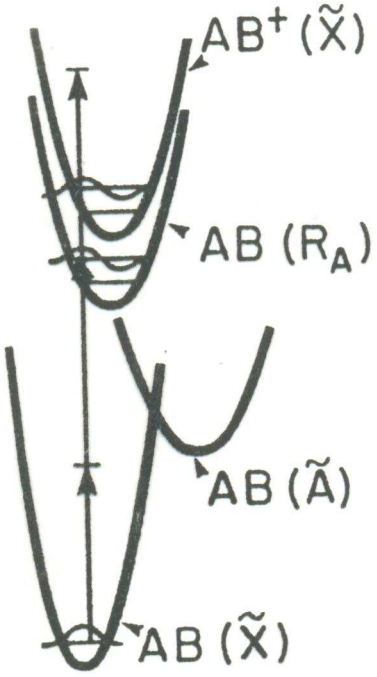

AB+ (X̃)
AB (RA)
AB (Ã)
AB (X̃)

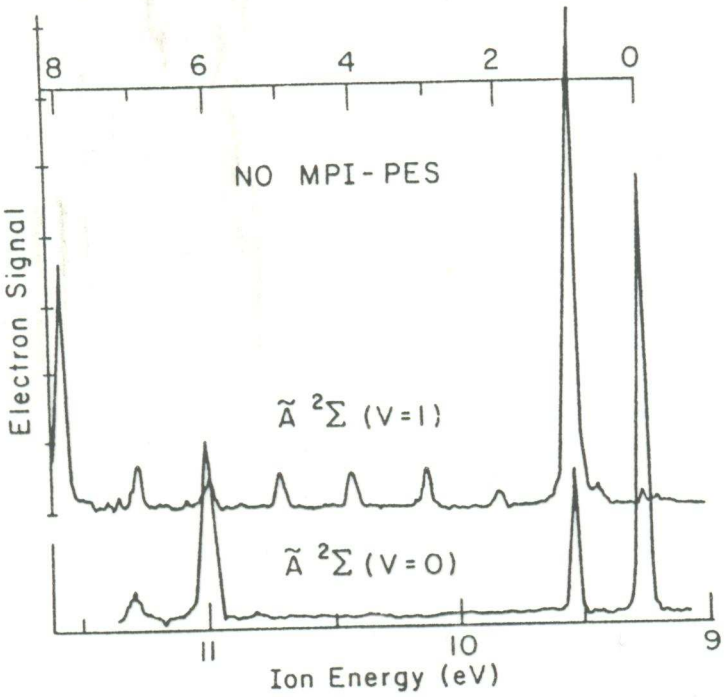
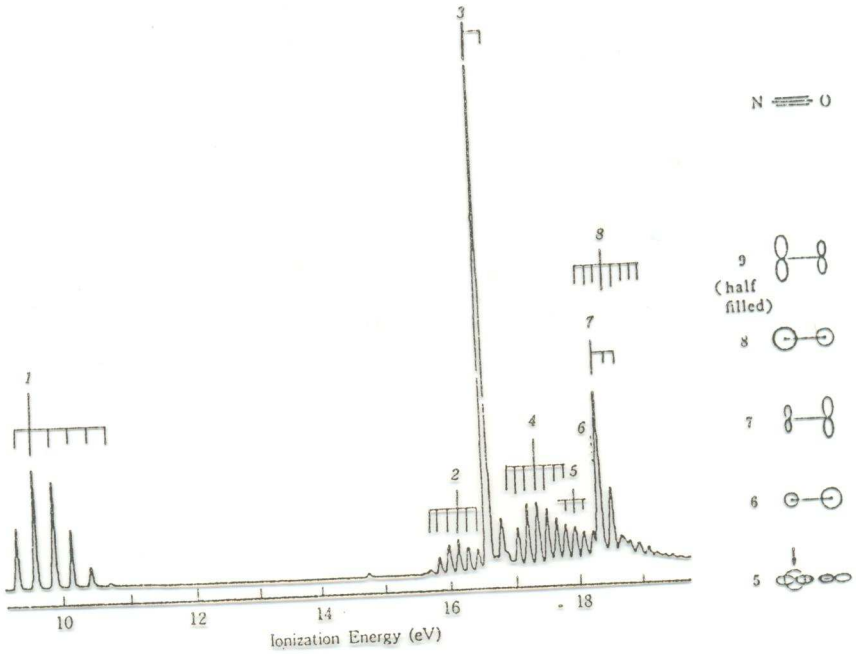
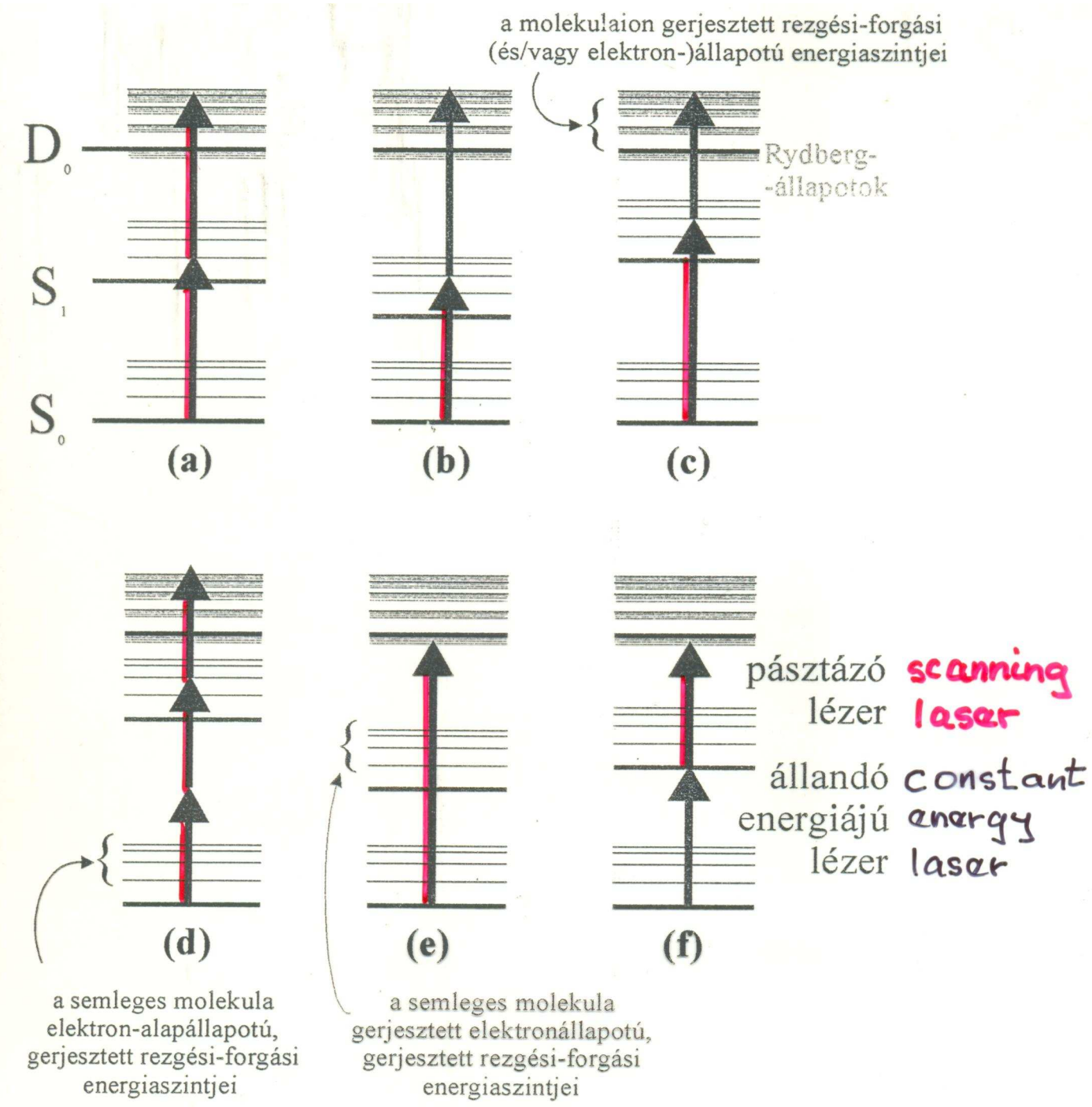


Figure 4. Examples of the MPI PES obtained when NO is ionized via a two-photon excitation of the Ã-state vibrational levels followed by a two-photon ionization. Adapted from Kimman, Kruit, and Van der Wiel.[28]

(10) NO Nitrogen Monoxide





Fontosabb REMPI és ZEKE technikák: (a) egyszínű (1+1) REMPI, (b) és (c) kétszínű (1+1') REMPI, (d) 2+1 REMPI, (e) XUV ZEKE, (f) 1+1' ZEKE

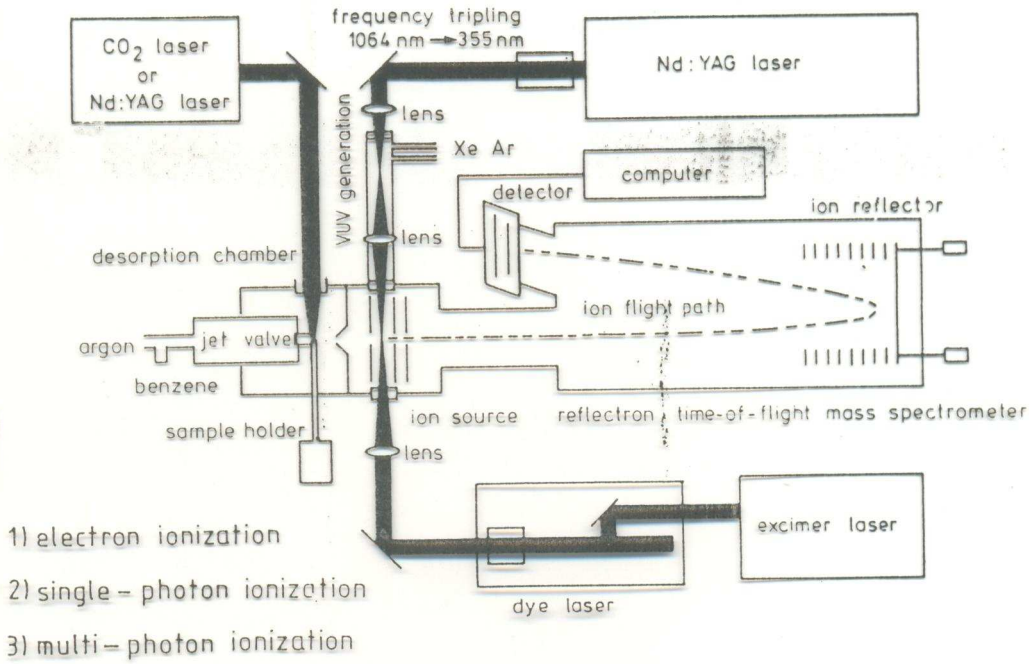


Fig. 3.2 The experimental set-up of two-colour photo-ionization with laser vaporization.

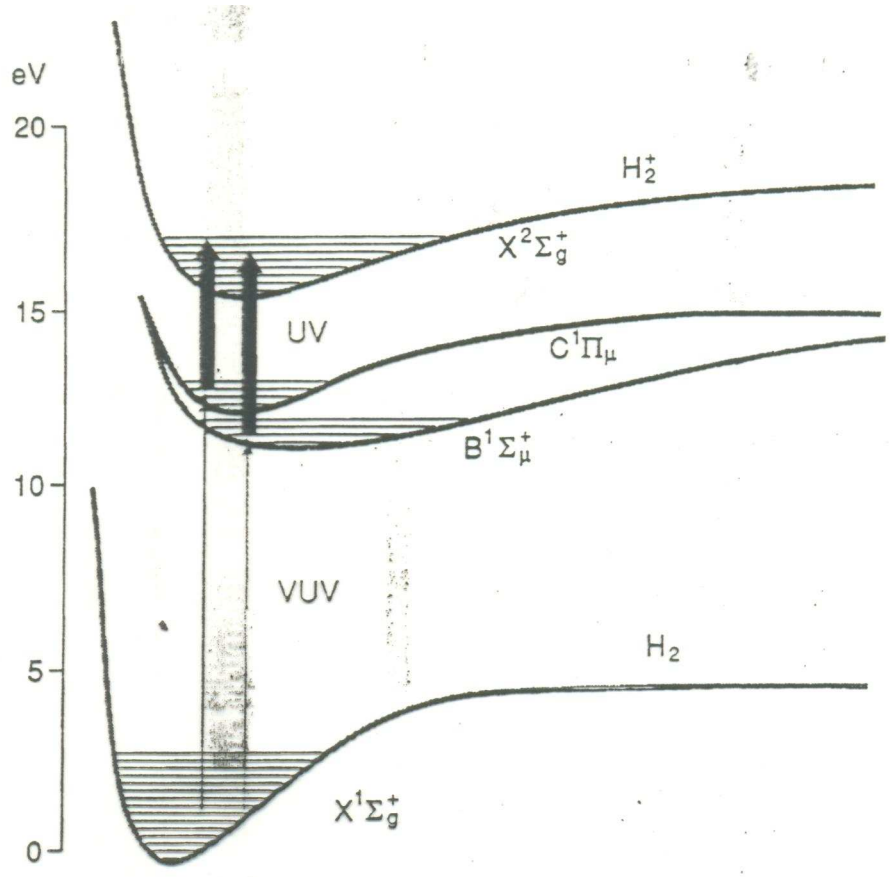


Figure 1. The (1+1) REMPI process is illustrated using the H_2 potential ene diagram. The H_2 molecule is excited by a weak VUV photon. A second intense U photon is then used to ionize the excited molecule.

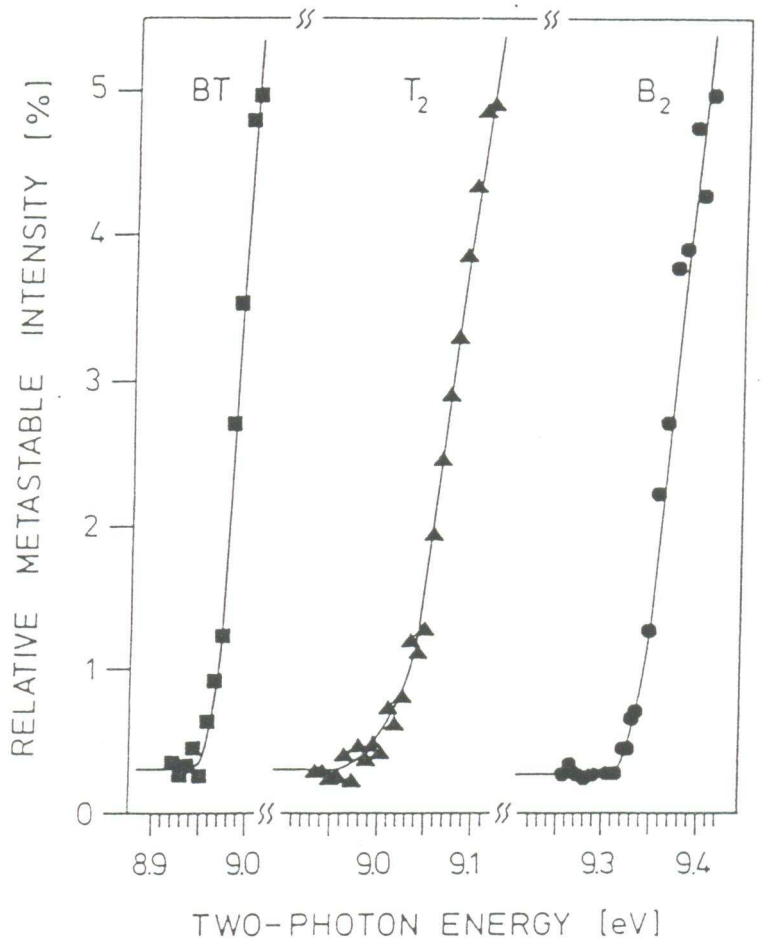


Fig. 3.10 The decomposition spectrum of benzene–toluene complexes as a function of excess energy[27].

Table 3.1. *Dissociation energies of clusters in the ground and ionic states from the Born-Haber cycle*[24,28,29]

	IP (eV)	AP (eV)	D_0 (meV)	E_0 (meV)
B_2	8.65±0.01	9.31±0.01	70±10	660±20
T_2	8.34±0.01	8.97±0.01	150±10	630±20
F_2	8.87±0.02	9.25±0.02	90±20	380±40
BF	8.75±0.02	9.24±0.02	80±20	490±40
BT	8.42±0.01	8.95±0.01	130±10	530±20
BC	9.12±0.02	9.32±0.02	80±20	200±40
BAr	9.222±0.001	9.260±0.005	17±5	38±5
BN_2	9.227±0.002	9.283±0.003	40±3	56±5
B_3	8.58±0.02	8.85±0.02	200±20	270±40
B_4	8.55±0.02	8.68±0.02	100±20	130±40
B_5	8.50±0.02	≤8.61	≤60	≤110

Note:
B, benzene; T, toluene; F, *p*-difluorobenzene; C, cyclohexane.

$$D_0 = AP - IP(B)$$

$$E_0 = AP - IP(B_2)$$

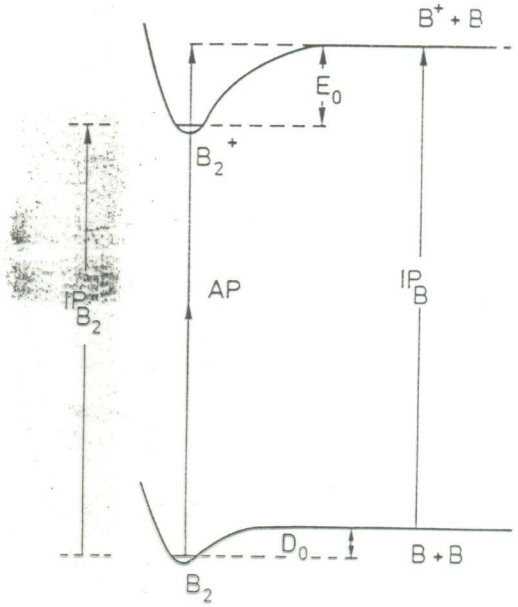


Fig. 3.11 A Born–Haber cycle for determining bond dissociation energies of complexes in the ion and also in the ground state. It requires the measurement of the appearance potential (AP) of fragments of the complex and the measurement of the ionization potentials of the complex and of the monomer[24].

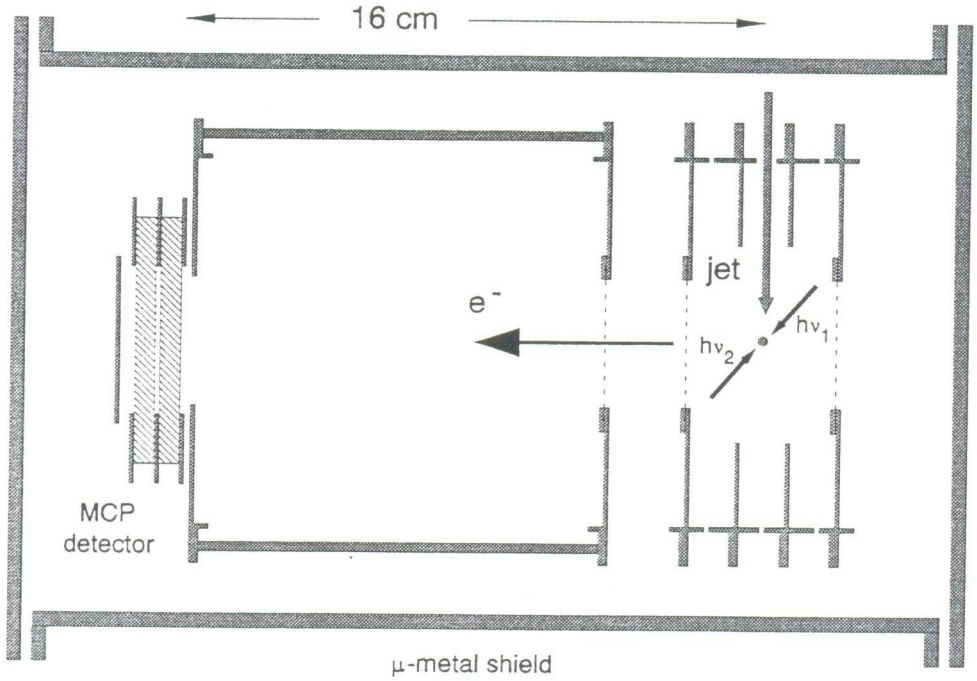
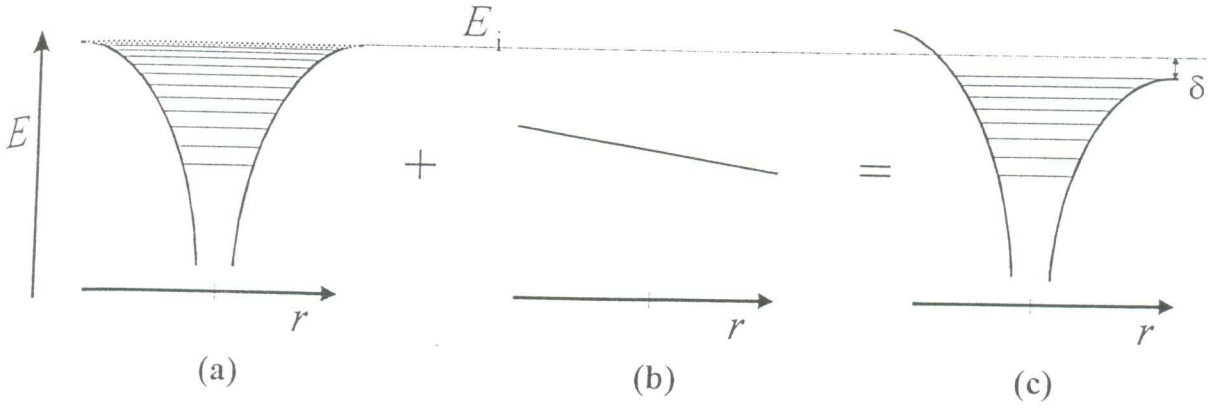


Fig. 6.5 Apparatus for detecting ZEKE electrons. The draw-out pulse is applied as a voltage ramp 1–2 μs after the laser pulse. The electrons drift some 16 cm to a multichannel plate detector in a nearly field-free region (created by use of a μ-metal shield). Two-colour excitation usually simplifies the results.



Lowering of the ionization energy due to an electric field

$$\delta E = 4\sqrt{F}$$

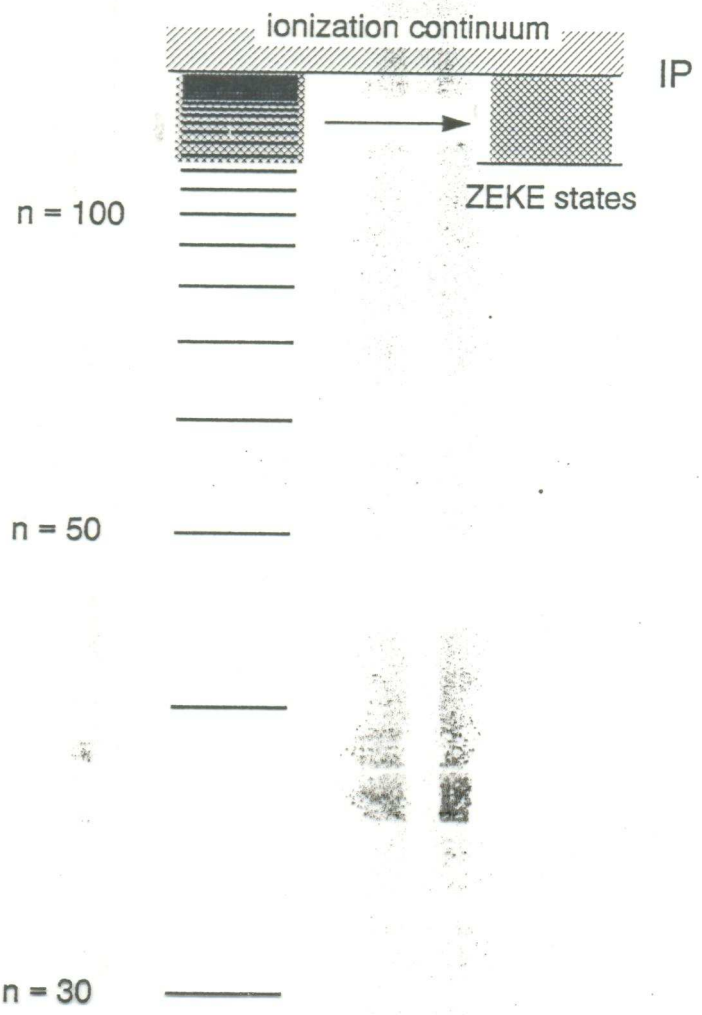


Fig. 6.3 One representative Rydberg series, here leading to the ionization potential (IP). The Rydberg states starting around $n=120$, by interaction with residual fields, are converted to long-lived ZEKE states shown on the right-hand side.

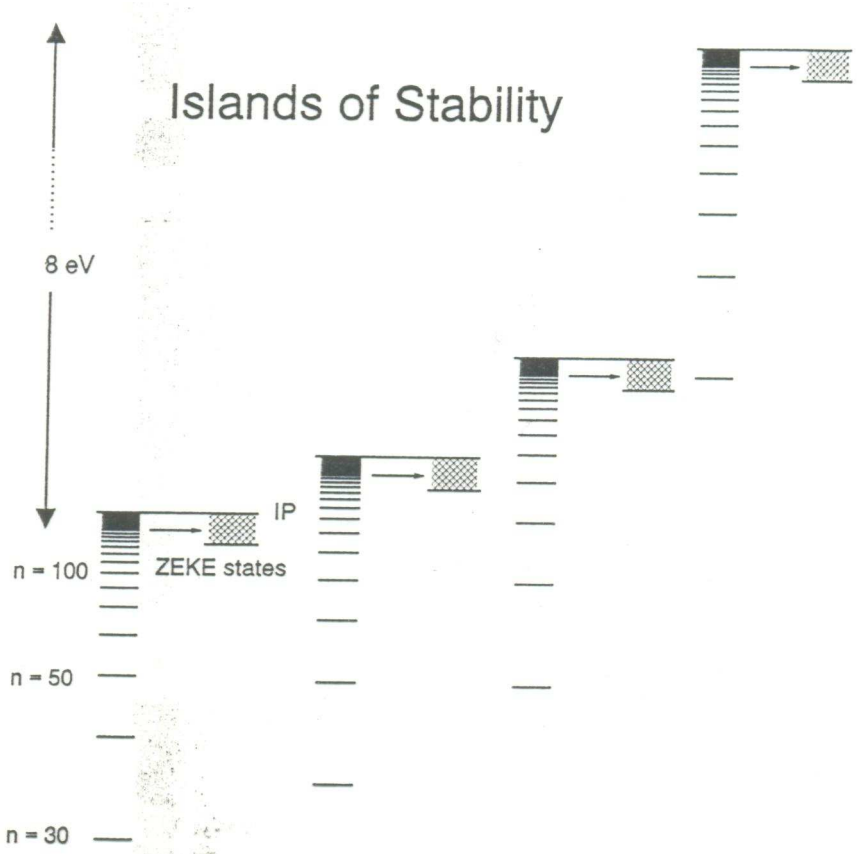


Fig. 6.4 Islands of stability. Here the ionization energy and three additional states at higher energy are shown as an example to show that each state has its own individual Rydberg series. The states at high n, typically near $n=100$ are converted by external fields and ions into special ZEKE states that have an abnormal lifetime, typically some three orders of magnitude longer than one would expect for these states by extrapolation from low n. These abnormally long-lived ZEKE states then exist as special islands of stability at high excess energies within the ionization continuum with a typical bandwidth of some 8 cm^{-1}, as depicted here. These bands can arise from a band of rotations, vibrations or electronic degrees of freedom.

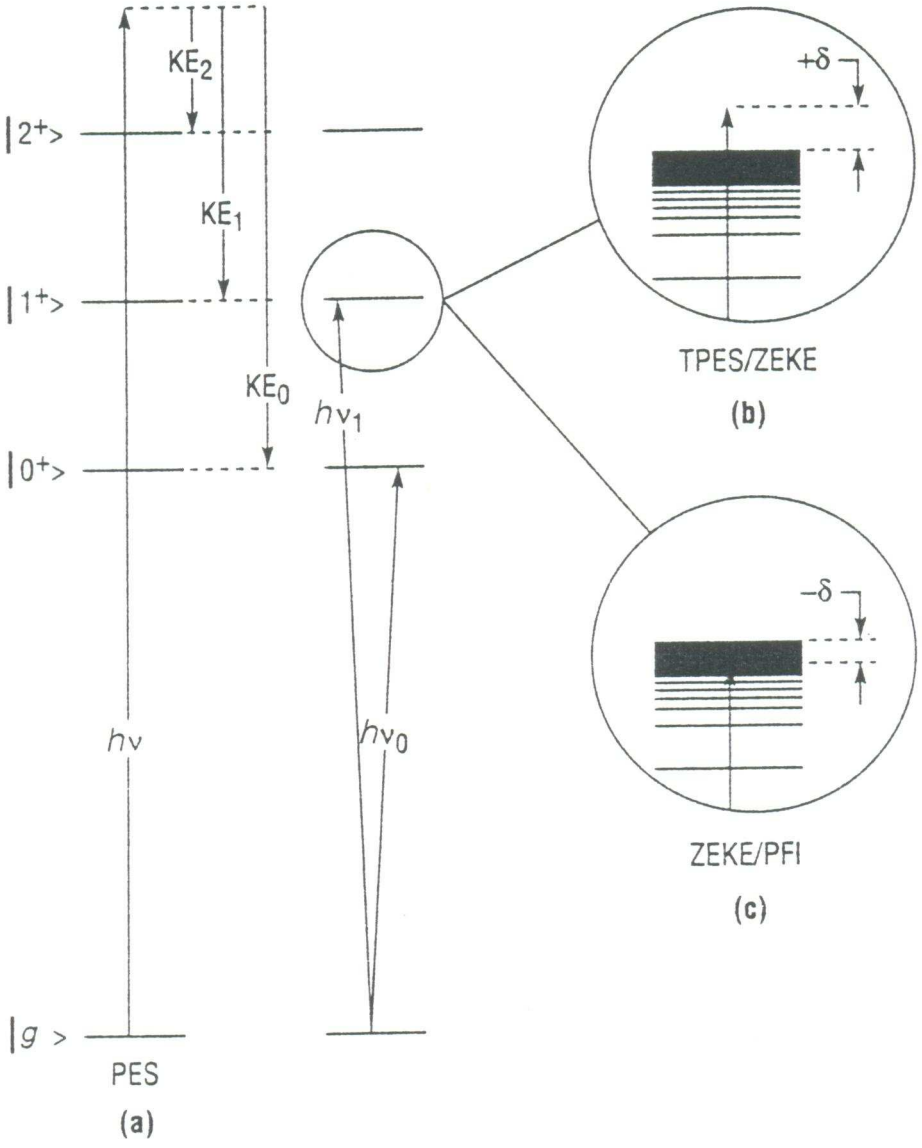


Figure 3.1 Schematic diagram illustrating various approaches to photoelectron spectroscopy: (a) conventional photoelectron spectroscopy (PES) where it is necessary to resolve differences in kinetic energy among the photoelectrons; (b) threshold photoelectron spectroscopy (TPES) where photoelectrons with kinetic energies less than $+\delta$ are detected and spectra are obtained by scanning the VUV radiation ($h\nu$). ZEKE (zero kinetic energy) refers to delayed pulsed extraction of above threshold electrons in the limit of $+\delta \rightarrow 0$; (c) pulsed field ionization (PFI) approach to threshold photoelectron spectroscopy. A delayed, pulsed electric field ionizes metastable high-n Rydberg states lying just below $(-\delta)$ the cation threshold

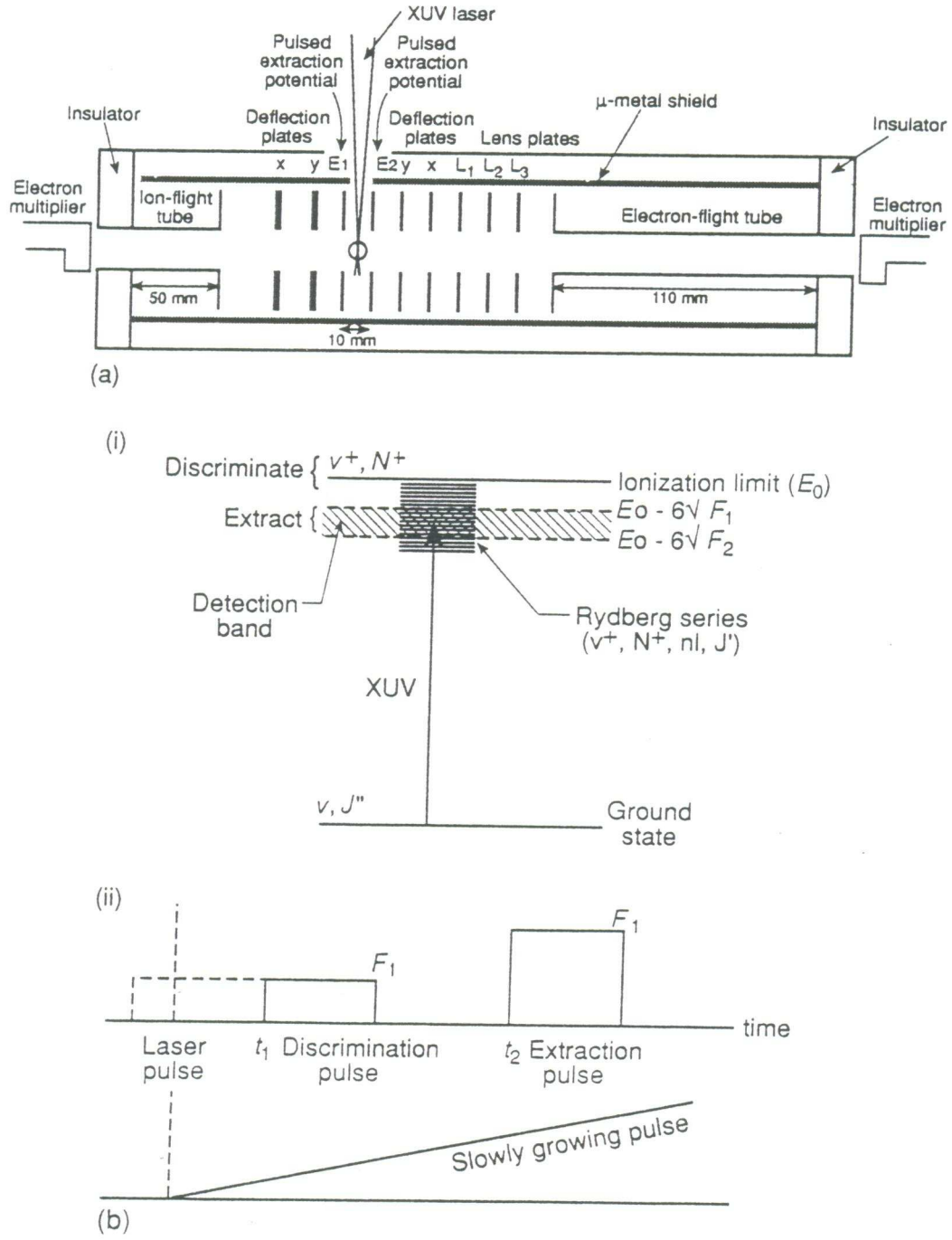


Figure 4.2 (a)Interaction region of the ZEKE photoelectron spectrometer. (b) (i) The energetics of excitation and field ionization by a pair of pulsed fields. (ii) Timing of the discrimination and extraction pulses. As an alternative a slowly, or stepwise, growing pulse as explained in the text is sometimes used (Lindner *et al.*, 1994)

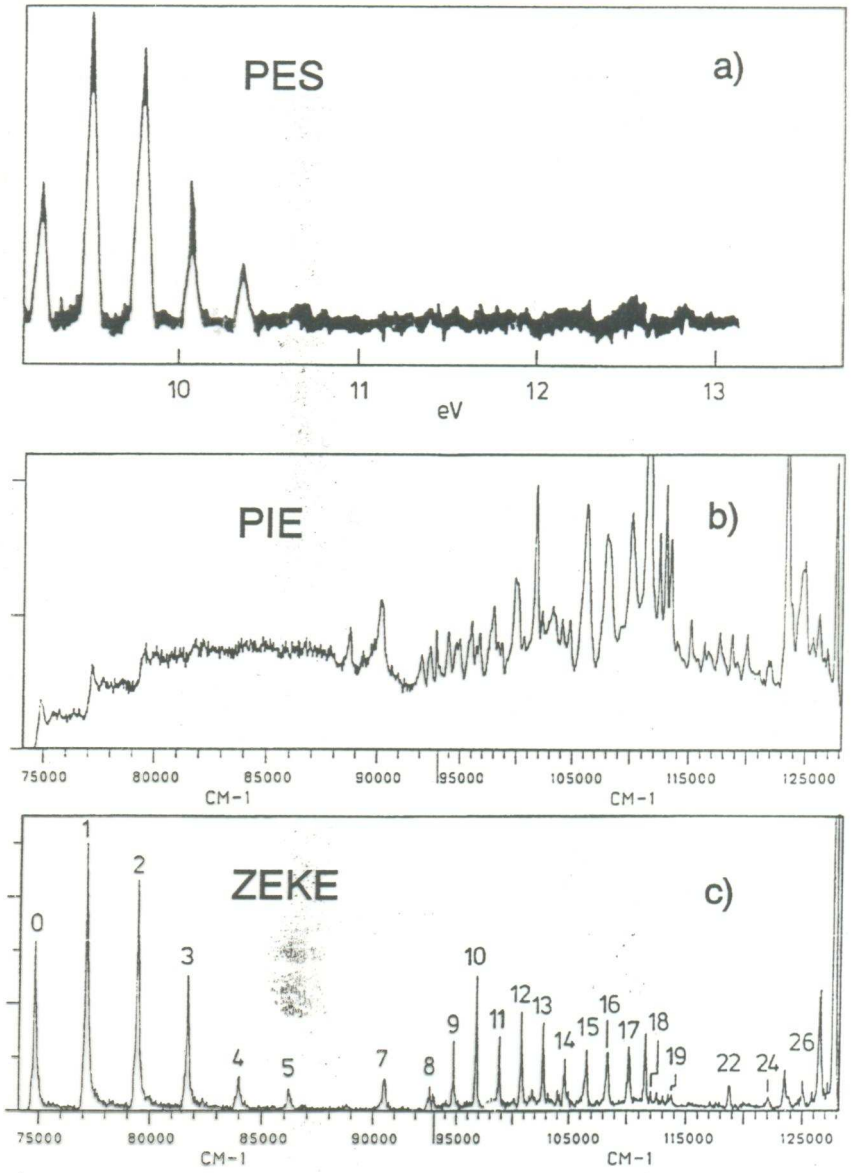


Fig. 8.4 A comparison of methods for nitric oxide. (a) The photoelectron spectrum from Turner, (b) the staircase function of PIE and (c) the threshold-ZEKE spectrum. Note that the vibrations go up to $\nu^+=26$, whereas only $\nu^+\leq 4$ is seen in the PES. This demonstrates a fundamental difference between the two spectroscopies.

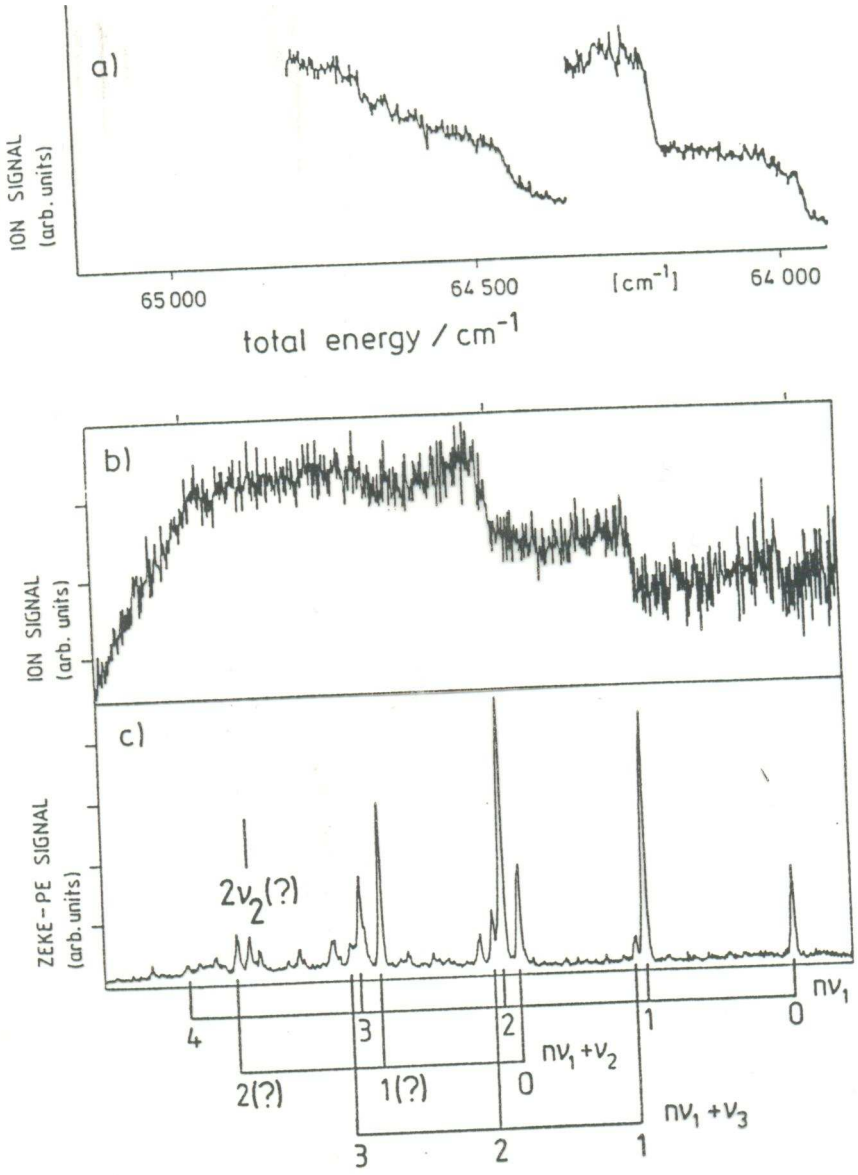


Figure 12 Two-photon two-color ionization of the phenol-H_2O (1:1) complex with the vibrationless S_1 state of the complex as intermediate resonance. Ion signal (m/e) = 112 with (*a*) constant field extraction (reproduced with permission from Ref. 117); (*b*) pulsed field extraction vs. total energy; (*c*) corresponding ZEKE spectrum with assignments of intermolecular vibrations (*b* and *c* reproduced with permission from Reiser et al, to be published).

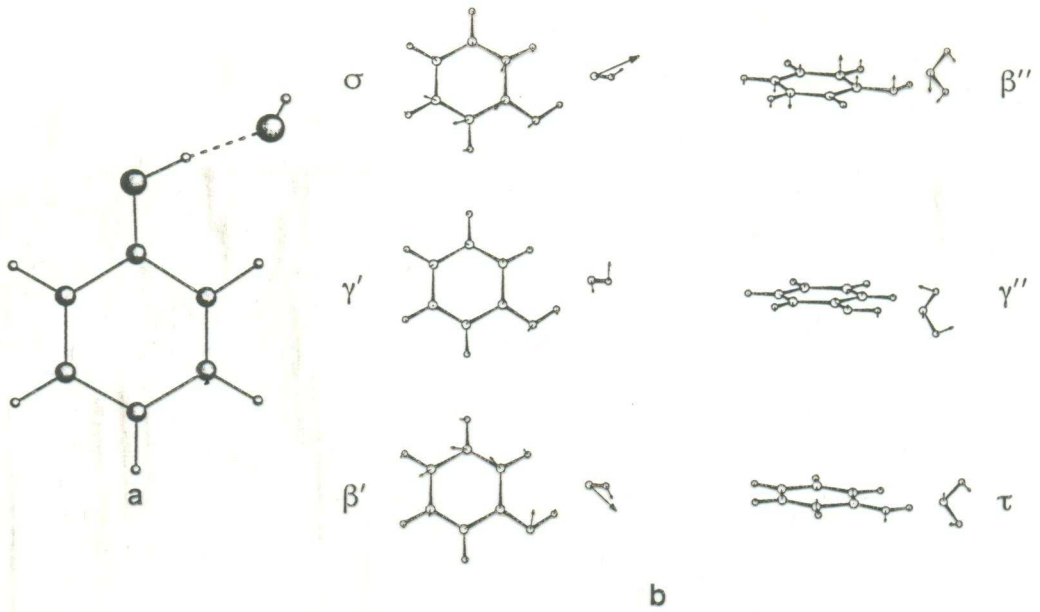


Figure 12. Part a is a sketch of the structure of the ionic 1:1 phenol–water complex (C_s symmetry, the phenyl pla
the symmetry plane). (Geometry taken from ref 158.) Part b shows the six intermolecular normal modes of the phe
water cation radical: σ is the stretch, τ is the torsion, β' and β'' are the in-plane and out-of-plane bends, while γ' a
are the in-plane and out-of-plane wags. (σ, γ', and β' have a′ symmetry; β'', γ'', and τ have a″ symmetry.) (Taken fro
158.)

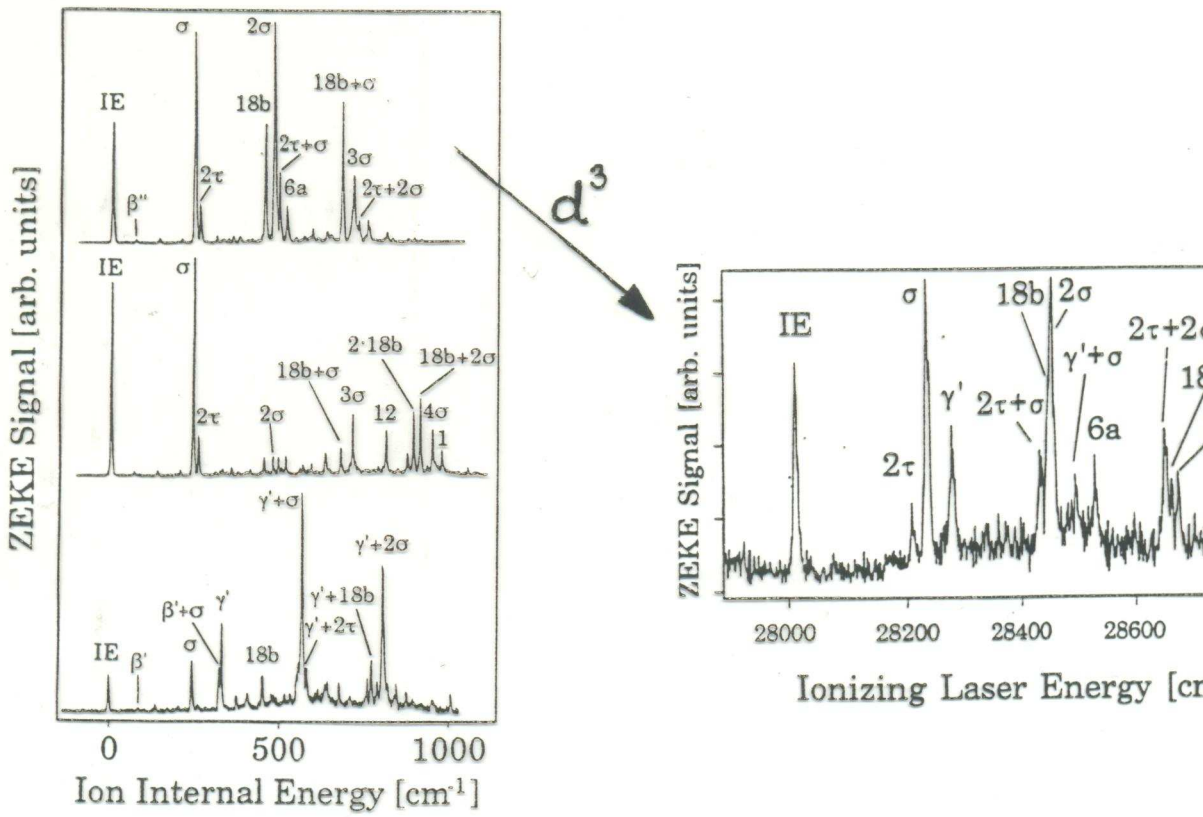


Figure 14. ZEKE spectra of the 1:1 phenol–water complex, [Ph–H_2O]-h_3, via different intermediate S_1 levels: S_1 0^0 (top), S_1 σ^1 (middle), and S_1 γ'^1 (bottom). (Taken from ref 135.)

with permission from Ref. 79 (*top*), Ref. 38 (*bottom*).]

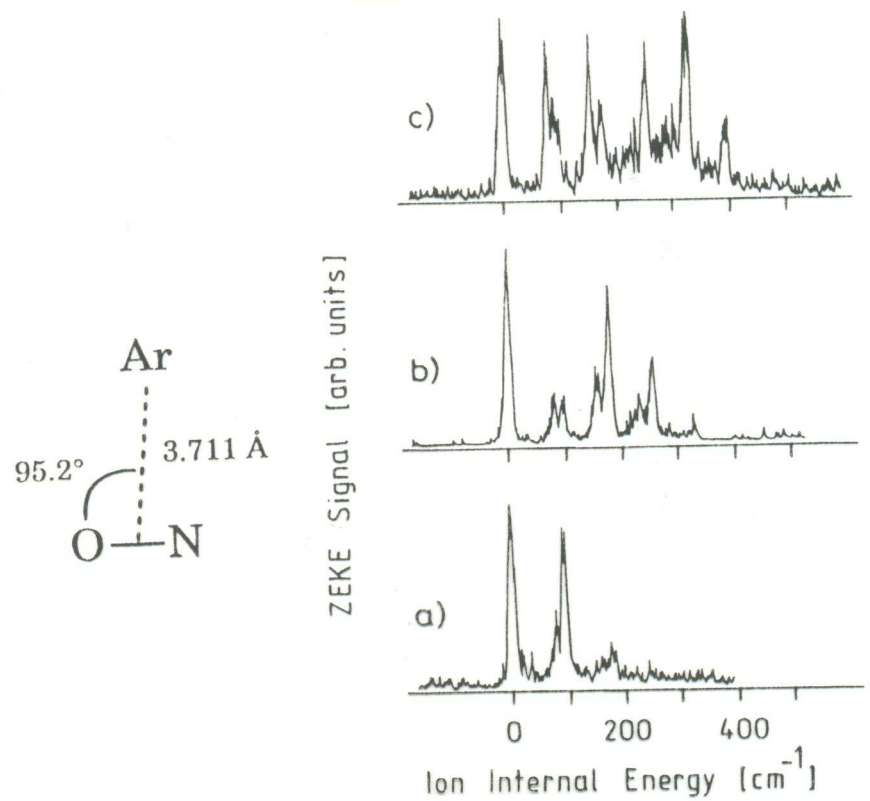


Figure 3. ZEKE spectra of NO–Ar via the $\tilde{C}$ state with zero (a), one (b) and two quanta (c) of the intermolecular stretch excited. (Taken from ref 31.)