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for Photon Energies from 5 eV to 30 eV

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The Vacuum Ultraviolet Spectrum of Naphthalen Vapour  
for Photon Energies from 5 eV to 30 eV<sup>†</sup>

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*The absorption spectrum of naphthalene vapour has been photo-electrically recorded within the photon energy range from 5 eV to 30 eV using synchrotron radiation. In addition to known  $\pi-\pi^*$  absorption bands at lower energies Rydberg series to the first and higher ionization limits are found and tentatively assigned. They partially overlap and are superimposed to broader bands which seem to be valence shell transitions originating from lower  $\pi$ - or  $\sigma$ - orbitals. The orbital nature of the excited states is discussed and tentative assignments are given.*

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The absorption spectrum of the naphthalene molecule has been experimentally studied in the visible and near ultraviolet region by George and Morris up to 6.5 eV (1) and by Angus, Christ and Morris between 6.5 and 8.3 eV (2). The range from 6.8 to 8.2 eV has recently been reinvestigated by Scheps, Florida and Rice (3). From a theoretical point of view these new experiments have been stimulated by the interest in interference phenomena between energetically degenerate excited states e.g. Rydberg states and quasi continuous  $\pi-\pi^*$  bands. In fact some of the peculiar absorption profiles observed in the naphthalene vapour spectrum at around 7.5 eV have been ascribed to antiresonances resulting from such interference effects (3,4,5). Additionally, recent progress in computational handling of many-electron-systems has renewed the interest in the electronic spectra of large hydrocarbon molecules, i.e. the excitations of  $\pi-$  as well as the more tightly bound  $\sigma$ -electrons. The results of molecular orbital calculations by Buenker and Peyerimhoff (6) and by Hofer and Hedges (7) for naphthalene, including all valence electrons, have recently become available.

A comparison with the experimentally determined absorption spectrum for the whole spectral range, where valence electron excitations are expected to occur, was not possible, since up to now only electron energy loss spectra (8) covered the whole spectral range of interest. These experiments were limited by a comparatively low resolution. It is, furthermore, a problem to obtain the absorption cross-section from the experimentally determined loss function in such experiments.

This letter reports on early results of our optical absorption measurements of naphthalene vapour in the VUV region for photon energies from 5 to 30 eV. Experimental details were given in previous publications (9,10). The intense

and continuous spectrum of the synchrotron radiation of the 7.5 GeV electron accelerator DESY was used as a light source. It allowed us to record the spectra photoelectrically. The maximum wavelength resolution was somewhat better than  $1 \text{ \AA}$  (corresponding to 0.01 eV at 10 eV). The absolute photon energies given with our results are correct within  $\pm 0.015$  eV. We additionally photographed some portions of the spectrum using a 2.2 m grazing incidence spectrograph (McPherson, model 247) in the range 4 to 9 eV with a slightly increased resolution.

Figure 1 gives a survey of the whole absorption spectrum. Above the strong  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  transition at 5.89 eV a band of medium intensity is observed with its center at about 7.7 eV. At higher energies a steep increase to a broad and intense continuum with a maximum at about 16 eV follows. The absorption cross-section then decreases towards higher energies. Several relatively sharp bands are superimposed on these main structure. For energies exceeding 12 eV there might still be some fine structure not displayed here. Because of the photoelectric recording together with the windowless absorption chamber possible fine structure in this range of high absorption is difficult to distinguish from noise arising from pressure fluctuations. Here we have reproduced an average spectrum based on several individual runs. The spectrum between 5 and 11 eV is shown on an expanded scale in Fig. 2.

For energies below 8.2 eV our results are in agreement with optical absorption data by George and Morris (1), Angus, Christ, and Morris (2) and Scheps, Florida, and Rice (3). With the exception of additional details displayed in the optical spectra the main features of the spectra are also in good agreement with the energy loss spectra of Ref. (8) and the energy

loss data obtained by Huebener, Mielczarek, and Kuyatt (11). As regards the electronic transitions the prominent bands at 5.9 and 7.7 eV are generally ascribed to  $\pi-\pi^*$  excitations. According to the extensive MO-calculations by Hummel and Ruedenberg (12) these transitions are polarized along the long molecular axis and are hence of the symmetry type  ${}^1B_{2u}$ . (The notation is in agreement with Ref. (13)). CNDO calculations performed by Hofer and Hedges (7) including all 48 valence electrons of the molecule yield further valence shell transitions at higher energies up to about 10 eV due to  $\sigma-\pi^*$  and  $\pi-\sigma^*$  excitations. However, it does not seem justified to assign observed bands at higher energies with these calculated transitions because there are quite large uncertainties in the theoretical calculations of transition energies and oscillator strength for such a large molecule. Furthermore, the calculations should be extended to even higher energies.

The observed fine structure of the spectrum is interpreted as being due to the excitation of Rydberg series which are accompanied by vibrational bands. Our interpretation, which in view of the complexity of the spectrum can only be tentative, is indicated in Fig. 2. To aid our assignment in this figure the ionization potentials (IP), as taken from the photoelectron spectra from Eland and Danby (14) and Turner, Baker, Baker, and Brundle (15), are given. The photoelectron spectra show three sharp bands for binding energies below 10.5 eV. Assuming that these first sharp maxima are due to the removal of  $\pi$ -electrons and that the calculated order of the MO occupied in the ground state (6) is correct, we make the following assignment for the IP: With increasing binding energy the  $\pi$ -MOs are  $1a_{1u}$  (8.15 eV),  $2b_{3u}$  (8.9 eV) and  $1b_{2g}$  (10.0 eV). The fourth and fifth  $\pi$ -orbital

$1b_{1g}$  and  $1b_{3u}$  are difficult to assign since the photoelectron spectrum shows overlapping bands above 11 eV.

Using the same arguments as outlined in our discussion on the benzene spectrum (10) we come to the conclusion that three allowed Rydberg series of d-symmetry ( $ndb_{1g}$ ,  $ndb_{2g}$  and  $ndb_{3g}$ ) are expected to converge to the first IP at 8.15 eV. In fact, three comparatively intense series have been observed ( $R_a$ ,  $R_b$  and  $R_c$  in Ref. (2)). In Fig. 2 the  $n=4$  members may be seen at 6.70, 6.74 and 6.78 eV. Since the quantum defects  $\delta$  for these three d-like series do not differ very much, only one series has been indicated in Fig. 2 with a quantum defect  $\delta = 0.85$ . Additionally, vibrational progressions with dominating spacing of 0.17 eV are observed. This energy corresponds to the totally symmetric  $a_g^{-v_4}$ -vibration of the carbon ring-structure (16). Its occurrence is most clearly seen in the spectrum for the  $n=4$  members, where we have additionally reproduced the corresponding observed vibrational structure of the ion taken from photoelectron spectra as an insert. The letters a, b, c for these levels should not be confused with the nomenclature in Ref. (2) for the Rydberg bands  $R_a, R_b, R_c$ .

We are unable to confirm the assignment of two more weak series given in Ref. (2) for this range. We are, furthermore, sceptical about the interpretation proposed earlier (3,4) for some of the absorption profiles as antiresonances, although our spectrum, which for the purpose of comparison is displayed on an extended scale in Fig. 3, is in excellent agreement with the data published by Scheps, Florida and Rice (3). (E.g., we also find no absorption profile above the 7.73 eV maximum which could be possibly interpreted as an antiresonance, as was the case in Ref. (2).) Those

structures which have been assigned to antiresonances in Ref. (3) are indicated by arrows in Fig. 3. The interpretation and analysis of this spectral range is very difficult because there are several accidental coincidences of presumed Rydberg bands and of vibrational bands belonging to other Rydberg states. Additionally, some of the observed bands in this range may be due to Rydberg series to the second or third IP (see below), a possibility not discussed so far. Finally, the uncertainties in the spectral behaviour of the underlying background absorption due to the  $\pi-\pi^*$ -band at approximately 7.7 eV make an unequivocal assignment impossible at the moment. Inspection of Fig. 3 suggests that some of the absorption profiles may well be merely accidental. Further investigations with improved resolution may settle these questions.

According to the selection rules we expect an intense s-series  $2b_{3u} + nsa_{1g}$  for the second IP at 8.90 eV. There is no clear indication of such a series in the spectrum and no vibrational structure, which would aid an assignment, is seen in the photoelectron spectrum. Tentatively taking the intense maximum at 7.83 eV as the n=4 member one arrives at a series with quantum defect  $\delta = 0.46$ , indicated in Fig. 2 by a dashed line. For the third IP at 10.00 eV two p-type series  $1b_{2g} + npb_{1u}$  and  $npb_{3u}$  are possible. The corresponding vibrational structure observed in the photoelectron spectrum (see insert) aids an assignment. In the absorption spectrum the vibrational structure is more clearly seen in the region at 9.13 eV (n=4) than for the range 8.3 eV, where we expect the first member of the series. The fact that the n=5 and n=6 members of the s-type series to the second IP are also expected to fall in that range at 8.5 eV may be the reason for this. We cannot decide whether the structure around 9 eV not assigned to the p-series and its vibrational bands may be due to the second p-series.



Finally, we have indicated a series to the fourth IP at 11.05 eV which may possibly correspond to the excitation of an  $\pi$ -electron from the  $1b_{1g}$  orbital. Two series  $1b_{1g} \rightarrow npb_{2u}$  and  $1b_{1g} \rightarrow npb_{3u}$  would be possible and the series indicated may explain the increase of absorption at 8.75 eV and the structure at 9.9 eV.

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Figure captions

- Fig. 1        Absorption spectrum of naphthalene vapour from 5 to 30 eV.
- Fig. 2        Absorption spectrum of naphthalene vapour from 5 to 11 eV.  
Ionization potentials and inserts are taken from photo-  
electron spectra from Turner, Baker, Baker, and Brundle  
(Ref. (15)). Indicated Rydberg series have been calculated  
using the given quantum defects.
- Fig. 3        Densitometer trace of the naphthalene absorption spectrum  
in the 7.5 eV range. Positions of absorption bands are given  
in eV. The incoming intensity is constant over this range.  
Arrows indicate structures assigned to antiresonances in Ref. (3).

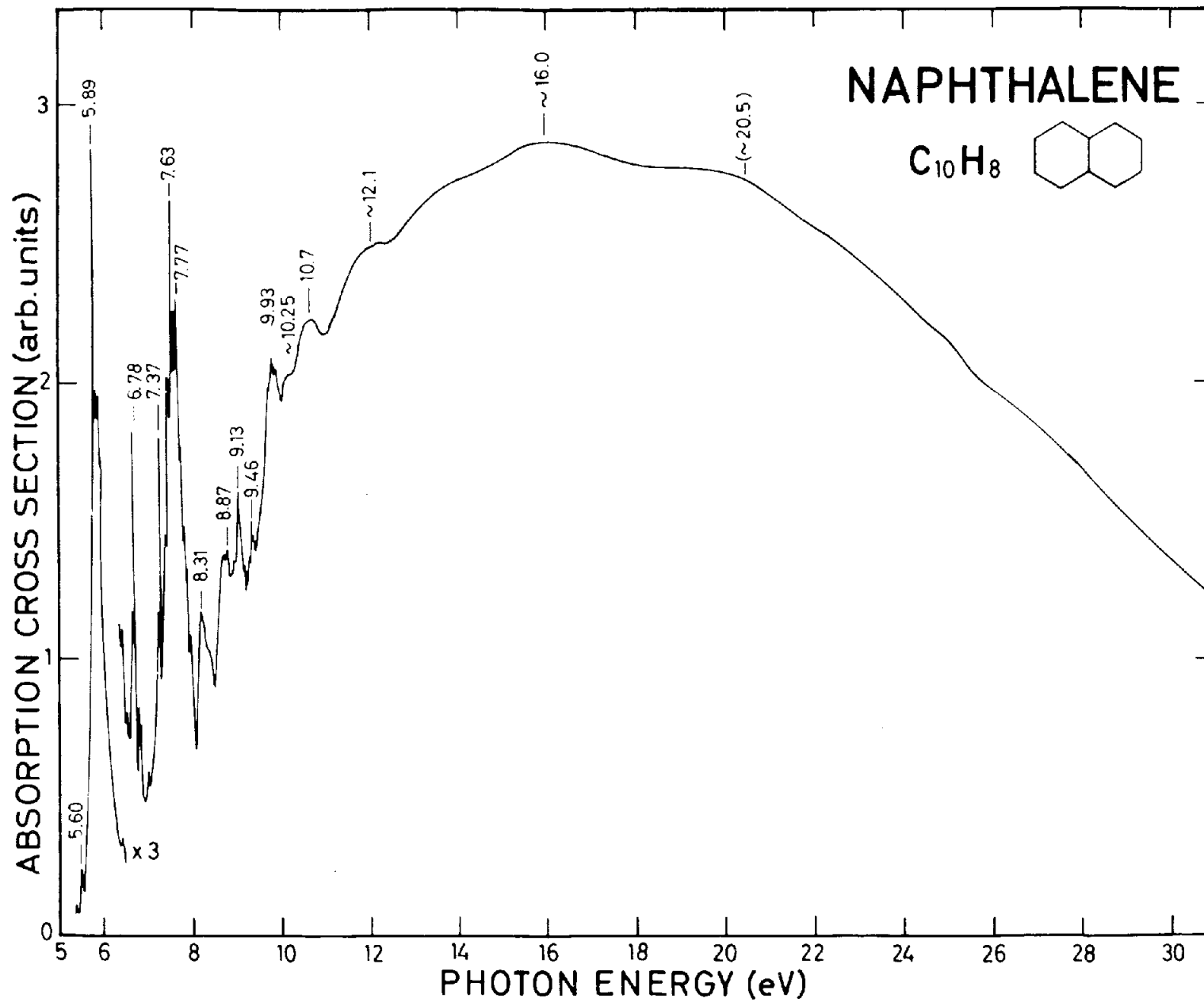


Fig. 1

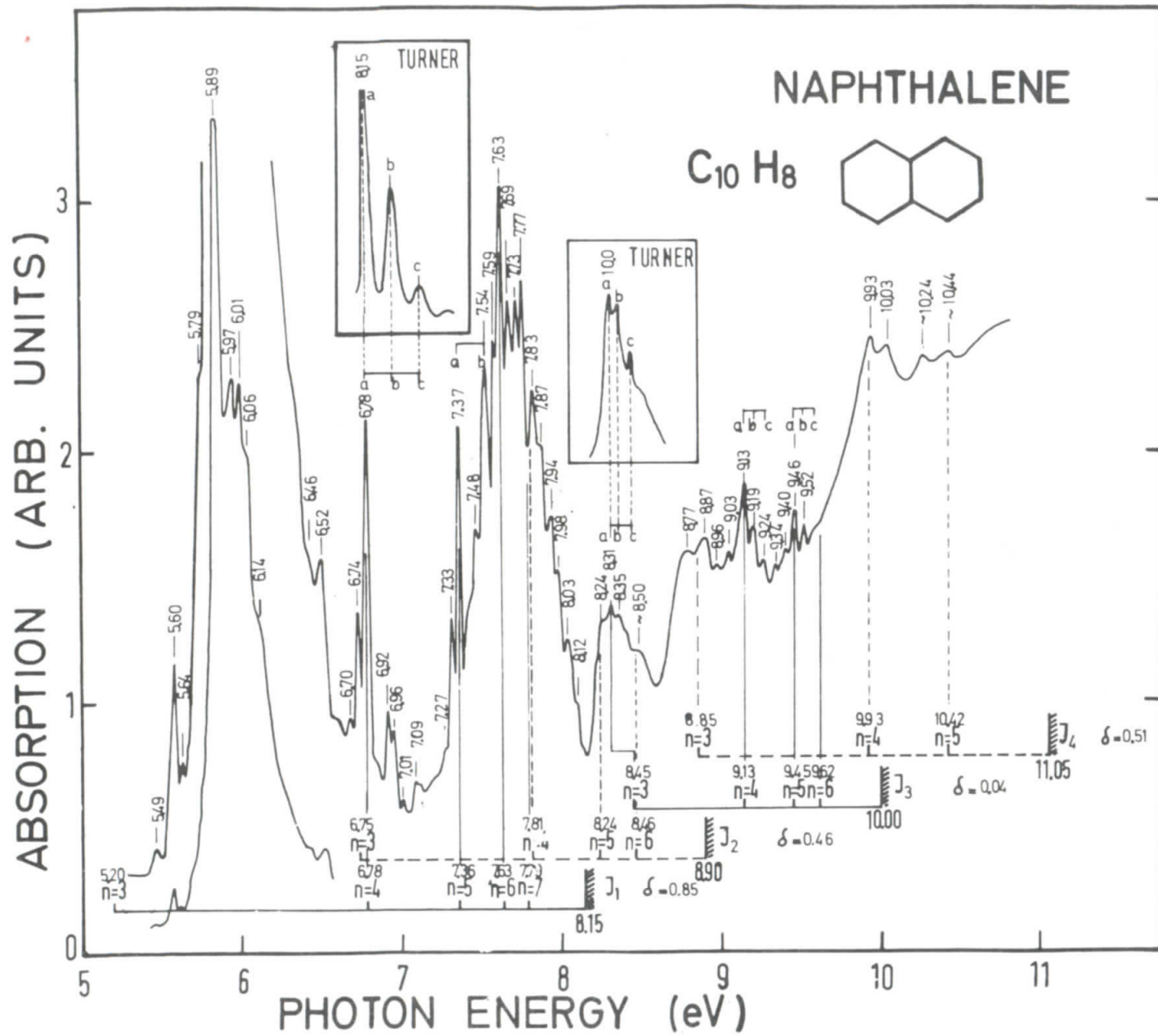


Fig. 2

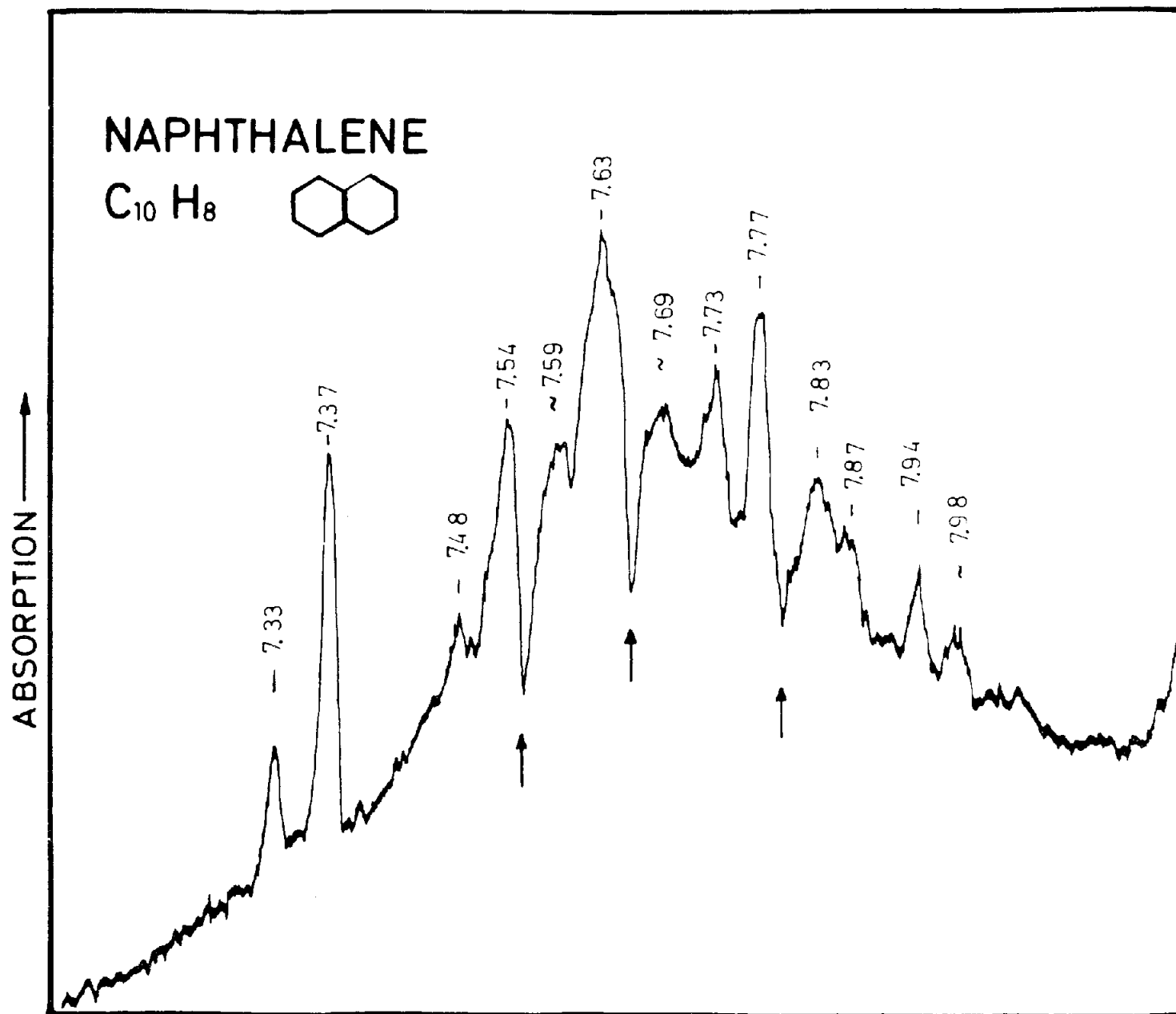


Fig. 3