GEOMETRY-DEPENDENT PHOTOIONIZATION STUDIES OF SMALL MOLECULES

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OUTLINE

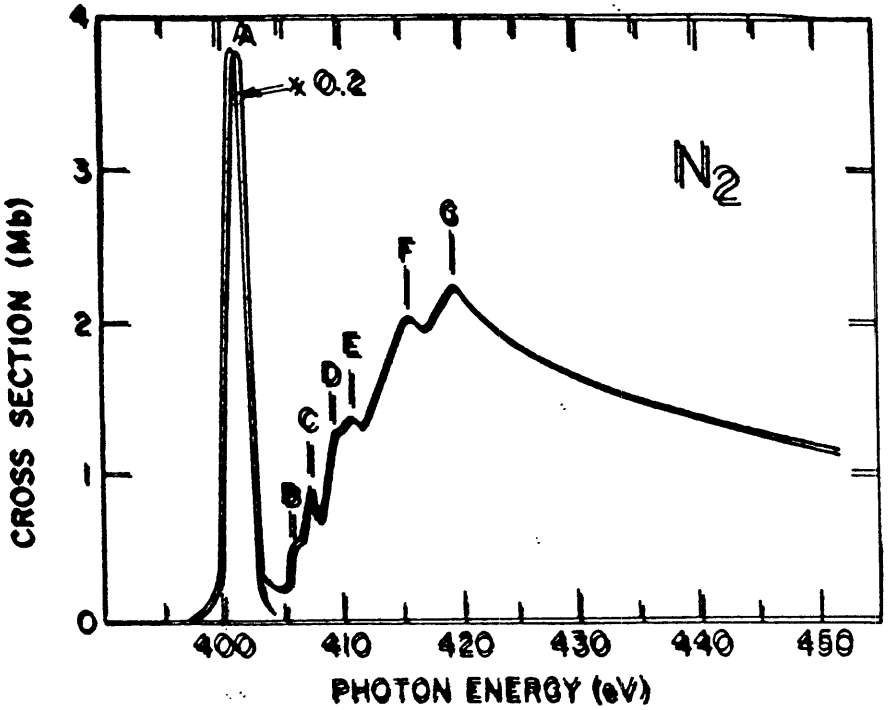
- The R Dependence of Shape Resonances in Small Molecules
- The R Dependence of Inner-shell Orbitals in Small Molecules
- The Bond-Angle Dependence of Shape Resonances in Small Molecules

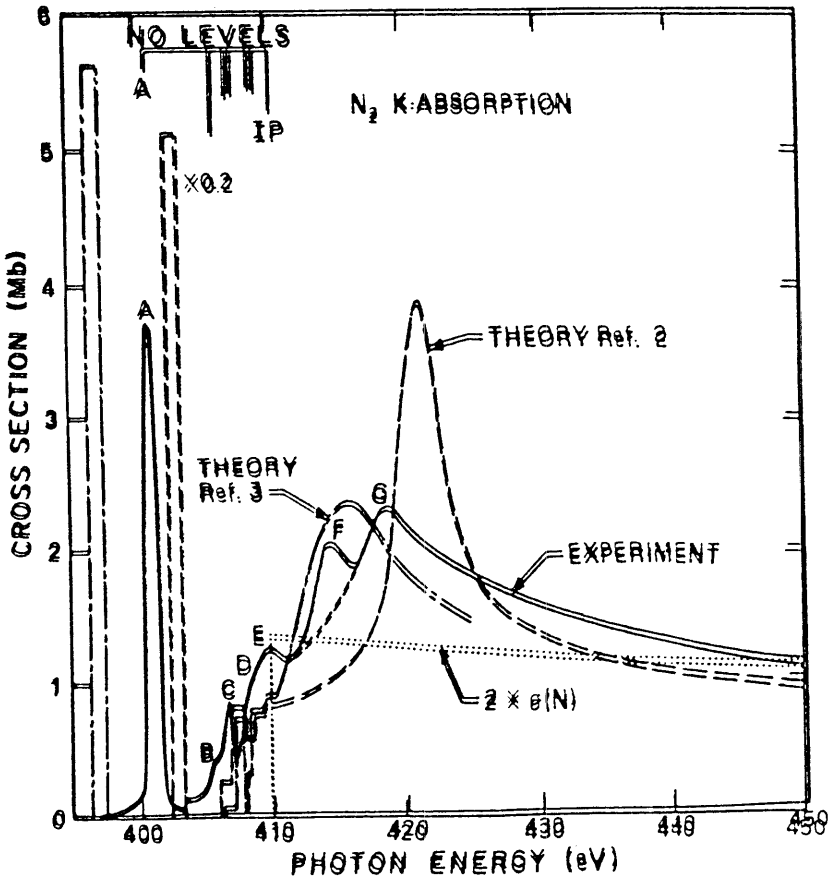
Shape Resonances and their R Dependence

- Centrifugal barriers and valence orbitals
- The R dependence of σ^* resonances: the correlation between resonance energy and bond length
- Can time-domain experiments probe this relationship directly?
- Why is it worth doing?

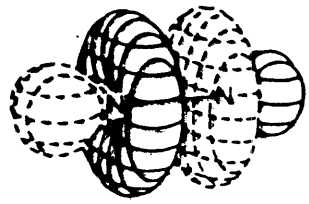
J. Stöhr, "NEXAFS Spectroscopy" (Springer, New York, 1992)
M. N. Piancastelli, J. Electron Spectrosc. Rel. Phenom. 100, 167 (1999

from A. Bianconi, H. Peterson, F. C. Brown, and R. Z. Bachrach, Phys. Rev. A 17, 1907 (1978).

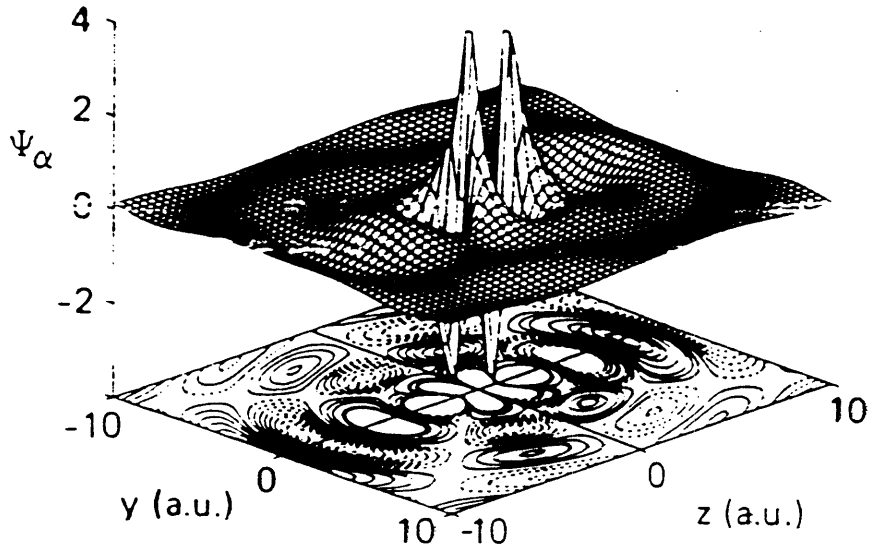




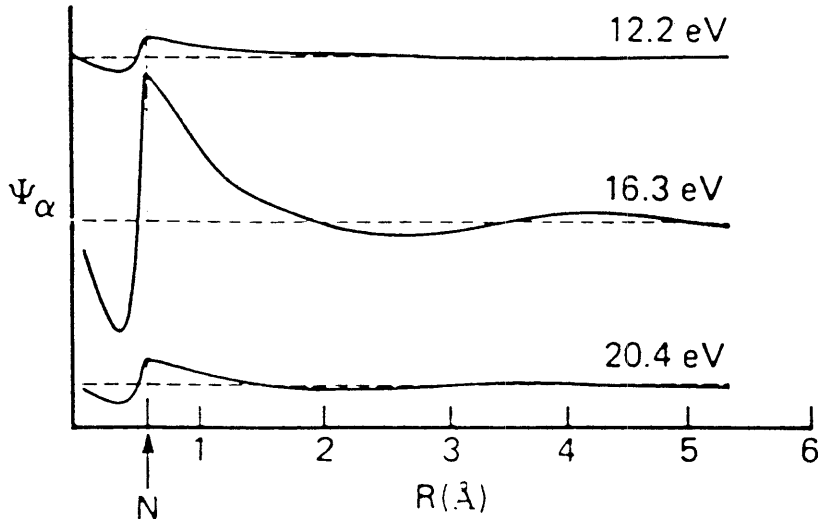
(a) N_2 $3\sigma_u^*$ Antibonding Orbital



(b) N_2 Resonant σ_u $\ell = 3$ Eigenchannel Wavefunction



(c) N_2 σ_u ℓ=3 Wavefunction on and off Resonance



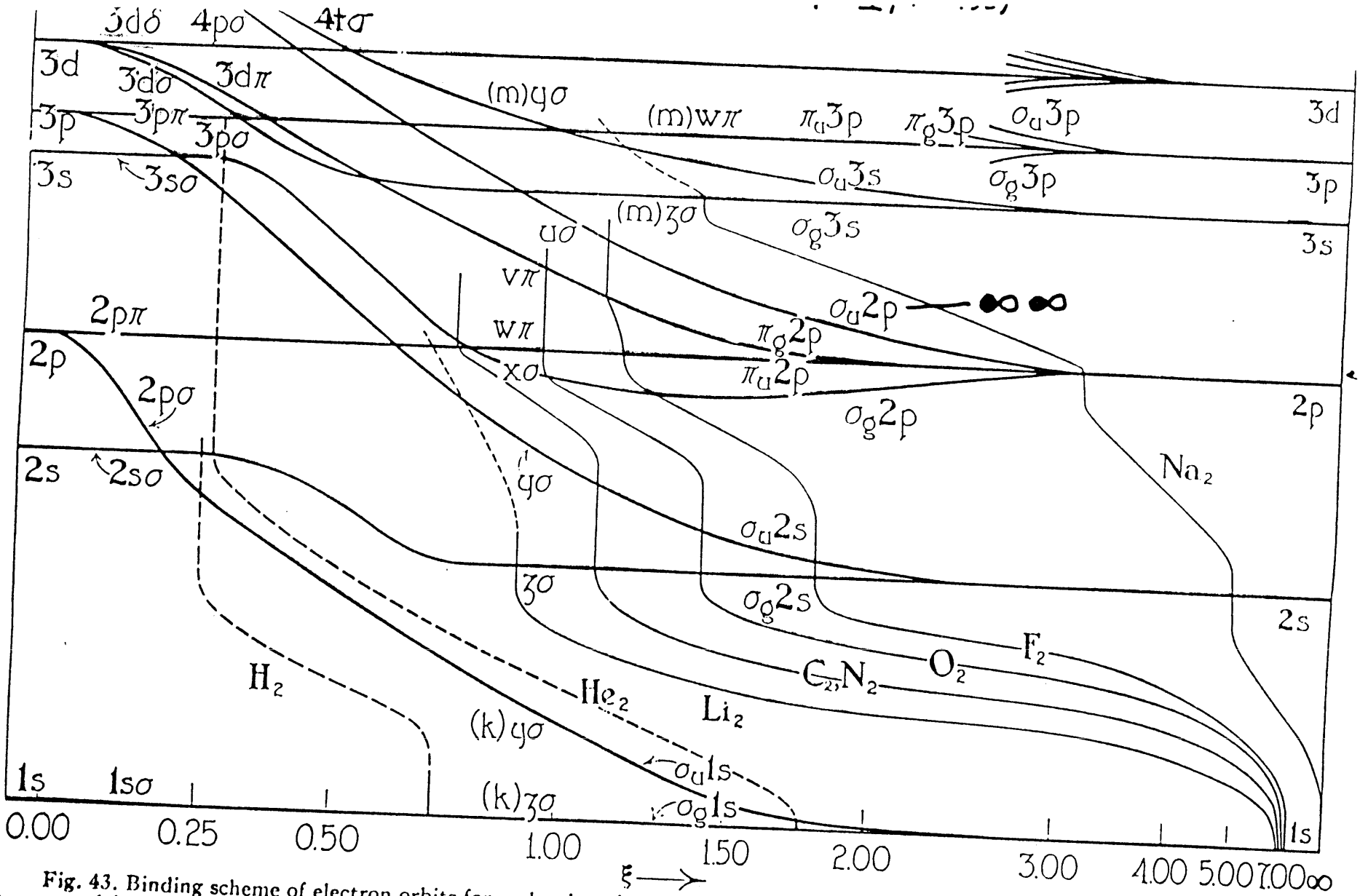
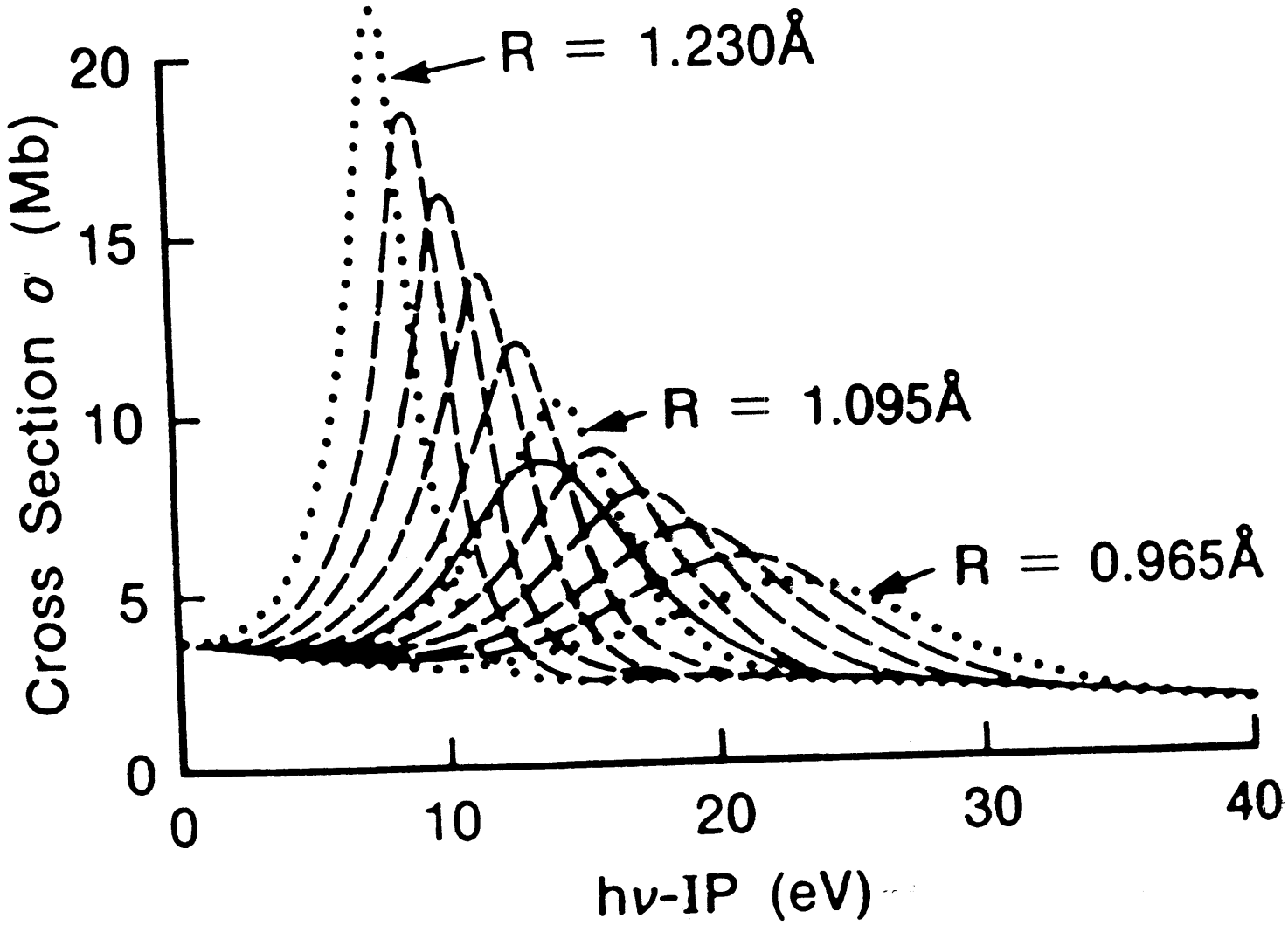


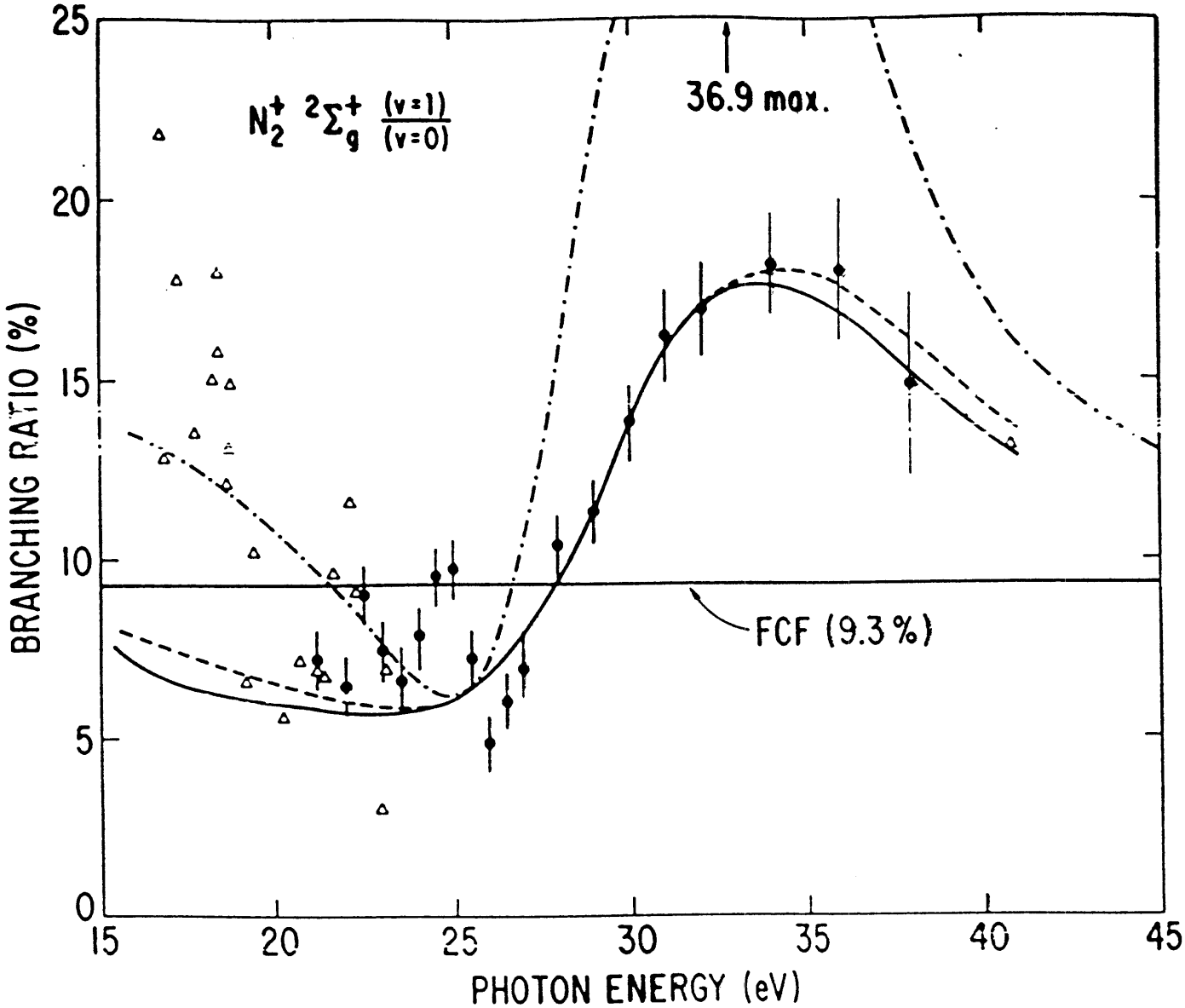
Fig. 43. Binding scheme of electron orbits for molecules whose nuclei are of the same element. Neither the abscissas ξ (distance between nuclei divided by mean diameter of electron orbit) nor the ordinates (negative energy of ionization of the electron) are plotted on a uniform scale, as will be seen from the figure. Also, from the nature of the figure, it is not possible for either ordinates or abscissas, especially the former, to have a quantitative significance. The ordinates on the right are, however, proportional to the logarithms of the binding energies of electrons in the N atom, except for the 2*s* level which has been arbitrarily shifted downward. Those on the left, except 2*s*, are proportional to a function of the logarithms of the binding energies of electrons in the Si atom, which is the united-atom corresponding to N_2. Thus the diagram is especially suited to the N_2 molecule, but is also satisfactory in a somewhat more qualitative way for other molecules. The thin lines going upward and to the left indicate roughly for various molecules the actual ξ values of various orbits, for stable molecular states. From these lines, the qualitative *order of binding* of orbit-types in each molecule can be seen, and at least a rough idea can often be obtained of the relative energy-differences between different orbit-types. (Cf. section D1 for further

from J.L. Dehmer, D. Dill, and S. Wallace, Phys. Rev. Lett. 43, 1005 (1979)
via J. Stöhr, "NEXAFS Spectroscopy" (Springer, New York, 1992).



Evidence for R Dependence

- Vibrationally resolved branching ratios and non-Franck-Condon effects
- Systematic studies of large classes of molecules
- Theoretical predictions



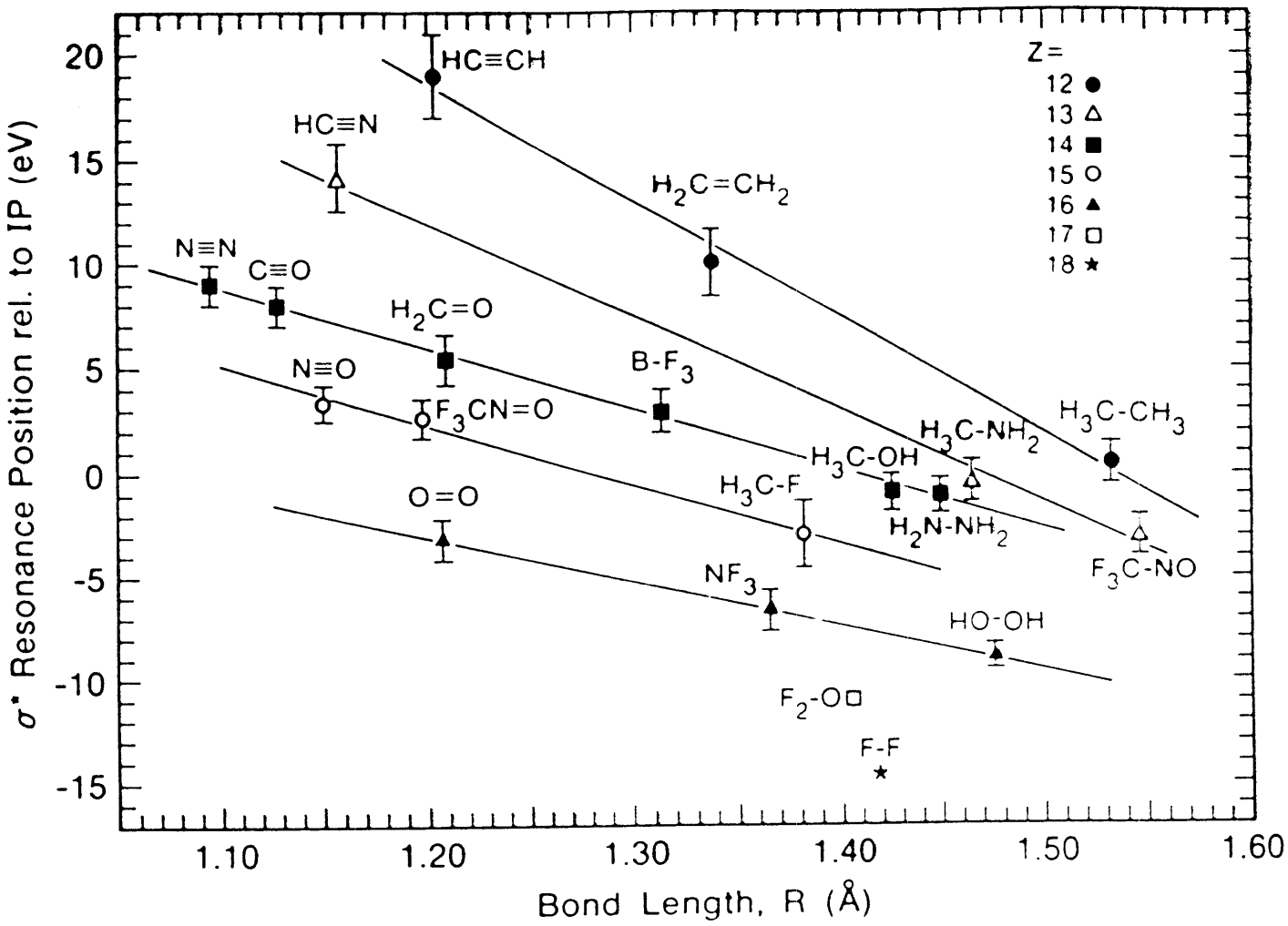
from J.L. Dehmer, A.C. Parr, and S.H. Southworth, "Handbook of Synchrotron Radiation, Vol. 2," edited by G.V. Marr (Elsevier, New York, 1987).

$$\left[\int d\tau\, \psi_e'^{*} D(r)\, \psi_e''\right]\left[\int dR\, \chi_v'^{*} \chi_v''\right] \qquad \text{FRANCK-CONDON}$$

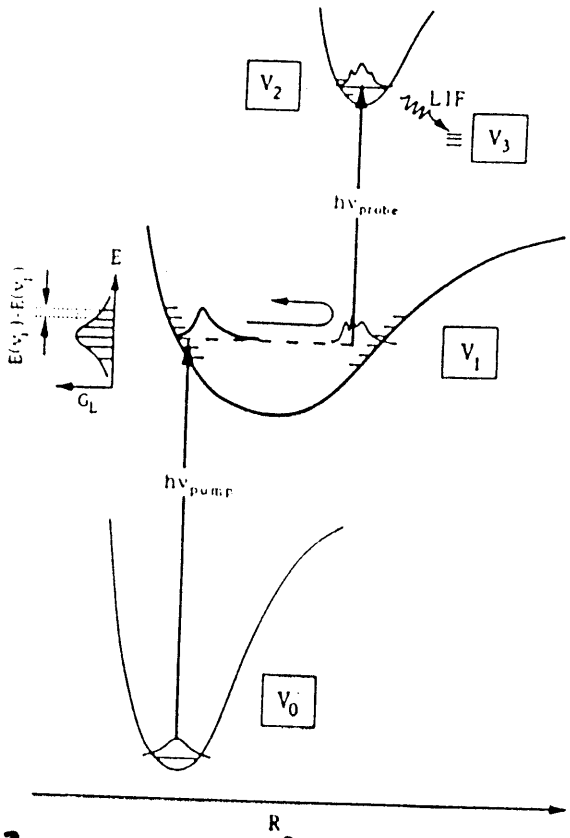
vs.

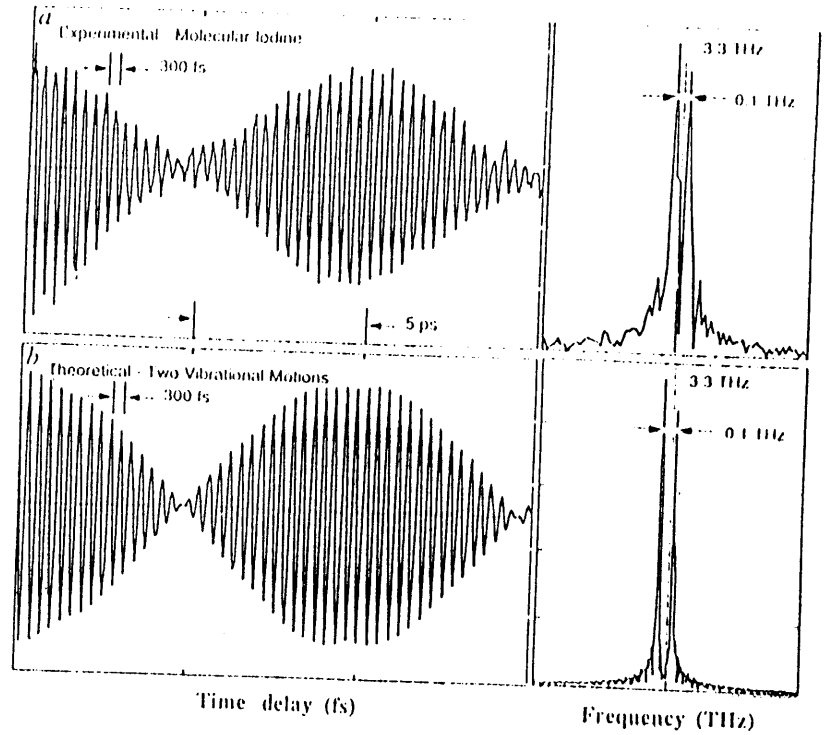
$$\int d\tau\, \psi_e'^{*}\left(\int \chi_v'^{*} D(R,r)\, \chi_v''\, dR\right) \psi_e''$$

from J. Stöhr, "NEXAFS Spectroscopy" (Springer, New York, 1992)



..., R.M. Bowman, and A.H. Zewail, Nature 343, 737 (
R. B. Bernstein, A.H. Zewail, Chem. Phys. Lett. 170, 321 (1990);
M. Gruebele, A.H. Zewail, J. Chem. Phys. 98, 883 (1993).





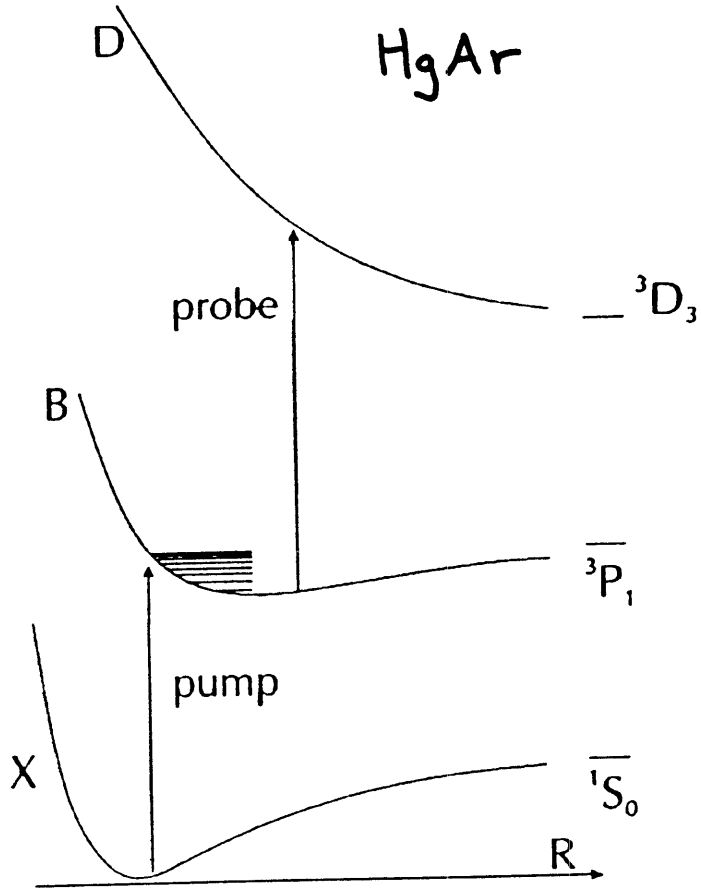
for the $B^3\Pi_{0^+_u}$ state of I_2, R can vary from ~2.7Å to ~5Å.

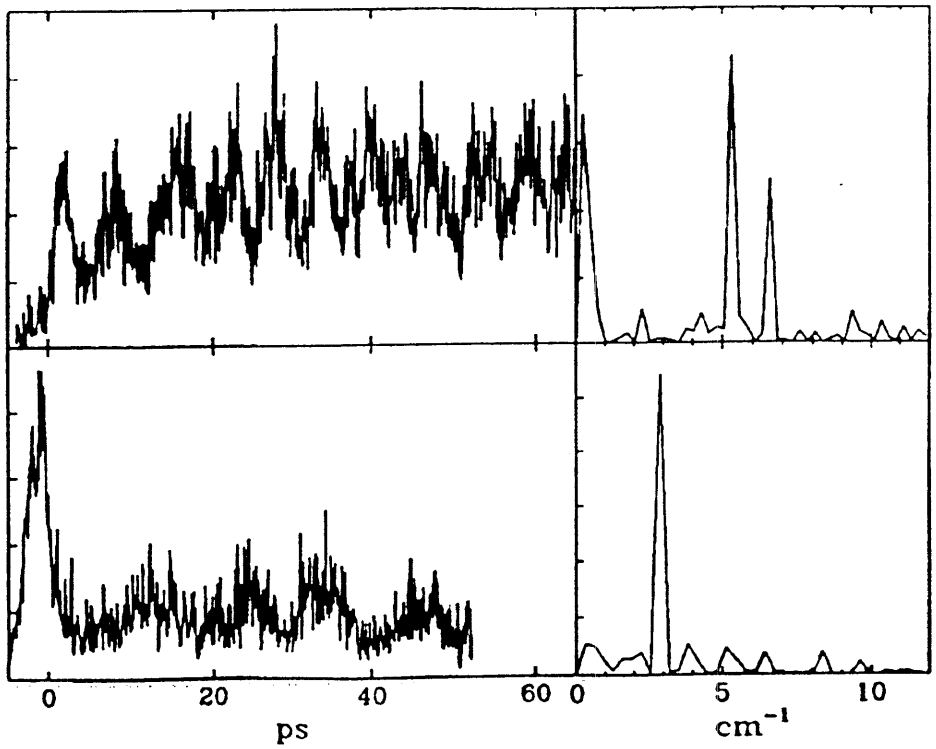
Table 1
Experimental data [4-6] and derived quantities [a]

λ_1 (nm)	τ (ps)	Γ_{id} [b]	E_v [c]	$\nu_{1\,eff}$ [d]	Γ_{corr} [e]	λ_{inv} [f] (nm)	$\Delta\lambda$ [g] (nm)
620	0.299	1012	513	16642	980	618.8	1.2
600	0.308	1233	104	16771	1109	595.6	4.4
550	0.411	2659	89	18271	2609	548.5	1.5
532	0.501	3172	0	18797	3135	531.0	1.0
520	0.606	3476	0	19231	3569	522.5	−2.5
505	1.10	4029	0	19802	4140	507.8	−2.8

[a] All energies are expressed in wavenumbers (cm^{-1}). [b] "Ideal" values of Γ_1 corresponding to perfect classical inversion.
[c] Corrections for thermal population of X-state. [d] "Effective" pump laser wavenumbers, corrected for E_v (column 4).
[e] $\Gamma_{corr} = \nu_{1\,eff} - \nu_0$, where $\nu_0 = 15662$ cm^{-1}.
[f] "Ideal" values of pump laser wavelength, i.e. the "inversion wavelengths" plotted in fig. 1a, calculated from $1/\lambda_{inv} = 1/\lambda_1 + (\Gamma_{id} - \Gamma_{corr})$
[g] $\Delta\lambda = \lambda_1 - \lambda_{inv}$, the discrepancy between the nominal pump laser wavelength and the "inversion wavelength".

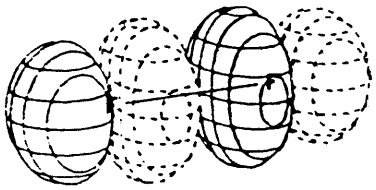
from L. Krim, B. Soep, and J. P. Visticot, J. Chem. Phys. 103, 9589 (1995).



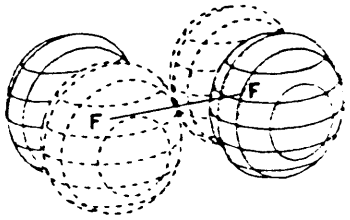


Near-edge Spectra as a Function of Time Delay

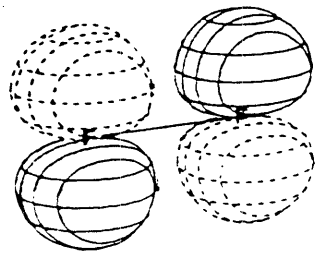
- Initial experiments at delays corresponding to the classical turning points
- Spectra away from R_e should be well separated from the ground state spectrum
- Relatively modest energy resolution is required
- Significantly extends sampled range of R
- Photoelectron spectroscopy of the new features



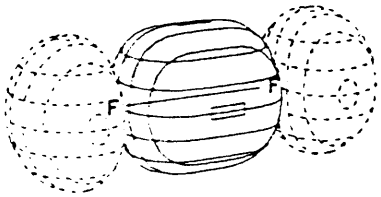
$3\sigma_u$ E= 0.3863



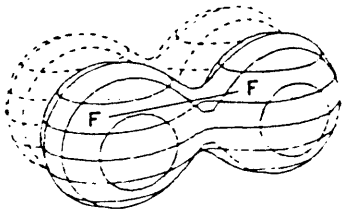
$1\pi_g$ E=-0.4318



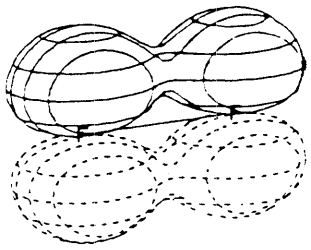
$1\pi_g$ E=-0.4318



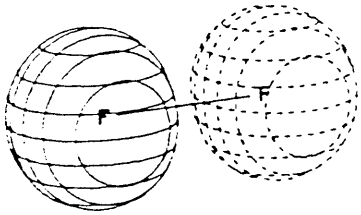
$3\sigma_g$ E=-0.5037



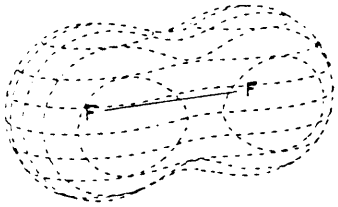
$1\pi_u$ E=-0.5645



$1\pi_u$ E=-0.5645

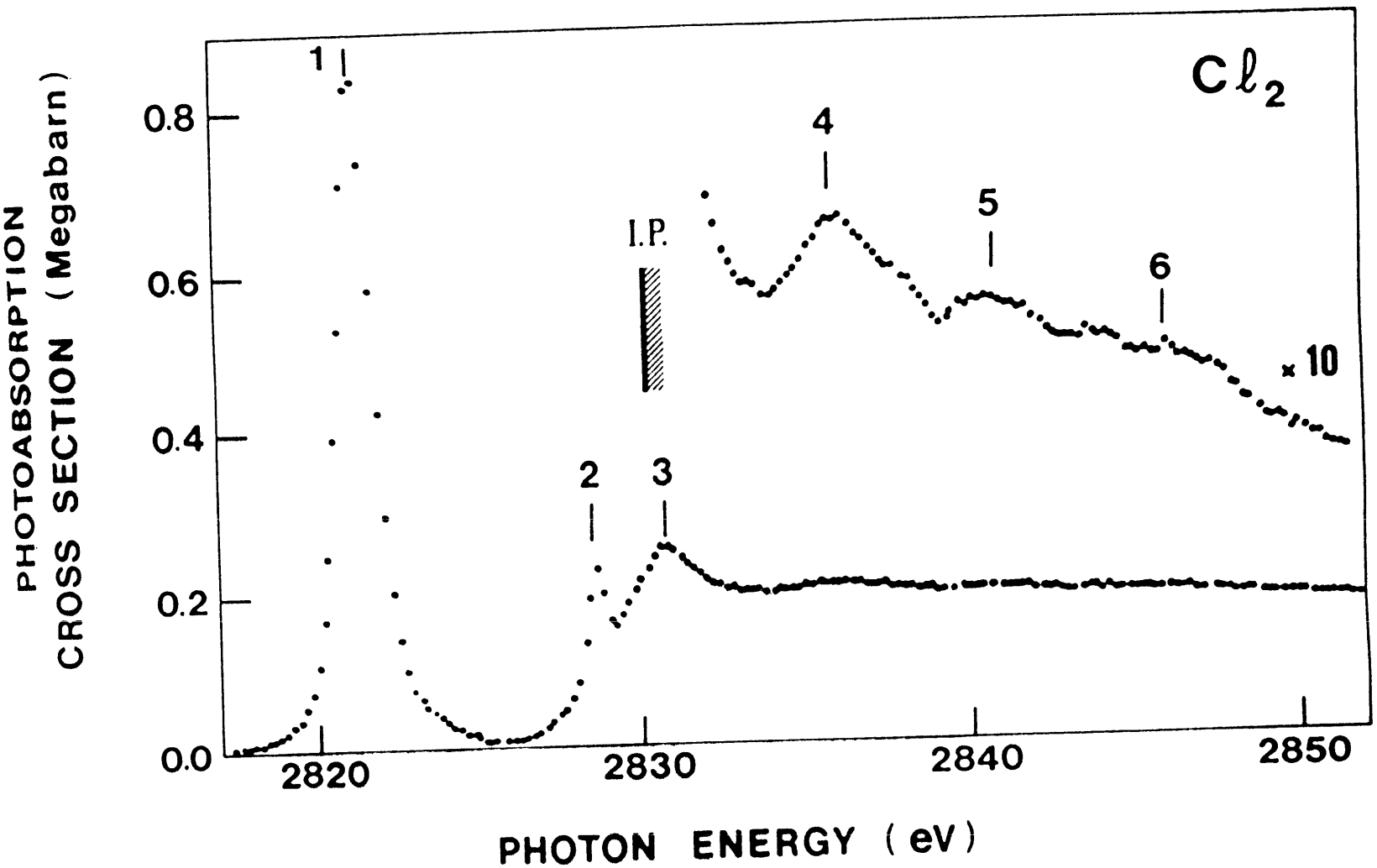


$2\sigma_u$ E=-1.3173

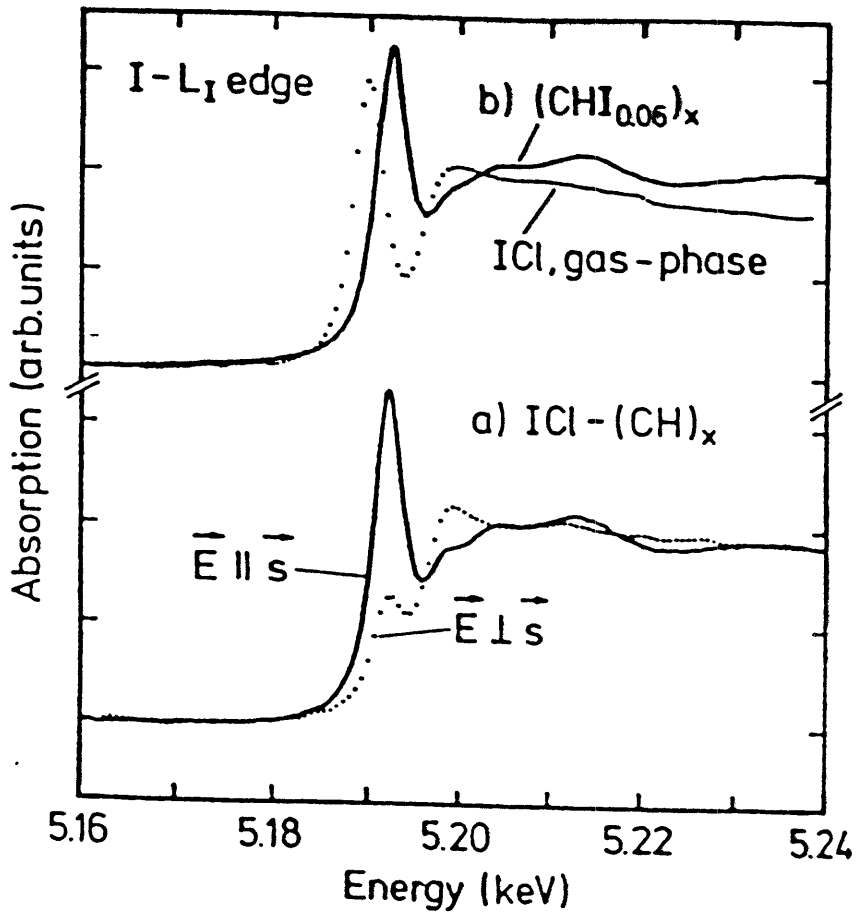


$2\sigma_g$ E=-1.5841

from: S. Bodeur et. al. Z. Physik D 17, 291 (1990).



W. Krone et al., Synthetic Metals 17, 479 (1987)



Feasibility

Nora says: with 10^{11} photons/sec monochromatized flux, a photoelectron spectrum can be obtained at the carbon edge of CO in ~20 minutes with S/N of ~100,000

Exciting 2% of the sample, this time is increased by a factor of 50

The monochromatized, sliced x-ray flux is 10^7 photons/sec, increasing the counting time by a factor of 10^4

Compromising on a S/N of ~1000, and if the counting statistics are the determining factor, the counting time is decreased by a factor of 10^4

This results in an overall factor of 50 increase, so a spectrum should take ~17 hours to collect

Wavelength scans with S/N of ~100 should also be feasible

The R Dependence of Inner-shell Orbitals and the Dipole Approximation

- The validity of the dipole approximation depends on the relative size of the target and the wavelength of the radiation

- At the I L_1 edge, $\lambda \sim 2.4$ Å; at the Cl K edge, $\lambda \sim 4.4$Å

- Vibrational wavepackets can be prepared in ICl that sample R ~ 2.3 to 4.6 Å, over which the validity of the approximation should change substantially*

- Experiments that probe this breakdown are somewhat more difficult, requiring angular distribution measurements or x-ray Raman scattering

* Lower energy edges could be used if necessary given more compact inner shells

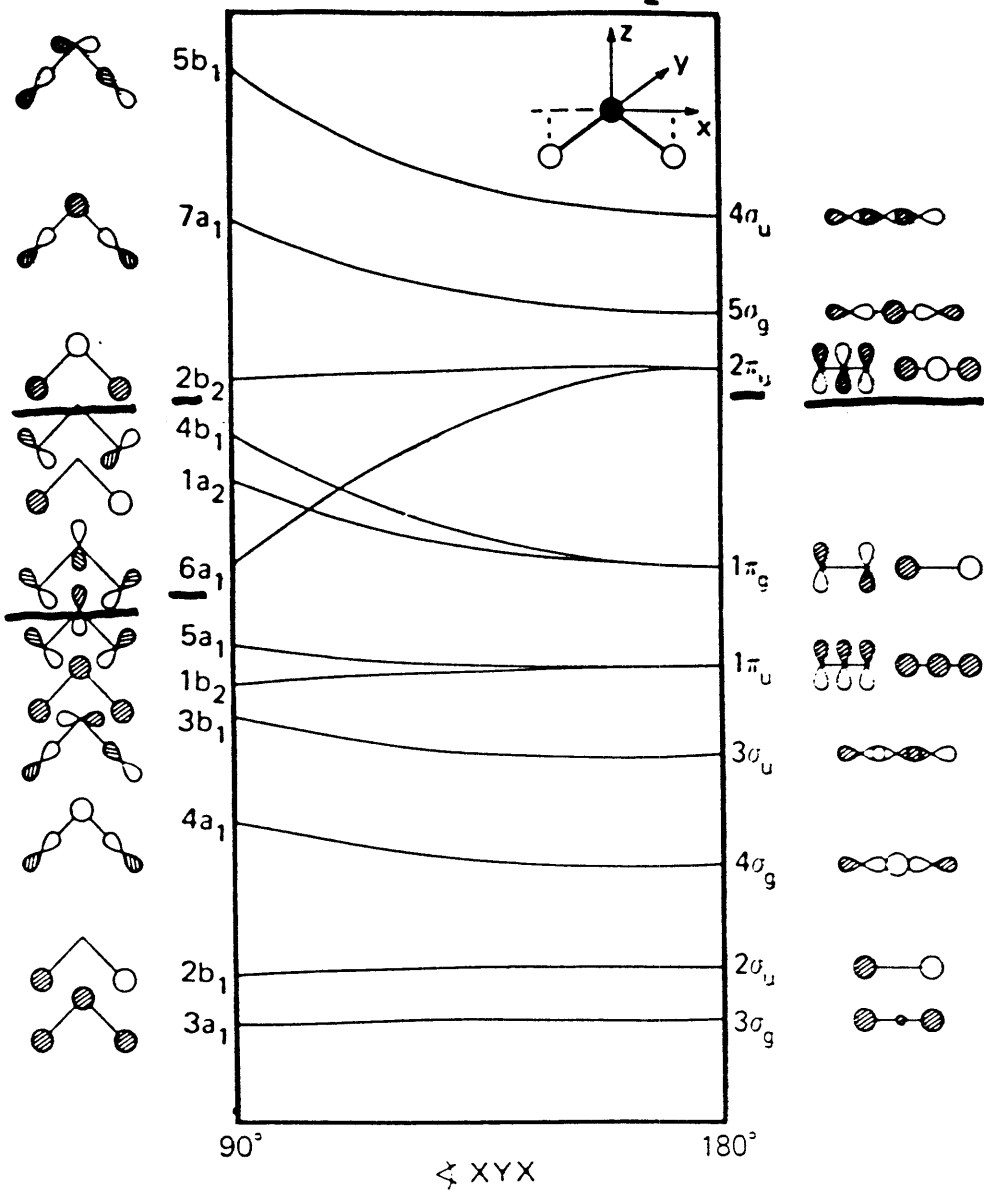
Dependence of Shape Resonance Energies on Bond Angle

- How do σ^* and π^* resonances depend on bond angle in polyatomic molecules?

- Can information on the bond angle be extracted from the resonance positions? Can this information also be extracted for molecules on surfaces?

- Produce a bending wavepacket by pumping a bent to linear transition, and sample this wavepacket at the bent geometry of the turning points

Walsh Diagram for YX_2



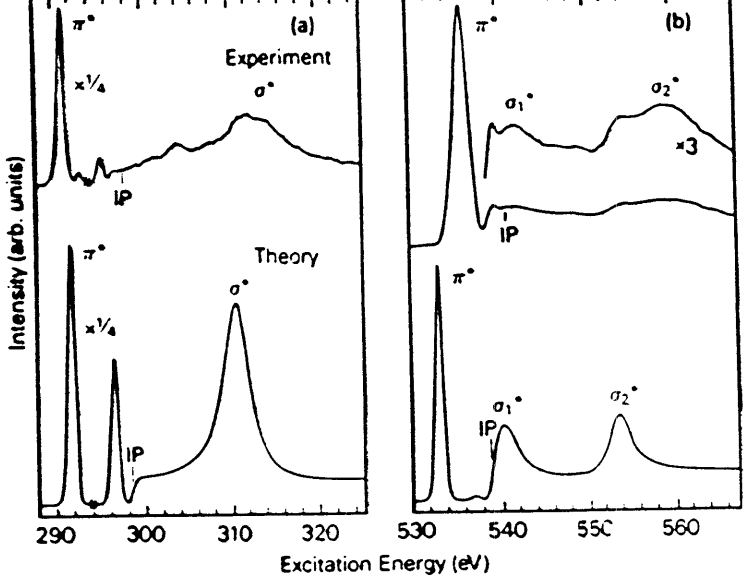


Fig. 6.24. Experimental [6.17, 104] and calculated [6.78] K-shell excitation spectra of carbon dioxide (O=C=O) at the C and O K-edges. At the O K-edge two σ^* resonances are observed due to interactions of the adjacent C=O bonds. The resonances labelled σ_1^* and σ_2^* correspond to transitions to the $5\sigma_g^*$ and $4\sigma_u^*$ MOs, respectively, which are depicted in Fig. 3.2. At the C K-edge the transition to the lower-energy $5\sigma_g^*$ orbital is forbidden by the dipole selection rule due to inversion symmetry and thus only one σ^* resonance is observed

X-M Tong and J-M Li, J. Phys. B 22, 1531 (1989)

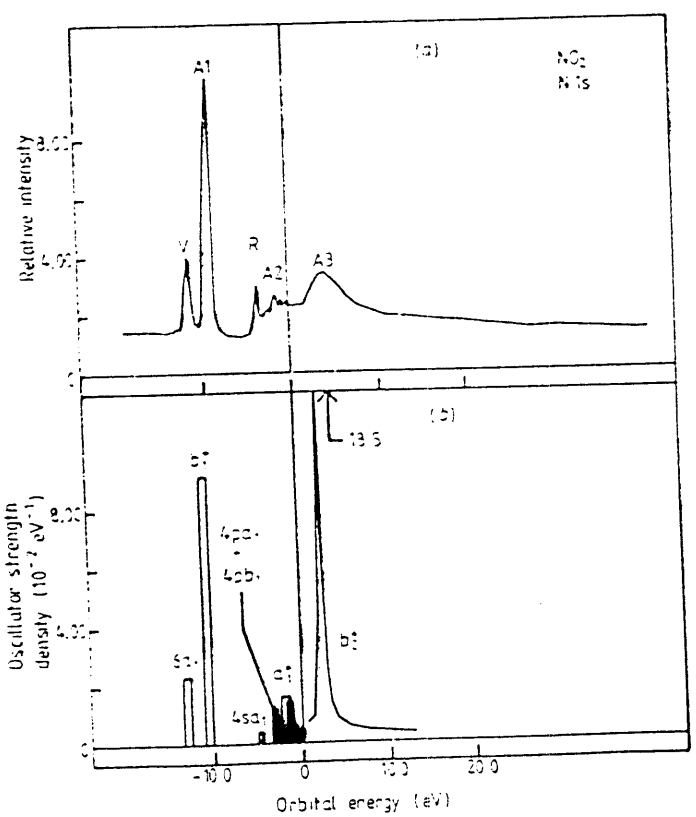


Figure 2. Near-threshold structure of the nitrogen K edge for the NO_2 molecule. (*a*) High-resolution electron energy loss spectrum. (*b*) Theoretical oscillator strength density.