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WINTER SCHOOL ON LASER SPECTROSCOPY AND APPLICATIONS

19 February - 2 March 2001

Photoelectron Spectroscopy with and without Photoelectrons

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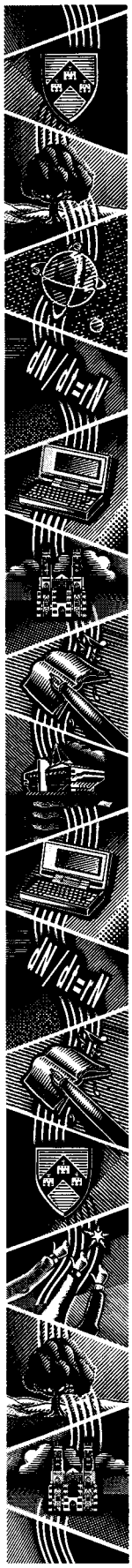
These are preliminary lecture notes, intended only for distribution to participants.



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Photoelectron Spectroscopy with and without photoelectrons:

From the photoelectric effect to ZEKE spectroscopy

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UK.

Outline

1) The origins of photoelectron spectroscopy
   Photoelectric effect
   Development of UVPES & XPS
   Experimental methods
   Factors affecting Resolution

2) Applications
   Atoms
   Diatomic Molecules
   Molecular Orbital Theory
   Koopmans' Theorem – closed and open shell
   Autoionisation
   Polyelectronic molecules

3) The quest for improved resolution
   Refinement of experimental conditions
   Laser REMPI-PES – state selection

4) Dispensing with energy analysis
   Threshold Photoelectron Spectroscopy
   Auto*ionisation revisited*

5) The next step: ZEKE spectroscopy
   Concepts
   Comparisons to PES
   Rydberg states and Field Ionisation
   Experimental details
   Improving resolution

6) Case Studies: *Electronically excited states, autoionisation, Rydberg excited van der Waals complexes.*

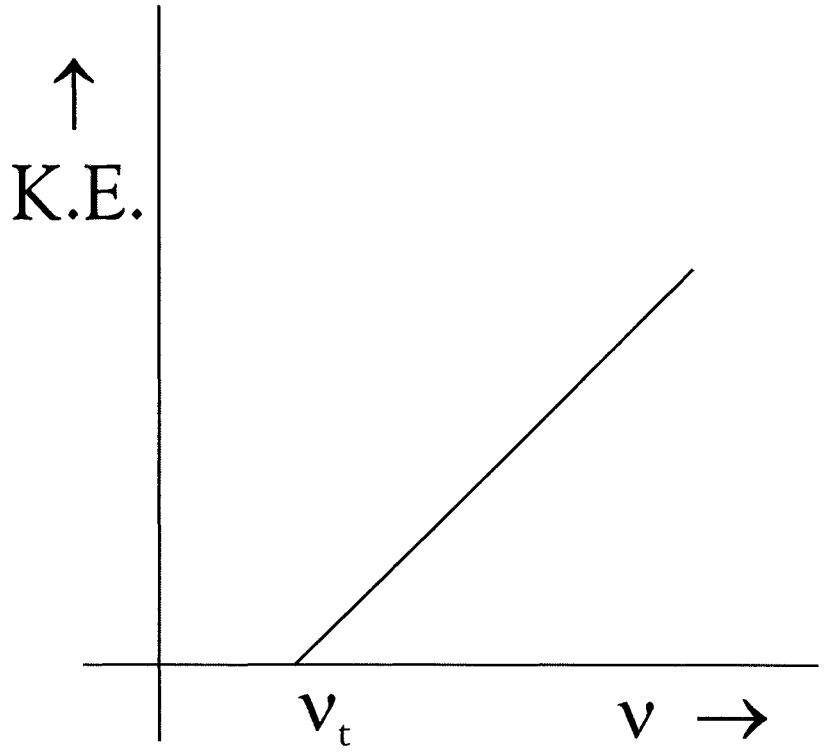
Origins of Photoelectron Spectroscopy

(a) The Photoelectric Effect

- First observed on surfaces of easily ionisable metals (e.g. Alkali metals).

$$h\nu = \tfrac{1}{2} m_e v^2 + \Phi$$

$$\text{K.E.} \propto h\nu .$$



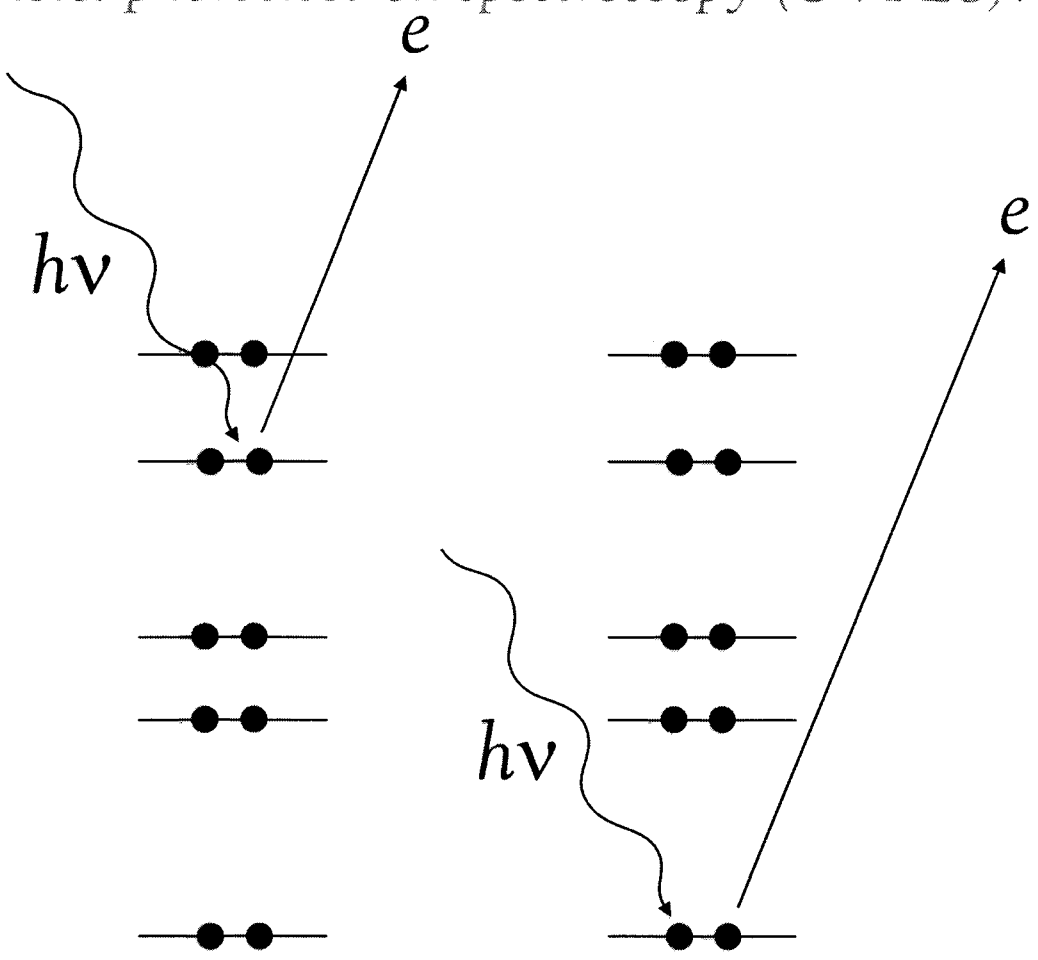
- Einstein[1] developed theory in 1905

For alkali metal surfaces, Φ is of the order of a few eV which requires near UV radiation.

[1] A. Einstein, Ann. Physik., 31 (1905) 132.

(b) The development of Photoelectron spectroscopy

- *1956 Siegbahn[2] invents X-ray photoelectron spectroscopy (XPS).*
- *1962 Turner et al.[3] and Vilesov et al.[4] develop ultraviolet photoelectron spectroscopy (UVPES).*



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[2] K. Seibgahn and K. Everson, *Nucl. Phys.*, **1** (1956) 137

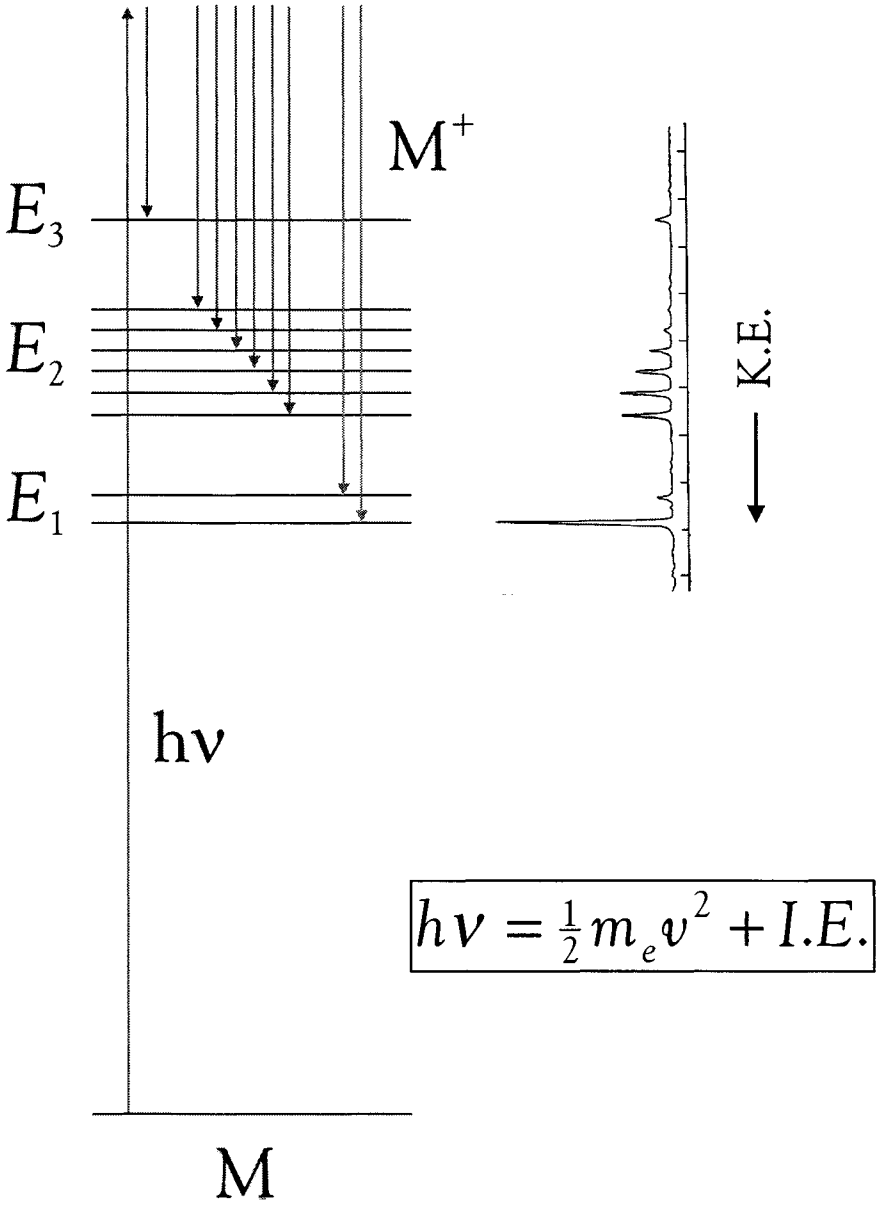
[3] M.I. Al-Joboury and D.W. Turner, *J. Chem. Phys.*, **37**, (1962) 3007.

[4] F.I. Vilesov, B.L. Kurbatov and A.N. Terenin, *Dokl. Akad. Nauk SSSR*, **138** (1961) 1329.

How does it work?

UVPES (*gas phase*) and **XPS** (*solid state & gas phase*) both involve the following process:

$$M + h\nu \rightarrow M^+ + e$$



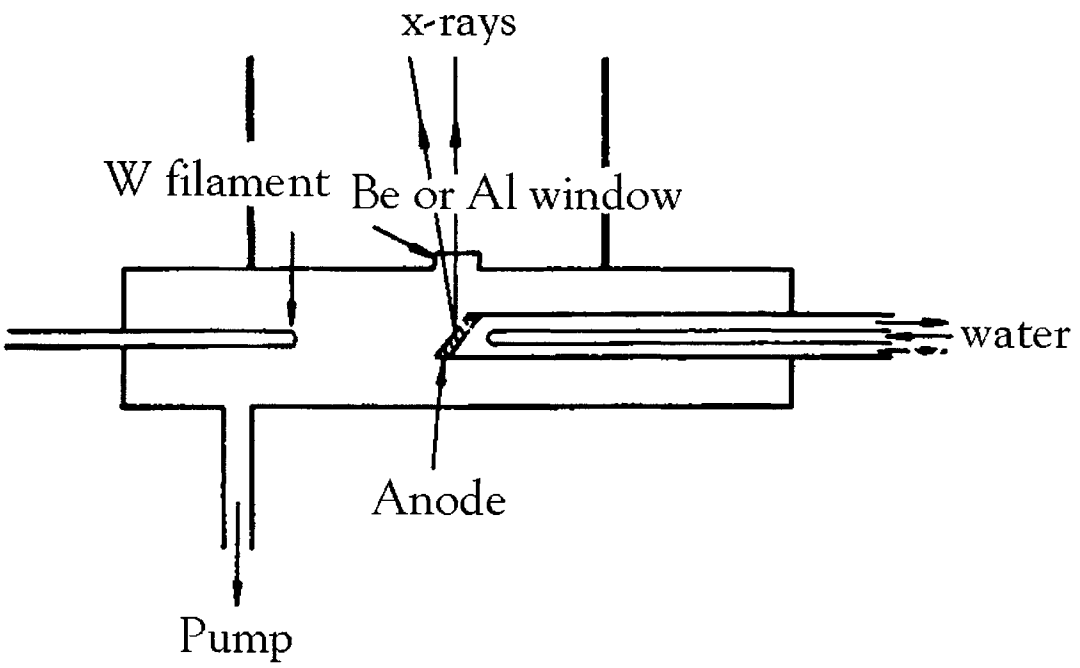
$$h\nu = \tfrac{1}{2} m_e v^2 + I.E.$$

The kinetic energy of the photoelectrons depends on the photon energy and the final state of the ion.

(a) Photon Source (preferably *monochromatic*)

XPS AlKα (1487 eV) or MgKα (1253 eV)

$$1s^2\,2s^2\,2p^5 \leftarrow 1s^1\,2s^2\,2p^6$$



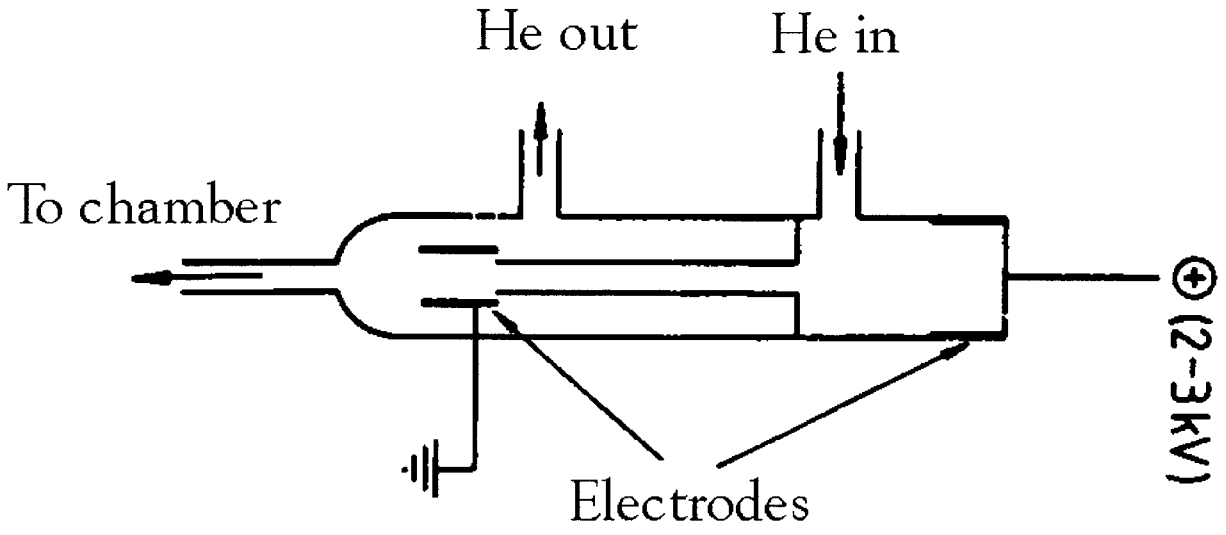
UVPES

- HeI (21.22 eV)

$$2^1P_1(1s^1 2p^1) \rightarrow 1^1S_0(1s^2)$$

- HeII (40.8 eV)

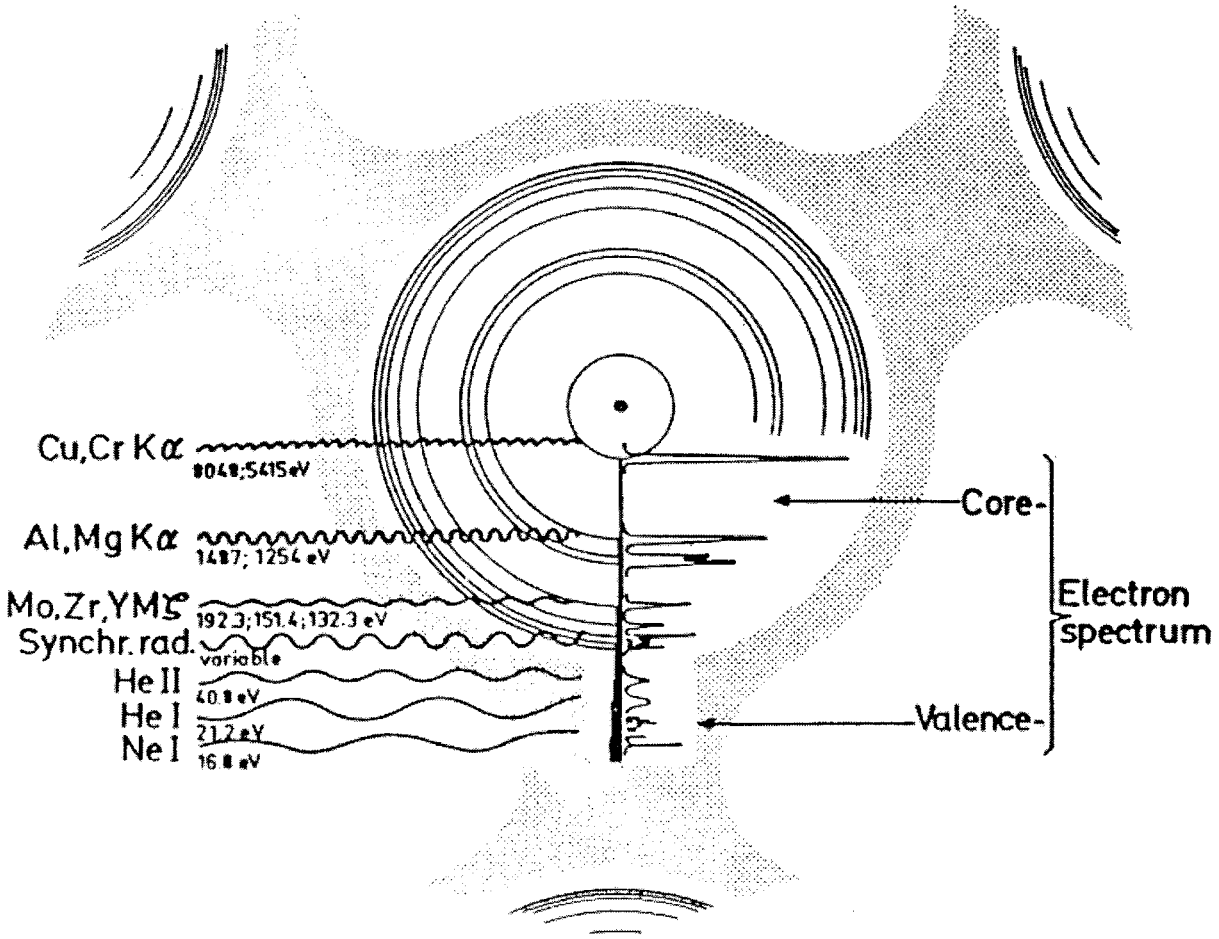
$$He^+\ 2^2P_{3/2,1/2}(2p^1) \rightarrow 1^2S_{1/2}(1s^1)$$



- NeI (16.67 and 16.85 eV)

$$^1P_1(2p^5 3s^1) \rightarrow 1^1S_0(2p^6)\ 16.67\ \text{eV}$$
$$^3P_1(2p^5 3s^1) \rightarrow 1^1S_0(2p^6)\ 16.85\ \text{eV}$$

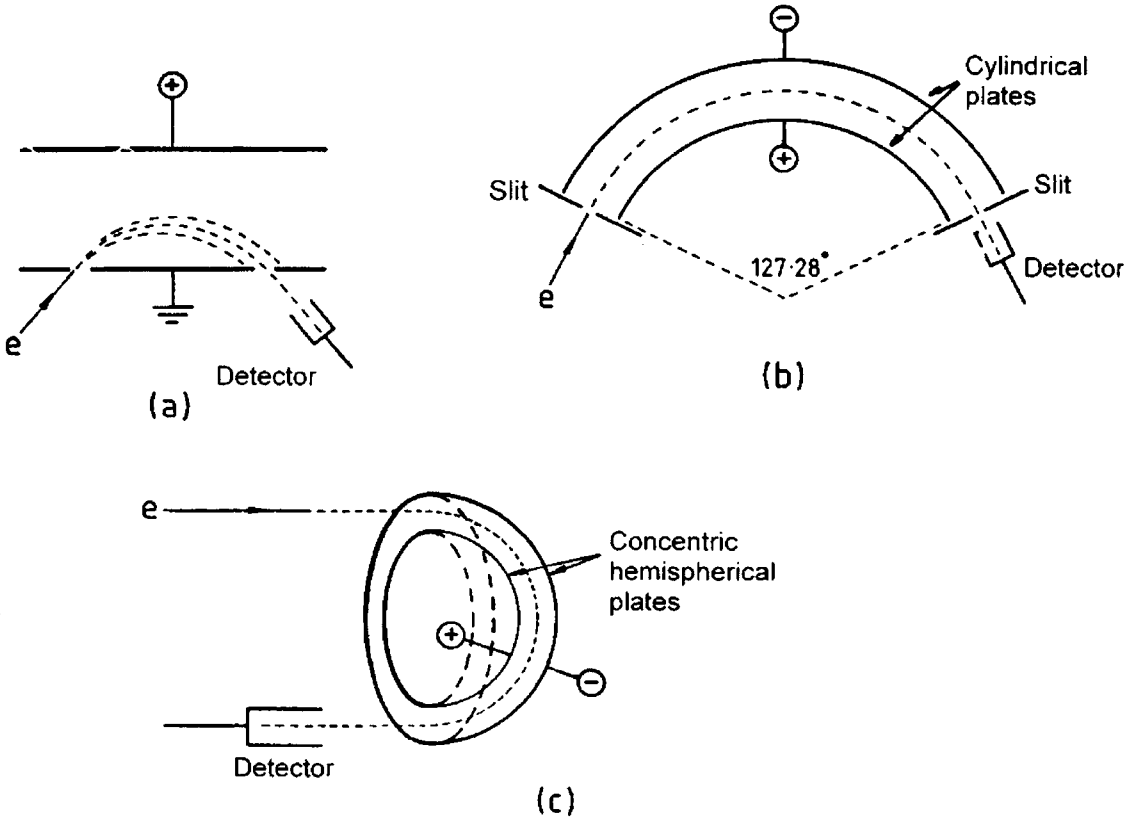
Summary



Types of radiation used in PES correlated to the regions of electronic stucture probed.

(b) Kinetic energy analysis

Deflection analysers: *Electrons with different energies follow different paths when subject to magnetic or electric fields*



(a) Parallel plate, (b) 127 cylindrical and (c) hemispherical analysers

Electrons of a kinetic energy E will reach the detector when

$$V = \frac{E}{e}\left(\frac{R_2}{R_1} - \frac{R_1}{R_2}\right)$$

for plates of radii R_1 and R_2 ($R_2 > R_1$).

(c) Resolution

(i) Radiation linewidth $\approx$ 3–4 meV (He I)
$\approx$ 0.2–1eV (AlKα)

(ii) Doppler broadening $\approx$ 4 meV (m=100, T=300 K, eKE = 10 eV)

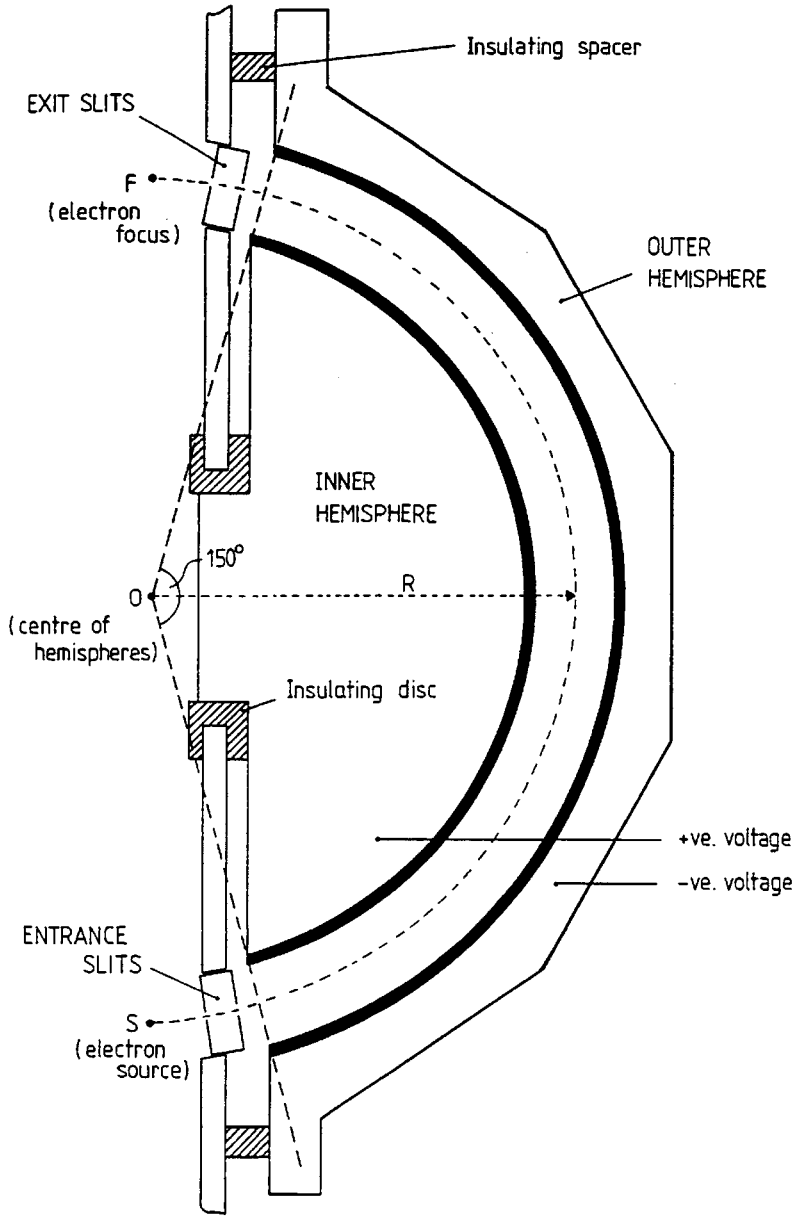
(iii) The analyser

$$\Delta E = \tfrac{1}{2} e \frac{V}{(R_2 - R_1)} \Delta R$$

where

$$\Delta R \approx S/2$$

is the variation in R and S is the total slit width.



Other factors affecting resolution

$$\Delta E = \tfrac{1}{2} e \frac{V}{(R_2 - R_1)} \Delta R = \frac{E}{R} \Delta R \approx \frac{E}{R} \frac{S}{2}$$

- The resolution improves as S is reduced (but transmission suffers).

- Resolution improves as the kinetic energy is reduced (but transmission suffers).

- ΔR depends on other factors such as stray electric/magnetic fields, local point charges (dirt!).

PES always involves a compromise between resolution and transmission.

- Typical resolution ≈ 10-20 meV = 80-160 cm^{-1}

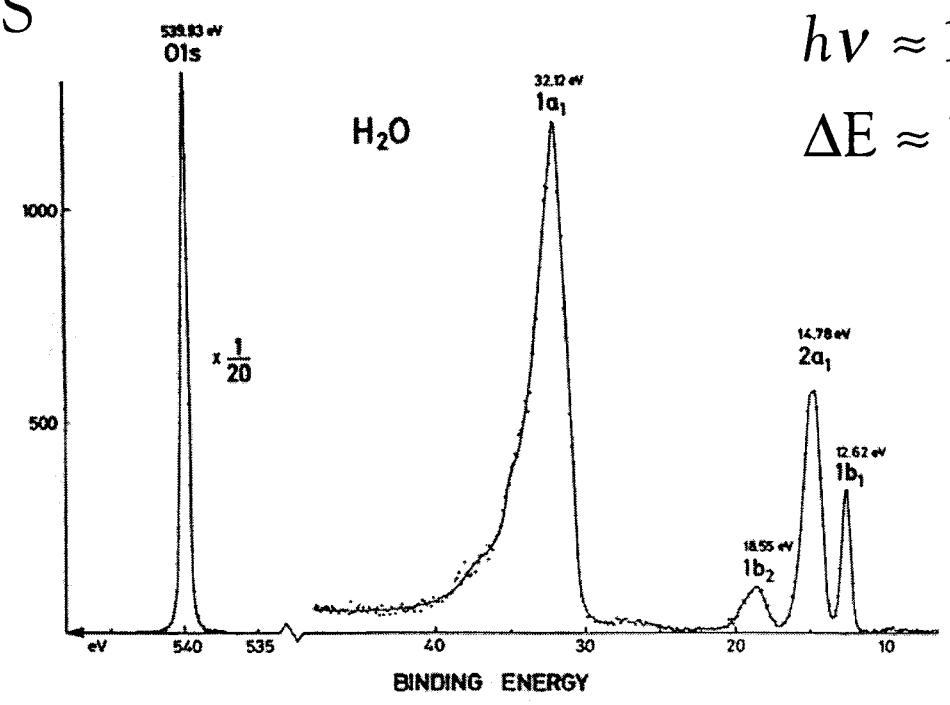
Vibrations – YES (mostly)
Rotations – NO!

XPS vs UVPES

(a) XPS

$h\nu \approx 1000\,\text{eV}$

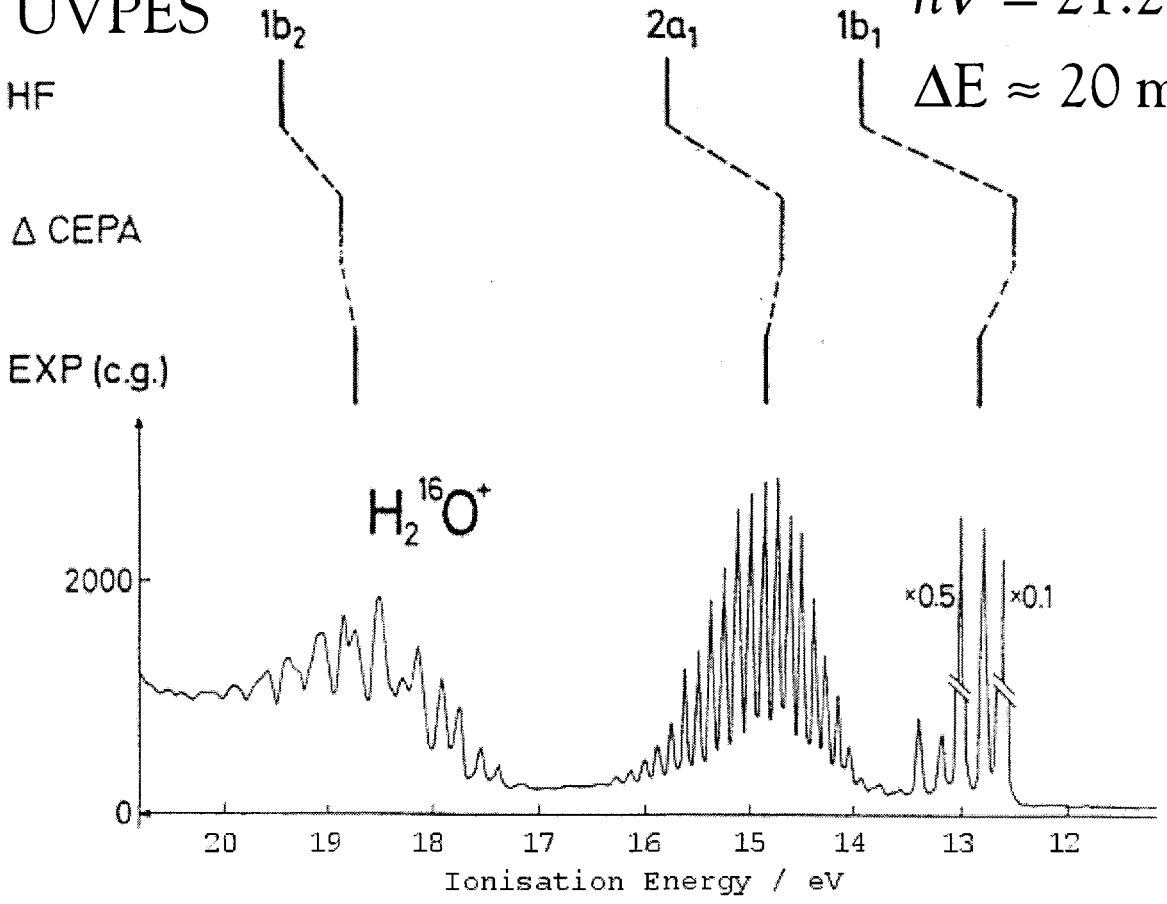
$\Delta E \approx 1\,\text{eV}$



(b) UVPES

$h\nu = 21.22\,\text{eV}$

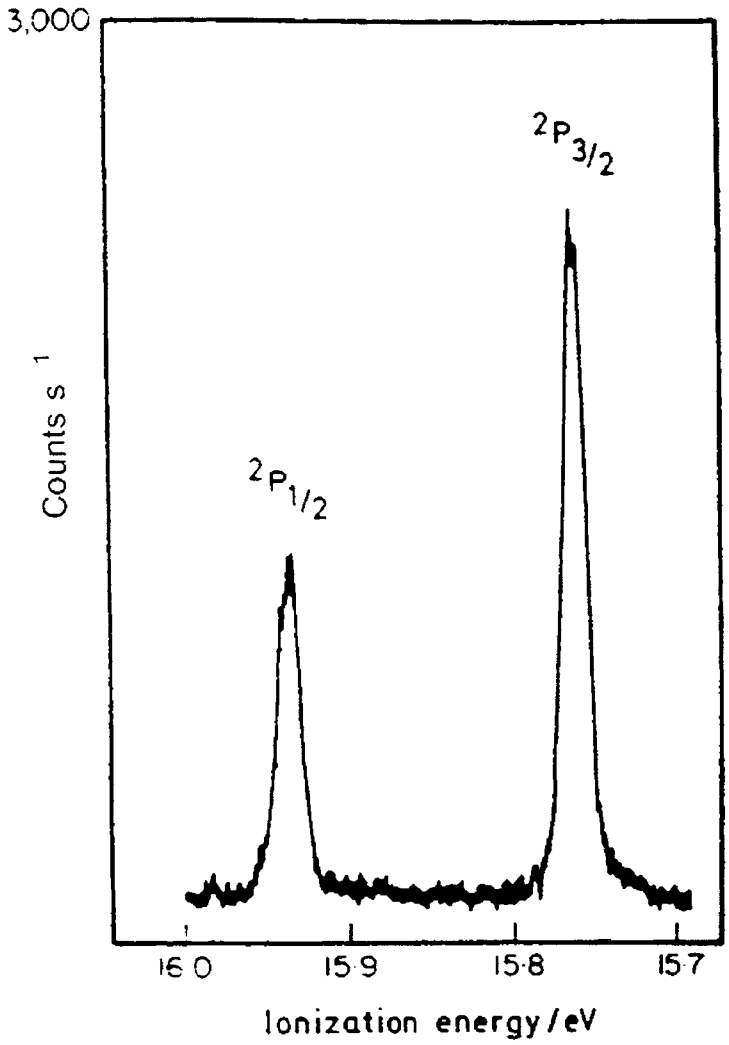
$\Delta E \approx 20\,\text{meV}$



UVPES of Atoms

PES of atoms provides little additional information over higher resolution techniques

$$KE = h\nu - IE_i$$



$$Ar^+ \ {}^2P_{3/2,1/2}(\ldots 3s^2 3p^5) \leftarrow Ar\ 1^1S_0(\ldots 3s^2 3p^6)$$

UVPES of Diatomic Molecules

$$KE = h\nu - IE_i - \Delta E_{vib} - \Delta E_{rot}$$

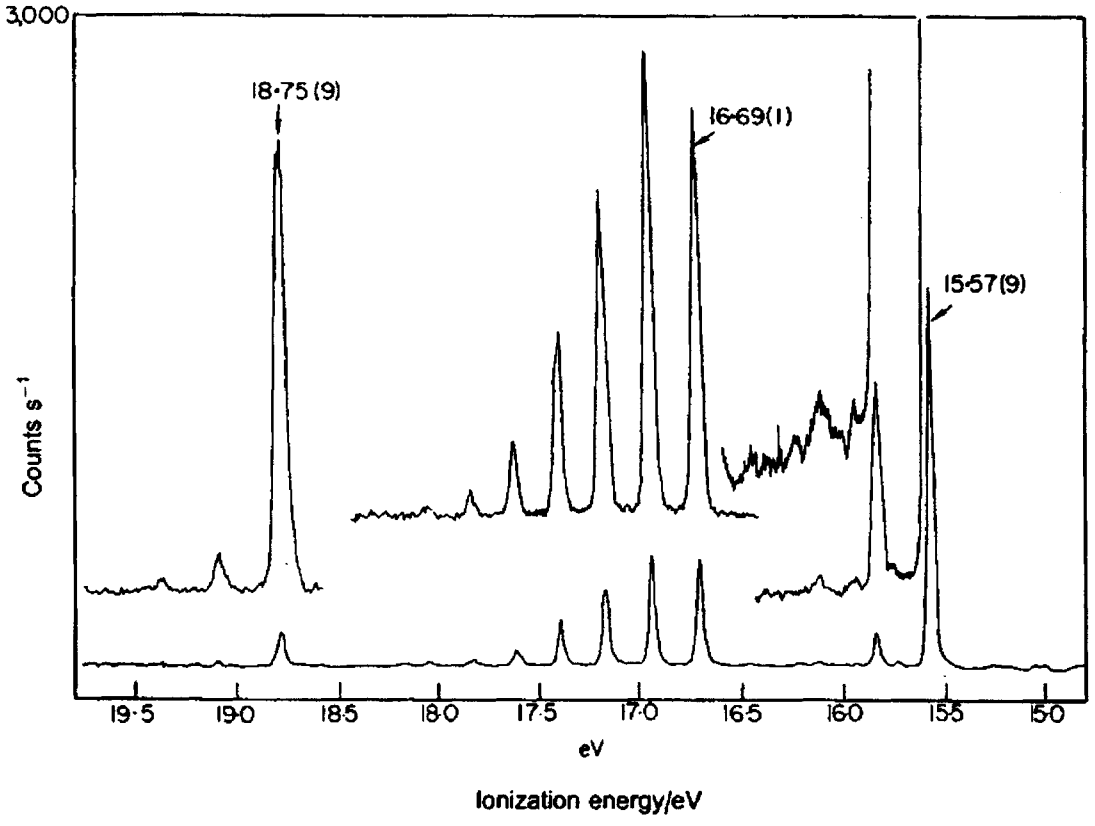
where ΔE_{vib} and ΔE_{rot} represent the internal vibrational and rotational energy of the ion.

How are molecular photoelectron spectra different from atomic PE spectra?

⇓

$\boxed{\Delta E_{vib} \text{ and } \Delta E_{rot}}$

The Photoelectron Spectrum of Nitrogen



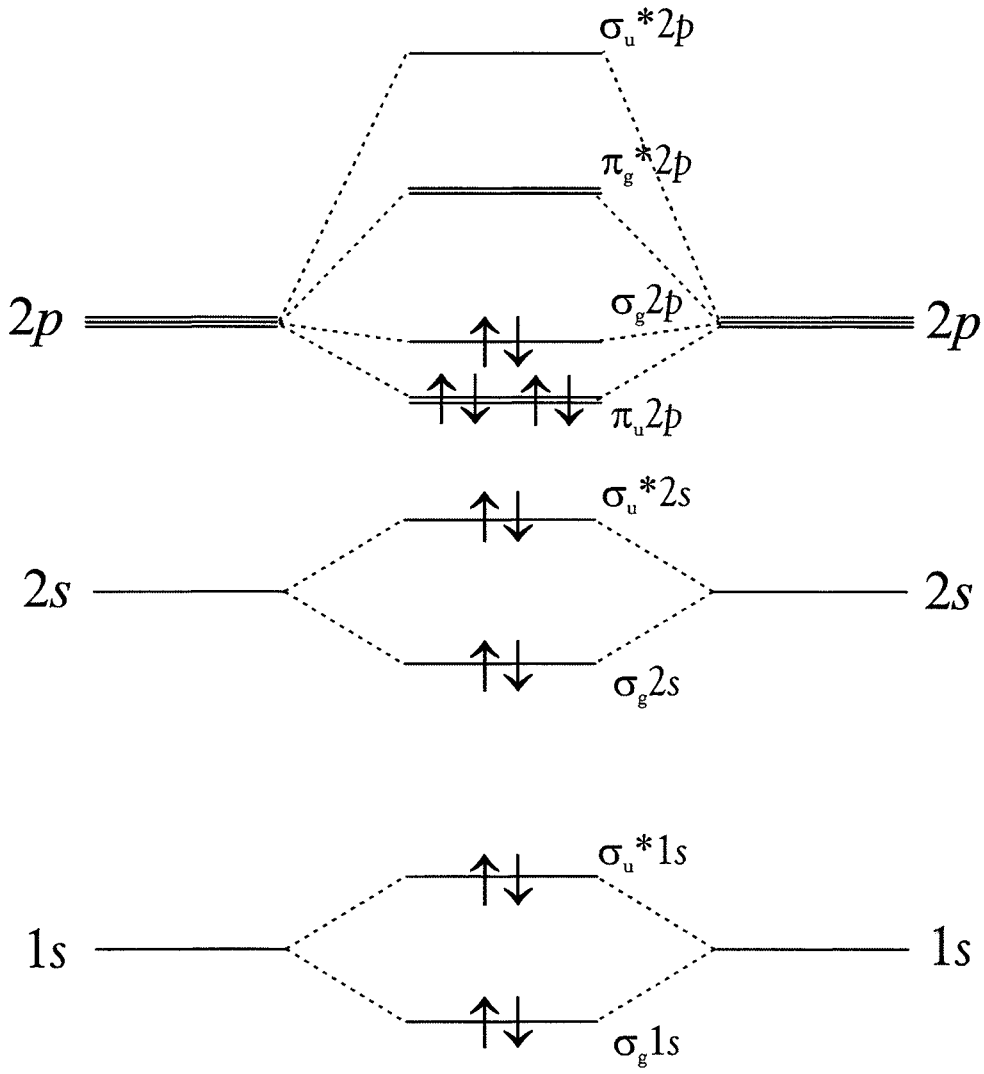
How can we explain the structure in a PE spectrum?

Molecular Orbital Theory

Molecular orbitals are constructed from linear combinations of **atomic orbitals** (LCAO)

$$\psi = \sum_i c_i \phi_i$$

MO diagram for N_2

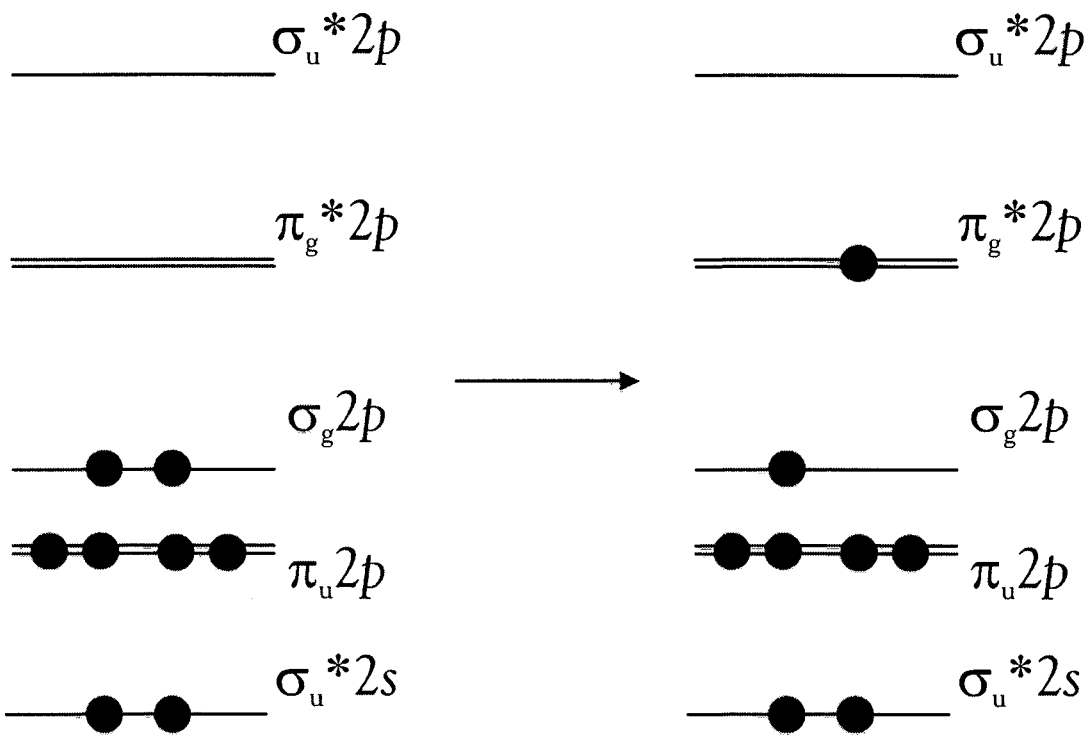


What is an electronic transition?

(a) The One-electron description

> *The excitation of an electron from an occupied MO to an unoccupied MO.*

e.g. N_2



(b) *Electronic transitions really occur between states!*

The ground electronic state configuration of N_2:

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$$

$$\Downarrow$$

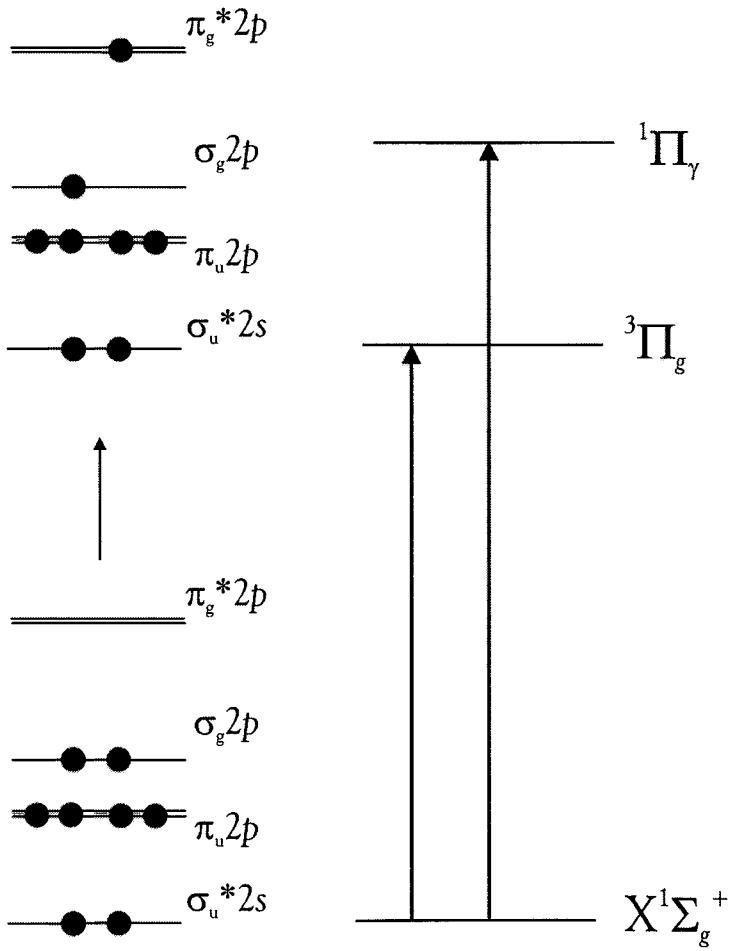
$$X^1\Sigma_g^+ \qquad \textbf{ONE state}$$

The excited configuration of N_2

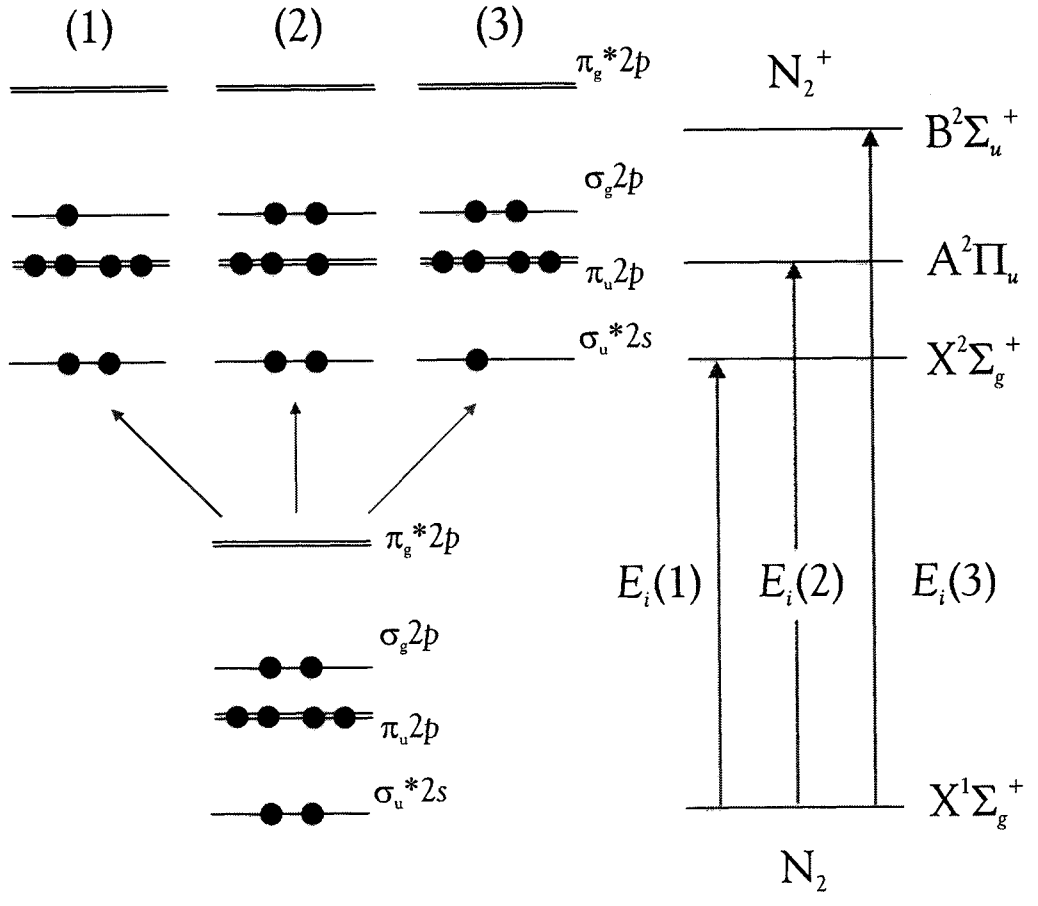
$$\ldots(\pi_u 2p)^4(\sigma_g 2p)^1(\pi_g^* 2p)^1$$

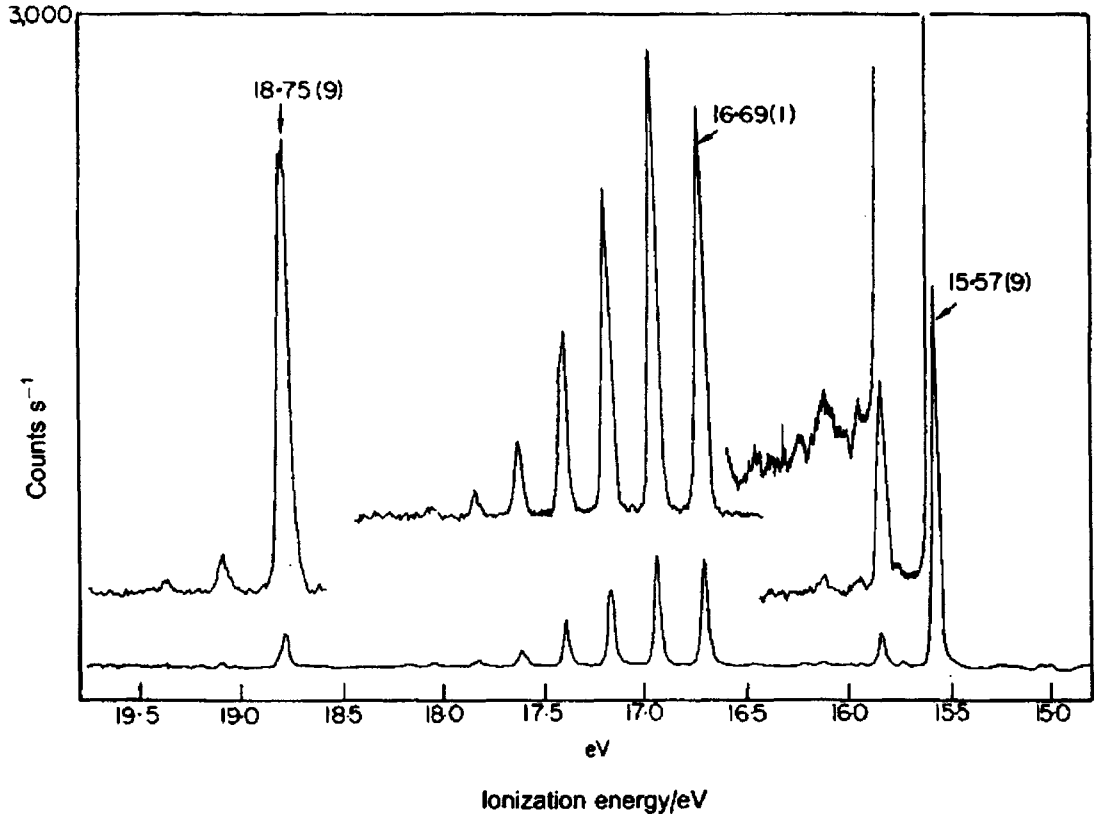
$$\Downarrow$$

$$^3\Pi_g,\ ^1\Pi_g \qquad \textbf{TWO states}$$



(c) *The one-electron description provides a good representation of ionisation in most closed shell molecules*





Koopmans' Theorem

'For a closed shell molecule, the ionisation energy for an electron in a particular orbital is approximately equal to the negative of the orbital energy'

$$I.E. \approx -\varepsilon_i$$

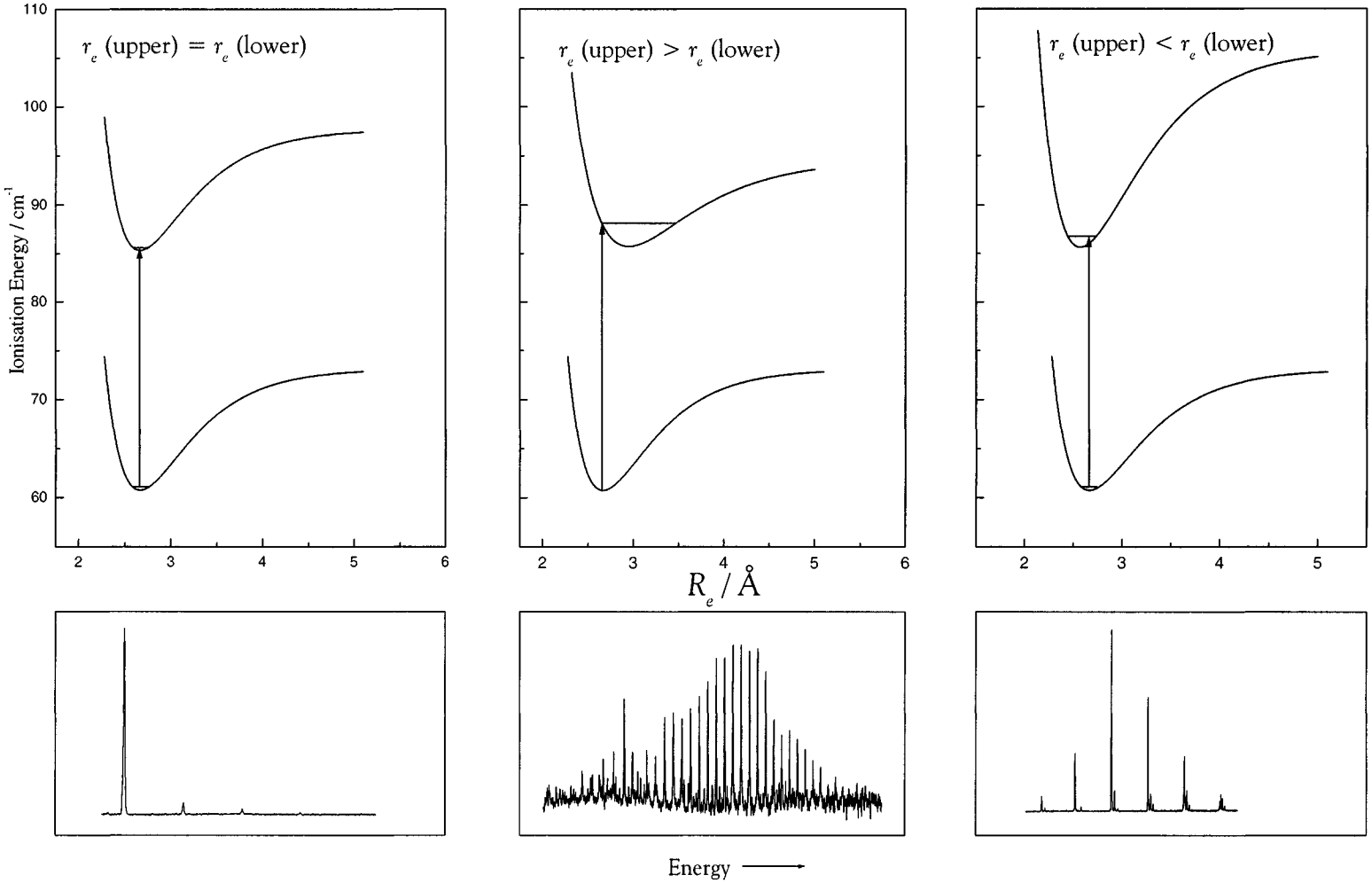
(1) Orbitals are an entirely theoretical concept.

(2) Their energies can only be obtained by calculation.

(3) Experimental ionisation energies are the measureable quantity which most closely corresponds to the orbital energy.

Understanding the origin of Vibrational Structure

The Franck-Condon Principle



Limitations of Koopmans' theorem:

(a) *Neglect of electron reorganisation*

Orbital relaxation, or reorganisation, may occur following ionisation.

$$I.E. \approx -\varepsilon_i + E_R$$

(b) *Neglect of electron correlation*

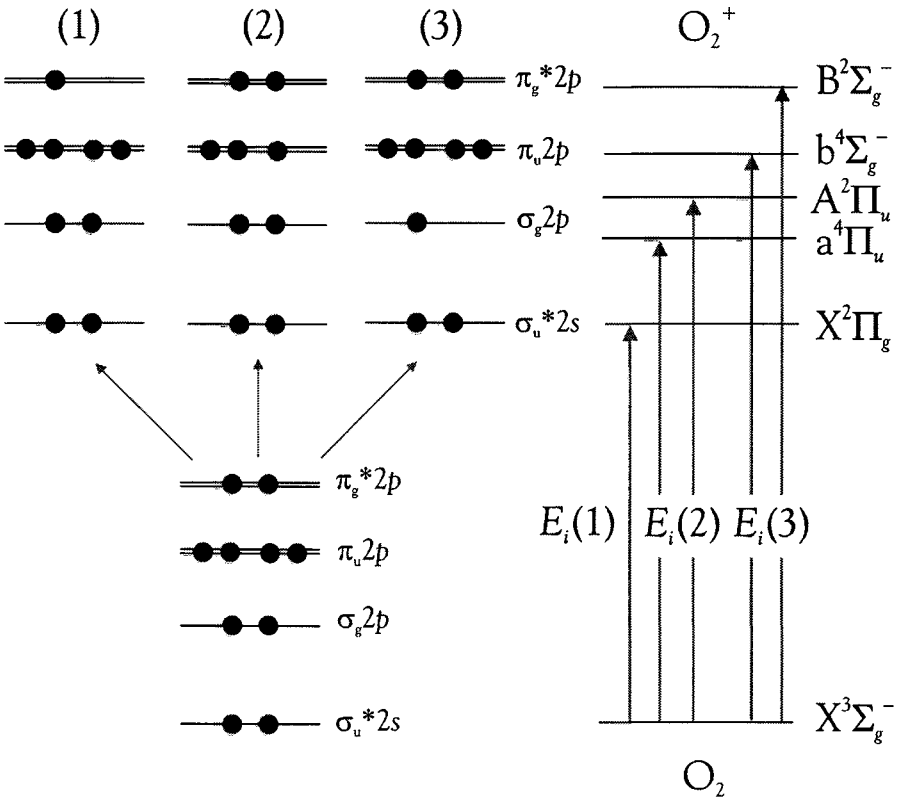
Electronic motion is **correlated** – electrons do not see an 'averaged out' charge of all the other electrons.

Both effects can be small, and fortuitously, in many cases cancel out!

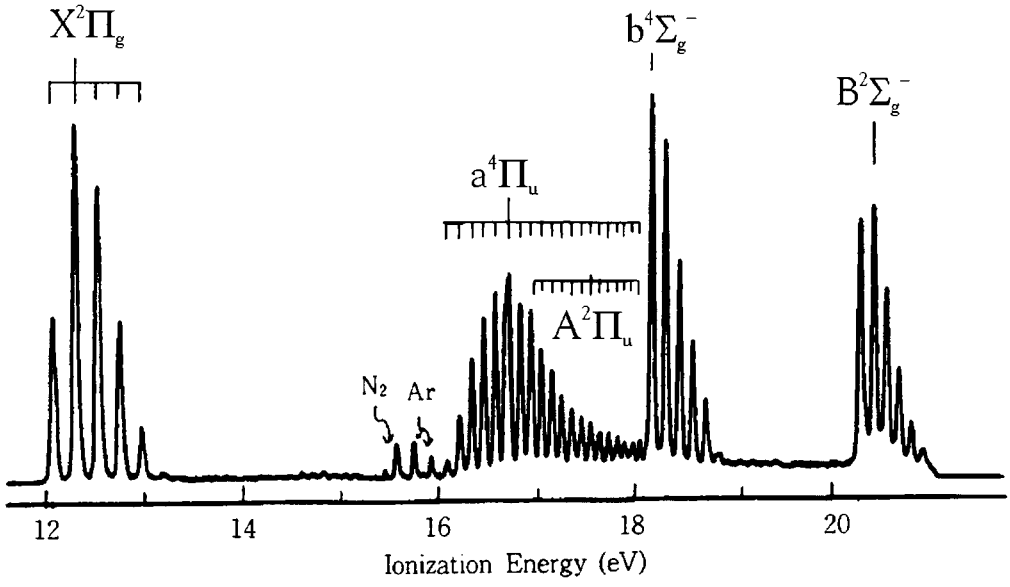
(c) *Fails to account for open shell molecules*

(c) Koopmans' theorem fails for open shell molecules

Oxygen



O_2 Oxygen



Autoionisation in PES

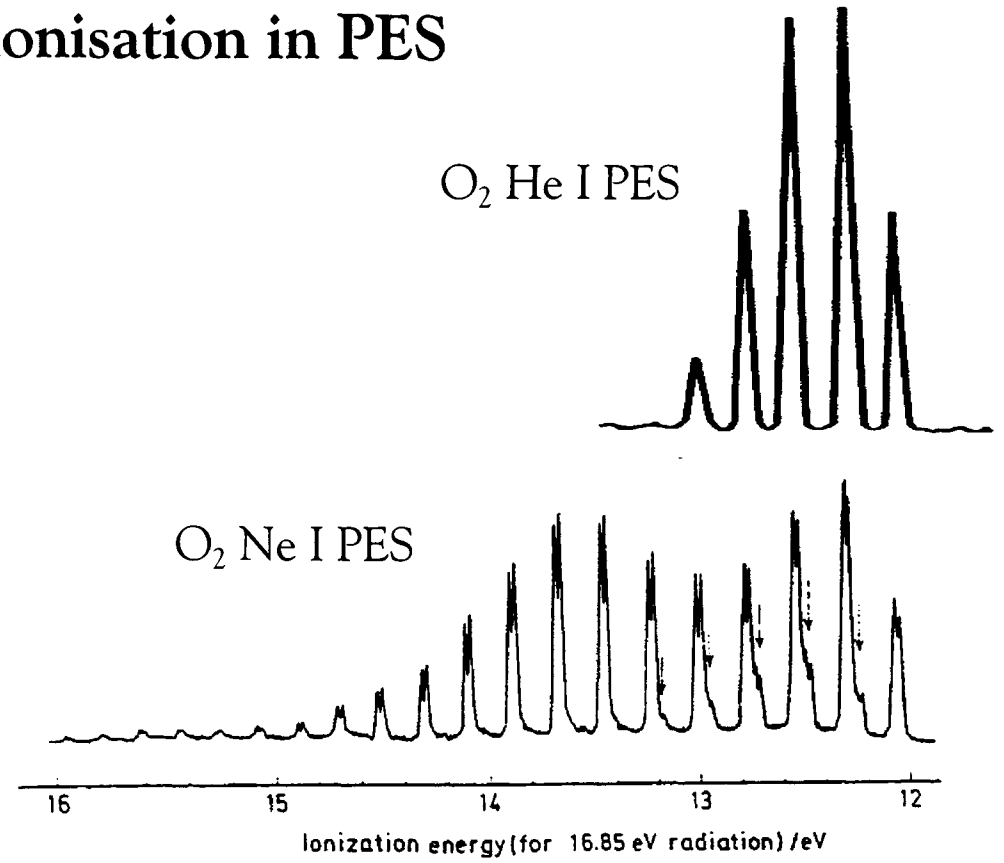
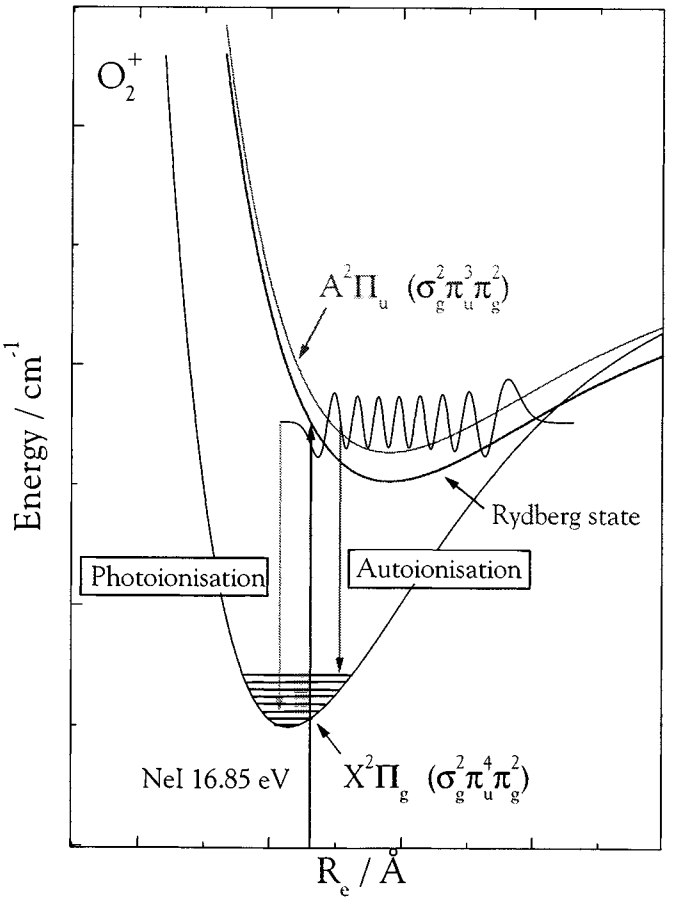


Figure 7.19 Autoionization in the $O_2^+(X^2\Pi_g) \leftarrow O_2\ (X^3\Sigma_g^-)$ band system using a NeI source. The bands marked with arrows are due to the 16.67 eV radiation and do not show autoionization
[Reproduced, with permission, from Eland, J. H. D. (1974). *Photoelectron Spectroscopy*, p. 63, Butterworths, London]

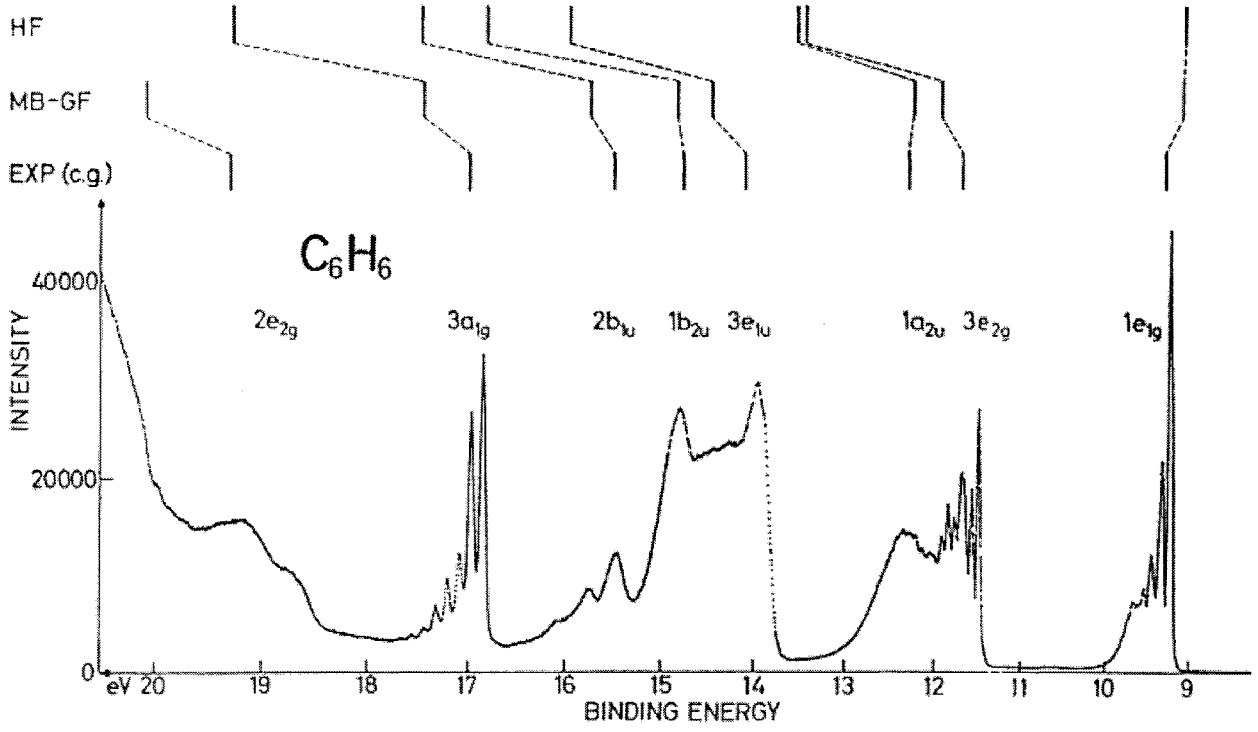


Polyelectronic Molecules

Benzene

- Partially resolved vibrational structure
  e.g. ν_1 (ring breathing mode) in $3a_{1g}$ band.

- Bands arise from ionisation from σ and π MO's.



The quest for higher resolution

- In the 1960's and 70's typical resolution no better than 10 meV (80 cm^{-1}).

- 1992 Balzer, Karlsson and Wannberg[5] improved to 4.5 meV (36 cm^{-1}) using mw electron-cyclotron-resonance source (linewidth 1.2 meV)

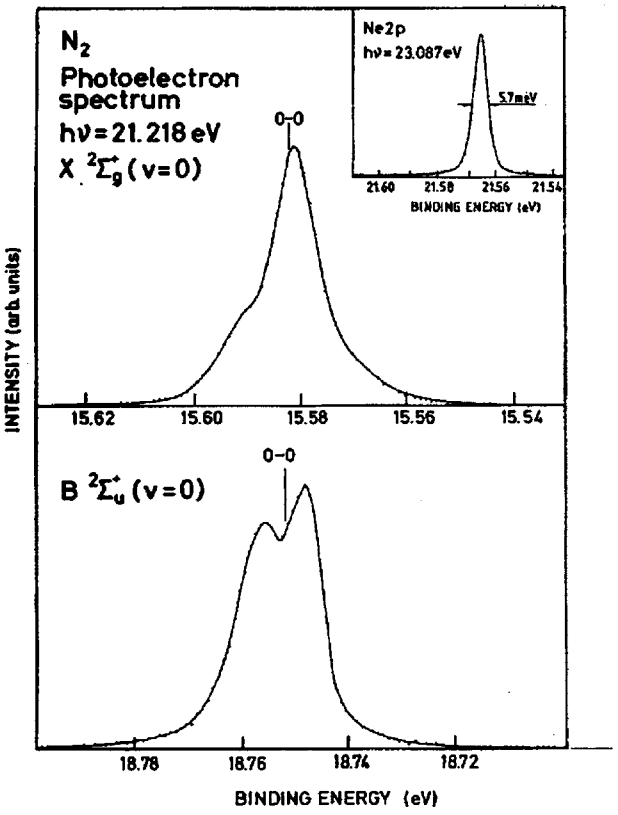


FIG. 1. The upper part shows the He I excited photoelectron spectrum corresponding to the $X\ ^1\Sigma_g^+(N_2, v=0) \rightarrow X\ ^2\Sigma_g^+(N_2^+, v=0)$ transition. The lower part shows the He I excited photoelectron spectrum corresponding to the $X\ ^1\Sigma_g^+(N_2,(N_2, v=0) \rightarrow B\ ^2\Sigma_u^+(N_2^+, v=0)$ transition. In the upper right part the Ne $2p_{3/2}$ line excited with the He I β radiation at 23.087 eV is inserted. The lines connecting the experimental points are drawn as guides to the eye.

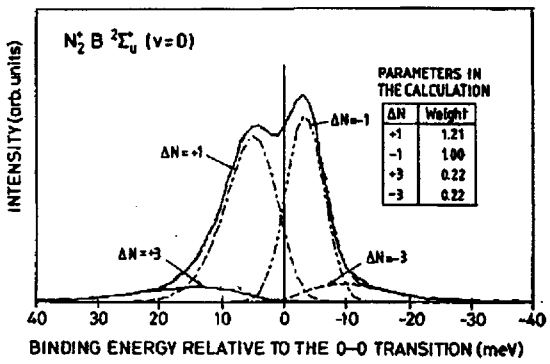
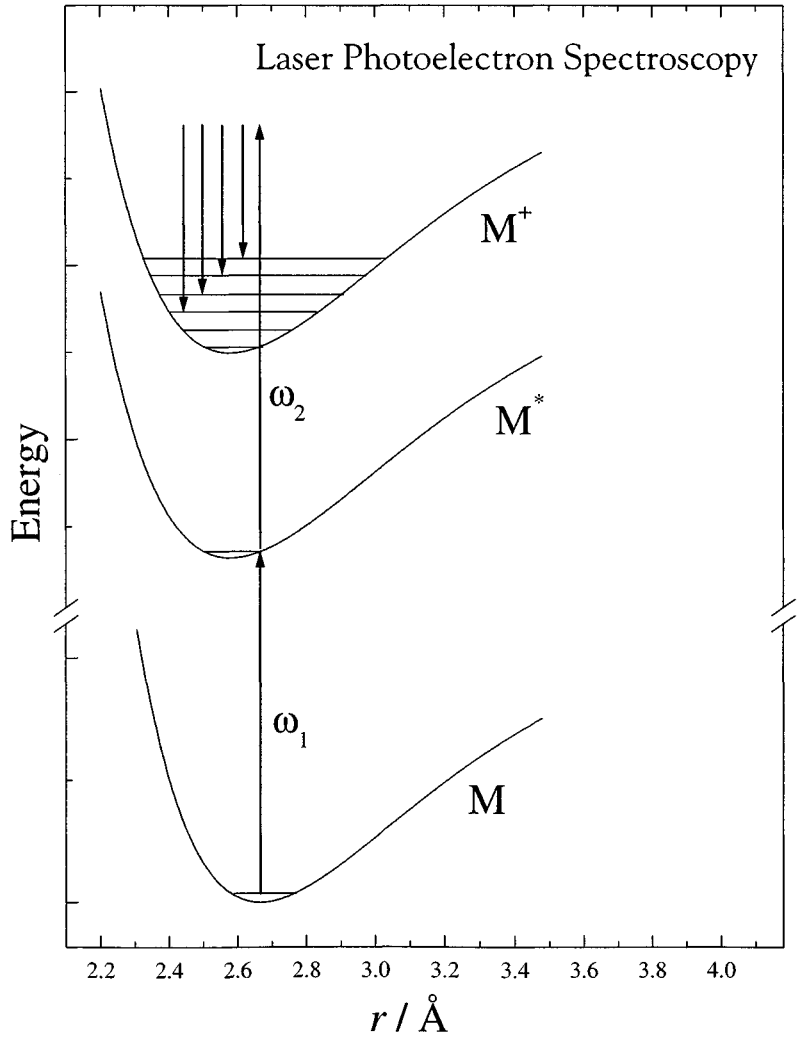


FIG. 3. The experimental (full line) and fitted theoretical (dashed line) $X\ ^1\Sigma_g^+(N_2, v=0) \rightarrow B\ ^2\Sigma_u^+(N_2^+, v=0)$ spectra shown together. The spectra are very similar and an obvious difference can be seen only at -12 meV from the zero level, where the intensity of the experimental spectrum is somewhat higher. For clarity, the subbands corresponding to transitions with $\Delta N = \pm 1$ and ± 3 are included. Also the weights used in the fitting of the theoretical spectrum are shown in the figure normalized to 1.00 for $\Delta N = -1$ subband. The energy scale refers to zero at the (unobserved) 0-0 transition.

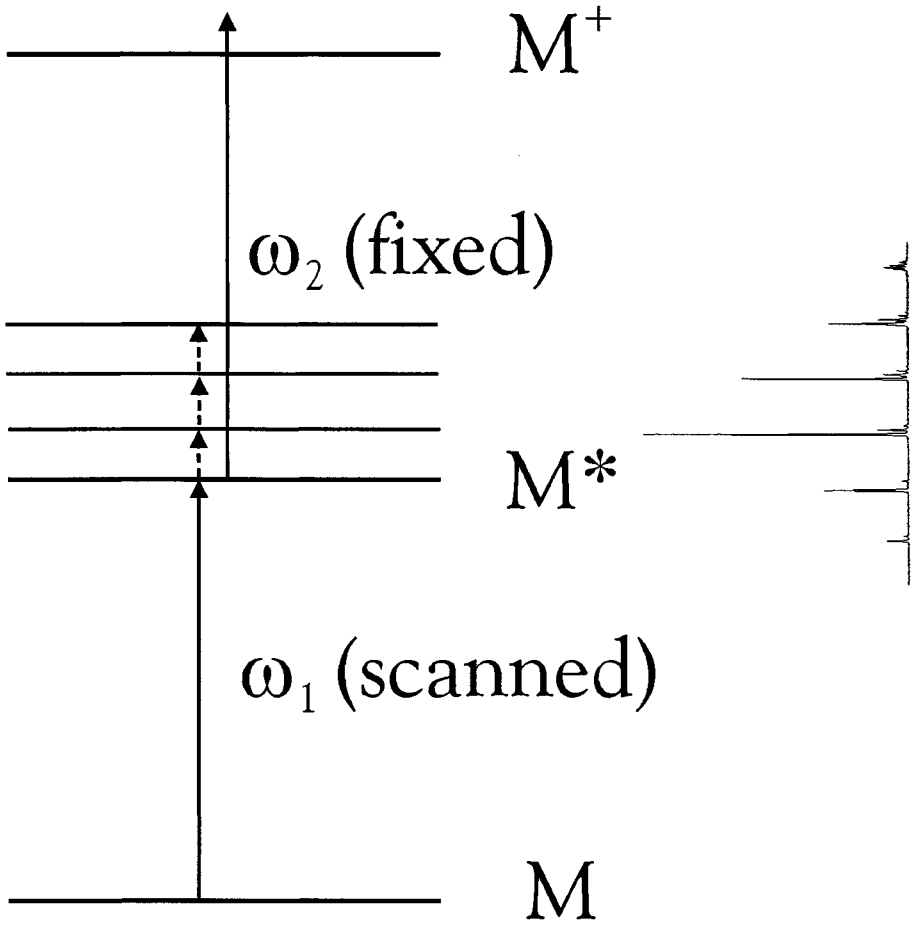
[5] P. Baltzer, L. Karlsson and B. Wannberg, *Phys. Rev A*, **46** (1992) 315

Laser Photoelectron Spectroscopy (1980's)

- Employs resonance enhanced multiphoton ionisation (REMPI) – a two step process.
- State selection
- Supersonic jets and molecular beams ($T_{trans} \approx 1$ K, $T_{rot} \approx 10$ K, $T_{vib} \approx 100$ K)
- Narrow laser linewidth (< 1 cm^{-1})
- Molecule specificity



REMPI spectroscopy characterises the intermediate state



A Case Study: The Ar-NO van der Waals Complex

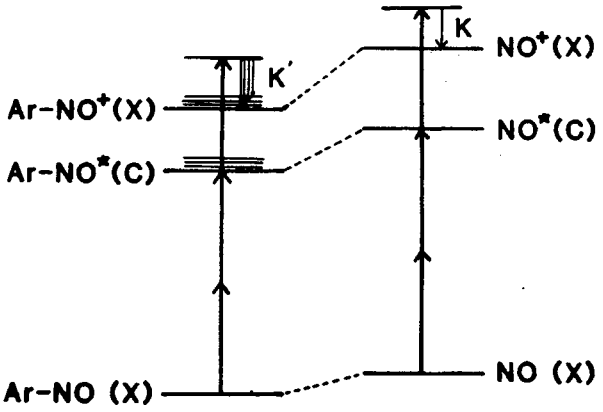


FIG. 5. Schematic energy level diagrams of NO and Ar–NO, relevant to (2 + 1) resonant multiphoton ionization through their Rydberg C states.

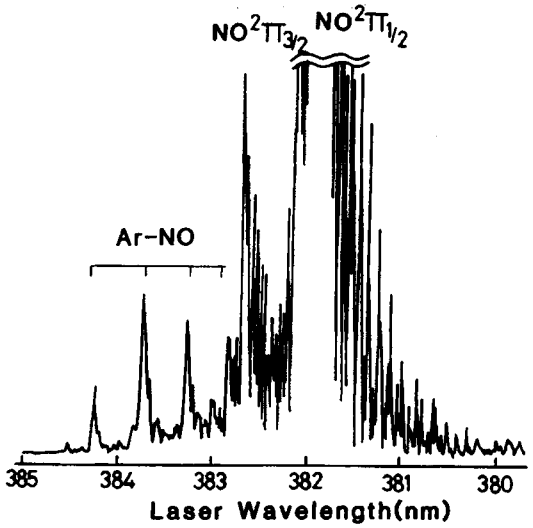


FIG. 1. An MPI ion–current spectrum obtained with a free jet of a mixture of 5% NO in Ar in the laser wavelength region 380–385 nm. The stagnation pressure was 1 atm.

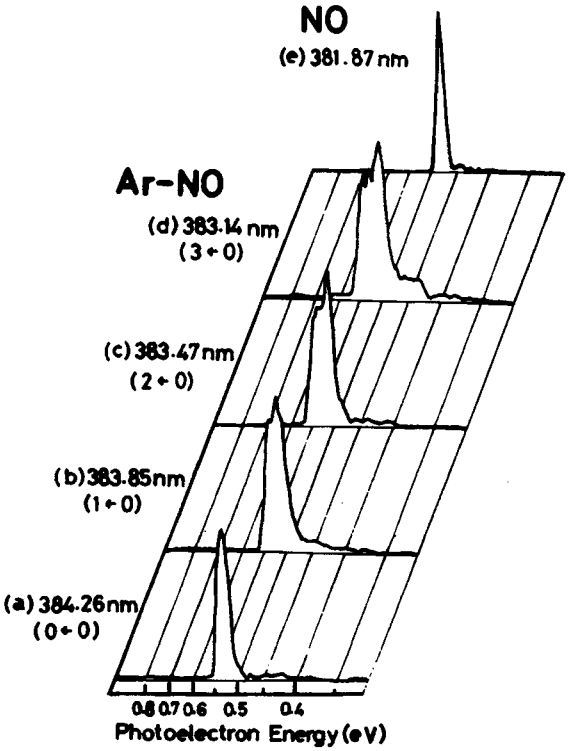


FIG. 4. Photoelectron spectra obtained by the (2 + 1) resonant multiphoton ionization of a free jet of the Ar–NO (5%) mixture at the ion–current peaks of the Ar–NO van der Waals complex [spectra (a)–(d)] and of the free NO molecule [spectrum (e)].

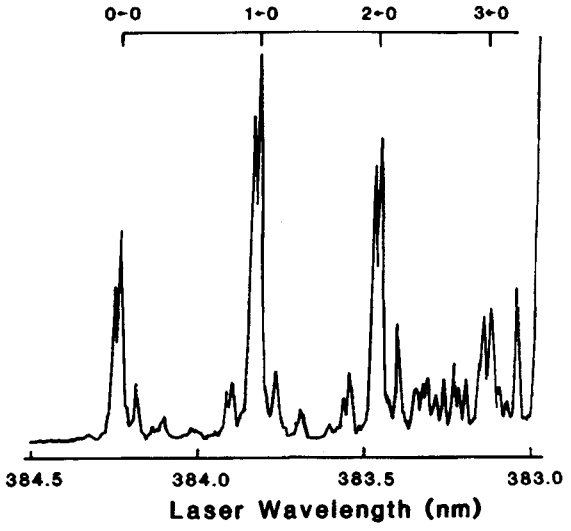


FIG. 2. An MPI ion–current spectrum attributed to the Ar–NO van der Waals complex, shown in an extended scale. The experimental conditions are the same as in Fig. 1.

Resolution of 20 meV, but molecule specificity!

K. Sato, Y. Achiba and K. Kimura, *J. Chem. Phys.*, **81** (1984) 57

Magnetic bottles, supersonic jets and lasers

- Late 1990's de Lange *et al.* obtained a resolution of 8 meV (64 cm^{-1}) using magnetic bottle electron energy analysis.

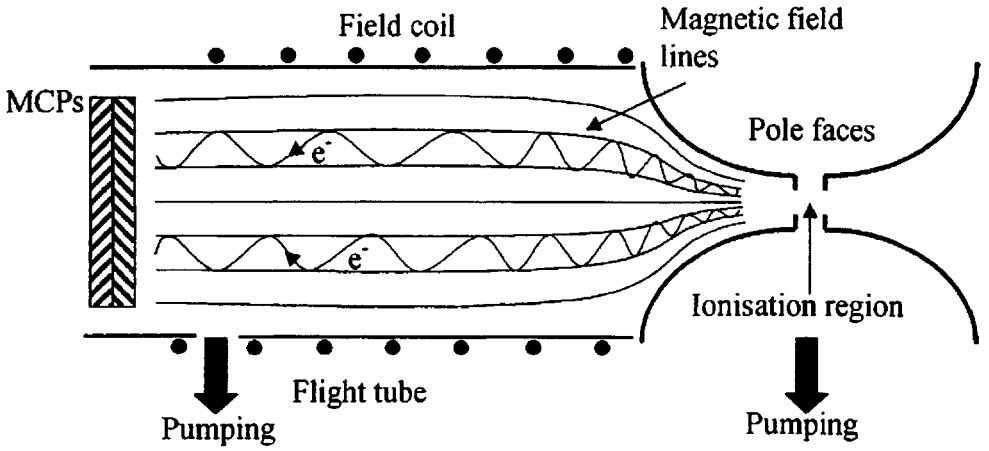


Fig. 1. Schematic of 'magnetic bottle' spectrometer showing the key functional elements.

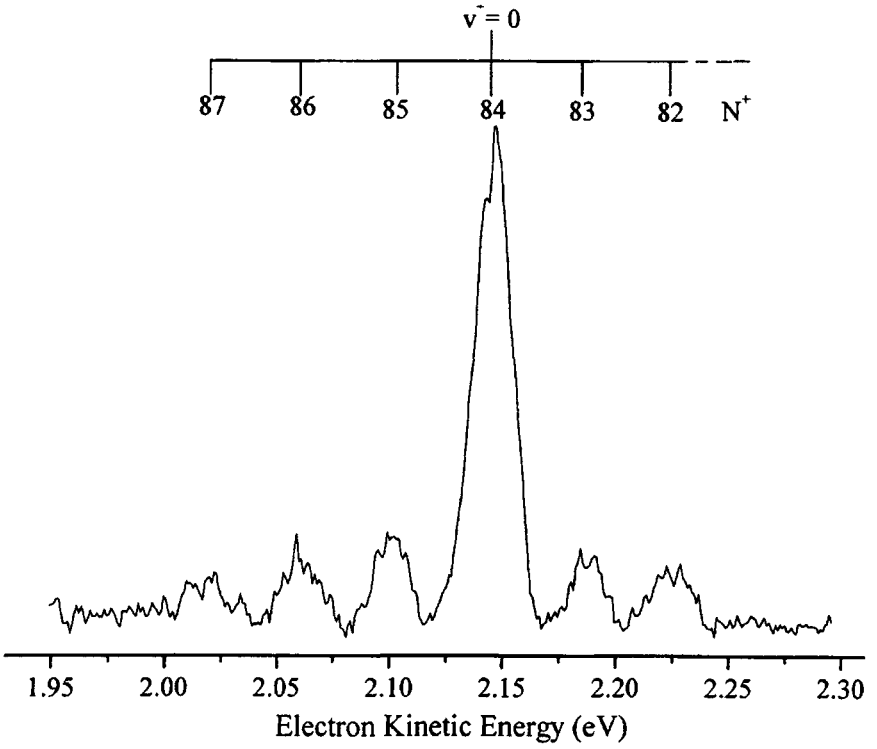


Fig. 4. Rotationally resolved photoelectron spectrum obtained by a one-photon ionisation from the Q(84) level of the intermediate $B^1\Sigma^-$ ($v' = 0$) state of rotationally excited CO.

Laser limited Photoelectron Spectroscopy?

Weinkauf *et al*[6] achieve 4 – 8 cm^{-1} resolution

- Minimising excess energy (<300 meV)
- Careful reduction of point charges in ionisation region
- REMPI state selection & time-of-flight energy analysis

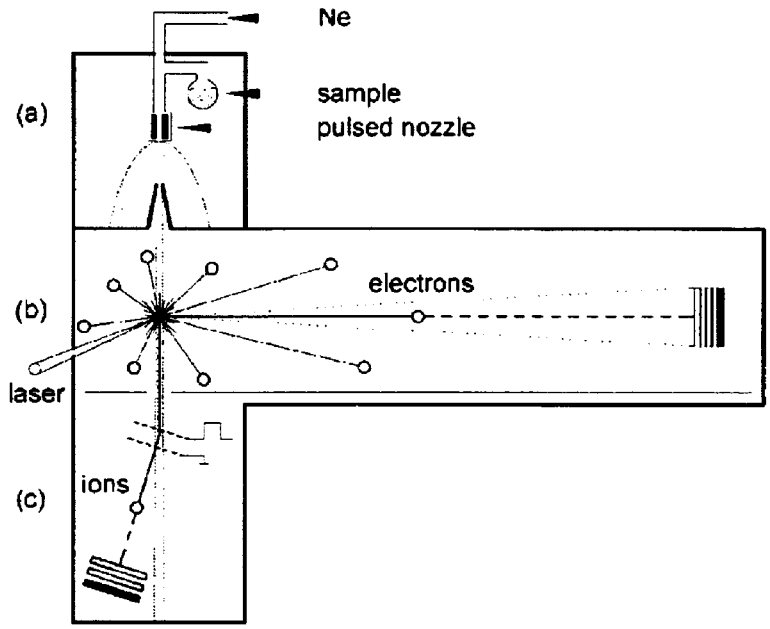
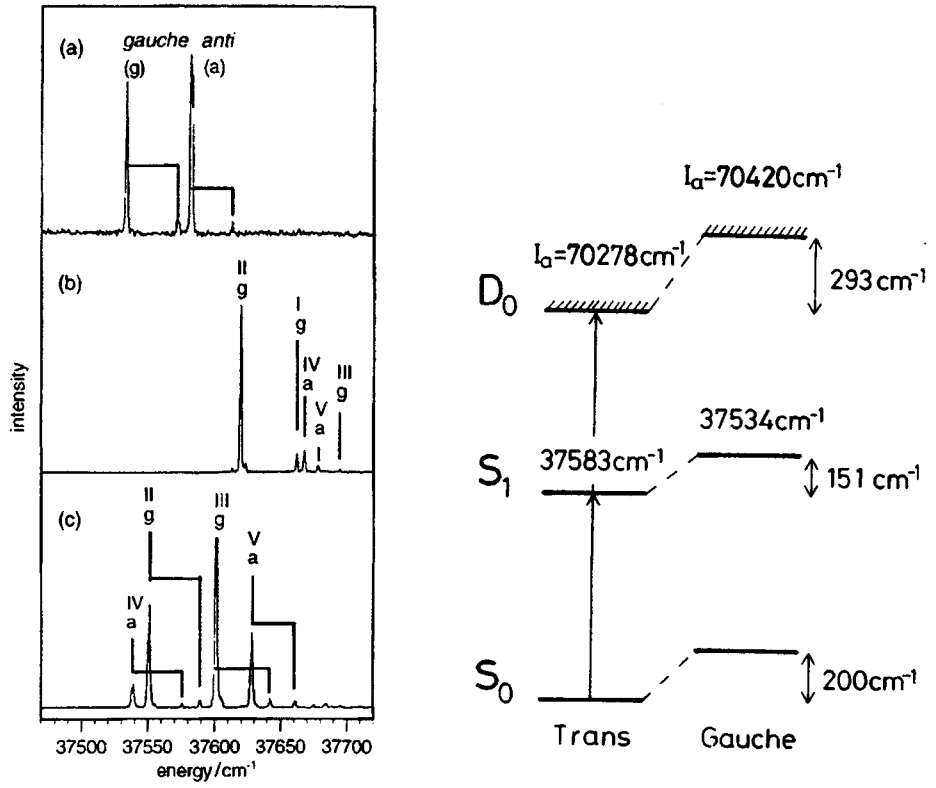


Fig. 2 Experimental setup of the MPI high-resolution photoelectron spectrometer: (a) inlet chamber, (b) field-free photoelectron spectrometer, (c) pulsed time-of-flight mass spectrometer. Note that MPI, MPI-PE and mass spectra can be recorded in the same instrument.

[6] R. Weinkauf, F. Lehrer, E.W. Schlag and A. Metsala, *Faraday Disscuss.* **115** (2000) 363

Photoelectron Spectrum of n-propylbenzene

(a) REMPI spectrum



(b) REMPI-PE spectrum

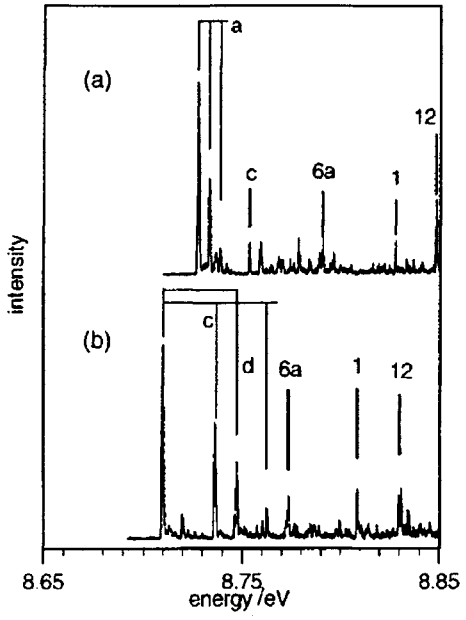
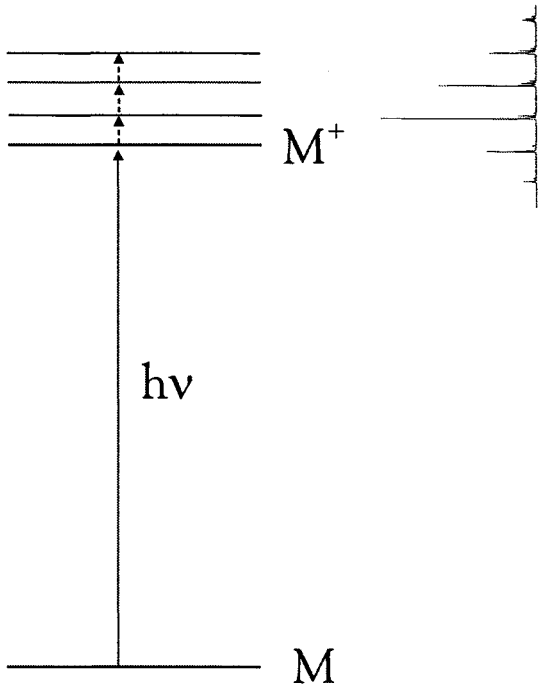


Fig. 6 The MPI-PE spectra of n-propylbenzene: (a) *gauche* and (b) *anti* conformer. The very different vibronic transition pattern allows a clear conformer assignment. The transition intensities show a relative small structural change upon ionization. The resolution of the MPI-PE spectrum is better than 8 cm^{-1}.

Dispensing with kinetic energy analysis

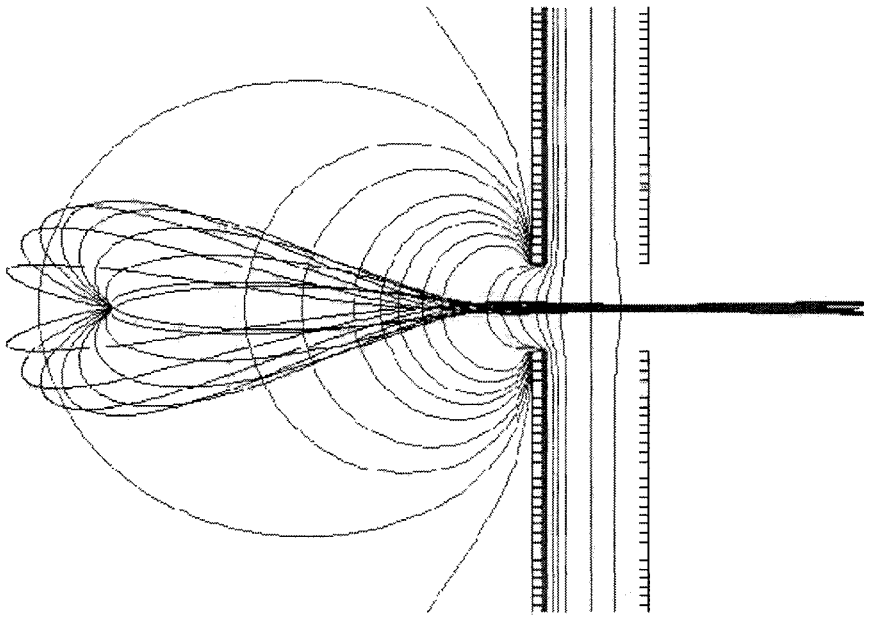
Threshold Photoelectron Spectroscopy (TPES)

- Collects threshold photoelectrons ('zero' energy) emitted when a resonant transition is excited.



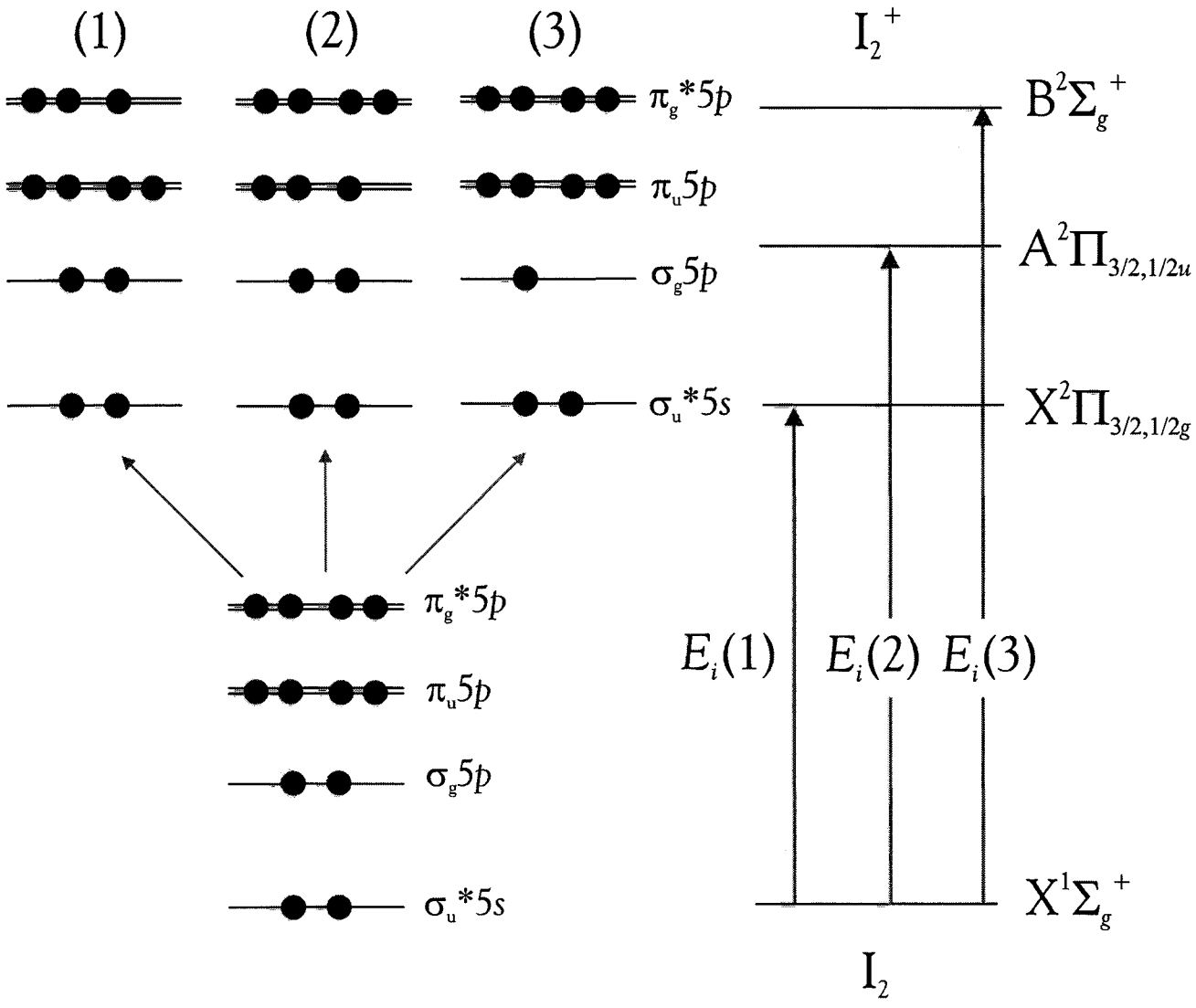
- Synchrotron radiation

- Penetrating field electron lens



Trajectories of 0.001eV electrons emitted from a point source are focused and collimated by the weak electric field from an 'extractor' electrode that penetrates through the 0 Volt aperture.

A Case Study: Molecular Iodine

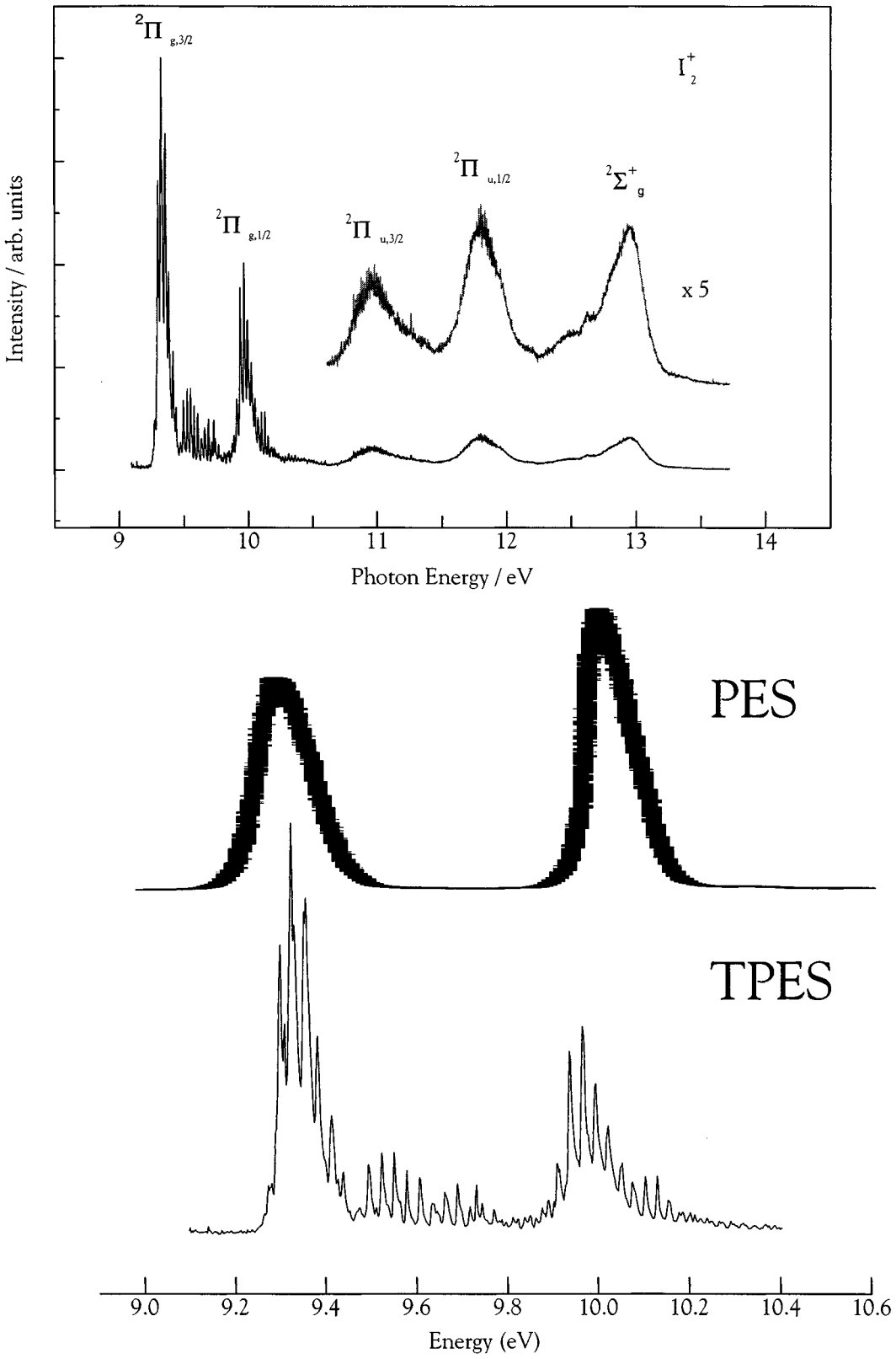


Each $^2\Pi$ state is split into two spin-orbit states

$$(\pi_g^*\ 5p)^3\ ^2\Pi_{3/2,1/2,g} \leftarrow (\pi_g^*\ 5p)^4\ ^1\Sigma_g^+$$

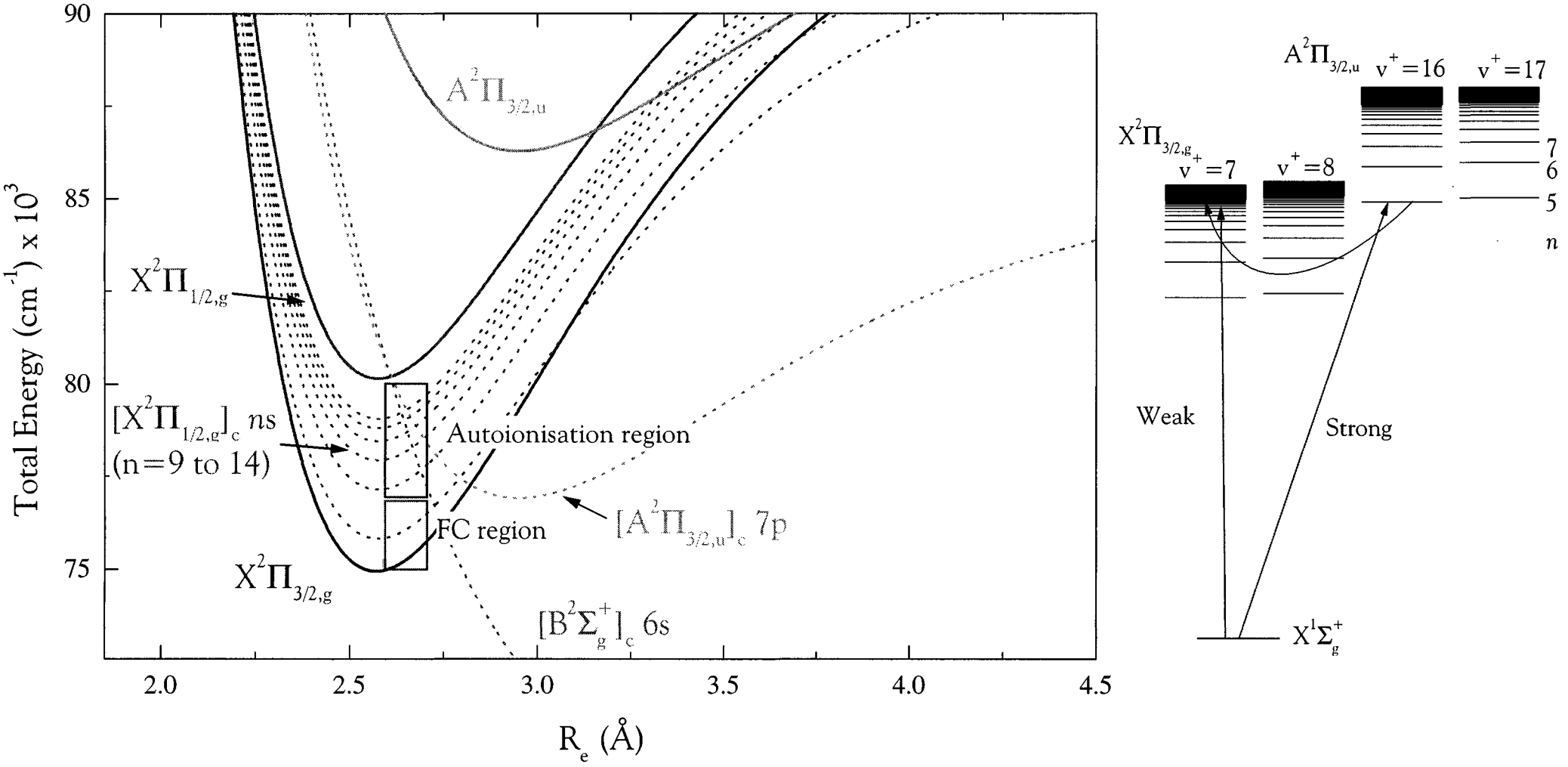
TPES of Molecular Iodine[7]

- Resolution ≈ 5 meV (40 cm^{-1})



[7] A.J. Yencha, M.C.R. Cockett, J.G. Goode, R.J. Donovan, A. Hopkirk and G.C. King, *Chem. Phys. Lett.*, **229** (1994) 347.

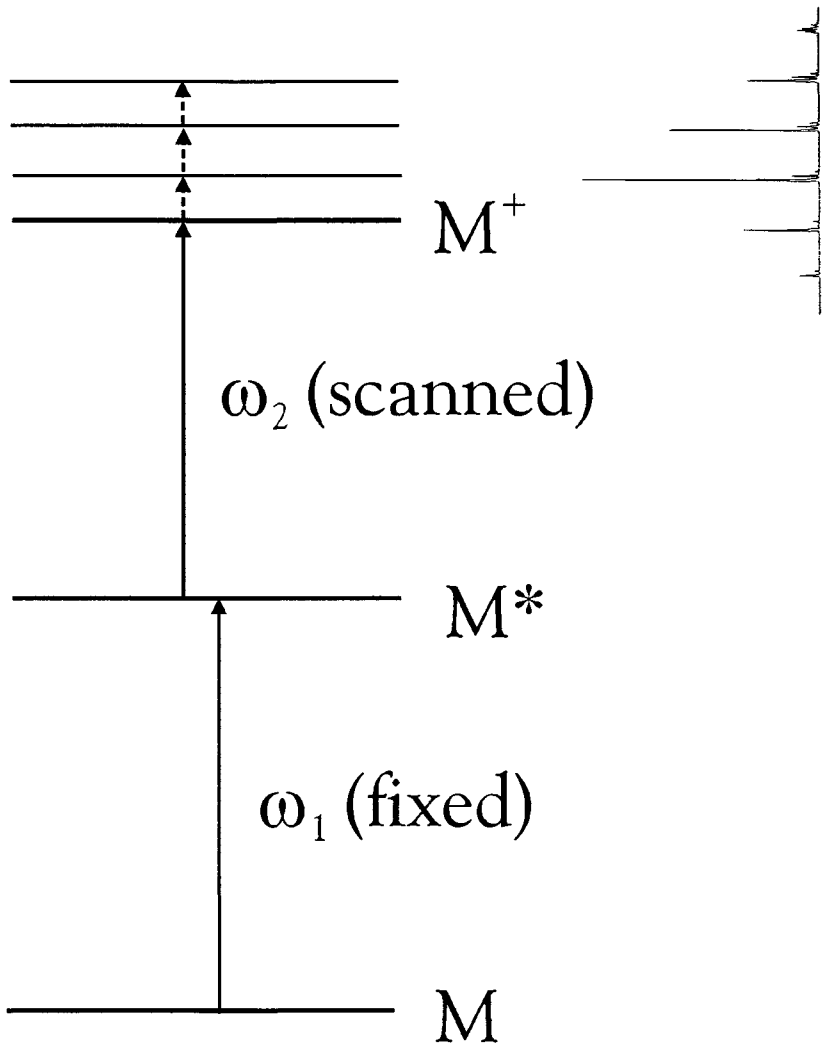
Autoionisation Revisited



The next step: Zero Electron Kinetic Energy (ZEKE) (photoelectron) spectroscopy

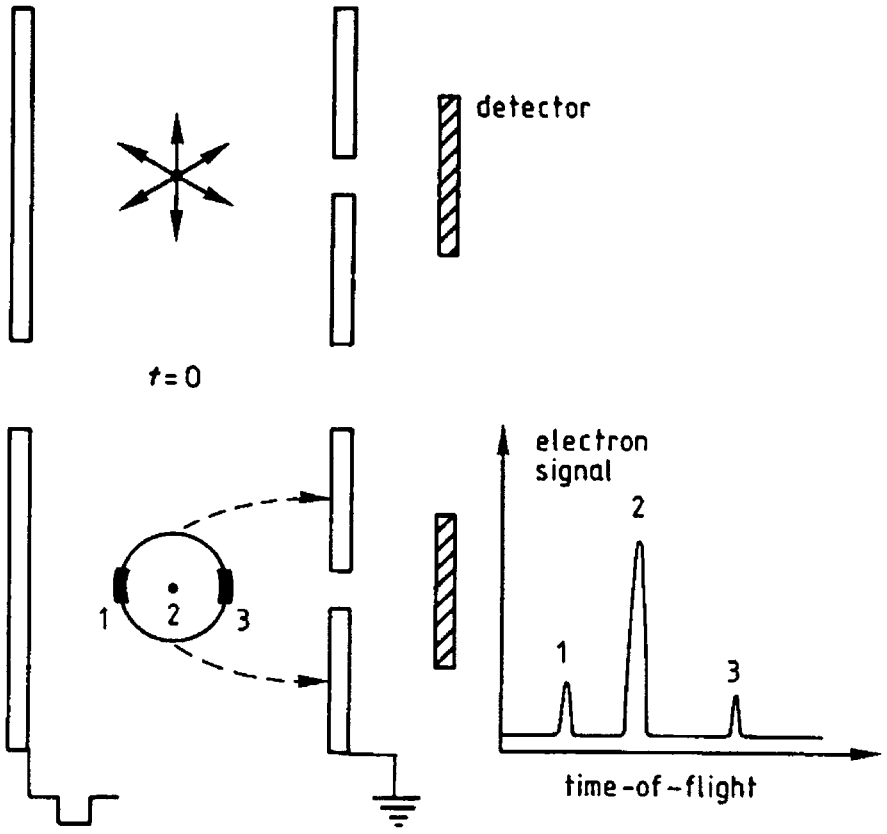
Lasers, delay, long life and Rydberg states

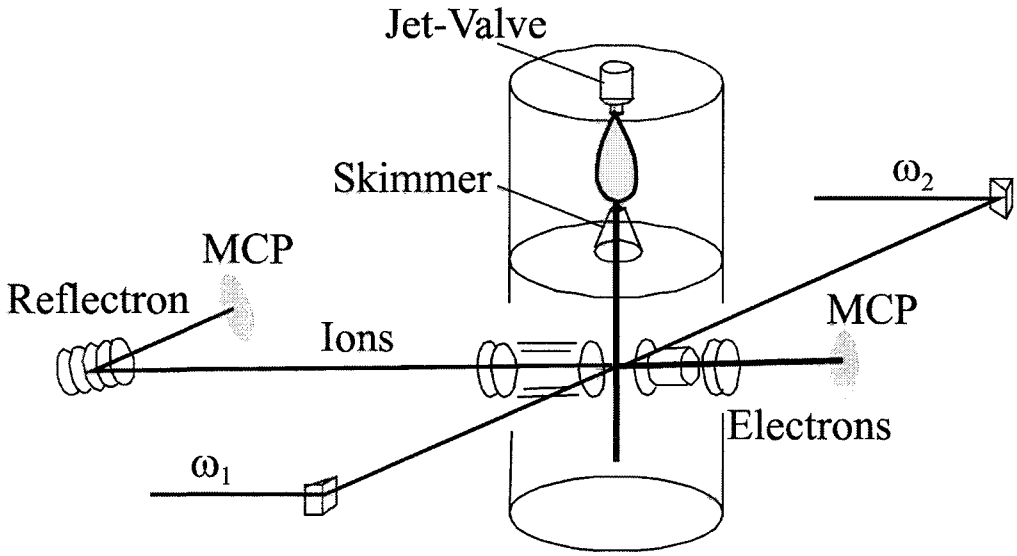
- **REMPI+TPES=ZEKE**



How do we separate 'ZEKE' electrons from 'fast' electrons?

We do nothing!





1984 The first ZEKE spectrum[8]

- Resolution better than ≈ 2 cm^{-1}
- Rotational structure

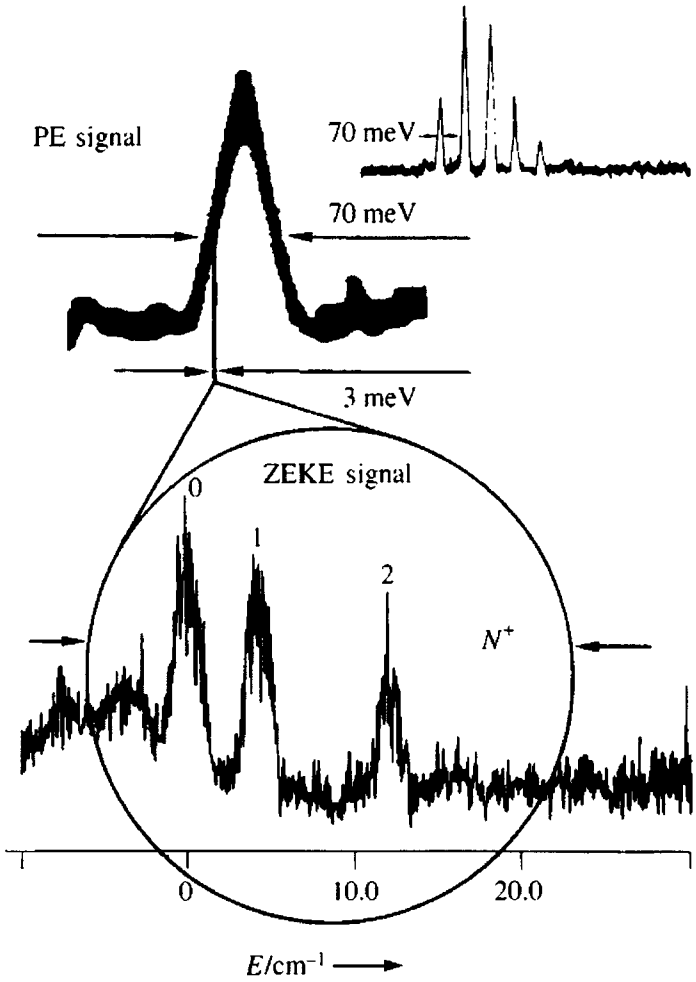
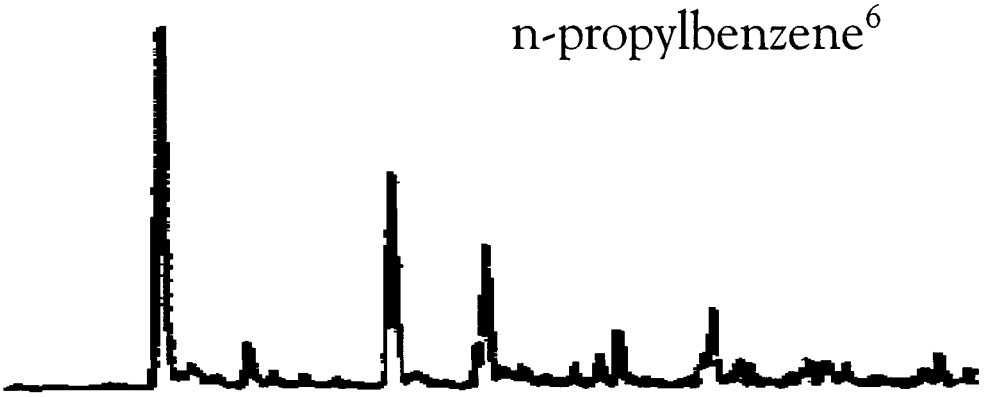


Figure 2. The first VUV photoelectron spectrum of NO[14] (top) with a vibrational progression from $v^- = 0$ to $v^+ = 4$ of the $^1\Sigma^+$ electronic ground state of NO^- and comparison of the $v^+ = 0$ peak with the first ZEKE spectrum obtained.[14] The ZEKE spectrum shows the lowest rotational states in the vibrational state $v^+ = 0$ with $N^+ = 0-2$.

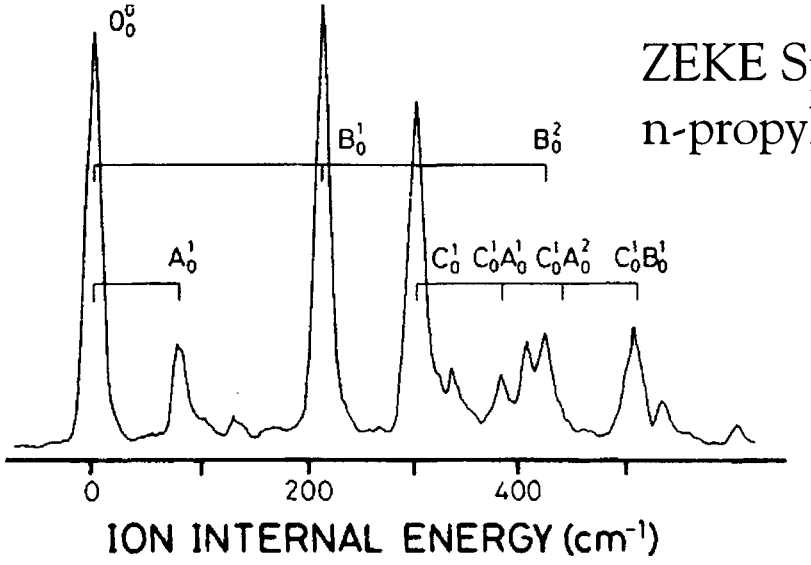
[8] K. Müller-Dethlefs, M. Sander and E.W. Schlag, *Chem. Phys. Lett*, **112** (1984) 291.

Is ZEKE spectroscopy 'real' photoelectron spectroscopy?

Photoelectron Spectrum of n-propylbenzene[6]



ZEKE Spectrum of n-propylbenzene[9]



[6]R. Weinkauf, F. Lehrer, E.W. Schlag and A. Metsala, *Faraday Disscuss.* **115** (2000) 363

[9]M. Takahashi and K. Kimura, *J. Chem. Phys.*, **97** (1992) 2920.

It looks like a duck, and walks like a duck but ...

- Late 1980's: ZEKE spectra are not equivalent to PE spectra.

- Each band is shifted by a few cm^{-1} to lower energy.

Are we really detecting 'ZEKE' electrons?

- ZEKE spectra frequently exhibit autoionisation.

Band intensities cannot be trusted!

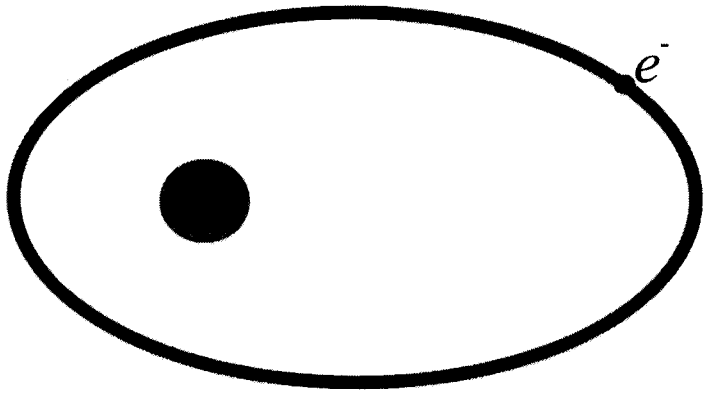
ZEKE electrons are not really photoelectrons

The Role of Rydberg States and Field Ionisation

What are Rydberg States?

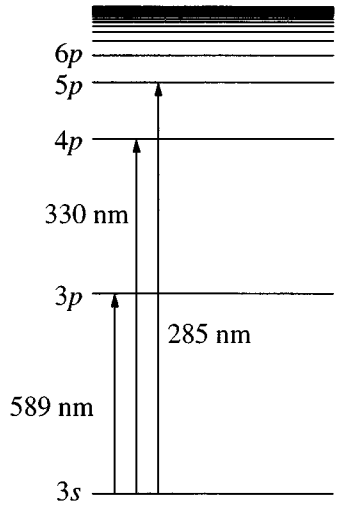
- Rydberg states are electronic states of high principal quantum number n.

- The electron occupies an orbital whose size is large relative to the dimensions of the ionic core.



Atoms:

Sodium $1s^2 2s^2 2p^6\ 4p^1\ {}^2P_{3/2,1/2} \leftarrow 1s^2 2s^2 2p^6\ 3s^1\ {}^2S_{1/2}$



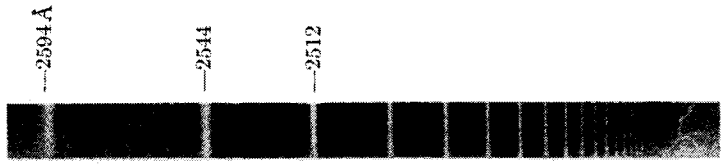
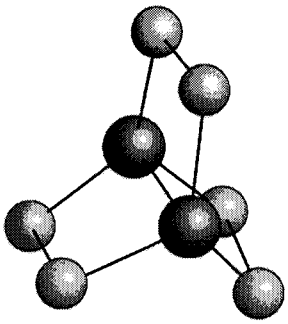


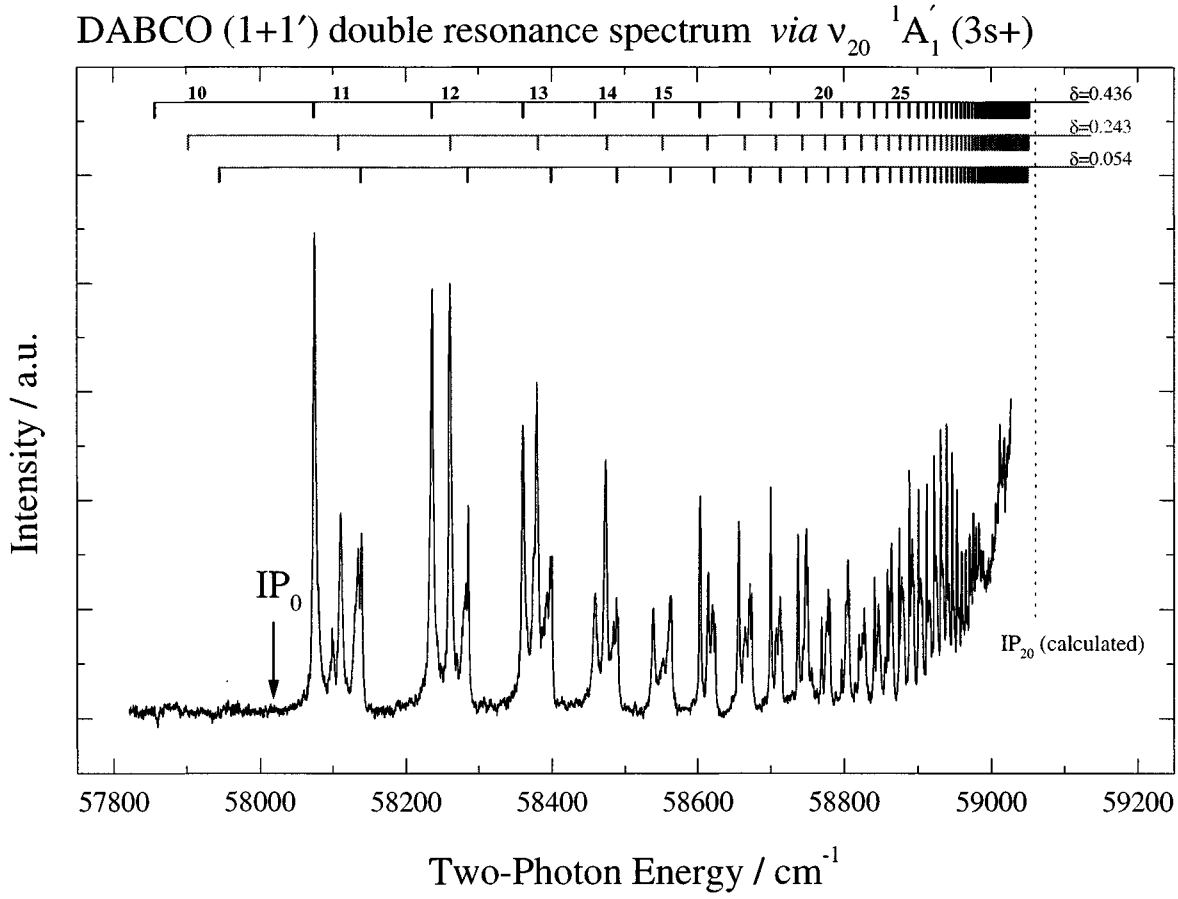
Fig. 2. Absorption Spectrum of the Na Atom [Kuhn (42)]. The spectrogram gives only the short wave-length part, starting with the fifth line of the principal series. The lines appear as bright lines on a dark continuous background, just as on the photographic plate.

Molecular Rydberg States

When is a molecule an atom?

- *At sufficiently high levels of electronic excitation, all molecules eventually resemble the hydrogen atom.*

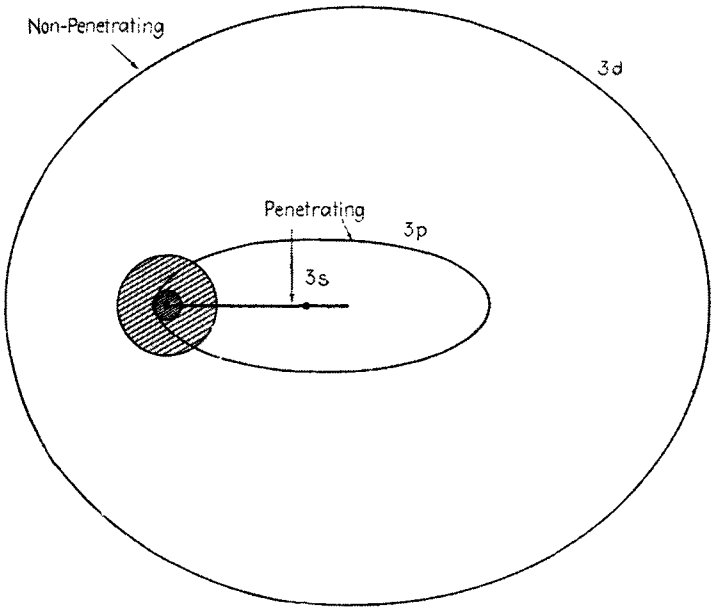




Lifetimes

Rydberg states are potentially HUGE.

$$r = \frac{n^2 \hbar^2 4\pi\varepsilon_0}{Ze^2 m}$$



n	r
1	0.53 Å
10	53 Å
100	5300 Å
200	21200Å

FIG. 7.3.—Comparison of the quantum-mechanical with the classical model of the neutral sodium atom. Three of the lowest possible states for the single valence electron are also shown.

Lifetimes

For *low*-ℓ, $\tau \propto n^3$

For *high*-ℓ, $\tau \propto n^5$

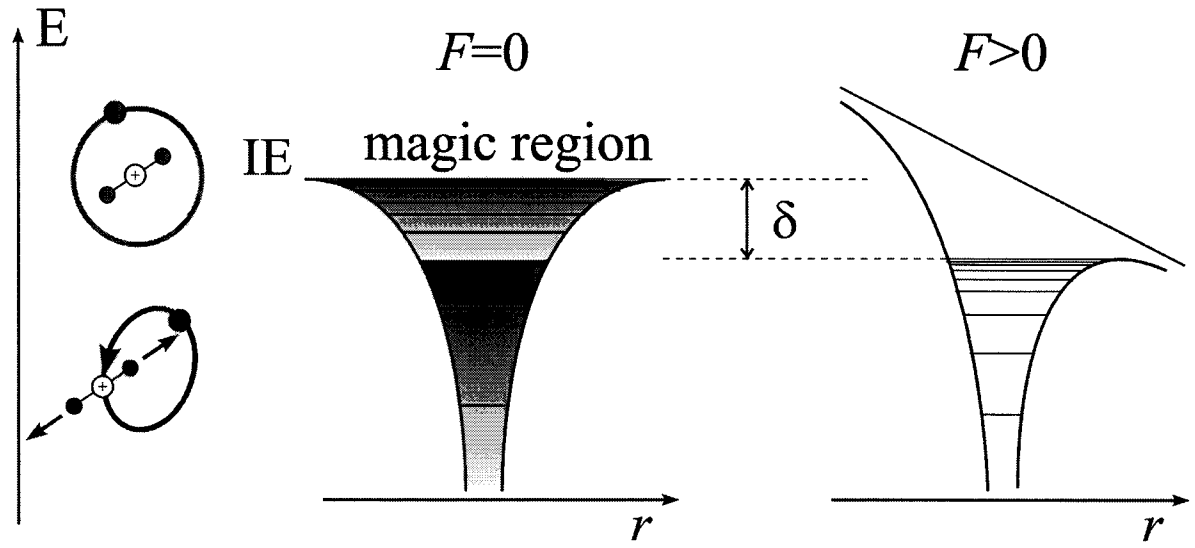
In sodium

$n = 30$; $\ell = 0$: $\tau = 32$ μs.

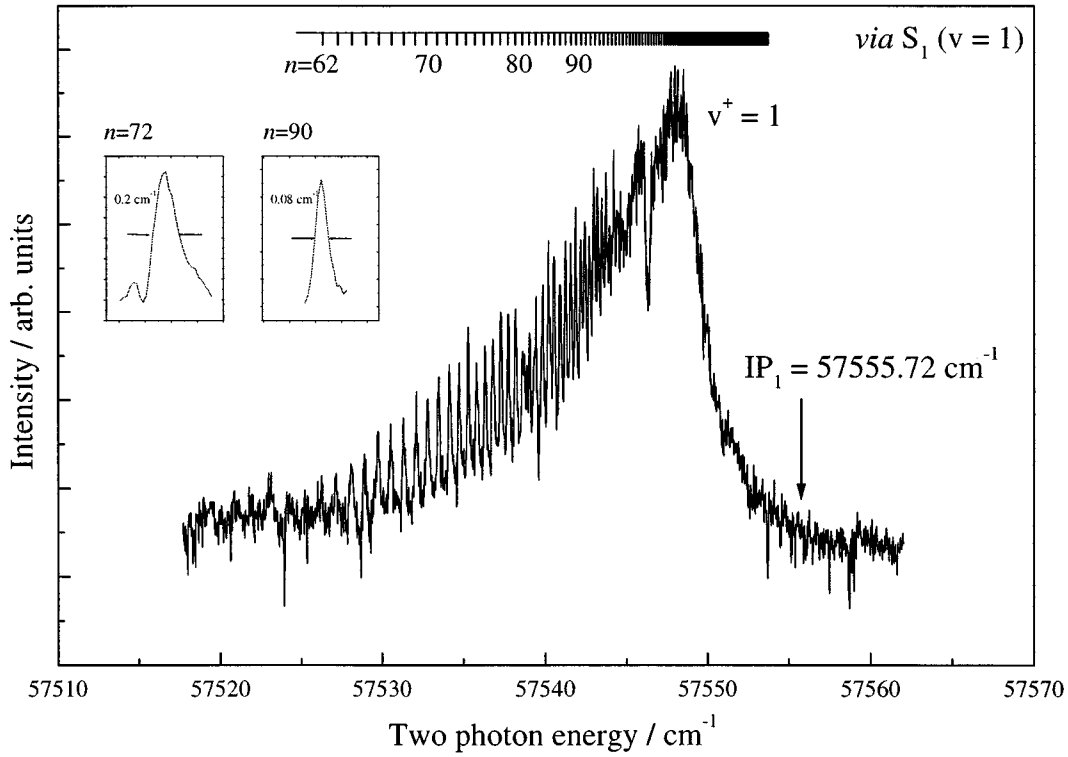
$n = 30$; $\ell = n - 1$ (*circular*): $\tau = 2.3$ ms

ZEKE spectroscopy relies on the existence of metastable high-n molecular Rydberg states.

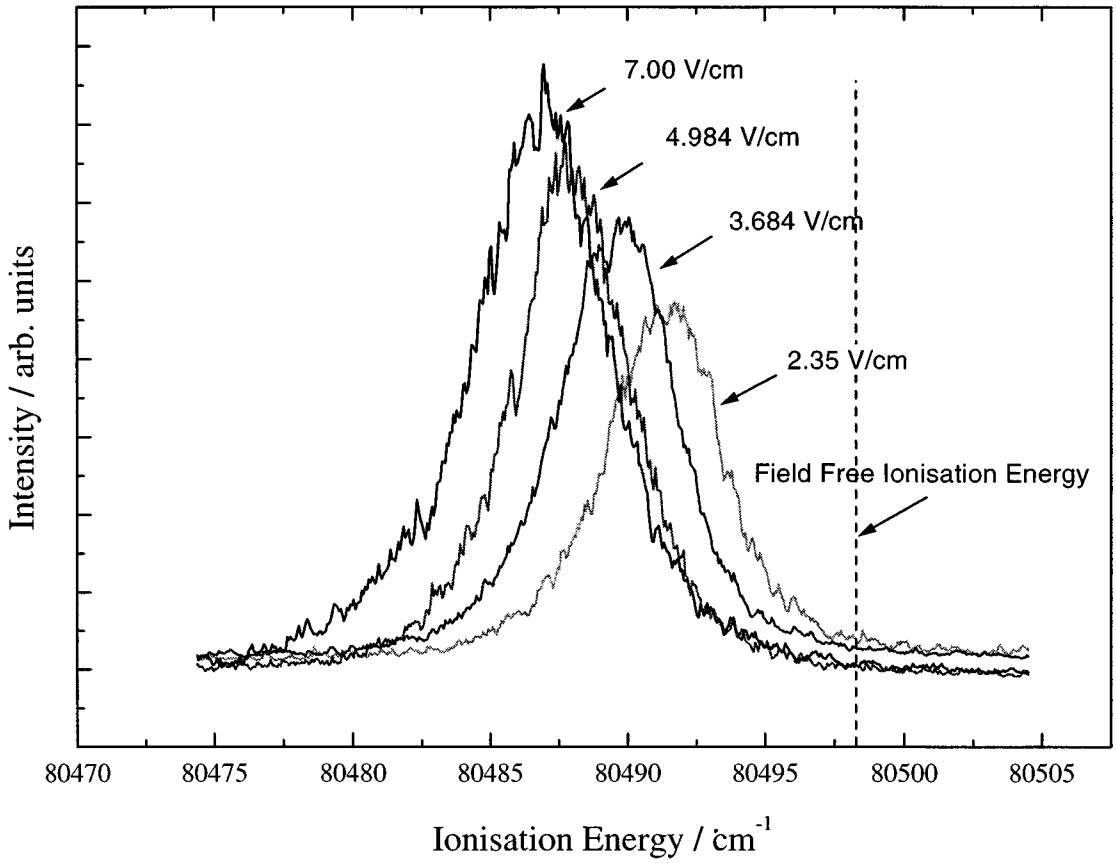
- ZEKE Rydberg states are high-n, high-ℓ, high-m_ℓ



- The signal comes from **below** threshold.



The position of a ZEKE band depends on field strength

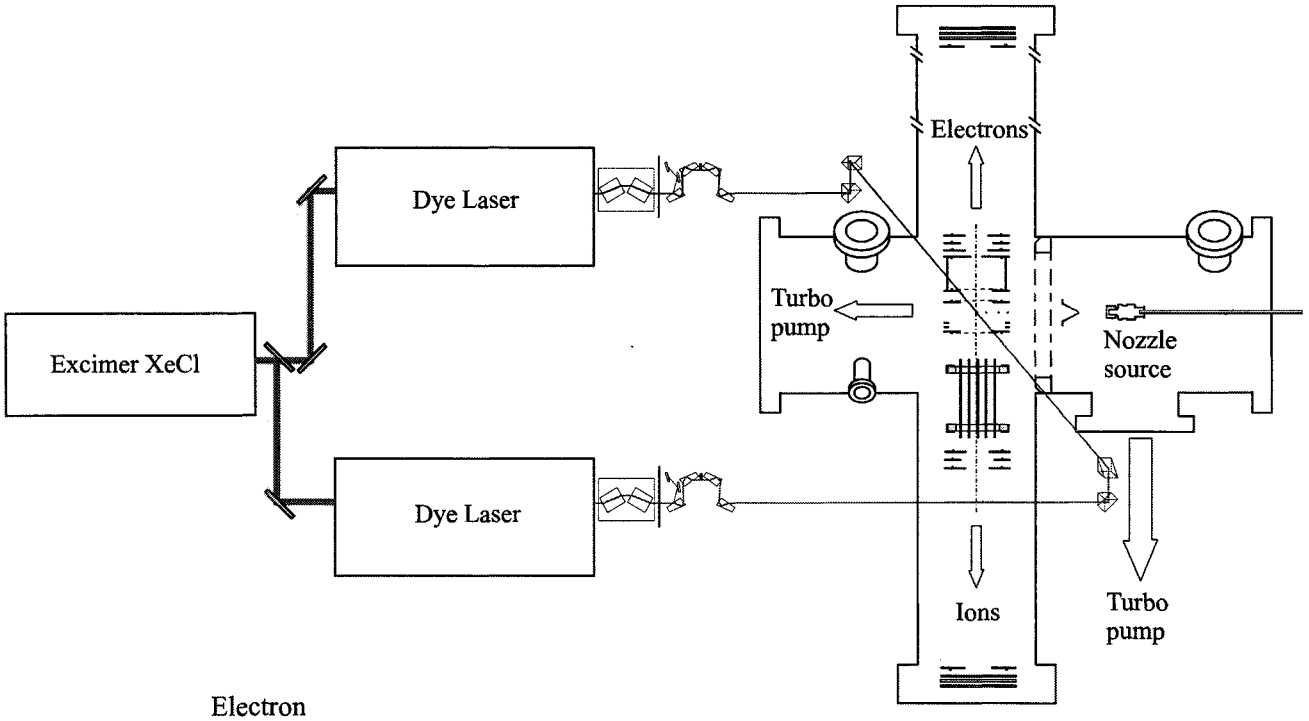


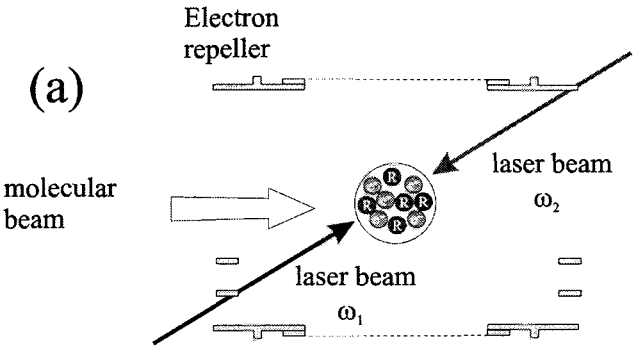
- The theoretical red-shifts for *pulsed* field ionisation are:

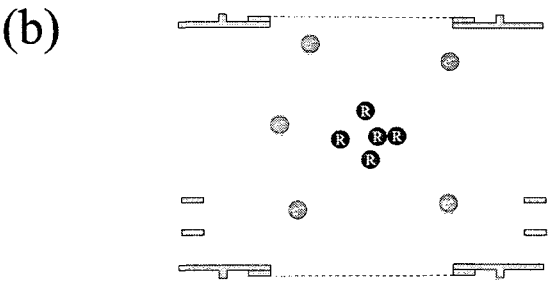
  $-3.1\sqrt{V}$ cm^{-1} for *diabatic* ionization measured at the band maximum

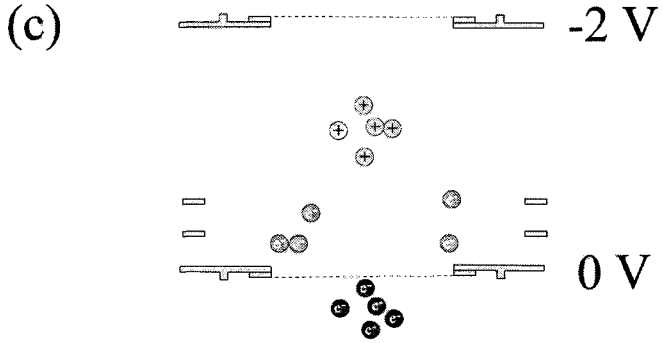
  $-4.6\sqrt{V}$ for *diabatic* ionization measured at the low wave number on-set of the band.

A typical ZEKE experiment









Improving the resolution

- Slow Rise-time and Stepped Pulses (< 0.25 cm^{-1})[10]

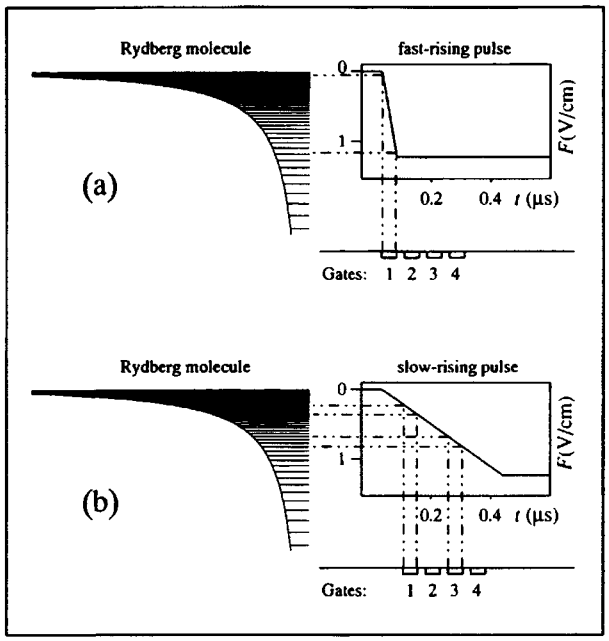


Figure 2.13 Pulsed field ionization of long-lived Rydberg states using a fast-rising (a) and a slowly rising (b) extraction pulse and collection within a certain time gate

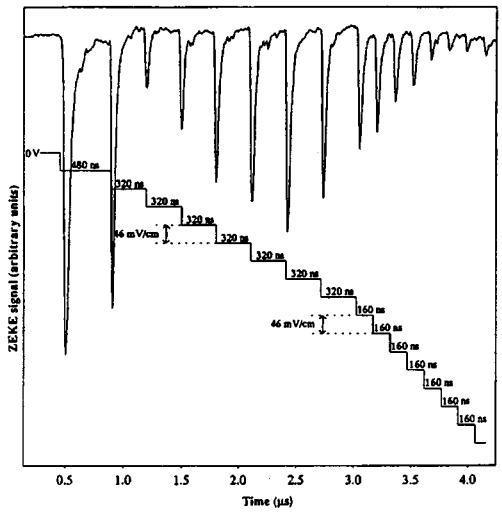


Figure 2.15 Shape of the multistep extraction pulse and resulting electron time-of-flight pattern. Each step changes the field strength by 46 mV/cm. The first laser populated the S_1 6^1 $^1E_{1u}$ ($J' = 4$, $K' = 4$, + l) intermediate rovibronic level; the second laser was tuned to an energy of 35 948 cm^{-1} (after frequency doubling). Each peak in the electron time-of-flight signal corresponds to a step of the extraction pulse. (Redrawn from Lindner *et al.*, 1994)

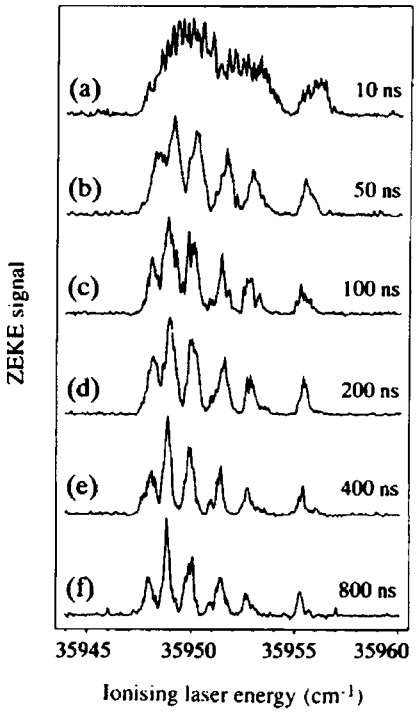
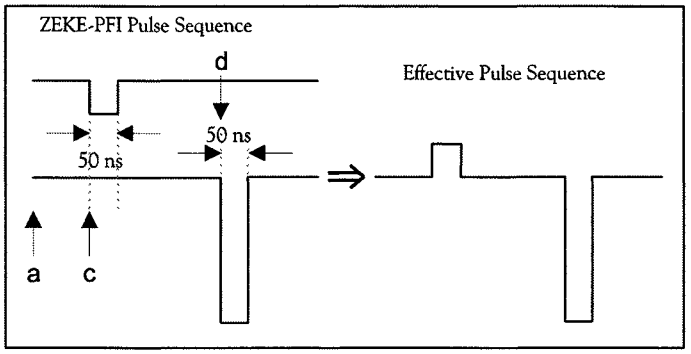
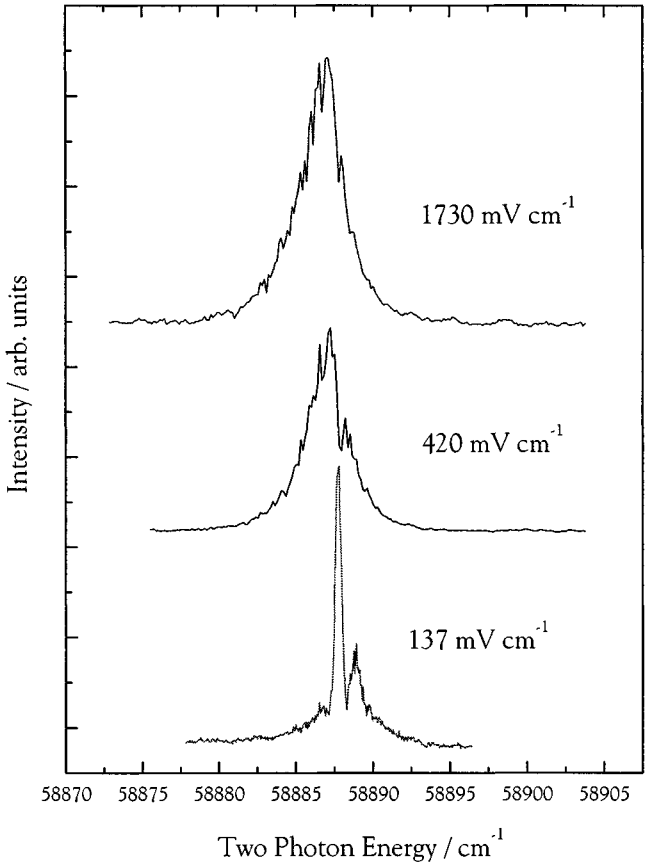


Figure 2.14 Spectral resolution of ZEKE detection as a function of the rise time of the extraction pulse. The spectrum of the D_0 $^2E_{1g}$←S_1 6^1 $^1E_{1u}$ ($J' = 2$, $K' = 2$, + l) transition of benzene was recorded using 1 + 1′-two-colour-REMPI. The rise time was varied from 5 to 600 ns but the final field strength was kept at 600 mV/cm. The width of the detection time gate was kept constant (20 ns). (Reproduced from Lindner *et al.*, 1994)

[10] R. Lindner, H.J. Dietrich and K. Müller-Dethlefs, *Chem. Phys. Lett.*, **228** (1994) 417.

- Double inverted pulses (< 0.5 cm^{-1})

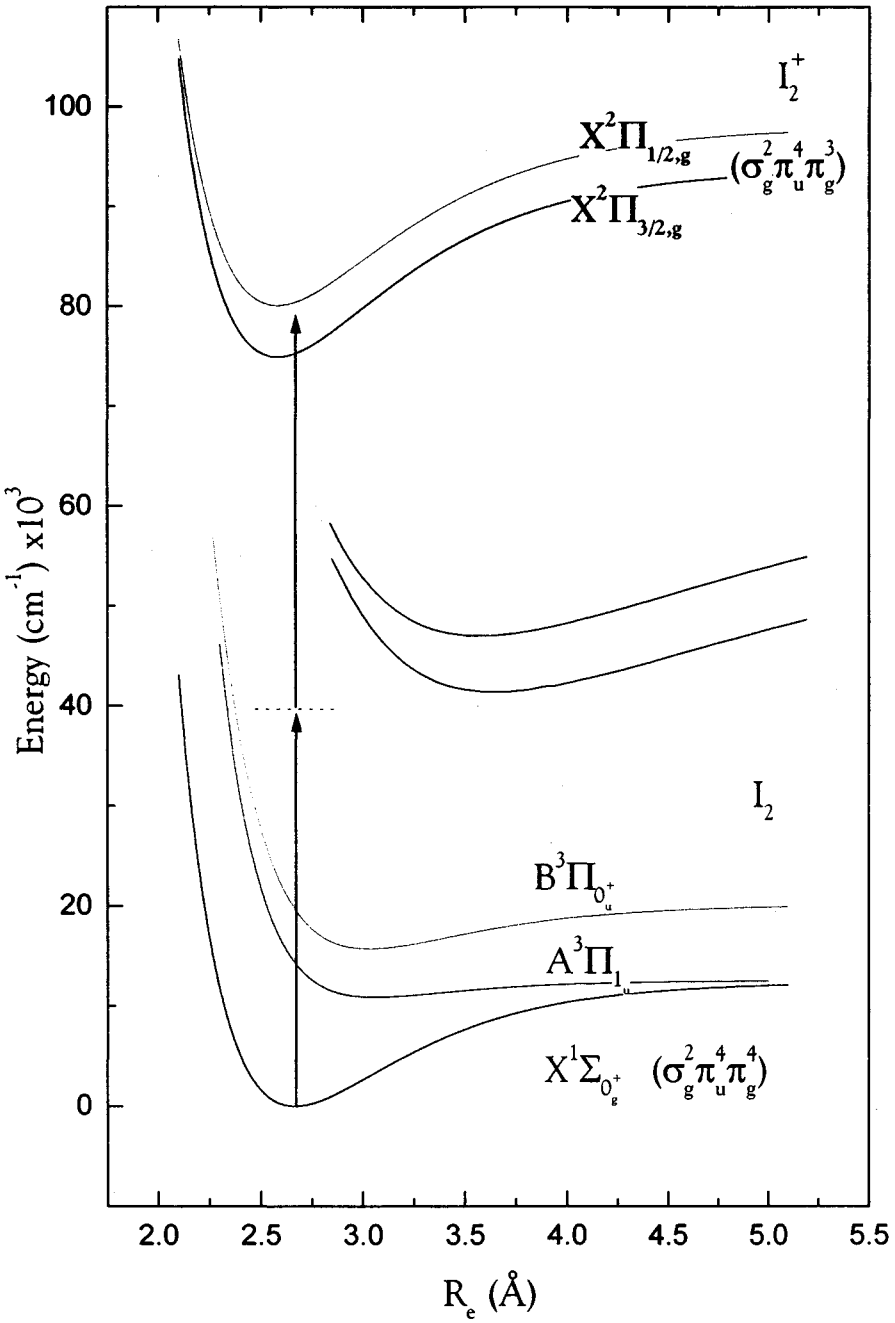


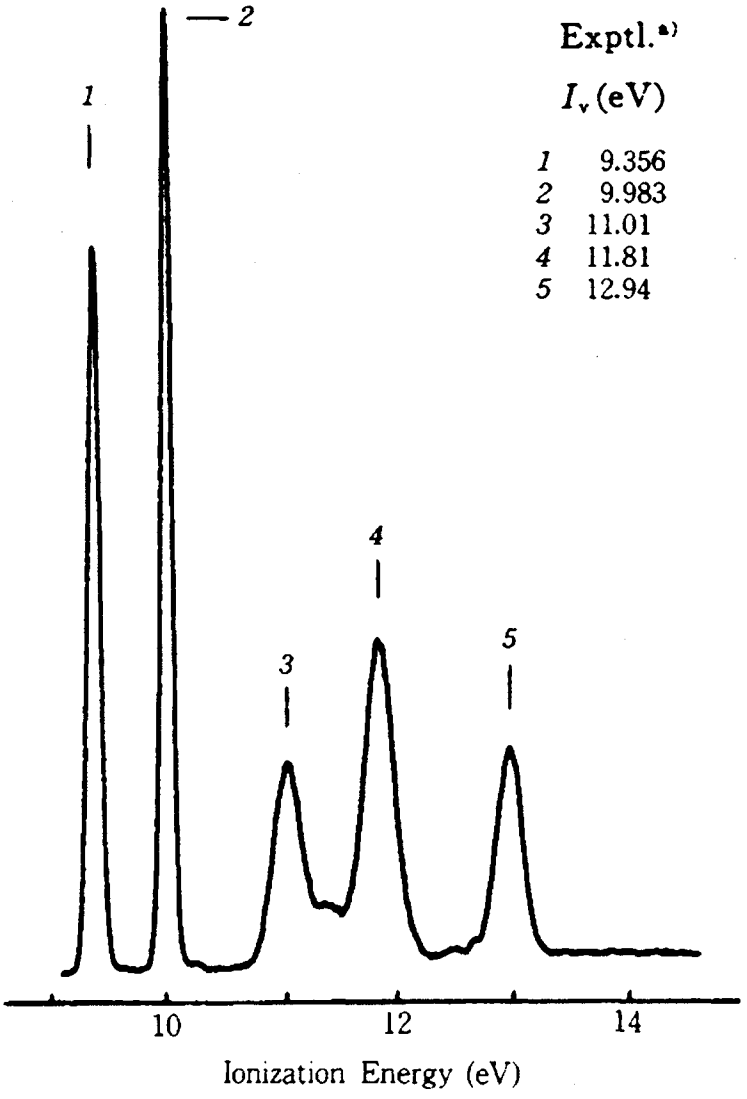


ZEKE spectra of DABCO[11] recorded at field strengths ranging from 137 mV cm^{-1} to 1730 cm^{-1}.

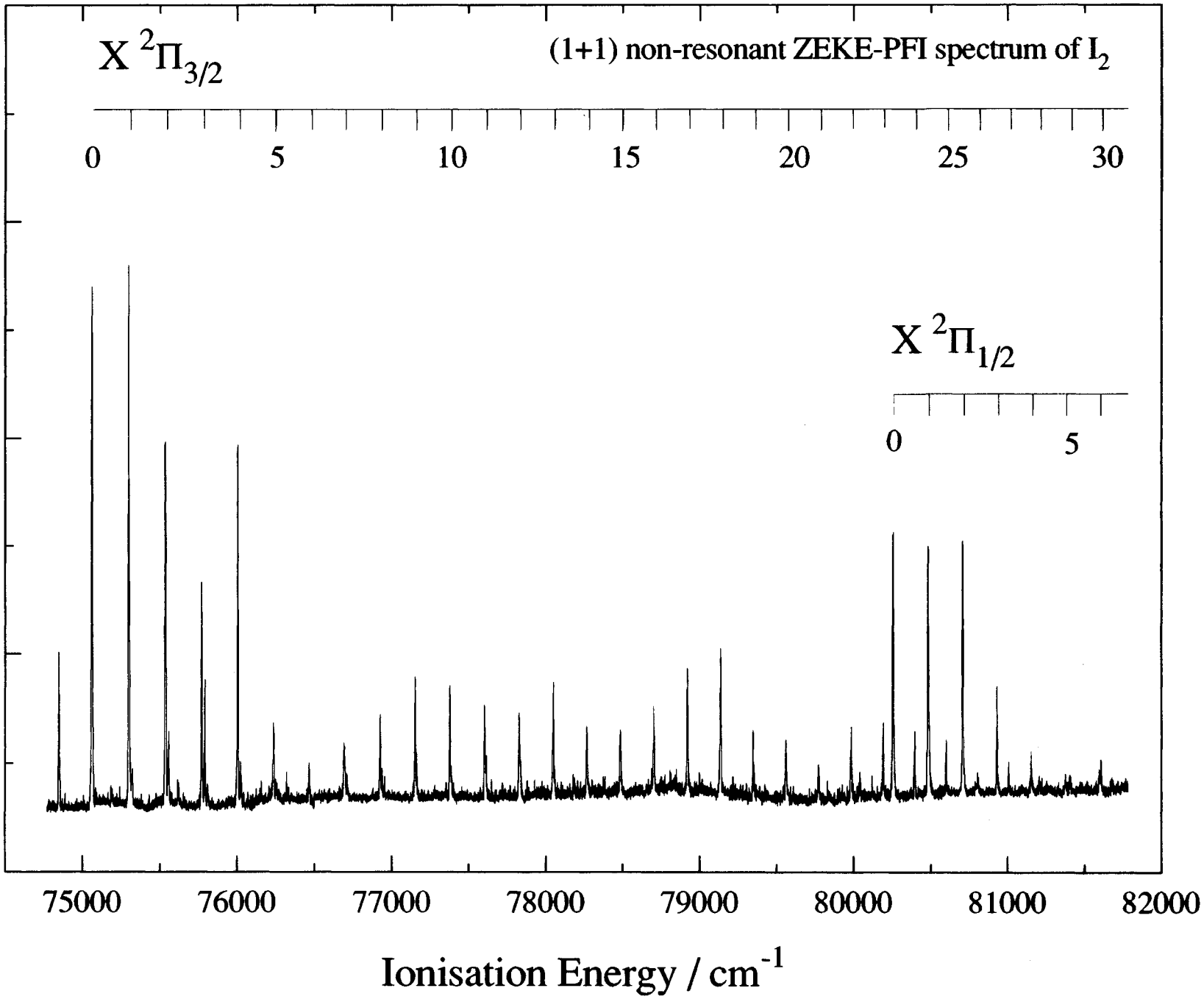
[11]M.J. Watkins and M.C.R. Cockett, *J. Chem. Phys.*, **113** (2000) 10560.

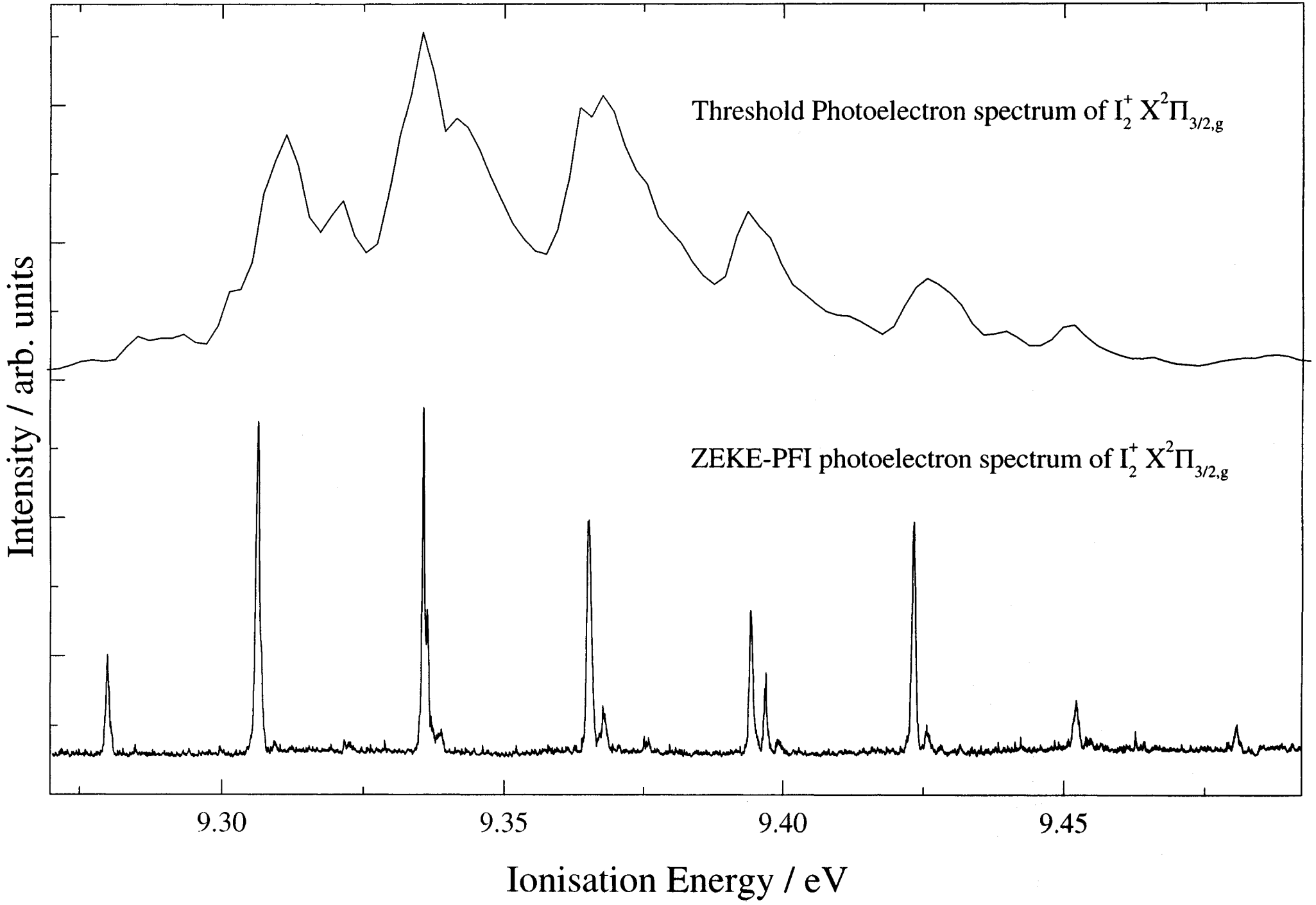
Non-resonant multiphoton ionisation:
The ZEKE spectrum of Molecular Iodine

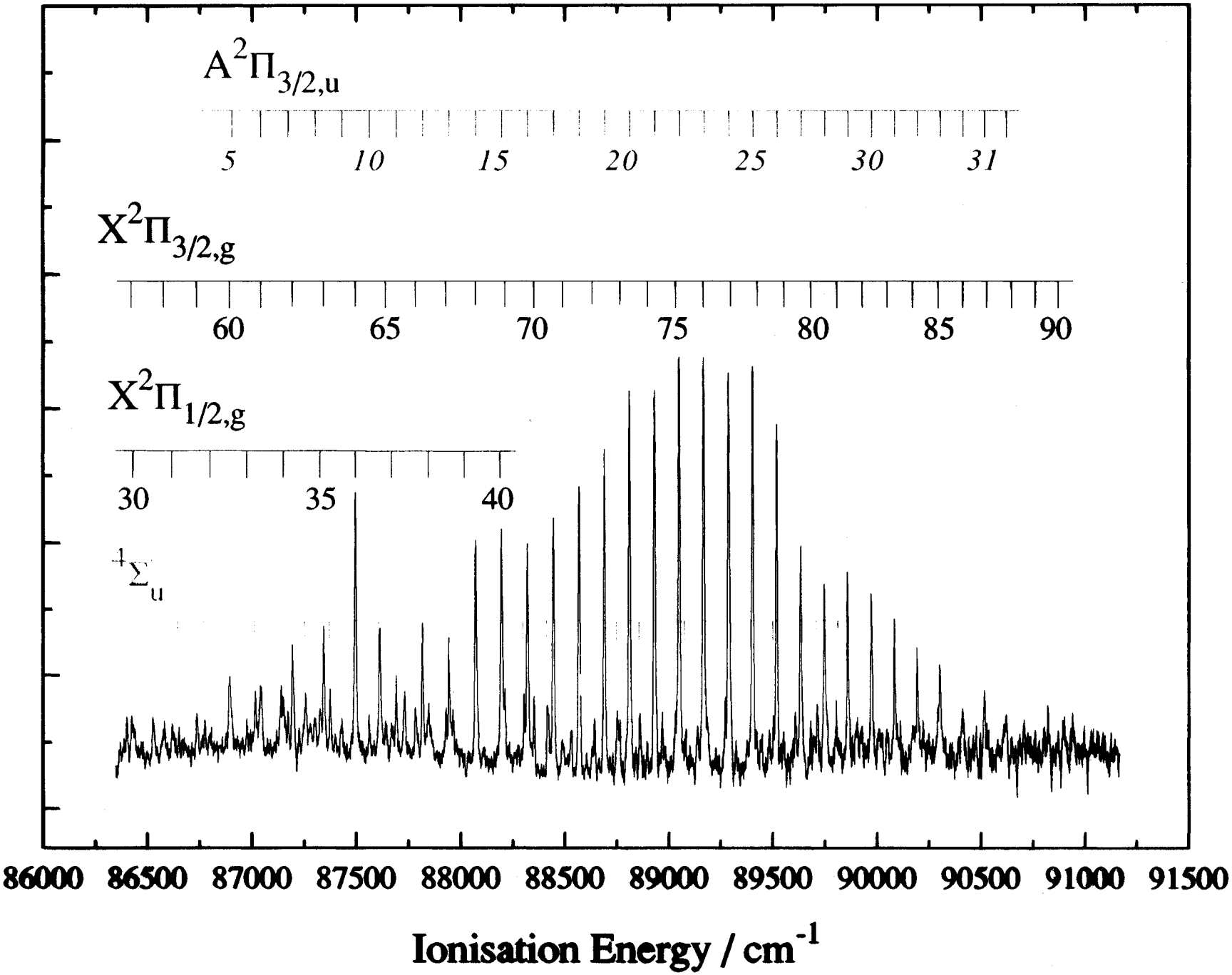


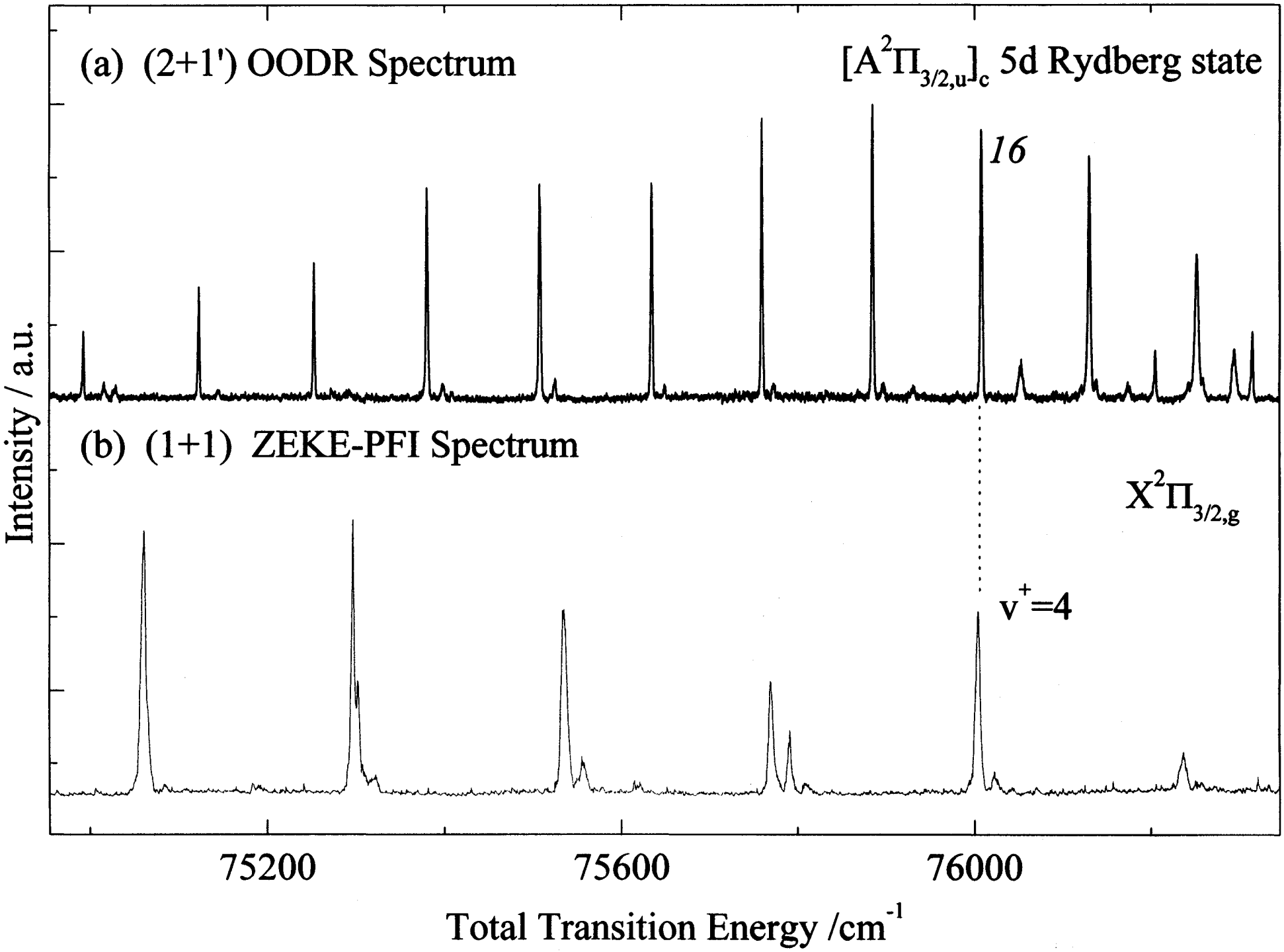


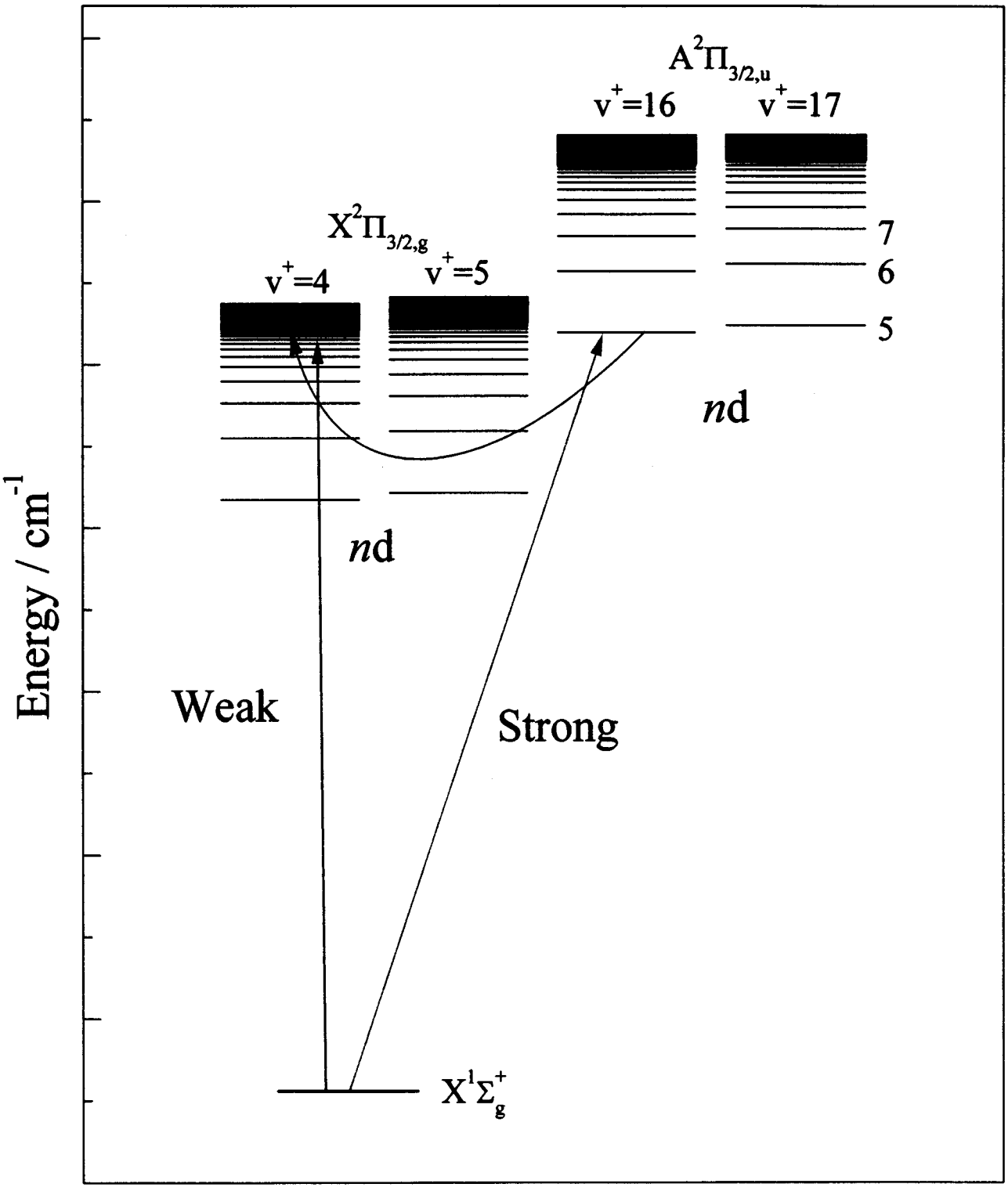
Exptl.[a]	
	I_v (eV)
1	9.356
2	9.983
3	11.01
4	11.81
5	12.94


X $^2\Pi_{3/2}$
(1+1) non-resonant ZEKE-PFI spectrum of I_2
0
5
10
15
20
25
30
X $^2\Pi_{1/2}$
0
5
75000
76000
77000
78000
79000
80000
81000
82000
Ionisation Energy / cm^{-1}


Threshold Photoelectron spectrum of $I_2^+ X^2\Pi_{3/2,g}$
ZEKE-PFI photoelectron spectrum of $I_2^+ X^2\Pi_{3/2,g}$
Intensity / arb. units
9.30
9.35
9.40
9.45
Ionisation Energy / eV

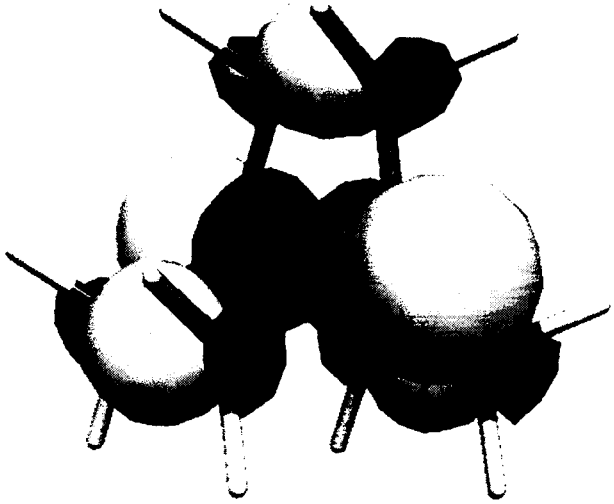

$A^2\Pi_{3/2,u}$
5
10
15
20
25
30
31
$X^2\Pi_{3/2,g}$
60
65
70
75
80
85
90
$X^2\Pi_{1/2,g}$
30
35
40
$^1\Sigma_u^+$
86000
86500
87000
87500
88000
88500
89000
89500
90000
90500
91000
91500
Ionisation Energy / cm^{-1}


(a) (2+1') OODR Spectrum
$[A^2\Pi_{3/2,u}]_c$ 5d Rydberg state
16
(b) (1+1) ZEKE-PFI Spectrum
$X^2\Pi_{3/2,g}$
$v^+=4$
Intensity / a.u.
75200
75600
76000
Total Transition Energy /cm^{-1}

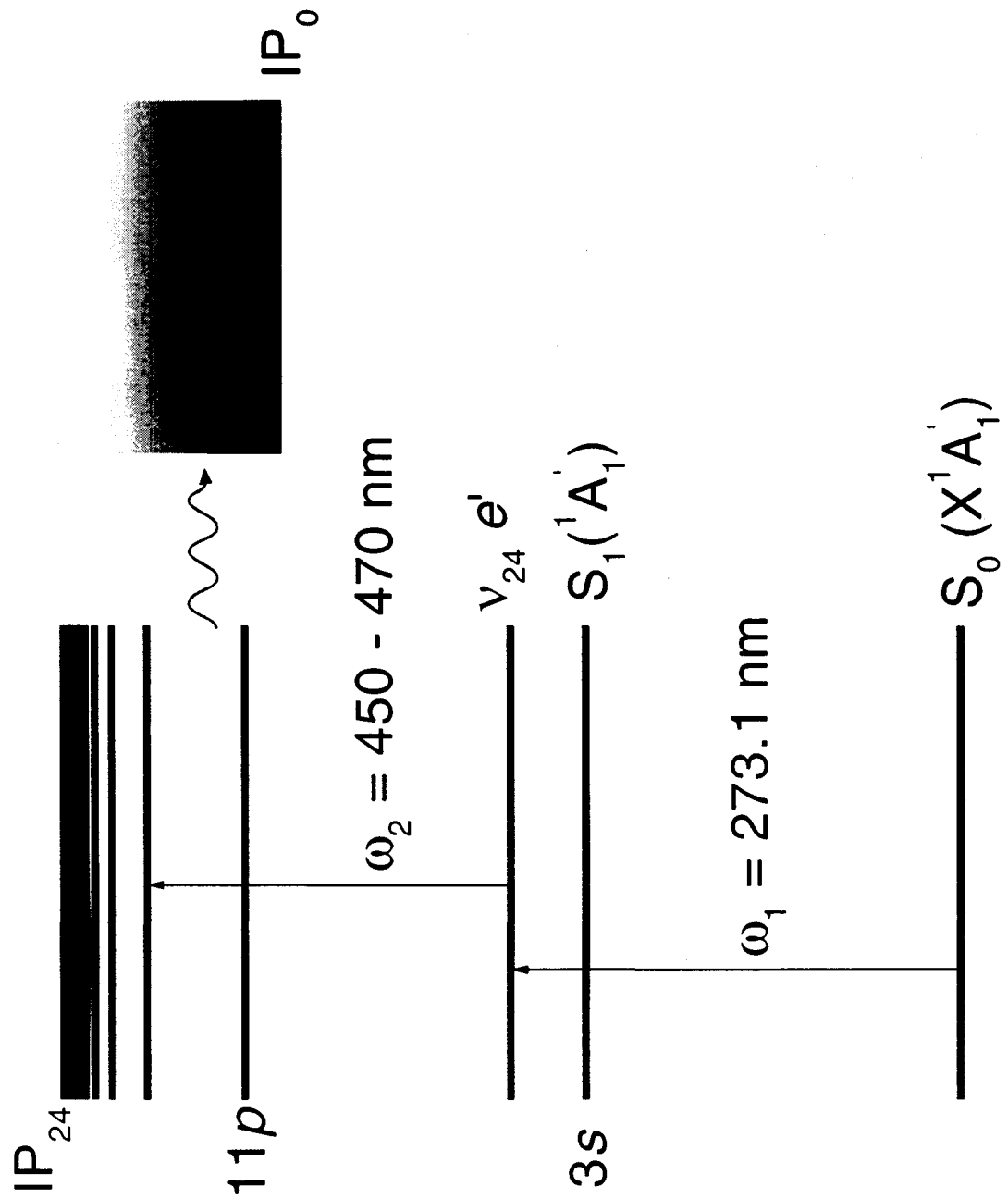

Energy / cm-1
A2Π3/2,u
v+=16
v+=17
X2Π3/2,g
v+=4
v+=5
7
6
5
nd
nd
Weak
Strong
X1Σg+

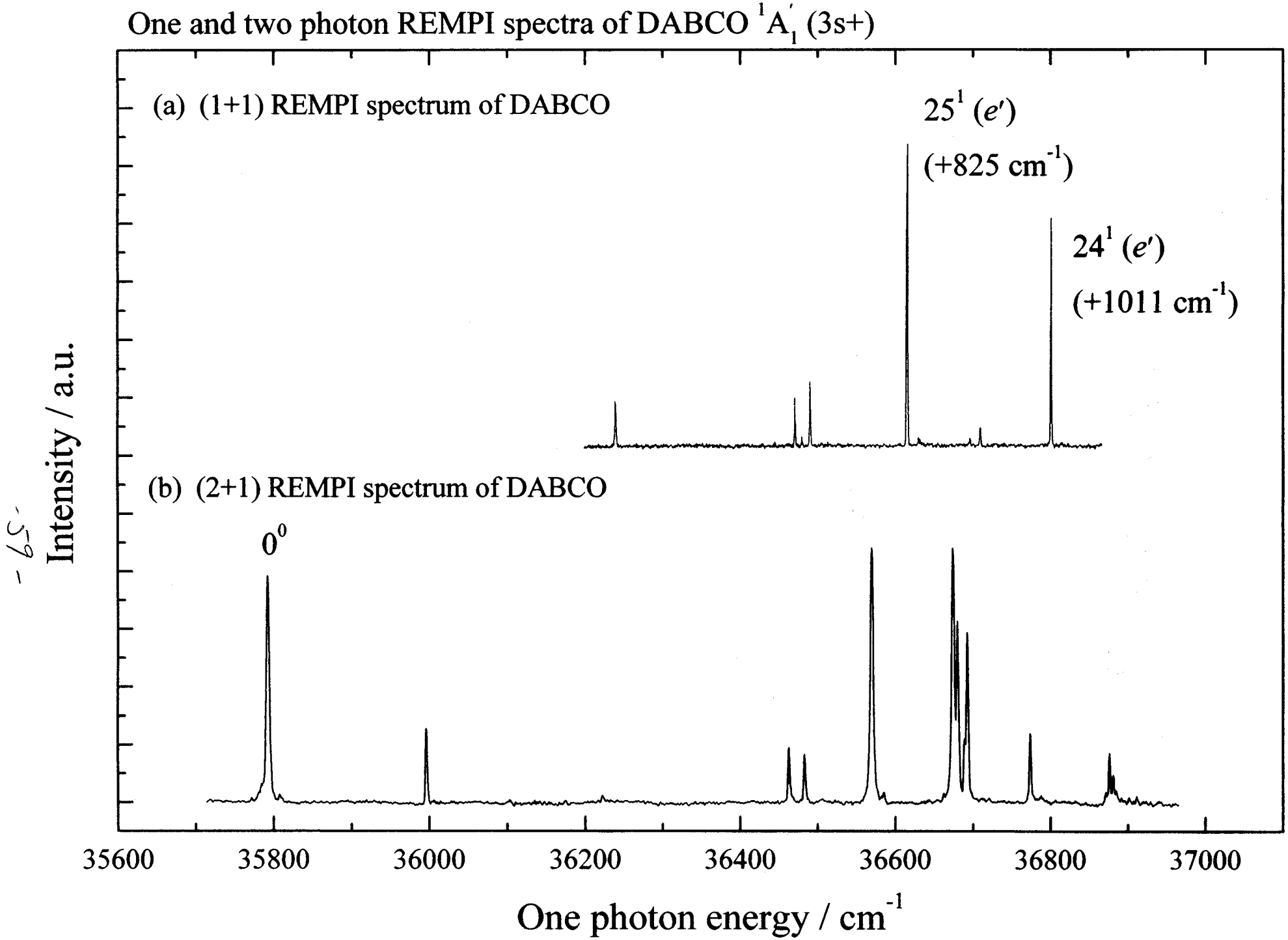
DABCO (RHF cc-pvdz)

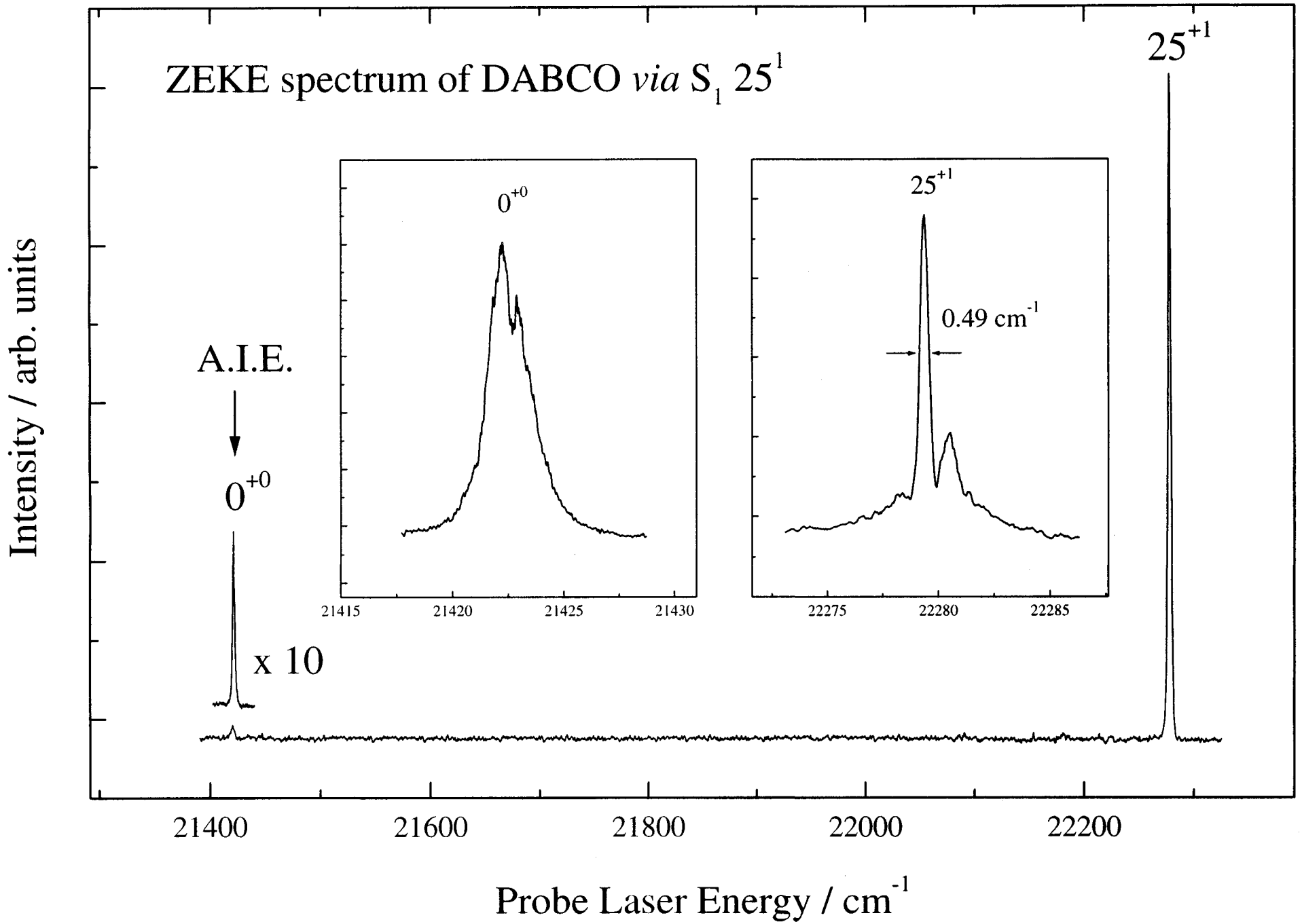
HOMO

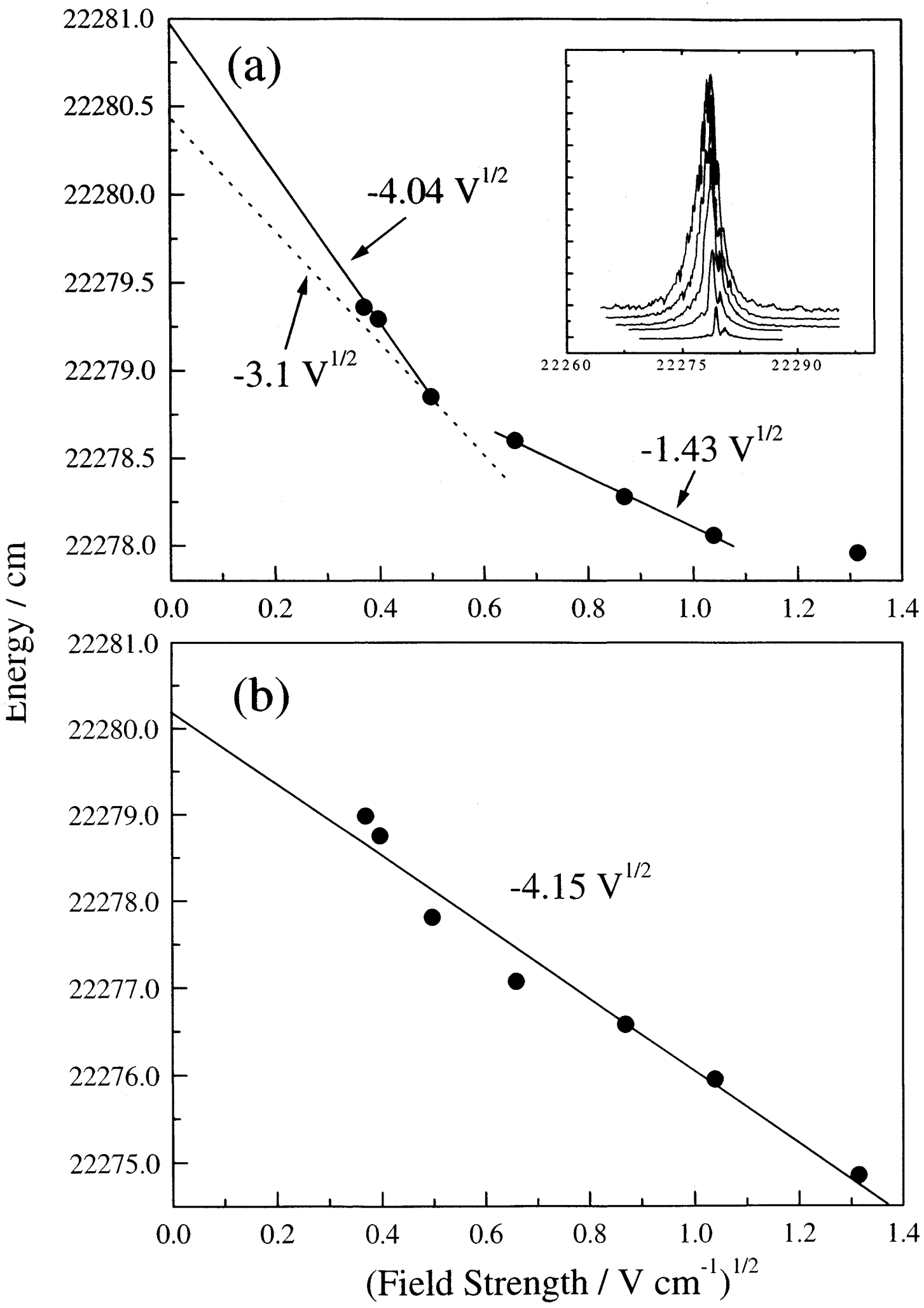


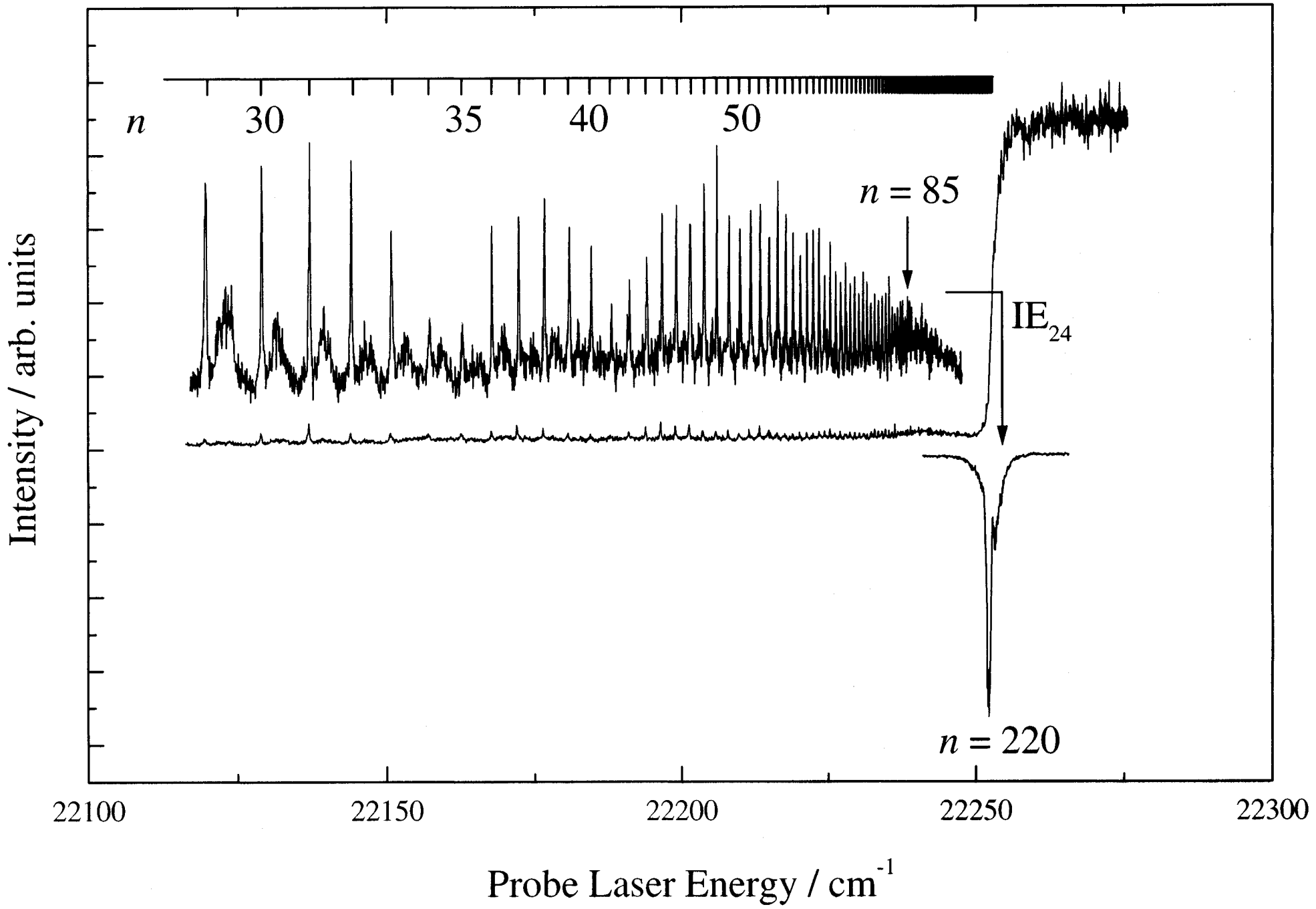
LUMO


IP0
IP24
11p
ω2 = 450 - 470 nm
ν24 e'
S1(1A1')
3s
ω1 = 273.1 nm
S0 (X1A1')


One and two photon REMPI spectra of DABCO $^1A_1'$ (3s+)
(a) (1+1) REMPI spectrum of DABCO
25^1 (e')
(+825 cm^{-1})
24^1 (e')
(+1011 cm^{-1})
(b) (2+1) REMPI spectrum of DABCO
0^0
Intensity / a.u.
35600
35800
36000
36200
36400
36600
36800
37000
One photon energy / cm^{-1}

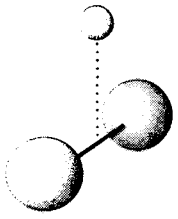

ZEKE spectrum of DABCO *via* S_1 25^1
25^{+1}
Intensity / arb. units
A.I.E.
0^{+0}
x 10
0^{+0}
21415
21420
21425
21430
25^{+1}
0.49 cm^{-1}
22275
22280
22285
21400
21600
21800
22000
22200
Probe Laser Energy / cm^{-1}


(a)
-4.04 V^1/2
-3.1 V^1/2
-1.43 V^1/2
22281.0
22280.5
22280.0
22279.5
22279.0
22278.5
22278.0
22260
22275
22290
(b)
-4.15 V^1/2
22281.0
22280.0
22279.0
22278.0
22277.0
22276.0
22275.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Energy / cm
(Field Strength / V cm^-1)^1/2


n
30
35
40
50
n = 85
IE24
n = 220
Intensity / arb. units
22100
22150
22200
22250
22300
Probe Laser Energy / cm-1

The van der Waals Interaction

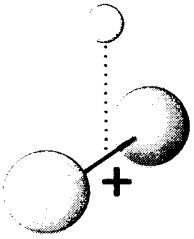
The Neutral



The dominant attractive force between neutral species is the Dispersion Interaction

$$V = -\frac{3}{2}\frac{\alpha'_M \alpha'_{Rg}}{r^6}\left(\frac{I_M I_{Rg}}{I_M + I_{Rg}}\right)$$

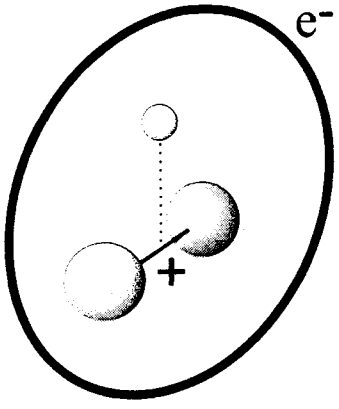
The Ion



In addition to the dispersion interaction, charge induced dipole forces assert themselves

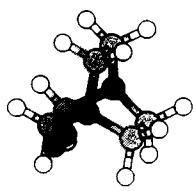
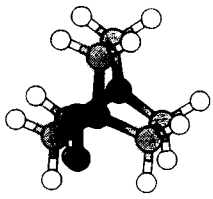
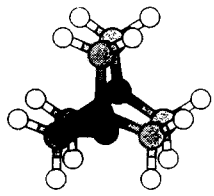
$$V = -\frac{\alpha_{Rg}}{2}\left(\frac{e^2}{(4\pi\varepsilon_0)^2 r^4}\right)$$

Rydberg States

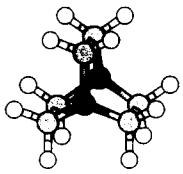
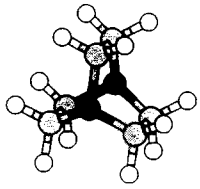
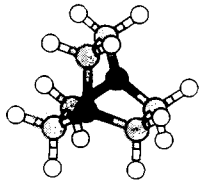
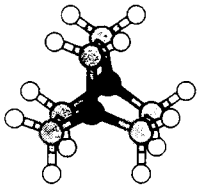
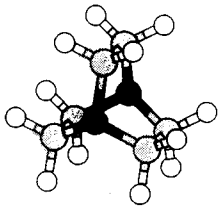
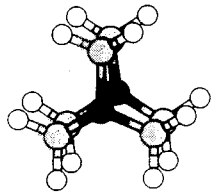


Depends on n, ℓ

HOW?



QUESTIONS

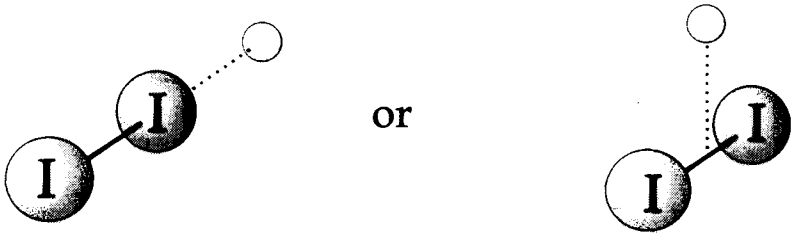
- What is the relationship between n and ℓ of the Rydberg electron and the binding energy of the complex?

- Can the formation of different isomers help us to learn more about the interaction?

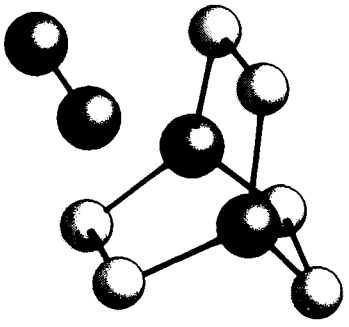
- How stable are very high-n Rydberg states to solvation?

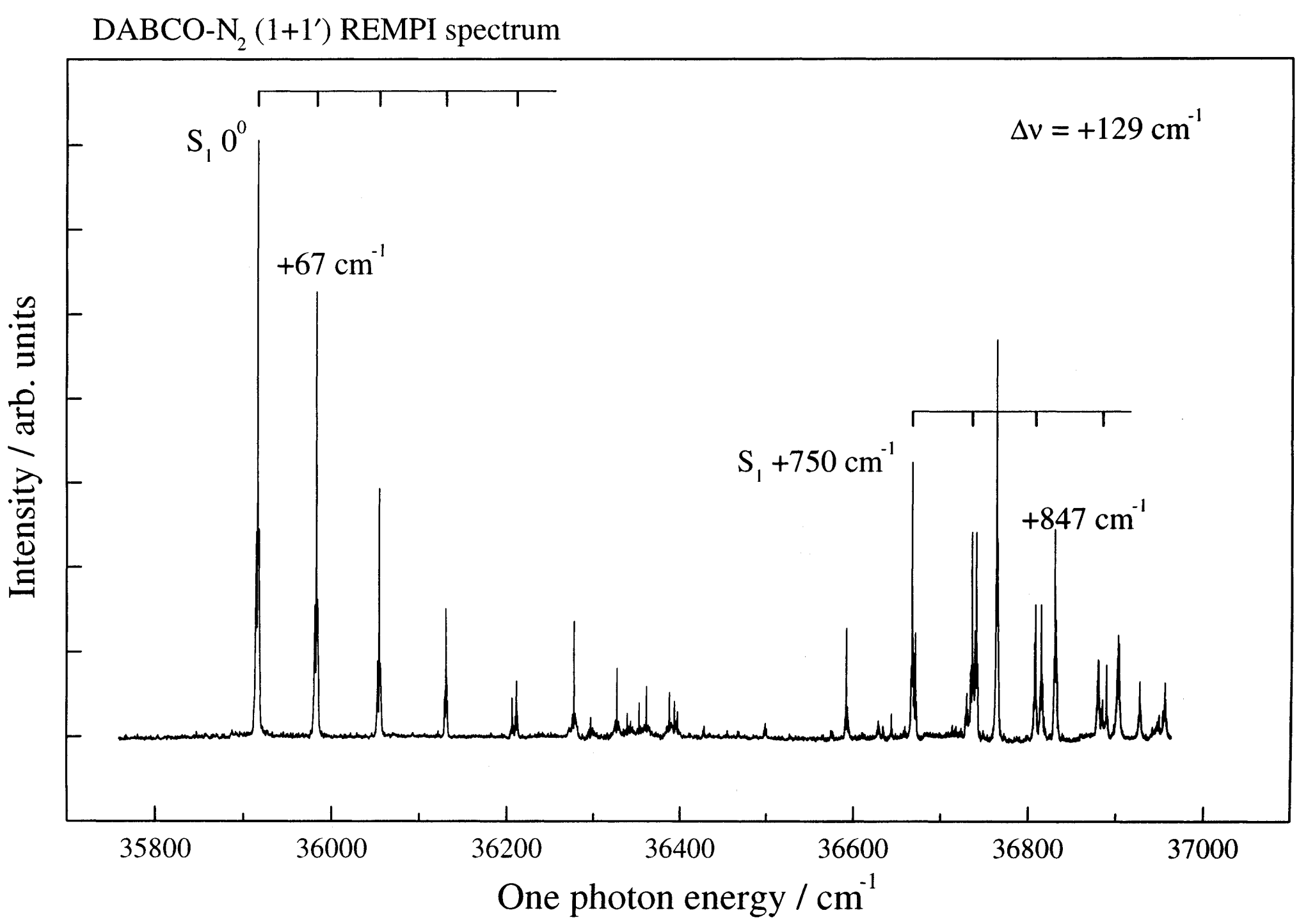
EXAMPLES

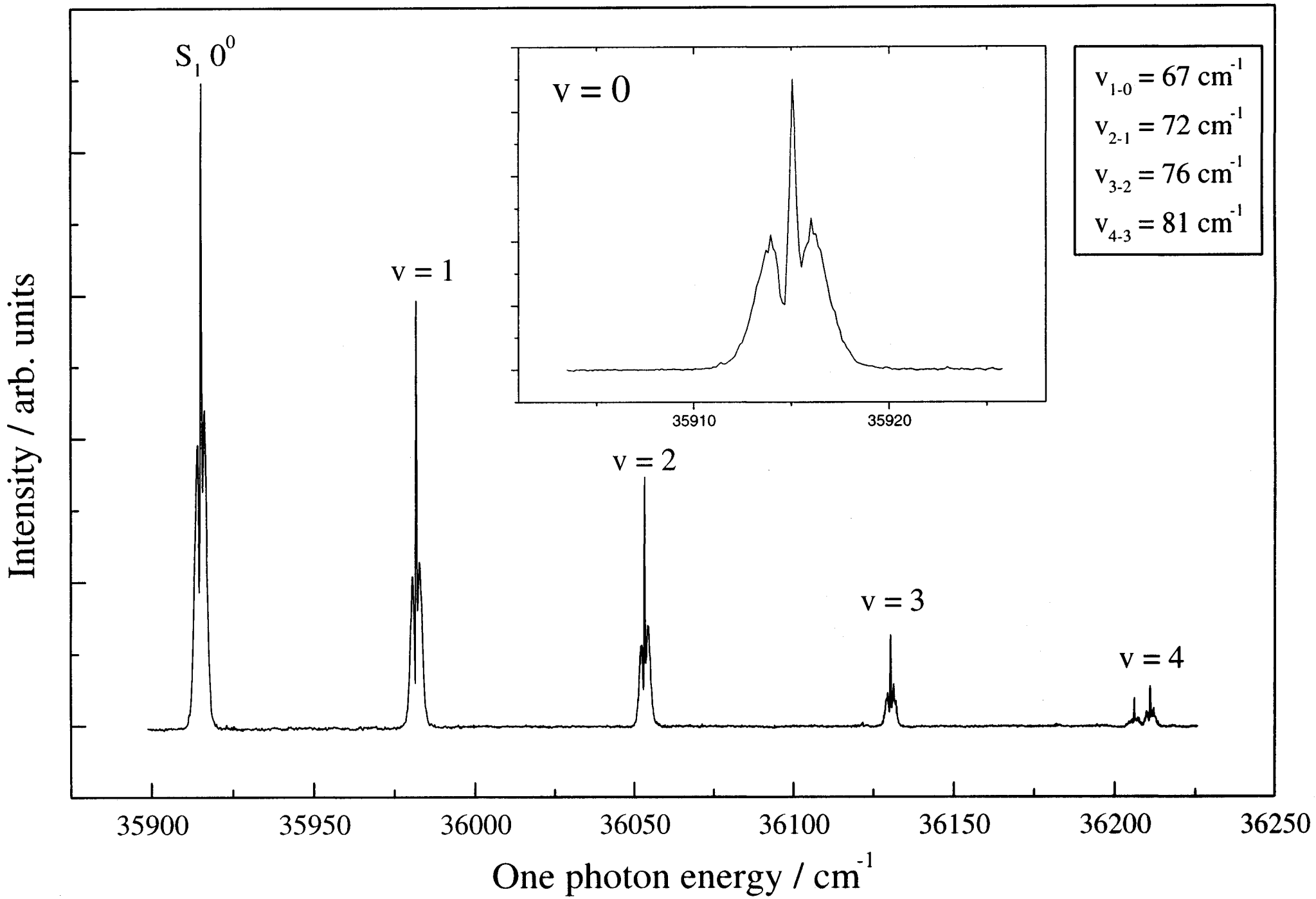
(a) I_2-Ar

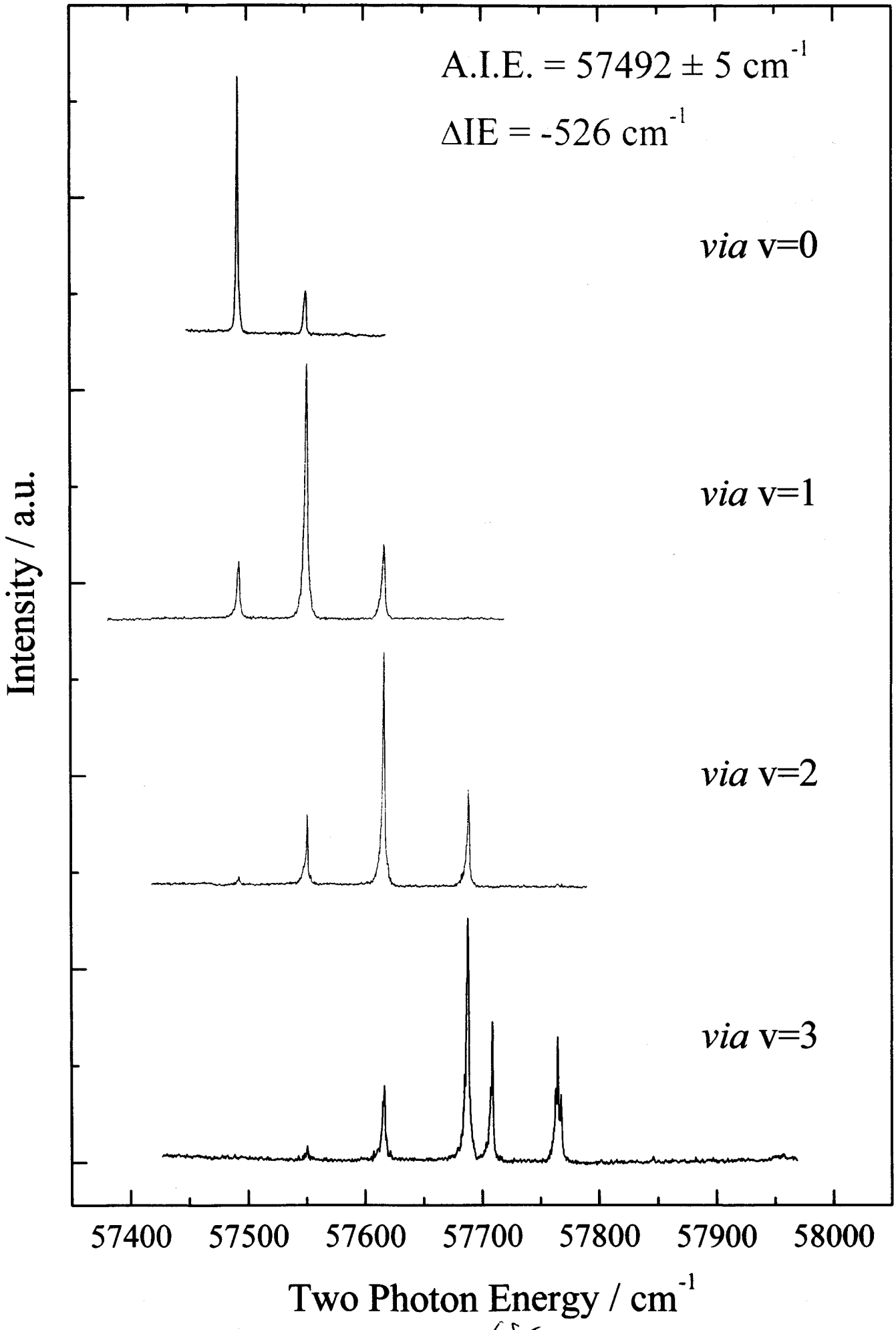


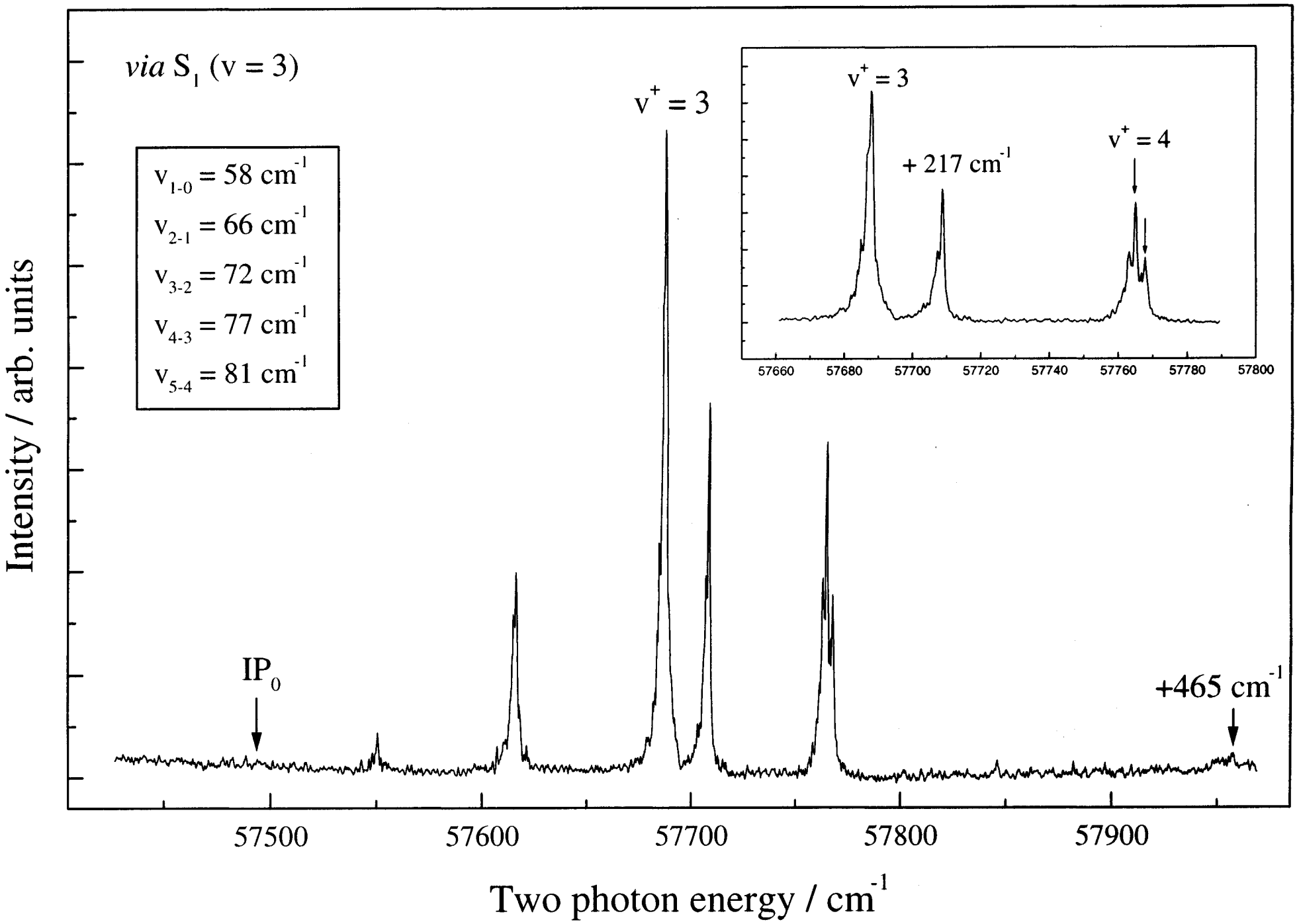
(b) DABCO-N_2

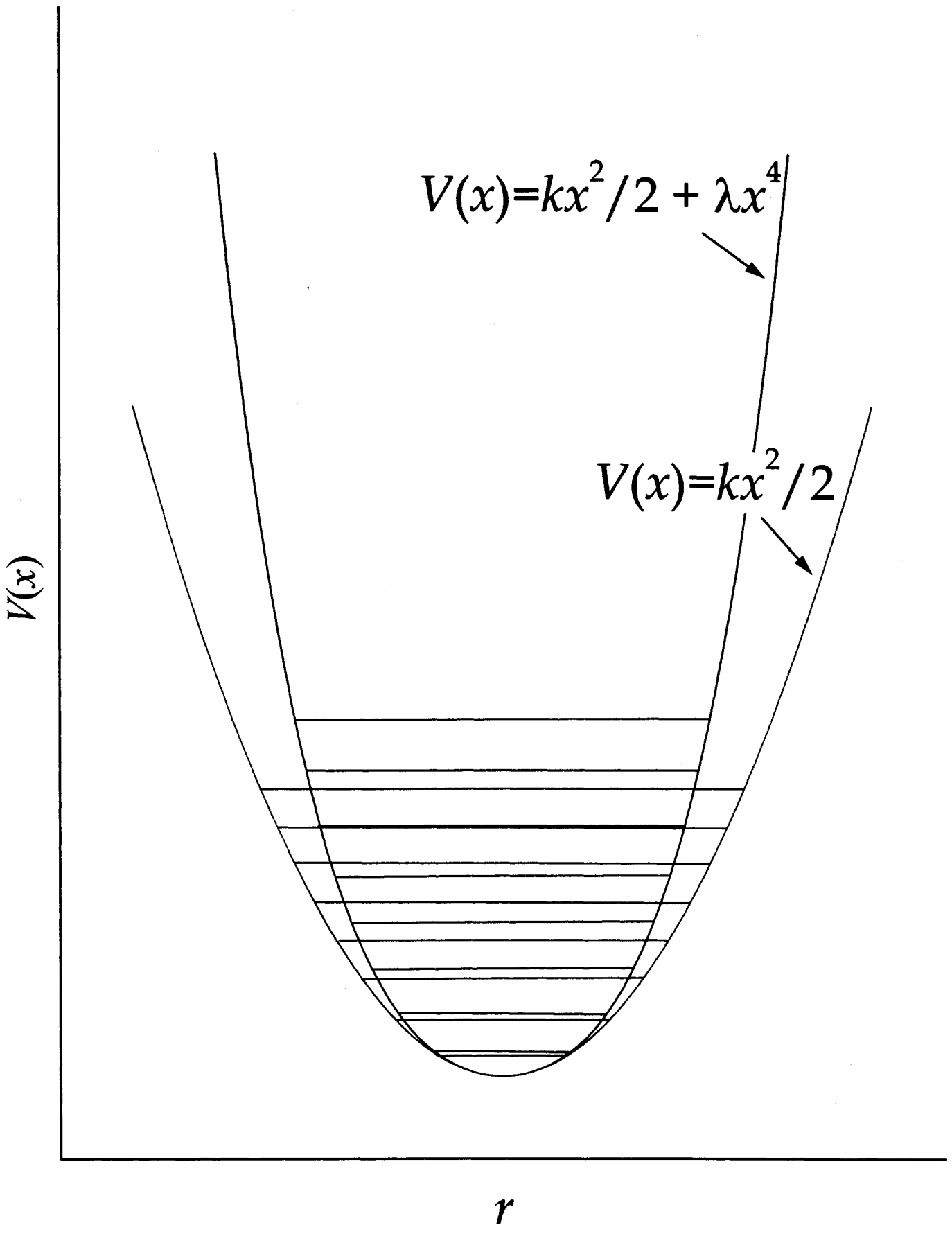



DABCO-N2 (1+1′) REMPI spectrum
S1 0^0
Δν = +129 cm-1
+67 cm-1
S1 +750 cm-1
+847 cm-1
Intensity / arb. units
35800
36000
36200
36400
36600
36800
37000
One photon energy / cm-1


S1 0^0
v = 0
35910
35920
v = 1
v = 2
v = 3
v = 4
v1-0 = 67 cm-1
v2-1 = 72 cm-1
v3-2 = 76 cm-1
v4-3 = 81 cm-1
Intensity / arb. units
35900
35950
36000
36050
36100
36150
36200
36250
One photon energy / cm-1


DABCO-N2 zeke spectra via 1A1' (3s+)
A.I.E. = 57492 ± 5 cm-1
ΔIE = -526 cm-1
via v=0
via v=1
via v=2
via v=3
Intensity / a.u.
57400
57500
57600
57700
57800
57900
58000
Two Photon Energy / cm-1


via S1 (v = 3)
v+ = 3
v1-0 = 58 cm-1
v2-1 = 66 cm-1
v3-2 = 72 cm-1
v4-3 = 77 cm-1
v5-4 = 81 cm-1
v+ = 3
+ 217 cm-1
v+ = 4
57660
57680
57700
57720
57740
57760
57780
57800
IP0
+465 cm-1
Intensity / arb. units
57500
57600
57700
57800
57900
Two photon energy / cm-1


$V(x)=kx^2/2+\lambda x^4$
$V(x)=kx^2/2$
$V(x)$
r

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