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# Fine Structure in the VUV Absorption Spectrum of Neopentane at 16 eV[+]

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*The photoabsorption of neopentane ($C(CH_3)_4$) has been measured for photon energies from 10 to 30 eV with synchrotron radiation. Sharp absorption bands are observed around 16 eV on top of a strong continuum. - They can be grouped into a p-like Rydberg series with accompanying vibrational subbands. The nature of the Rydberg states is discussed.*

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[+] work supported in part by DFG

The alkane spectra are of fundamental importance for the general understanding of molecular vacuum ultraviolet (VUV) spectra because a large number of molecules carries alkyl groups. Consequently the spectra of these completely saturated hydrocarbons have attracted considerable attention recently[1,2,3]. The electronic spectra are located in the far UV with the maximum of the absorption cross section at around 16 eV. Usually the spectra are diffuse and no vibrational structure could be observed with ethane as an exception[4,5]. As regards Rydberg excitations, which were believed to be non existend in the alkane spectra for many years, Robin[3] has positively identified such bands belonging to the first ionization potential for a number of molecules. The assignment was based on a comparison of the absorption features to high-resolution photoelectron spectra, the observations of high pressure effects and the systematics in term values for a series of analogous molecules. There seemed to be only little chance of observing extensive Rydberg series to higher ionization limits, since - as discussed by Herzberg[6] - in almost all cases the transition in the Franck Condon range would go to the repulsive part of the potential curve of the upper state and hence would be structureless and diffuse.

This letter reports on results of an optical absorption measurement of neopentane vapour in the VUV region for photon energies from 10 to 35 eV, in which we could identify a p-like Rydberg series located at around 16 eV. Experimental details were given in previous publications[2,7]. 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 wavelength resolution was

2 Å corresponding to 0.02 eV at 10 eV. The absolute photon energies given with our results are correct within ± 0.015 eV. No absolute determination of the absorption cross section was made. A rough estimate gives an approximate value of 150 Mb at 16 eV.

In Fig. 1 a survey of the absorption spectrum from the onset at about 7.2 eV up to 35 eV is shown. For photon energies below 10 eV the spectrum as reported by Sandorfy[1] is given. The absorption cross section rises from the onset with broad bands centered at 7.95 eV, 8.55 eV (shoulder), 9.20 eV and 10.5 eV to a maximum at about 15 eV and decreases smoothly towards higher photon energies. We observe on top of the strong continuum a number of comparatively sharp and narrow absorption bands which are displayed on an expanded scale in the insert. Although the band shapes in this spectral region are very assymetric suggesting that one observes Fano-Beutler type absorption profiles[8] we have not tried to fit the line shapes to such a profile. It is fairly clear that the ambiguities in accounting for the large background absorption would be large. Note, that the relative change of the cross section is only of the order of 10% of the total cross section in this spectral range. Further it was not possible to isolate the vibrational subbands unambiguously for a meaningful line shape analysis.

In table 1 we have given the analysis of the observed absorption features together with information about the electronic structure gained from photoelectron spectroscopy. For the ionization potentials we have quoted the band centers of the photoelectron spectra obtained by Evans et al.[9] (see also the photoelectron spectrum of $C(CH_3)_4$ as obtained by Jonas et al.[14]).

The symmetry designation used here follows the analysis of Murrel and Schmidt[10] assuming $T_d$ symmetry. It is based on the ab-initio convention and includes the carbon 1s level.

By comparison of the absorption spectra from linear and highly branched alkanes and on the basis of the term values Robin[3] has given the Rydberg assignment $4t_2 \rightarrow 3s$ and $4t_2 \rightarrow 3p$ for the absorption bands at 7.95 and 8.55 eV. Our tentative Rydberg assignment of the bands at 9.20 and 10.5 eV is based on the same assumptions, namely that for a 3s excitation a term value of the order of 3.3 eV and for a 3p excitation a term value of approximately 2.2 eV are expected.

The bands at 15.46, 16.59 and 17.00 eV can easily be identified as due to a Rydberg series with p character originating from the bonding $2a_1$ orbital. According to the Rydberg formula $E_n = E_\infty - R/(n-\delta)^2$, where $E_n$ denotes the excitation energy of the n-th band $E_\infty$ the ionization potential, R the Rydberg constant, and n and $\delta$ the main quantum number and the quantum defect respectively, one obtains for the term values $T_n = E_\infty - E_n$ : $T_3 = 2.22$ eV, $T_4 = 1.09$ eV and $T_5 = 0.68$ eV. We note that these term values and the quantum defect (one obtains for instance from the n=4 member $\delta=0.46$) are very similar to those of the observed p-type series in benzene[11] and perdeuterated benzene[12] in the 15-17 eV spectral range ($C_6H_6$: $T_3 = 2.22$ eV, $T_4 = 1.03$ eV, $C_6D_6$: $T_3 = 2.21$ eV).

We assign the remaining bands with a spacing of 0.17 eV to a vibrational progression based on the totally symmetric C-H deformation mode $\nu_2$ of symmetry species $a_1$ as indicated in the insert of Fig. 1 (see also table 1). This vibration has a frequency of 178 meV in the ground state[13] and 165 meV in the ionized molecule as observed in the photoelectron spectrum[9,14]. In addition to this progression the photoelectron spectra show a further weaker progression with the same spacing being displaced by 65±5 meV with respect to the one mentioned above. This weaker progression has been attributed to the combination of $\nu_2 + \nu_3$ where $\nu_3$ is the totally symmetric C-$CH_3$ stretching mode with a frequency of 0.091 eV in the ground state[13]. The absorption bands or shoulders at 15.58 and 15.77 eV and at 16.69 eV and 16.87 eV are assigned as corresponding counterparts . They too, have a spacing of about 170 meV characteristic for $\nu_2$. However, the displacement from the purely electronic Rydberg transition is 0.12 eV for the n=3 and 0.10 eV for the n=4 band, rather than 0.065 eV. Our observation thus indicates a strengthening of the C-C bonds upon removal of an electron from the $2a_1$ orbital in accord with the characterization of this MO as being strongly C-H bonding and weakly C-$CH_3$ antibonding[14].

Furhter experiments with higher resolution would give more precise data on this point and could make a line shape analysis possible. In addition it seems interesting to investigate the decay of these Rydberg states via autoionization into continuum states by means of photoion and fluorescence spectroscopy.

Table 1 Tentative Rydberg assignment of the neopentane absorption bands
(a): Ref. 9, (b): Ref. 3, (c): this work

| MO | | Ionization Potential[(a)] | Absorption[(c)] | Term value[(c)] | Assignment[(c)] |
|---|---|---|---|---|---|
| $4t_2$ | A | 11.0 | 7.95 | 3.05 | $4t_2 \rightarrow 3s$ [(b)] |
| | | | 8.55 | 2.45 | $4t_2 \rightarrow 3p$ [(b)] |
| $1t_1$ | $B_1$ | 12.58 | 9.20 | 3.38 | $1t_1 \rightarrow 3s$ |
| | | | 10.5 | 2.08 | $1t_1 \rightarrow 3p$ |
| $1e$ | $B_2$ | 13.91 | 10.5 | 3.4 | $1e \rightarrow 3s$ |
| $3t_2$ | $B_2$ | 15.24 | - | - | --- |
| $2a_1$ | C | 17.68 | 15.46 | 2.22 | $2a_1 \rightarrow 3p$ |
| | | 17.74 | 15.58sh | | $3p+\nu_3$ |
| | | 17.84 | 15.63 | | $3p+\nu_2$ |
| | | 17.91 | 15.77sh | | $3p+\nu_2+1\nu_3$ |
| | | 18.01 | 15.81 | | $3p+2\nu_2$ |
| | | 18.08 | 15.98 | | $3p+3\nu_2$ |
| | | 18.18 | | | |
| | | 18.24 | 16.59 | 1.09 | $2a_1 \rightarrow 4p$ |
| | | 18.34 | 16.69 | | $4p+\nu_3$ |
| | | $\nu_2$ : 165±5 meV | 16.75 | | $4p+\nu_2$ |
| | | $\nu_3$ : 65 ±5 meV | 16.87sh | | $4p+\nu_2+1\nu_3$ |
| | | | 19.91 | | $4p+2\nu_2$ |
| | | | 17.00 | 0.68 | $2a_1 \rightarrow 5p$ |
| | | | (17.07) | | $4p+3\nu_2$ |
| | | | (17.15) | | $5p+\nu_2$ |

$2t_2$ not yet observed
$1a_1$ expected at $\approx$23 eV
from methane $2a_1$ symmetry

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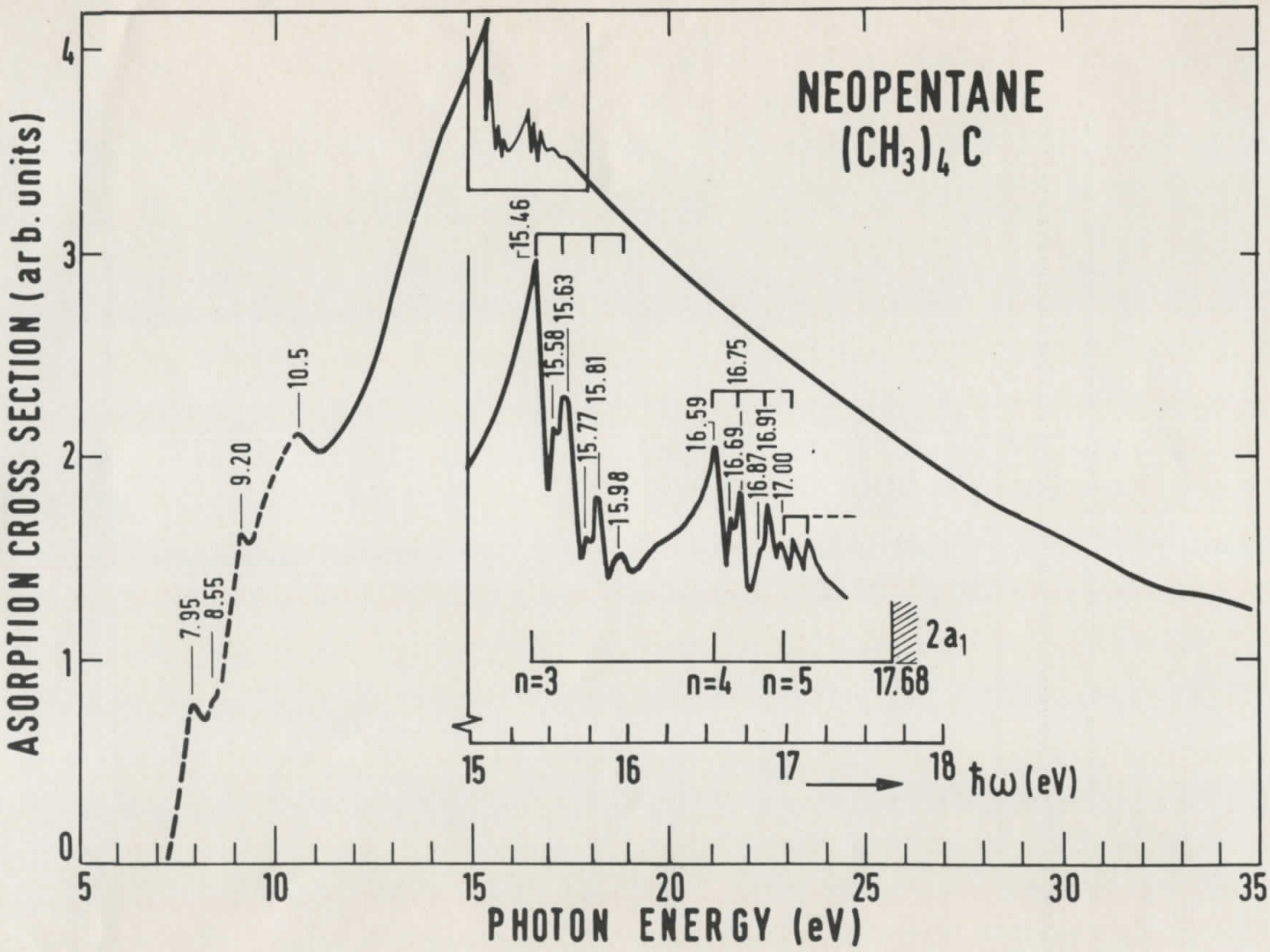
## Figure Caption

Absorption spectrum of neopentane for photon energies between 5 and 35 eV. Below 10 eV the spectrum reported by Sandorfy[1] (dashed curve) is given.


NEOPENTANE
$(CH_3)_4C$
ASORPTION CROSS SECTION (ar b. units)
PHOTON ENERGY (eV)
0
1
2
3
4
5
10
15
20
25
30
35
7.95
8.55
9.20
10.5
15.46
15.58
15.63
15.77
15.81
15.98
16.59
16.69
16.75
16.87
16.91
17.00
n=3
n=4
n=5
17.68
$2a_1$
15
16
17
18
$\hbar\omega$ (eV)