

# VACUUM ULTRA-VIOLET SPECTROSCOPY

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The far ultra-violet spectral region, also known as the Schumann region, is roughly and conventionally defined as that lying between 2000 Å and the limit of the soft X-rays. The study of both emission and absorption radiations in this region has not been utilized much until relatively recently for several reasons. The first of these is probably that, until a few years ago, practically no spectroscopic apparatus for this region was commercially available. Anyone who desired to carry out research in this field had to build his own apparatus. Today the situation is completely changed, and many good instruments built in Belgium, Britain, France, Italy, Japan and the United States are now commercially available. It is highly probable that the situation with regard to instruments which prevailed until recently produced an exaggerated sense of the difficulties which exist in the utilization of such apparatus. During the present survey, we will take into consideration only the difficulties in utilizing this spectral region, since the operator is not concerned with the difficulties of instrument construction.

Difficulties encountered in vacuum ultra-violet spectroscopy can arise from

- (a) absorption of the radiations by atmospheric gases;
- (b) absorption of the radiations by the optical materials;
- (c) light sources;
- (d) detectors;
- (e) the necessity of working with gases or vapours.

The difficulty with atmospheric gases could be overcome by filling the optical path with some transparent gas; but it is better to eliminate all atmospheric gases, in particular oxygen, from the optical path. Absorption of radiations by oxygen begins to be noticeable at wavelengths slightly greater than 2000 Å (with the system of Schumann-Runge bands), and its intensity increases rapidly towards the shorter wavelengths. The different electronic transitions of oxygen give rise to many other absorption regions so that, in the presence of oxygen, the only portion of the Schumann region which is at all usable lies between 1100 and 1200 Å.

The second major component of the atmosphere, nitrogen, is almost transparent down to about 1000 Å. Below this wavelength, the absorption increases, and becomes very intense below 850 Å. Other minor atmospheric components (water vapour, carbon dioxide, rare gases, *etc.*) are present at such low partial pressures, especially after evacuation, that they may be neglected. Using the known values of the absorption coefficients of the various atmospheric gases, the losses in this region may be readily calculated<sup>1</sup>. Consider, for example, an optical path, 2 m long, of a spectrograph of medium dispersion equipped with a 1 m concave grating. In this case, a residual pressure of  $3 \times 10^{-3}$  mm Hg corresponds to an intensity loss of

about 30 per cent, which is the maximum loss that may be permitted for qualitative research. For quantitative work, in which the loss of radiation must not be greater than 1 per cent, the residual gas pressure should not exceed  $10^{-4}$  mm Hg. This low final pressure can be maintained in two ways:

(a) with an apparatus that, once evacuated, is really vacuum-tight (termed static vacuum);

(b) by continuous pumping (dynamic vacuum).

This second method is to be preferred because, in practice, a really vacuum-tight spectrograph is nearly impossible to construct; and, even if the joints and materials were truly vacuum-tight, a certain quantity of gas is slowly, but continuously, evolved by the walls of the apparatus, from all its micro-porosities, and from the photographic material. Thus, an efficient pumping train is necessary for the continuous removal of gases and vapours. Because of these circumstances, the equipment which is required is a little more complex than that for the usual spectrographic apparatus, and a certain amount of skill in high vacuum technique is demanded from the operator. Today, these difficulties may be easily overcome, thanks to modern standards of vacuum equipment and technique.

In an apparatus designed for the Schumann region, a "clean" vacuum, *i.e.* a vacuum really free from residues of mercury vapour and of organic matter, is particularly important. These vapours normally come from the greases needed for the lubrication of the driving axes of the external controls and from the fluids of the diffusion pumps. These materials should, therefore, be chosen very carefully so that their own vapour pressure is less than  $10^{-6}$ – $10^{-7}$  mm Hg. The pumping train itself must be equipped with a good cold trap (filled with carbon dioxide snow, or, better, with liquid air) rationally designed so that every trace of mercury and oil will be removed. A better method of obtaining the vacuum is to use a Roots pump, *i.e.* a completely mechanical pump, without vapours, capable of reaching a very clean vacuum rapidly without the need of cold traps. Such pumps are commercially available at reasonable prices. To obtain the desired vacuum rapidly, the tubing, connections and valves must be designed with optimal dimensions.

The absorption of radiations by optical materials is a severe limitation which must be taken into consideration when planning this type of research. There are no materials which transmit light with wavelengths covering the whole Schumann region: the best quality silica, only 0.1 mm thick, is transparent down to 1650 Å; good quality calcium fluoride or lithium fluoride transmit radiations with wavelengths as low as 1100–1200 Å; there is no material which is transparent beyond this limit. Thus, no prisms or focusing lenses can be constructed for use at wavelengths less than 1200 Å. Furthermore, it is not possible to make focusing lenses achromatic, as required for good, homogeneous illumination of the slit with light of adequate spectral range, or for uniform focusing of each wavelength on the detector. Consequently, prism apparatus of the classical type are relatively rare, spectrographs equipped with a concave grating being preferred. The first advantage of the grating instrument is that it introduces only one reflecting surface into the optical path. This surface has the double task of diffracting and focusing the radiations. This single surface is particularly important because the

reflecting power of suitable materials rapidly decreases as the wavelength decreases. A second advantage of the grating is its nearly linear dispersion, and strictly linear variation of the dispersion, so that measurements of wavelength are greatly facilitated. On the other hand, grating spectrographs have the disadvantage of a certain loss of light due to the diffraction on both sides of the incident beam, even with specially treated gratings. If the spectral field of interest is limited to the range above 1200 Å, it is still possible to utilize calcium fluoride or lithium fluoride windows to separate the light source from other parts of the spectral apparatus. Below 1200 Å, it is no longer possible to introduce any kind of windows, so that work on absorption is technically very difficult, if not impossible. Studies on molecular spectroscopy below 1200 Å are, therefore, virtually restricted to emission spectroscopy in completely windowless apparatus, in which the molecules under investigation are acting as their own light source.

The next point is concerned with the light sources, particularly for absorption spectroscopy. The ideal light source would be one giving a continuous spectrum with a constant background intensity. Again, until a few years ago, the only possibility of obtaining such a continuous spectrum in the Schumann region was represented by the Lyman continuum, produced by a strongly condensed electric discharge in a capillary. It is not necessary to enumerate all the difficulties arising from the use of this kind of light source. Fortunately, the situation is now much better, thanks to the discovery of the rare gas continua.

The fundamental work of Tanaka, Wilkinson and their associates<sup>2-6</sup> succeeded in making available as light sources emission continua that can be excited by simple methods. These have a sharp cut-off on their lower wavelength limit, and are also limited on the long-wave side, so that higher orders may be used with grating spectrographs without any danger of mutual overlapping of different orders. For instance, with only two light sources of the simple discharge type (with different electrical feeding), one filled with hydrogen and the second with krypton, it is possible to explore continuously the whole absorption spectrum from 1236 to 4000 Å, *i.e.* from the practical limit of transparency of lithium fluoride windows to the visible region. In fact, the krypton continuum extends from 1236 to 1700 Å, and the hydrogen continuum begins at about 1700 Å and extends to about 4000 Å. With a similar argon source, the region from 1067 to 1500 Å can be covered. Thus, if selected windows are available, no difficulty exists in investigating the absorption spectra of the great majority of neutral molecules down to their ionization potential, which normally lies between 1100 and 1200 Å. With neon and helium sources, and accepting the restriction that windowless apparatus must be utilized, the continua can be extended down to about 600 Å.

The next point is concerned with the detectors. As in other spectral regions utilized for investigating the molecular electronic spectra, they can be either photographic or photo-electric. Special sensitive plates are used in this region since the gelatin incorporating the silver bromide in the usual photographic plates is opaque for these radiations. For very careful work, *e.g.*, if a profile of a narrow line is desired, plates and films are now commercially available with very little gelatin and with the sensitive silver bromide

concentrated at the surface, so that they can be used down to the extreme limit of this spectral region.

Such plates and films are very delicate and must be handled very carefully: the slightest contact of the sensitive surface with any solid, even with very soft paper, leaves a trace that will be developed as a spectral trace and can give rise to considerable trouble in the evaluation of the spectra. This difficulty may be overcome with a little experience in dark-room technique. For all but very special work, it is possible to use normal photographic plates after sensitizing the surface with a suitable fluorescent compound. Sodium salicylate has proved to be among the best of these, and possesses many advantages: it can be coated on to the surface in a reproducible manner simply by using a 2 per cent methanolic solution; it is not decomposed by the radiations; its quantum yield of fluorescence is constant over the whole Schumann region; and it does not require the use of a special desensitizing bath before development. It can be concluded that the difficulties encountered with the photographic plate detector are practically the same as those for classical photographic spectrography.

Some attempts have been made to utilize photo-electric cells and ionization counters as detectors, and intensity measuring devices in conjunction with monochromators, but the results obtained are still poor. With closed detectors, difficulties arise from the opacity of the envelopes, and from the probable inconstancy of the fluorescent coating over long periods of time. On the other hand, when using open detectors, much higher vacua are required, the danger of poisoning the photosensitive layer becomes appreciable, and there are mechanical difficulties associated with sharp focusing on the exit slit. Because of these difficulties, photo-electric detectors are less commonly employed in this spectral region. Nevertheless, a number of commercial photo-electric monochromators is now available for this region.

The last point concerns the fact that investigations on molecular spectroscopy are practically restricted to the gas- or vapour-phase because the liquid or solid states permit investigations of only very thin samples. In the case of solid samples, it is difficult to prepare a sample of uniform thickness that may be accurately measured; for work on solutions, the only solvents partly transparent in this region are saturated hydrocarbons, such as very pure *n*-hexane, which, in thin layers (about 0.1 mm), transmit light down to a wavelength of 1700 Å.

Molecular spectroscopic investigations are, therefore, usually restricted to gases or vapours. The difficulties encountered are almost the same as for the spectroscopy of gases or vapours in other spectral regions. The equipment is not at all complicated. Even with the limitations mentioned above, much information can be obtained by vacuum spectroscopy which is useful for both molecular physics and chemistry.

To conclude this brief survey of experimental difficulties, it can be stated objectively that these difficulties are not really greater than those encountered in other fields of spectroscopy. It is, therefore, desirable that spectroscopists should direct more and more of their attention to this spectral region. This is especially so because we can often give a correct interpretation of the observed phenomena only when we can extend the spectral investigation at least down to the limit of the transparency of lithium fluoride.

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A few examples can be given to illustrate the usefulness of this region for solving various problems. The first is concerned with the correct interpretation of the electronic structure of some molecules<sup>7-10</sup>.

In principle, two different electronic structures can be assigned to some simple unsaturated heterocyclic molecules with a five-membered ring: a dienic structure without interaction between the  $\pi$ -electrons of the skeletal carbon atoms and the non-bonding electrons of the heteroatom, or a structure with homocyclic conjugation involving both the  $\pi$ - and the non-bonding electrons. To decide between the two possibilities we have to assume that, if the former structure were correct, we should find a spectrum resulting approximately from a superposition (more or less disturbed) of some bands originating from the dienic system and of some other bands originating from the non-bonding electrons. In other words, we should obtain a spectrum corresponding more-or-less to a superposition of the spectrum of a cyclic diene (*e.g.* cyclohexadiene; this would be better than cyclopentadiene to avoid any effects due to hyperconjugation of the methylene group) and of that of the saturated parent molecule containing the same heteroatom. The thiophene spectrum should then be similar to the superposition of the cyclohexadiene and tetrahydrothiophene spectra. However, if the second hypothesis is the right one, we should obtain for thiophene a spectrum completely different from the superposition discussed above. The same argument can be developed for selenophene. Even a superficial comparison of the thiophene and selenophene spectra with those of the corresponding saturated compounds shows that the spectra of the unsaturated compounds cannot be considered as a superposition of the spectra of cyclohexadiene and of the corresponding saturated compound. We are forced, therefore, to assign to the unsaturated compounds a cyclic conjugation similar in some aspects to that of benzene. Now, if we carry out a first approximation calculation with the LCAO-MO method of the excited levels of these unsaturated molecules, including more than the first excited level, we find that the results are confirmed by the experimental findings<sup>10,11</sup>. This confirmation is only possible because the spectra in the Schumann region, covering more than one electronic transition, are available.

Another very fruitful field of research in this region is represented by the possibility of determining ionization potentials of molecules, either photographically by extrapolating the Rydberg series, or by attaching to the exit slit of a vacuum monochromator a suitable ionization chamber<sup>12-14</sup>.

A vacuum monochromator is clearly superior to an accelerated electron source in producing monoenergetic beams whose energy can be very accurately measured. The determination of ionization potentials can, therefore, be carried out more accurately by photo-ionization than by electron impact, even if the focussing on the exit slit of the monochromator is not particularly sharp. On the other hand, when measuring ionization potentials by extrapolation of the Rydberg series, the spectroscopic method is still superior to the electron impact method, even if the spectral lines sometimes become broader and more diffuse or if the Rydberg series are not very long.

Another good example of what can be achieved by vacuum spectroscopy is the thorough investigation of the NO and NO<sup>+</sup> spectra, by means of which a

very interesting perturbation among different electronic states, caused by crossing of their potential curves, can be interpreted<sup>15-19</sup>. The results obtained in this research can, of course, be used as a guide for other similar investigations.

Recently, the spectra of thin layers of ice, solid ammonia and solid methane have been investigated in the Schumann region, and compared with the gas spectra<sup>20</sup>. As a result, it can be said that strong hydrogen bonding is highly probable in solid ammonia and ice, but not in solid methane.

Some exocyclic ketones have been investigated in this region<sup>21</sup>, giving evidence of  $n \rightarrow \sigma^*$  transitions and of transitions attributable to  $\sigma$ -electrons. In general, it is to be expected that the broad and very little explored field of the  $\sigma$ -transitions can be opened up purely by investigations in this spectral region.

Other results of vacuum spectroscopy have been summarized recently in a number of good reviews<sup>22-24</sup>, and in a very good bibliography<sup>25</sup>.

In conclusion, it can be said that the results of spectroscopic research in this field are often of the same type as those obtained from other spectral regions in which molecular electronic spectra can be observed. However, such problems as transitions involving  $\sigma$ -electrons, and the determination of ionization potentials, can be investigated only in this region. The combination of near ultra-violet and vacuum ultra-violet spectroscopy renders possible a plausible interpretation of the observed phenomena, such as was illustrated above for two heterocyclic compounds, because the availability of more spectral data pertaining to different electronic transitions permits a reliable comparison with the results of theoretical calculations.

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