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Optical Studies of Molecular Crystals in the Vacuum Ultraviolet Using Synchrotron Radiation

by

E. E. Koch
Sektion Physik der Universität München

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OPTICAL STUDIES OF MOLECULAR CRYSTALS IN THE VACUUM ULTRAVIOLET USING SYNCHROTRON RADIATION[†]

E.E. Koch

Sektion Physik der Universität München,
8 München 40

I. INTRODUCTION

Several experimental problems encountered in studies of the optical properties of gases and solids in the vacuum ultraviolet (VUV) and soft X-ray region were essentially overcome during the last few years. This was due to the development of new vacuum spectrometers, ultrahigh vacuum sample chambers, new detectors and improvements on light sources. The utilization of synchrotron radiation[1] as an intense, highly polarized continous light source was one of the major breakthroughs. Since 1953, when synchrotron radiation was used for the first time for optical experiments in the VUV by Hartman and Tomboulian[2], spectroscopic work using this unique light source has matured in many ways. The techniques and results obtained have been summarized in a number of review articles[3-9], which reflect the extend of recent activities as well as the various lines along which research is carried out at the different synchrotron radiation laboratories.

In the following, the emphasis will be placed on those experiments which have been performed during the last three years at the Deutsches Elektronen-Synchrotron DESY on molecular crystals in the excitonic region of the spectrum. Experimental results for molecular crystals formed by rare gases, atmospheric gases and simple hydrocarbon molecules will be discussed.

Since, in molecular crystals, the covalent bonding within the molecule is strong in comparison with the van der Waals binding between the molecules, electronic excitation lines of an individual molecule will appear in the optical results from the crystalline solid as excitons, often shifted but little in energy.

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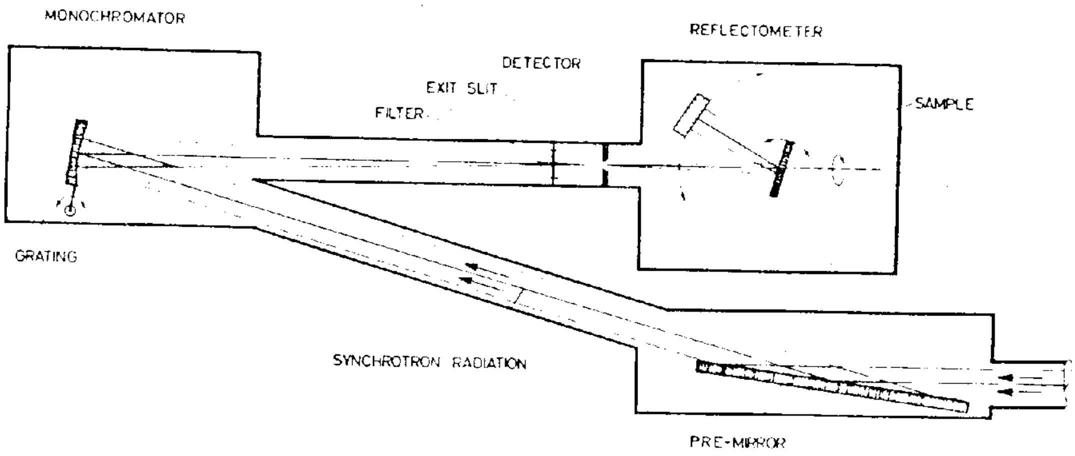

Fig. 1 Sketch of the experimental setup cut perpendicular to the synchrotron plane (Ref. 11)

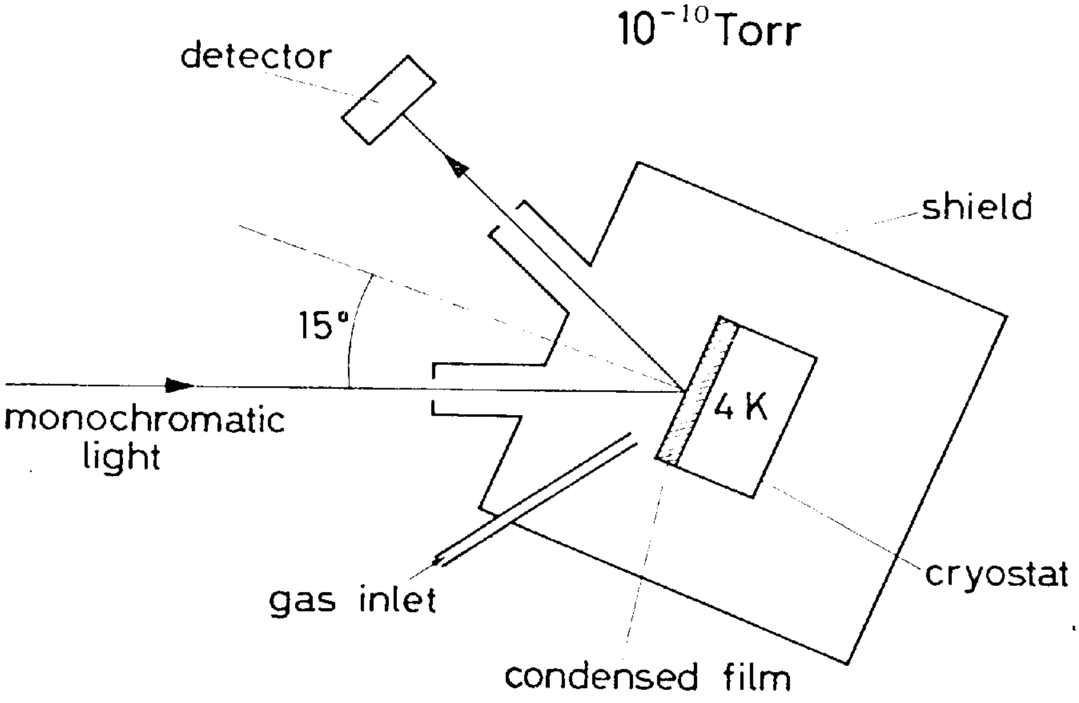

Fig. 2 Sketch of the reflection experiment on condensed films of molecular crystals (Ref. 27)

Comparison between results from the vapour and solid phase therefore gives valuable information about the properties of these excitons. In single crystals containing more than one molecule per unit cell the crystal field splitting (Davydov-splitting) and also the influence of longitudinal macroscopic fields can be studied. Only recently have studies of secondary processes such as fluorescence and photoemission using synchrotron radiation as the primary VUV-radiation source been undertaken.

II. EXPERIMENTAL ASPECTS

As the large oscillator strength of singlet excitons makes absorption measurements in the VUV for most molecular crystals impossible, investigation of them has to be done by reflection spectroscopy. Using synchrotron radiation, which makes it possible to cover a large range of frequencies, a fact important for subsequent Kramer-Kronig analysis, this technique has been shown to be a very useful tool. Figures 1 and 2 are sketches of the monochromator and experimental setup presently used for such studies at DESY. The reflectometer or cryostat and multiplier are mounted into an ultrahigh vacuum system attached to the exit slit of the monochromator with a vertical dispersion plane especially designed for use with synchrotron radiation[10,11]. The best resolution obtained with this instrument, which uses the size of the electron beam within the synchrotron as an entrance slit, is 0.5 Å. In future experiments, improved resolution will permit more accurate determinations of line shapes and vibrational structure. Further, experiments using internal modulation techniques such as thermoreflectance or electroreflectance are in preparation. Thus detailed information about exciton phonon coupling may be obtained. The high degree of polarization of the synchrotron light makes it an excellent source for spectroscopic measurements on anisotropic single crystals. Details of the evaluation of optical constants from reflection spectroscopy with polarized light on monoclinic crystals, which form the largest group of organic molecular crystals are given in Ref. 12.

The high intensity of synchrotron light in the VUV allows the study of secondary processes such as photoemission[13] and the fluorescence radiation from molecular crystals excited with primary VUV photons[14]. This promising field, the results from which will contribute to a better understanding of dynamical processes, e.g., exciton decay via various channels and energy transfer processes[15], will benefit from the availability of high current storage rings. Presently, at DESY, a photon flux behind the exit slit of a normal incidence monochromator (one grazing incidence reflection at the premirror, at 4.5 GeV, 30 mA)[16] of 3 x 10^9 Photons/Å sec is obtained at 600 Å $\hat{=}$ 20.66 eV. This photon flux will be increased by a factor of up to 100 when the high current

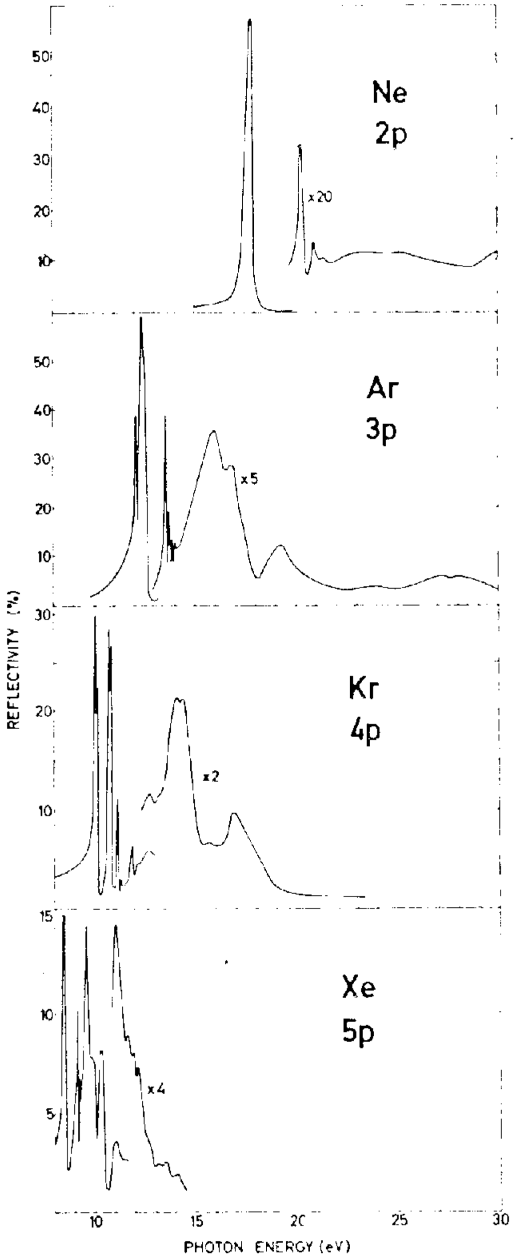

Fig. 3 Reflectance of solid Ne, Ar, Kr and Xe for an angle of incidence of 15° (Ref. 38)

storage ring DORIS, which is presently under construction will be in operation.

III. EXCITONIC EXCITATIONS IN SOLID RARE GASES

The absorption edge of solid rare gases, often considered to be the most simple molecular crystals, is characterized by a number of narrow lines followed by broader continuum-like structures at higher energies (Fig. 3). Comparison is made in Fig. 4 between the positions of resonance lines in the gas due to the excitation of those p-electrons forming the filled outer shells of the rare gas atoms, with the maxima in ε_2, the imaginary part of the dielectric function, for the solid. The latter was deduced via Kramers-Kronig analysis from the reflectance data$^{17-19,38}$. Such an analysis is also necessary for a discussion of the line shapes. The excitation of roughness induced surface plasma waves may influence the high reflectivity of a sample in the reflectance band severely causing a dip or shoulder. The interpretation of these lines in the case of

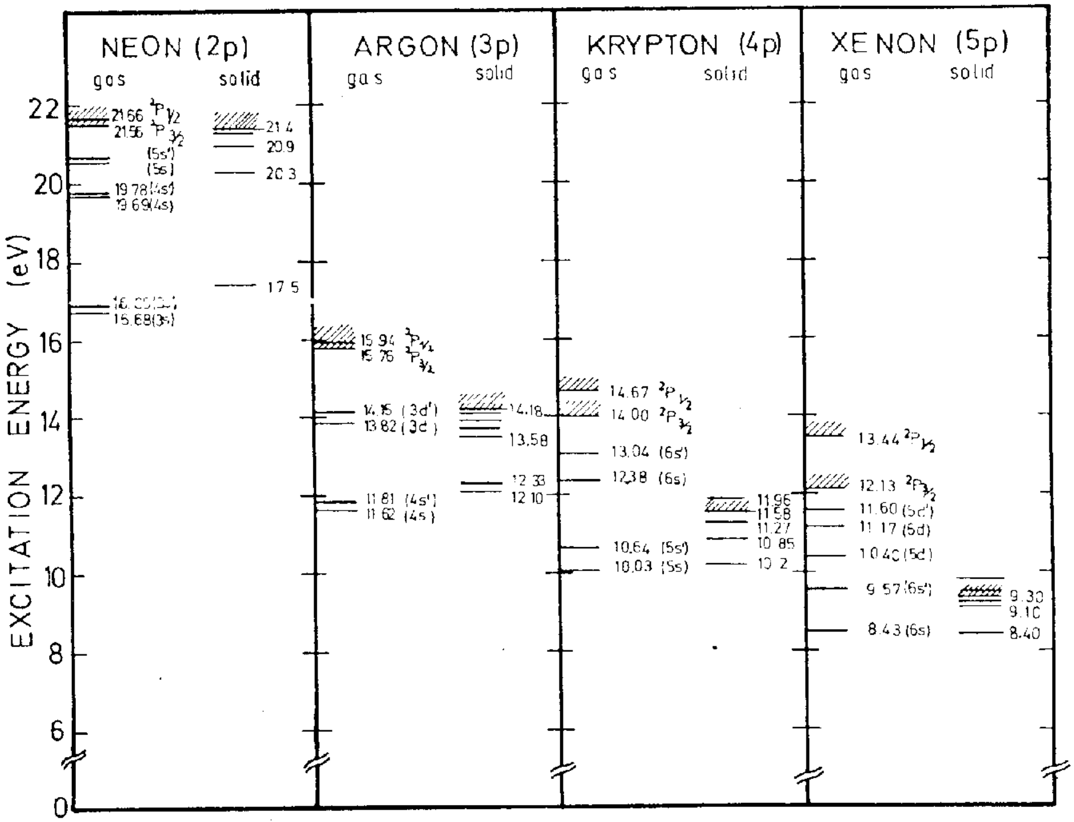

Fig. 4 Excitation energies of rare gas atoms and solids for the onset of outer p-shell electron transitions

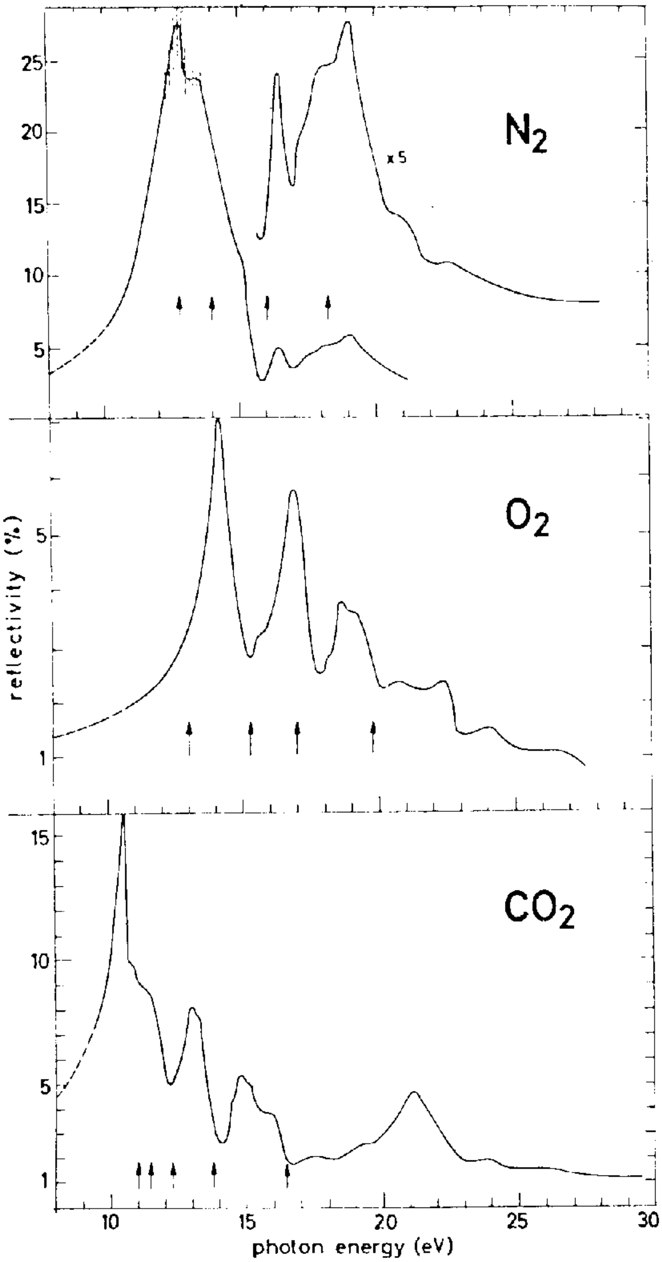

Fig. 5 Reflectance of solid N_2, O_2 and CO_2 at an angle of incidence of 15°. Arrows indicate the positions of the main absorption bands in the gaseous phase. (Ref. 38)

argon, krypton, and xenon in terms of Wannier excitons by Baldini[20] has been subsequently refined. For instance, in a recent analysis by Rössler and Schütz[21], in which the electron hole interaction was considered as a perturbation of the one-electron band model, the calculated binding energies, oscillator strengths and relative hydrogenic defects compare favorably with data deduced from experiment. Photoemission yield spectra from solid argon, krypton, and xenon[13] in the whole range of p-valence shell electron excitation show weak emission below the band gap caused by the decay of excitons. This range is followed by a steep increase of the photoemission yield to ∿ 0.5 electrons per incidence photon.

For a recent discussion of the interband transitions as well as the inner shell excitations in solid rare gases[22] and solid rare gas mixtures[23], see, for instance, the paper by Kunz and Mickish[24].

IV. ATMOSPHERIC MOLECULES

Discrete structure in the absorption continua of N_2 and O_2 was found several years ago by Codling and Madden[25] using synchrotron radiation. In contrast to the gaseous phase only broad bands are generally observed in the reflection spectra of solid N_2, O_2[26] and CO_2[27] (Fig. 5) in the range 10 to 30 eV. There is no obvious correlation between the bands in the solid and the gas and in order to establish a rough correlation, a considerable chemical shift due to the crystal potential has to be assumed. There is one surprising exception in solid N_2, where one observes a progression of sharp reflectance bands in the solid at about 13 eV (Fig. 6). For this $b^1\Pi_u$ transition, 14 bands with a vibrational spacing of 0.1 eV are observed. Compared to the gas, they are no longer perturbed by Rydberg bands[28]. The solid bars in Fig. 6 indicate the positions and strengths of the corresponding bands in the gaseous phase[29]. The vibrational structure is more regular in the solid as regards the spacing as well as the intensity distribution. No such sharp vibrational structure could be observed in solid O_2 and CO_2. Since these molecular crystals are more complicated than the solid rare gases, comparatively little theoretical work has been done in order to understand their electronic properties.

V. ORGANIC MOLECULAR CRYSTALS

In the photon energy range from 5 to 35 eV, the excitations of all but the C 1s-core electrons of organic materials can be studied. An example of a homolog series of molecules are the n-alkanes[10], which are pure σ-electron systems. The first pronounced reflectance maxima for solid methane and ethane (Fig. 7) are not much shifted from the absorption maxima for the gas phase[30].

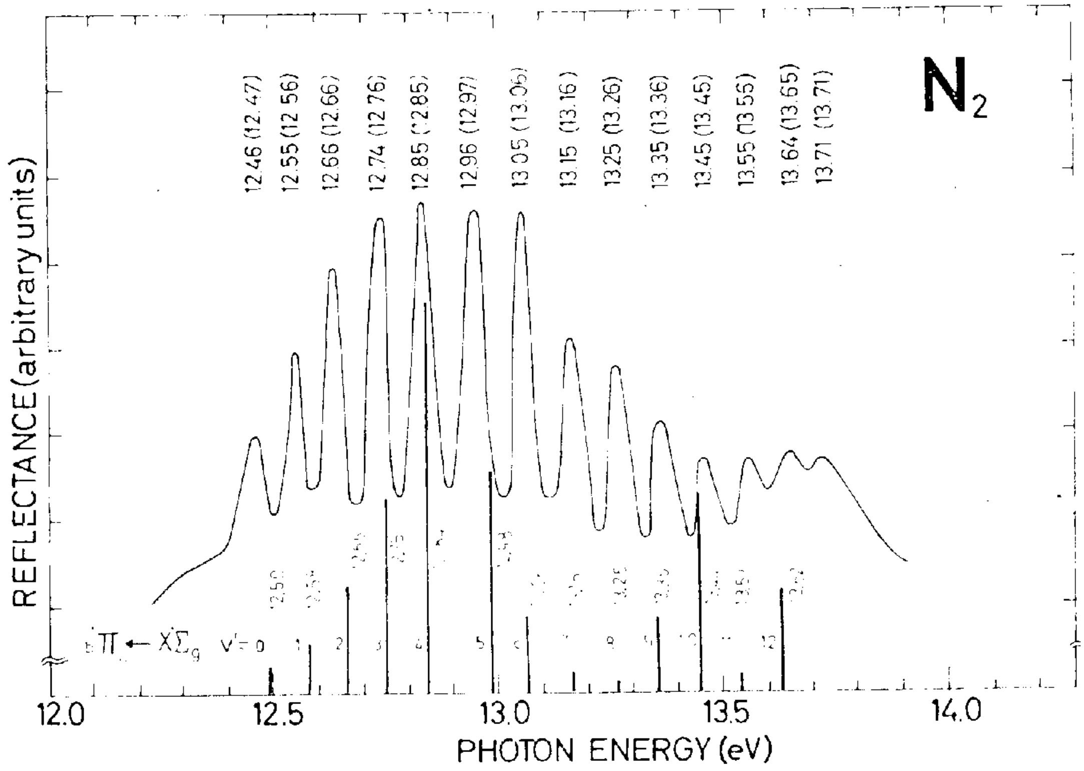

Fig. 6 Reflectance of solid N_2 at 10° K for an angle of incidence of 15°, showing the $b^1\Pi_u$ vibrational levels. The values given by Buxton and Duley[28] are added in brackets. Position and strengths of vapour bands[29] are indicated as vertical bars. (Ref. 26)

For solid ethane, the vibrational levels observed in the vapour are smeared out. The fact that, also at higher energies, the main solid reflectance maxima coincide with the principal absorption peaks, indicates that the electronic structure of these molecules is not much influenced by the solid environment.

For solid ethylene and benzene[11], the fine structure due to Rydberg series[31] has disappeared in the solid. These extravalence excitations are significantly distorted by scattering processes involving the neighbouring molecules. Recent photoyield measurements on solid benzene show an onset of the yield at about 8.70 eV[32]. This shift of 0.55 eV from the first ionization potential in the vapour at 9.25 eV, is nearly the same as the gas to solid shift for the $^1E_{1u}$ band (6.69 eV to 6.26 eV).

An assignment of absorption bands of the anthracene molecule[33] has been obtained using information from studies of the anisotropic reflectance from single crystals[34]. The optical con-

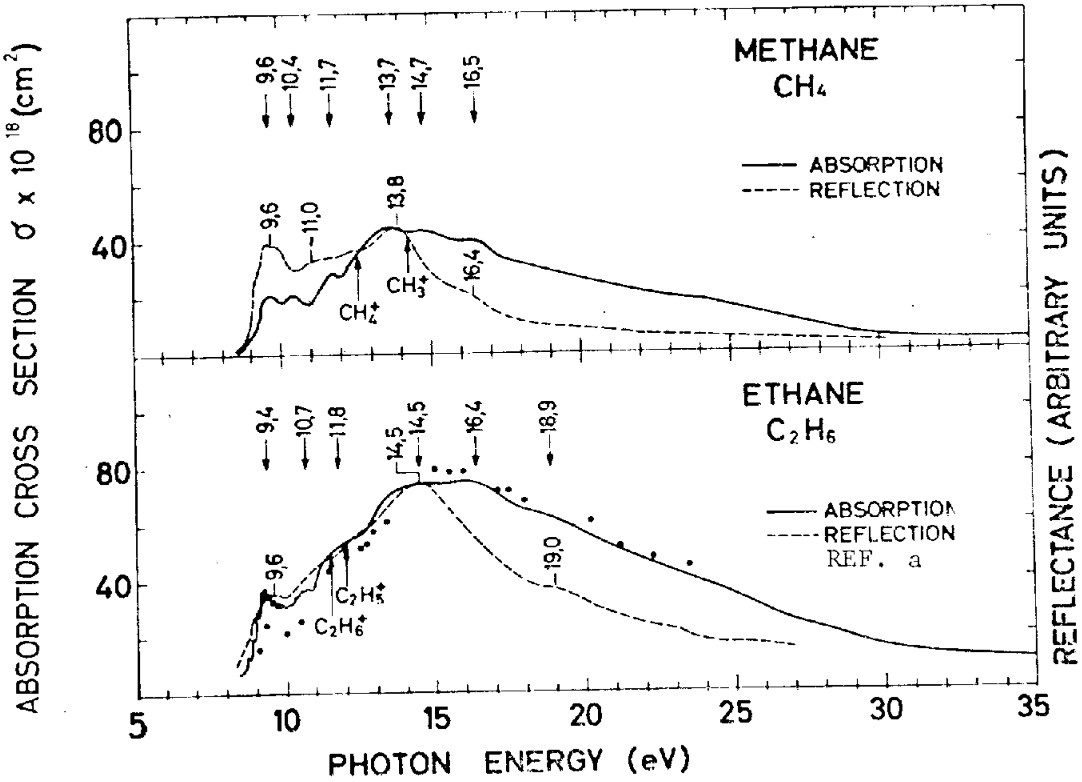

Fig. 7 Absolute absorption cross sections for methane and ethane (solid line) and reflectance for solid films of methane and ethane. Ref. a: R.J. Schoen, J.Chem.Phys. 37, 2032 (1962) (Ref. 10)

stants in the photon energy range between 4 and 10.5 eV could be derived from the reflectance over a large range of frequencies for the most important directions of polarization ($\underline{E} \parallel \underline{b}$ on (001) and $\underline{E} \parallel \underline{L}$ $\underline{E} \perp \underline{L}$ on the (010) plane) (Fig. 8, see next page). In particular, the influence of longitudinal fields on the exciton bands was studied experimentally by means of non normal incidence reflection and theoretically from the point of view of experimentally obtained frequency dependent dielectric functions[35]. The results obtained are in good quantitative agreement with recent theoretical results based on the microscopic theory of exciton bands in molecular crystals[36-37].

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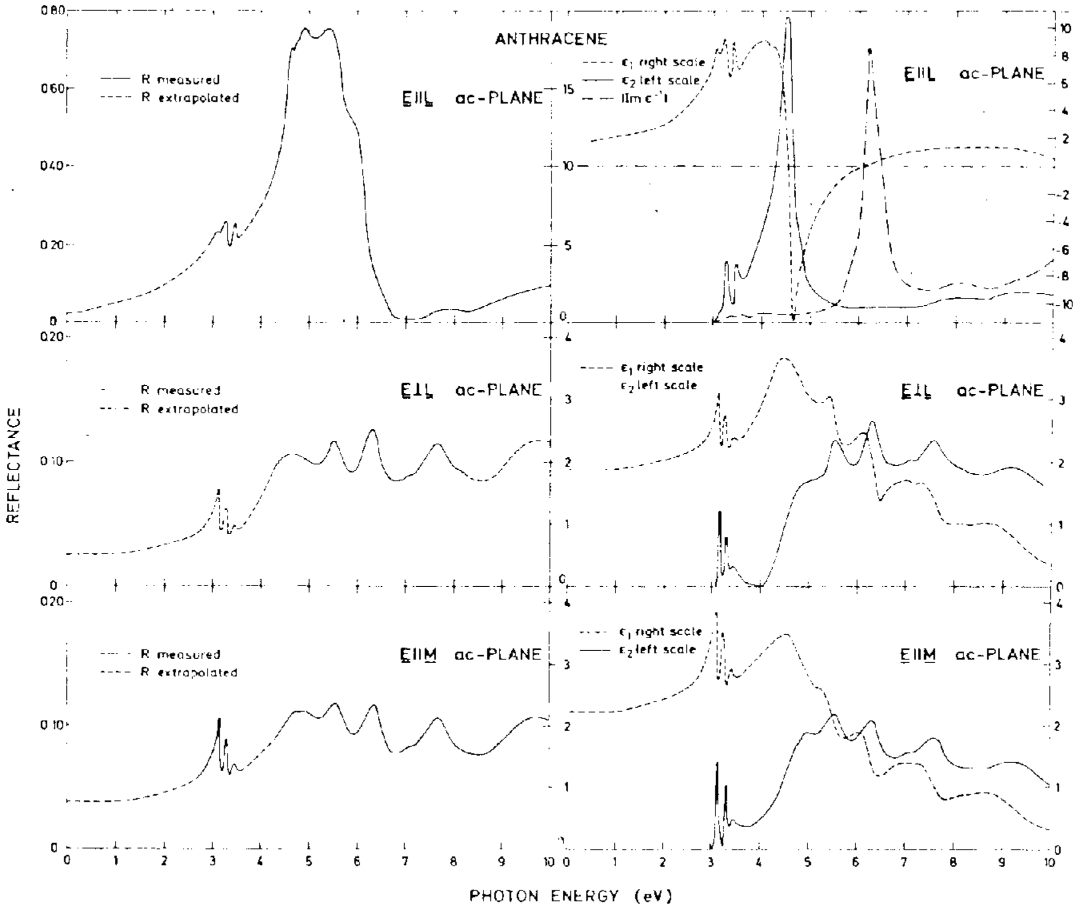

Fig. 8 Reflectance of anthracene single crystals for s-polarized light at near normal incidence (7.5°) from the (010)-plane for E ∥ L and E ⊥ L and E ∥ M and dielectric functions deduced from it. (Ref. 35)

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