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Optical Absorption of Gaseous Methane, Ethane, Propane and Butane
and Reflection of Solid Methane and Ethane in the Vacuum Ultraviolet[†]

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The absorption spectra of gaseous n-alkanes have been investigated for photon energies from 8 to 35 eV where excitations of the σ electrons are expected to occur. For methane and ethane the spectra are compared to reflectance measurements on solid films. A new monochromator designed for work with synchrotron radiation and a windowless absorption cell made it possible to resolve considerable new structure.

[†] Supported by the Deutsches Elektronen-Synchrotron

Introduction

Detailed spectroscopic work on hydrocarbons in the far vacuum ultraviolet, where transitions of the tightly bound σ electrons are expected to occur, has not been performed as yet. On the other hand there is much current interest in developing quantitative theories for the electronic structure of these systems (1). The n-alkanes are of special interest because transitions of the σ -electrons are not masked in these completely saturated hydrocarbons by transitions of delocalized π -electrons. Their spectra have been extensively studied during the last years for photon energies below 11 eV (2,3) and were discussed in terms of N-V transitions of the σ -electrons (4).

All these measurements on n-alkanes indicated a steep increase of the absorption cross section towards higher energies, and in fact Ditchburn (5) and Metzger and Cook (6) (for the case of methane) and Schoen (7) (for the other n-alkanes) found maxima of the absorption cross section around 16 eV. However, because of light source problems (with exception of Ref. (6) only line sources had been used) these investigations of the spectra above 10 eV remained imperfect, and any detailed structure would not have been detected. For the solidified gases optical measurements are reported only up to 11 eV (8). Therefore we have reinvestigated the absorption spectra of the n-alkanes and have for comparison measured the reflectance of the solid phase using the continuous spectrum of the 7.5 GeV electron synchrotron DESY as a light source (9).

Experimental

The absorption experiments were performed with a monochromator which was newly constructed for use with synchrotron radiation (Fig. 1). Light emitted

tangentially from the electron orbit passes through a beam pipe over a distance of about 40 m towards the monochromator. On this way the light is reflected at half the distance (20 m) upwards by a plane mirror (angle of incidence is 83°). Its plane of incidence is lying perpendicular to the synchrotron plane.

The monochromator is operating in a modified Wadsworth mounting similar to the instrument previously described (10). The monochromatic beam emerges from the exit slit horizontally; the angle α between entrance and exit arm is fixed to 14° . In contrast to the older mounting advantage is taken of a dispersion plane perpendicular to the synchrotron plane. Since the vertical extension of the electron beam in the synchrotron is smaller (~ 2 mm) than the horizontal extension (~ 10 mm), the resolution in the vertical Wadsworth mounting is improved. Since furthermore the plane of incidence of the premirror as well as that of the grating are perpendicular to the synchrotron plane this arrangement produces an even higher degree of polarization (11).

A 2400 lines/mm Bausch & Lomb grating blazed at 300 \AA with a concave radius of 1999.5 mm was used, yielding a linear dispersion of $4 \text{ \AA}/\text{mm}$. The spectral resolution of the monochromator using a slitwidth of 250μ was about 1 \AA over the whole spectral range up to 45 eV. The energy calibration was checked to be accurate within $\pm 1.5 \text{ \AA}$, i.e. to about 0.01 eV at 10 eV.

The windowless absorption chamber of 40 cm length is separated from the monochromator by a differential pumping system. The gas pressure in the

absorption chamber (for these measurements in the range from 0.005 to 0.02 Torr) is measured by a precision membrane-vacuummeter (Datametrix Model 1014). Under these conditions the pressure in the monochromator stayed at a few 10^{-4} Torr while in the beam pipe the pressure remained in the 10^{-6} Torr range. The influence of this residual gas was estimated and taken into account when the absolute cross sections were calculated. The light traversing the sample chamber hits a sodium salicylate screen deposited on a glass window and is converted into longer wavelength photons which are measured by a photomultiplier (EMI 9502 B). The gases were obtained from L'Air Liquide. Their purity was 99.995 % for methane and 99.95 % for the other gases. The absolute cross sections given with our results are not corrected for possible fluorescence of the samples or for straylight. The estimated error is of the order of ± 20 %. The technique used in the reflectance measurements was essentially the same as in our measurements of solid rare gases (12). The films were deposited at temperatures below 30° K on different alkali halide single crystals which served as substrates. The light reflected from the samples at an angle of incidence of 15° was detected with an open photomultiplier (Bendix model 306). In the case of methane the films were evaporated at different temperatures of the substrate; some films were annealed. However, the overall spectral distribution remained unchanged, although the absolute value of the reflectance changed markedly. As no absolute calibration of the reflectance was made during the measurements, the reflectance is presented in arbitrary units.

Results and Discussion

Our results are summarized in Figure 2. Here the absolute absorption cross section for the four molecules is given in an energy range from 8 to 35 eV. The arrows on top of each spectrum give the energy positions of the main

peaks of absorption. For methane and ethane the reflection spectra for the solidified gases are also shown together with the energy positions of the reflectance maxima. Measurements of the cross section by Schoen (7) are included for ethane, propane and butane. With the exception of ethane the spectra do not show any sharp structure. The spectral range below 11 eV is well known from other experiments. We remark, however, that the maxima seem to be more pronounced in our measurements as compared to those reported in the literature, probably due to the improved experimental conditions. From methane to butane the centers of the first two bands shift systematically to lower energies. For ethane the energy positions of the vibrational levels of these two bands are in excellent agreement with those measured by Lombos et al. (2). For ν_1 to ν_{11} we find 8.68, 8.81, 8.95, 9.10, 9.23, 9.38, 9.53, 9.69, 9.83, 9.97 and 10.12 eV respectively. A second though less clearly developed vibrational structure is found at 10.50, 10.63, 10.78, 10.93, 11.08, 11.26 and 11.38 eV. (The scale of Fig. 2 prevents a clear presentation of these transitions.)

For all alkanes the first two bands are followed by a large increase of the absorption cross section. This increase up to approximately 15 eV is not entirely structureless, as was concluded from measurements with line sources. Quite pronounced peaks and/or shoulders appear, such as the peak at 11.7 in methane or the two peaks at 12.7 and 14.2 eV in the propane spectrum. At least three broad bands between 13 and 16 eV contribute to the pronounced absorption. The cross sections then decrease smoothly to higher energies. Further marked structure is not expected to occur before the onset of transitions from the K shell of carbon at approximately 290 eV (13).

The absolute values of the cross section for the pronounced absorption between 13 and 16 eV increase nearly linearly (43 Mb, 75 Mb, 95 Mb, 125 Mb for methane to butane respectively) and more rapidly than the absorption cross section of the first peak (18 Mb, 35 Mb, 45 Mb, 60 Mb).

The first pronounced reflectance maxima for solid methane (9.6 eV) and ethane (9.6 eV) are not much shifted as compared to the gas phase. They seem to have the same origin and may be attributed to the same transition (${}^1F_2 \leftarrow {}^1A_1$) and (${}^1F_u \leftarrow {}^1A_{1g}$) as in the gas phase (2, 4). For ethane the vibrational levels influenced by the solid environment have disappeared. On the slope to higher energies some not too well marked structure is superimposed for both substances. Again, as in the lower energy part, the reflectance maxima coincide with the main absorption peak. Above the maximum the reflectance drops markedly. There are slight shoulders at 16.4 and 19.0 eV for methane and ethane respectively and no further structure is observed up to the limit of the experiment.

We have inserted into Fig. 1 the onset of photoionisation and photodissociation (14, 15). The fact that these processes for all molecules occur at lower energies than the main strong absorption suggests that these intense peaks are not entirely due to ionisation and dissociation. A definite interpretation has to wait until more experimental (mass-spectroscopic work) and theoretical work (calculations of the excited states at higher energies) is at hand.

Acknowledgment

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Figure captions

Fig. 1 Sketch of the monochromator with absorption cell cut perpendicular to the synchrotron plane
(TMP turbo molecular pump, DP diffusion pump, VP fore pump, V valve, DV needle valve, RV reduction valve, TV gate valve, SR beam pipe, SY synchrotron radiation, SB apertures, G grating, DA excentric pivot, WLT wavelength drive, Fi filter, AS exit slit, A absorption cell, S ample, M_1 , M_2 pressure gauges, LS sodium salycilat screen, F window, PM photomultiplier)

Fig. 2 Absolute absorption cross sections for methane, ethane, propane and butane (solid line), and reflectance for solid films of methane and ethane (dashed line). Values from Ref. (7) are dotted. Positions of the main structures are indicated by arrows on top of each curve. First ionisation and dissociation thresholds from Ref. (15, 16) are marked by arrows below each curve.

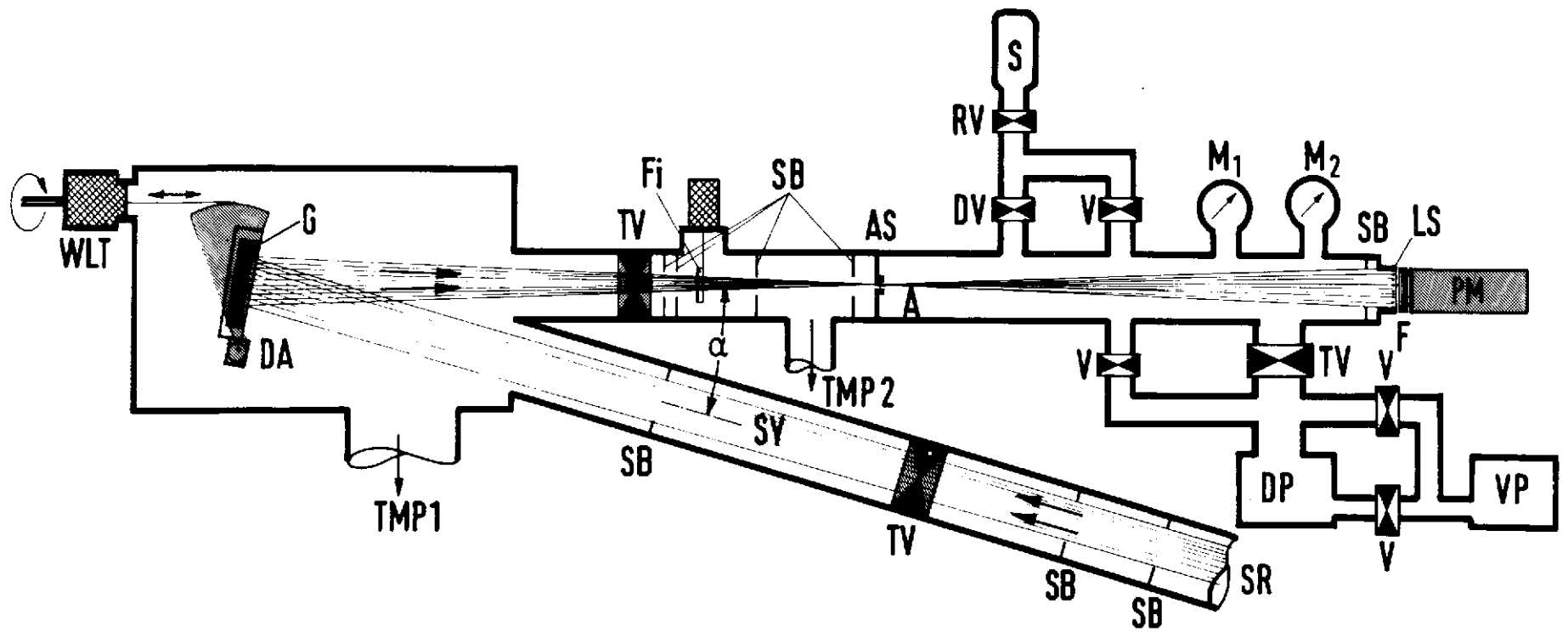


Fig. 1

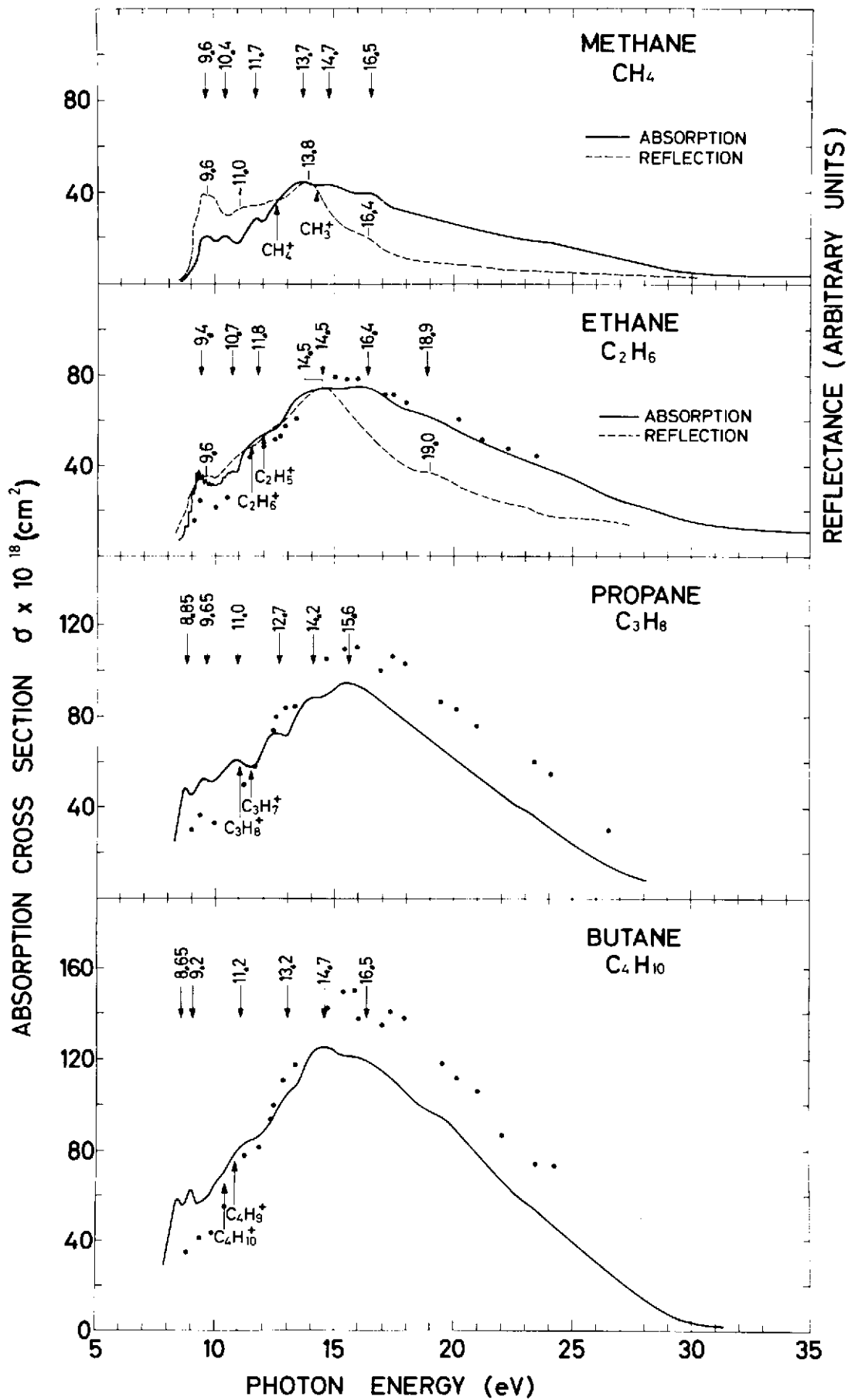


Fig.2

