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All-Union Vitamins Institute, Moscow

U.D.C. 543.42.062

SPECTRA OF ORGANIC MOLECULES IN THE FAR AND VACUUM ULTRAVIOLET

O. V. Agashkin and A. E. Lyuts

CONTENTS

1. Introduction 428

2. Chromophores in the vacuum ultraviolet region 428

3. The spectra of saturated hydrocarbons 429

4. Hydrocarbons containing double and triple bonds 430

5. Saturated compounds containing nitrogen, oxygen, and halogens 432

6. Complex chromophores 436

7. Application of absorption spectra in the far and vacuum ultraviolet to the analysis of the composition and structure of materials. 438

1. INTRODUCTION

When we study absorption in the visible, the ultraviolet, or the Schumann regions of the spectrum, we are observing a single process: the transfer of electrons to higher energy levels under the influence of light. However, for purely historical reasons, the unnatural classification of electronic spectra by wavelength is still retained. At first, only the visible region was experimentally accessible. Later, when quartz optics and photocells were developed, we became acquainted with the ultraviolet region. Lastly, by using diffraction techniques and LiF and CaF_2 optics, we were able to reach the vacuum ultraviolet region. This is a relatively recent achievement; the technical difficulties still act as a psychological barrier against the widespread application of vacuum ultraviolet spectra in structural problems involving polyatomic molecules. At least two psychological factors militate against the adoption of the vacuum region by chemists. The first is the widespread belief that the necessary techniques are extremely complex and inaccessible. The second, and more important, obstacle is that we know a great deal about the origin of absorption bands in the near ultraviolet and in the visible region, whereas we know practically nothing of the nature of bands in the Schumann region. Thus, the frequent temptation to look beyond the limits of 220 nm is usually demolished by the commonsense question: what shall we learn about this molecule by going further into the short-wavelength region? There are no correlations at all, in this region, between the position and intensity of bands on the one hand and structure on the other hand. Even the spectra themselves are so few that no attempt has been made to classify them systematically.

The aim of the present article is to review the most important results obtained by applying absorption spectra in the far and vacuum ultraviolet to the solution of problems in molecular structure. We hope to convince the reader that the vacuum region is not altogether barren from the chemist's point of view, that the new spectra can be treated as extensions of many existing spectra, and lastly that the techniques involved in recording these spectra have now reached a level comparable to those of the near ultraviolet and infrared region, so that all these regions can now be exploited on an equal footing.

Electronic spectra in the vacuum ultraviolet do not constitute an isolated aspect of theory. To understand these spectra and to make practical use of them, we need a basic knowledge of spectroscopy and of quantum chemistry. Existing textbooks on these subjects are quite good, and deal with the subject at quite different levels. Readers wishing to familiarise themselves with the basic theory are referred to the book by Barrow[1]. A group of three books[2,3,4], read in conjunction, would give a firmer grasp of the subject. Readers approaching spectroscopy from a chemical background will perhaps find the books by Jaffe and Orchin[5] and by Murrell[6] best suited to their needs.

The minimum background knowledge needed to read the present article is the following. We shall assume familiarity on the part of the reader with the form of the complete energy spectrum of a molecule, with the properties of the states giving rise to this spectrum, with possible inter-state transitions, and with the reasons for intensity differences between the observed bands. An appreciation of the origin of the fine structure of electronic bands will be important, as well as the ability to extract from it information on molecular structure. Lastly, it will be necessary to understand some other effects associated with the absorption of light. The review articles by Mason[7] and by Ramsay[8] give a very compact account of all these problems.

The order of presentation of the subject matter will be as follows. We shall first of all discuss the possibility of establishing a relationship between the characteristics of absorption in the far and vacuum ultraviolet and characteristic structural elements. We shall then examine in detail the individual spectra of various classes of organic compounds. Electronic transitions will be designated according to Mulliken's classification[9] and also by the localised orbitals classification[3].

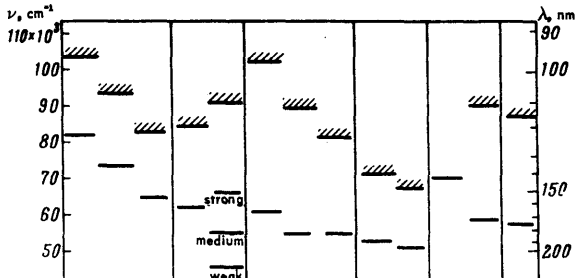
The spectra obtained up to 1944 were classified in the review articles by Sponer[10] and by Platt and Klevens[11]. The fullest account of subsequent work is given by Turner[12]. The books by Phillips[13] and by Rao[14] include a factual summary and a bibliography of vacuum spectra.

2. CHROMOPHORES IN THE VACUUM ULTRAVIOLET REGION

Electronic spectra are widely used in the study of problems of chemical structure, particularly when chromophoric groups are present in the molecules and characteristic frequencies exist. We shall try to establish whether the concept of a chromophore can in any sense be carried over to the new region. It is immediately apparent that by no means every absorption in the vacuum ultraviolet can be ascribed to the presence of a known chromophore in the molecule. In particular, it is obvious that any organic molecule with saturated bonds absorbs light in this region, whereas not every such molecule contains a chromophoric group in the usual meaning of the word. The term chromophoric is applied to those groups or atoms in a molecule which give rise to absorption by the molecule at the longest wavelengths. The definition is not too loose, since it has been known for a long time that a chromophore does not always produce a colour. We shall retain the term auxochromic for those groups which shift the spectrum towards longer waves. However, a given group can behave either as a chromophore or as an auxochrome in different molecules. For example, in the ethane molecule the C–C bond is a chromophore, and the C–H bonds are auxochromic in the most favourable case. In methane, the C–H bonds are fully chromophoric.

However, this is not merely a matter of terminology. The chromophore concept is a fruitful one if it can be shown that a characteristic absorption is associated with each chromophore. This idea is illustrated in Table 1, which summarises existing information on the longest-wavelength allowed transitions of a series of organic mole-

TABLE 1. Chromophores.



$\log\epsilon_{max}$	4.0	4.0	3.17 2.18 3.40	3.52 3.60		4.2
Oscillator strength, f	0.342		0.046 0.005 0.035		0.0247: w.	
Transition	$\sigma \rightarrow \sigma^*$	$\pi \rightarrow \pi^*$ trans	$n \rightarrow \sigma^*$	$n \rightarrow \sigma^*$	$\pi \rightarrow \sigma^*$; $n \rightarrow \sigma^*$	$\pi_0 \rightarrow \sigma$
Chromophore	C–H; C–C; C–C(=C)–C	C=C; C≡C	H–O–H; H–O–C; H–O–C(=O)	C–N–H; C–N(=C)–C	C–F; C–Cl	C=O
Molecule	CH_4; C_2H_6; $C(CH_3)_4$	C_2H_4; C_2H_2	H_2O; CH_3OH; $(CH_3)_2O$	$(CH_3)_2NH$; $(CH_3)_3N$	CF_4; CH_3Cl	H_2CO
References	15; 16; 17; 18	19; 20; 17	21; 21; 22	23; 23	16; 24	7

cules, each of which is the simplest carrier of that chromophore and could therefore stand at the head of a whole family of related compounds. The first impression gained from the Table is definitely unfavourable. Matters improve slightly if the chromophores are classified by transition type: this brings order into the groups in which only one type of long-wavelength transition is possible.

In the paraffin series transitions of the type $\sigma \rightarrow \sigma^*$ only are possible. These transitions occupy the shortest wavelength region. Unsaturated compounds give bands associated with $\pi \rightarrow \pi^*$ transitions, close to the lower absorption edge of the paraffins. All three long-wavelength bands of acetylene are due to these transitions. For oxygen-containing saturated compounds, the transitions of lowest energy will be $n \rightarrow \sigma^*$ transitions. These transitions may turn out to be forbidden (as in methanol), depending on whether the highest filled states taking part in the transition are $2p$ or $2s$. The $n \rightarrow \sigma^*$ transitions localised at an amino nitrogen atom occur at even longer wavelengths. In alkyl halides $n \rightarrow \sigma^*$ transitions are peculiar. They are undoubtedly forbidden, which suggests that an appreciable fraction of $n(2p)$ states takes part in the transition. In ketones, aldehydes, and carboxylic acids, competition of absorption in the long-wavelength region is possible between the $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $n \rightarrow \sigma^*$ transitions. Within the limits of Table 1, it is impossible to demonstrate any regularities for these compounds: we shall discuss their spectra in greater detail in the subsequent Sections. At this point, however, it is important to draw attention to the behaviour of the ionisation potentials. They follow the long-wavelength allowed transitions very closely indeed. In some cases the relationship between ν_{max} for the long-wavelength band and the ionisation potential is not merely monotonic, but actually linear.

We shall now turn to the published spectroscopic data, following the classification given in Table 1.

3. THE SPECTRA OF SATURATED HYDROCARBONS

The highest filled orbitals in saturated hydrocarbons are bonding σ-orbitals. In these systems absorption can occur only by transitions of the molecule to the σ* antibonding state or to Rydberg levels. The simplest member of this series is methane. A knowledge of its spectrum should resolve the problem of the absorption associated with the chromophore C–H in all compounds containing this chromophore. Clearly, we can only talk about the absorption region, since in saturated compounds the electrons are not localised in an individual bond but belong to the whole molecule to an appreciable extent. Figs. 1*a* and 1*b*, taken from the work of Duncan[16] and of Weissler[25], give some idea of the full spectrum of methane. The total oscillator strength, measured by the area between the long-wavelength absorption edge and the onset of ionisation, is 6.1: this is practically the same as the theoretical limit, since the higher molecular orbitals contain just six $2p\sigma$-electrons. This means that all possible transitions for electrons of the valence shell ($N \rightarrow V$ and $N \rightarrow R$ transitions) are concentrated in that interval. From this point of view, the band with a maximum at 1250 Å is due to a $\sigma \rightarrow \sigma^*$ transition, whilst the shorter-wavelength region of the spectrum relates to forbidden Rydberg series converging towards the ionisation potential (12.99 eV).

Unfortunately, the chromophore carrier C–C (ethane) has not been studied in the same detail. We only know[17] that its long-wavelength absorption maximum lies at 1350 Å. This is undoubtedly an $N \rightarrow V$ transition, involving excitation of one of the σ-electrons of the C–C bond to the antibonding σ* state. Further increase in the number of carbon atoms in the straight-chain alkane series causes the band associated with this transition to shift towards longer wavelengths (Fig. 2). Curve *a* of Fig. 2, based on

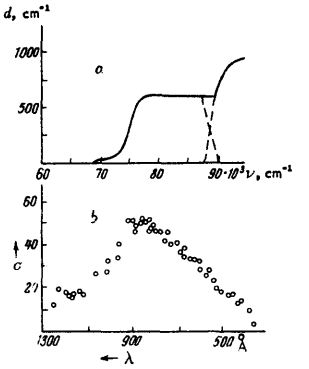


Fig. 1. Absorption spectrum of gaseous methane:
a) absorption coefficients of methane in the region 60 000–95 000 cm^{-1};[16] *b*) absorption cross-sections of methane in the region 1300–500 Å.[25]

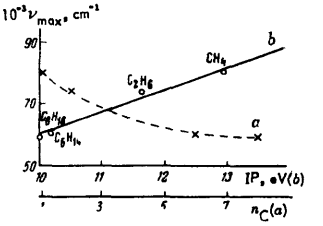


Fig. 2. Relation between the frequency of the long-wavelength absorption maximum of saturated normal hydrocarbons and (*a*) chain length and (*b*) ionisation potential.

experimental data[18,26,27], justifies the conclusion that the wavelength of the absorption maximum for straight-chain alkanes remains practically constant beyond C_6. Despite the scarcity of experimental data, this conclusion seems reasonable, because delocalisation of bonding σ-electrons can extend only over a limited region. Further lengthening of the hydrocarbon chain ceases to affect the distribution of charge among the bonds, and therefore also the absorption spectrum. It is important to remember the linear relationship between ionisation potential and the frequency of the long-wavelength absorption maximum, which suggests that the energy of the highest occupied orbital increases monotonically with the length of the chain. Evidently, when the number of carbon atoms is large enough the energy diagram of the molecule can be described by zones similar to those of a dielectric. Furthermore, branched hydrocarbons absorb at higher wavelengths than their straight-chain isomers[18]. Cyclic hydrocarbons also give spectra at longer wavelengths than the straight-chain linear hydrocarbons, but in this case the wavelengths of the maxima and the oscillator strengths are a function of strain in the ring[28,29]. This is the reason why straight-chain hexane and heptane are often used as solvents in the far ultraviolet. According to Platt and coworkers[30], 0.3 mm layers of these compounds are transparent down to 1705 Å: this is adequate in a large number of cases.

4. HYDROCARBONS CONTAINING DOUBLE AND TRIPLE BONDS

Here we have to deal with two types of $N \rightarrow V$ transition. The first of these originates in exactly the same way as the transition discussed above. The second, on the other hand, is associated with $\pi \rightarrow \pi^*$ excitation. We can predict some of the features of absorption arising from this particular transition on the basis of current ideas. Firstly, this absorption should occur at longer wavelengths, if only because π-bonding is weaker than σ-bonding, and, secondly, the transition should be symmetry allowed.

Let us consider the spectrum of the simplest carrier of the C=C chromophore (ethylene), shown in Fig. 3. The envelope of the fine structure in the region 1400–2000 Å is a very broad band with a maximum at 1620 Å. This is the band which is assigned to an $N \rightarrow V$, $\pi \rightarrow \pi^*$ transition. Studies of its long-wavelength slope[19] revealed a vibrational structure, which becomes diffuse as the dissociation limit (1620 Å) is approached. The absorption showing fine structure, which forms the maximum of the diffuse band and begins at 1750 Å, is caused by an $N \rightarrow R$ transition, where R is the first Rydberg state. The system of doublets denotes transitions to different vibrational levels of this Rydberg state. By using deuteriated materials, Wilkinson and Mulliken[19] were able to show that the long-wavelength components of the doublets correspond to the vibrations of the C=C bond, whereas the short-wavelength components

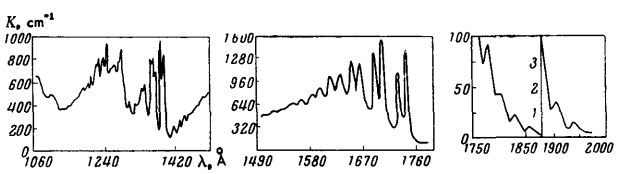


Fig.3. Absorption spectrum of gaseous ethylene[31].

are the even transitions of the oscillations associated with the torsional vibration $\tau_{H-C-H'}$. The higher terms of the Rydberg series lie at 1322, 1247, and 1225 Å, and converge towards the ionisation limit at 10.45 eV, in good agreement with the values of ionisation potential obtained by other methods[26,27].

Let us now return to the $N \rightarrow V$ transition. The long-wavelength side of the band has a vibrational structure whose intensity distribution shows that excitation of the molecule produces an anomalously large increase in the C–C distance: the strongest components of the structure give[19] $\Delta v > 10$. Theoretical analysis[32] of the vibrational structure gives $r_{C-C} = 1.69$ Å as compared with 1.335 Å for the ground state[19]. In the spectrum of tetradeuterioethylene we find, in addition to the stretching vibration bands, bands which can only be ascribed to τ_{H-C-H} vibrations. The difference between the vibrational quantum numbers for these transitions is again very large, which suggests, by the Franck–Condon principle, a very large difference in the angle between the HCH planes in the upper and lower electronic states. This difference is close to 90°. It is difficult to overemphasise the importance of these conclusions. They mean, effectively, that the V-state of ethylene is non-planar. Analysis of many spectroscopic results led Walsh[33] to the conclusion that (1) the planes of the methylene groups are mutually perpendicular; (2) the C–H and C–C bonds form a pyramid at each of the carbon atoms; (3) each carbon atom lies slightly outside the plane passing through the bisector of the H–C–H angle of the opposite methylene group. The first of these conclusions can be readily understood without detailed analysis of the experimental data. Antibonding in the π^*-state is a maximum for the planar configuration of the nuclei, when the carbon $2p$-orbitals are mutually parallel. The repulsion energy will be a minimum, by symmetry considerations, when these orbitals are oriented at right angles to each other. Under these conditions the planes of the methylene groups also will diverge by about 90°. The resulting molecular orbital will no longer be a pure π^*-orbital, and the total bonding will increase to a maximum. Thus, the potential energy of the ethylene molecule, both in the ground and in the excited states, is a periodic function of the angle between the planes of the methylene groups (Fig. 4). The two curves are out of phase by 90°. This means that excitation brings the system into a state of maximum repulsion energy. If the lifetime of the excited

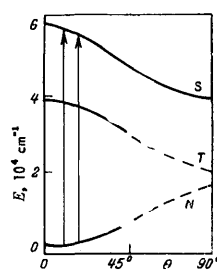


Fig.4. Variation of the potential energy of ethylene with the angle of twist between the planes of the methylene groups for the ground (N), singlet (S), and triplet (T) excited states[7].

state is long enough, the molecule, having dissipated the excess of energy, will be in a state of zero vibrational energy and non-planar nuclear configuration. Such a molecule will behave in a very unusual way in a number of reactions. Equally important is the fact that, when returning to the electronic ground state, the molecule can adopt (with equal probabilities) either the original nuclear configuration or a configuration involving a 180° rotation. With ethylene itself this is immaterial, but if we consider instead *trans*-dichloroethylene, say, we can expect to obtain a new substance, *cis*-dichloroethylene, as a result of this process. The *cis-trans* isomerisation reaction of ethylene derivatives is a very common one. This is evidence that we are indeed dealing with a long-lived excited state, which is a triplet in this case[34]. The Rydberg states correspond to planar nuclear configurations[18], and when a molecule is excited to these states there is no significant change in the shape or in the reactivity of the molecule.

Let us now consider what happens to the $N \rightarrow V$ transition when the ethylene molecule is perturbed in various ways. The introduction of an alkyl substituent into ethylene causes a shift of the band towards longer wavelengths. Longer alkyl substituents give an enhanced shift, but the effect tapers off when the number of carbon atoms in the radical is large (Fig. 5). Similar changes are found in the ionisation potential. Increasing the number of alkyl substituents has exactly the same effect[35-37]. In every case we can envisage a delocalisation of the π-electrons, leading to an increase in the energy of the ground state and a decrease in the energy of the excited state.

A second vinyl or carbonyl group, not conjugated with the first, has practically no effect on the absorption characteristic associated with the $N \rightarrow V$ transition in a C=C double bond[38]. The intensities of non-interacting C=C groups present in the same molecule are additive[39]. All these observations open the way for analytical applications of spectra in the far ultraviolet, at least to alkenes. Table 2 can be used as a key to analytical applications.

Cyclic alkenes are a special group of alkenes. If we compare a linear and a cyclic alkene having the same number of carbon atoms, the cyclic compound is usually found to absorb at shorter wavelengths than the linear compound, the difference increasing with the amount of strain in the ring. The integral intensities or oscillator strengths for the transitions decrease as the strain increases[29,40]. If the molecule contains more than one unsaturated bond, and

TABLE 2. Average position and maximum intensity of the absorption bands (Å) of olefin vapours[39].

Alk-1-enes	1750±25	11800±1200
cis-Alk-2-enes	1765±15	12300±200
trans-Alk-2-enes	1790±10	11700±800
2-Alkylalk-1-enes	1875±15	8900±1200

conjugation between these bonds is established, the spectrum is so strongly shifted towards longer wavelengths that it can appear in the near ultraviolet and thus fall outside the frequency range relevant to the present article. A great deal of relatively recent information on the spectra of unsaturated conjugated systems and of alkenes can be found in Turner's[12] and Mason's[7] reviews, and in the monographs by Rao[14], Murrell[6], and Phillips[13].

The chromophore C≡C is in many ways similar to the previous one. The longest-wavelength transition is again the $N \rightarrow V$ transition from a bonding π-state to an antibonding π^*-state. The electronic structure is still more complicated in this case because the π-states are doubly degenerate. If we choose the Z axis in the direction of the bond, we can consider filled π_x and π_y states, and free antibonding π_x^* and π_y^* orbitals. Ignoring singlet–triplet transitions, we can set up four combinations of these states, but not every one of these can be realised. If the molecule in the excited state is linear, three of the four combinations lead to forbidden transitions and only one can be realised. If, on the other hand, the excited molecule is bent, three allowed transitions are possible, one of which should be relatively weak, by analogy with the corresponding forbidden transition for the case of a linear upper state[41]. This transition should be modified by two types of vibration: by C≡C stretching vibrations and by bending vibrations arising from changes in the H–C–C angle. The spectrum indicates a decrease in the H–C–C angle and an increase in the C–C internuclear distance in the first excited state. Fig. 6 shows the spectrum of gaseous acetylene. Four absorption bands are found in the range 1400–2400 Å. The band with the longest wavelength has a vibrational structure with a red shift, indicating that the internuclear distance increases during excitation. King and Ingold[42] have made a vibrational analysis of the structure. They found evidence for two vibrations: a C≡C stretching vibration with a frequency of 1385 cm^{-1} (as compared with 1974 cm^{-1} in the ground state) and a scissor bending vibration of frequency 1049 cm^{-1} (as compared

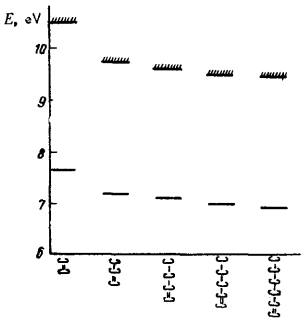


Fig. 5. Relationship between the frequency of the long-wavelength absorption maximum and ionisation potential in the olefin series.

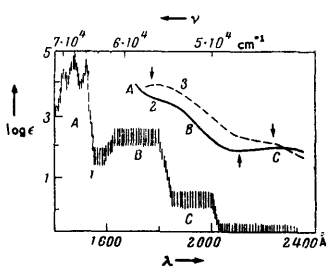


Fig. 6. Absorption spectra[45] of acetylene vapour (curve 1) and of hexane solutions of oct-1-yne (curve 2) and oct-2-yne (curve 3).

with 612 cm^{-1} for the ground state). The transition was found to be polarised at right angles to the plane of the bent molecule, whence it follows that the configuration of the nuclei in this particular excited state has a centre of symmetry. This means that the equilibrium configuration is bent in the *trans* direction. The other two $N \rightarrow V$ transitions correspond to excitation to linear states[43] with an even greater increase in C–C internuclear distance, since the corresponding frequency is lowered to 800 cm^{-1}. Relatively recently Wilkinson carried out a more careful vibrational analysis using deuteriation, and was able to confirm the earlier conclusions[44]. Absorption at wavelengths shorter than 1500 Å is associated with $N \rightarrow R$ transitions. Analysis of this region has shown that the fine structure of the spectrum can be reduced to two Rydberg series converging to a single ionisation limit at about 92 000 cm^{-1}.

Alkylation of acetylene lowers the frequency of all the bands due to $N \rightarrow V$ transitions. At the same time, the intensity of these bands increases. Fig. 6 shows the spectra of two octyne isomers. Bands having the same origin are labelled with the same letter. Other examples have confirmed that alkylation decreases the frequency and increases the intensity. An even stronger red shift and increase in intensity are obtained when hydrogen is replaced by a heteroatom (particularly nitrogen)[46], or by a second $-C{\equiv}CH$ group[47].

The changes occur in the same sense for all bands associated with $N \rightarrow V$ transitions. In the case of heteroatoms, the anomalously large increase in intensity may be due to charge transfer of non-bonding electrons to the free π-orbitals.

The hydrocyanic acid molecule, being isoelectronic with acetylene, should have a similar spectrum: this is confirmed by the work of Herzberg and Innes[48]. However, in this case there are two transitions giving a ben configuration of the molecule: the $\Sigma^+ \rightarrow \Sigma^-$ transition with a band in the region of 1600–2000 Å, and the $\Sigma^+ \rightarrow \Delta$ transition whose absorption lies in the region of 1550–1700 Å.

5. SATURATED COMPOUNDS CONTAINING NITROGEN, OXYGEN, AND HALOGENS

The spectroscopic properties of these compounds are largely determined by the properties of the heteroatoms. The most characteristic feature of their electronic structure is the presence of non-bonding electrons occupying the highest filled levels. We shall consider first the nitrogen compounds.

1. The Chromophore $-\overset{|}{N}-$

We were able to list only five papers on the electronic spectra of aliphatic amines. Yet, these spectra should be a fruitful field of study in short-wave spectroscopy. The simplest carrier of the chromophore is ammonia. Because it has three equivalent N–H σ-bonds and a non-bonding electron pair, ammonia should give rise to a very simple spectrum consisting of one $N \rightarrow Q$ transition, one $N \rightarrow V$ transition at a shorter wavelength than the previous one, and a series of Rydberg transitions. Thompson and Duncan[49] studied the frequency range from 45 000 to 120 000 cm^{-1} and discovered four ammonia bands in this region, which they assigned to Rydberg transitions of the non-bonding pair. Sun and Weissler[25] found a continuum similar to the methane continuum at the short-wavelength end of this range, possibly arising from $N \rightarrow V$ transitions of the electrons localised at the N–H σ-bonds. If this is the case, one of the bands found by Thompson and Duncan[49] should be assigned to the $N \rightarrow Q$ transition. It was recently shown that this interpretation is not definitive: if the four transitions are arranged in a single Rydberg series, the series converges to a potential of 11.58 eV, whereas photoionisation experiments give[50] 10.154 ± 0.01 eV. Vibrational and rotational analysis led Walsh and Warsop[51] to conclude that if the Q-branch frequencies of purely electronic transitions are considered, the Rydberg series including only three transitions (2168, 1434, and 1330 Å) converges towards a reasonable limit (10.1 eV). This is a series of transitions to the 3*s*, 4*s*, and 5*s* atomic states. The other two transitions at 1665 and 1286 Å can be combined into an $n \rightarrow n'p$ series, where n' is the principal quantum number, which takes the values 3 and 4. Vibrational analysis confirmed Walsh's theoretical prediction[52] that ammonia is planar in excited states. The strongest argument is provided by deuteriation experiments. The ratio of the w_{e_2} frequencies for ammonia and ND_3 is the same as the value calculated by the product rule if both molecules have D_{3h} symmetry and the vibration being considered belongs to class A_2''. Another important effect of excitation is an increase in length of the N–H bond. However, in the limiting case involving ionisation of the molecule the N–H bond should be shorter than in the ground state of the neutral molecule because the electron repulsion energy is decreased. Since we expect these changes to be continuous, we may think that, as the excitation energy increases in the sequence 3*s*, 4*s*, 5*s*.... $\dot{N}H_3$, the bond length increases more and more slowly and eventually starts to decrease. All this is difficult to reconcile with identity of configuration in all excited states, including the ground state of the $\dot{N}H_3$ ion†. The increase in length of the N–H bond was confirmed for the first excited state by Douglas[54] on the basis of an analysis of the rotational structure (1.08 Å as against 1.01 Å in the ground state). Douglas also showed that practically all electronic transitions in ammonia show signs of predissociation, and we must therefore assume strong interaction between singlet and unstable triplet states. It would appear that, somehow, there is no room for the $N \rightarrow Q$ transition in the range we are discussing. It is possible, however, that this transition falls into the long-wavelength region with alkylated ammonias.

Förster and Jungers[55] recorded the spectrum of methylamine and its deuterium derivatives in the region 2500–2000 Å. They observed a single electronic transition in this region, with a resolved vibrational structure, which can be described by the formulae

$$CH_3NH_2 \quad \nu = 41\,680 + \upsilon_1 \times 650 + 1000 \ cm^{-1}$$
$$CD_3NH_2 \quad \nu = 41\,780 + \upsilon_1 \times 600 + 870 \ cm^{-1}$$
$$CH_3ND_2 \quad \nu = 42\,540 + \upsilon_1 \times 515 + 1000 \ cm^{-1}$$
$$CD_3ND_2 \quad \nu = 42\,580 + \upsilon_1 \times 500 + 825 \ cm^{-1}.$$

Thus, the electronic transition giving rise to the band at the highest wavelength is modified by two vibrational frequencies. One of these is strongly affected by deuteriation at the nitrogen atom, the other by deuteriation at the carbon atom. This allows us to ascribe the frequency 650 cm^{-1} to

† See also Duncan's comments[53] in connection with the force constants of the bending vibrations of the planar and the pyramidal structure.

scissor bending vibrations of the N–H bond, and 1000 cm^{-1} to vibration of the methyl group. The corresponding frequencies in the ground state are 783 and 1127 cm^{-1}. Since no other frequencies appear in the vibrational structure, we are dealing with an $N \rightarrow R$ transition of non-bonding electrons to the nearest Rydberg state.

It would nevertheless be very surprising if no room were found for the $N \rightarrow Q$ transition among the long-wavelength transitions in alkylamines: the transition should be strong, since the transition moment in this case is large[56].

Tannenbaum and coworkers[23] have systematised the spectroscopic data on alkylamines (see Fig. 7). They found three broad overlapping bands in the range 45 000–65 000 cm^{-1}. The maximum of the band at the shortest wavelength lies outside the above limits with primary and secondary amines, and can be seen only in tertiary amines. The long-wavelength band, on the other hand, is visible only in primary amines: it strongly overlaps the middle band in secondary amines and is quite invisible in tertiary amines because of the intense middle band. Table 3 gives a fuller account of the influence of structure on the spectroscopic characteristics of an amine.

It can be seen from Table 3 that the long-wavelength band is not markedly affected by substitution. This confirms the suggestion that the long-wavelength transition is the first Rydberg transition of non-bonding electrons of the nitrogen atom to the 3s atomic state of nitrogen. The second transition in the amine series is sensitive to substitution, and can therefore be interpreted as an $N \rightarrow Q$ transition of the non-bonding electrons to the antibonding σ^*-orbital. The decrease in frequency of the second band maximum and the sharp increase in intensity upon alkylation suggest that in this case the n-electrons are excited to antibonding orbitals localised mainly at C–N bonds. Thus, as far as the second transition is concerned, we can envisage charge transfer of n-electrons, leading to a decrease in binding energy and dipole moment in the excited state of alkylamines.

There is another way of testing whether these bands have been correctly assigned to n-electron transitions. When alkylamines are dissolved in acids, the proton of the acid is taken up by the nitrogen, forming a salt and binding the n-electrons. Under these conditions, absorption in the region under discussion vanishes completely[23]. Dissolution of alkylamines in water or alcohols causes a characteristic short-wavelength shift in both bands, resulting from the formation of a hydrogen bond which lowers the energy of the n-electrons.

The relationship between the spectroscopic characteristics of alkylamines and the basicity of the nitrogen atom is particularly important. Fig. 8 shows the n-electron levels in the two lowest unoccupied orbitals relative to the first ionisation energy, taken as $E = 0$. It is evident that the energy of the n-electrons increases with alkylation. This is accompanied by a decrease of the frequency of maximum absorption for the $n \rightarrow \sigma^*_{C-N}$ transition. It is natural to assume that the basicity of the nitrogen increases in this series. Measurements of the ionisation constant confirm that the basicity increases from ammonia to secondary amines, but the measured basicity of tetriary amines turns out to be anomalously low. It is believed that the increase in basicity is cancelled out by steric hindrance to proton addition. Hence it is reasonable to distinguish intrinsic basicity, resulting from the electronic structure of the molecule, from the realisable basicity, which is determined by the steric factors of the reaction as well as by the electronic structure. It is obvious that the spectroscopic characteristics of an isolated molecule should correlate with the intrinsic basicity. This may be the reason for the lack of reasonable correspondence between the pK_B values and the spectroscopic characteristics of cyclic

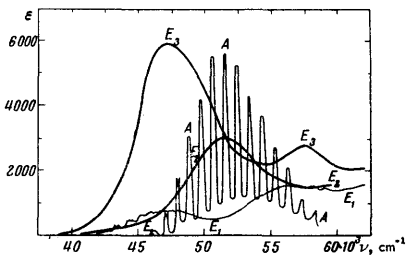


Fig. 7. Absorption spectra of gaseous ammonia (A), ethylamine (E_1), diethylamine (E_2), and triethylamine (E_3)[23].

TABLE 3. Positions of band maxima and transition intensities in amines.

	Ammonia	Methyl-amine	Dimethyl-amine	Trimethyl-amine	Ethyl-amine	Diethyl-amine	Tri-ethyl-amine
First band							
max. position, cm^{-1}	51500	46500	45000	44000	47000	(45000)	—
ϵ_{max}	5600	600	(100)	900	800	(300)	—
f	0.079	0.017	0.0017	0.016	0.019	(0.0028)	—
Frequency of 0–0 transition	46140	41690	—	—	42870	—	—
Second band							
Max. position, cm^{-1}	66000	57500	52500	50250	56500	51500	47250
ϵ_{max}	—	2200	3300	3950	1600	3000	(5900)
f	0.0095	0.084	0.10	0.13	0.050	0.10	(0.18)
Frequency of 0–0 transition	60135	(50360)	45870	—	—	—	—
Difference between maximum frequencies of first and second band, cm^{-1}	14500	11000	7500	6250	9500	6500	—

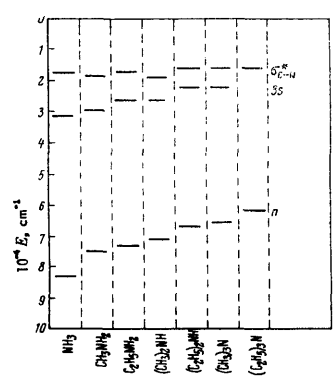


Fig. 8. Ground and nearest excited states of various aliphatic amines[23,26,27].

amines[57]. We should consider yet another factor which may limit the realisable basicity. The non-bonding electron pair of the nitrogen in amines occupies a hybrid orbital, formed by the superposition of s- and p-atomic orbitals. If the s-character is predominant, the resulting orbital is localised close to the nucleus and therefore resides within the van der Waals sphere of the atom. In the opposite limit, when the n-electrons are effectively in a pure p_Z state (e.g. in the pyridine molecule), the electron density distribution is more diffuse and part of the electron cloud can extend beyond the van der Waals sphere. However, the most directional orbital of the carbon atom will be an sp^3-hybrid bonding orbital. This maximises the probability of direct contact between the interacting species — the first step in the process of proton addition. In this sense, the hybrid strength or the value of the homopolar dipole moment is an important characteristic of the basicity[3]. Thus, we can say that the basicity of an amine should increase as the ionisation potential decreases and as the homopolar dipole increases. Information on the homopolar dipole may possibly be obtained by analysing the intensities of the $n \rightarrow \sigma^*_{C-N}$ transitions in different amines, assuming that the orbital of the n-electrons can be approximated by the combination $a2s + b2p$ and estimating the ratio a/b. In general, the intensity of $n \rightarrow \sigma^*$ transitions is surprisingly sensitive to structural changes. For example, axial or equatorial methyl groups at C_2 in cyclic amines cause absorption at practically the same frequencies, but the maximum intensities of the corresponding bands differ by a factor of three or four[58]. These anomalous changes in intensity suggest the presence of some specific intramolecular interactions (between the methyl group and n-electrons) which only an equatorial methyl group can undergo. Changes in ring strain also give rise to remarkable changes in band intensity. The oscillator strength for the $n \rightarrow \sigma^*_{C-N}$ transition[57] is 0.11 for piperidine and 0.05 for pyrrolidine. The intensities fall off appreciably when amines are dissolved in polar solvents, the effect increasing with the polarity of the solvent[57,58]. The bands also suffer a short-wavelength shift, which can be taken to indicate that n-electrons are involved in the transition.

The great sensitivity of the spectroscopic characteristics of amines towards structural changes in the molecules and towards the properties of the medium justifies our hope that spectroscopic studies will soon become a standard method of investigating this large and important class of compounds.

In conclusion we note that the tendency to form planar configurations in the excited state should persist in alkylamines. This cannot fail to have a significant effect, particularly in the isomerisation of cyclic amines, alkylation, and above all in the preparation of amides.

2. The Chromophore -O-

The chromophore -O- is common to water, alcohols, and ethers, but the attention given to these compounds by research workers has differed widely. About 90% of the papers on the electronic spectra of oxygen-containing saturated compounds relate to water. The remaining 10% are shared between ethylene oxide and all other alcohols and ethers. This state of affairs is quite reasonable, since water, being the simplest of all carriers of the chromophore, is the natural touchstone of theory. A preliminary idea of the absorption spectrum of water can be obtained by considering, in Mulliken's approximation, the molecular orbitals of the ground and of the lowest excited state. According to Mulliken[59,60], the ground state of the H_2O molecule, ignoring the $(1s)^2$ electrons, can be represented as follows:

Orbitals	$(2sa_1)^2$	$(yb_2)^2$	$(za_1)^2$	$(2xb_1)^2$	$^1A_1$
Localisation	O	HOH	HOH	O	
Ionisation potential, (eV)	32	18	17	12.7	

The second line shows the atom or group at which the state orbital is localised. The third line gives the energy of these orbitals or ionisation potential calculated in the zeroth approximation (except for the last). Thus, the highest orbital is the orbital of non-bonding $(2xb_1)^2$ electrons, which are localised mostly at the oxygen atom. The nearest excited state can be obtained from the ground state by moving one of the electrons $(2x)$ to the first Rydberg $3s$ atomic orbital of the oxygen, leading to the state $(2sa_1)^2(yb_2)^2(za_1)^2(2xb_1)(3sa_1)$. This state can be a triplet $^3A_1$ or a singlet $^1A_1$. The band observed[21] at 1667 Å can be assigned to a transition of the molecule to this state. The anomalously large width of this band is ascribed to predissociation, leading to $O + H_2$ $(^1\Sigma_g^+)$[59], but an alternative interpretation is possible[61]. The region below 1250 Å shows a series of absorption bands: these can be combined in a Rydberg series, whose members have a vibrational and rotational structure. By analysing the fine structure for H_2O and D_2O, Bell[61] was able to estimate the changes in bond length and bond angle accompanying excitation. Absorption at 1240 Å lengthens the O–H bond by 0.065 Å and increases the angle by 5.2°. The corresponding value for the band system at 1219 Å is 0.067 Å. Bell's analysis also shows that the oxygen n-electrons are bonding, whilst the 3s and 3p atomic orbitals are to some extent antibonding in the water molecule. Bell considers this to be the cause of the continuum at 1655 Å.

In the alkyl derivatives of water only the long-wavelength transition can be associated with the oxygen atom. Alkylation brings about several interesting changes. Replacement of hydrogen by methyl lowers the transition frequency by 5500 cm^{-1} and decreases the intensity by an order of magnitude. Increasing the length of the radical by one unit raises the intensity but has little effect on the frequency. Further increase in the length of the radical lowers the intensity again, but for a secondary alcohol with the same number of carbon atoms the intensity is higher. These changes are summarised in Table 4.

The intensity of this band begins to increase with chain length[30] in the spectra of alcohols with still longer straight-chain hydrocarbon radicals.

Replacement of hydroxylic hydrogen by an alkyl group causes a sharp increase in the intensity of the long-wavelength transition. Also, this transition is accompanied by

TABLE 4.[21]

Substance	Frequency, cm^{-1}	ϵ	f	Ionisation potential, eV
Water	60000	1480	0.0460	12.59
Methanol	54500	150	0.005	10.86
Ethanol	55100	320	0.008	10.50
1-Propanol	54600	240	0.006	10.15
2-Propanol	55300	620	0.015	10.09

a clear vibrational structure in the spectra of ethers. Methyl ether and ethyl ether show this behaviour most clearly (Fig. 9)[62]. The first band has structure with spacing of about 400 cm^{-1}, which can be ascribed to C–O–C bending vibrations in the excited state. The structure of the second band of methyl ether includes the frequencies 2100 and 1300 cm^{-1}, corresponding apparently to stretching and bending vibrations of the methyl group[22,62]. This means that the second band is generated by a transition to antibonding levels of the alkyl substituents, and not to oxygen atomic levels. The spectrum of ethylene oxide[63] is strongly displaced towards short wavelengths as compared with non-cyclic ethers. The bands of 1,3-dioxan occur at shorter wavelengths than those of 1,4-dioxan[64]. This allows us to conclude that in 1,3-dioxan the two oxygen atoms are independent. Another interesting observation is that absorption in 1,4-dioxan is stronger than in tetrahydropyran, but not by a factor of two, as would have been expected if the oxygen atoms had been independent (see Fig. 10). A vibrational band structure observed in cyclic ethers can be assigned to deformation of the ring

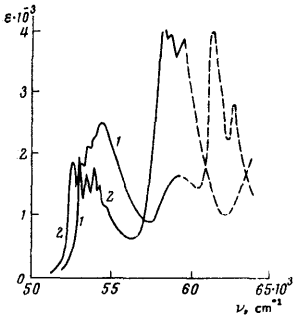


Fig. 9. Absorption spectra of gaseous ethyl ether (curve 1) and methyl ether (curve 2)[62].

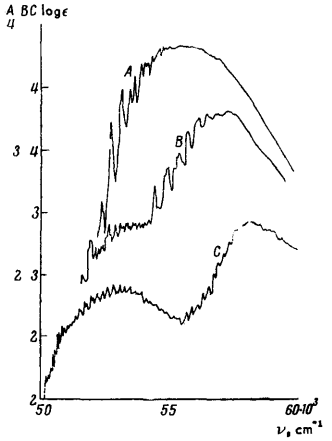


Fig. 10. Absorption spectra of gaseous 1,4-dioxan (*A*), tetrahydropyridine (*B*), and tetrahydrofuran (*C*)[65].

(frequencies in the region of 200 cm^{-1})[65,66]. The absence of one of the bands from the dioxan spectrum is ascribed to the higher symmetry of this compound. Furthermore, because of the presence of a centre of symmetry, the electronic band of 1,4-dioxan cannot show out-of-plane vibrations. The whole of the experimental data on the vacuum spectra of alcohols and ethers suggests that the long-wavelength bands are due to a transition involving non-bonding electrons. The $N \rightarrow V$ transitions in these compounds are concentrated in the region 500–1300 Å, and are weakly perturbed by the proximity of the hydrocarbon part of the molecule to the oxygen atom. In particular, the absorption by methyl, ethyl, n-propyl, and n-butyl alcohols has a maximum at 800 Å, and the intensity ratio of the bands is in strict proportion to the ratio of the number of C–H bonds (3 : 5 : 7 : 9), with a slight discrepancy in the case of n-propyl alcohol[67].

The identification of $n \rightarrow 3s$ and $n \rightarrow \sigma^*$ transitions is a controversial problem in saturated oxygen-containing compounds, as it is in aliphatic amines. This is because the first term of the Rydberg series is not described as a rule (see, for example, Walsh and Warsop[51]) by the Rydberg formula, and therefore the position of the first transition cannot be determined rigorously. The $n \rightarrow \sigma^*$ transition also is to be expected in the long-wavelength part of the spectrum.

Tsubomura[56] and others consider that the absorption spectra of water, alcohols, and ethers can be given a unified interpretation by postulating that: (1) the long-wavelength band is due to an $n \rightarrow \sigma^*$ transition where the n-orbital is a pure $2p$ atomic orbital of oxygen; (2) σ^*_{C-O} lies below σ^*_{H-O}; (3) the matrix element of the Hamiltonian for the σ^*-orbitals is small. If these assumptions are correct — and several arguments can be put forward in favour of the last two — the orbitals σ^*_{C-O} and σ^*_{O-H} in these spectra are non-interacting, but the σ^*-orbitals in water and in the ethers interact strongly owing to degeneracy. This explains why the first transition occurs at longer wavelengths in the ethers than in the alcohols. Calculation of the oscillator strengths for water, alcohols, and ethers, based on the same postulates, leads the authors to conclude that the values should decrease in the sequence water, ethyl ether, ethanol. The observed values are 0.084, 0.041, and 0.013 respectively. The qualitative agreement between calculation and experiment indirectly confirms the validity of the assumptions (including the first). Thus there are arguments in favour of both the $N \rightarrow Q$ and the $N \rightarrow R$ [62] interpretation of the long-wavelength transition. There can be no doubt, however, that the nature of this transition is molecular rather than atomic, since its characteristics are strongly dependent on the nature of the substituent groups. Thus it is meaningful to envisage some composite molecular orbital as the upper state of the first transition.

3. The Halogen Atom Chromophore

The electronic structure of the C–Hal bonds is very similar to that of the C–O bond. However, the observed absorption may lie in the far ultraviolet (70 000 cm^{-1} for CF_4 [20]) as well as in the near ultraviolet (40 000 cm^{-1} for CH_3I [7]). This absorption is due to transitions from n-electron levels. As in the case of alcohols, the intensity is low (see Table 5). The long-wavelength transition can be interpreted as an $n \rightarrow \sigma^*$ transition with the same justification as in the case of the oxygen-containing compounds.

TABLE 5.

Substance	λ, Å	ε	f	References
CF_4	1250	—	0.024	19
CCl_4	1740	2500	0.063	56
$CHCl_3$	1755	1000	0.026	56
CH_2Cl_2	1790	510	—	56
CH_3Cl	1690	370	0.01	56
CH_3Br	2040	200	—	7
CHI_3	3490	230	—	7
CH_2I_2	2915	1320	—	7
CH_3I	2575	365	—	7

TABLE 6.

λ_{max}, Å	Oscillator strength	Assignment		
		transition	symmetry of upper state	selection rules
1700	0.5	$\pi \rightarrow \pi^*$	$^1A_1$	allowed
1800	0.02	$n \rightarrow \sigma^*$	$^1B_2$	allowed
2800	0.0004	$n \rightarrow \pi^*$	$^1A_2$	forbidden by symmetry
3500	10^{-5}	$n \rightarrow \pi^*$	$^3A_2$	forbidden by symmetry and multiplicity

6. COMPLEX CHROMOPHORES

We have so far considered only chromophores which absorb in the far and vacuum ultraviolet. In this sense, the chromophores were simple ones. We shall now discuss the short-wavelength absorption of the familiar chromophores, which we shall term complex because they absorb both in the near and in the far ultraviolet. The simplest of these is the carbonyl group in saturated systems.

The C=O Chromophore

The simplest carrier of this chromophore is formaldehyde, whose ground state can be described as

$$[(1s_C)^2(1s_O)^2(2s_O)^2(\sigma_{CH})^2(\sigma_{CH})^2(\sigma_{CO})^2(\pi_{CO})^2(n_O)^2]\,A_1.$$

Transitions to the following excited states are possible:

$$\ldots(\pi_{CO})^2(n_O)(\pi^*),\quad A_2$$
$$\ldots(\pi_{CO})(n_O^2)(\pi^*),\quad B_1$$
$$\ldots(\pi_{CO})^2(n_O)(\sigma^*).\quad B_2$$

These transitions give rise to absorption bands at relatively long wavelengths. The next transition (towards shorter wavelengths) may be due to excitation of an electron from one of the bonding σ-levels, either σ_{CH} or σ_{CO}. An analysis of the symmetry of the initial and of the final state is needed to establish which of these transitions actually occurs, and with what intensity. Remembering that the formaldehyde molecule has C_{2v} symmetry, we can ascribe a definite symmetry also to the electronic configurations of the various states, which gives us a basis for applying the selection rules. These rules tell us that the $A_1 \rightarrow A_2$ transition is forbidden by symmetry, since all three components of the dipole moment of the transition are equal to zero, whilst the $A_1 \rightarrow B_1$ and $A_2 \rightarrow B_2$ transitions are allowed. If we allow also for spin conservation, the $^1A_1 \rightarrow {}^3A_2$ transition must have the lowest intensity, because the spin of the electron changes. Table 6 [1] lists the approximate positions of typical absorption bands for formaldehyde and symmetrical ketones, the oscillator strengths, and assignments of the bands to the appropriate transitions.

Formaldehyde, in particular, has the following set of absorption bands[7]: 3100 Å (ε = 5), 1749 Å (ε = 18000), and 1555 Å (ε = 23000). Their assignment presents no difficulty if we remember that none of these bands are caused by singlet–triplet transitions. With other symmetrical ketones, however, the situation may be more complicated, and further investigation is needed to distinguish $N \rightarrow Q$ and $N \rightarrow V$ transitions. In this respect, a characteristic property of the transitions, such as the shift in the maximum absorption frequency on going from the gas to a solution, can be of considerable help, if the ketone molecules become solvated by molecules of the solvent. Under these conditions the $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands are shifted towards shorter wavelengths, whilst the $\pi \rightarrow \pi^*$ band moves towards longer wavelengths[14,68].

Let us return to formaldehyde. The band at 1749 Å is diffuse, possibly as a result of predissociation. This band is fairly confidently assigned[69,70] to the $n \rightarrow \sigma^*$ transition. The band at 1555 Å has a clear vibrational structure whose spacing (1250 cm^{-1}) is probably related to stretching vibrations of the C=O group in the excited state[69]. This band is confidently assigned[70] to a $\pi \rightarrow \pi^*$ transition. Rydberg absorption begins at 1397 Å. The two series which are observed converge to an ionisation potential of 10.83 ± 0.01 eV.

Alkyl substituents shift the $n \rightarrow \sigma^*$ transition towards longer wavelengths (1749 Å for formaldehyde, 1816 Å for acetaldehyde, 1950 Å for acetone)[7]. The $\pi \rightarrow \pi^*$ transition does not show a definite trend (1555 Å for formaldehyde, 1650 Å for acetaldehyde, 1540 Å for acetone). The ionisation potential rises continuously with alkylation and with the length of the alkyl chain.

Acetone and other aliphatic ketones show yet another band in the 1500–1700 Å region, whose assignment raises special difficulties. Its intensity increases with the degree of branching at the α carbon atom[71,72], whilst at the same time the band shifts towards longer wavelengths. Holdsworth and Duncan[71] analysed the behaviour of this band, and concluded that a $\sigma_{C-C} \rightarrow \sigma^*_{C-O}$ transition with charge transfer was involved. This assignment is supported by two additional arguments. Firstly, if we arrange the molecular states of acetone and, say, ethane on a single energy scale (ethane being chosen as the simplest model of an alkyl substituent containing the C–C bond), we find that the transition $\sigma_{C-C} \rightarrow \sigma^*_{C-O}$ falls exactly in the region of 55000–60000 cm^{-1} (see Fig. 11). Secondly, the intensity of the $n \rightarrow \sigma^*$ transition decreases[71] in the aliphatic ketone series as the intensity of the transition under discussion increases. Similar effects are found in cyclic ketones[73,74].

The carbonyl group in amides, acids, and esters is no longer an isolated chromophore. The absorption spectra of these compounds cannot be treated as an additive combination of the spectra of the elementary chromophores. The spectrum of formamide, in particular, consists of a broad band with a maximum at 1717 Å and a weak band with a maximum at 1345 Å.[75] The broad band has a fine structure some of whose components can be combined into a Rydberg series converging at 10.2 eV. The spectrum of dimethylformamide is similar to that of formamide but displaced towards longer wavelengths[75]. Nagakura assigned

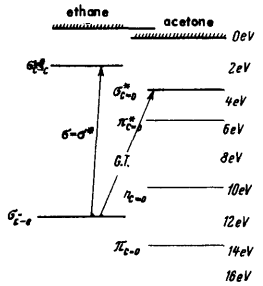


Fig. 11. Diagram of possible charge transfer in carbonyl compounds.

these bands[76] on the basis of the calculated electronic spectrum of formamide. Using the same calculation, the band at 1717 Å is shown to be associated with charge transfer and the band at 1345 Å with a $\pi \rightarrow \pi^*$ transition. Another paper by Nagakura and coworkers[77] gives the absorption spectra of formic and acetic acids and of ethyl acetate as well as the calculated electronic spectrum of formic acid. According to their calculation, the formic acid band with a maximum at 1590 Å is of $\pi \rightarrow \pi^*$ type to the extent of 46.2% and has 44.7% of charge-transfer character.

The  Chromophore

Aromatic compounds have attracted, not surprisingly, most of the attention of theoretical chemists. Benzene itself has undoubtedly been the object of practically every variant of the quantum-chemical methods. The basic difference between benzene and the chromophores discussed above is that the $2p\pi$ electrons in benzene cannot be localised at any individual carbon atom. All six $2p\pi$ electrons belong to the molecule as a whole. According to Pauli's principle, they should be distributed among three orbitals. Since these electrons are the least firmly bound in the molecule, their transitions should give rise to the long-wavelength part of the benzene spectrum. The simplest variant of the quantum-chemical calculation of the states of a π-electron system (the Hückel method) leads to a ground state in which the six π-electrons are distributed over two levels, the upper level being degenerate. The lower of the two nearest excited states is also doubly degenerate. Fig. 12 shows the energy diagram of the states and the shape of the corresponding molecular orbitals. The long-wavelength spectrum of benzene, reproduced in Fig. 13, is in fact determined by transitions to the

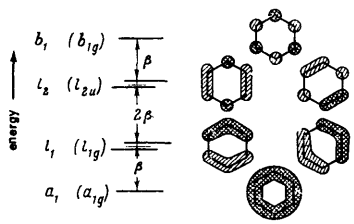


Fig. 12. Energy level diagram and orbital shapes in the benzene molecule[1].

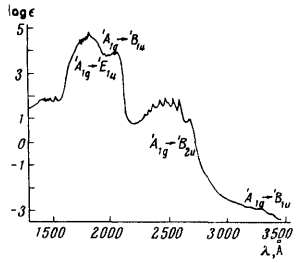


Fig. 13. Absorption spectrum of benzene[1].

two nearest excited states. The transition giving the longest wavelength is evidently forbidden on the grounds of change in multiplicity. The 2500 Å band is associated with the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition, forbidden by symmetry. The allowed $^1A_{1g} \rightarrow {}^1E_{1u}$ transition gives a band at 1800 Å, which is diffuse owing to predissociation. At still shorter wavelengths we find a fine structure caused by Rydberg absorption, and further still we find another Rydberg series[78]. Both these series converge to an ionisation potential compatible with the values obtained by other methods[26]. Platt and Klevens[79] studied the effect of alkyl substitution on the spectrum of benzene, and found that the 1800 Å band is gradually shifted towards longer wavelengths by alkylation in the sequence toluene, *o*-, *m*-, and *p*-xylene. The intensity of the observed band increases in the same order. The influence of lower symmetry on the spectrum of an aromatic system was investigated by El-Sayed[80]. As expected, the spectra of pyridine, pyrimidine, and pyrazine turned out to be more complex, but each of the changes, relative to the benzene spectrum, follows naturally from the lower symmetry which removes the degeneracy from an initially degenerate state. A review article by Stevenson[81] is devoted to the effect of chemical substitution on the electronic spectra of aromatic compounds, but, of course, it deals mainly with the near ultraviolet.

We have thus surveyed the spectra of practically all the most important organic chromophores. We must stress the fact that care was taken to avoid discussing substances in which several chromophores interact so strongly that they behave as a combined chromophore in which the characteristics of the components are lost. With this important exception, we may conclude that the chromophore concept remains a fruitful one in the far and vacuum ultraviolet. In other words, we can assign to each isolated functional group a fully characterised band or set of bands in the absorption spectrum which is an analytical criterion of this chromophore. Furthermore, we know in practically every case the qualitative and quantitative effect of the immediate environment, provided that it does not destroy the "isolation" of the chromophore being considered. The impact of intramolecular interactions on short-wavelength electronic spectra is undoubtedly of much greater interest, but unfortunately it is still too early to consider this topic: the fund of published data is too small. It should be remembered, however, that the far ultraviolet region is being intensively investigated at present, and the results should be available before long.

Our next question is: are the far and vacuum ultraviolet regions already of use to the chemist at the time of writing? In this connection we shall consider several examples of the practical application of short-wavelength electronic absorption spectra.

7. APPLICATION OF ABSORPTION SPECTRA IN THE FAR AND VACUUM ULTRAVIOLET TO THE ANALYSIS OF THE COMPOSITION AND STRUCTURE OF MATERIALS

The far and vacuum ultraviolet regions are the only source of information on electronic absorption spectra which can be applied to determining the composition of mixtures and the structure of compounds containing only saturated bonds (and which therefore do not absorb in the near ultraviolet and visible regions). Fig. 14 shows the spectrum of cholestanol[82]. The structural elements of this compound are cyclohexane and the hydroxy-group. Neither cyclohexane nor cyclohexanol have an absorption comparable to that of cholestanol. It follows that the excess absorption of cholestanol (as compared with cyclohexanol) can be ascribed to the quaternary carbon atom.

The isolated ethylene group gives an even more characteristic absorption. Cyclohexene and the sterols containing a cyclohexene ring (such as cholesterol and stigmasterol) give a band with a maximum at 180 nm (Fig. 15)[82]. Increasing the degree of substitution at the ethylene bond produces a monotonic shift of the band towards longer wavelengths, up to 200 nm.

The problem of the electronic structure of five-membered unsaturated heterocycles can be solved quite easily with the help of absorption spectra in the far ultraviolet.

Two structural variants of these compounds are possible. In the first the diene system does not interact with the heteroatom; in the second conjugation occurs between the n-electrons of the heteroatom and the π-electrons of the double bond. In the first case the absorption spectrum should be simply the sum of the spectra of the diene system and of the n-electrons. For example, the spectrum of thiophen should be indistinguishable from a superposition of the spectra of cyclohexadiene and tetrahydrothiophen. If the second variant is the correct one, the spectrum will have nothing in common with the superposition. Experiment settles the question unambiguously in favour of the second alternative. Thus, spectra in the far ultraviolet have confirmed the aromaticity of thiophen and selenophen[83].

Spectra in the vacuum ultraviolet have helped to characterise the main intermolecular interactions in solid ammonia, water, and methane. By comparing the spectra of the gaseous and of the solid compounds, it was found that hydrogen bonds play a very important role in the first two compounds, but are absent in the third[84].

Another very important aspect is that spectra in the far and vacuum ultraviolet provide information about a great

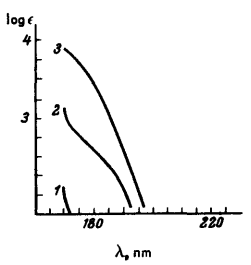


Fig. 14. Absorption spectra of cyclohexane (curve 1), cyclohexanol (curve 2), and cholestanol (curve 3)[82].

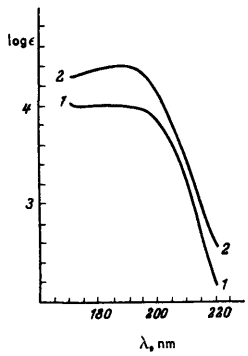


Fig. 15. Absorption spectra of cholesterol (1) and stigmasterol (2)[82].

number of molecular transitions. This adds substantially to the reliability of quantum-chemical calculations of the electronic structures and of the spectra themselves. The more we can check the predicted transitions the more realistic is the result of the calculation. Between three and five bands in the region 1500–2200 Å have been found in styrene, benzaldehyde, acetophenone, and benzonitrile. Satisfactory agreement with the observed spectra was obtained in a calculation which allowed for interaction between the ground state, a partially excited configuration, and a configuration including intramolecular charge transfer. The contribution of the charge-transfer configuration was 58% for styrene, and 68% for benzaldehyde (for the bands in the region of 2300 Å). The same investigation provided information about the electron affinity of the C=C and C=O groups.

In conclusion, we should mention another important field of application of the vacuum ultraviolet region: the determination of adiabatic ionisation potentials. In addition to the absorption spectra, which enable the Rydberg series to be observed and analysed, photoionisation spectra are also valuable in this context[26,27,86].

It should be understood that the applications listed here are only a very small fraction of the field and are given simply as illustration. The reader is referred to the bibliographic handbook published by Comstock in 1960 for a fuller review of the literature on this subject[87].

The analytical application of vacuum ultraviolet spectra in chemistry has been discussed in review articles by Kaye[88], and by Jones and Taylor[39].

References to the techniques and experimental methods can be found in the reviews by Price[89], Tousey[90], Lüscher[91], Inn[92], and Romand and Vodar[93].

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Institute of Chemical Sciences of the Academy of Sciences of the Kazakh SSR, Alma-Ata