

REVIEW

STRUCTURES OF ELECTRONICALLY EXCITED MOLECULES

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(1) INTRODUCTION

When energy is taken up in the various degrees of freedom of a free molecule, the change of shape or structure (relative to a centre-of-mass fixed origin) as its translational, rotational or vibrational energy is increased, is in general small and gradual. Changes of nuclear energy are effectively irrelevant to chemical structure, but an increase of electronic energy in a polyatomic molecule can cause a distinct and abrupt change in its shape and dimensions. When one speaks of a particular molecular entity as having a particular shape, one should explicitly specify the electronic state to which one refers, i.e., usually the ground state. However, electronically excited states have important roles in the chemical reactions of many substances, particularly if the reaction is initiated photochemically. Thus, a knowledge of how the structures of electronically excited molecules differ from those of the ground state is essential to the understanding of those chemical reactions. We are concerned primarily with molecular conformations (i.e. bond lengths and bond angles) in various electronic states, and only secondarily with electron configurations (i.e., ordered assignments of electrons to atomic and molecular orbitals of definite spatial characteristics) in those simpler cases in which this practice is illuminating. In this article we first consider atoms as

vehicles for summarising some basic principles, then proceed to diatomic, triatomic and more complex polyatomic molecules. The molecules to be discussed have been selected both as instances of the kinds of phenomena generally occurring, and also to indicate some methods and their accuracies for such structure determinations. All energies and frequencies are expressed in wavenumber units ($\text{cm}^{-1} = 10^{-2} \text{m}^{-1}$); dimensions of atoms and molecules are expressed as lengths in Ångstrom units ($= 10^{-10} \text{m}$) and as angles in degrees. Force constants have units of $\text{hN}-\text{m}^{-1}$ ($= 10^5 \text{d}-\text{cm}^{-1}$).

(2) ATOMS

Experimentally, only energy differences are obtainable. Bohr's simple treatment of one-electron atoms gave a set of energy levels which correlated almost exactly with measurements from atomic spectra:

$$E_n = - \frac{k^2 m e^4}{2 \hbar^2} \frac{M}{m+M} Z^2 \frac{1}{n^2} \frac{1}{hc} .$$

E_n represents the energy of the atom (apart from nuclear and translational contributions) in a particular bound energy state; m and M are the electronic and nuclear masses, respectively; e , \hbar , c are the universal fundamental constants for electronic charge, Planck's constant of action ($\hbar = h/2\pi$), and the velocity of light, respectively; k represents the proportionality constant in the Coulomb law relation ($k = (4\pi\epsilon_0)^{-1}$); and Z represents the proton number of the nucleus. In the simplest Bohr theory the energy of a particular one-electron atom depended only on the (principal) quantum number n , which could take integral values greater than zero. From this theory one can also calculate the radius of the orbits, supposed circular:

$$r = n^2 \hbar^2 (m+M) (mMkZe^2)^{-1}$$

The information can be displayed diagrammatically for the hydrogen atom, as in Fig. 1. Recently, some radio frequency emission lines emanating from outer space have been interpreted as being of hydrogen atoms for which n is of the order of 100 for both states; the Bohr radius of the atom in such states is therefore of the order of 5000 Å.

Quantum mechanically, one calculates the same energies as from the Bohr equation above, but the orbits can be described much less definitely. The precise radius of a Bohr orbit is replaced by a radial distribution curve different for each orbital. An orbital can be described, following Mulliken¹, as "something as much like an orbit as is possible in quantum mechanics" or as a one-electron eigenfunction which is a mathematical solution of the appropriate Schrödinger equa-

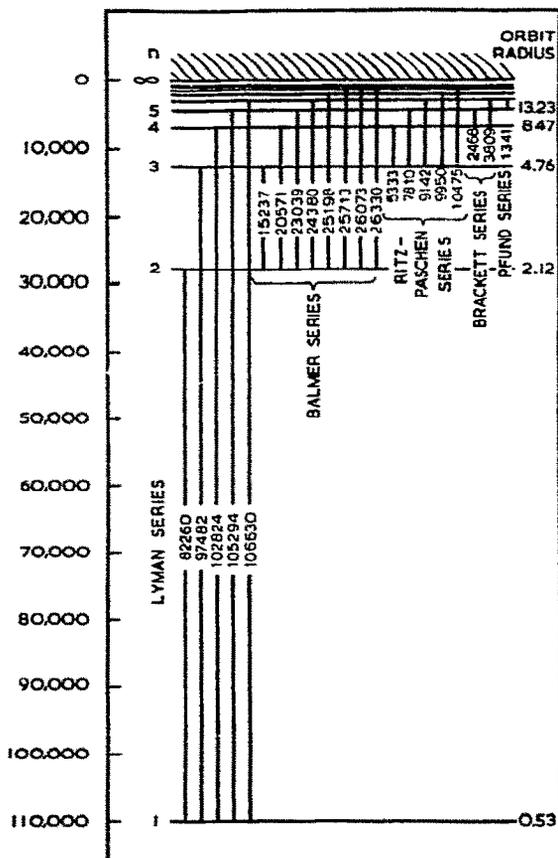


Fig. 1. Grotrian diagram of the hydrogen atom. The ordinate and the transition intervals are expressed in wave-number units (cm^{-1}), while the orbit radii at the right edge are in Angstrom units.

tion. A particular orbital is specified by three quantum numbers: n , l (related to the total orbital angular momentum) and m_l (related to a component of the orbital angular momentum); for one-electron atoms there is a possible $(2l+1)$ -degeneracy of energy levels of the same value of n , but for many-electron atoms without applied fields only the m_l -degeneracy remains. However, the maxima of the probability distribution functions are still approximately equal to the definite radii of the simple Bohr theory. For the ground state of the hydrogen atom, the predicted value of 0.53 \AA is satisfactorily close to half the collision diameter measured by gas kinetic methods. There seem to exist no comparable data for excited atomic states of one-electron atoms. However, we expect the theory to be adequate at least in the case of one-electron atoms, so the prediction that the size of these atoms depends on the square of the principal quantum number n is sufficient for the present purposes.

We have so far accepted that there are discrete energy states of atoms and

that such energy states are in general characterised by different probability distribution functions of electron separation from the nucleus leading to a different size of atom in those states. How do atoms proceed from one energy state to another? An electronic transition is said to occur whereby the quantum numbers specifying the occupied orbital change according to certain selection rules. The net result of the transition is that the electron is transferred from one orbital to another, usually with simultaneous absorption or emission of radiation. The energy change for the one-electron atom can be represented by the relation:

$$\Delta E = \nu = R(n_2^{-2} - n_1^{-2}).$$

This equation represents the difference of terms T , which can be represented in general by:

$$T = A - (Z - p)^2 R(m + a)^{-2}$$

in which A is the ionisation energy, Z is the proton number of the nucleus, p the number of core electrons, R is the Rydberg constant, m is a running number, and a is the quantum defect. In the case of the one-electron atom, $p = a = 0$ and m is identical to the quantum number n .

For many-electron atoms, the size of the atom or atomic ion (the so-called Van der Waals radius) is effectively determined by the outer-shell or valence electrons. All atoms, of course, are observed (time-average) to be spherical in shape in the absence of strong external influences. For many-electron atoms (and later for molecules) as for one-electron atoms we will employ the orbital approximation, in connection with the aufbau principle. In other words, we take the orbitals of the one-electron atom and add electrons to them in order of increasing energy to compose the atom of the required atomic number. The more readily observable electronic transitions in absorption are then considered to represent the excitation of valence electrons, i.e. those in orbitals belonging to the occupied shell of greatest n -value in the ground state being transferred to orbitals of successively increased n -values culminating in ionisation (complete separation of electron and remaining atom fragment). Sets of such transitions are generally called Rydberg series, for both atoms and molecules. Formally a transition such as that of the sodium atom, $3p \leftarrow 3s$ (in absorption), producing the well-known D-lines, is also a Rydberg transition but, for molecules, we will distinguish wherever possible between valence-shell transitions in which the principal quantum number of any of the atomic orbitals combined into the molecular orbitals does not change, and Rydberg transitions contrarily. We are concerned only with one-electron transitions in this article.

As a general conclusion, the effective size of atoms increases very rapidly with increasing principal quantum number of the excited valence electron.

(3) DIATOMIC MOLECULES

The excited electronic states of molecules, and the transitions involving them, will be discussed in terms of molecular orbitals, composed, in general, as linear combinations of atomic orbitals. Formally one ought to base discussion on true delocalised molecular orbitals, what Mulliken¹ calls spectroscopic molecular orbitals but, for our descriptive purposes, more localised molecular orbitals will also serve. To some degree of approximation, again acceptable for this account, we can distinguish among bonding, non-bonding and anti-bonding orbitals, both as the source orbital of a transition and as the destination.

As Herzberg has remarked², the study of the spectra of hydrogen (both atomic and molecular) has played a preeminent role in the development of our understanding of the structure of matter and of the universe. Thus it is appropriate for us to take hydrogen for our first example. The ground state of the hydrogen atom has the $1s$ -orbital singly occupied. To compose our molecular orbitals, we can take our $1s$ amplitude functions for the individual atoms to add constructively or destructively, thus yielding two molecular orbitals, one bonding and the other anti-bonding. Double occupancy of the bonding orbital by the two electrons provided by the atoms constitutes the ground state ${}^1\Sigma_g^+$ of the hydrogen molecule for which we can designate the spin orbital as $\sigma^1(1s+1s)^2(\alpha\beta-\beta\alpha)$. A spin-orbital describes not only the spatial characteristics of the state of the electron but also its spin state; the latter can play an important role in interactions between electrons as electrons of parallel spin state (i.e., both α or both β) are correlated further apart, in general, than electrons of antiparallel spin (one α and the other β), in accordance with Hund's rule. An excitation of one electron to the anti-bonding orbital renders an excited electronic state, ${}^3\Sigma_u^+$, of configuration $\sigma(1s+1s)^1\sigma(1s-1s)^1(\alpha\alpha, \beta\beta, \alpha\beta+\beta\alpha)$, in which α and β refer to spin states of quantum number $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$, respectively. Because of electron repulsion, the anti-bonding effect of one electron in the $\sigma(1s-1s)$ orbital always exceeds, for such a related pair of orbitals, the bonding effect of one electron in the $\sigma(1s+1s)$ orbital. Thus this excited state proves to be unstable with respect to dissociation into neutral atoms in their ground states. However, a very important application of this unstable state results from the emission continuum produced after electron bombardment of gaseous hydrogen serves to populate the ${}^3\Sigma_g^+$ state (counterpart of the ${}^1\Sigma_g^+$ state shown in Fig. 2) from which the radiative transition to ${}^3\Sigma_u^+$ occurs; hydrogen and deuterium lamps in commercial spectrophotometers function in the 27000–60000 cm^{-1} range by this mechanism.

If we permit the use of one excited hydrogen atom (or more), we can produce some stable excited states of the hydrogen molecule. The next available atomic orbitals, after $1s$, are the $2s$ and $2p$ orbitals; of increased principal quantum number, states formed with use of these orbitals are termed Rydberg states. From these orbitals, there are three possibilities for bonding: the $2s$ -orbital can partic-

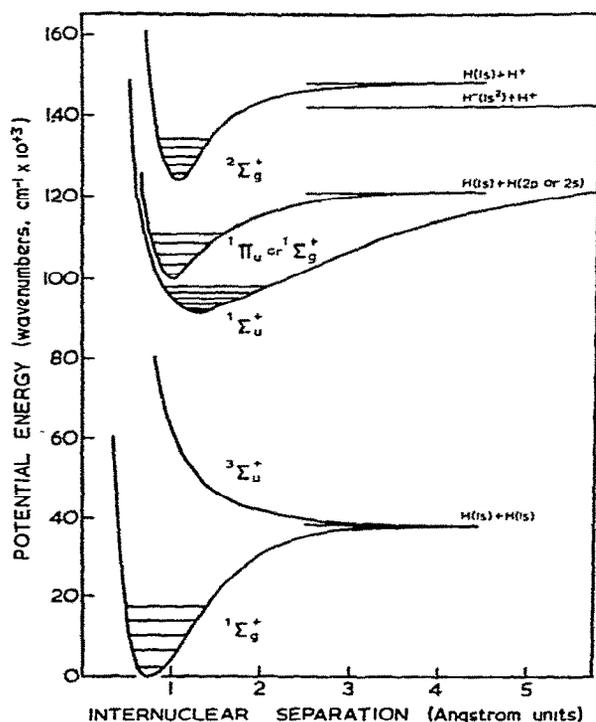


Fig. 2. Potential curves of some states of H_2 and H_2^+ . The sets of horizontal lines in the troughs of the curves represent vibrational levels, whereas the horizontal lines asymptotic to the curves at the right represent the dissociation limits. The ${}^1\Pi_u$ and ${}^1\Sigma_g^+$ states are effectively indistinguishable on the scale of this diagram.

ipate in only a sigma bond, but the $2p$ -orbitals can lead to either sigma or pi bonds depending on whether the p -orbital is directed parallel to the internuclear axis or perpendicular to it, respectively. The known stable singlet states which arise from these possibilities are included in Table 1. Data characterising the states, such as state symbol, equilibrium internuclear separation, harmonic vibration frequency and force constant, are specified in the Table, along with minimum energy relative to the ground state.

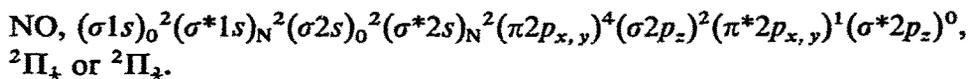
TABLE 1

DATA FOR SOME ELECTRONIC STATES OF MOLECULAR HYDROGEN, TAKEN FROM A MUCH MORE EXTENSIVE COLLECTION OF HERZBERG³

| Configuration | State | r_e | ω_e | k_e | T_e |
|----------------------------------|--------------------------------|----------------------|-----------------|-------|--------|
| $(\sigma_g 1s)^1$ | $(H_2^+) \quad {}^2\Sigma_g^+$ | 1.06 | 2297 | 1.57 | 124429 |
| $(\sigma_g 1s)^1(\sigma_g 2s)^1$ | ${}^1\Sigma_g^+$ | 1.01 | 2589 | 1.99 | 100063 |
| $(\sigma_g 1s)^1(\pi_u 2p)^1$ | ${}^1\Pi_u$ | 1.03 | 2443 | 1.77 | 100043 |
| $(\sigma_g 1s)^1(\sigma_g 2p)^1$ | ${}^1\Sigma_u^+$ | 1.29 | 1357 | 0.55 | 91690 |
| $(\sigma_g 1s)^1(\sigma_u 1s)^1$ | ${}^3\Sigma_u^+$ | $\rightarrow \infty$ | $\rightarrow 0$ | 0 | 38284 |
| $(\sigma_g 1s)^2$ | ${}^1\Sigma_g^+$ | 0.74 | 4395 | 5.73 | 0 |

Let us consider the data in Table 1 and the potential curves in Fig. 2. The binding in the excited states, as indicated qualitatively by the force constant, is much less effective than in the ground state. The minima in the potential curves are usually more shallow, and the bond lengths usually greater. (The equilibrium internuclear separation and equilibrium force constant are in general valid bases of comparison as they are, apart from any slight residual effects, isotopically invariant. Of course the harmonic frequencies for the same isotopic molecule in various electronic states are directly comparable as well.) In the form of the attractive part of the curve the $^1\Sigma_u^+$ state differs markedly from the other curves because this is an ionic state ($H^+ H^-$). The attraction at large separations corresponds to the Coulomb potential whereas, for the atomic states (dissociating into neutral atoms as opposed to ions), the force of attraction is exponential in nature. At smaller separations, the ions can no longer be regarded as point masses, so repulsion between nuclei plays its usual role and a minimum in the potential curve results. The dissociation energy of this ionic state, 50242 cm^{-1} , exceeds that of the ground state, 38284 cm^{-1} . The other two listed stable excited states of the neutral hydrogen molecule, namely $^1\Pi_u$ and $^1\Sigma_g^+$, resemble the ground state of the hydrogen molecular ion H_2^+ , also listed for comparison. This phenomenon is quite general, but not invariable: Rydberg states resemble the ground state of the corresponding molecular ion formed on complete removal of the excited electron. The molecular orbital newly occupied as a result of a Rydberg excitation is generally so diffuse in nature, because of its size, that any bonding or anti-bonding effect is usually relatively slight. Thus molecular orbitals formed from extra-valence shell atomic orbitals might be considered to be non-bonding, in common with 'lone pair' orbitals in the valence shells and core or inner shell orbitals.

Another diatomic molecule for which abundant accurate data of many electronic states are available is nitric oxide, NO. This molecule is notable for other properties: although it is an odd molecule, i.e., one containing an odd number of electrons, it shows little tendency to dimerise, or even to disproportionate into molecular nitrogen and oxygen, relative to which it is thermodynamically unstable. Another feature which complicates the assignment of electron configurations to excited states of NO is the multiplicity of atomic states arising from the configurations of the unexcited atoms. Thus, the nitrogen atom configuration, $1s^2 2s^2 2p^3$, gives rise to three states 4S , 2D and 2P , and the oxygen configuration, $1s^2 2s^2 2p^4$, also leading to three states 3P , 1D and 1S ; the states 4S of N and 3P of O are the ground states of the atoms. One can postulate the following configuration of the ground state of the nitric oxide molecule:



In fact, two states result, depending whether the components of orbital and spin angular momentum along the internuclear axis are additive ($^2\Pi_{\frac{1}{2}}$) or subtractive

(${}^2\Pi_{\frac{1}{2}}$). Strictly, the latter state, although lying 123 cm^{-1} above the ${}^2\Pi_{\frac{3}{2}}$ state, ought not to be considered electronically excited as both states have the same orbital configuration. (In the compound symbols specifying the particular states, the superscripted numeral is essentially related to the number of unpaired electrons in the molecule, the Greek majuscule designates the character of the orbital angular momentum of all the molecule's electrons, and the following subscripted number or fraction is related to the total (i.e. spin plus orbital) angular momentum. Reference 3 defines these terms and details some technical applications. For the purpose of this article, the structural aspects are emphasised, and the symbols may be considered to constitute specifying labels of states, with additional significance for other purposes.)

Whereas for the hydrogen molecule the molecular states arising from the unexcited atomic states are only two in number, one stable and the other unstable, for nitric oxide there are many possible states, both stable and unstable, resulting from various combinations of the atomic states specified above. For some of the low-lying excited states of NO^{3-5} listed in Table 2, there is no general agreement on the molecular orbital configuration, but the states of the separated atoms have

TABLE 2

DATA FOR SOME ELECTRONIC STATES OF NITRIC OXIDE AND RELATED SPECIES³⁻⁵

| Molecule | Configuration | State | r_e | ω_e | k_e | T_e |
|----------------|------------------------------|-------------------------|-------|------------|-------|--------|
| N_2^+ | $\pi^4\sigma^1$ | ${}^2\Sigma_g^+$ | 1.12 | 2207 | 20.09 | 125650 |
| | $\pi^4\sigma^1\sigma^{*1}$ | ${}^1\Sigma_u^+$ | 1.45 | 752 | 2.33 | 104481 |
| | (Rydberg?) | ${}^3\Pi_u$ | 1.15 | 2035 | 17.08 | 89147 |
| | $\pi^4\sigma^1\pi^{*1}$ | ${}^1\Pi_g$ | 1.21 | 1692 | 11.81 | 69290 |
| N_2 | $\pi^4\sigma^2$ | ${}^1\Sigma_g^+$ | 1.09 | 2360 | 22.97 | 0 |
| | $\pi^4\sigma^1\pi^{*1}$ | ${}^1\Pi$ | 1.19 | 1609 | 11.39 | 148000 |
| NO^+ | $\pi^3\sigma^2\pi^{*1}$ | ${}^3\Sigma^+$ | 1.34 | 1170 | 6.02 | 126600 |
| | $\pi^4\sigma^2$ | ${}^1\Sigma^+$ | 1.06 | 2377 | 24.85 | 74757 |
| | $\pi^3\sigma^2\pi^{*2}$ | ${}^2\Pi_{\frac{1}{2}}$ | 1.42 | 1040 | 4.76 | 45958 |
| | | ${}^2\Pi_{\frac{3}{2}}$ | 1.42 | 1037 | 4.73 | 45922 |
| | $\pi^4\sigma^2(\sigma 3s)^1$ | ${}^2\Sigma^+$ | 1.06 | 2371 | 24.73 | 43966 |
| NO | $\pi^4\sigma^2\pi^{*1}$ | ${}^2\Pi_{\frac{1}{2}}$ | 1.15 | 1904 | 15.94 | 123 |
| | | ${}^2\Pi_{\frac{3}{2}}$ | 1.15 | 1904 | 15.94 | 0 |

been established; for instance, the ${}^2\Pi$ state dissociates into $\text{N } {}^2D$ and $\text{O } {}^3P$. The lowest excited state which has been definitely characterised is ${}^2\Sigma^+$ which dissociates into $\text{N } {}^4S$ and $\text{O } {}^5S$. The oxygen atom has the excited state, $1s^22s^22p^33s^1$; therefore ${}^2\Sigma^+$ is a Rydberg state. Comparison of ${}^2\Sigma^+$ with the ${}^1\Sigma^+$ ground state of the molecular ion NO^+ reveals incontrovertible similarities in bond length, harmonic frequency and force constant, as mentioned earlier for H_2 . In this case, the equilibrium internuclear separations of ${}^2\Sigma^+$ of NO and ${}^1\Sigma^+$ of NO^+ are smaller than that of ${}^2\Pi_{\frac{1}{2}}$, the ground state, and the harmonic frequency of vibration, and

consequently the force constant, are greater. These unusual effects reflect the occupancy in the ground state of an anti-bonding π^* -orbital. When that electron is either promoted to a non-bonding Rydberg orbital or removed completely, more effective net bonding is achieved. The ionisation energy of nitric oxide is unusually small, about 71800 cm^{-1} , for a similar reason.

Let us consider some molecules related to NO by successive electron removal. The ground state of NO^+ has already been mentioned. Table 2 includes two excited states of NO^+ in which an electron has been removed from either a π - or a σ -bonding orbital to the π^* -orbital last occupied in the ground state of NO. The force constants are reduced, the bond lengths increased, by comparison with the ground state of NO^+ . The ground state of N_2 is isoelectronic with that of NO^+ , so its properties bear comparison, and also those of N_2^+ which is known. The previously stated trends still apply: the equilibrium internuclear separation in the excited state changes to reflect the difference of bonding effect of the excited electron; Rydberg states resemble the ground states of the corresponding molecular ion. The phenomena shown in the diatomic molecules here selected as examples, occur generally in other diatomic molecules. Increasing the number of atoms per molecule beyond two necessitates the introduction of further effects than those already mentioned.

(4) TRIATOMIC AND TETRA-ATOMIC MOLECULES

First we consider some symmetric triatomic dihydrides, then some related molecules containing only one hydrogen atom. The most readily observable structural property of diatomic molecules which changes upon an electronic excitation is the internuclear separation between the two bonded atoms. For polyatomic molecules, not only bond lengths can change, but also bond angles. The change of an interbond angle is of course entirely equivalent to a change in internuclear separation of the nuclei of non-bonded atoms. However, the change in structure expressed in angular terms tends to be more enlightening from the point of view of valence theory. Both the dihydride and the monohydride examples in this section demonstrate striking angular changes as well as bond length variations among sundry electronic states.

Of the three molecules^{6,7} listed in Table 3, one is a stable diamagnetic species but the other two are reactive radicals in their ground states. The radicals are characterised by unpaired electrons, of essentially non-bonding nature, in their valence shells. Various electronic states are available for excitations, but allowed optical transitions are restricted according to certain selection rules. The electrons promoted to form, respectively, the $^3\Sigma_u^-$ and 1B_1 Rydberg states of CH_2 and OH_2 come from non-bonding orbitals in the ground state configurations, so no large changes in structure occur, but the bond lengths increase significantly,

TABLE 3

ELECTRONIC STATES AND STRUCTURES OF FIRST-ROW DIHYDRIDES^{6,7}

| XH_2 | State | r_{XH} | Angle | T_0 |
|-----------------|--|----------|-------|---------------|
| OH ₂ | ¹ B ₁ | 1.01 | 107° | 80625 |
| | ¹ A ₁ | 0.96 | 105° | 0 |
| | ² A ₁ | 1.00 | 144° | 10249 |
| NH ₂ | ² B ₁ | 1.02 | 103° | 0 |
| | ¹ B ₁ | 1.05 | 140° | $\chi + 7400$ |
| | ¹ A ₁ | 1.11 | 102° | $\chi < 8000$ |
| CH ₂ | ³ Σ _u ⁻ | 1.08 | 180° | 70634 |
| | ³ Σ _g ⁻ | 1.03 | 180° | 0 |

as shown in Fig. 3. The ¹B₁ and ²A₁ states of CH₂ and NH₂, respectively, are almost linear. In fact, with a few quanta of the bending vibration in those states, the molecule passes through the linear conformation during the oscillation

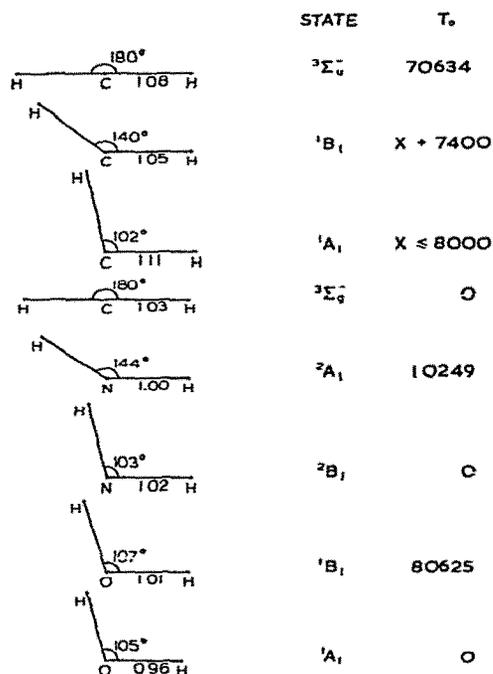


Fig. 3. Conformations of some dihydrides of C, N and O.

which is of comparatively large angular amplitude (in the vicinity of 100 degrees): thus CH₂ and NH₂ in those states are quasi-linear. There is only a small energy difference (denoted χ) between the ³Σ_g⁻ and ¹A₁ states of CH₂; the triplet state is of *less* energy due in part to the *lesser* repulsion of the odd electrons correlated apart because of their parallel spins. For the homologous SiH₂ radical⁸, only bent singlet low-lying states, ¹A₁ and ¹B₁, are known. As well as the forementioned

similarity between the 1B_1 and 2A_1 states of CH_2 and NH_2 , respectively, one can note the similarities of angle in the 1A_1 , 2B_1 and 1A_1 states of CH_2 , NH_2 and OH_2 , respectively; the electrons successively added to produce this series of dihydrides seem to have little effect on the shape of the molecules.

Another group of hydrides^{6,9} formed from first-row atoms is listed in Table 4. Unlike the ground state, the excited states of HCN are bent, but the ${}^1A'$

TABLE 4

ELECTRONIC STATES AND STRUCTURES OF RELATED HXY AND H_2XY MOLECULES^{6,9,10}

| Molecule | State | r_{XH} | r_{XY} | Angle | T_0 |
|-----------------------|----------------|----------|----------|-------------|-------|
| H_2CO | ${}^1A''$ | 1.09 | 1.32 | 116° | 28188 |
| | ${}^3A''$ | 1.09 | 1.31 | 114° | 25194 |
| | 1A_1 | 1.10 | 1.20 | 122° | 0 |
| HNO | ${}^1A''$ | 1.04 | 1.24 | 116° | 13154 |
| | ${}^1A'$ | 1.06 | 1.21 | 109° | 0 |
| | ${}^2A''$ (II) | 1.04 | 1.19 | 180° | 9294 |
| HCO | ${}^2A'$ | 1.15 | 1.18 | 123° | 0 |
| | ${}^1A'$ | 1.14 | | 141° | 65644 |
| | ${}^1A''$ | 1.14 | 1.33 | 115° | 54620 |
| HCN | ${}^1A^*$ | 1.14 | 1.30 | 125° | 52256 |
| | ${}^1\Sigma^+$ | 1.06 | 1.16 | 180° | 0 |

state is probably quasi-linear as for NH_2 above. When one electron is added to the basic HCN configuration it must enter an anti-bonding π^* -orbital in the ground state. By bending, the molecule can lose the anti-bonding effect at the expense of the bonding effect of the corresponding π -orbital (in the same plane). The electron promoted in HCN to produce a low-lying excited state will occupy the same orbital, so the molecule could have a bent conformation, as observed. The similarity between the first ${}^1A''$ state of HCN and the ground state ${}^2A'$ of HCO is striking, in support of this concept, as illustrated in Fig. 4. On the other hand, if the additional electron in HCO (exceeding the electron complement of HCN) is promoted, its anti-bonding effect can be decreased, and the linear conformation can be resumed. Once again the similarity in CH bond length and interbond angle between the ${}^1\Sigma^+$ state of HCN and the ${}^2A''(\text{II})$ state of HCO is remarkable. As the main anti-bonding effect applies mainly to the CN and CO bonds, their lengths increase in the excited states in both cases. One would expect Rydberg states of HCO to have linear conformations with bond lengths similar to those of the ${}^2A''(\text{II})$ state. When a further electron is added to HCO to produce HNO, according to the aufbau principle, its influence will reinforce that of the previous electron (added to HCN to produce HCO); therefore the interbond angles in the various states will in general be decreased by comparison with HCO, as observed. One would predict no linear conformations of Rydberg states of HNO. Although methanal (formaldehyde) is certainly not a triatomic molecule, it can

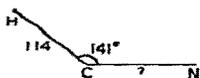
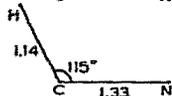
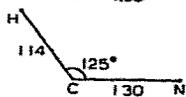
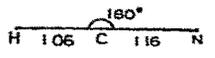
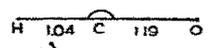
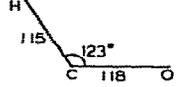
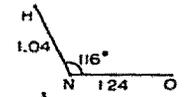
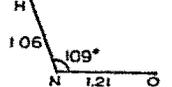
| | STATE | T. |
|---|--------------|-------|
|  | $^1A'$ | 65644 |
|  | $^1A''$ | 54620 |
|  | $^1A''$ | 52256 |
|  | $^1\Sigma^+$ | 0 |
|  | $^2A'(\pi)$ | 9294 |
|  | $^3A'$ | 0 |
|  | $^1A''$ | 13154 |
|  | $^1A'$ | 0 |

Fig. 4. Conformations of some monohydrides of C, N and O.

be related to HNO in that a proton placed in the nitrogen lone pair orbital in the molecular plane can be considered to lead to the electronic configuration of H_2CO . Thus the ground state of H_2CO has a planar conformation¹⁰. However, promotion of an oxygen non-bonding electron into the π^* -orbital will produce an effect analogous to the similar excitation in HCN: the molecular frame will lose its planar conformation. In the $^3A''$ state, the oxygen atom is situated 35° off the plane defined by the methylene group⁶; in the $^1A''$ state, the corresponding angle is 31° , as illustrated in Fig. 5. The effect of electronic transitions involving essentially only the XY atoms on the direction and length of the HX bonds is also noteworthy in all these HXY and H_2XY molecules.

(5) DETERMINATION OF STRUCTURES

Now that some instances of monatomic, diatomic and triatomic molecules have been presented, the determination of their structures can be briefly explained in that context. The only structural parameter which an atom can have is size because, in the absence of strong electromagnetic fields, it must be spherical in shape. In connection with the discussion of the hydrogen atom, allusion was made to an estimate of the size of the ground state derived from gas kinetic measurements. Such experimental information is available for many monatomic gases in

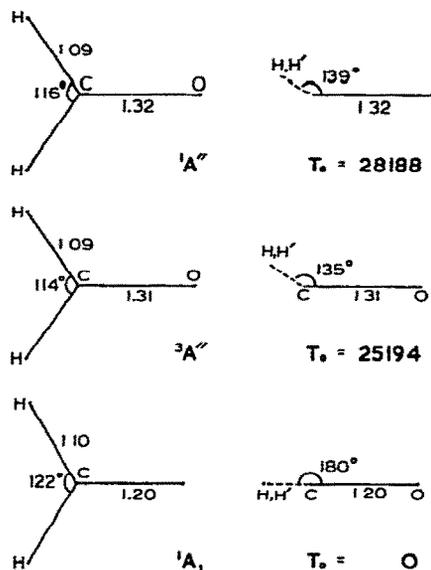


Fig. 5. Conformations of some states of methanal.

the ground electronic states, but for few, if any, excited states. In the case of one-electron atoms, in particular, the size of any electronic state may be estimated from the results of quantum mechanical calculations, but some criterion for relating size to total electron density at a particular radius from the nucleus is necessary. Approximate computations can also be made for more complex atoms. Thus, for excited states of atoms, we must in general, rely upon sizes derived theoretically rather than experimentally.

With molecules consisting of more than one atom, the size problem for excited states still applies. However, because nuclear amplitudes of motion are much smaller than electronic amplitudes, a different measure of molecular size and shape is available. The equilibrium separations between various nuclei can be expressed in either length or angular coordinates. For instance, the separation of the carbon and hydrogen nuclei in the 1A_1 state of methanal¹⁰ is quoted above as 1.10 Å and the angle between the two CH internuclear vectors is 116°. Thus the significant determination of the structures of molecules comprising two or more atoms is the establishment of magnitudes of internuclear separations. As with atomic sizes, these can be theoretically calculated, but the results are usually unreliable at the desired level of accuracy.

At the present time, therefore, we must depend mostly on experimentally derived structure determinations for the desired accuracy. However, the standard methods of structure determination are largely inapplicable for various reasons. The diffraction methods require fairly large concentrations, or at least large proportions, of these molecules to be in their excited state of interest. Even if large concentrations or proportions of molecules could be maintained in an

excited state by some pumping process, pure rotation or vibration-rotation spectra may still not be useful if the radiative lifetime of the excited state were of the order of vibrational periods. In the latter event, the quantum mechanical indeterminacy principle would mean that only rotationally diffuse spectra could be obtainable.

The only really general method for attaining accurate structure determinations of molecules in excited states applies the very mechanism of formation of these excited states (but not the only formation process). The formation of an excited state from the ground state involves, according to the orbital approximation used here, the transfer of an electron from one orbital to another of greater energy. This excitation process can be effected by absorption of light of accurately measurable wavelength. The corresponding de-excitation processes produce emission spectra. Such electronic transitions may be accompanied by vibrational and rotational transitions. If discrete rotational fine structure can be detected and assigned, a rotational analysis may be effected of which the basic principles are identical to those employed in analysing the rotational structure associated with the fundamental vibration of a light diatomic molecule, e.g. HCl. Then accurate bond lengths and bond angles can be calculated directly from the rotational constants, supplemented by these quantities for isotopically substituted molecules as required. The excited state structures of all molecules so far mentioned have been determined in this way. As the number of atoms in a molecule increases, the difficulty of deriving rotational constants of the (physically unattainable) equilibrium vibration-less state increases much more rapidly. Therefore in larger molecules we must often be reluctantly content with the approximate structural parameters pertaining to the state of zero-point energy; these are not quite isotopically invariant. Even if discrete rotational structure cannot be analysed or even detected (the diffuseness perhaps resulting from predissociation), band contours can provide accurate data which can be interpreted to produce rotational constants of useful accuracy in some cases. In the absence of such rotational contour data, relative vibrational intensities in the band systems of an electronic transition can still be used to provide estimates of changes in structural parameters during the transition between the two electronic states but the accuracy is further decreased. Finally, the nature of the vibrations appearing in progressions (series of bands of similar separation) accompanying electronic transitions can furnish clues to the change of shape of the molecule between the two states. Applications of these methods are demonstrated in the remaining sections of this article.

(6) SOME CARBON HYDRIDES

Methane alone of the simplest hydrocarbons has no well characterised excited states because of continuous absorption. Ethene and ethyne have absorption spectra amenable to structural deductions.

Ethyne (or acetylene) shows an abundant spectrum⁶ in the region of 44000 cm^{-1} , rotational analysis of several bands of which proves the structure of the excited state to be a bent, centrosymmetric trans conformation. The electronic transition involves the excitation of an electron from a strongly bonding π -orbital to a strongly anti-bonding π^* -orbital. Occupancy of the latter causes such an unfavourable anti-bonding effect that, in order to reduce the repulsion, the molecule bends within one plane such that the bonding and anti-bonding orbitals singly occupied become non-bonding 'lone-pair' orbitals. The electronic transition is therefore accompanied by a long progression (a series with numerous members) in a bending vibration. The excited conformation has CCH interbond angles of 120° , as illustrated in Fig. 6, and is therefore similar to the ground state

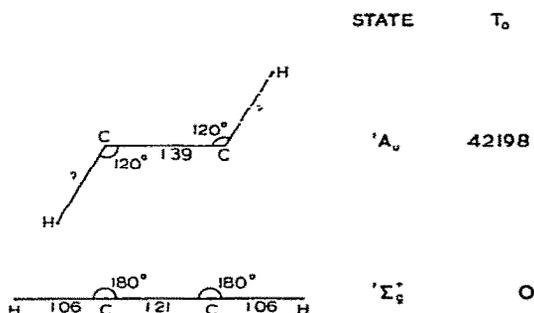


Fig. 6. Conformations of two states of ethyne.

structure of $\text{HN}=\text{NH}$, di-imide¹¹. Also, the equilibrium internuclear separation of the carbon atoms increases from 1.21 \AA to 1.39 \AA as a result of the transition in which the net bonding between these atoms is substantially reduced. In other excited states of Rydberg character, the anti-bonding effect is insufficient to prevent a linear conformation, indicated by the presence of only bond-stretching (totally symmetrical) vibrations in various progressions.

Ethene (or ethylene) has not so far been successfully treated by rotational analysis for its structure in the excited state produced by the $50,000\text{ cm}^{-1}$ transition. The diffuse vibrational progressions have been variously interpreted as consisting of a stretching mode involving the carbon-carbon bond¹², twisting vibrations involving the torsional mode¹³, and a combination of bending and torsional vibrations involving out-of-plane deformations¹⁴. The corresponding structures are respectively an elongated and twisted molecule with an increased carbon-carbon bond length, one with the two methylene groups twisted by 90° , and a form with the two carbon atoms both above the plane defined by the four hydrogen atoms. Although these structures were the results of increasingly sophisticated vibrational analyses, a definitive assignment of structural parameters must await the attainment of some definite rotational information. Either discrete

rotational lines or well-defined band contours may be observable in the extremely weak bands which lie below $45,000\text{ cm}^{-1}$.

The first Rydberg transition of ethene has been subjected to vibrational analysis¹⁵. The progressions involve the carbon-carbon valence-stretching vibration, indicating a substantial increase in the equilibrium C-C bond length in this state, and the torsional vibration, indicating lack of planarity of equilibrium conformation. In fact, fitting of the torsional frequencies to an assumed potential function produced an estimate of a 26° angular twist of the methylene group relative to one another. From the resemblance of the appearance of spectra of higher Rydberg transitions of ethene to that of the 57340 cm^{-1} system, the inference has been drawn that the molecular ion C_2H_4^+ is also non-planar. Vibrational structure in photoelectron spectra has been stated to support this inference¹⁵. However, to the extent that valence-shell transitions are distinct from Rydberg transitions, implications of the conformation of Rydberg states applied to the shape of the ethene molecules in the state resulting from the 50000 cm^{-1} transition are not valid.

(7) SOME MOLECULES CONTAINING NITROGEN

In this section we consider a group of molecules containing nitrogen atoms, of which the structures of their excited states, by comparison with related molecules, are interesting because of the special effects conferred by the inclusion of nitrogen atoms.

Electronic absorption spectra of the methyleniminyl radical H_2CN have been studied. Although the band contours under medium dispersion seem well defined¹⁶, recent spectra at great dispersion¹⁷ reveal rotational diffuseness which prevents determination of the structure of the various electronic states by the usual method. Nevertheless, some conclusions as to the shape of the molecule are possible. The simplicity of the spectrum indicated, by the scarcity of vibrational bands, that no appreciable change of shape occurs between the ground and excited states. The similarity of band contours to some vibration-rotation bands of (ground state) methanal under similar dispersion indicates similar conformations, i.e., planar in all the combining states. Contrast with the $^1A''$ and $^3A''$ states of methanal is noteworthy; as mentioned earlier, their conformations deviate much from planarity. For F_2CN , the conformation in both the two known states¹⁸, ground and excited, is planar. For D_2CN and HDCN some weak vibrational structure is found in the spectrum and has been assigned to totally symmetric fundamentals in the upper states. But for each of H_2CN , HDCN and D_2CN , a band more intense than that observed at smallest frequencies (to which the fundamental vibration frequencies were related) occurs at an interval unrecognisable as a vibration frequency. A similar phenomenon occurs for F_2CN .

The postulate of additional electronic transitions for these bands seems necessary. However the non-appearance of vibrational bands in conjunction with these apparently purely electronic transitions means that the structure in the excited state must be very similar to that of the ground state. Only a single band has been observed¹⁹ for the HNCN radical, and rotational analysis confirmed that the geometrical dimensions change very little in that electronic transition. H_2CN may be considered to be isoelectronic with nitric oxide for which the spin-orbit coupling of the ground configuration produced two states separated by 123 cm^{-1} . However large spin-orbit effects in polyatomic molecules necessary to account for the unrelated bands being separated by about 500 cm^{-1} for the isotopic methyleniminyl radicals (or 138 cm^{-1} for F_2CN) are apparently unprecedented.

Electronic absorption spectra of diazomethane, H_2CNN , have been studied through a considerable frequency range. The first transition, responsible for the yellow colour of this substance, consists in the gas phase of a long progression in a bending vibration of small frequency. A bent skeleton in the upper state was deduced²⁰. Isoelectronic (and isostructural in the ground state) ketene, H_2CCO , shows a similar effect, and in that case the retention of planarity in the excited state was postulated²¹. However, a further progression in a larger frequency vibration adjoins the first system of diazomethane, so a second electronic transition is indicated. As the vibration frequency is appropriate to a skeletal valence-stretching vibration, no change in shape seems required, merely an increase in the CNN bond lengths. Another vibrational band progression in a very intense absorption system beginning near 44000 cm^{-1} also has a band interval appropriate to a skeletal-stretching vibration. Again, a moderate increase in CNN band distances is indicated; the analogous transition of ketene shows a similar effect⁶. For Rydberg transitions of diazomethane that have been studied, planar conformations of all observed states were indicated²². Furthermore, the apparent absence of vibrational intervals assigned to in-plane skeletal bending modes suggests that linear heavy-atom arrangements occur, as in the ground state. Thus, only the first excited state, of all those known, and including states of the molecular ion H_2CNN^+ by inference, seems to have a bent skeleton. All these deductions of the shapes of the excited molecules have resulted from considerations of the vibrational structure accompanying the various electronic transitions, it being taken for granted that the ground state structure is accurately determined separately (for H_2CNN from pure rotational spectra in the microwave region²³).

Methanal azine, $\text{H}_2\text{C}=\text{N}-\text{N}=\text{CH}_2$, is one of three dienes which merit consideration; the others are glyoxal, $\text{O}=\text{CH}-\text{CH}=\text{O}$, and butadiene itself, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$. Of the three separate excited states indicated by electronic transitions of methanal azine¹⁶, that of least energy seems to be unstable with respect to direct dissociation. The second transition consists of a long progression in a vibration frequency suitable for a bending or torsional mode, corresponding to a large change of the appropriate interbond angle in the excited state. The third

transition apparently has diffuse vibrational structure corresponding to a skeletal stretching frequency in the excited state. There is no doubt of a progression of such a vibration for butadiene. In each case, the excitation of an electron from the bonding π_2 -orbital to the anti-bonding π_3^* -orbital is expected to produce just such an effect. The transition involving promotion of an oxygen non-bonding electron into the π_3^* -orbital of glyoxal is accompanied by resolvable rotational fine structure. The decrease of the central CC bond length is probable but the increase of length of the CO bonds is certain²⁴. Qualitative accordance with the predictions of simple molecular orbital theory is agreeably obtained.

Nitrosomethane, H_3CNO , while not directly related to the previous three nitrogenous molecules, is included in this section because the structure determination for its electronically excited state illustrates a further method. As a rotational analysis of the electronic absorption spectrum had not at that time proved possible²⁵, estimates of the geometry change on electronic excitation were obtained using the Franck–Condon principle, not only qualitatively as implied earlier in this article, but quantitatively. In symmetry-allowed electronic transitions, the Franck–Condon factors govern the relative intensities of the various vibrational bands, and are functions, in part, of changes of equilibrium geometrical parameters. Comparison of the observed intensity distribution in the short progressions comprising the H_3CNO spectrum enabled the choice of the following changes of parameters on excitation:

- Change in CN bond length, $-0.03 \pm 0.015 \text{ \AA}$;
- Change in NO bond length, $0 \pm 0.02 \text{ \AA}$;
- Change in CNO interbond angle, $+8.6 \pm 1.5 \text{ degrees}$

As the ground state structure has now been determined from microwave spectroscopic measurements²⁶, the structure of the excited state can be estimated from the data above. In fact, the development of powerful computational techniques of rotational band contour analysis since that study of H_3CNO would now permit estimates of the molecular geometry more accurate than those cited above, particularly if the band contours were not smooth but consisted in part of some distinct fine structure.

(8) CYCLIC MOLECULES

Of a few cyclic molecules which could illustrate some remaining topics, benzene is exemplary in many respects. It can be considered to be composed of twelve sigma-type strong bonds holding the carbon and hydrogen atoms in a regular hexagonal framework, with additional bonding due to six electrons in π -type orbitals in the ground state. The π -electrons are most readily excited. The change of shape of the benzene molecule on excitation should be much less than

the change of shape of the ethene molecule in a similar excitation for several reasons: in benzene, only one π -electron of six is excited compared with one of two for ethene; the orbital newly occupied most readily on excitation is also a π -type orbital, albeit partly anti-bonding, but sufficiently delocalised that the effect felt in any one bond is much reduced from the similar case in ethene; finally, the cyclic form of the benzene molecule inhibits some deformations, such as twisting of the bonds²⁷.

In the excited state reached by optical excitation in the $40,000\text{ cm}^{-1}$ region, these expectations are abundantly fulfilled. In both ground and excited states the equilibrium nuclear conformation is a regular planar hexagon. The excited structure is established most convincingly by a rotational analysis²⁸, in which the C–C bond length is shown to increase from 1.397 \AA to 1.435 \AA and the CH bond length to decrease from 1.08 \AA to 1.07 \AA , from ground to excited state, respectively. Bond length differences thus calculated agree excellently with those derived from vibrational analyses (Franck–Condon factors)²⁹, and also from some empirical rules based on vibration frequencies³⁰.

Rotational analysis of phenol was also achieved, but only with the aid of a band contour computation. The discussion³¹ of the principles and practice of such a method in connection with phenol emphasised the difficulty of succeeding in a complete structural determination for such a (relatively) large molecule. In this instance, the most concrete possible inference of structure was the relative decrease of C–O bond length in the excited state (resulting from the 39350 cm^{-1} optical transition). It is noteworthy that, even in the case of benzene, which was shown to be a very symmetrical molecule in the excited state alluded to above, a rotational contour computation contributed greatly to the success of the structure determination²⁸. With the aid of band contour analysis and spectra of several isotopically substituted species, the first determination of the geometrical structural parameters of an aromatic molecule from information derived entirely from its electronic spectrum was accomplished³² for *s*-tetrazine (1, 2, 4, 5-tetraazabenzene). For this molecule the electronic transition in the visible region is accompanied by an increase of C–N bond length of 0.06 \AA and a (greater) decrease of N–N separation of 0.10 \AA .

Another cyclic molecule worthy of note is the tropyli radical, C_7H_7 . An electronic absorption spectrum of this species has been observed³³ in which the three bands can be fitted to an equation:

$$\nu = 50329 - R(n+0.046)^{-2}$$

in which $n = 3, 4$ or 5 . The resemblance of this relation to the term equation presented in Section 2 for atoms indicates that these bands comprise a Rydberg series with the very small ionisation energy of 50329 cm^{-1} . All three bands were relatively narrow, only the first appearing diffuse, and no accompanying vibrational structure was detected. Therefore no appreciable change in shape or geo-

metrical parameters occurs during the electronic transitions, and the molecular ion as well as the Rydberg states can be deduced to have structures virtually identical with that of the ground state.

A method for distinguishing between Rydberg and valence-shell transitions has been suggested. Experimental evidence was obtained to indicate that Rydberg absorptions disappear in dense phases, such as compressed gases or solid solutions^{34,35}. Some theoretical justification³⁶ for such phenomena was cited in the necessity, for existence of such states, of the condition that the mean free path of the optically excited electron must exceed the circumference of its orbit. The radius of a circular orbit (or distance of maximum probability) for a Rydberg state of ethene was calculated³⁵ to be 6.7 Å. More recent experiments³⁷ demonstrate that, instead of disappearing altogether, these transitions are shifted (by 3500 cm⁻¹ in the case of ethene) to greater frequencies. However, the vibrational progressions of the trapped molecules in the dense media are similar to those of the free molecule in the corresponding electronic states. Thus the implication is apparent that the geometrical structure of the excited states, in these cases, does not vary greatly with medium.

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