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SMR/115 - 68 **

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(21 January - 22 March 1985)

Topical Meeting on Multiphoton Processes

TWO-STEP-PHOTOIONIZATION SPECTROSCOPY OF BENZENE

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Lecture Notes Trieste 1985
Lasers, atomic and molecular physics

2-Step-Photoionization Spectroscopy of Benzene

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Background - History

MPI of molecules and atoms known for long
But: As a higher order process small efficiency.
High laser power turns on multitude of NL phenomena
Better: UV Lasers – res.-enhanced
2-step process
(high yield/selectivity)

⇓

Study fragmentation

⇓

Spectroscopy of intermediate States

⇓

Ionization mechanism

⇓

use the ions

⇙ ⇓ ⇘

Spectroscopy MS Ion-molecule interaction etc.

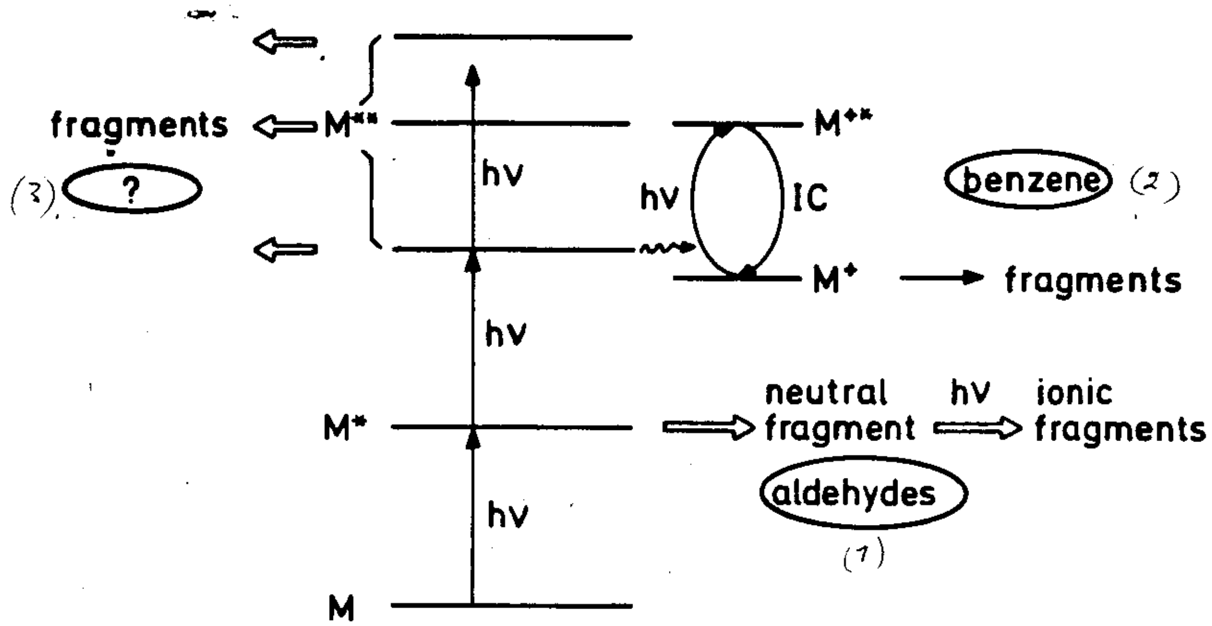
Background - Problems

Res.-enhanced multiphoton ionization of polyatomic molecules proposed for use in:

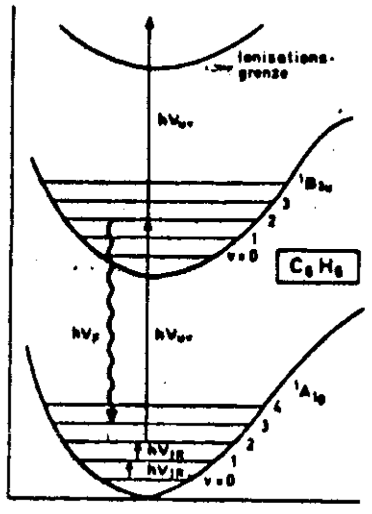
(1) Molecular spectroscopy.
Spectral dependence of ionizing step
Lifetimes unknown

(2) Mass Spectrometry
What is the total ion yield? / spectral dependence of it? / fragmentation pattern? /
In general: Predictability of spectra!

(3) Photochemistry
Needed. Well defined ion states / cold ions / know the role of neutral fragments generated at the same time



UV - Laser multiphoton can go different ways: (1) Photo dissociation of intermediate state; (2) molecular (so-called "soft" ionization; (3) superexcited state ionizes with lots of internal energy

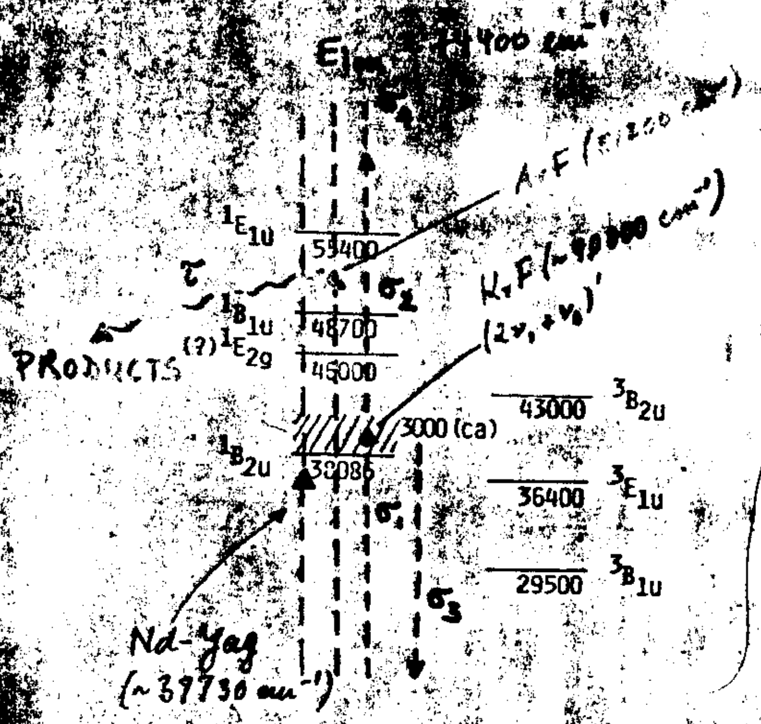


$\tilde{X}$ Electron becomes non-bonding
→ nuclear configuration similar to S_0

S_1 Electron becomes antibonding
⇒ change in nuclear coordinates

S_0

Photoionization Spectroscopy $S_1 \rightarrow \tilde{X}$ spectral structure
Qualitative and simplified picture for benzene



Energy relationships for benzene (see p. 4) using diff. laser wavelengths

$$d[C_6H_6]^*/dt = \sigma_1 I [C_6H_6] - [(\sigma_2+\sigma_3)/I + 1/\tau][C_6H_6^*]$$

$$d[C_6H_6^+(0)]/dt = \sigma_2 I [C_6H_6^*] - \sigma_4 I [C_6H_6^+(0)]$$

$$d[C_6H_6^+(n)]/dt = \sigma_4 I \{[C_6H_6^+(n-1)] - [C_6H_6^+(n)]\}$$

$$n \geq 1$$

rate equation for the 3 levels populations involved in the process

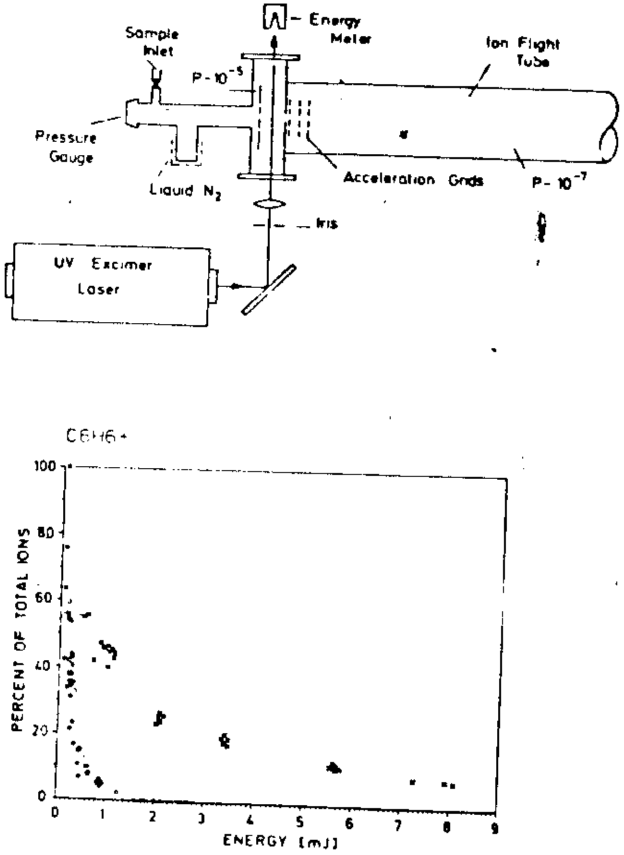
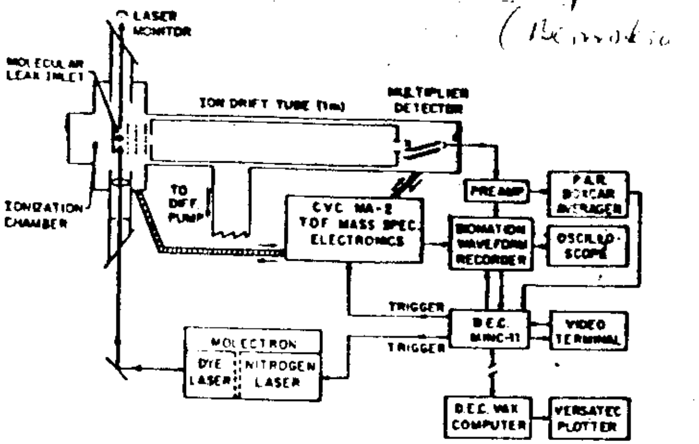


Fig. 1: Apparatus used for generating mass spectra of polyatomic molecules by UV-laser induced ionization (top) and experimentally observed percentage of total ion signal represented by the C_6H_6 parent ion (x=KrF, o=ArF laser)

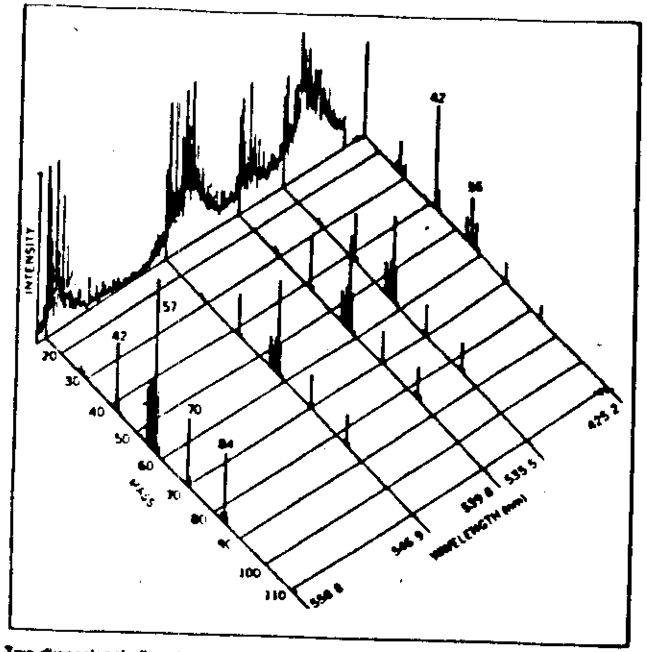
Final experimental scheme: TOF mass spectrometer

(Reilly, Kompa)

Second exptl scheme : Two-dimensional mass spectrometry (Bernstein et al)

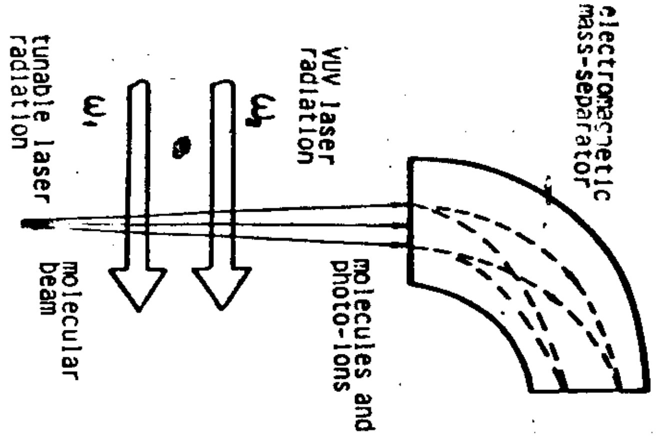


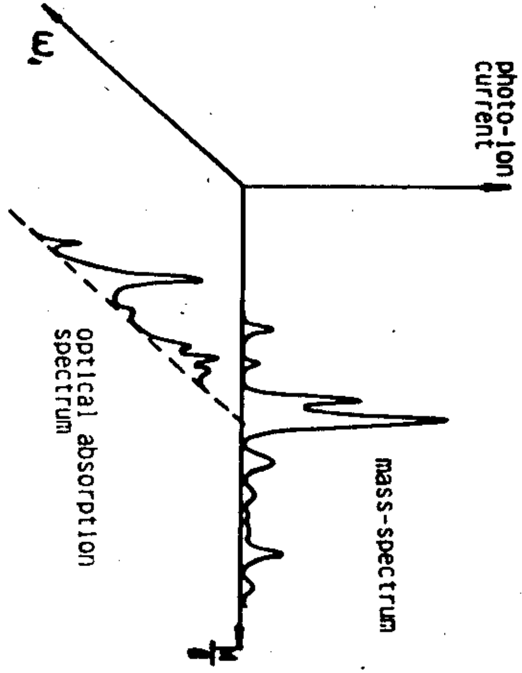
. 1. Schematic diagram of the laser ionization TOF mass spectrometer system. See text (section 2) for details.



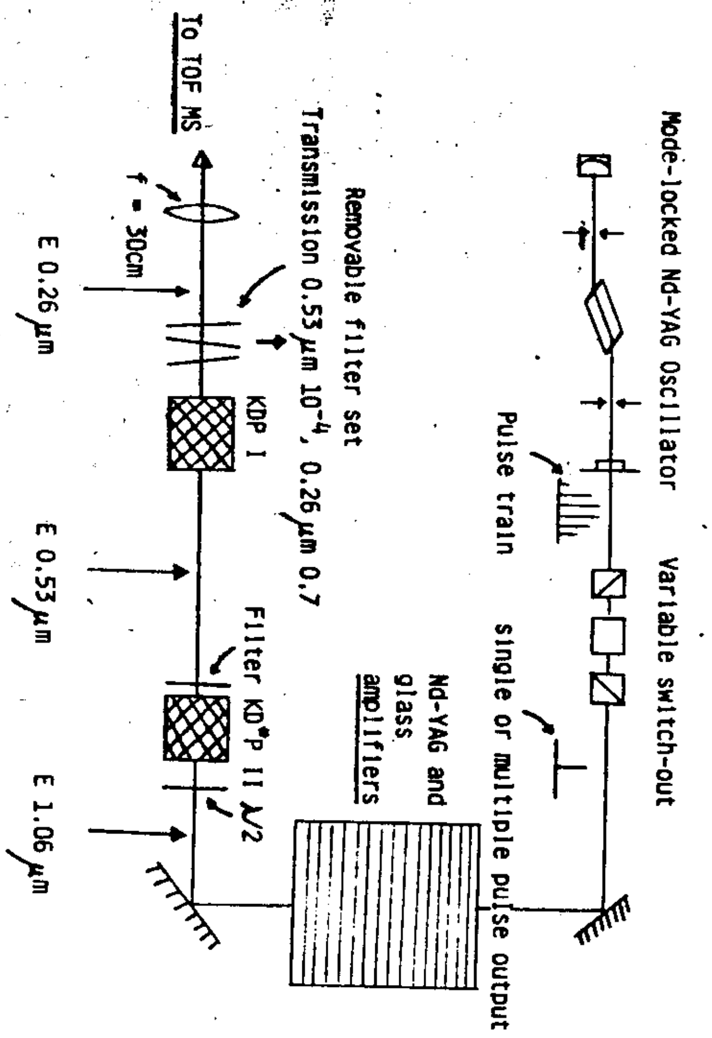
Two-dimensional vibronic/mass spectrum of triethylenediamine [N(C$_2$H$_4$)$_3$N] obtained via laser multiphoton ionization mass spectroscopy. Back-panel: total ionization wavelength spectrum, sticks: relative intensities of fragment ions. (Adapted from reference 17.) Figure 7

Third exptl scheme (after Letokhov et al)
ideal experiment

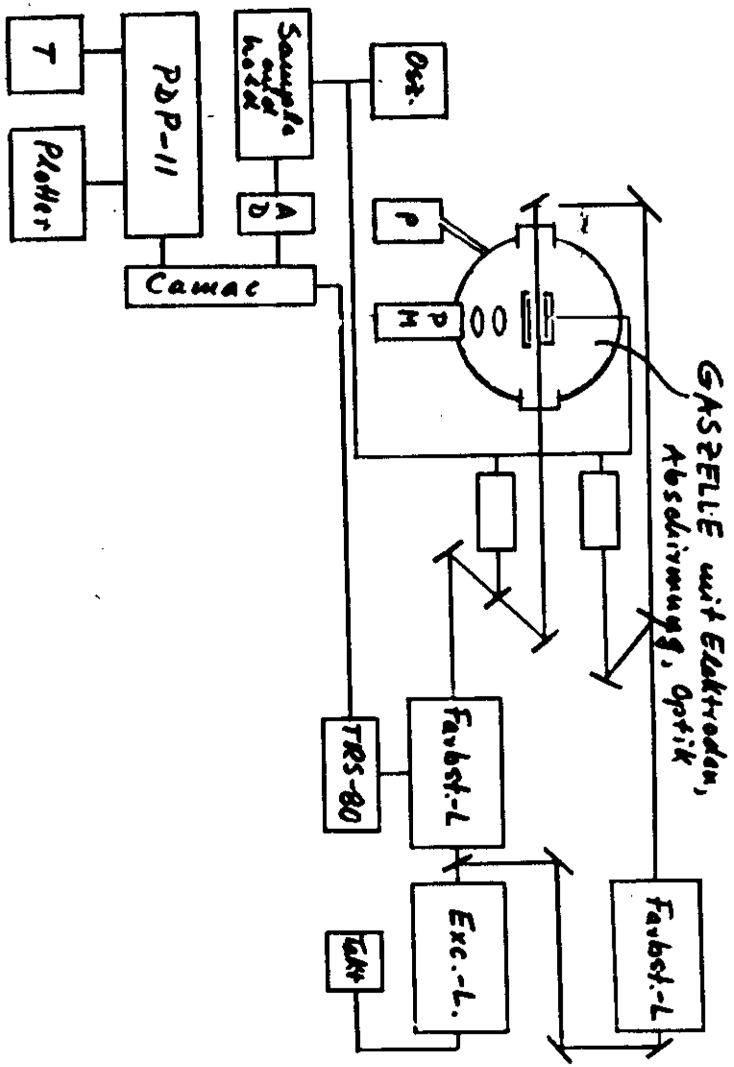




After Antonov, Letokhov and Shibanov



4. exptl. scheme: ps-Expt.
see later



5. exptl. scheme. Ionization spectroscopy (Ion currents + LIF) with two independently tunable dye lasers (Müller, Kompa)

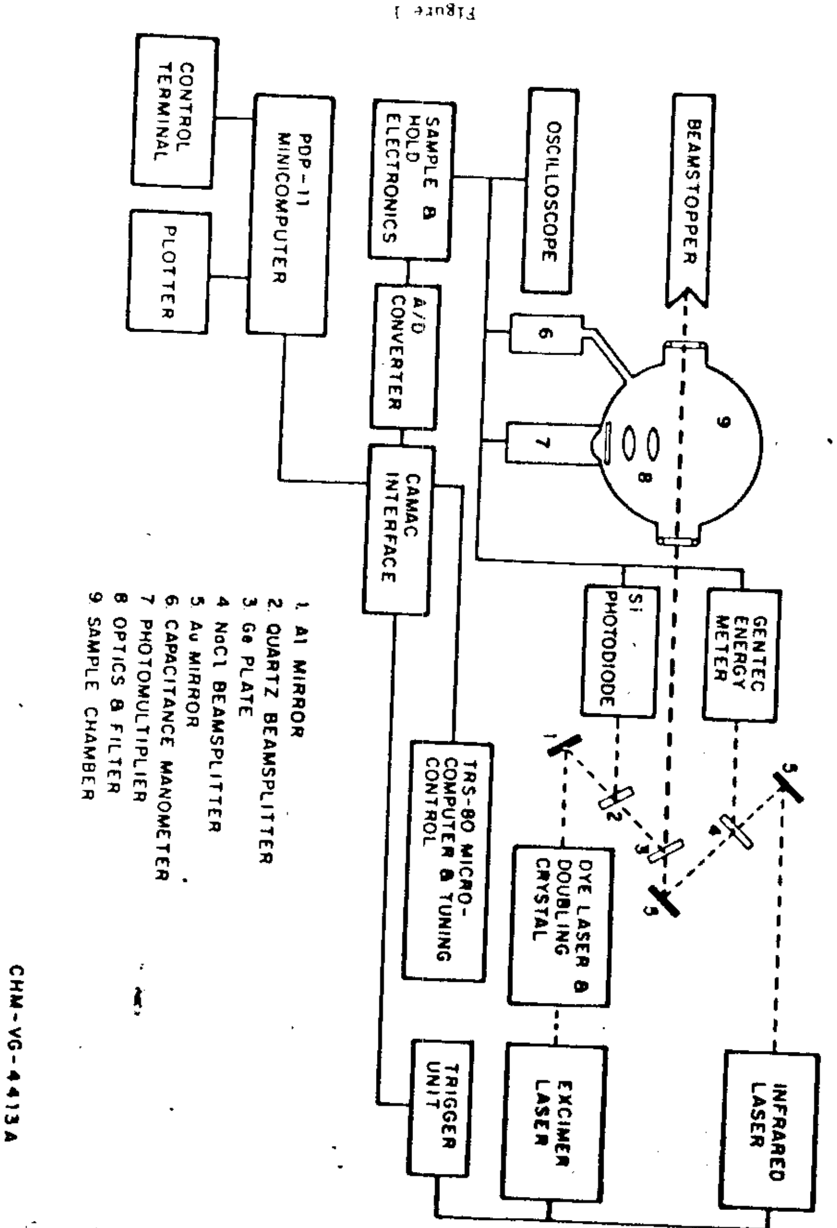


Figure 1

[illegible] [illegible] [illegible]: Apparatus used for [illegible] of vibrationally excited benzene [illegible], Miller, Compton) see later

Primary fragmentation paths of benzene molecular ion (all with threshold energies around 4 eV, all occuring from the electronic groundstate of $C_6H_6^+$)

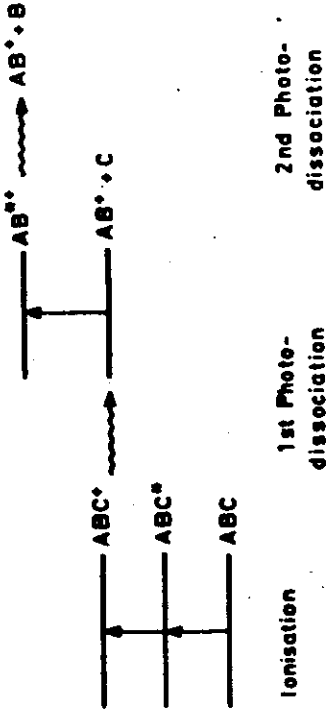
$C_6H_6^+ \longrightarrow C_6H_5^+ + H$

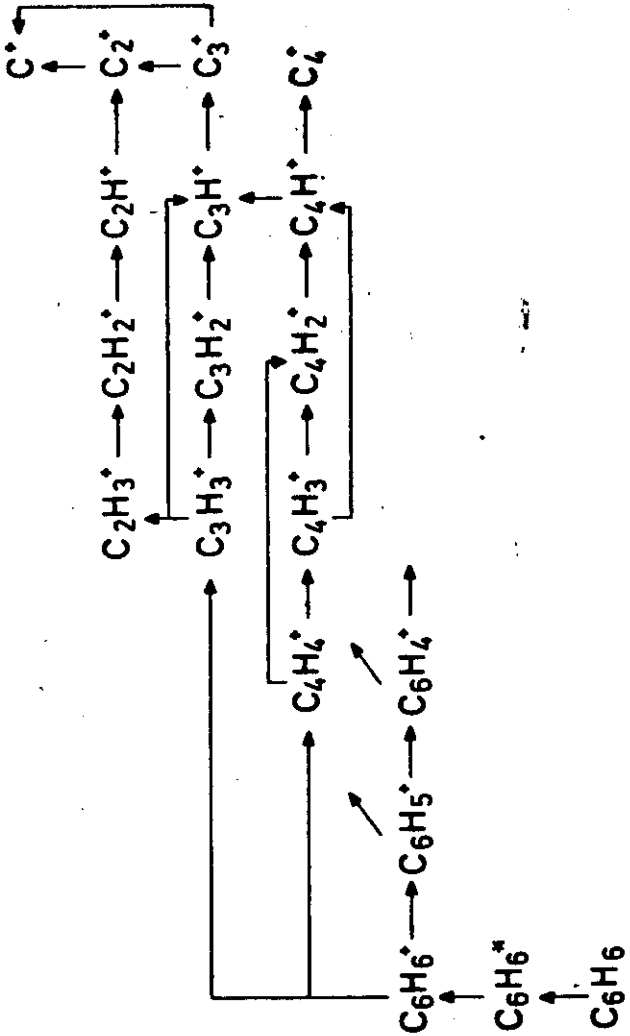
$\longrightarrow C_6H_4^+ + H_2$

$\longrightarrow C_4H_4^+ + C_2H_2$

$\longrightarrow C_3H_3^+ + C_3H_3$

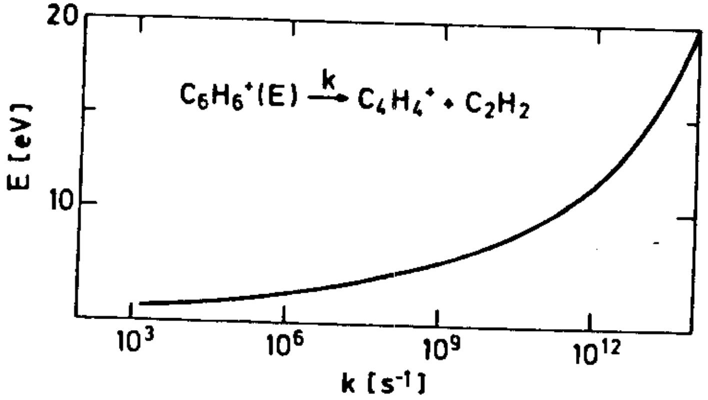
"Ladder switching" in benzene ionization and fragmentation. Question. Can this switching scheme be interrogated by ps- experiment?





Fragmentation tree for benzene ionization and subsequent photodissociation (Kebenhol et al.)

RRKM estimate of benzene fragmentation rate as function of excess energy: e.g. 11 eV excess internal energy deposited in the ion will cause fragmentation within a 10 psec.



PICOSECOND UV-LASER INDUCED MULTIPHOTON IONIZATION AND FRAGMENTATION OF BENZENE

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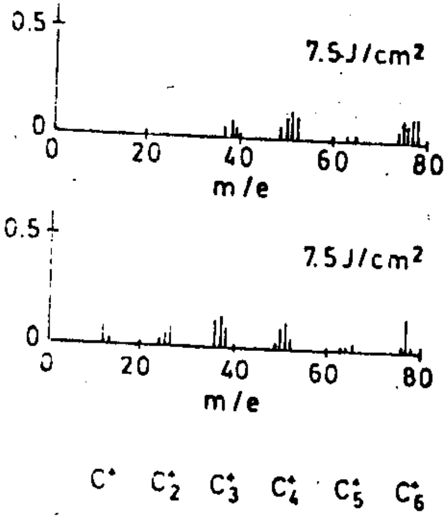


With psec laser indeed secondary fragmentation can be suppressed ⟹ by the time the first photoion events have occurred the laser has already terminated. The upper mass spectrum (psec) is therefore hard showing any small mass fragments. For comparison in the lower spectrum the results for nsec-laser excitation are displayed.

Statistical Model for the Fragmentation of Benzene by Multiphotonionization

(F. Rebentrost, A. Ben-Shaul)

Fragmentation tree with consecutive branchings

$$C_mH_n^+ \rightarrow C_kH_l^+ + C_{m-k}H_{n-l}$$

Obtain probability function

$$P_{ij}(E_i, E_j) = \alpha_{ij}\, \rho_j(E_j) \times \int d\epsilon_t\, \rho_n(E_n - \epsilon_t)\, \rho_t(\epsilon_t) / \Omega_i(E_i)$$

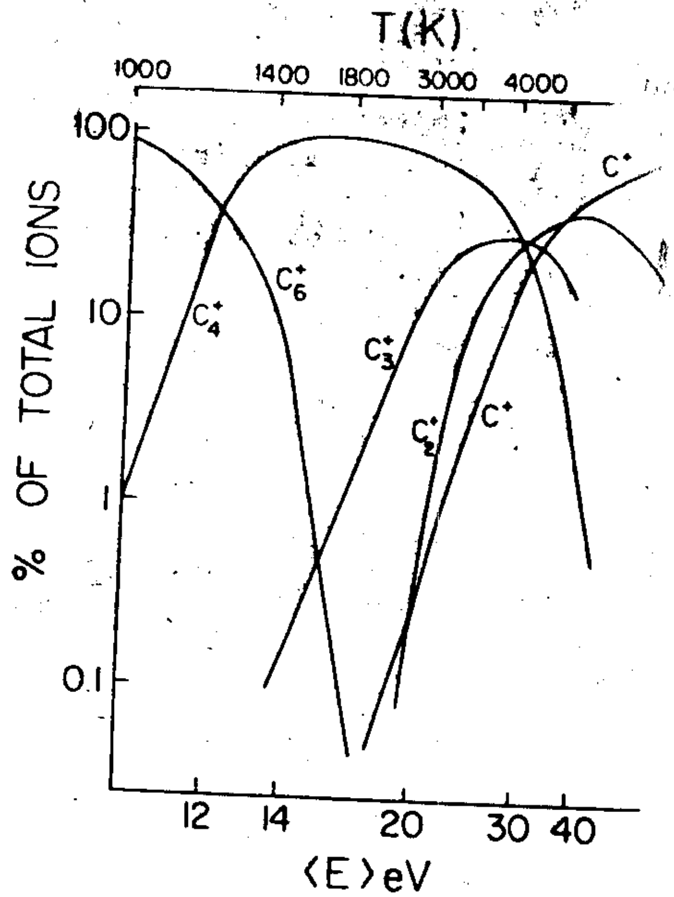
ρ_j, ρ_n internal state densities of product ion j^+ and its corresponding neutral

Ω_i = total phase space density at Energy E_i

α_{ij} = reaction path degeneracy

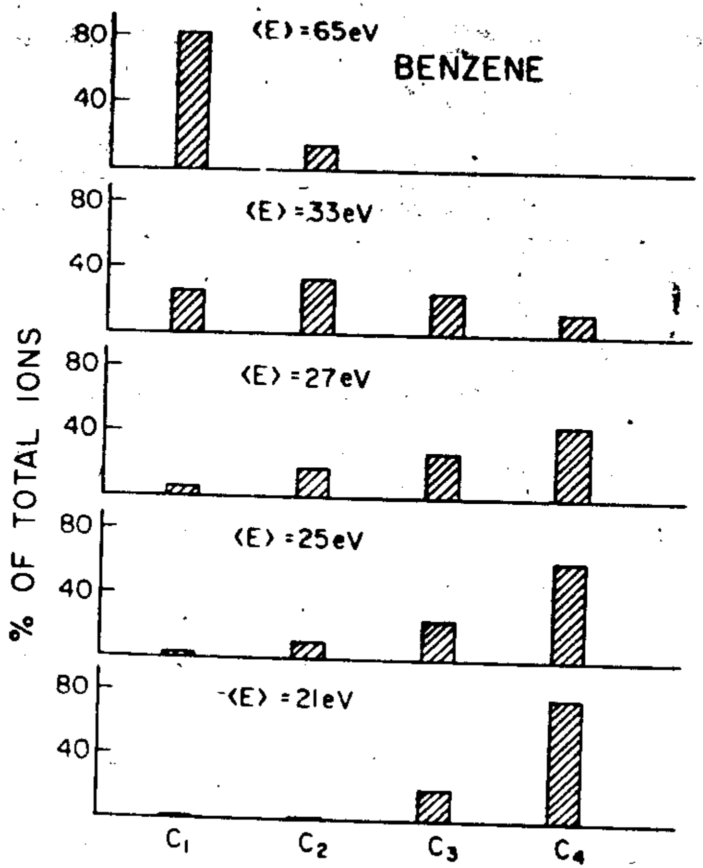
The prominent route for formation of C^+ involves the sequence

$$C_6H_6^+ \rightarrow C_4H_4^+ \rightarrow C_4H_3^+ \rightarrow C_4H_2^+ \rightarrow C_4H^+ \rightarrow C_3H^+ \rightarrow C_3^+ \rightarrow C^+$$



Statistical fragmentation sequence in conventional mass spectrometry to be compared with laser data.

Fig 2



Statistical calculation for benzene fragmentation extending the graph of p. 20; for conclusions see next page.

FIG 1

Conclusions

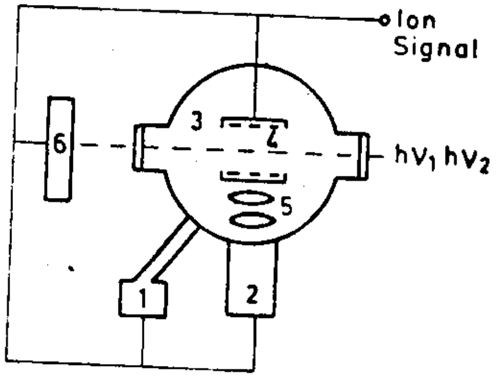
(1) Model with multiple fragmentation states good description; support for statistical content of model: (see also Silberstein and Levine)

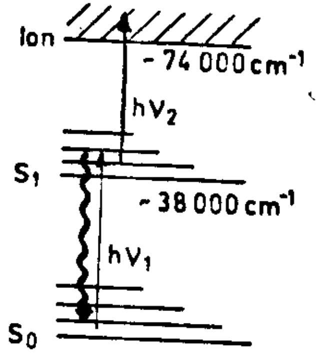
(2) Fragmentations observed by [illegible] and other methods are linked, however much higher energies can be populated

(3) Energy is the main controlling factor no laser frequency dependence expected as long as species absorb

(4) Future: Application to [illegible] suggested; Ionization spectroscopy as efficient probing technique; More information on intermediates needed for generalization; High excitation rates may lead to non-statistical behavior.

Ion current measurements and Comparison with LIF





Problems in the interpretation of 2-Photon-ionization experiments

– suggested solutions

(1) Recombination

numerical elimination

e^- scavengers

(2) Secondary ionization ($h\nu$, E/p, e^-)

choice of experimental parameters

(3) Intermediate State decay

choice of $h\nu$ and laser power

(4) Ion secondary fragmentation

p sec - pulses

low p

theoretical modelling

2-Step-Photoionization of Benzene: Rate equations

$$\frac{dN_0}{dt} = -\sigma_{ex}^{r} I(t)/h\nu \cdot (N_0 - N_1)$$

$$\frac{dN_1}{dt} = \sigma_{ex}^{T} I(t)/h\nu \cdot (N_0 - N_1) - (k_r + k_{nr}) N_1 - \sigma_{ion} I(t)/h\nu \cdot N_1$$

$$\frac{dN_2}{dt} = \sigma_{ion} I(t)/h\nu \cdot N_1$$

approximately (S_{Fl}, S_{ion} are the numbers of photons and ions)

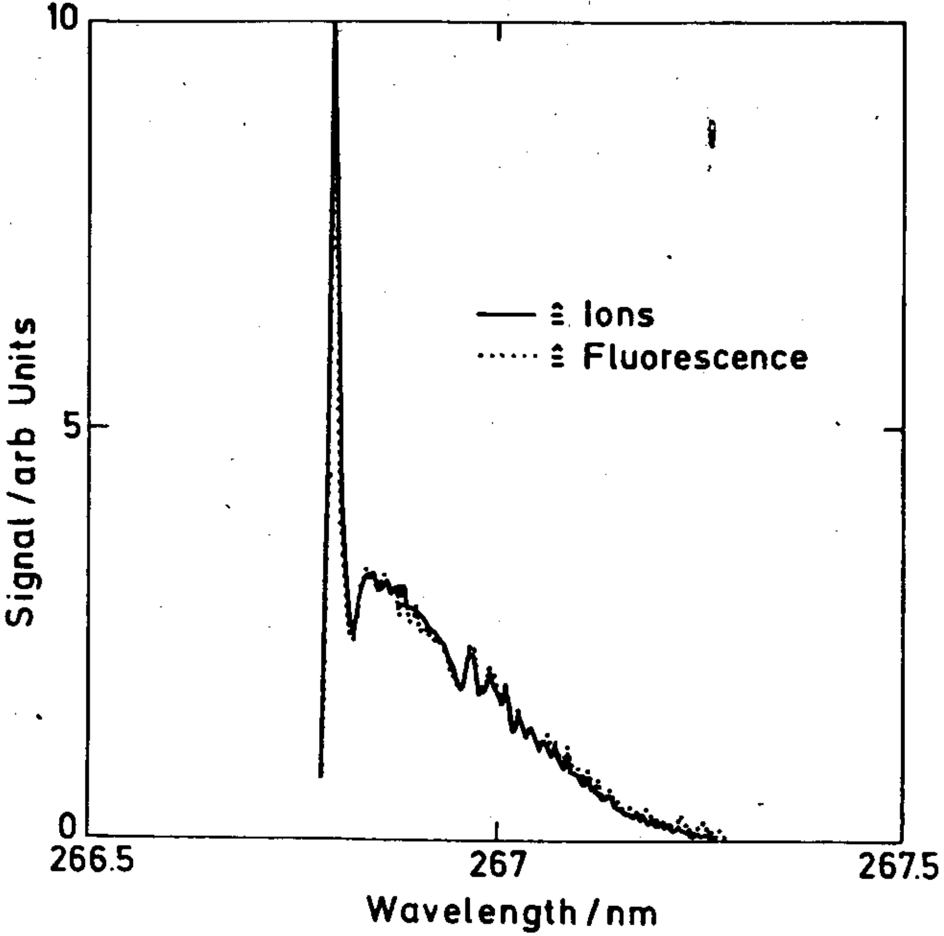
$$S_{Fl} = c_1 \sigma_{ex}^{ph} \cdot E \cdot N \cdot F/L$$

$$S_{ion} = c_2 \sigma_{ex}^{ph} \sigma_{ion} \cdot E^2 \cdot N \cdot F/L$$

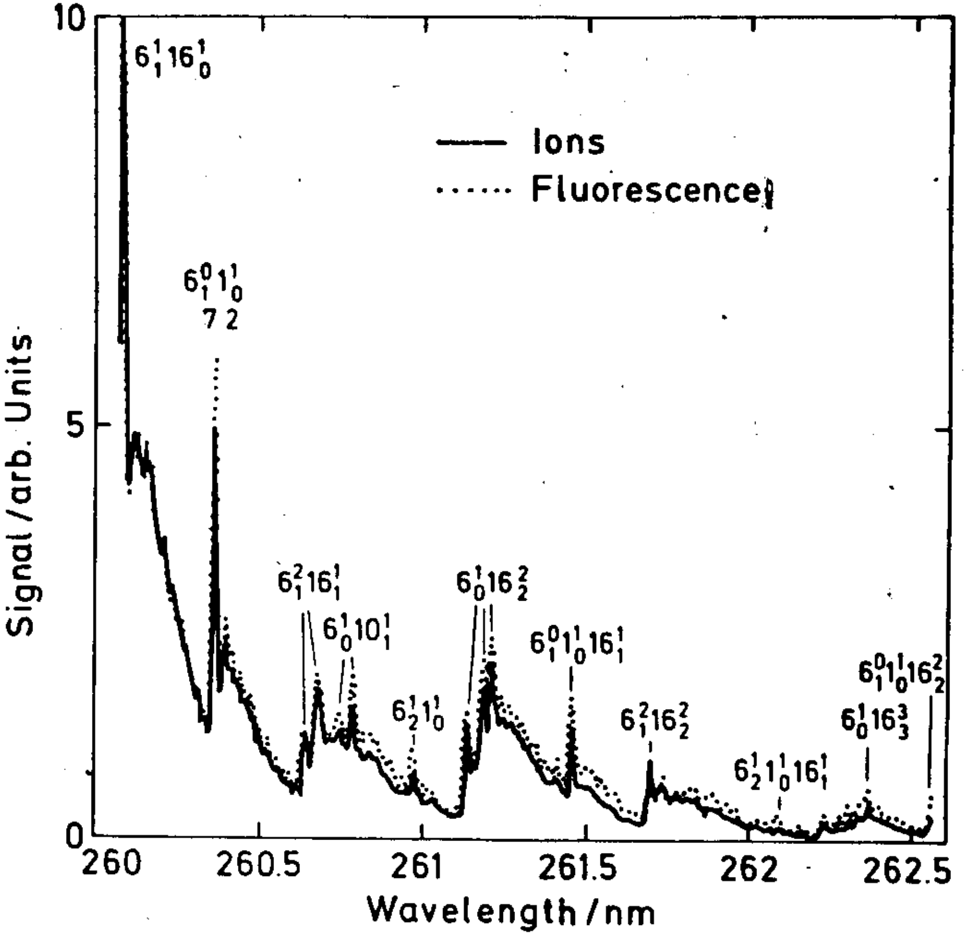
Ionization out of $6_0^1 16_1^1$ in S_1 ($\lambda = 260.08$ nm)

$$\sigma_{ex}^{ph} \approx 1.3 \cdot 10^{-18}\ \mathrm{cm}^2$$

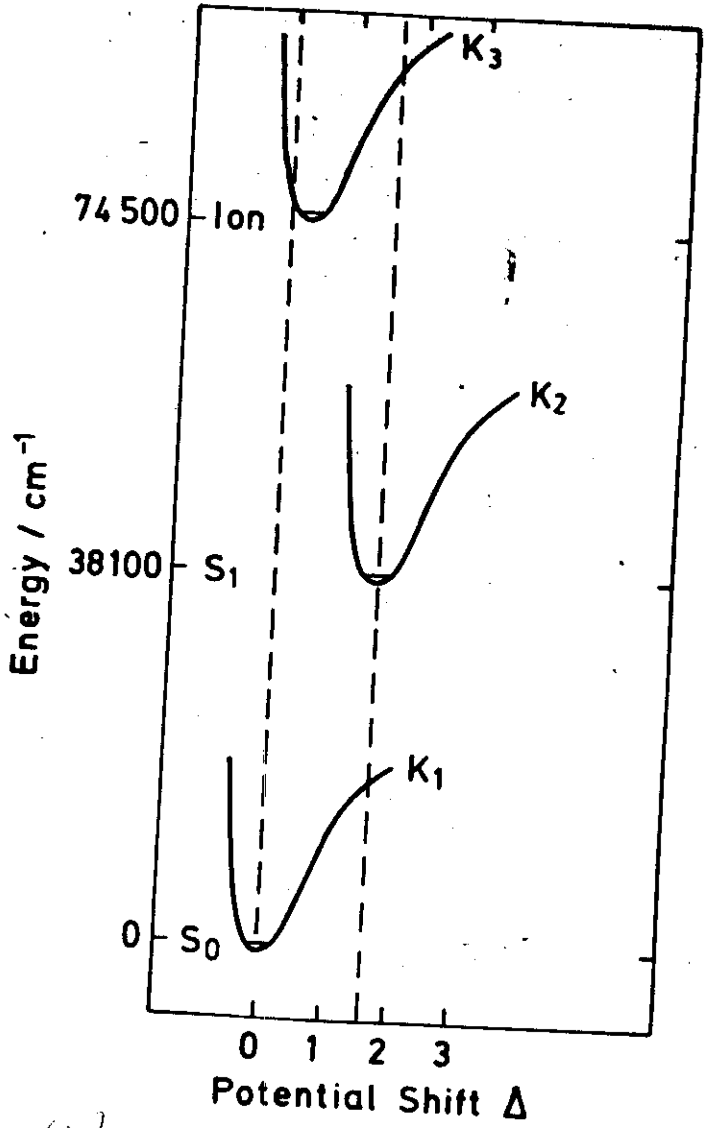
$$\Rightarrow \sigma_{ion} = 2.6 \pm 0.5 \times 10^{-17}\ \mathrm{cm}^2$$



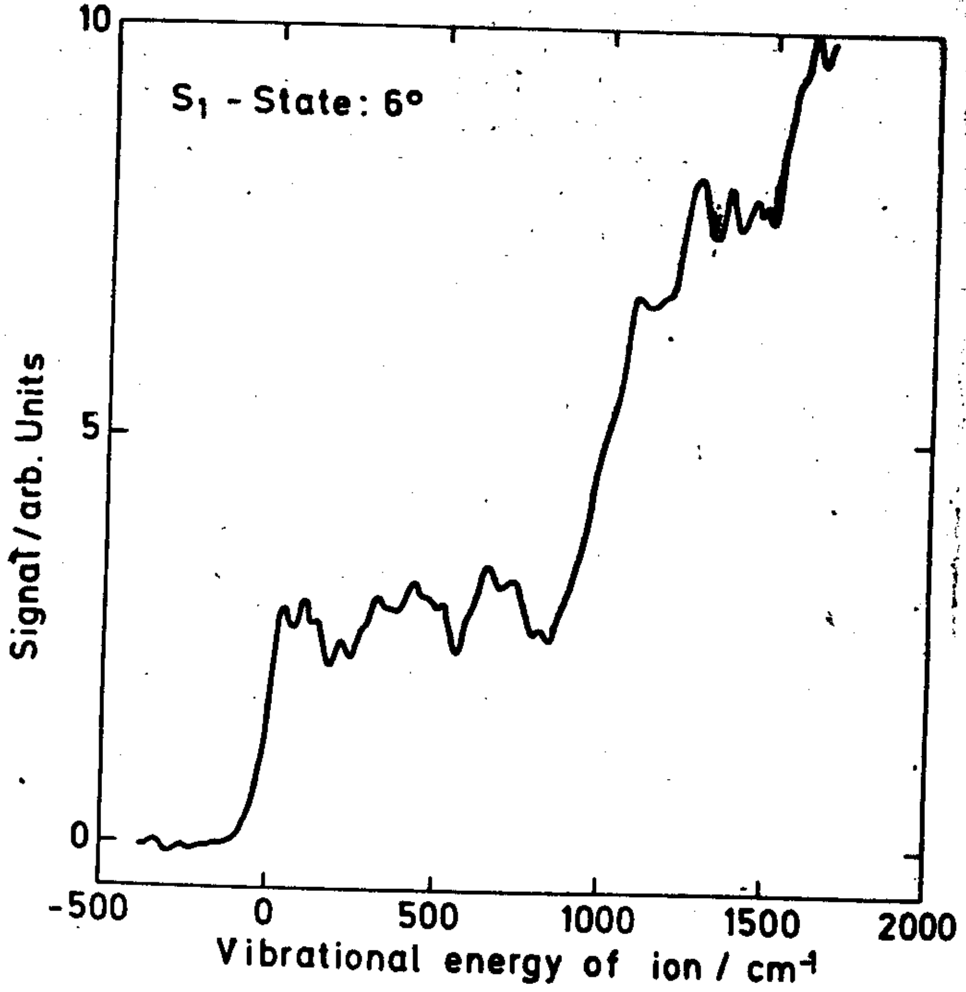
With suitable care the ion and LIF spectra seem to overlap in some spectral ranges: No features added by the second step $S_1 \Rightarrow X^+$



On an extended spectral scale differences between ion and LIF spectra appear: No new spectral lines are seen, however, intensities (= probabilities for ionization from certain vibronic levels in S_1) change ⇒ Franck Condon factors different?



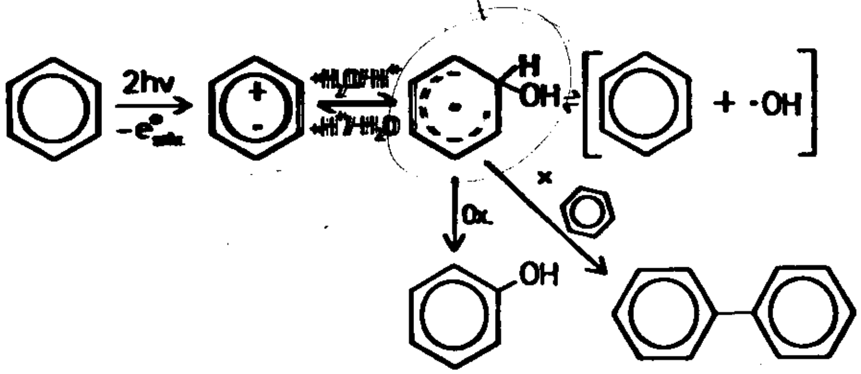
Exemplification of Franck-Condon argument on p. 97 for one partial normal coordinate



At the onset of ionization the yield of ions increases discontinuously (stepwise). The steps should be related to ion vibrational levels but no simple relationship found so far: Work in progress.

[redacted]

Ionic Photochemistry: Opposed to the one-photon product which is much different 2-Photon excitation yields phenol C_6H_5-OH as an interesting product. This can be generated through the same intermediate also in radiation chemistry.



Bildung des Hydroxycyclohexadienyl-Radikals

Conclusion: Ionic photochemistry works! Other substitution reactions (to introduce other substituents into the benzene ring) can be carried out in the same way.