INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392-I

SMR/100 - 67

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(24 January - 25 March 1983)

# Lasers in Chemistry II

H. SCHRÖDER

Max-Planck-Institut für Quantenoptik
8046 Garching bei München
Fed. Rep. Germany

## Problems in Laser Isotope Separation

the photon absorption is very weak

(1) multiphoton processes

(2) small pressure ( no collisions ! )

(3) small concentration of the rare isotope

---

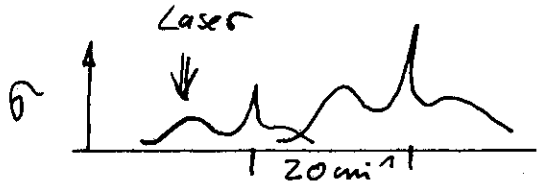
possible solutions

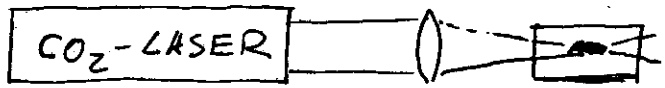
(1) longer path lengths by reprocessing

(2) higher pressure with shorter pulses

(3) increase of the absorption cross section with a broad band laser or with 2 laser frequencies

## Laser isotope separation by IR multiphoton excitation is in principle very simple




$p \leq 0.5$ mbar

$\phi_c \gtrsim 12$ J/cm²

$$^{32}SF_6 \xrightarrow{h\nu} {}^{32}SF_4 \xrightarrow{OH^-} H\,{}^{32}SO_3^-$$

$$CF_3I \xrightarrow{h\nu} CF_3 + I \longrightarrow C_2F_6 + I_2$$

$-22.5°$ $\quad -81°$

| | $SF_6$ | $CF_3I$ |
|---|---|---|
| abundance | $^{32}S : {}^{34}S$ | $^{12}C : {}^{13}C$ |
| natural | 95 : 4.2 | 98.9 : 1.1 |
| after separation | 20 : 80 | 45 : 55 |
| Laser frequency | 944.2 $cm^{-1}$ | 1072.2 $cm^{-1}$ |
| laser energy/shot | 20 J | 8 J |
| | 17000 | 2000 shots |
| Yield | 10 mmol | 10 mmol |
| | 1.5 g $^{32}SF_6$ | 2 g $^{12}CF_3I$ |
| expense | 1500 Quanta/molec. | 100 Quanta/molec. |
| | ≙ 15 Mol Quanta | 1 Mol Quanta |
| absorbed energy | 20% | 40% |

Scaling of ...

| | | |
|---|---|---|
| Laser energy | $E_L$ | $\left.\begin{matrix}\\\\\end{matrix}\right\} \phi_L = \frac{4E_L}{\pi D^2}$ |
| diameter | $D$ | |
| divergency | $N_F \lambda / D$ | |
| pulse length | $t_p$ | |

---

| | |
|---|---|
| max. molecular density | $1/l \cdot t_p = n_m$ |
| absorption length | $1/\sigma \cdot n_m = L_m$ |
| N. of absorbed quanta for dissociation | $q_m$ |
| → energy density | $\phi_m = q_m/\sigma$ |

---

Rayleigh length $\quad L_R = D^2/\lambda N_F$

---

you have to refocus the beam at $\quad L_{ref.} = L_R \phi_L / \phi_m$

N. of refocussing $\quad z = L_m / L_{ref.}$

$$z = \left(\frac{\pi\lambda}{4}\right) \frac{N_F t_p}{E_L} + \frac{1}{\sigma^2}$$

## Irradiation of the rare isotope

abundance $h$

$\Longrightarrow$ $\tau_i = h^{-1} \tau_0$

$L_{mi} = h^{-1} L_{mo}$

max. number of refocussing : 50

$N_F = 1$

| | $h$ | $\sigma$ [cm²] | $\Phi_m$ [J/cm²] | 100ms | 3 µs |
|---|---|---|---|---|---|
| $^{13}CF_3Br$ | 0.011 | $10^{-19}$ | 2.5 | 0.6 J | 18 J |
| $CF_3D$ | $1.5 \cdot 10^{-4}$ | $7 \cdot 10^{-20}$ | 10 | 240 J | |

Mechanism of IR multiphoton excitation is basically a spectroscopic question:

**Why can molecules absorb tens of photons without completely moving out of resonance?**

Determine level positions, anharmonicities ... (from relatively low levels)

High vibrational states:
Spectral widths are not much different to those of fundamentals

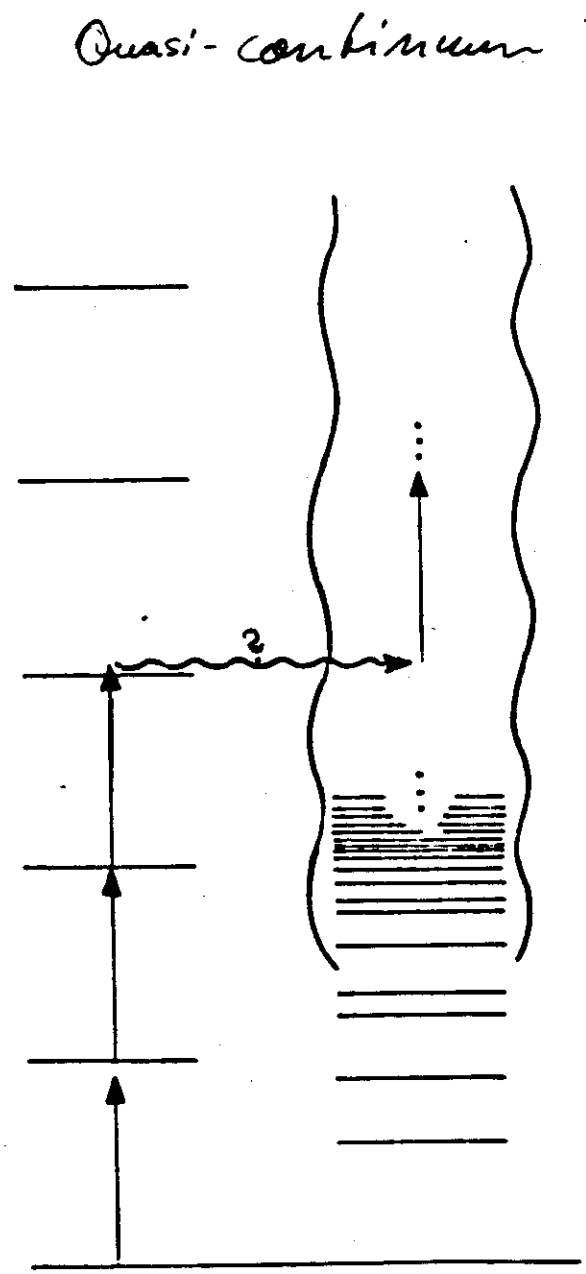
1) Evidence
2) How does the molecule come up ? (Survey of contributing mechanisms)
3) Understanding details

Table 3. Infrared bands close to multiphoton excitation frequencies

| Molecule | excited at ($cm^{-1}$) | IR bands ($cm^{-1}$) and relative intensities |
|---|---|---|
| $O_3$ | 1037.4 /9/ | 1042.1 /335/<br>1103.2 |
| $CF_3Br$ | 1040-1082.3 /46-49/ | 1084 (1) /335,336/<br>1095 (0.1)<br>1119.6 (0.1) |
| $CF_3I$ | 1028.1-1082.3 /49-62/ | 1028.1 (0.1) /335,337/<br>1075.2 (1)<br>1081.0 (0.1) |
| $CF_2Cl_2$ | 920.8-931.0<br>1081.1-1080.0 /31-41/ | 882 (0.3) /338/<br>992 (1)<br>1102 (1) |
| $CrO_2Cl_2$ | 969-984 /65/ | 990<br>1000 single band /65/ |
| $CH_3CN$ | 933.0, 1046.9 /88-91/ | 920 (1) /336/<br>1041 (1) |
| $N_2F_4$ | 944.2, 975.9 /31a,113, 114/ | 933 to 1031 /339/<br>(7 strong bands) |
| $CH_3NH_2$ | 1031.5-1070-5 /115, 118-120/ | 931 (0.1) /336/<br>945 (0.1)<br>1044 (1)<br>1140 (0.3) |
| $SF_5Cl$ | 904.9, 914.9 /126,127/ | 909 /340/<br>947<br>1029 |
| $SF_6$ | 930-1056 /5/ | 948 (1) /333/<br>992 (0.01)<br>1140 (0.001) |
| $C_2H_5Cl$ | 973.3 /206/<br>2850-3050 /21/ | 974 (2 modes9 (1) /21,335/<br>1081 (0.06)<br>2880 to 3013<br>(5 strong bands) |
| $C_2F_6$ | 1087.9 /210/ | 1025 (0.005) /336/<br>1063 (0.005)<br>1117 (1) |
| $CF_3COCF_3$ | 944.2-983.3 /225-229/ | 971 (1) /336<br>1027 (0.05)<br>1070 (0.05) |
| $SF_5NF_2$ | 908.5-957.8 /224/ | 885 ( 1) /22.<br>910 ( 1)<br>950 ( 1)<br>and several less intense bands |
| $S_2F_{10}$ | 920.8-944.2 /178/ | 909<br>938<br>960 |

Fup, Kompa PLE 30 (1980)





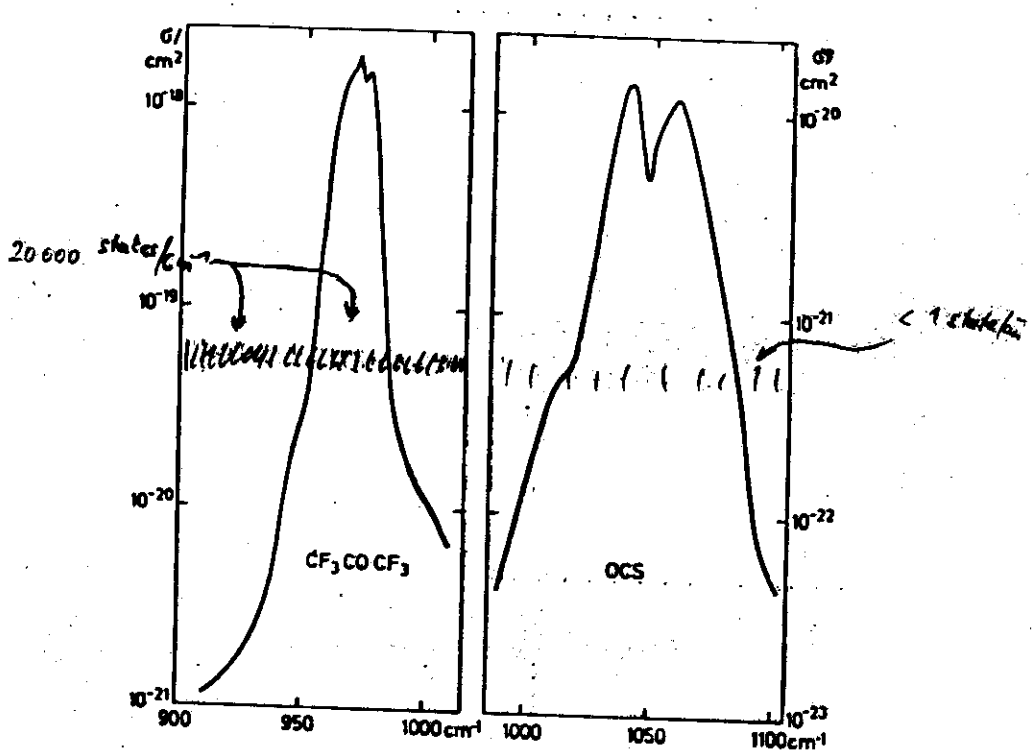



Fig. 1 Infrared spectra of a small molecule (carbonyl sulfide) and of a molecule (hexafluoroacetone), which is in the quasicontinuum of states at 313 K, the temperature of measurement. Spectral slit width was 1 $cm^{-1}$. Higher resolution reveals rotational structure and a slightly higher cross section for COS.

Fuß, Kompa PLF 30 (1980),
Progr. Quantum El. (1981)



$CF_3Br \xrightarrow{e\text{-impact}} CF_3Br^+(v) \xrightarrow{h\nu_{CO_2}} CF_3^+$

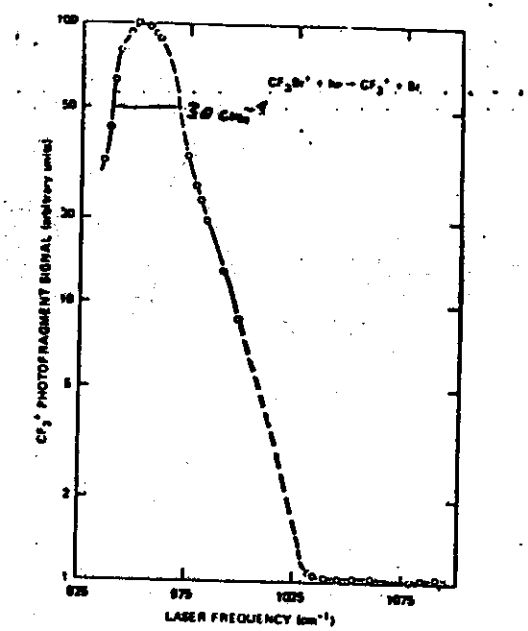
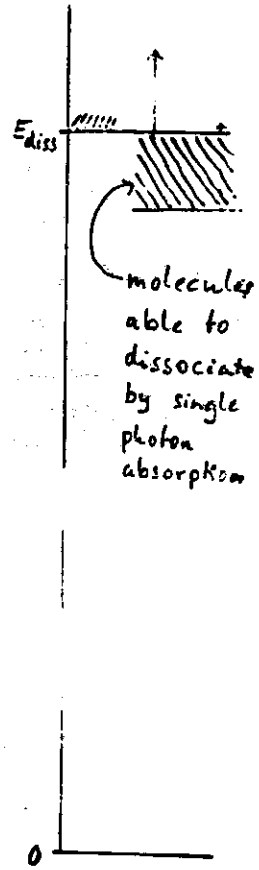
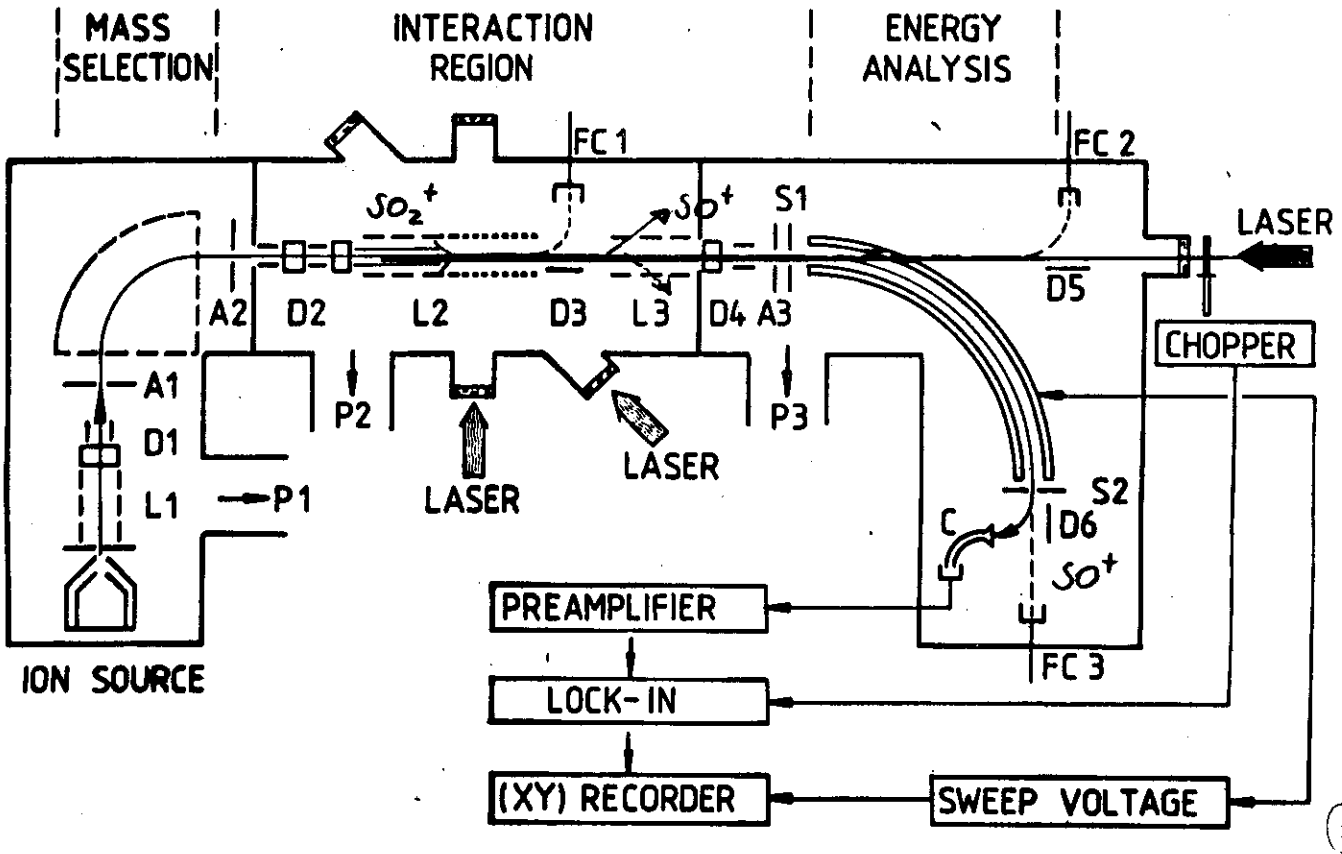



FIG. 4. Frequency dependence of $CF_3^+$ fragment yield from $CF_3Br^+$ corrected for laser power variations. Dashed line indicates $CO_2$ laser tuning gaps.

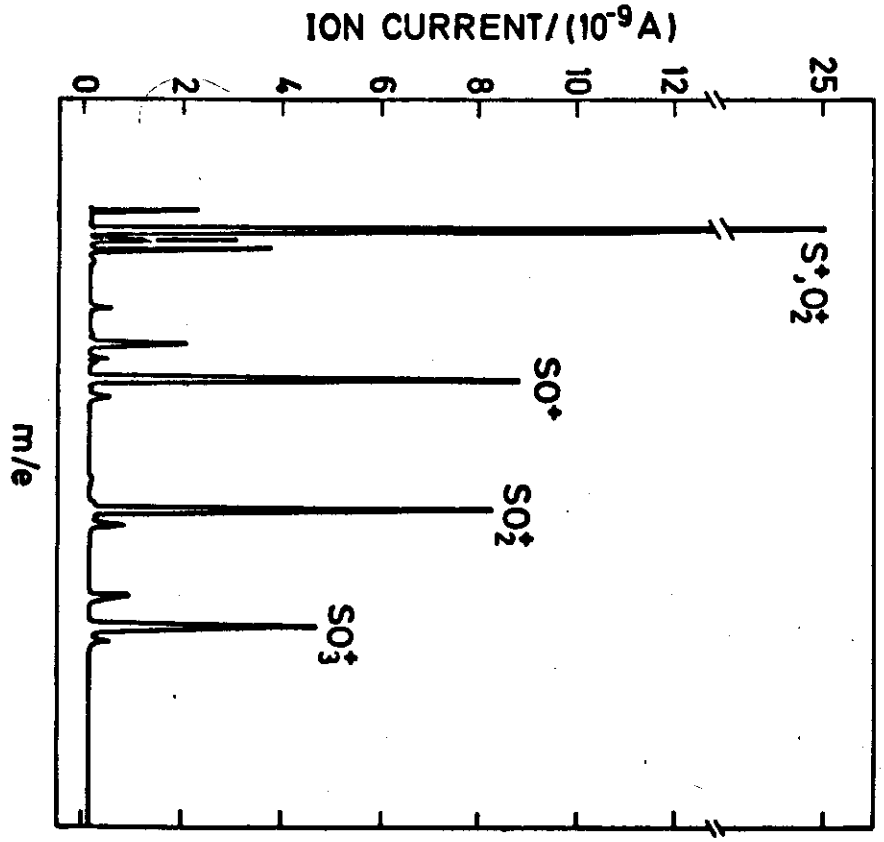
Coggiola, Cosby, Peterson
J. Chem. Phys. 72 (1980) 6507



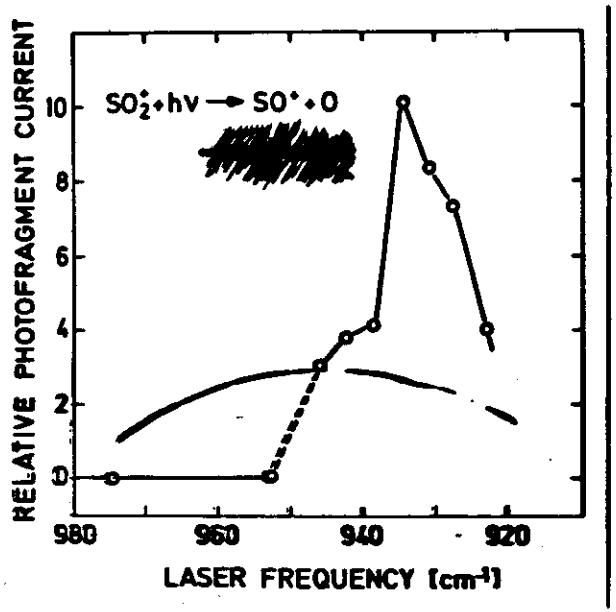
H. Stein


MASS SELECTION
INTERACTION REGION
ENERGY ANALYSIS
FC 1
FC 2
$SO_2^+$
$SO^+$
S1
LASER
A2
D2
L2
D3
L3
D4
A3
D5
CHOPPER
A1
D1
L1
P1
P2
P3
LASER
LASER
C
S2
D6
$SO^+$
PREAMPLIFIER
FC 3
ION SOURCE
LOCK-IN
(XY) RECORDER
SWEEP VOLTAGE

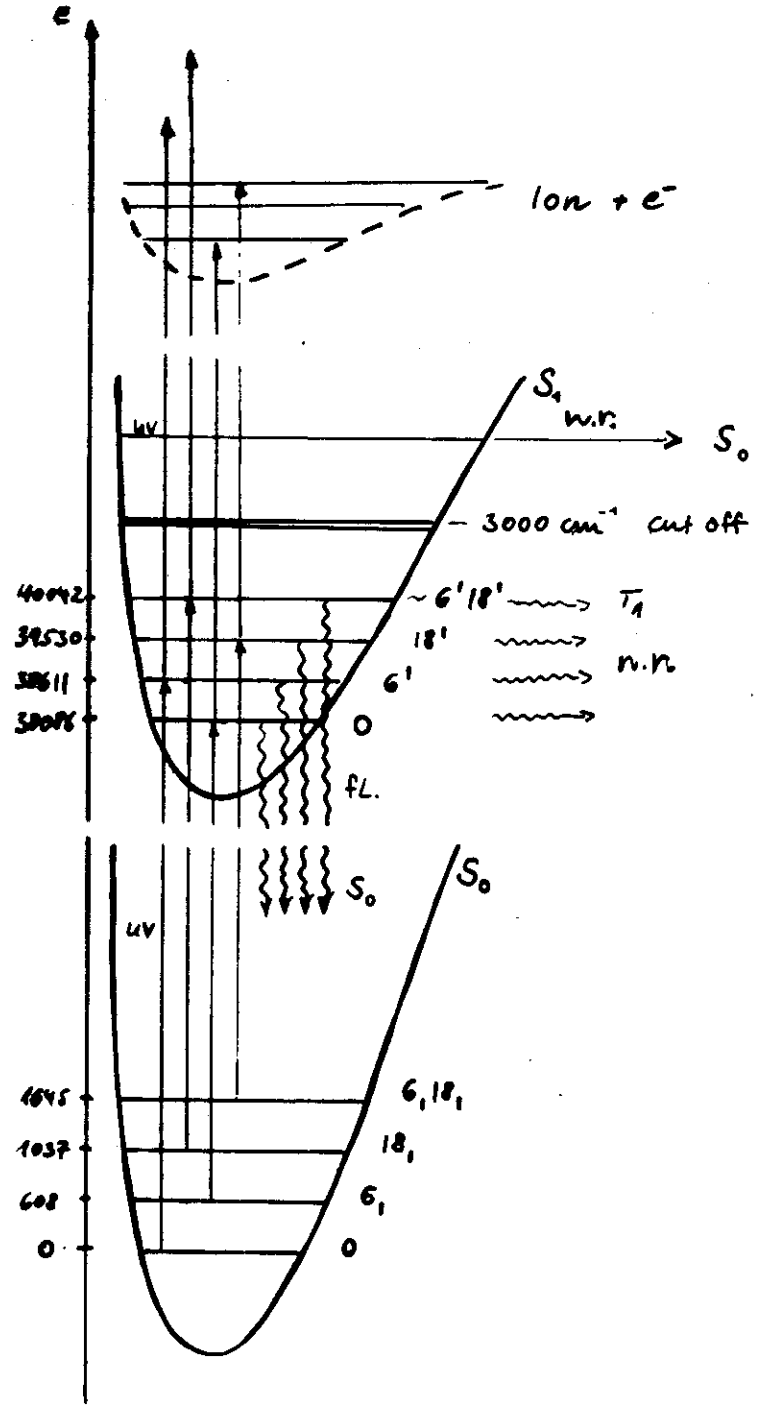
(11)


ION CURRENT/($10^{-9}$ A)
0
2
4
6
8
10
12
25
m/e
$S^+,O_2^+$
$SO^+$
$SO_2^+$
$SO_3^+$

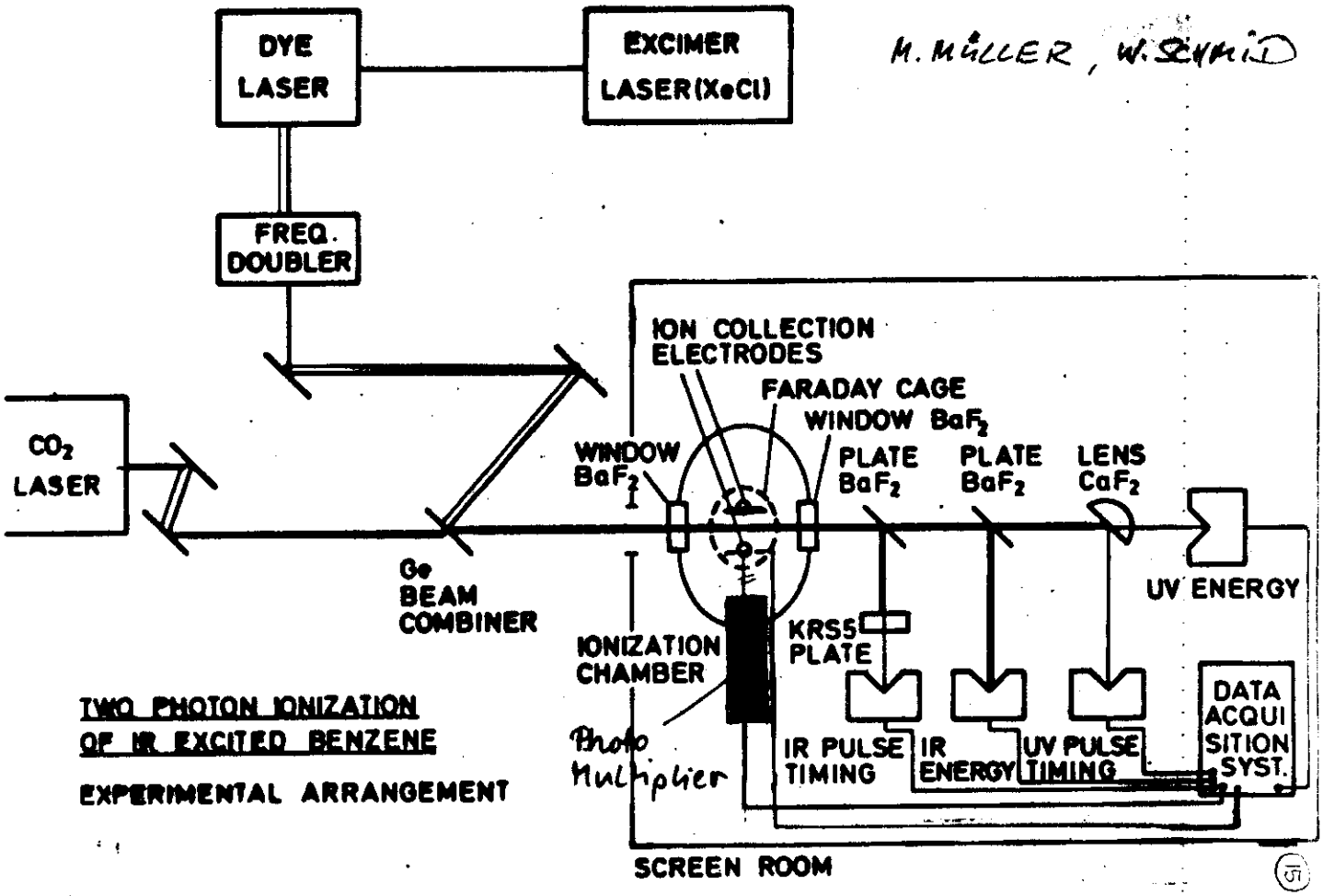
(12)


RELATIVE PHOTOFRAGMENT CURRENT
$SO_2^* + h\nu \rightarrow SO^* + O$
10
8
6
4
2
0
980
960
940
920
LASER FREQUENCY [cm⁻¹]




E
Ion + e⁻
$S_1$
n.r.
$S_0$
UV
3000 cm⁻¹ cut off
40042
39530
38611
38098
~ 6'18'
18'
6'
0
$T_1$
n.r.
fl.
$S_0$
$S_0$
UV
1645
1037
608
0
$6_1 18_1$
$18_1$
$6_1$
0

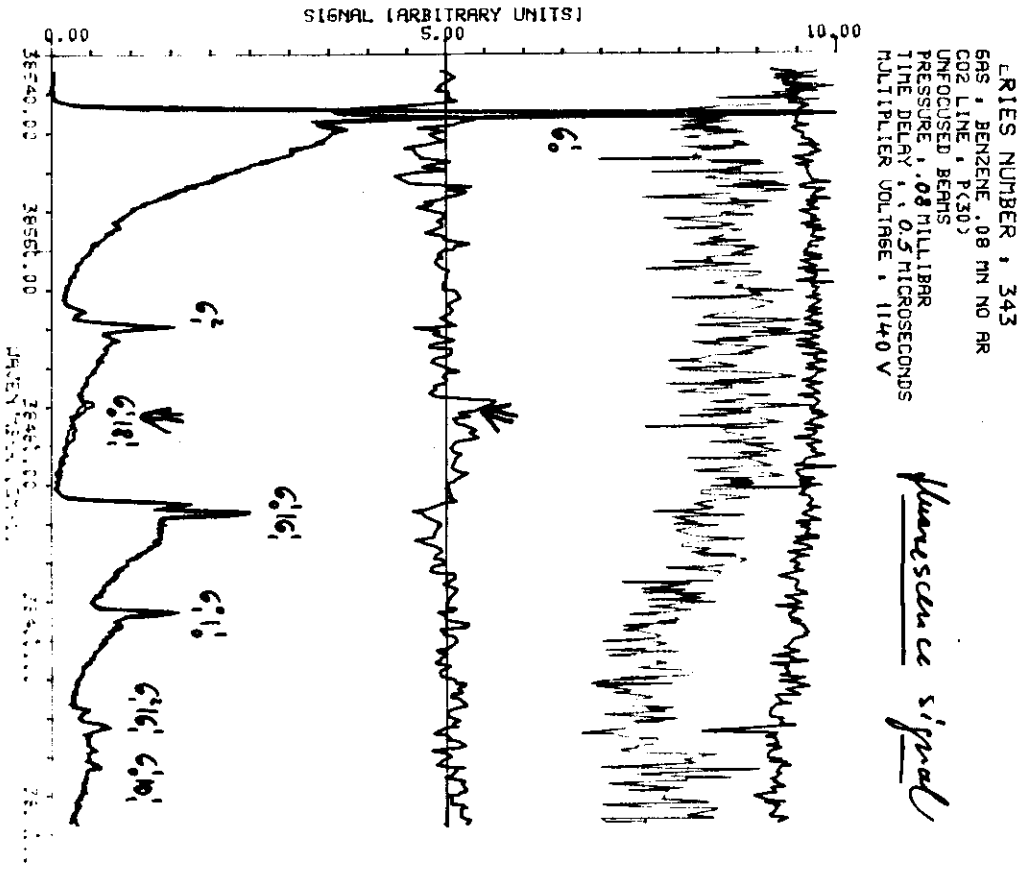
M. MÜLLER, W. SCHMID




TWO PHOTON IONIZATION OF IR EXCITED BENZENE

EXPERIMENTAL ARRANGEMENT

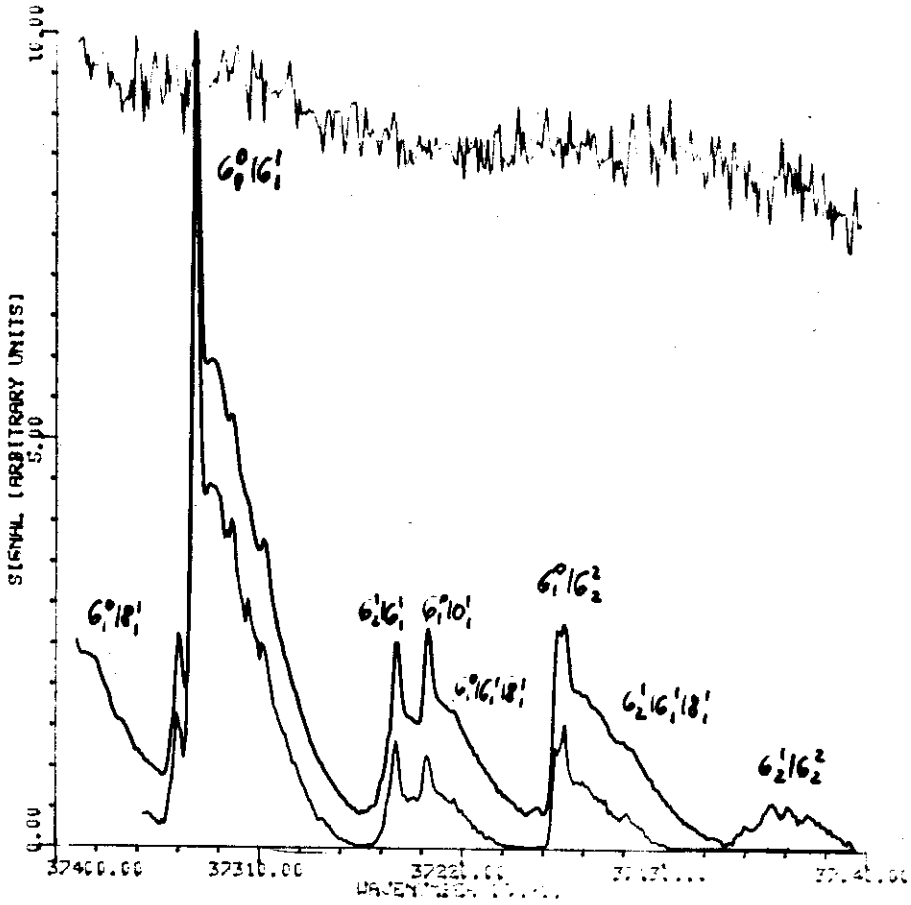
(15)



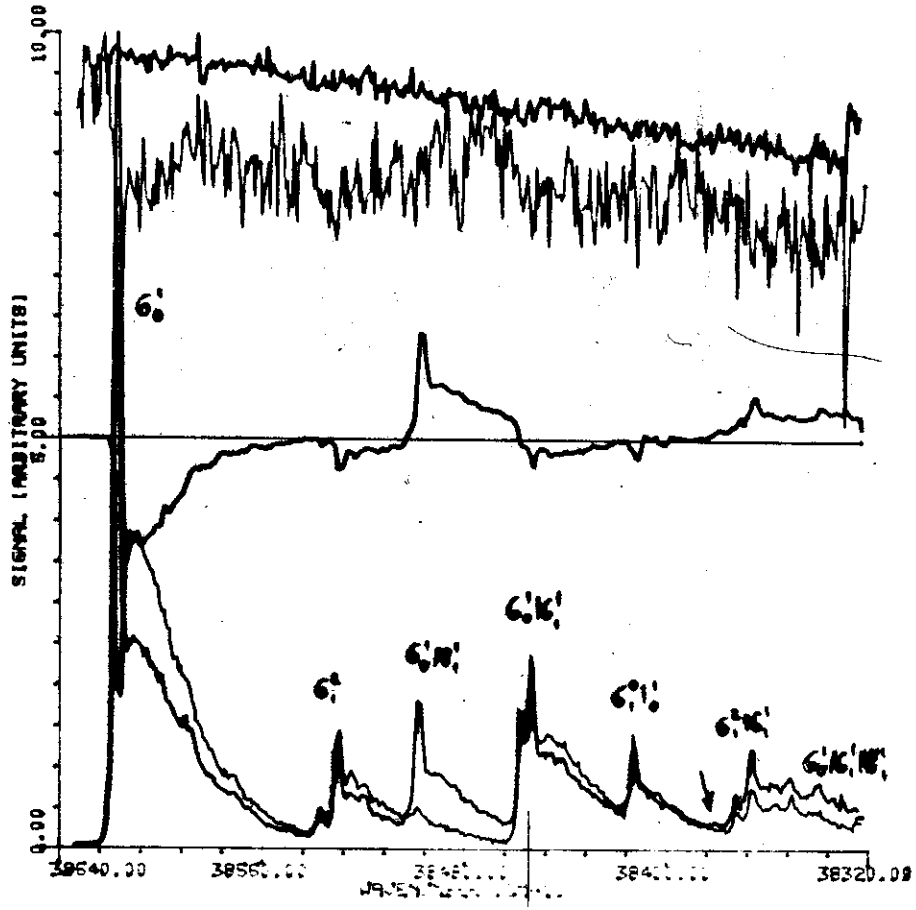

(16)

GAS : BENZENE
CO2 LINE : ABS
UNFOCUSED BEAMS
PRESSURE : 0.2 MILLIBAR
TIME DELAY : 0.00 MICROSECONDS

Absorption
Jon Signal




SERIES NUMBER : 341
GAS : BENZ - 0.08 MB + AR
CO2 LINE : P(28)
UNFOCUSED BEAMS
PRESSURE : 18.1 MILLIBAR
TIME DELAY : 0.5 MICROSECONDS
MULTIPLIER VOLTAGE : 1140 V



SERIES NUMBER : 374
GAS : BENZ-0.08 MB, AR TO 20 MB
CO2 LINE : P(30)
UNFOCUSED BEAMS
PRESSURE : 18.3 MILLIBAR
TIME DELAY : 0.5 MICROSECONDS
MULTIPLIER VOLTAGE : 970 V