

86

Topics in Current Chemistry

Fortschritte der Chemischen Forschung

Spectroscopy

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Spectroscopy



Springer-Verlag
Berlin Heidelberg New York 1979

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ISBN 3-540-09462-8 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-09462-8 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data. Main entry under title: Spectroscopy. (Topics in current chemistry ; 86) Bibliography: p. Includes index. 1. Spectrum analysis – Addresses, essays, lectures. I. Series. QD1.F58. vol. 86 [QD95] 540'.8s. [543'.085]. 79-16331

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Typesetting and printing: Schwetzingen Verlagsdruckerei GmbH, 6830 Schwetzingen. Bookbinding: Konrad Tritsch, Graphischer Betrieb, 8700 Würzburg
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Photochemistry and Spectroscopy of Simple Polyatomic Molecules in the Vacuum Ultraviolet

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1 Introduction

The distinction between the ultraviolet and the vacuum ultraviolet regions is essentially terrestrial, arising from the unique planetary atmosphere we still (thankfully) enjoy. This distinction has, however, a spectroscopic quality as well, since excitation in the vacuum ultraviolet explores the energy range from intravalency shell transitions to photoionization thresholds and beyond. Any attempt to describe the nature of the primary photochemical process must begin with the characterization of the excited state initially populated by light absorption, and in consequence spectroscopic considerations will be of central importance in this review. Transitions which lie at energies below the first ionization limit may be intravalence and/or Rydberg in nature, and this aspect of the characterization is a problem which exercises theoreticians, spectroscopists and photochemists alike. In considering photochemistry, the utility (and limitations) of electronic state correlation diagrams in rationalising experimentally observed branching ratios as a function of the exciting wavelength will be emphasised, but the more important information concerning the details of potential energy surfaces over which photodissociation proceeds is only just beginning to appear. The discussion will stop short of photoionization processes, except where these compete against dissociation to neutral products or help in the understanding of electronic transitions in the vacuum u.-v.

Apart from its intrinsic interest, the investigation of photochemical processes in the vacuum u.-v. is of much value in relation to other studies, for example, the determination of bond dissociation energies, the molecular dynamics of photodissociation, the kinetics of electronically excited atomic and molecular species, the photochemistry of planetary atmospheres, and the development of chemical laser and laser amplifier systems based on metastable products of vacuum u.-v. photodissociation. There is a great deal of current interest among plasma physicists in the use of rare gas-metastable atom exciplexes, derived from O (1S), S (1S) and Se (1S), as energy storage media in high-power gas laser amplifier systems. The variety of applications will become apparent as the review progresses. It is not intended to be a comprehensive catalogue, however, but rather an extended essay discussing in depth the spectroscopy and photochemistry of a representative sample of simple polyatomic molecules. We feel this is a more valuable exercise than the listing of a large number of systems at a relatively superficial level.

The review was completed in June 1978 and covers literature published up to March 1978; some earlier reviews and monographs are listed¹⁻²⁵ to provide leading references.

2 The Nature of Molecular Electronic States Populated in the Vacuum Ultraviolet

The vacuum u.-v. region begins at photon energies around 600 kJ mol^{-1} (6 eV), sufficient to excite electronic transitions in all but the very simplest of molecules. The

initial semantic problem to be overcome concerns the language used to define the "nature" of the photoexcited state. This may be based on an operational, experimental description which follows an analysis of the absorption spectrum, or it may be a theoretically based description which follows an analysis of the results of molecular orbital/configuration interaction calculations. In developing a proper understanding of the character of the photoexcited molecule, each approach borrows from the results of the other until the two types of description converge.

The most important operational description in the vacuum u.-v. region identifies "Rydberg" transitions on the basis of two criteria.

- (i) Their membership of a well-characterised Rydberg series with term values

$$T_n = \text{I.P.} - \nu_n = \frac{R}{(n - \delta)^2} \quad (1)$$

where I.P. is a molecular ionization potential (normally obtained from the photoelectron spectrum), ν_n is the frequency of the absorbed photon, R is the Rydberg constant, n is an integer and δ is the quantum defect. The magnitude of δ reflects the degree to which the upper orbital penetrates the molecular core: increasing penetration increases the electron binding energy and hence the term value T_n . It also reflects departure from simple H-atom behaviour and varies with the "quantum number l ". Typical values are $\delta(ns) \sim 1$, $\delta(np) \sim 0.6$, $\delta(nd) \sim 0.1$ for Rydberg states when $l = 0, 1, 2$, respectively (but see later discussion).

- (ii) Rydberg excited states are highly sensitive to external perturbation, e.g. collisional broadening under the influence of high pressures of inert diluent gases, because the large volume of the Rydberg orbitals allows substantial electron density in regions remote from the molecular core. Robin in particular has exploited the onset of pressure broadening as a diagnostic experimental method¹⁾.

Theoretical descriptions measure the degree of Rydberg and/or intravalency shell character in the upper electronic state by

- (i) assessing the effect of adding long-range Rydberg functions to the basis set,
- (ii) considering the LCAO expansion of the excited molecular orbital and calculating its Coulomb integral (as a measure of diffuseness), and
- (iii) comparing SCF/CI predictions for the electronic state energy with that observed experimentally²⁶⁻²⁸⁾.

However, as later discussions will indicate, the molecular orbital character may change dramatically with changes in the molecular geometry, particularly as the molecule distorts along the path to dissociation, so that an electronic state initially of Rydberg character may subsequently become largely intravalence. Such changes will affect the contours of the potential surface over which the molecule moves as it evolves from its initial photoexcited state into the separating molecular fragments. Unfortunately, detailed knowledge of the geography of the potential surface, which is so important in any discussion of the molecular dynamics of photodissociation, is almost entirely unknown, (except to the molecule, which enjoys the privilege of exploring that unfamiliar terrain).

When the upper states possess Rydberg character, the electronic transitions populate molecular orbitals which are so large and diffuse that to a first approximation

they are centred on a molecular core which is "seen" as atom-like, so that the details of the molecular geometry exert only a minor perturbation on the orbital character. From the photochemist's point of view, the larger the volume of the Rydberg orbital, the less influence it will have on the molecular bonding; thus the photoexcited molecule will tend to an equilibrium geometry characteristic of the molecular ion. It might then be supposed that, unless the ion is unstable with respect to dissociation, the population of states with a high degree of Rydberg character would not be expected to lead to direct dissociation. In conformity with this, it is often found that Rydberg transitions exhibit sharp spectral features, especially when the originating orbital is non-bonding in character (e.g. the transition $5pe \rightarrow 6sa_1$ ($\tilde{B}^1 E \leftarrow \tilde{X}^1 A_1$) in CH_3I , largely localised on the I atom). In some instances, the sharp structure may even include resolvable rotational features, even though neighbouring transitions are wholly diffuse or at best have ill-defined vibrational band structure. A particularly dramatic illustration of this type of behaviour is provided by H_2O (and D_2O) (see Section 3.1); the first two electronic transitions each generate broad continua which reflect intravalence, antibonding character in the upper state, or the introduction of such character as the molecule moves on the upper potential surface, but another transition which is superimposed on the second continuum has a rotationally structured contour. The structure is sharp enough to display a reduction in the spectral line-width upon deuteration, associated, no doubt, with the change in the rate of radiationless transfer out of the bound Rydberg state into the underlying continuum (see Sect. 3.1). If there are large differences in the equilibrium geometry and force constants for the two states, Franck-Condon considerations may restrict the rate of predissociation from the Rydberg state.

A high degree of intravalence character can be expected when the electronic transition has a term value larger than that of the least energetic Rydberg transition in the atoms on which the molecular orbitals are centred. For example, it might be expected that the first continuum in the u.-v. absorption of H_2O , which has a term of 41800 cm^{-1} , would be largely intravalence in character, since the largest term value in the O atom is 33100 cm^{-1} , corresponding to the transition $2p \rightarrow 3s$. The broad continuum is believed to reflect the strong O—H₂ antibonding character of the orbital populated in the upper state (see Sect. 3.1.1). In contrast to a Rydberg state, the nature of the upper orbital has a major influence on the character of the photoexcited molecule, a feature that was first recognised and rationalised in Walsh's Rules²⁹.

Mixed Rydberg/intravalency character may be expected when the intravalency orbital has an energy close to that of an atomic Rydberg orbital, and the same symmetry. The mixing may depend on the molecular geometry and it will, in principle, generate a conjugate pair of excited states, one of which will emphasise Rydberg and the other, intravalence character. Transitions into the latter may not be readily identified if they produce broad continuous absorption underlying sharp, primarily Rydberg, transitions. These descriptions have been discussed at length by Robin¹ who has argued the case for the separate existence of these conjugate Rydberg/intravalency shell transitions in the "no-man's land" where the two extremes overlap. Higher Rydberg orbitals retain their purity since they lie too far above the valence energy levels for mixing to be significant.

2.1 Influence of the Molecular Core

In the lower lying Rydberg states, orbitals with $l > 0$ will be split by the asymmetry of the molecular core. The splittings decrease as n increases and the orbitals become increasingly diffuse; in a linear system, for example, the separate components $\lambda = l, l-1 \dots 0$ become nearly degenerate. Under these conditions, the Rydberg states form "complexes", e.g. the " p -complex" comprising $p\sigma$ and $p\pi$ states, or the " d -complex" comprising $d\sigma$, $d\pi$ and $d\delta$ states (see Ref.³⁰). In practice, there are several other interactions which may affect the energies and the character of Rydberg states and complicate the task of spectral analysis. These include

(i) Interactions between states differing in both n and l ; for example, an nd state for which the quantum defect $\delta \sim 0$ will be nearly iso-energetic with the $(n+1)s$ state, for which $\delta \sim 1$, since they will have very similar term values. If the two states have the same symmetry under the point group of the molecular core, they will interact strongly.

(ii) The electron spin coupling scheme may change as n increases, from the Russell-Saunders scheme when n is low, to separate core (Ω_c) – optical electron (ω), (Ω_c, ω) coupling when n is large. In the latter case the distinction between pairs of singlet and triplet states, whose energies are separated by the electron exchange integral

$$2K = 2 \langle \phi_C \phi_R | \frac{e^2}{r_{12}} | \phi_C \phi_R \rangle$$

disappears, since the overlap between the core orbitals ϕ_C and the Rydberg orbital ϕ_R becomes very small. A $\pi_C \rightarrow \pi_R$ transition in a linear molecule such as ICN, for example, would generate an ionic core for which $\Omega_c = \frac{3}{2}$ or $\frac{1}{2}$ and a Rydberg orbital

for which $\omega = \frac{3}{2}$ or $\frac{1}{2}$. Under (Ω_c, ω) coupling these will lead to two pairs of

states $\left\{ \left(\frac{3}{2}, \frac{3}{2} \right), \left(\frac{3}{2}, \frac{1}{2} \right) \right\}$ and $\left\{ \left(\frac{1}{2}, \frac{3}{2} \right), \left(\frac{1}{2}, \frac{1}{2} \right) \right\}$ separated by an energy close to the spin-orbit coupling in the molecular ion, while each pair is split further to generate ten states in all³¹. The correlations for this situation are represented in Fig. 2.1.1. When n is low and Russell-Saunders coupling prevails, the singlet transitions will be far more intense, but as n increases the "singlet" and "triplet" components will approach equal intensity, although the reducing overlap between the core and the Rydberg orbitals will lead to a decline in their net oscillator strength.

(iii) The degree of penetration into the molecular core, and hence the magnitude of the quantum defect δ , is dependent on the size and symmetry of the Rydberg orbital and the size and architecture of the molecular core. The more the Rydberg state is aware of its molecular parentage, the less will it conform to the simple, atom-like Rydberg formula. Strong mixing of intravalency and Rydberg character will lead to large departures from the latter behaviour; since this mixing may be prevalent in (but not exclusive to) the lower lying states, the first member of the Rydberg progression may often be out of step with the succeeding ones, though in view of the interactions

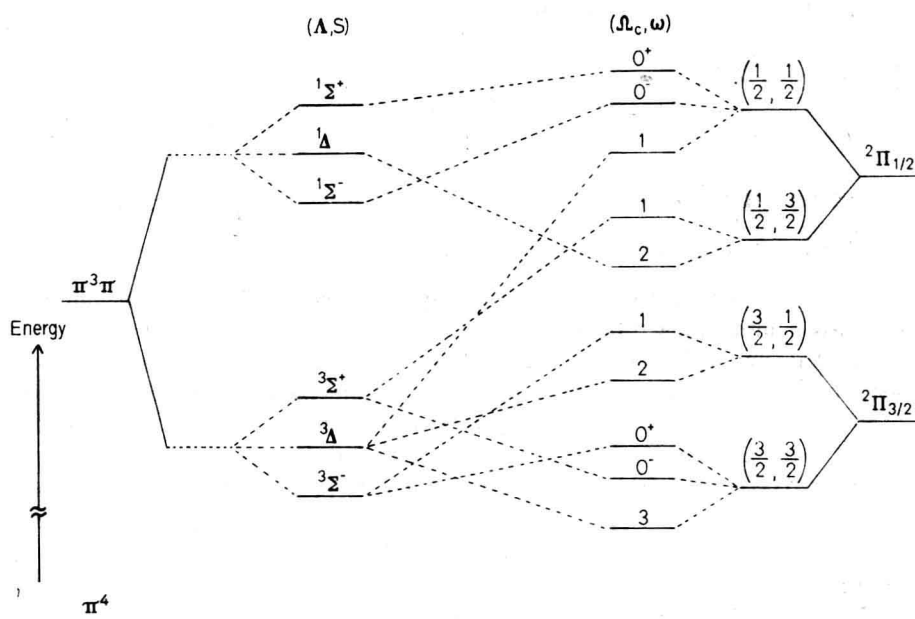


Fig. 2.1.1. Schematic correlation between (Λ, S) and (Ω_c, ω) coupling for the $\pi^3\pi$ configuration in a linear molecule

which can arise from other sources, generalisations should be treated with caution. Robin¹⁾ has presented a thorough discussion of the consequences of orbital penetration into the molecular core and of the influence of substituents on the values of δ in the ns Rydberg progressions (where the orbital penetration is greatest) in homologous series of organic molecules.

To summarise, it should be clear that the characterization of the lower-lying states of polyatomic molecules populated by absorption in the vacuum ultraviolet region is no easy task, either theoretically or experimentally. The transitions may generate broad continua which can only be assigned on the basis of theoretical considerations: furthermore, the orbital composition in the upper state may be strongly dependent on the interatomic distances. Where the transitions are structured, it is relatively rare for the rates of radiationless transfer to be slow enough to allow resolution of the rotational structure and hence allow the assignment of the orbital symmetry of the excited state. Assignments are generally achieved through comparisons with isovalent molecules and "united atoms", by appeal to theoretical calculations, and by comparison of observed and anticipated term values. A fourth route which is developing involves the analysis of photofragment excitation spectra, the polarization of fragment fluorescence, the predictions of correlation diagrams linking the excited parent molecular states with the observed photofragment states and the energy disposal amongst them. The remainder of the review is devoted to a survey of the inter-relation between the molecular spectroscopy of the parent molecule and its photochemistry in the vacuum ultraviolet. The discussion is limited to simple polyatomic systems.

3 Spectroscopy and Photochemistry

3.1 H₂O and D₂O

3.1.1 Spectroscopy

In its ground state the electronic configuration of the water molecule may be written

$$(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2; \tilde{X}^1A_1$$

Fig. 3.1.1 summarises the nodal properties of the valency shell orbitals, including the two virtual antibonding orbitals $4a_1$ and $2b_2$. These might be expected to contribute to the character of the lower-lying excited states, though the electronic absorption spectrum of water lies well in the vacuum u.v. region, and the term values of some of the lower-lying transitions are comparable with those for the $2p \rightarrow 3s$ and $3p$ transitions of the O atom. Much of the debate regarding the assignment of electronic transitions in H₂O (and D₂O) has centred on the relative proportion of Rydberg/intra-valency character in the upper states¹⁾. There is less argument over the description of the vacated orbitals since the "lone pair" electrons in $3a_1$ and $1b_1$ are much less tightly bound than the rest.

The absorption spectrum of H₂O is shown in Fig. 3.1.2: that of D₂O is broadly similar³²⁾. The first continuum, with $\lambda_{\max} \sim 167$ nm, was originally assigned by Mulliken³³⁾ to the leading member of the Rydberg progression $1b_1 \rightarrow nsa_1 (\tilde{A}^1B_1 \leftarrow \tilde{X})$,

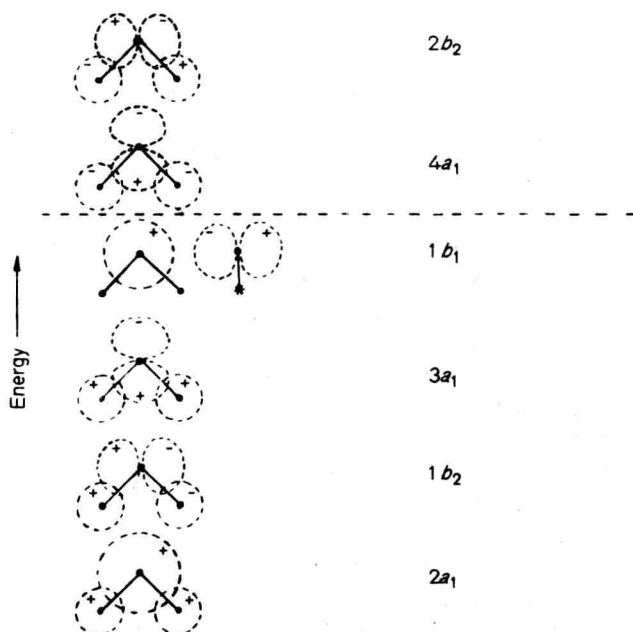


Fig. 3.1.1. Molecular orbitals of the ground electronic state of H₂O in terms of LCAO's. Orbitals are symmetrical with respect to the molecular plane except for the $1b_1$ orbital, where two views are given (after Herzberg, Ref. ³⁾)

$n = 3, 4, 5 \dots$; however, the excited states associated with higher members of the series^{32, 34}) and the corresponding molecular ion³⁵⁻³⁸) (in the 2B_1 state) are all bound rather than dissociative, with geometries and frequencies similar to those of the neutral molecule in its ground state³). McGlynn and co-workers, who have presented a thorough review of the vacuum u.v. absorption spectroscopy of water, discerned a very diffuse progression in the bending vibrational frequency ν_2' , superimposed on the broad continuum³²), with a value $\sim 20\%$ greater than the frequency in the ground state, ν_2'' . This behaviour is consistent with excitation of an electron from the non-bonding orbital ($1b_1$) into an upper orbital which encourages H-H bonding, i.e. one of symmetry a_1 , since this must allow the possibility of in-phase overlap between the $1s_H$ orbital functions. By definition, the Rydberg orbital $3sa_1$ is less likely to achieve this result than the intravalency shell $4a_1$ m.o., and McGlynn et al.³²) conclude that the continuum $\lambda_{\max} \sim 167$ nm is associated with a predominantly intravalency shell transition into a strongly bent upper state, $1b_1 \rightarrow 4a_1$ ($\tilde{A} {}^1B_1 \leftarrow \tilde{X}$). In support of this, they note that the photo-electron band associated with the ionization from the $1b_1$ orbital has a very different structure³⁵⁻³⁸) (see Fig. 3.1.3) implying that in the optical transition the geometrical changes are promoted by the character of the newly populated m.o., rather than by that of the vacated orbital. The inclusion of intravalency shell character in states which involve the $3sa_1$ or $3pb_2$ Rydberg orbitals can also be justified on theoretical grounds³⁹); the two O-H antibonding orbitals are of symmetry a_1 and b_2 (see Fig. 3.1.1).

In a linear configuration the $\tilde{A} {}^1B_1$ state correlates with one component of ${}^1\Pi_u$; the other component, 1A_1 , has been assigned to the second broad continuum centred around 128 nm, upon which is superimposed much more pronounced vibrational structure (see Fig. 3.1.4). Its appearance is similar to the $\tilde{X} {}^1A_1 \rightarrow {}^2A_1$ photo-electron band³⁵⁻³⁸) (see Fig. 3.1.3) suggesting excitation of an electron from the H-H bonding orbital, $3a_1$, into the non-bonding Rydberg orbital, $3sa_1$. This view is reinforced by the long progression in the bending frequency with $\nu_2' < \nu_2''$ and by the comparable values for the quantum defect δ in equivalent transitions in the te-

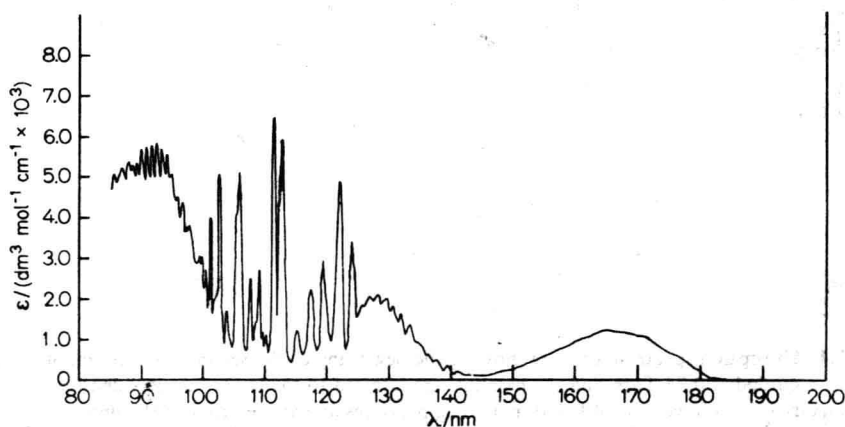


Fig. 3.1.2. Vacuum ultraviolet absorption spectrum of H_2O (after Watanabe and Zelikoff, Ref.⁸⁶)

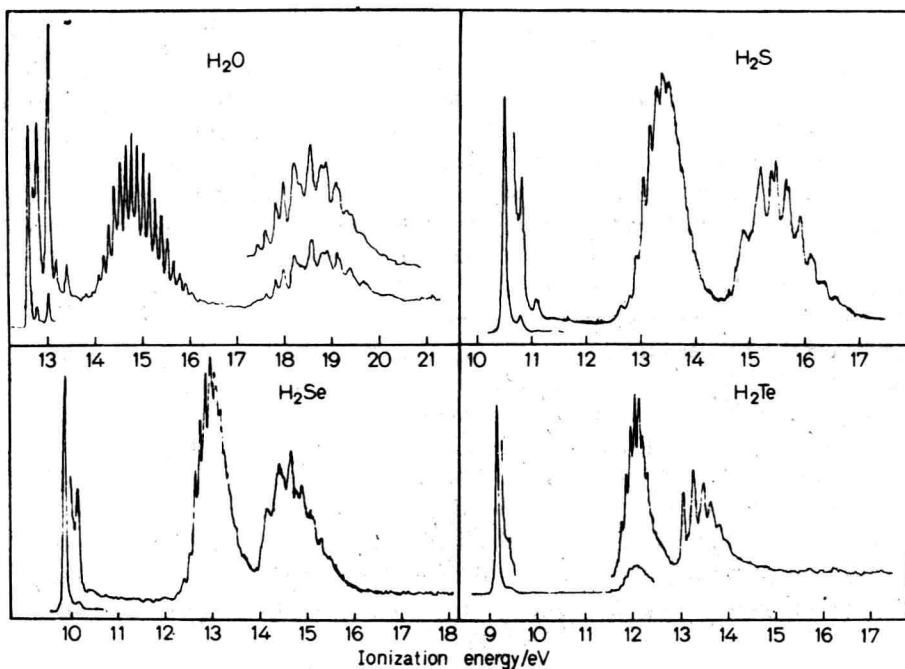


Fig. 3.1.3. He I photoelectron spectra of H_2O , H_2S , H_2Se and H_2Te (after Potts and Price, Ref. 36))

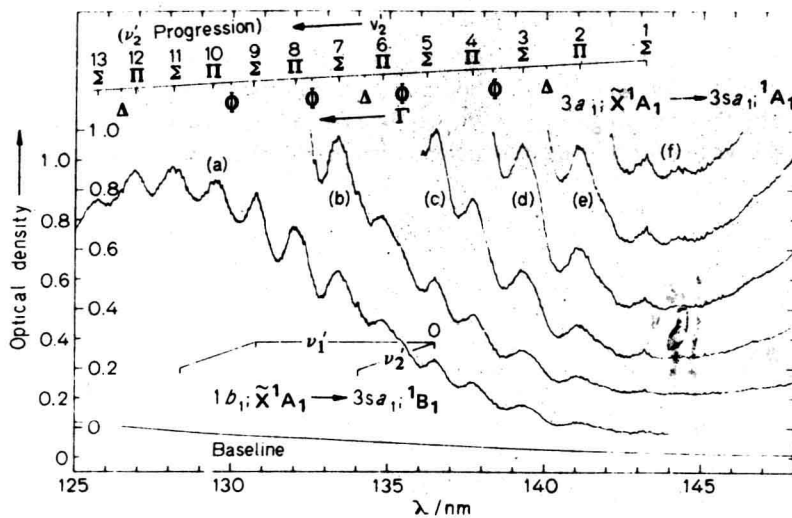


Fig. 3.1.4. Absorption spectrum of H_2O showing the beginning of the second continuum. Spectrum (a), recorded at 0.75 Torr, and the baseline, are referred to the lower "optical density" scale. Spectra (b) – (f) were recorded at increasing pressures and are referred to the upper "optical density" scale. The figure shows the proposed electronic and vibrational assignments of McGlynn et al. (after Ref. 32))