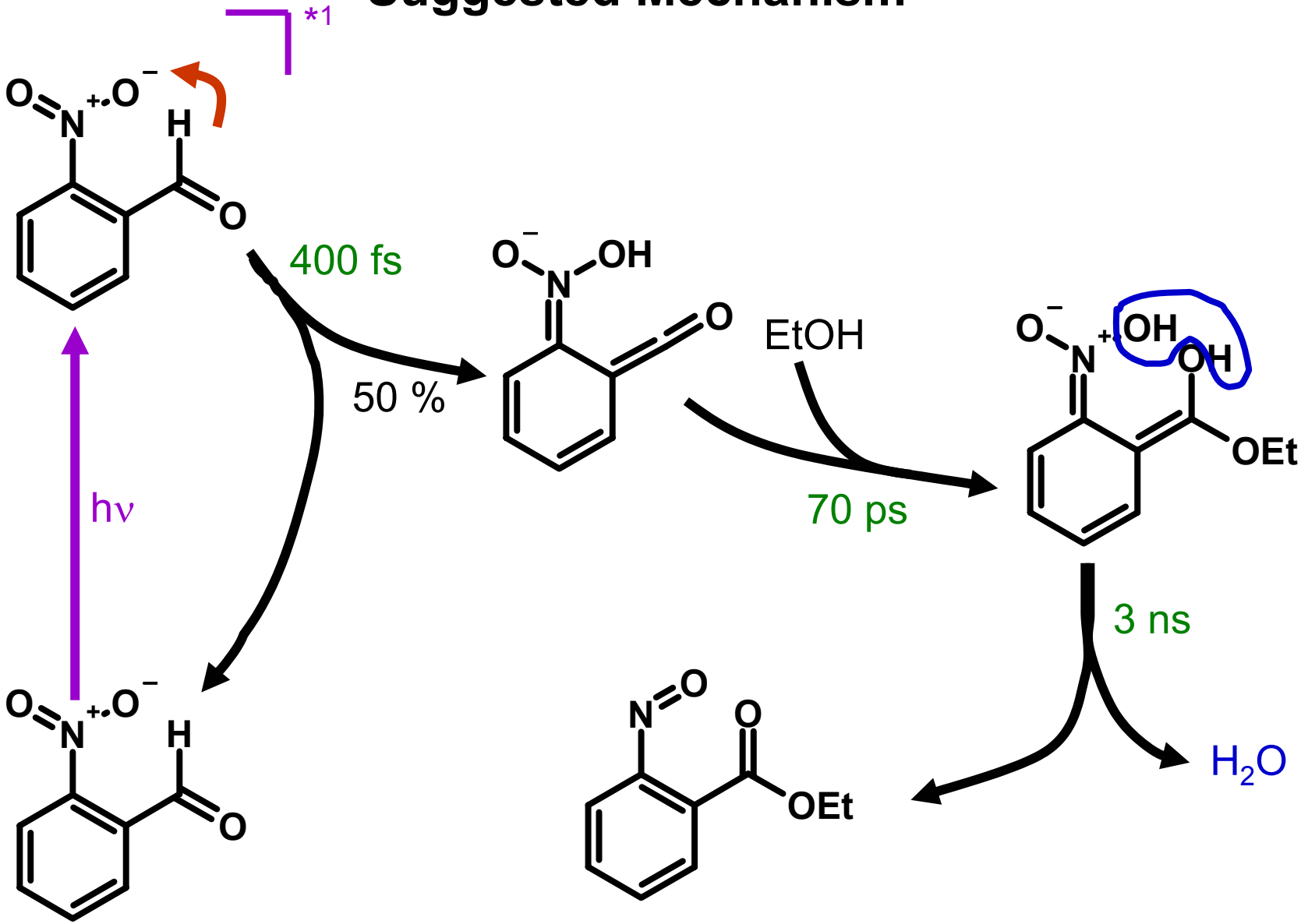


Structure of NBA available thanks to X-ray diffraction

Nice agreement between calculation (B3LYP, 6-311G**) and experiment

Gives confidence that we can predict spectra of intermediates!

Suggested Mechanism



Take Home Message

Summing up

- Monitored photo-redox-reaction of NBA with three femtosecond techniques
- UV/Vis spectroscopy yields precise time constants
- Ketene intermediate identified by IR spectroscopy
- First application of femtosecond stimulated Raman scattering for study of photoreaction
- **Outlined an „evidenced based“ mechanism**