DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-83-16
October 1983

PARTIAL CROSS SECTION AND AUTOIONIZATION RESONANCES IN THE VALENCE SHELL PHOTOEMISSION FROM SOLID ACETYLENE

by

J.-H. Fock

II. Institut f. Experimentalphysik, Universität Hamburg

E.E. Koch

Hamburger Synchrotronstrahlungslabor HASYLAB at DESY

ISSN 0723-7979

NOTKESTRASSE 85 · 2 HAMBURG 52

DESY SR-83-16
October 1983

ISSN 0723-7979

Partial cross sections and autoionization resonances in the valence shell photoemission from solid acetylene*

J.-H. Fock[#]

II. Institut für Experimentalphysik, Universität Hamburg
D-2000 Hamburg, 50, Germany

and

E.E. Koch

Hamburger Synchrotronstrahlungslabor HASYLAB at DESY
D-2000 Hamburg 52, Germany

Abstract

Photoelectron energy distribution curves from solid acetylene were measured for excitation energies up to 30 eV using synchrotron radiation. The partial cross sections are discussed in comparison to theory and other experiments. The $1\pi_u$ valence band cross section shows a pronounced autoionisation resonance with a shoulder and a peak 2.5 and 5.0 eV above the vacuum level which originates from the resonant decay of the $2\sigma_u \rightarrow 1\pi_g$ valence excitation (discrete shape resonance).

---

* Work supported in part by Bundesministerium für Forschung und Technologie (BMFT) from Funds for Research with Synchrotron Radiation

[#] now at: Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80, Germany.

submitted to Chem. Phys. Letters

1. Introduction

Studies of molecular photoemission cross sections over extended energy regions have enhanced our understanding of final state effects generally and have stimulated a fruitful and intense competition between theory and experiment in elucidating the dynamics of the photoionisation process [1]. In this general area, photoemission from acetylene (C_2H_2) has been the subject of a number of recent studies [2-8]. Experimentally, for the gas phase a sharp minimum in the partial cross section of the $1\pi_u$-level has been observed at $h\nu \approx 14$ eV, a few eV above threshold and different explanations involving two transitions have been suggested for the resulting two peak structure [3-7]. However, in a recent calculation including electron correlation effects the cross section data and the minimum observed in photoemission asymmetry parameter for the $1\pi_u$-photoionisation have been identified as arising from one single autoionization resonance ($2\sigma_u \rightarrow 1\pi_g$) [8].

In this letter we describe the results of photoemission experiments from solid C_2H_2, which are part of a larger project concerned with final state effects and resonances in condensed gases [9,10]. Cross section determinations close to threshold for solid gases are generally not hampered by degenerate autoionizing *Rydberg* states which can make such measurements and their interpretation more difficult in the gas phase. Thus in solid gases higher excited *non Rydberg* states and shape resonances are dominating. Indeed for solid acetylene our experiment shows similar to the gas phase clear evidence for a pronounced autoionization resonance in the photoionization cross section of the $1\pi_u$-orbital with a shoulder and peak 2.5 and 5.0 eV above threshold. This clearly supports the viewpoint that this structure originates from the resonant decay of the $2\sigma_u \rightarrow 1\pi_g$ *valence* excitation. In a simple MO picture we locate the empty $1\pi_g$ virtual MO involved in the autoionisation about 2.0 - 3.0 eV below threshold. Furthermore, we arrive at a consistent description of this final state resonance in X-ray absorption-, UPS- and electron scattering-experiments by correlating the energies of the discrete shape resonance observed in X-ray absorption [11,13], the energy of the empty valence MO involved in the UPS experiments and the $1\pi_g$-shape resonance observed at 1.8 - 2.6 eV kinetic energy in electron scattering experiments [14,15]

2. Experimental Details

We used our previously described apparatus [10] at the DORIS II storage ring as a synchrotron radiation source with a 3 m normal incidence monochromator at HASYLAB in Hamburg. Angle integrated photoelectron energy distribution curves (EDC's) were measured with a double pass cylindrical mirror analyzer (CMA) for excitation energies ranging from $h\nu$ = 10 eV up to 30 eV. The count rates were $\sim 10^4\ s^{-1}$ for the C_2H_2 valence bands with an overall resolution (monochromator and electron analyzer) of 0.1 - 0.2 eV, which was found to be sufficient for an accurate determination of EDC features which have typical widths of 1.1 - 1.6 eV (fwhm).

Research grade C_2H_2 gas was condensed under UHV conditions (pressure before and after condensation $\sim 3 \times 10^{-10}$ Torr) on a helium-cooled gold substrate. The temperature of the substrate was ~20 K. To avoid charging problems during photoemission, the sample thickness was limited to roughly 10 nm.

For the determination of photoemission intensities the EDC's for each excitation energy have been normalized to the intensity of the photon flux impinging on the sample. Secondly a smooth structureless background was subtracted from direct emission peaks to account for electrons originating from the aged gold substrate and for scatterd electrons. Finally, the area under each primary emission peak in the EDC's was determined by fitting the experimentally determined four peak structure by gaussians. It turned out that in all cases a fit with one gaussians for each peak was sufficient (see Fig. 1).

As we discussed elsewhere in detail [10], the largest uncertainity in the cross section determination rests in the unknown transmission function of the electron analyzer at low kinetic energies ($\leq$ 4 eV). It contributes most of the total errors in the relative cross sections which we estimate may be as high as 30 %.

3. Results and Discussion

Acetylene is a small linear unsaturated hydrocarbon (point group $D_{\infty h}$), isoelectronic with N_2. Compared to the latter, however, two additional unoccupied MO's are present which are derived from the two hydrogen 1s orbitals. The following electron configuration, including the lowest virtual MO's results:

$$\underbrace{(1\sigma_g)^2(1\sigma_u)^2}_{\text{core}} \quad \underbrace{(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2}_{\text{occupied valence MO's}} \quad \underbrace{(1\pi_g)^0(4\sigma_3)^0(3\sigma_u)^0(4\sigma_u)^0}_{\text{empty MO's}}$$

The occupied states of the molecule are well understood [16-19] and the photoelectron spectrum is easily interpreted. In Fig. 1 a comparison is shown of an EDC obtained for solid C_2H_2 with the gas phase photoelectron spectrum. All four occupied valence levels are visible and a clear one-to-one correspondence to the gas phase photoelectron spectrum emerges which is typical for monomolecular van der Waals solids [9,10]. Thus it is easy to assign the peaks for solid C_2H_2 to the photoemission from the valence bands formed by the $1\pi_u$, $3\sigma_g$, $2\sigma_u$ and $2\sigma_g$ MO's of the molecule respectively. The 27.5 eV configuration interaction satellite which is clearly visible in XPS spectra [18,20] has a vanishing intensity for photon energies below $h\nu$ < 50 eV. The binding energies and widths of the valence bands together with the assignments are collected in table 1 where also the gas-phase results [16-19] are given for comparison. The resulting gas-to-solid shifts are 0.6 eV for the vertical ionization potentials and 1.7 eV to 2.3 eV for the adiabatic ionization potentials. These relaxation shifts are mainly due to screening of the hole in the solid [10]. We note in passing that these values, representative for bulk acetylene, are by about 0.9 eV lower than those reported for acetylene on Ni-metal surfaces [21]. Probably in the latter case the film thickness was still fairly low and stronger screening via metal electrons may have been active.

Here we are particularly interested in the $h\nu$-dependence of the partial photoionisation cross sections for the valence bands. In Fig. 2 a family of EDC's is shown measured at different photon energies. In this plot peaks originating from the same initial state, i.e. having the same binding energy, move to higher kinetic energies when the photon energy is increased. From these spectra the relative partial cross sections were determined by fitting each peak with a gaussian after suitable background subtraction. The result of this analysis is shown in Fig. 3 and may be directly compared to gas phase partial cross sections for acetylene [2-5,8]. For each orbital we observe marked changes of the photoionisation cross section with photon energies. In the following we discuss these cross sections in more detail.

$1\pi_u$ - Orbital. For gaseous acetylene the cross section of the $1\pi_u$-orbital is, similar to the N_2-case, the largest and derives most of its intensity from the atomic $1\pi_u \rightarrow \varepsilon\delta_g$ channel. It shows a double peak structure in the 10-20 eV range with a sharp minimum at around 14 eV. Our solid state cross section shows a very similar behaviour with a strong peak at $h\nu$ = 16 eV and a dip around 14 eV, while the first maximum is broadened and only visible as a shoulder at $h\nu$ = 13.5 eV.

This structure in the $1\pi_u$-cross section has been attributed to at least one autoionizing valence state, namely $2\sigma_u \rightarrow 1\pi_g$ [3,4,22], but additional autoionization processes have been proposed including the $3\sigma_g \rightarrow 3\sigma_u$ [22] and $2\sigma_u \rightarrow 4\sigma_g$ [3,4] valence transitions, shape resonances [5] and the $3\sigma_g \rightarrow 3p\sigma_u$ Rydberg transition [6]. However, according to the calculation by Machado et al. [4], the two proposed valence transitions are too far off in energy so that besides the $2\sigma_u \rightarrow 1\pi_g$ valence transition only the proposed Rydbergy transition remains as a plausible second candidate for the autoionization. The similarity of the cross sections for gas and solid makes it highly unlikely that a Rydberg state, which is expected to be heavily quenched in the solid, is responsible for the autoionization. Thus we conclude, that only one, namely the $2\sigma_u \rightarrow 1\pi_g$ valence transition (discrete shape resonance) causes the structure in the $1\pi_u$-cross section. This is in complete agreement with the recent calculation by Levine and Soven [8], where the authors find, that a single Fano-autoionization profile is sufficient to explain the $1\pi_u$-cross section. Moreover, the calculation shows, that oscillator strength of the discrete $1\pi_u \rightarrow 1\pi_g$ valence transition is shifted to the continuous part of the spectrum and contributes to the observed resonance.

This last point leads us to briefly comment on the occurance of shape resonances in C_2H_2. From a naive point of view four resonances corresponding to the empty $1\pi_g$, $4\sigma_g$, $3\sigma_u$ and $4\sigma_u$ MO's could be expected. Only the $1\pi_g$-shape resonance is well characterized both in X-ray absorption [11-13] where it occurs 5.4 ± 0.2 eV below threshold, and in electron scattering [14,15]. As discussed above the same MO forms a discrete shape resonance ($\pi \rightarrow \pi^*$ valence transition) about 2.0 - 3.0 eV below threshold when the $2\sigma_u$ orbital is excited.

According to dipole selection rules both the $1\pi_g$ and $4\sigma_g$ shape resonances can be reached from the $1\pi_u$-orbital, but, up to now, these transitions have not jet been identified unequivocally in the acetylene VUV-absorption spectrum (e.g. [23]). The calculation by Machado et al. [4] does not include the $1\pi_u \rightarrow 1\pi_g$ transition while the $1\pi_u \rightarrow 4\sigma_g$ transition is assigned to the so called $\tilde{D}$-band at 9.2 eV which in turn has been assigned by Åsbrink et al. [23] on the basis of their HAM calculation to the $1\pi_u \rightarrow 1\pi_g$ transition.

Thus, at present the absorption spectrum is poorly understood and does not yield further insight in the assignment.

$3\sigma_g$-Orbital. In the $3\sigma_g$ cross section the $3\sigma_u$ and $4\sigma_u$ shape resonances might be expected. Our data (Fig. 3) show large values close to threshold and a smooth decrease to higher photon energies without any significant structure. This behaviour is in general agreement with the gas phase results [3] and the calculation by Machado et al. [4] which identifies the high intensity close to threshold with the $3\sigma_u$-shape resonance. We note, however, that the $3\sigma_g$ and $2\sigma_u$ cross sections could not be determined close to threshold (no data points in Fig. 3) because of the background of scattered electrons. In the experiment no indication of the additional $4\sigma_u$-shape resonance is found.

$2\sigma_u$ - Orbital. Our data show a smooth decreasing cross section in agreement with the gas phase [3]. From the $2\sigma_u$-orbital the $1\pi_g$- and $4\sigma_g$- shape resonances can be reached. The autoionization of the former and its influence on the $1\pi_u$ cross section has already been discussed above. According to the calculations by Machado et al. [4] $2\sigma_u \rightarrow 4\sigma_g$ forms a discrete transition at $h\nu$ = 17.7 eV which has not been identified experimentally. It is expected to contribute to the discrete spectrum close to threshold.

In Fig. 4 we have plotted the energies of shape resonances as observed in X-ray absorption [11-13], gas- and solid-phase photoemission and electron scattering [14,15]. For the photoemission the occupied valence MO's and the derived valence bands respectively are also shown, together with the resonant autoionization process involving the $2\sigma_u \rightarrow 1\pi_g$ transition.

For the $1\pi_g$ shape resonance a clear regular energy shift is observed going from X-ray absorption where the resonance is 5.4 ± 0.2 eV below threshold to electron scattering where it occurs ~ 2.0 eV above threshold. This increase reflects the increasing Coulombic repulsion of the electron. Similar trends for the shape resonances have been observed and discussed for N_2 and CO_2 [9,10]. Fig. 4 explains what is meant by the term discrete shape resonance [24], where the transition reaches an orbital, that lies below the corresponding threshold for photoemission. In this respect $1\pi_g$ forms a discrete shape resonance in x-ray absorption. In photoemission from the valence shell it becomes only detectable via the autoionization process.

Furthermore, inspection of Fig. 4 suggests, that the hitherto unassigned $1\pi_u \rightarrow 1\pi_g$ ($\pi \rightarrow \pi^*$) valence transition (discrete shape resonance) can be expected about 2 - 3 eV below threshold. A plausible candidate for this transition would be the $\tilde{D}$-band at $h\nu = 9.2$ eV [23]. This assignment is supported by the absorption spectrum of the solid and the matrix isolated species, which both show a braod absorption band in this region. The higher lying resonances are not well characterized for acetylene and the assignment in Fig. 4 for the $3\sigma_u$ and the $4\sigma_g$ resonances is entirely based on a comparison with theory [4].

In summary we have determined the partial cross sections for photoemission out of the valence orbitals of solid acetylene. The $1\pi_u$ cross section shows a broad and strong autoionizing resonance which is due to the $2\sigma_u \rightarrow 1\pi_g$ discrete shape resonance/valence transition. This behaviour is similar to the gas phase. Our results make it very probably, that only one valence transition is responsible for the observed structure, because non-valence transitions are expected to be only weak in the solid phase.

The energy of the $1\pi_g$ virtual orbital shows a regular shift in going from x-ray absorption via valence band photoemission to electron scattering.

Acknowledgement

We thank H.-J. Lau for his help during the experiments.

Initial Orbital	Solid (this work)			Gas Ref. [16,19]		Shift	
	IP_{vert} [eV]	FWHM [eV]	IP_{ad} [eV]	IP_{vert} [eV]	IP_{ad} [eV]	IP_{vert} [eV]	IP_{ad} [eV]
$1\pi_u$	11.04	1.16	9.7	11.49	11.40	0.45	1.7
$3\sigma_g$	16.24	1.32	14.7	16.7	16.36	0.5	1.7
$2\sigma_u$	17.99	1.61	16.1	18.7	18.38	0.7	2.3
$2\sigma_g$	22.83	1.14	21.5	23.5	-	0.7	-

Table 1: Vertical (IP_{vert}) and adiabatic (IP_{ad}) ionisation potentials, full width half maximum (FWHM) and energy shift between gas and solid acetylene. For the solid phase the adiabatic ionisation potential has been determined according to the formula

$IP_{ad} = IP_{vert} - (1.2 \times FWHM)$

Experiment	Initial orbital	Solid (this paper)		Gas (a) (b)		Assignment
		$h\nu$	E_{kin}	$h\nu$	E_{kin}	
X-ray absorption	$1\sigma_u$	-	-	285,8$\pm$0.2	-5.4$\pm$0.2	$1\sigma_u \rightarrow 1\pi_g$
				288.1 to 295	-3.0 to +3.9	$1\sigma_u \rightarrow 4\sigma_g$ (c)
	$1\sigma_g$	-	-	309	18	$1\sigma_g \rightarrow 3\sigma_u$ (c)
Valence shell photoemission	$1\pi_u$	13.5	2.5	13.3	1.8	mainly $1\pi_u \rightarrow \varepsilon\delta_g$ and autoionisation of $2\sigma_u \rightarrow 1\pi_g$
		16.0	5.0	15.3	3.8	
	$3\sigma_g$	~19.0	~2.8	~ 18.0	~1.3	$3\sigma_g \rightarrow 3\sigma_u$ (c)
	$2\sigma_u$	16.0	-2.0	15.3	-3.4	$2\sigma_u \rightarrow 1\pi_g$
Electron scattering(d)	continuum	-	-	-	1.8 to 2.6	continuum $\rightarrow 1\pi_g$

Table 2: Experimentally determined final state resonances in the cross sections of acetylene. All energies are referred to the vacuum level, $E_{vac} = 0$, where the minus sign indicates that the resonances occur in the discrete part of the spectrum.

(a) Ref. [4,11-13]
(b) Ref. [3,22]
(c) This assigment, based on the calculation of Ref. [4] is only tentative , see text.
(d) Ref. [14,15]

References

1. J.L. Dehmer, D. Dill and A.C. Parr, in: Photophysics and Photochemistry in the VUV, ed.: S. McGlynn, G. Findley and R. Huebner, Reidel Publ. Comp., Dordrecht, 1983
2. R. Unwin, I. Khan, N.V. Richardson, A.M. Bradshaw, L.S. Cederbaum and W. Domcke, Chem. Phys. Letters 77, 242 (1981)
3. P.W. Langhoff, B.V. McKoy, R. Unwin and A.M. Bradshaw, Chem. Phys. Letters 83, 270 (1981)
4. L.E. Machado, E.P. Leal, G. Csanak, B.V. McKoy and P.W. Langhoff, J. Electr. Spectrosc. Relat. Phenom. 25, 1 (1982)
5. J. Kreile, A. Schweig and W. Thiel, Chem. Phys. Letters 79, 547 (1981)
6. A.C. Parr, D.L. Ederer, J.B. West, D.M.P. Holland and J.L. Dehmer, J. Chem. Phys. 76, 4349 (1982)
7. P.R. Keller, D. Mehaffy, J.W. Taylor, F.A. Grimm and T.A. Carlson, J. Electr. Spectrosc. Relat. Phenom. 27, 223 (1982)
8. Z.H. Levine and P. Soven, Phys. Rev. Letters 50, 2074 (1983)
9. H.J. Lau, J.H. Fock and E.E. Koch, Chem. Phys. Letters 89, 281 (1982) and J.-H. Fock, Dissertation, Universität Hamburg, 1983
10. J.H. Fock, H.J. Lau and E.E. Koch, Chem. Phys., in press
11. W. Eberhardt, R.-P. Haelbich, M. Iwan, E.E. Koch and C. Kunz, Chem. Phys. Letters 40, 180 (1976)
12. A.P. Hitchcock and C.E. Brion, J. Electr. Spectrosc. Relat. Phenom. 10, 317 (1977)
13. M. Tronc, G.C. King and F.H. Read, J. Phys. B12, 137 (1979)
14. K.D. Jordan and P.D. Burrow, Acc. Chem. Res. 11, 341 (1978)

15. E.H. van Veen and F.L. Plantenga, Chem. Phys. Lett. 38, 493 (1976)

16. D.W. Turner, C. Baker, A.D. Baker and C.R. Brundle, Molecular Photoelectron Spectroscopy, Wiley Interscience, New York 1970

17. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules, Japan Scientific Societies Press, Tokyo, 1981

18. R.G. Cavell and D.A. Allison, J Chem. Phys. 69, 159 (1978)

19. G. Bieri and L. Åsbrink, J. Electr. Spectrosc. Relat. Phenom. 20, 149 (1980)

20. A.M. Bradshaw, W. Eberhardt, H.J. Levinson, W. Domcke and L.S. Cederbaum, Chem. Phys. Lett 70, 36 (1980)

21. J.E. Demuth and D.E. Eastman, Phys. Rev. Letters 32, 1123 (1974)

22. T. Hayaishi, S. Iwata, M. Sasanuma, E. Ishiguro, Y. Morioka, Y. Iida and M. Nakamura, J. Phys. B 15, 79 (1982)

23. L. Åsbrink, C. Friedh and E. Lindholm, Chem. Phys. 27, 159 (1978)

24. J L. Dehmer and D. Dill, J. Chem. Phys. 65, 5327 (1976)

Figure Captions

Fig. 1 Comparison of the gas phase photoelectron spectrum (from Ref. [17,18], upper panel) with a photoelectron energy distribution curve for solid acetylene (this work, lower panel). The deconvolution of the EDC for solid acetylene into four bands is also shown. Crosses mark the measured EDC while the solid line gives the sum of the individual bands.

Fig. 2 Photoelectron energy distribution curves for polycrystalline solid C_2H_2 for excitation energies ranging between 10 and 30 (38) eV. In this plot the same initial states follow inclined lines. The four valence bands are denoted by the one-electron MO-notation.

Fig. 3 Relative partial ionisation cross sections for the $1\pi_u$-derived, $3\sigma_g$-derived and $2\sigma_u$ derived valence bands of solid acetylene. The arrows mark the onset for photoemission from these bands.

Fig. 4 Schematic energy scheme for the electronic structure of acetylene. In the left column shape resonances observed in X-ray absorption are shown [4,11-13]. In the middle part the electronic band structure of gaseous and solid acetylene as derived from photoemission experiments is depicted. In the right part results from electron scattering on gas phase acetylene [14,15] are shown. In this picture energies are refered to the vacuum level ($E_{vac} = 0$) and negative energies denote discrete shape resonances below threshold or initial energies of occupied valence bands. The resonant autoionisation involving the $2\sigma_u \rightarrow 1\pi_g$ transition is also indicated.

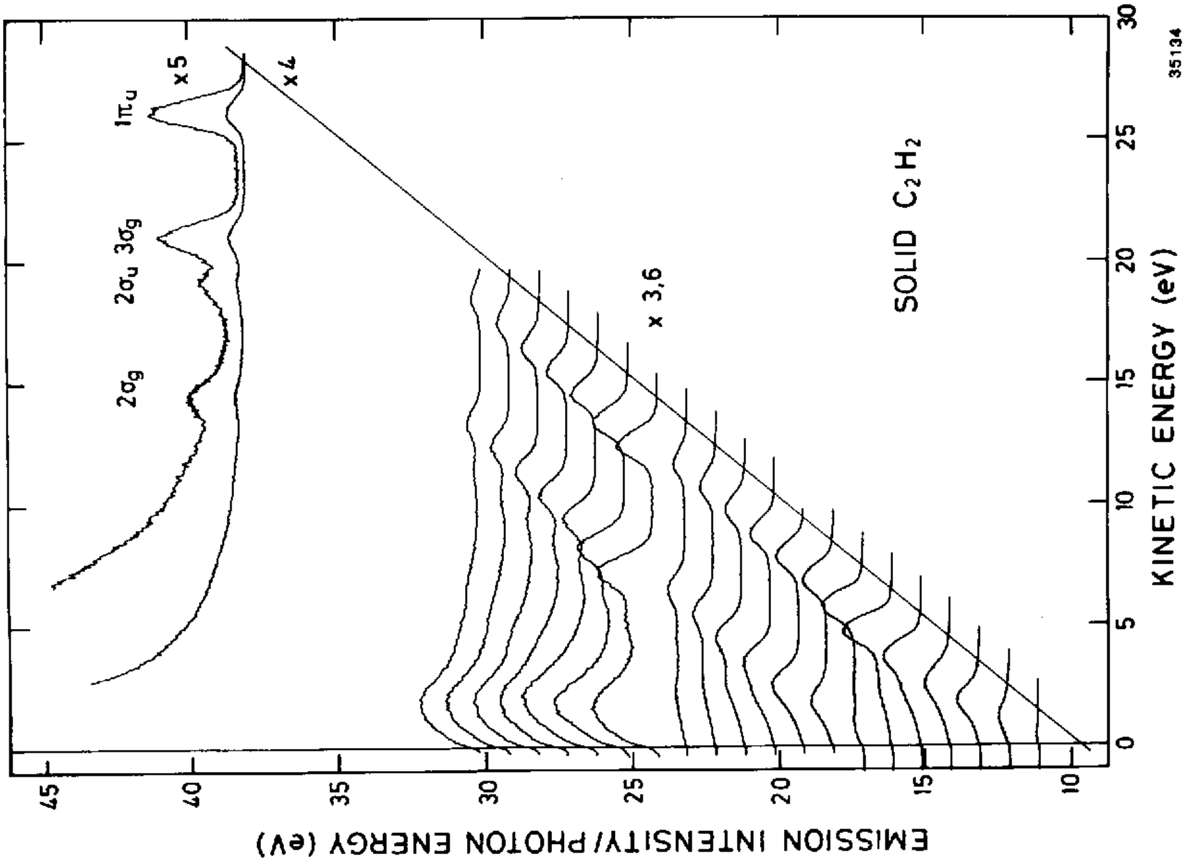
SOLID C_2H_2
$1\pi_u$
x 5
x 4
$2\sigma_u$ $3\sigma_g$
$2\sigma_g$
x 3,6
KINETIC ENERGY (eV)
0
5
10
15
20
25
30
EMISSION INTENSITY/PHOTON ENERGY (eV)
45
40
35
30
25
20
15
10
35134

Fig. 2

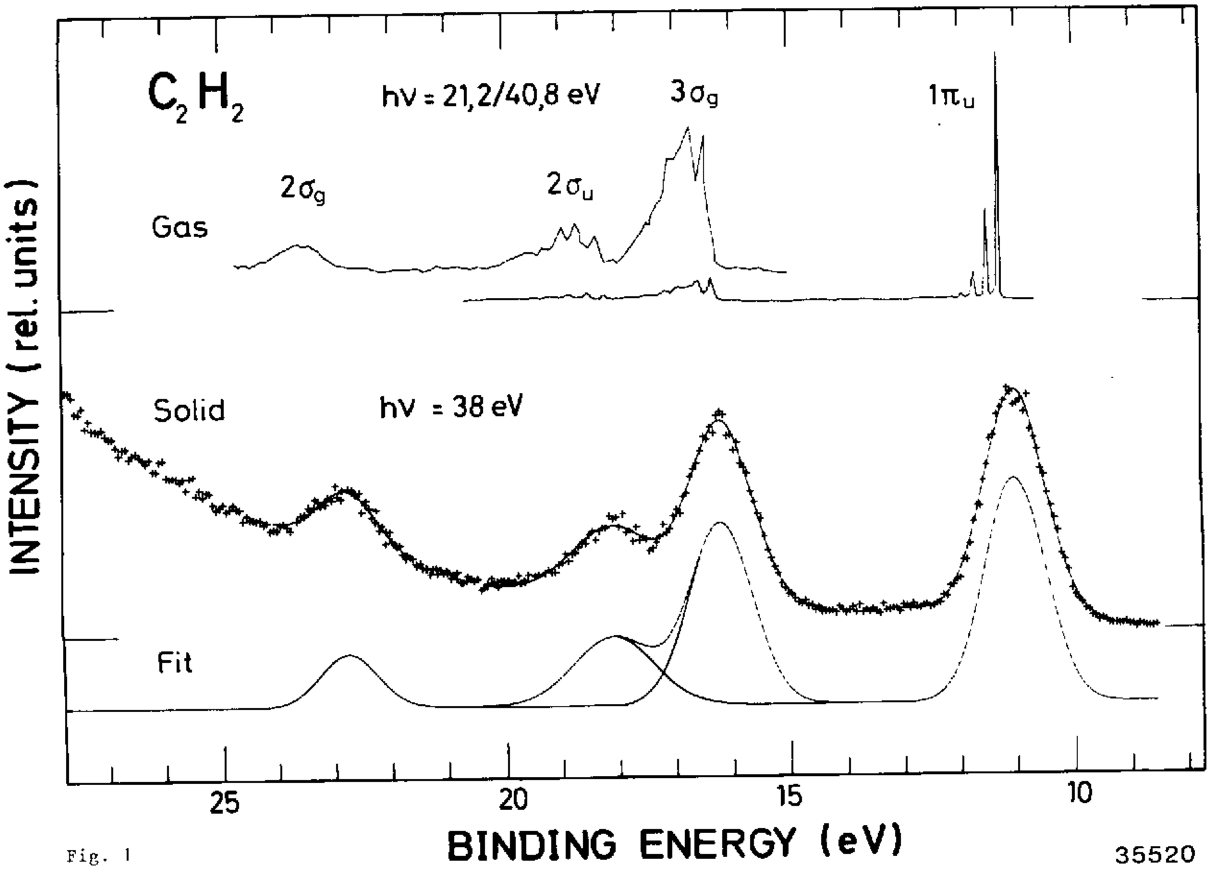
C_2H_2
hν = 21,2/40,8 eV
$3\sigma_g$
$1\pi_u$
$2\sigma_g$
$2\sigma_u$
Gas
Solid
hν = 38 eV
Fit
INTENSITY (rel. units)
25
20
15
10
BINDING ENERGY (eV)
35520

Fig. 1

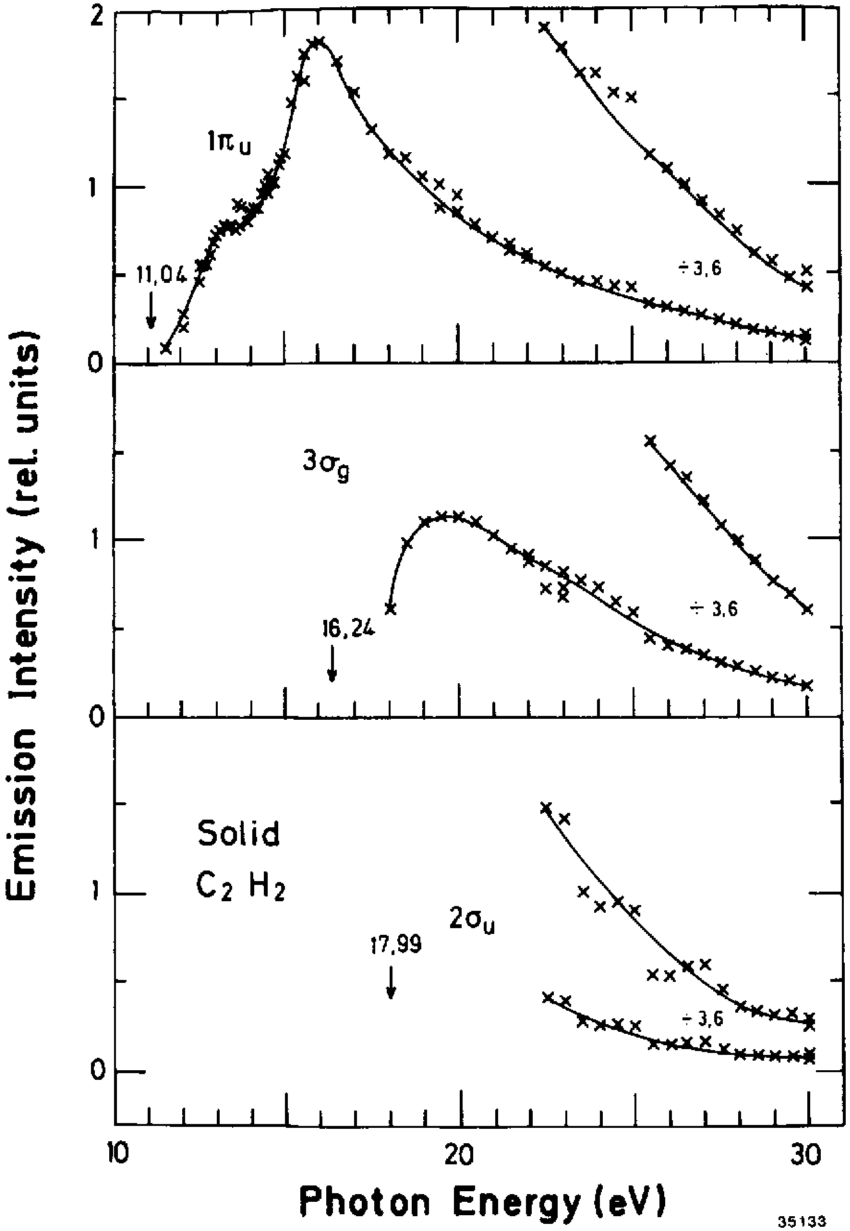
Emission Intensity (rel. units)
Photon Energy (eV)
10
20
30
0
1
2
1π_u
11,04
÷ 3,6
3σ_g
16,24
÷ 3,6
Solid
C₂ H₂
2σ_u
17,99
÷ 3,6
35133

Fig. 3

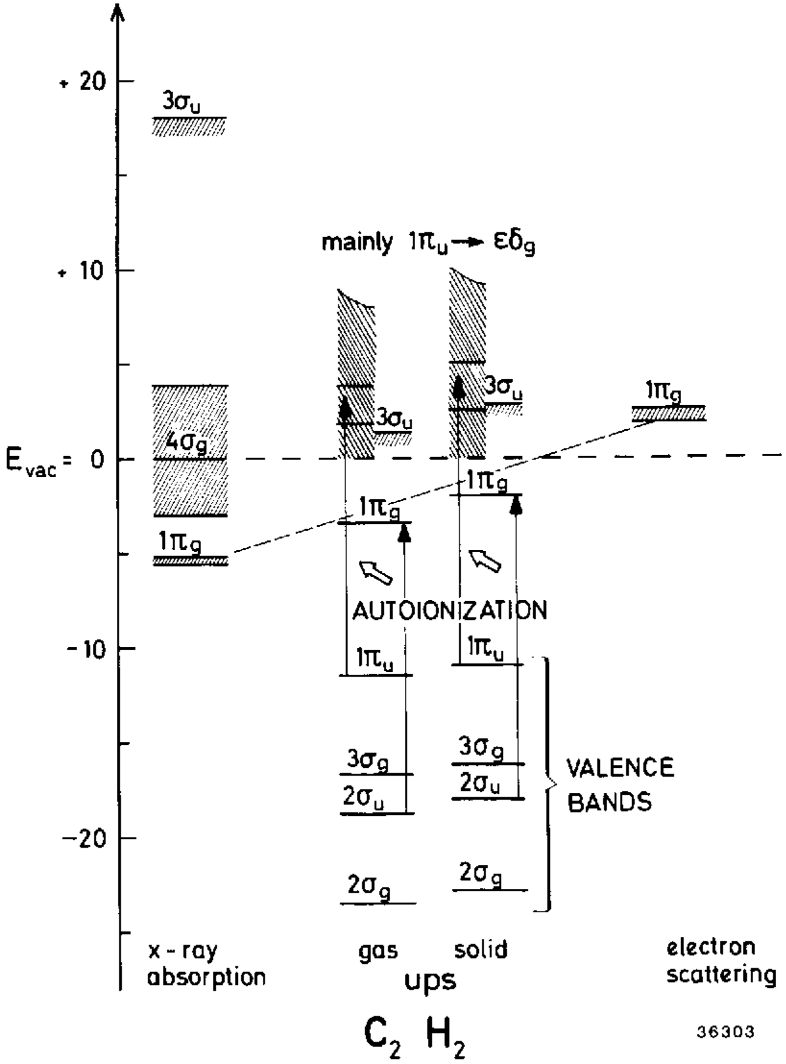
+ 20
+ 10
E_vac = 0
- 10
- 20
3σ_u
4σ_g
1π_g
mainly 1π_u → εδ_g
3σ_u
1π_g
3σ_u
1π_g
1π_g
AUTOIONIZATION
1π_u
1π_u
3σ_g
2σ_u
3σ_g
2σ_u
2σ_g
2σ_g
VALENCE BANDS
x - ray absorption
gas
solid
ups
electron scattering
C₂ H₂
36303

Fig. 4