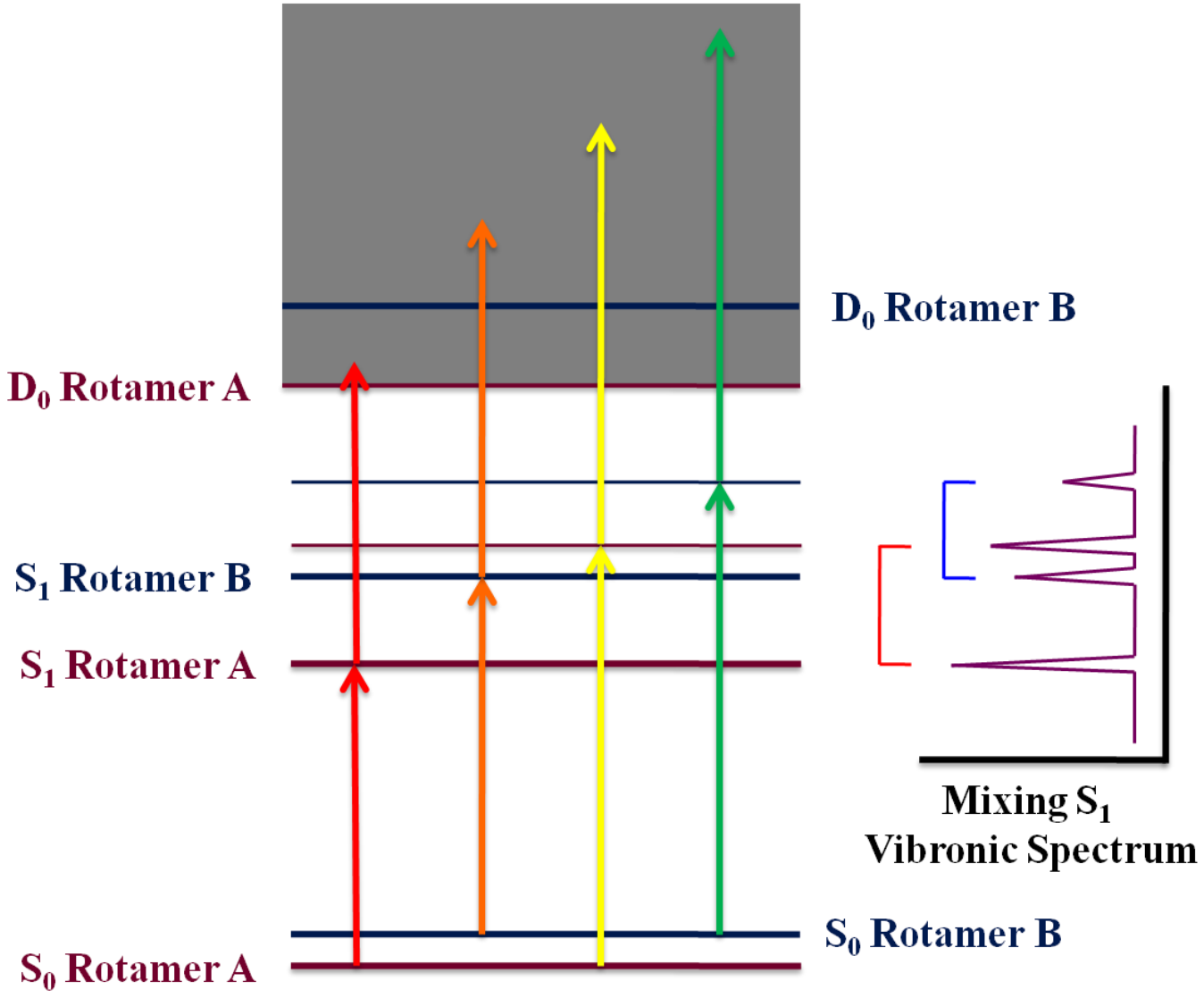
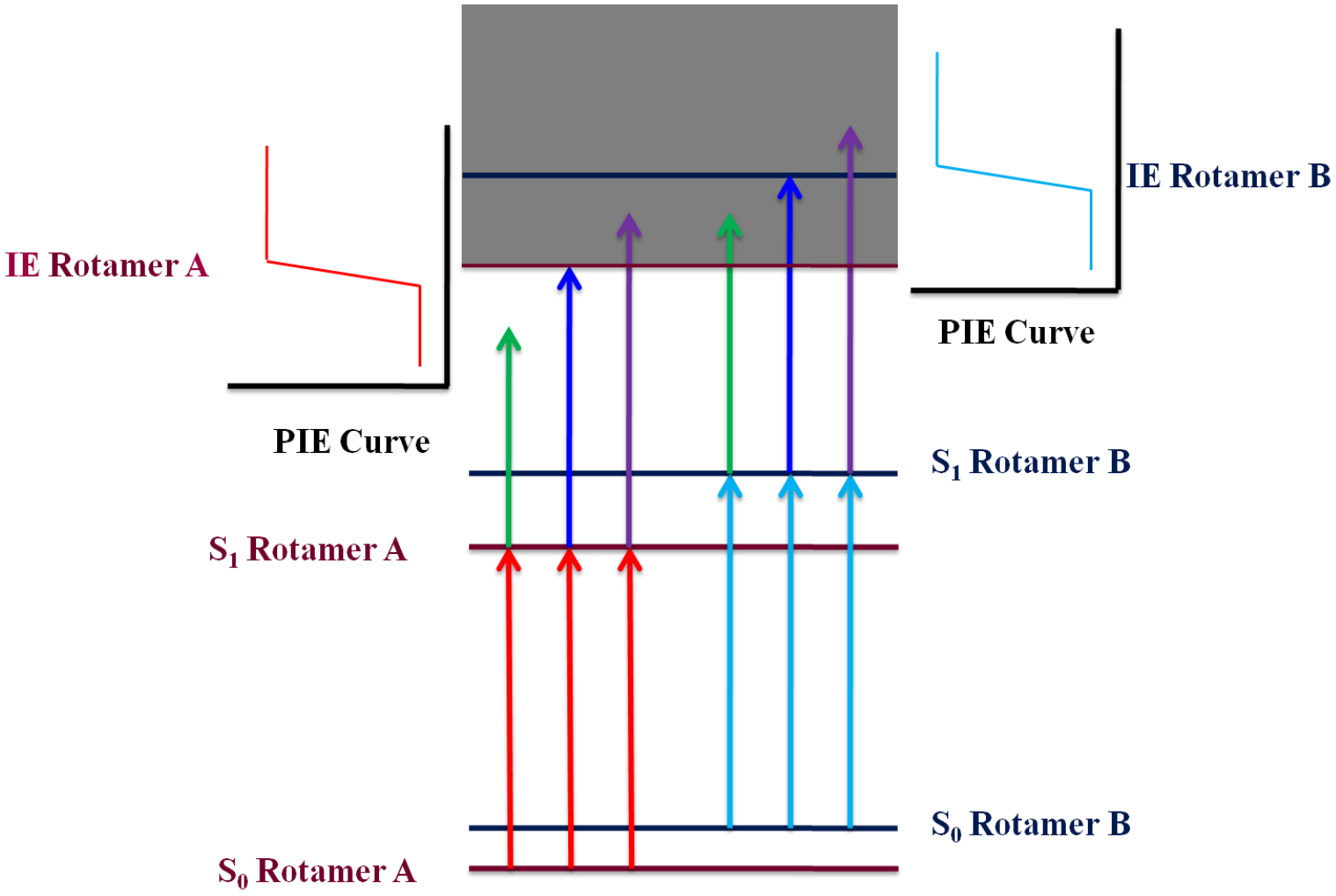
One-color resonant two-photon ionization (1C-R2PI)



Photoionization efficiency (PIE) curve By 2C-R2PI

Ionization:
Laser 2 freq. scanned

Excitation:
Laser 1 freq. fixed (species selection)



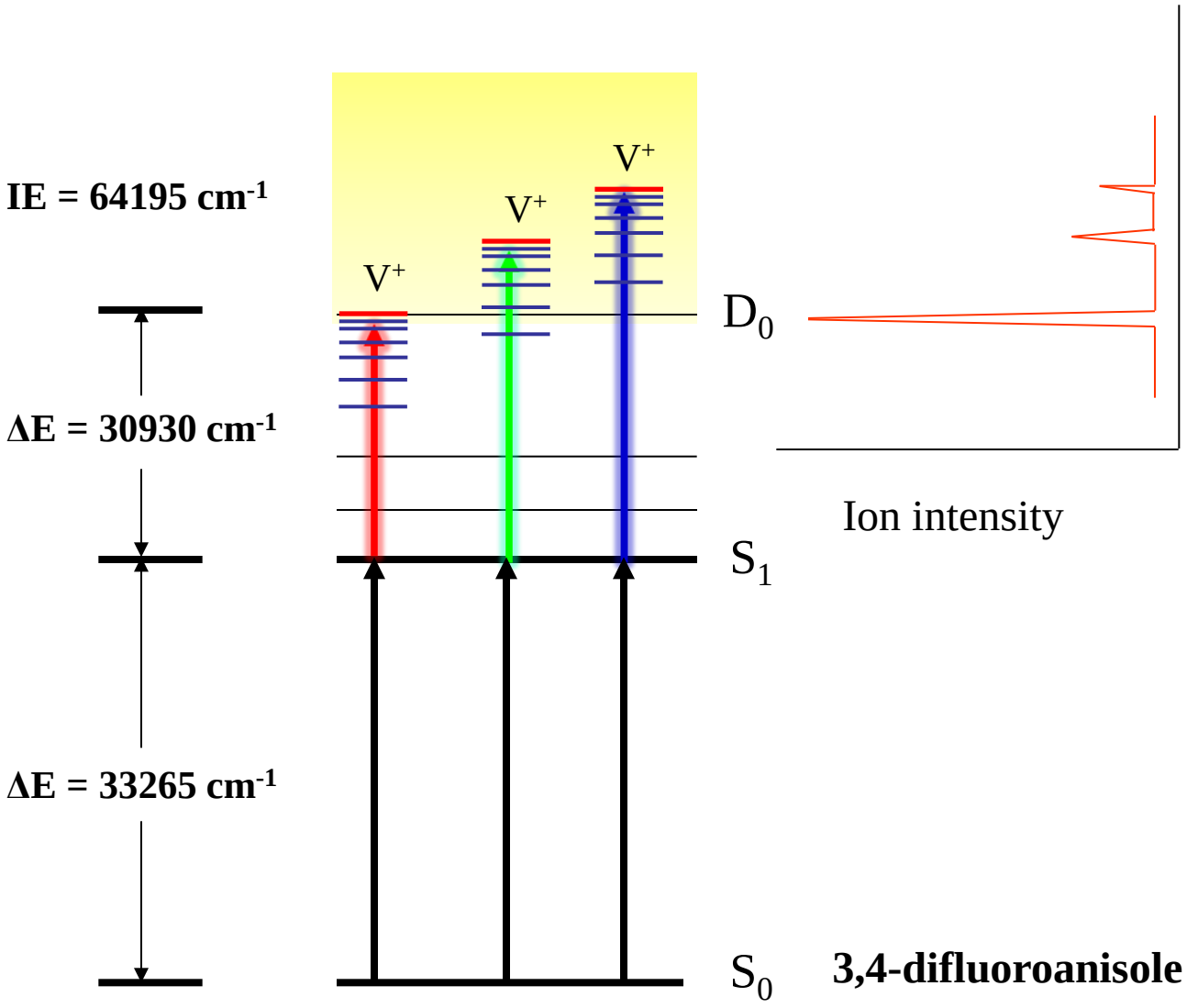
Mass-analyzed threshold ionization (MATI)

PFI after 10 µs

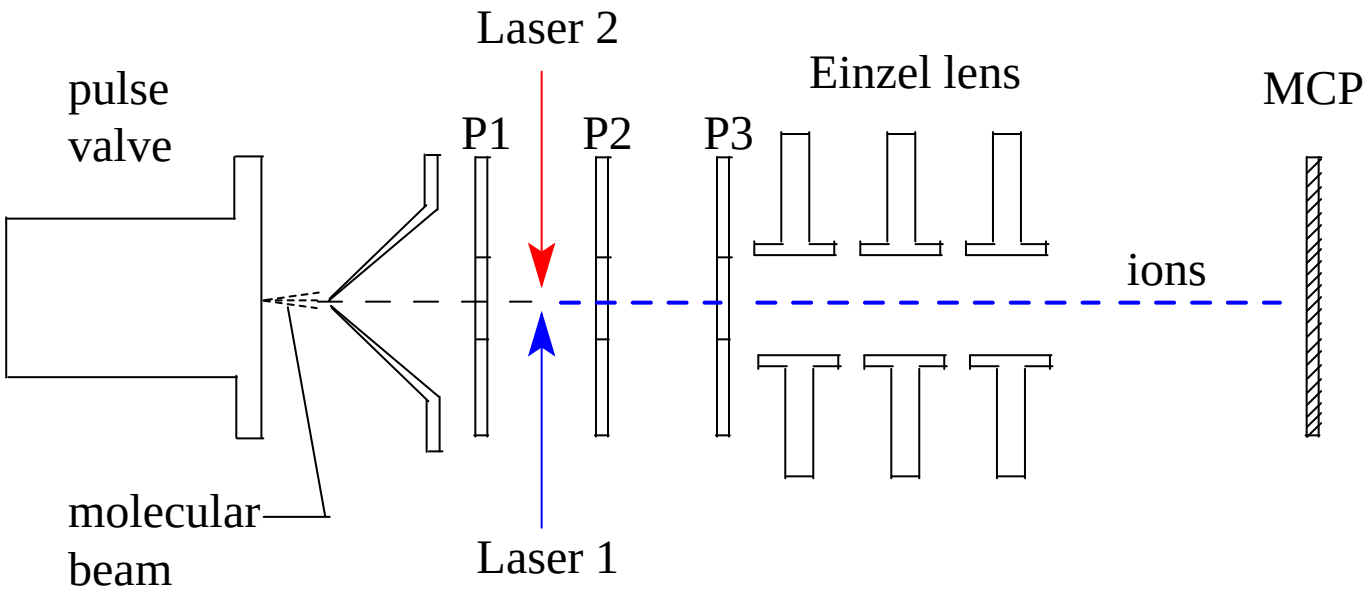
Excitation: Laser 2 freq. scanned

Excitation: Laser 1 freq. fixed

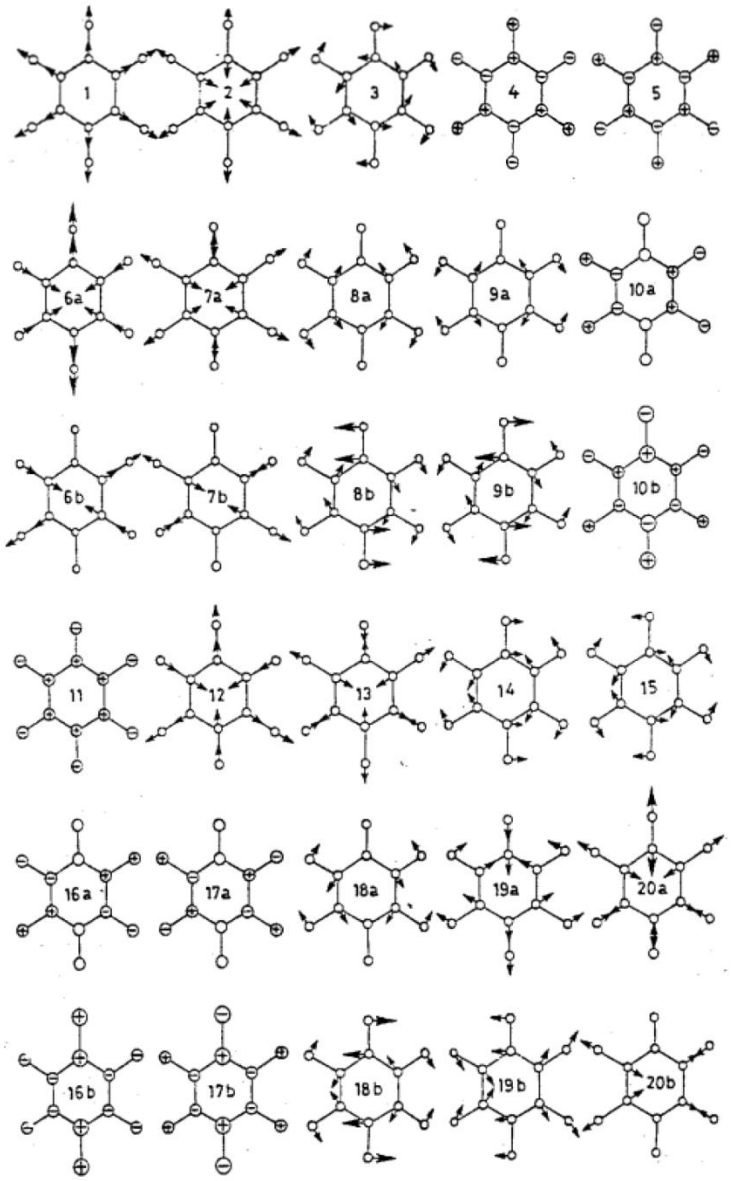
species and state selection



TOF MS for REMPI and MATI experiments



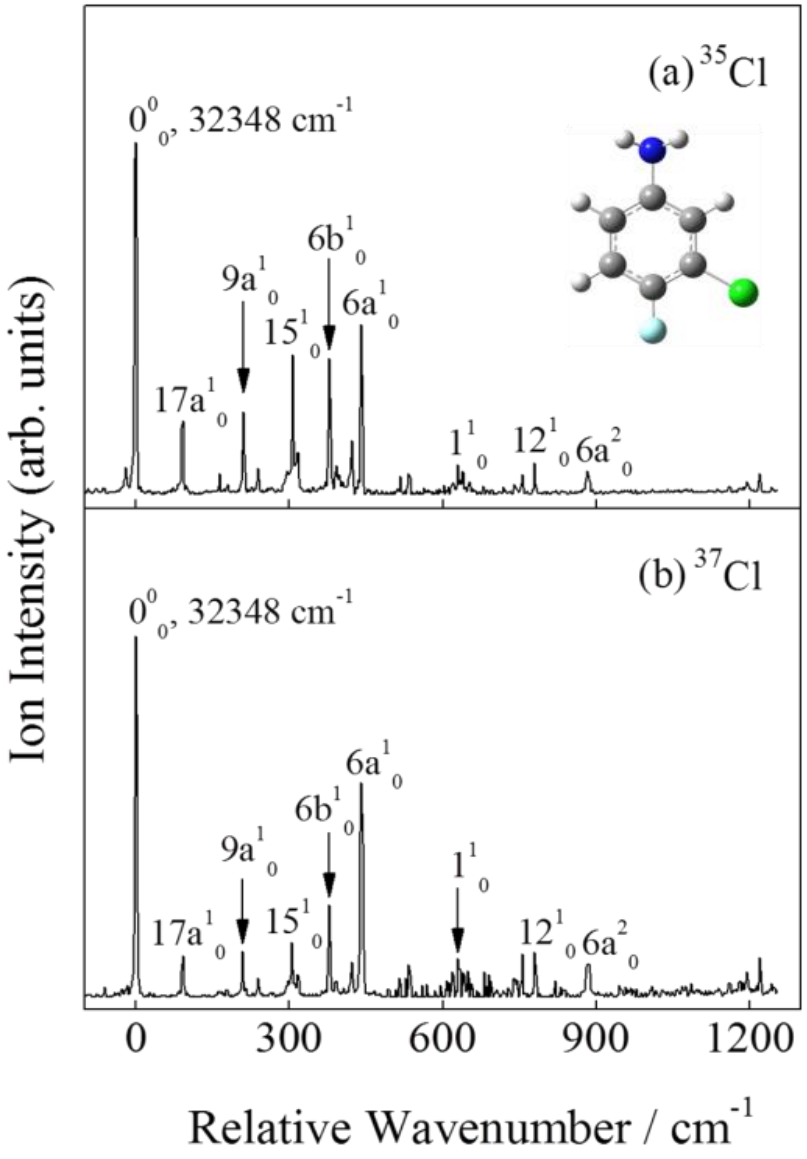
Normal vibrations of benzene



1. Tangential vibrations
   (a) C-C stretching: 8a, 8b, 19a,19b,14
   (b) C-X in-plane bending: 3, 9a, 9b, 15, 18a, 18b
2. Radial vibrations
   (a) radial skeletal: 1, 12, 6a, 6b
   (b) C-X stretching: 2,7a, 7b, 13, 20a, 20b
3. Out-of-plane vibrations
   (a) out-of-plane skeletal: 4,16a,16b
   (b) C-X out-of-plane: 5, 10a, 10b, 11, 17a, 17b

Assignment of vibrational spectra of seven hundred benzene derivatives, G. Varsanyi, Wiley, New York, 1974.

Vibronic spectra of 3-chloro-4-fluoroaniline isotopologues



recorded by using
1C-R2PI method

Substituent-sensitive bending

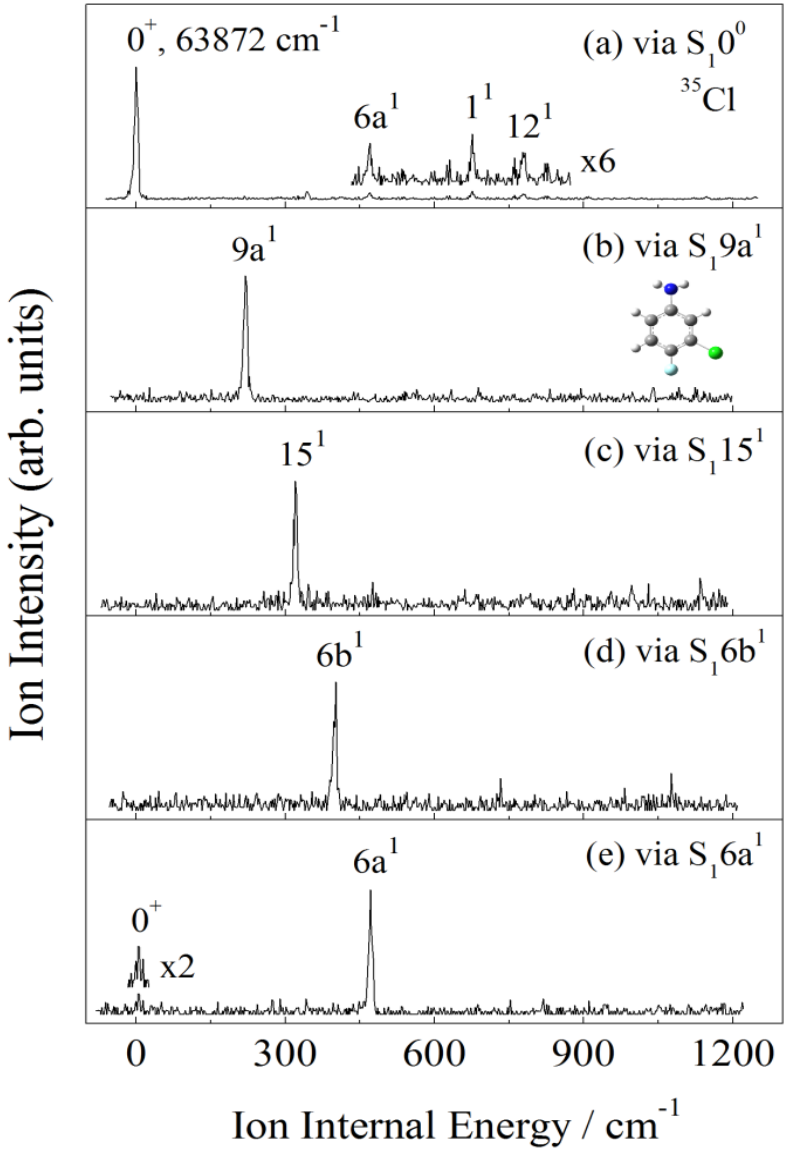
$17a^1_0$, γ(CCl), γ(CH)
$9a^1_0$, β(CCl), β(CF), β(CN)
15^1_0, β(CF), β(CN)
I^2_0, γNH(wag)

In-plane ring deformation

$6b^1_0$, β(CCC)
$6a^1_0$, β(CCC)
1^1_0, breathing
12^1_0, β(CCC)

3-Chloro-4-fluoroaniline studied by resonant two-photon ionization and mass-analyzed threshold ionization spectroscopy
K.W. Lo, W.B. Tzeng, J. Mol. Spectrosc. 288 (2013) 1-6

MATI spectra of ^{35}Cl 3-chloro-4-fluoroaniline



recorded by using
2CR2-MATI method
via 5 intermediate states

Substituent-sensitive bending

$9a^1_0$, β(CCl), β(CF), β(CN)
15^1_0, β(CF), β(CN)

In-plane ring deformation

$6b^1_0$, β(CCC)
$6a^1_0$, β(CCC)

Geometries & vibrational coordinates of $D_0 \sim S_1$

Laser Chemistry

Spectroscopy, Dynamics and Applications

Helmut H. Telle *Swansea University, UK*
Angel González Ureña *Universidad Complutense de Madrid, Spain*
Robert J. Donovan *Edinburgh University, UK*

1807 BICENTENNIAL WILEY 2007 BICENTENNIAL

John Wiley & Sons, Ltd

Page 254

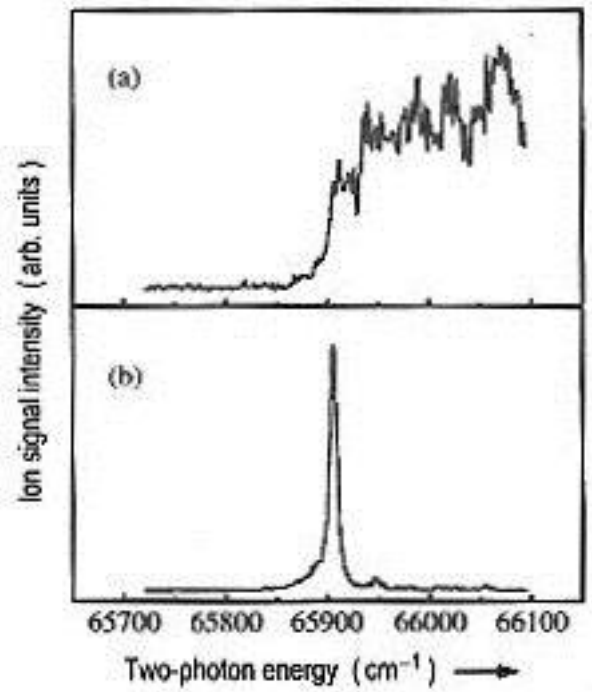
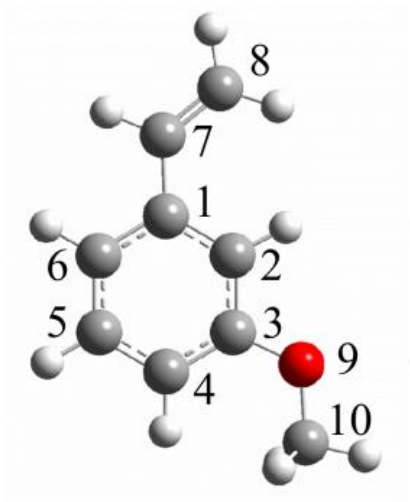


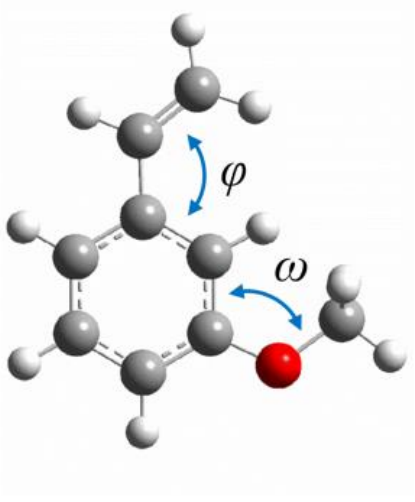
Figure 18.7 Ionization of *p*-methylphenol via the $S_1 0^0$ intermediate state, using the methods of (a) 2C-R2PI and (b) MATI. Reproduced from Lin *et al. J. Chem. Phys.*, 2004, **120**: 10515, with permission of the American Institute of Physics

Jung-Lee Lin, Changyong Li, Wen-Bih Tzeng
J. Chem. Phys. 120, 10513-10519 (2004)

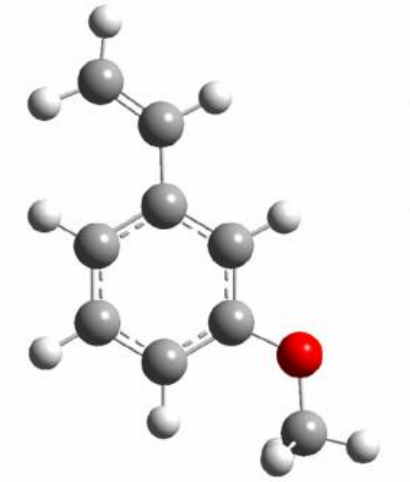
Rotamers of 3-methoxystyrene



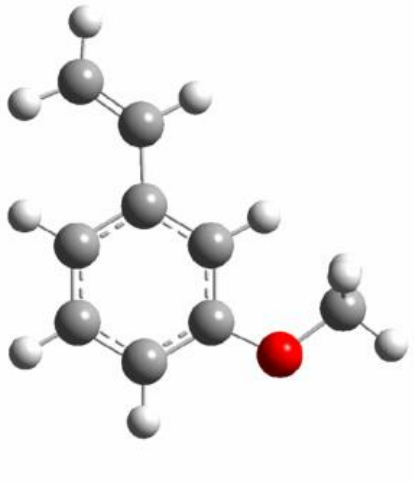
Rotamer I



Rotamer II



Rotamer III

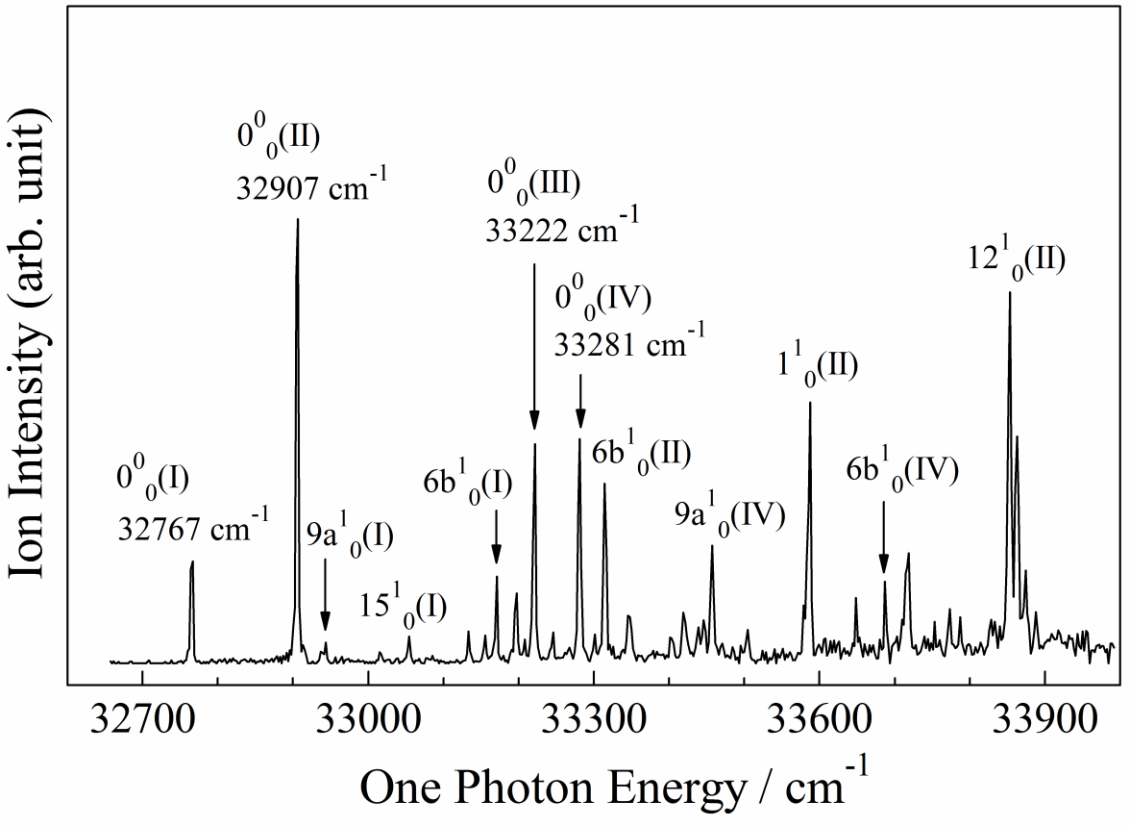


Rotamer IV

These stable four rotamers of *m*-methoxystyrene have been found to be co-exist in the chemical sample by using (1) resonant two-photon ionization and mass analyzed threshold ionization spectroscopy and (2) DFT calculations.

Identification of four rotamers of m-methoxystyrene by resonant two-photon ionization and mass analyzed threshold ionization spectroscopy, Y. Xu, S.Y. Tzeng, V. Shivatare, K. Takahashi, B. Zhang, W.B. Tzeng, J. Chem. Phys. 142 (2015) 124314.

Vibronic spectrum of 3-methoxystyrene



recorded by using
1C-R2PI method

Substituent-sensitive bending

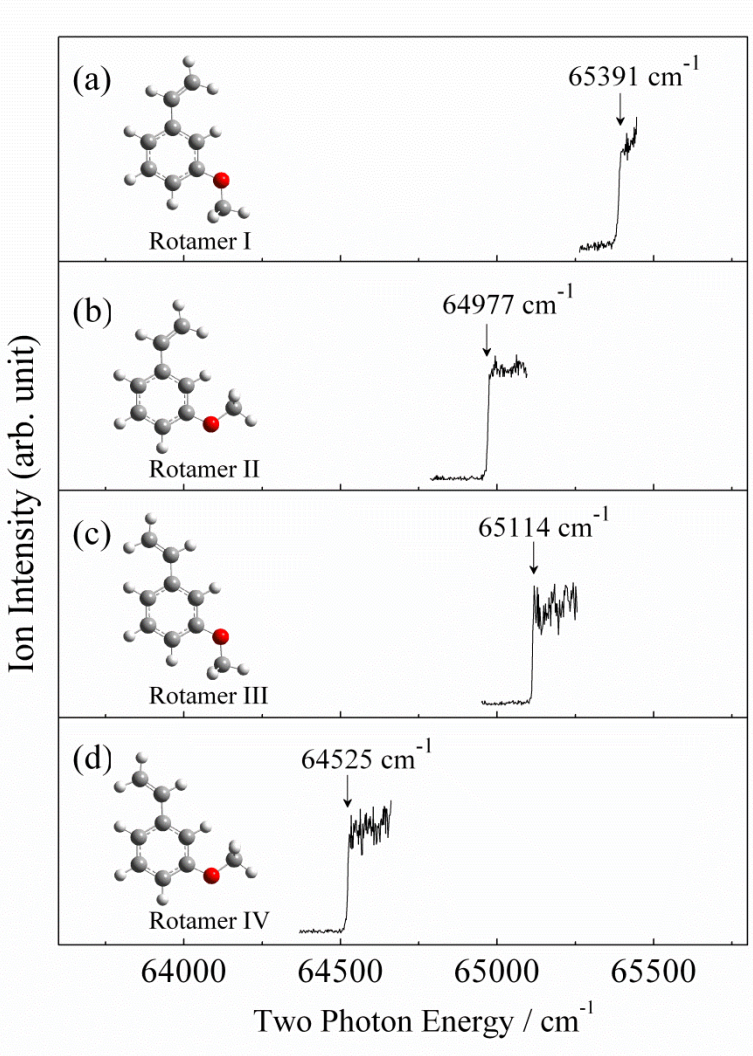
$9a^1_0$, β(ring-vinyl)
15^1_0, β(ring-methoxyl)

In-plane ring deformation

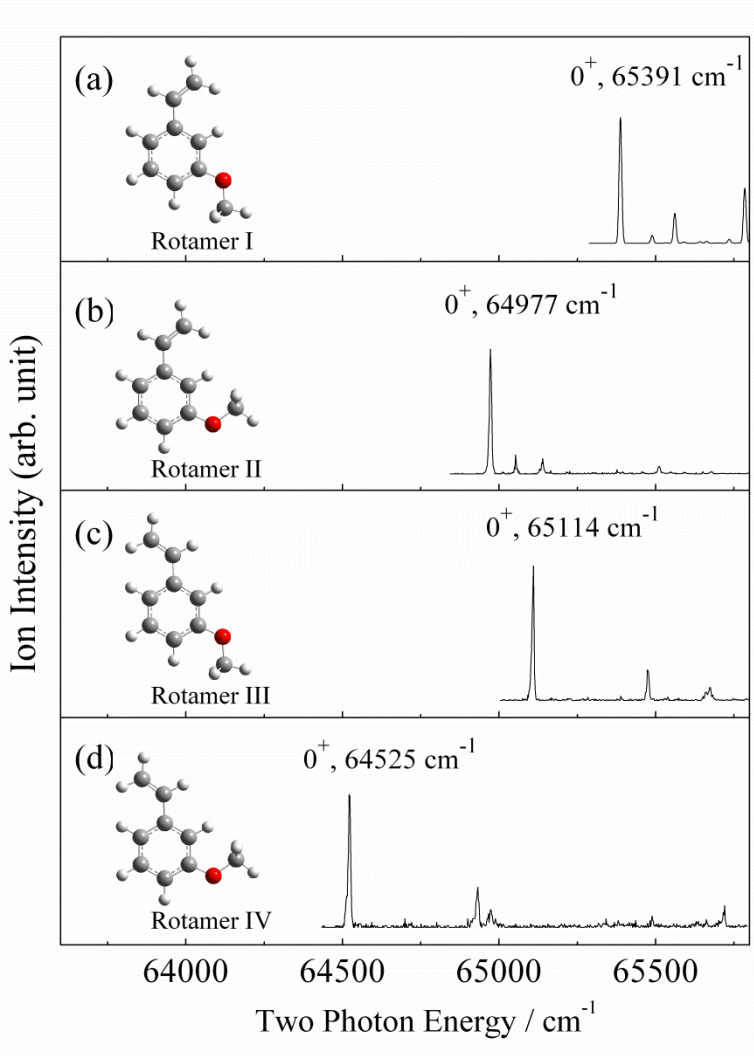
$6b^1_0$, β(CCC)
$6a^1_0$, β(CCC)
1^1_0, breathing
12^1_0, β(CCC)

Rotamer	0^0_0 (in cm^{-1})	IE (in cm^{-1})
I	32,767	65,391
II	32,907	64,977
III	33,222	65,114
IV	33,281	64525

PIE curves of rotamers of 3-methoxystyrene by 2C-R2PI
via their respective 0^0_0 states

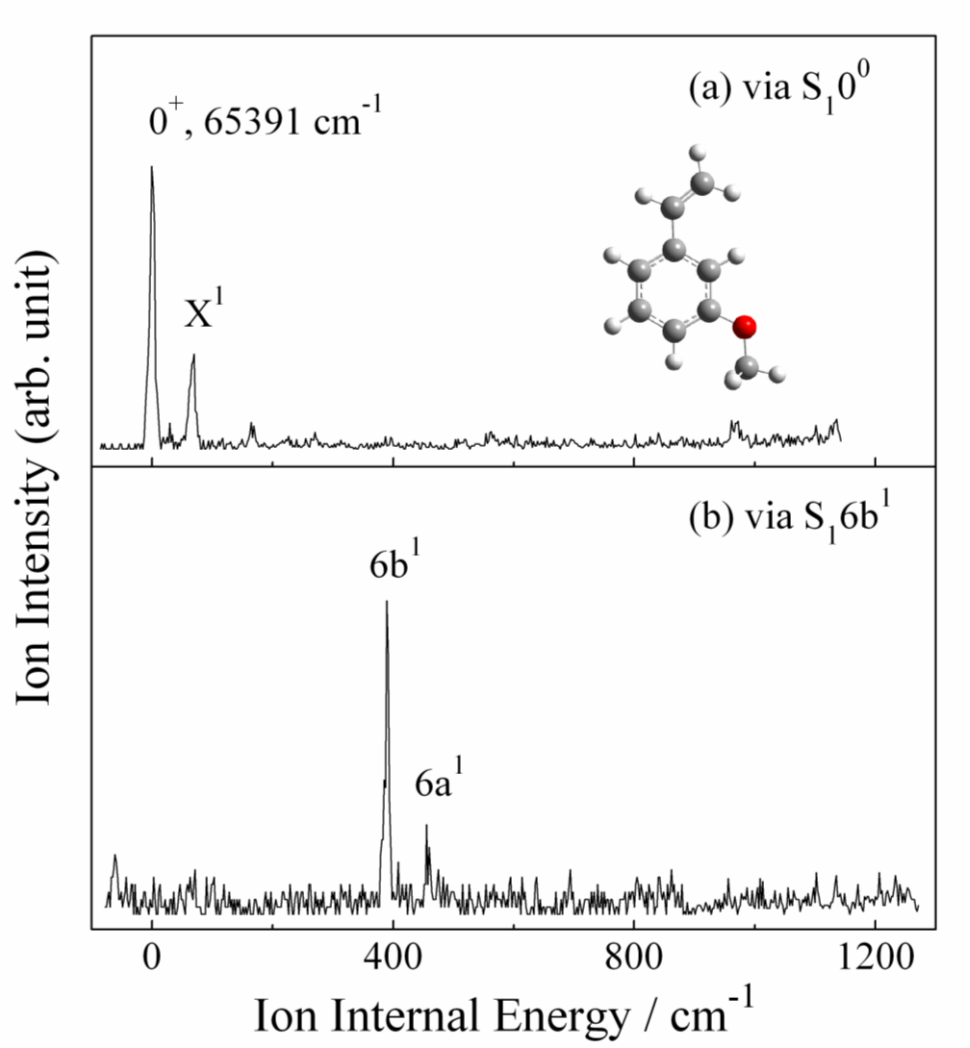


Cation spectra of rotamers of 3-methoxystyrene by MATI
via their respective 0^0_0 states



(species selection)

MATI spectra of 3-methoxystyrene (I)



recorded by using
2CR2-MATI method
via 2 intermediate states

Substituent-sensitive bending

X^1_0, $\gamma(O–OCH_3)$

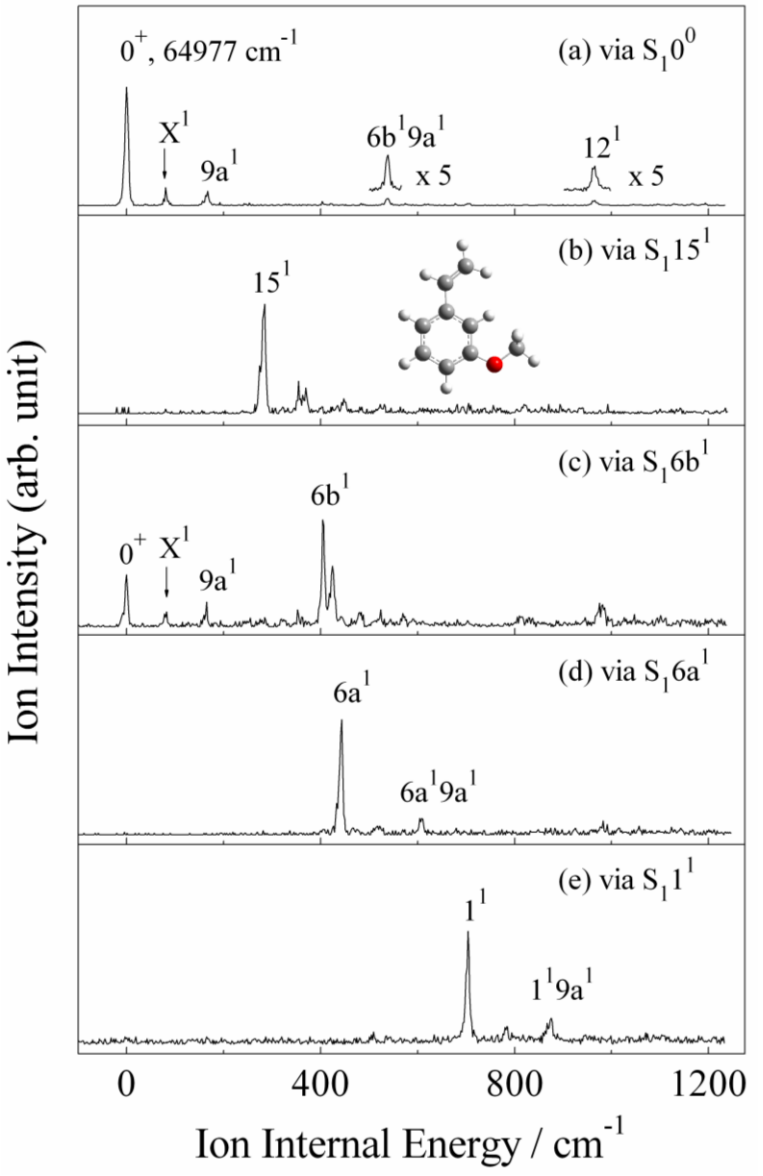
In-plane ring deformation

$6b^1_0$, $\beta(CCC)$
$6a^1_0$, $\beta(CCC)$

Geometries & vibrational coordinates of $D_0 \sim S_1$

(species and state selection)

MATI spectra of 3-methoxystyrene (II)



recorded by using
2CR2-MATI method
via 5 intermediate states

Substituent-sensitive bending

X^1_0, γ(O–OCH_3)

$9a^1_0$, β(ring-vinyl)
15^1_0, β(ring-methoxyl)

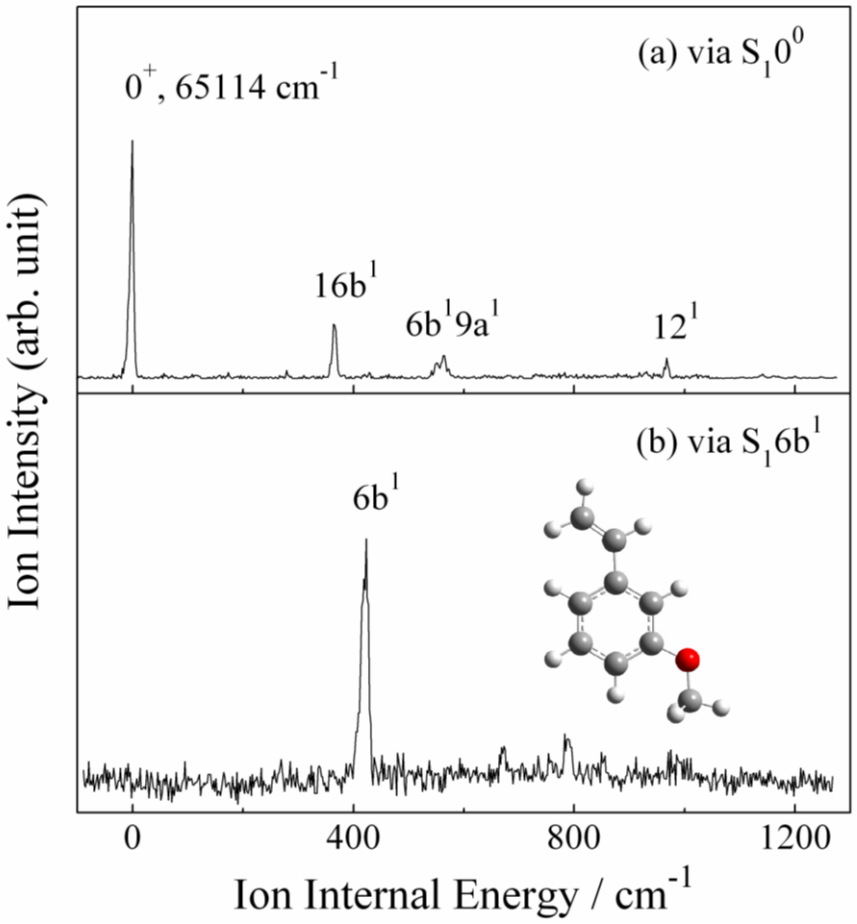
In-plane ring deformation

$6b^1_0$, β(CCC)
$6a^1_0$, β(CCC)
1^1_0, breathing
12^1_0, β(CCC)

Geometries & vibrational coordinates of $D_0 \sim S_1$

(species and state selection)

MATI spectra of 3-methoxystyrene (III)



recorded by using
2CR2-MATI method
via 2 intermediate states

Substituent-sensitive bending

$9a^1_0$, β(ring-vinyl)

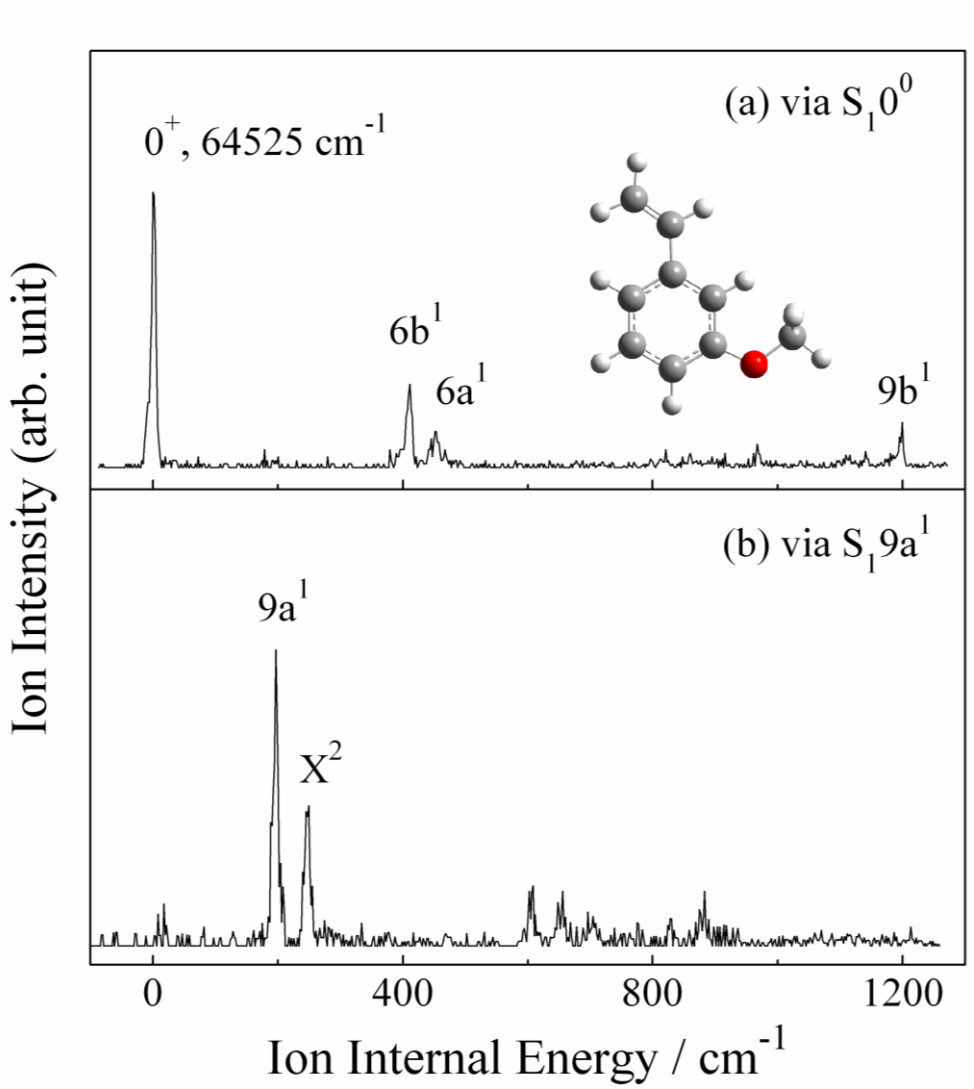
In-plane ring deformation

$6b^1_0$, β(CCC)
$16b^1_0$, γ(CCC)
12^1_0, β(CCC)

Geometries & vibrational coordinates of $D_0 \sim S_1$

(species and state selection)

MATI spectra of 3-methoxystyrene (IV)



recorded by using
2CR2-MATI method
via 2 intermediate states

Substituent-sensitive bending

X^1_0, γ(O–OCH_3)

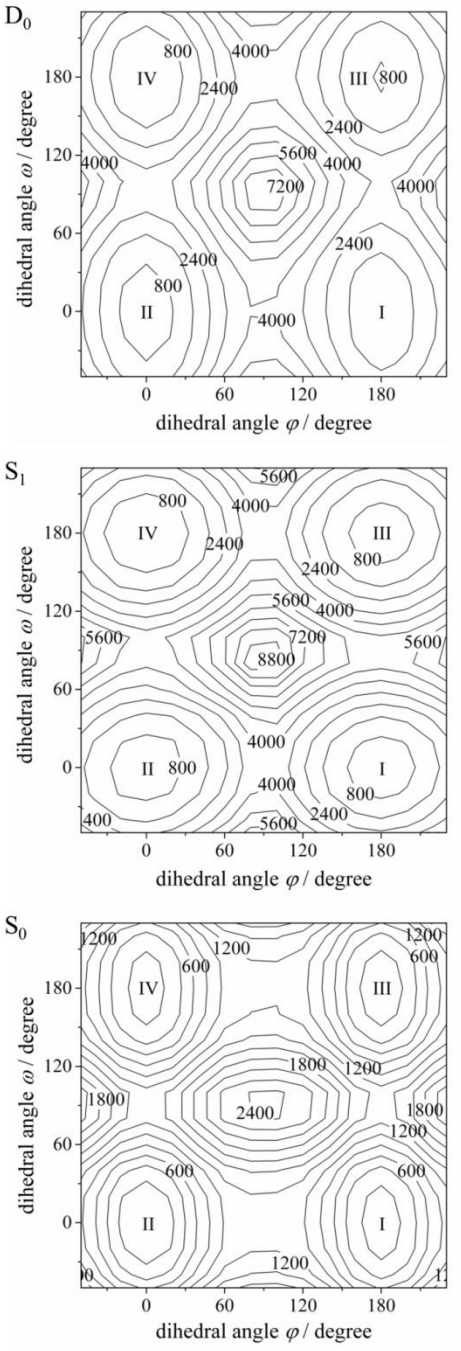
$9a^1_0$, β(ring-vinyl)

In-plane ring deformation

$6b^1_0$, β(CCC)
$6a^1_0$, β(CCC)
$9b^1_0$, β(ring-H)

Geometries & vibrational coordinates of $D_0 \sim S_1$

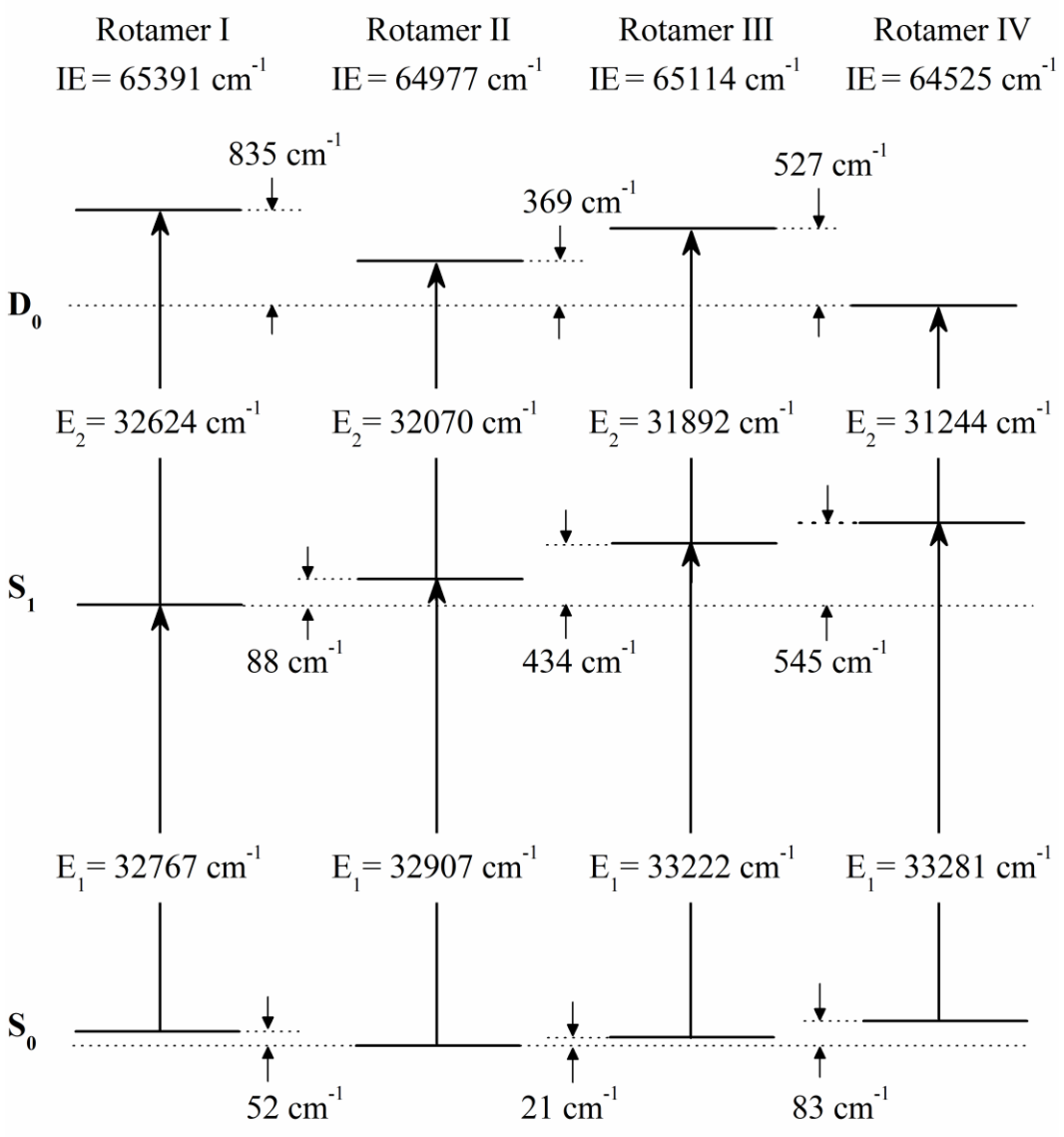
(species and state selection)



2-d potential energy surfaces for interconversion of 4 rotamers of 3-methoxystyrene in the S_0, S_1, and D_0 states by the B3PW91/6-311++G(d,p) calculations.

The calculated barrier of the ring-OCH_3 rotation of 3-methoxystyrene in the S_0, S_1, and D_0 states are 1156, 3712, and 3644 cm^{-1}, whereas those of the ring-vinyl rotation are 1332, 6047, and 2354 cm^{-1}, respectively.

Schematic diagram of energy level for rotamers of 3-methoxystyrene

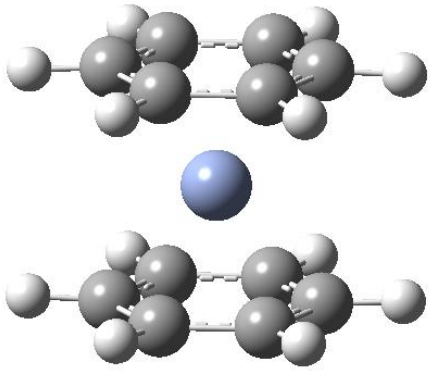


E_1 and E_2 are the measured values, obtained from our REMPI and MATI experiments

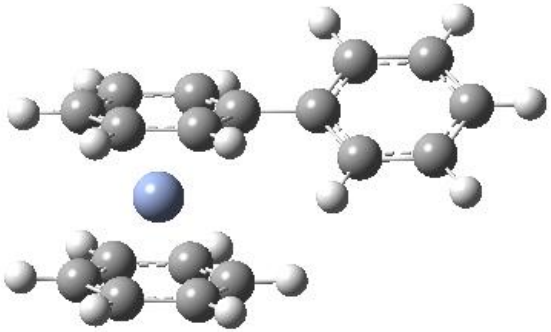
Relative total energy of the rotamers are obtained from the B3PW91/6-311++G(d,p) calculations.

Some organometallic sandwich molecules

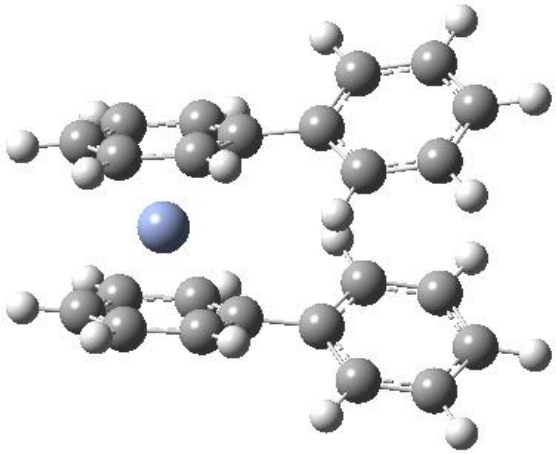
Bis(η^6-Benzene)Chromium
Bz2Cr
Molecular weight : 208 a.m.u.



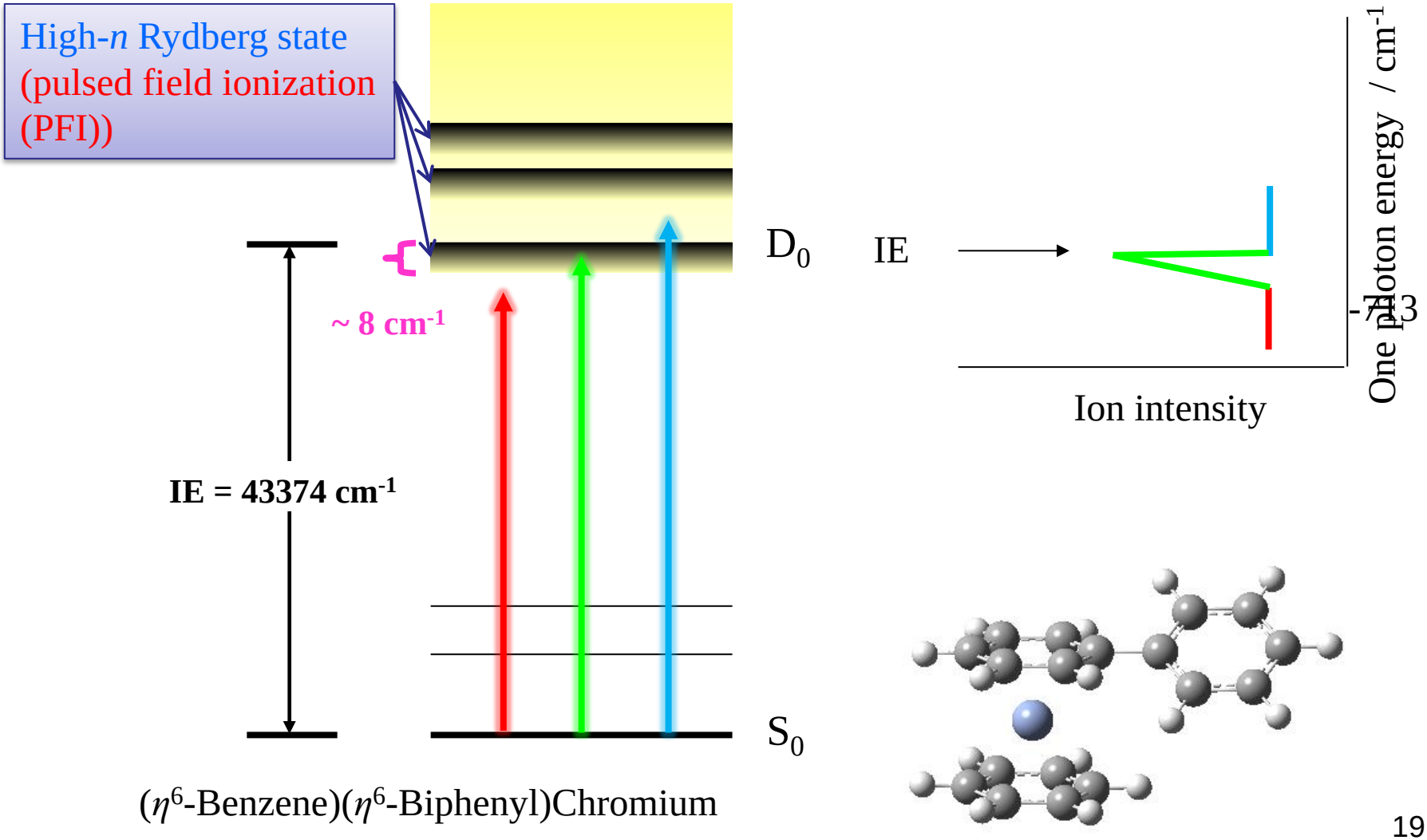
(η^6-Benzene)(η^6-Biphenyl)Chromium
BzPh2Cr
Molecular weight : 284 a.m.u.



Bis(η^6-Biphenyl)Chromium
(Ph2)2Cr
Molecular weight : 360 a.m.u.



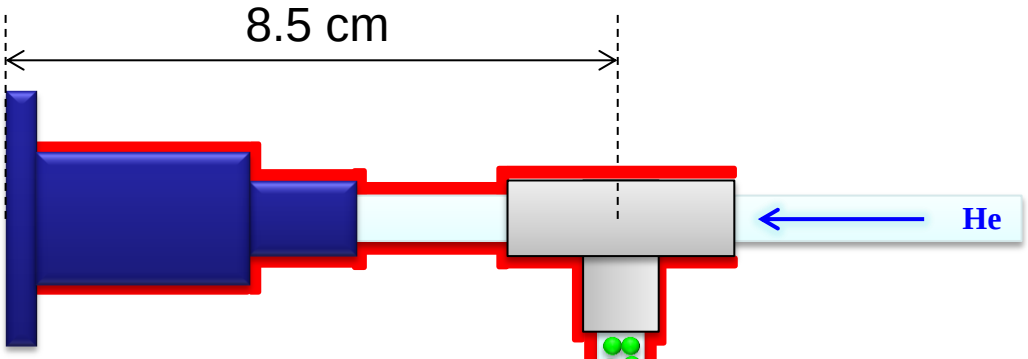
One-photon MATI spectrum of (η^6-Benzene)(η^6-Biphenyl)Chromium

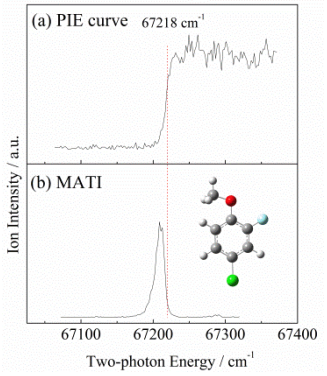


(η^6-Benzene)(η^6-Biphenyl)Chromium

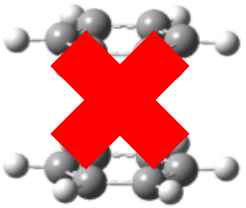
Modification on sample container of pulsed valve

Ver. 1



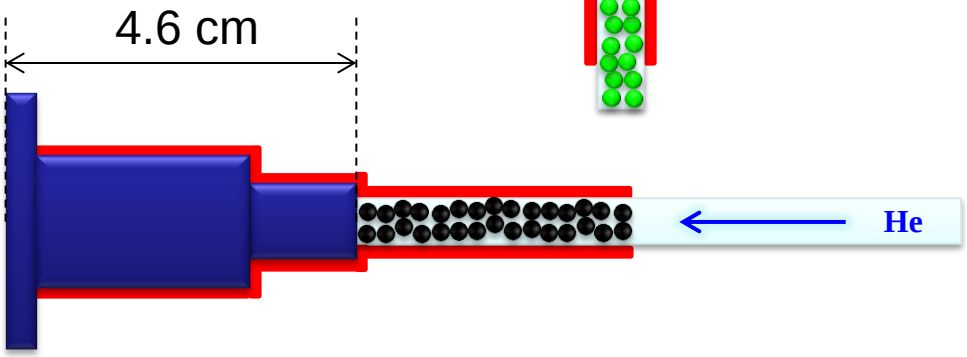


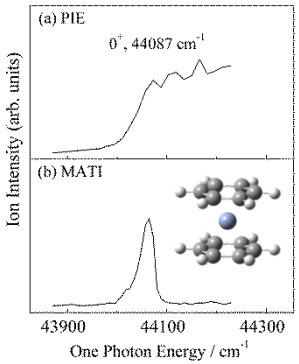
4-Chloro-2Fluoro-anisole



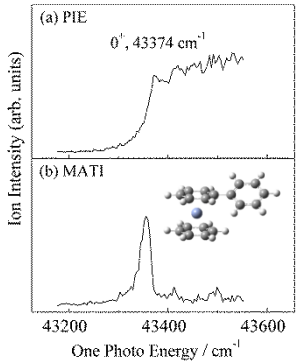
Bis(η^6-Benzene) Chromium

Ver. 2



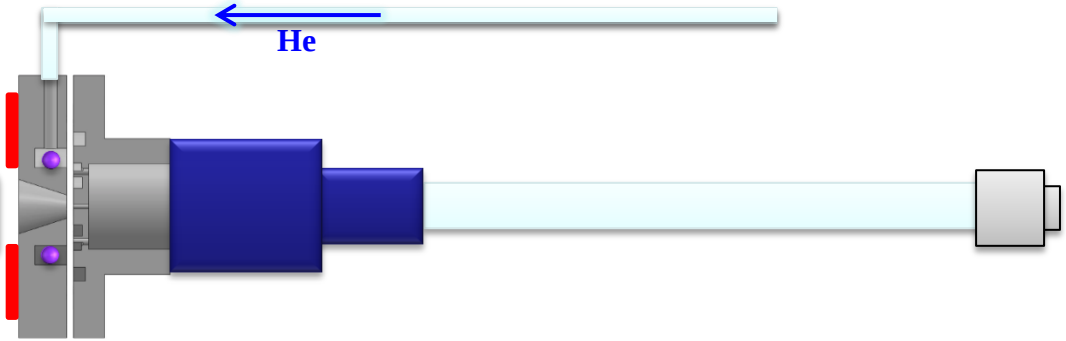


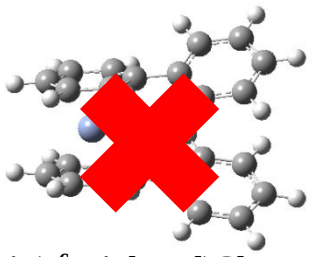
Bis(η^6-Benzene) Chromium



(η^6-Benzene)(η^6-Biphenyl) Chromium

Ver. 3

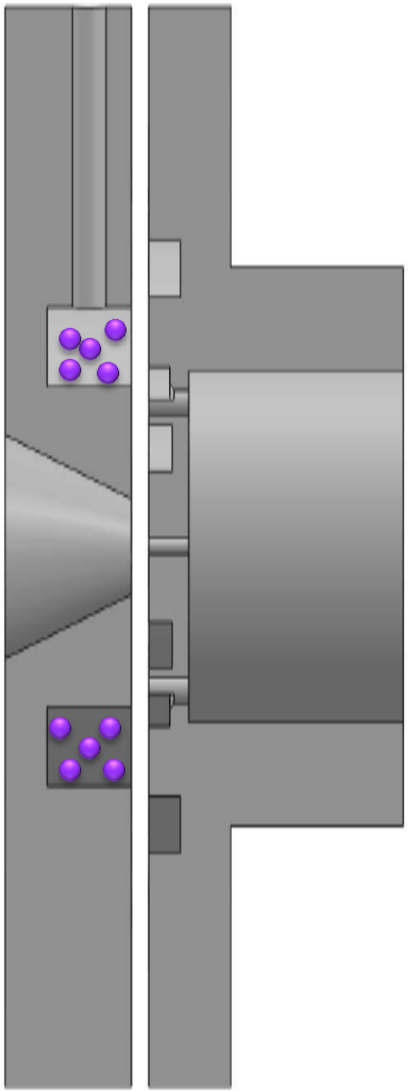


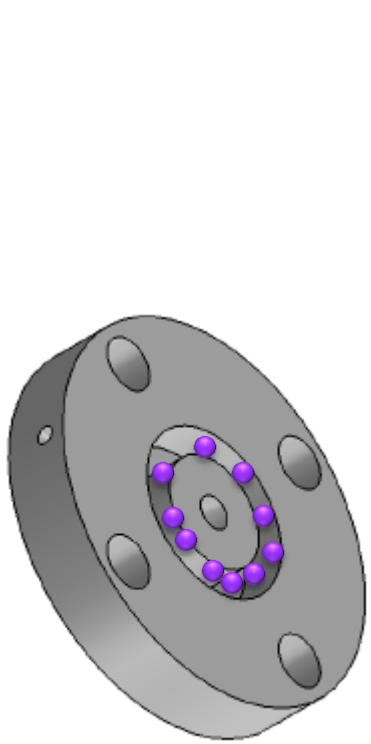


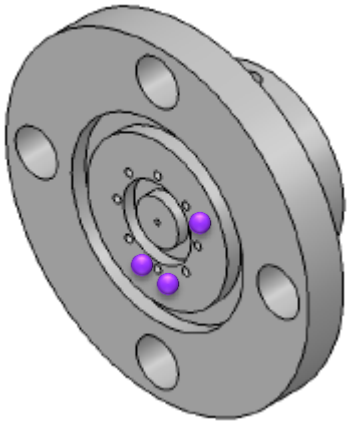
Bis(η^6-Biphenyl)Chromium

Experiment Setup

Ver. 3

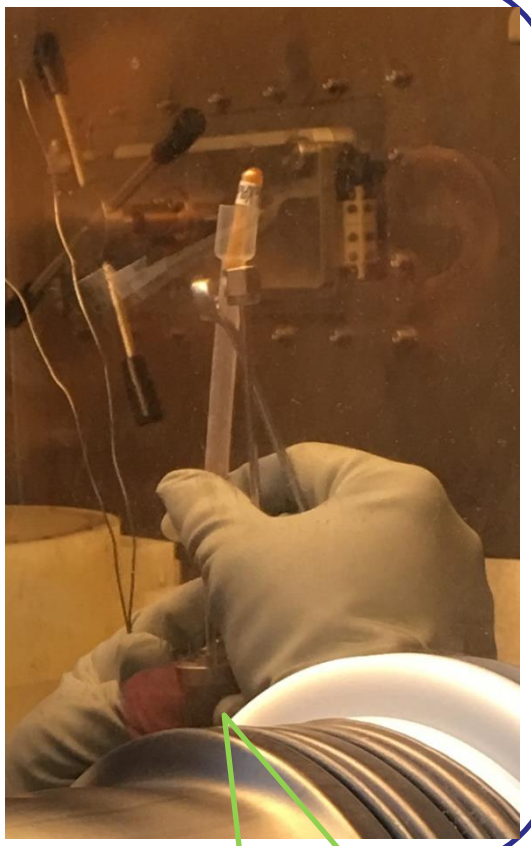


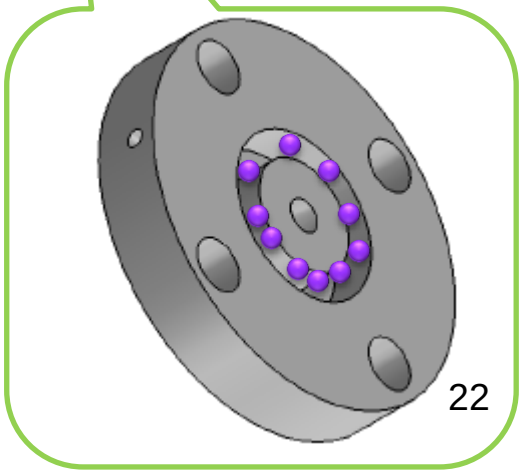




Experiment Setup

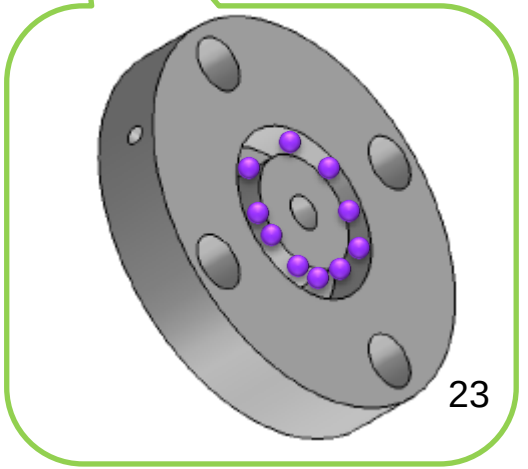
Ver. 3

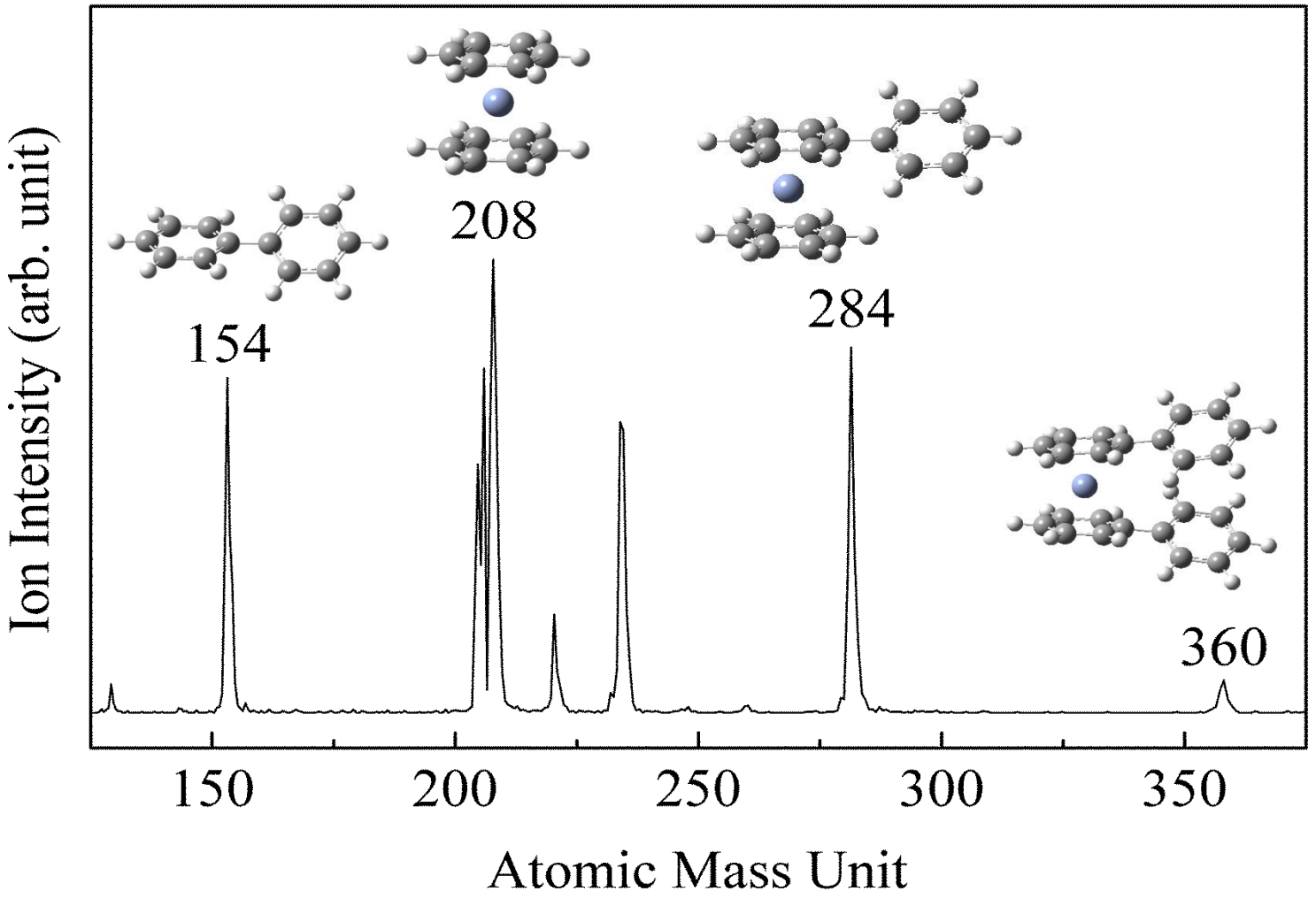




Experiment Setup

Ver. 3

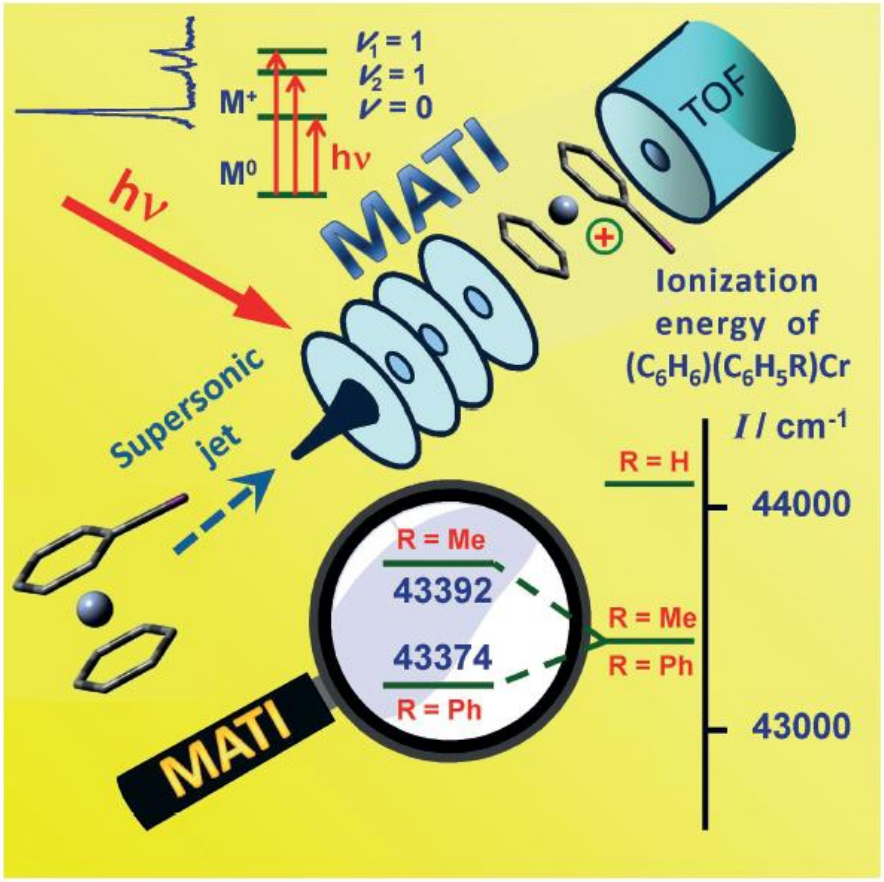



Ion Intensity (arb. unit)
154
208
284
360
150
200
250
300
350
Atomic Mass Unit

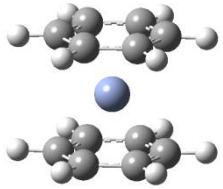
Substituent Effects | *Hot Paper*

Fine Substituent Effects in Sandwich Complexes: A Threshold Ionization Study of Monosubstituted Chromium Bisarene Compounds

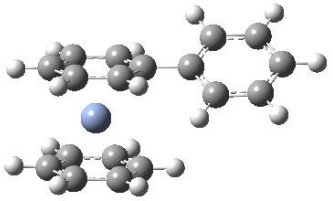
Sergey Yu. Ketkov,*[a] Gennady V. Markin,[a] Sheng Y. Tzeng,[b] and Wen B. Tzeng*[b]



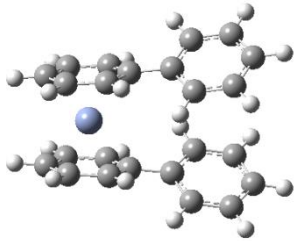
Chem. Eur. J. 2016, 22, 4690 – 4694 Wiley Online Library 4690
© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Bz_2Cr



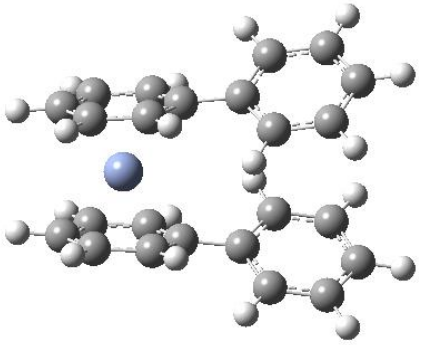
$BzPh_2Cr$

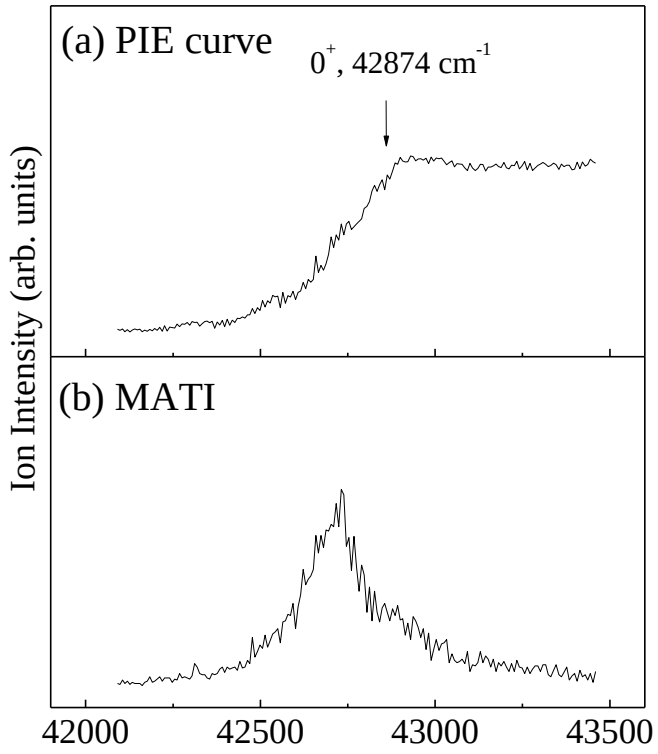


$(Ph_2)_2Cr$

Molecule	IE	δIE
Bz_2Cr	44087	0
$BzPh_2Cr$	43374	-713
$(Ph_2)_2Cr$	42874	-1213

Chem. Eur. J., 22 (2016) 4690





Bis(η^6-biphenyl)chromium

Ver. 3

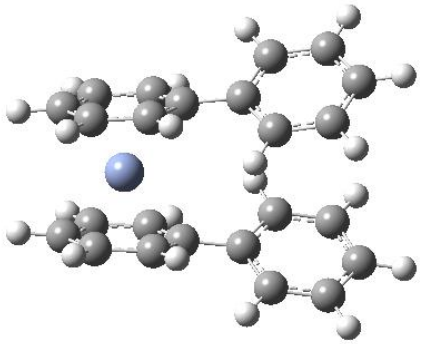
PIE curve
P0= 1468 torr
P1= 4.0*10^{-8} Torr
Focus= +380 V
Heating: 232 ^{o}C

Ver. 3

MATI
P0= 1663 torr
P1= 8.0*10^{-8} Torr
U1: AMP= 4.00 V offset= -1.25 V
Focus= +380 V
Heating: 232 ^{o}C

IE (exp) = 42874 ± 10 cm^{-1}

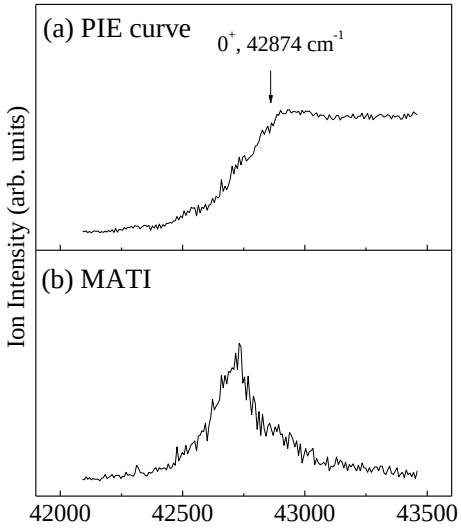
Results

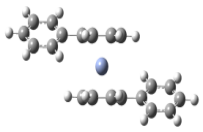
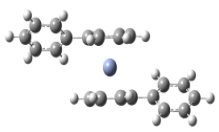
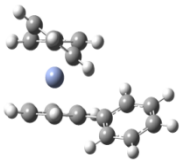
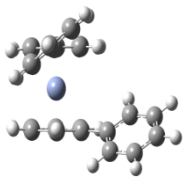
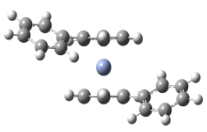
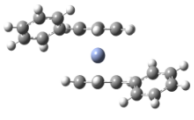
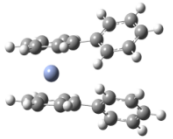
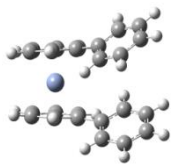


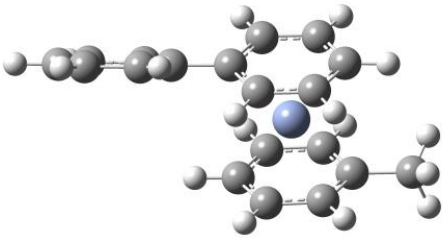
Bis(η^6-biphenyl)chromium
[$(Ph_2)_2Cr$]

IE (exp) = 42874 ± 10 cm^{-1}

Ver. 3



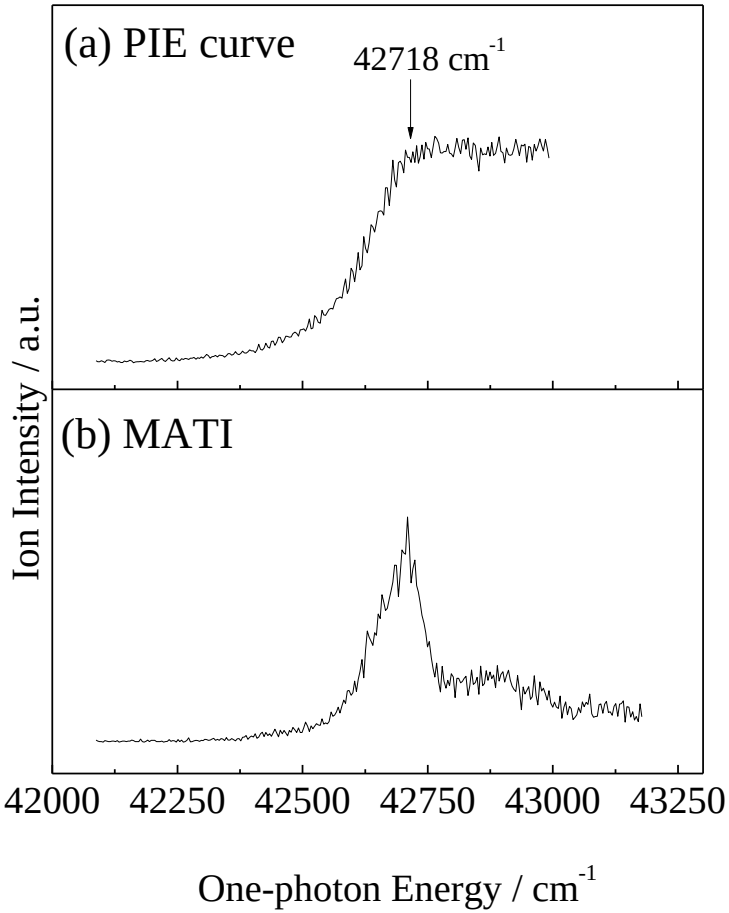
$(Ph_2)_2Cr$								
B3PW91 6311++g(d,p)	$(Ph_2)_2Cr\_p\_a$	$(Ph_2)_2Cr\_p\_s$	$(Ph_2)_2Cr\_o\_a$	$(Ph_2)_2Cr\_o\_s$	$(Ph_2)_2Cr\_m\_a$	$(Ph_2)_2Cr\_m\_s$	$(Ph_2)_2Cr\_e\_a$	$(Ph_2)_2Cr\_e\_s$
S_0 (ZPE)	-1970.546597	-1970.546681	-1970.547123	not converge	-1970.546725	-1970.546381	not converge	-1970.544451
D_0 (ZPE)	-1970.354524	-1970.354515	-1970.354892	not converge	-1970.354552	-1970.354377	not converge	-1970.352133
IE(Hartree)_cal	0.192073	0.192166	0.192231		0.192173	0.192004		0.192318
IE (cm^{-1})_cal	**42155**	**42176**	**42190**		**42177**	**42140**		**42209**
de	**719**	**698**	**684**		**697**	**734**		**665**
de(%)	**1.7**	**1.7**	**1.6**		**1.7**	**1.7**		**1.6**



(η^6-biphenyl)(η^6-toluene)chromium

Ver. 3

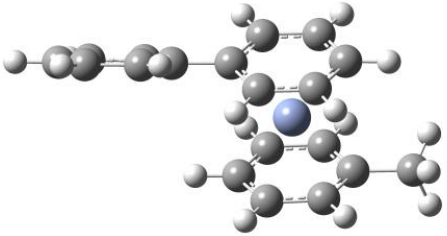
PIE curve
P0= 1969 torr
P1= 1.0*10^{-7} Torr
Focus= +600 V
Heating: 124 ^{o}C



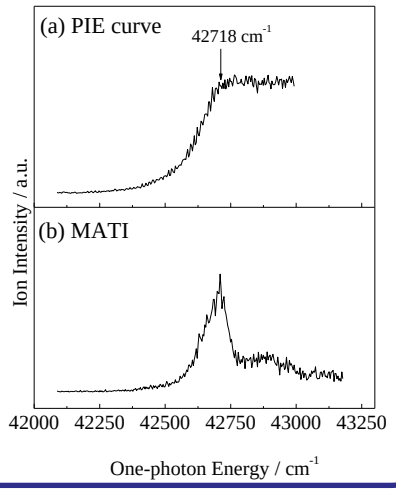
Ver. 3

MATI
P0= 1720 torr
P1= 1.0*10^{-7} Torr
U1: AMP= 2.50 V offset= -1.25 V
Focus= +100 V
Heating: 124 ^{o}C

IE (exp) = 42718 ± 10 cm^{-1}

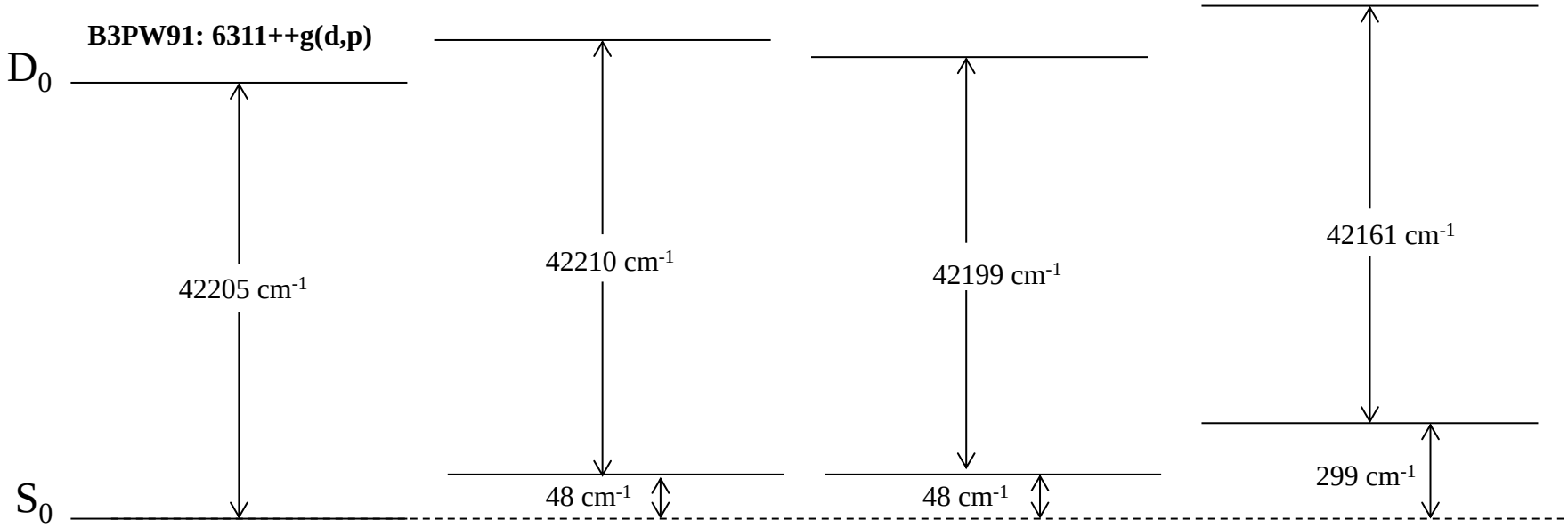


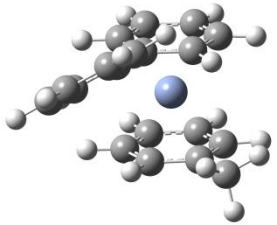
Ver. 3



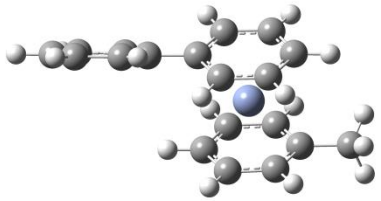
(η^6-biphenyl) (η^6-toluene)chromium (CrPh2PhMe)

IE (exp) = 42718 ± 10 cm^{-1}

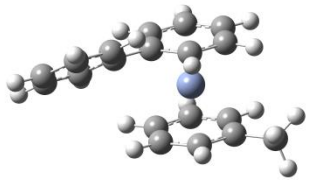




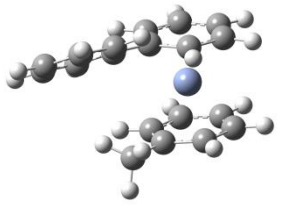
CrPh2PhMe_o



CrPh2PhMe_p



CrPh2PhMe_m



CrPh2PhMe_s