9.13. Molecules (or fractions of molecules) with II-nd type of oscillations.

The two types of oscillations introduced in §9.5.4.2 are distinguished by the moment of inertia of the molecule or its structures. For the molecules with I-st type of oscillations, discussed so far, the moment of inertia is quite small and has been neglected.

For molecules with a larger moment of inertia, the centrifugal forces could not be ignored. They contribute to the rotational energy. For homonuclear diatomic molecules this energy is given by Eq. (9.3). If this forces are smaller than the E_B energy, the molecule possesses a I-st type of vibrations, otherwise it may posses a II-nd type of vibrations. **In the II-nd type of vibrations, the inertial forces work against the quantum quasishrink effect. This may cause a deterioration of the quantum conditions.**

The deteriorated quantum conditions may affect the process of photon emission (absorption). The signature of II-nd type of vibrations is not so apparent from the optical spectrum. However, it could be identified by the Photoelectron (PE) spectrum. The distinguishing signatures in the PE spectrum are the following:

A. For molecules with a I-st type of oscillations:

(a) The bottom level of the the PE spectrum is smooth.

(b) The bonding system of H_2 (or D_2) contributes to a narrowly spaced and well separated peaks

(c) the bottom level of H_2 (D_2) peaks are not shifted

B. For molecules with a II-nd type of oscillations:

- appearance of quite wide peaks with larger separation
- appearance of H_2 (D_2) signatures with elevated bottom level of the peaks
- appearance of H_2 (D_2) signatures overimposed on wide peaks

According to BSM analysis, the wide peaks with larger separation are indicators of deteriorated quantum conditions. If examining the wide peaks with higher resolution PE spectroscopy, it is apparent that some of them have a fine structure, others do not. The fine structure is indication that quantum conditions exists, but they might be from superimposed PE spectrum of some groups containing H_2 (D_2) bonding possessing a I-st type of vibrations. This conclusion has experimental confirmation, when interpreting the PE spectrum of H_2S and D_2S. Such spectra are provided by Eland, C. J, (1979). They are shown in Fig. 9.42**.**

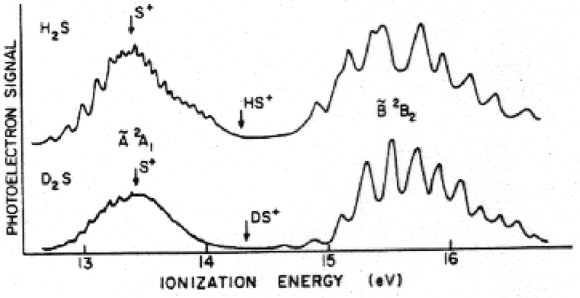

Fig. 9.42
PE spectrum of H_2S and D_2S (Courtesy by Eland, (1979))

The left part of the spectra is from a neutral molecule, while the right part - from an ion. The H_2S^+ ion is obtained after one of the bonding electrons is lost. The possible molecular structure of this ion is shown in Fig. 9.43.

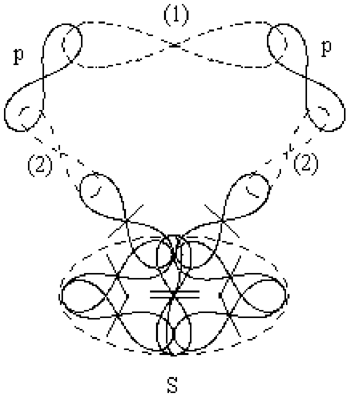

Fig. 9.43
Possible configuration of H_2S^+ ion. The number in bracket shows the subharmonic number of the quantum orbit. The top quantum orbit could be also of (2) subharmonic. Every quantum orbit contains a single electron.

In the shown possible configuration, the structure of H_2S^+ molecule appears symmetrical in respect to the polar axis of sulphur (S element). The quantum orbits are also symmetrical. The single electron in the top orbit (between both protons), is not paired. The effective positive charge may modulate the surrounding CL space in proximity of the molecule. In comparison to the neutral H_2S, the electrons are not so well paired and their quantum interactions with the CL space should be larger. Then the wide PE peaks in Fig. 9.22 may correspond to deteriorated quantum conditions, mentioned above. The left part of the PE spectrum contains the familiar PE spectrum of H_2 but with a significantly elevated bottom level. So the left slope of the left wide peak could be contributed by I-st type vibrations of H_2S with well defined quasishrink effect, while the right slope could be a result of deteriorated quantum conditions valid for a II-nd type of vibrations for H_2S^+ molecule. The confirmation of this conclusion comes also from the comparison of the fine structures of the left wide peak for the H_2S and D_2S, which is provided by the bonding electrons. In case of D_2S, this structure is shifted to smaller E_{IP} energies (larger E_K energy). This could be explained by the increased IG forces from the D_2 type of bonding.

Summary:

- **The I-st type of the molecular vibrations could be identified by the PE spectrum**
- **The complex molecules may contain groups with I-st and II type of vibrations**
- **Only the I-st type of vibrations provides a strong discrete optical spectrum**

9.14. Information about the molecular configuration, provided by the photoelectron spectrum

The PE spectrum may provide additional information about the molecular configuration by the following features:

(a) The energy spacing between the peaks in the I-st type of vibrations

(b) Angular distribution of the photoelectrons

(a): The energy spacing between the peaks in I-st type of vibrations is weakly dependent on the interactions between the bonding and nuclear quantum orbits. A stronger interaction corresponds to larger spacing. This is known from the existing theory of PE spectra. For the BSM model, this feature may provide a valuable information about the atomic internuclear separation. It may allow to identify the possible configuration of different excited states of the O_2 molecule, discussed later in this Chapter.

(b): The angular distribution of the PE, known as an “anisotropy parameter” is successfully measured, when the molecules are properly oriented in respect to the analyser magnetic field. The anisotropy parameter can be evaluated from the experimental angular distribution of the photoelectrons. Such distribution for H_2 is shown in Fig. 9.44 (From. Carlson, T.a and Jonas A.E (1971).

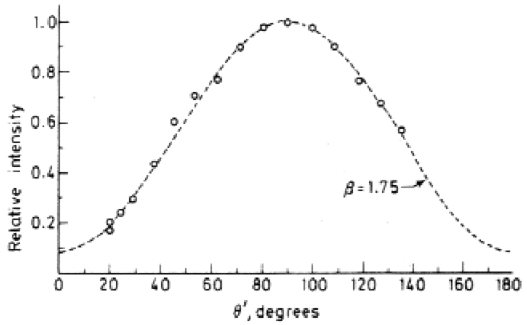

Fig. 9.44

Experimental angular distribution of the photoelectrons from ionization of hydrogen by He I line (From Carlson et al. (1971)

The anisotropy parameter β is evaluated by the least square fit to a theoretical equation:

$$I(\theta) = 1 + \frac{3\beta}{4 - 2\beta}\sin^2(\theta') \qquad (9.46.A)$$

where: I - is the relative intensity of PE signal
θ' - angle of distribution

The anisotropy parameter is measured for number of molecules in different states and it varies between 1.8 (for H_2) and some minus values for some molecules. It also has different value for different states of one and a same molecule. When plotting the function $I(\theta')$ we obtain a sense of the position of the plane of the bonding quantum orbit in respect to the molecular orientation along its vector of velocity. In case of H_2 molecule, the parameter β is a largest one. **Consequently, the parameter β is a signature of the orbital plane orientation in respect to the molecular axis of the rotational motion.** For two different states of N_2 it obtains value of 0.6 and 0.65.

If the bonding orbits are more than one and with good rotational symmetry, then the parameter β is low. For the inert gases the parameter β is not related with the bonding orbits but with the photoelectrons from the internal completed layer of protons. For this reason the β parameter is informative about the shape of the nuclei of these atoms. For example, the shape of the Ar nucleus is closer to a sphere, but the nucleus of Kr or Xe is not. Fig. 9.39 shows plots of β parameter for H_2 and for some inert gases.

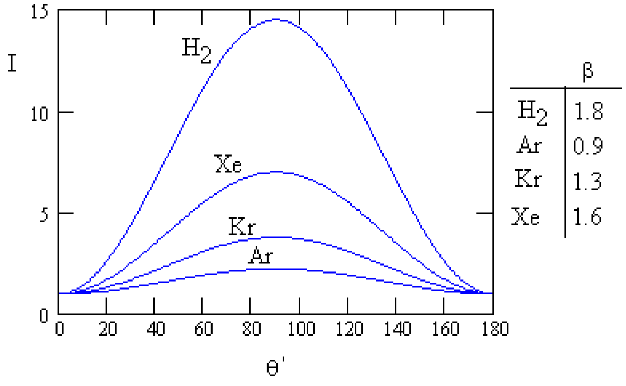

Fig. 9.45

Angular distribution of photoelectrons from PE spectra and corresponding β para-meter for different gazes

9.15. IG energy balance for system of diatomic homonuclear molecule

9.15.1 IG Energy of a bonding system

In the presented examples of H_2 and D_2 molecules, the IG energy balance was satisfied for the first harmonic quantum orbit. Let considering the ortho-I state of H_2, whose IG energy balance is described by Eq. (9.23). If using $L_q(n)$ instead of $L_q(1)$, where $n > 1$, the Eq. (9.23) is unbalanced quite a bit. The imbalance $E_V(\Delta)$ (eV) for quantum orbits with different subharmonic number *n* is shown in Table: 9.5

Table 9.5

subharmonic number (n)	$L_q(n)$ [A]	$E_V(\Delta)$ [eV]
1	Lq(1)	6.27
2	Lq(2)	1.6326E6
3	Lq(3)	3.166E6
4	Lq(4)	4.487E6

where: $L_q(n) = L_q(1)/n$

We see that for larger subharmonics the IG balance of the system is disturbed quite a lot. If the obtained imbalance, however, is compensated by a proper IG field between two atoms, a new balance could be obtained, valid for the whole system. In such case, the bonding energy would be expressed by the same equation (9.23) but instead of length $L_q(1)$ we will have $L_q(n)$ where *n* - is the subharmonic number. $n > 1$. In this point, however, one question arises: Do bond systems which are similar but with quantum orbits of higher subharmonic number have the same dependence of vibrational number? For this reason we must consider two cases:

Case (A). Assumption that the term $\alpha^4\pi(\upsilon_m - \upsilon)^2$ is one and a same for quantum orbits with different subharmonic number

In this case, the total momentum energy as a function of the quantum number υ is:

$$B_{H2}(n, \upsilon) = \frac{C_{IG}}{q[r_n(n, \upsilon)]^2} - \frac{2E_q}{q} - \frac{2E_K}{q} + 6.26 \text{ (eV)} \qquad (9.47)$$

$$r_n(n, \upsilon) = [L_q(n)](1 - \alpha^4\pi(\upsilon_m - \upsilon)^2) + 0.6455L_p \qquad (9.47.a)$$

where; $B_{H2}(n, \Delta)$ is the momentary energy of the bonding system of protons (corresponding to H_2 ortho-I type system), $0.6455L_p$ - the locus distance from the central point of Hippoped curve, υ - is the vibrational level (referenced to the equilibrium distance),

For bonding system of deuterons, the momentum bonding energy is equivalent to the total energy of D_2 molecule given by Eq. (9.27). Applying for subharmonic numbers of *n*, we obtain a momentary bonding energy of deuterons, denoted as B_{D2}.

$$B_{D2}(n, \upsilon) = \frac{C_{IG}}{q[r_n(n, \upsilon)]^2} - \frac{2E_q}{q} - \frac{2E_K}{q} + 6.235 \text{ (eV)} \qquad (9.49)$$

$$r_n(n, \upsilon) = [L_q(n)](1 - 0.5\alpha^4\pi(\upsilon_m - \upsilon)^2) + 0.6455L_p \qquad (9.49.a)$$

There are two special points of the vibrational curve defining two special values for the momentary bonding energy:

(a) the equilibrium point defines a **momentary bonding energy at equilibrium** ($\upsilon = 0$).

(b) the dissociation point defines a **momentary bonding energy at dissociation limit** (for some value of υ_m)

Note: υ_m has a finite value. This means the vibrational curve has a limit number of vibrational numbers according to BSM models. From the BSM point of view, the large quantum numbers in QM model are results of deformations of the shape of the quantum orbits as discussed in section 9.5.7.4.

The single valence bonding system between two atoms in the molecule could be regarded as bondings of H_2 or D_2 system. In fact D_2 system bonding is more typical as seen from the Atlas of the Atomic Nuclear Structure (ANS). Therefore, the Eq. (9.47) is valid for a bonding system of protons while the Eq. (9.49) - for a bonding system of Deuterons.

Case (B). Assumption that the term $\alpha^4\pi(\upsilon_m - \upsilon)^2$ is dependent on the quantum number of the orbit

Larger subharmonic numbers means smaller length of the particular quantum orbit. If considering that IG energy of heavier than H_2 and D_2 molecule causes a larger bending of the vibrational ladder, then the above term may have some kind of inverse proportional dependence on *n*. If assuming that this is correct, the same rule should be valid also for the Lq(1). The correct dependence cold be determined only by studying the vibrational properties of diatomic molecules for which photoelectron and optical spectra are available. Some study of this problem by using the photoelectron and optical spectra of O2 molecule is presented separately as BSM_Appendix9_1.

9.15.2 Energy balance in diatomic molecules

The momentary bonding energy could be compensated by a proper IG potential between the atomic nuclei involved in the molecule. For a stable connection of atoms into a molecule, the average IG energy of the total system should be in balance. The average IG energy means that the system may vibrate around the momentary balance equilibrium state in a similar way as the H_2 and D_2 molecules. Then the IG energy may be regarded as comprised of two components: DC (constant component, like "direct current") and AC (alternative component). Such system includes:

- the CL space occupied by the volume of the integrated Bohr surfaces of both atoms and bonding system.

- the elementary particles of both atoms (comprised of helical structures with their internal RL(T) lattices).

- the bonding system comprised of one or more pair of protons(deuterons).

The energy interactions diagram of a simple molecule of two atoms connected by electronic bonds is schematically illustrated in Fig. (9.46). It is assumed that the bonding system is comprised of deuterons (a more typical case).

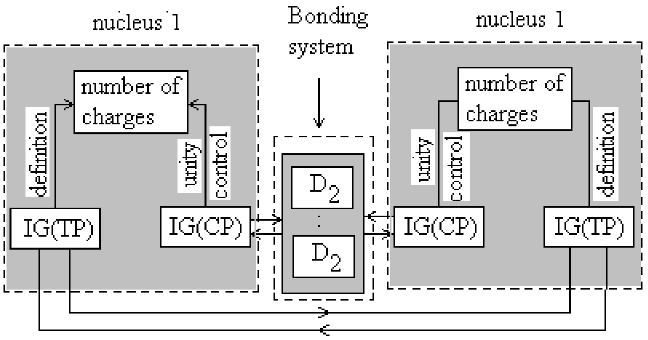

Fig. 9.46
Energy interaction diagram of simple diatomic molecule

The IG(TP) of the atomic nucleus provides a charge definition (by RL(T) of the FOHSs), while the IG(CP) provides a charge unity control for all proton charges. The bonding system, shown in Fig. 9.46 contains two deuteron's pair. In order to be balanced for particular quantum orbits from the possible quantum orbit set, it needs some amount of external IG energy of IG(CP) type (IG energy between the two atoms). Such type of energy should be provided by the molecular system, but it should be balanced by IG(TP) energy, in order the whole system (including the CL space) to be brought to an average IG energy balance. The momentary energy of the molecule may oscillate around the equilibrium point, so the total IG energy should have a DC and AC components as in the case of H_2 (D_2) molecule. Then the energy balance conditions could be formulated as *Electronic Bonding* (EB) conditions:

EB conditions: At the equilibrium point of vibrations, the momentary imbalance of the total AC type IG energy of the molecule should be equal to zero.

The bonding system imbalance involves IG(CP) energy, so the necessary interaction should be of this type, as shown in Fig. 9.46. It is difficult to estimate directly the IG(TP) energy supplied by both atoms, but it could be estimated by the total balance of the system. This energy is subtracted from the total system energy, so it has to be compensated. The possible compensation could come from IG attractions involving IG(TP) fields of both nuclei. If the internuclear distance was known, the IG(TP) forces could be estimated by using the known value of C_{IG} factor and the number of hadrons in the nuclei. Then the IG energy could be estimated as a work for separation of the nuclei from the internuclear distance to infinity. Practically, the condition for infinity in CL space is obtainable at distance of few nuclear lengths (due to a fast drop of IG forces with the distance in CL space). More useful, however, appears the inverse task: an estimation of the internuclear distance, when the energy balance is determined. This parameter could be verified with the observational data, so it may serve as a validation parameter for the unveiled molecular configuration.

It is reasonable to consider that the proportionality between the nuclear atomic mass and the atomic mass unit (valid for the Newtonian mass) is preserved also for the intrinsic masses of the nuclei. For approximate calculations, we may accept two simplification:

- neglecting the difference between the masses of neutron and proton and using the proton mass only (in fact they both contain one and a same intrinsic matter)
- neglecting the mass deficiency (nuclear binding energy) especially for atoms with a low Z number.

For neutral molecules, when estimating the IG(TP) forces between the two nuclei at a distance r_n, we should exclude the protons involved in the bonding system, as their forces and energies are directly involved in the bonding system balance. Having in mind that the factor C_{IG} is normalized to the intrinsic proton mass, the IG force between two identical nuclei could be expressed as:

$$F_{IG} = \frac{C_{IG}(A-p)^2}{r_n^3} \qquad (9.51)$$

where: C_{IG} - is the intrinsic factor, defined by Eq. (9.13.a) and expressed by Eq. (9.17), A - is the atomic mass of the participating atom, p - is the number of protons per atom, involved in the bonding system

In Eq. (9.51), only the protons are excluded from the attractive IG forces between the two nucleus. (In fact the distance between neutrons over proton saddle are closer than the internuclear distance but IG field between them could be partly affected by the proximity fields of the protons). This assumption leads to more reasonable final results, as shown in §9.16.2, tested especially for the Oxygen molecule.

Having in mind that $E_{IG}(TP) = 2\alpha E_{IG}(CP)$ and integrating Eq. (9.32) on a distance r, we get:

$$E_{IG}(TP) = 2\int_{r_n}^{\infty} \frac{2\alpha C_{IG}(A-p)^2}{r^3} dr = \frac{2\alpha C_{IG}(A-p)^2}{r_n^2} \qquad (9.52)$$

The factor 2 in front of the integral takes into account the two branches of aligned prisms along *abcd* axes, involved in one cell unit of CL space.

For a momentary AC type of balance at equilibrium distance, the $E_{IG}(TP)$ energy given by Eq. (9.52) should be equal to the energy $B_{D2}(n, \Delta)$ multiplied by the number of connected protons (per one atom) involved in the binding system. Deviations of internuclear distance from the equilibrium value of r_n will make a system imbalance, which is characterised by quantum vibrational energy levels. For a bonding system of protons, this deviation is given by Eq. (9.47), while for deuterons - by Eq. (9.49). The total IG(TP) energy necessary for momentary balancing of the bonding system is:

$$E_{IG}(TP) = \frac{2\alpha C_{IG}(A-p)^2}{(r_n \pm [\Delta r(\upsilon)])^2} \qquad (9.53)$$

where Δr is the change of the internuclear distance due to the different vibrational quantum numbers.

For case of D_2 bonding, it is obtainable by differentiation of the internuclear distance given by Eq. (9.49.a) on vibrational number υ. Having in mind that $\Delta\upsilon = 1$ we obtain:

$$\Delta r = L_q(n)\pi\alpha^4(\upsilon_m - \upsilon) \qquad (9.53.a)$$

If equating the energy of $E_{IG}(TP)$ in (eV) with energy $B_{D2}(n, \upsilon)$ we get AC balance condition only for $\upsilon = 0$. For $\upsilon \neq 0$ the imbalance energy is the vibrational energy level. **Therefore, the vibrational energy levels (for D_2) are equal to the difference between the energies given by Eq. (9.49) and Eq.**

(9.53) for different integer values of υ. We can denote them as ΔE.

$$\Delta E = \frac{2\alpha C_{IG}(A-p)^2}{(r_n \pm [\Delta r])^2} - B_{D2} \qquad (9.54)$$

The energy balance B_{D2}, defined by Eq. (9.47) is for one valence connection. The diatomic molecules (or groups) usually do not have more than three valence connections. So for more than one valence connection we may express the balance energy by simply multiplying the energy term B_{D2} by the valence factor *p*. The final equation for the vibrational levels in diatomic homonuclear molecule obtains a form:

$$\Delta E(p, n, \upsilon) = \frac{2\alpha C_{IG}(A-p)^2}{[r_n \pm [\Delta r(n, \upsilon)]]^2} - pB_{D2}(n, \upsilon) \qquad (9.55)$$

where: *A* - is the atomic mass in atomic mass units (for one atom), *p* - is the number of protons involved in the bonding system (per one atom), *n* - is the subharmonic quantum number of the quantum orbit, r_n - is the internuclear distance at the equilibrium, Δr - is the change of the internuclear distance in function of vibrational quantum number υ

The participation of $L_q(n)$ parameter in Eq. (9.55) does not exclude a serially connected quantum loops. In the following analysis, however, only single quantum loops are discussed.

The application of (9.55) is limited for diatomic mainly homonuclear molecules with electronic bonding system. Such molecules are possible for the elements from 15, 16, and 17 vertical group of the Periodic table (but possible applications for other groups are not excluded).

If applying the equation for $n = 1$, we see that the B_{D2} energy is in order of few eV. In order to get equilibrium balance, the internuclear distance for O_2 molecule, for example, has to be in order of 0.12 *nm*. This of cause is not reasonable for any molecule due to the finite nuclear size of the atomic nucleus (defined by the finite size of the proton and neutron). **Consequently: the case of $n = 1$ is not valid for any molecule, but H_2 and D_2 only.** This facilitates the task for determination of the configurations of molecules of heavier atoms by excluding the bonding orbit $L_q(1)$.

The obtained Eq. (9.55) is of great importance for BSM. It provides the opportunity to find the real structure of some simple diatomic molecules, if the optical and PE spectra are available. By careful analysis of such spectra, the parameters *n*, Δ, and r_n could be determined. The analysis could be simultaneously assisted by finding the proper spatial configuration, working with the known three dimensional shape of the proton, (neutron), and the set of quantum orbits, defined with their shape and dimensions. The Δr parameter is quite small in comparison to r_n, as in the H_2 and D_2 molecule. Therefore, we can use the well defined dimensions of the quantum orbit in free CL space.

Such type of analysis is applied in the next paragraph for the Oxygen molecule and its possible states.

Note: The vibrational levels calculated by Eq. (9.55) are approximate due to a simplification that the IG mass of the nucleus is located in a point. However, the nucleus of every atom has a finite dimensions according to BSM models, so this is a source for error. Another smaller source for error could be the ignored spin-orbit interactions. For this reason the calculated distances could be used only for determination of molecular configuration.

From Eq. (9.55) we may derive a direct expression for the internuclear distance for a homonuclear diatomic molecule. Having in mind that the change of the internuclear distance for vibrating molecule is intrinsically small, we may use the distance at equilibrium at which $\upsilon = 0$ and the momentary energy is zero $\Delta E(p, n, \upsilon) = 0$ Then solving Eq. (9.55) for r_n we obtain:

$$r_n(n, A, p) = (A-p)\sqrt{\frac{2\alpha C_{IG}}{pE_B(n)}} \qquad (9.56)$$

Eq.(9.56) could be easily modified for heteronuclear molecules.

9.15.3. Electronic bonds with quantum orbits formed by serially connected quantum loops.

We have considered so far that the trace of any quantum orbit is formed by a single quantum loop. The condition of quantum orbit, however, is satisfied for more than one quantum loops, connected serially. This was discussed for Hydrogen in §7.4 and the possible quantum orbits in such case were given in Table 7.1. There are not theoretical restrictions such orbit to exists in bonding systems between atoms in molecule. If the quantum orbit, for example, contains two quantum loops of third harmonic, it will still have kinetic energy of $13.6/3^2 = 1.511$ (eV) per electron, but its linear dimension will be twice the linear dimension of third subharmonic orbit. Consequently quantum orbits of serially connected quantum loops increases the set of possible lengths of quantum orbits. When this set is combined with the limited angular freedom of polar bonded protons, additional options for total energy balance for connected in molecule atoms are obtained. The derived equations for the bonding length and vibrational levels are easier modifiable for this option. For the bonding energy expression the serially connected loops will affect the kinetic energy in Eq. (9.49) and the internuclear distance in Eq. (9.49.a). For the total energy balance of the molecule, the serially connected loops will affect r_n and Δr_n in Eq. (9.53).

The derived equations are used in BSM_Appendix9_1 for analysis of different states of the O2 molecules in order to obtain their configurations.

***Summary*:**

- **The vibrational energy levels for diatomic molecules could be approximately estimated by Eq. (9.55). Using the simplification that IG mass is in a point and ignoring QM spin-orbital interaction, it may provide only approximate value.**
- **Diatomic molecules or groups with atomic mass larger than 4 could not have a bonding orbit of first harmonic.**
- **By simultaneous cross analysis of the PE and optical spectrum with the help of Eq. (9.55) the real structure of the diatomic molecules and their different states could be obtained.**

9.16. Oxygen molecule and its different states.

The analysis of different states of O_2 molecule in order to obtain the corresponding molecular configurations is provided in BSM_Appendix9_1. For this purpose PE and Optical spectra of O_2 molecule are used. Here only some final results are shown.

Fig. (9.48) shows the PE spectrum provided by K. Kimura et al. (1981).

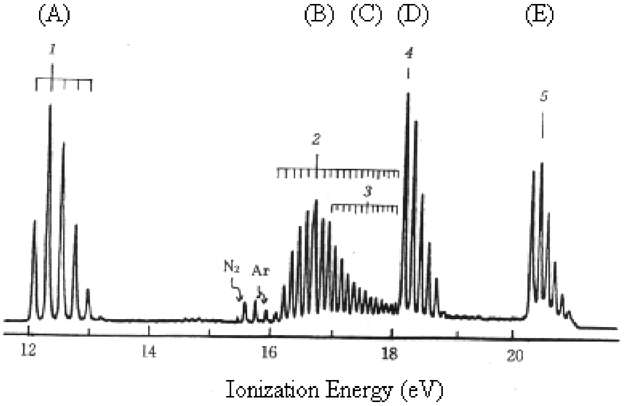

Fig. 9.48. PE spectrum of oxygen molecule excited by He I radiation (Turner et all., courtesy of K. Kimura et al., (1981))

According to BSM analysis, the different bands of PE spectrum correspond to different molecular configurations or states. They are denoted by the alphabets (A), (B), (C), (D), (E) states (BSM annotation), put in the top of the figure. Note that the (C) and (D) states are partly overlapped. The possible configurations of the {D} and {A} states are shown in Fig. (9.50).

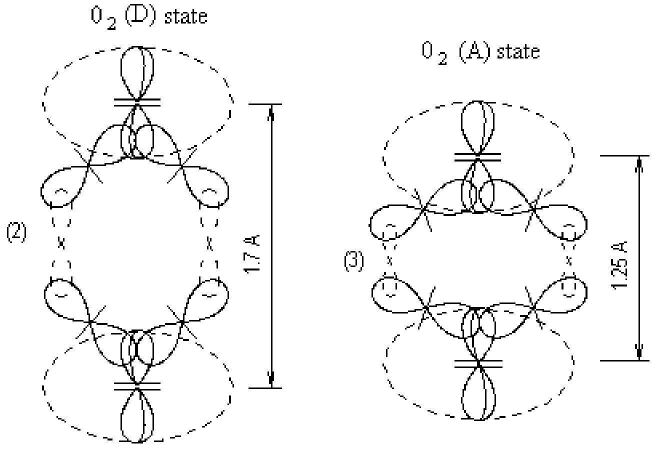

Fig. (9.50)
Possible configurations of O_2 molecule in {D} and {A} states (by BSM)

Fig. 9.52 shows the possible configuration of {E} state of O_2 molecule. Eq. (9.55) is not directly applicable for this state without modifications, because the quantum orbits are not aligned with the common internuclear axis.

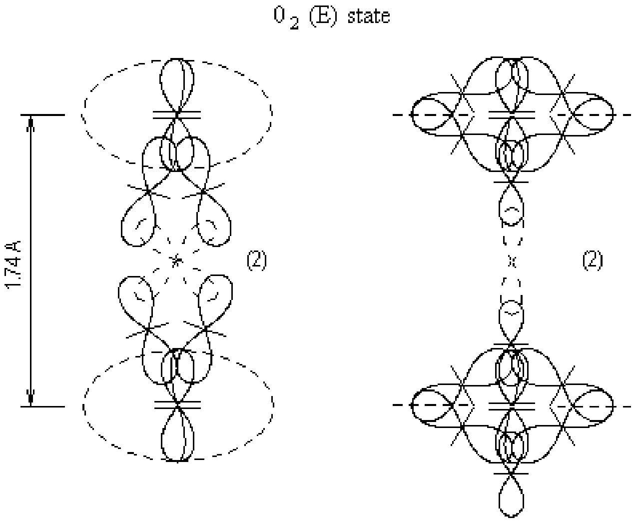

Fig.9.52

A possible configuration of (E) state of O_2 molecule

The calculated values of r_n (rounded) by Eq. (9.56) and those matching the spatial configuration by using a drawing method, are given in Table 9.6.

Calculated (rounded) values for r_n Table 9.6

r_n (A)	$L_q(2)$ (1 bond)	$L_q(2)$ (2 bonds)	$L_q(2x)$ (2 bonds)	$L_q(3)$ (2 bonds)
by Eq. (9.56)	2.57 A	1.695 A		1.217 A
by drawing	2 A	1.7 A	1.74 A	1.25 A
state	(B), (C)	(D)	(E)	(A)

The calculated distances could not be considered accurate as some elaborate methods of Quantum Mechanics. They are shown only for identification of the possible molecular configuration.

9.16.8 $(OH)^-$ ion.

The possible configuration of (OH)- ion is shown in Fig. 9.62 It is assumed, that the plane of the two bonding orbits are parallel, so they exhibit a maximal QM spin interaction. In such case the polar angular position of the valence protons is influenced by the QM spins of the two orbits even for bonding orbits with different subharmonic number.

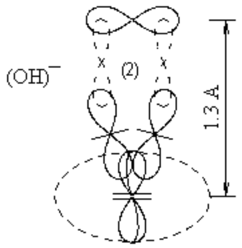

Fig. 9.62

A possible configuration of $(OH)^-$ Every bonding orbit contains two electron with opposite QM spin. (the bonding orbits are shown in the drawing plane for simplicity, although they are perpendicular to the drawing).but rotated

The shown configuration is characterized, also, by the following feature: The planes of the three sets of orbits: the He nucleus orbits, the orbits of GBclp protons, and the bonding orbits are mutually orthogonal. The described features might be important factor for the stability of OH^- ion.

9.17 NH_3 molecule

The Nitrogen atom has 3 free valence protons (deuterons) and two equatorial EB protons in its external shell. Two of the three valence protons are bonded to one pole and another one to the second pole. In NH_3 molecule every valence proton of N is connected to one hydrogen atom (proton). The bonding orbits are perhaps of second subharmonic number. The configuration is difficult to be shown by small number of views. The study of the optical spectrum of NH_3 indicates two minima of the vibrational curve, corresponding to lower energy and higher energy states. The two possible states according to BSM have the following configuration:

A. Lower energy state:

This states may correspond to a large polar angles of the three deuterons as in the water molecule in a gas phase. The connected protons are aligned by the valence deuterons.

B. Higher energy state:

This states may correspond to smaller polar angles of the polar bonded deuterons of nitrogen atom. The positions of the bonding quantum orbits in this state may play a stabilizing role in the following way. Their long axes become parallel to the polar axis of the nitrogen atom. In such configuration their magnetic fields could be coupled with the magnetic fields of the orbits of the two equatorial EB bonded deuterons. In such condition, the molecule obtains four symmetrically aligned quantum orbits in respect to the polar axis. The QM spin interaction in such case should be quite large. This may provide a stable molecular configuration.

9.18 Molecules with folded vibrational-rotational spectra

From the previous paragraph we see, that the valence protons of the nitrogen atom is asymmetrical in respect to the polar axis. When participating in molecular groups it propagates its asymmetrical feature to them. For molecules and groups with a large asymmetry, the bending centrifugal forces become so large that the optical spectrum is additionally distorted. The large asymmetry between P and R branches causes a folding of R branch. A typical example of such molecule is HCN.

The four protons (deuterons) in the Carbon atom posses a polar axial symmetry but rotated at 90 deg. It is apparent that the obtained bonding connection $C \equiv N$ is quite asymmetrical. The single valence bond between the carbon and hydrogen additionally increases the asymmetrical properties of the molecule.

A possible configuration of HCN is shown in Fig. 9.63.

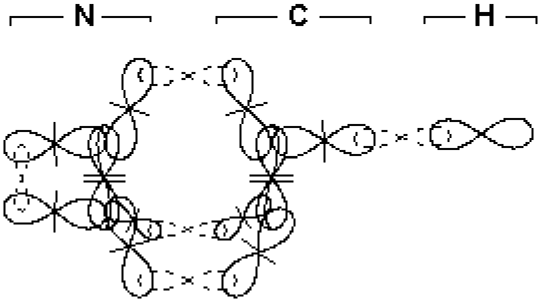

Fig. 9.63. A possible configuration of HCN molecule

Fig. 9.64 shows a stretched P branch and folded R branch of one of the optical transitions of HCN molecule. The folded R branch of HCN molecule evidently is from the CN bondings, caused by the asymmetrical bending forces around the common axis.

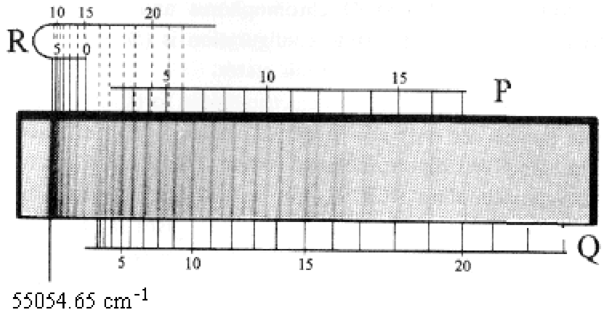

Fig. 9.64. Absorption band of $\tilde{A}\ ^1A'' - \tilde{X}\ ^1\Sigma^+$ transition of HCN molecule (courtesy of P. F. Bernath, (1995)

The first contributing factor is the asymmetry of the $C \equiv N$ bonding system in respect to the molecular axis of rotation and the second one is the asymmetrical position of the proton, bonded to the carbon.

For explanation of the folded R branch we may use the following simple example of a three leg chair on a horizontal plane. Let the top of the chair is tipped by a horizontal force causing a rotation around its vertical axis. There will be two different moments of the motion: when two legs are in contact with the horizontal plane and when only one leg is in contact. Now suppose, that the top of the chair is loaded with mass that is displaced from the central axis of rotation. Let also consider, that the horizontal plane is partly soft. We arrive to a similar conditions as for the bonding connection and IG attractive forces between C and N nuclei. The motion analysis of the example with three leg chair leads to the following conclusion:

The folding of the R branch is a result of changed momentary energy balance for one of the electrical bonds of CN group due to a redistribution of the IG forces.

9.19 CO_2 molecule

The carbon atom in CO_2 molecule is in the middle, so this molecule is highly symmetrical. For calculation of the internuclear distance, Eq. (9.56) could be used with small modification.

- considering CO system as a single molecule
- replacing the factor $(A - p)$ with the product $[(A_1 - p)(A_2 - p)]^{1/2}$, where: A_1 is the carbon atomic mass A_2 is the oxygen atomic mass. The factor 2 in front of *p* for C atom takes into account the exclu-

sion of 4 protons, as participating in the bonding system.

The obtained internuclear distance for CO group, according to the above consideration is about 1.284 A (angstroms) for a second subharmonic orbit. One view of the obtained configuration is shown in Fig. 9.65.

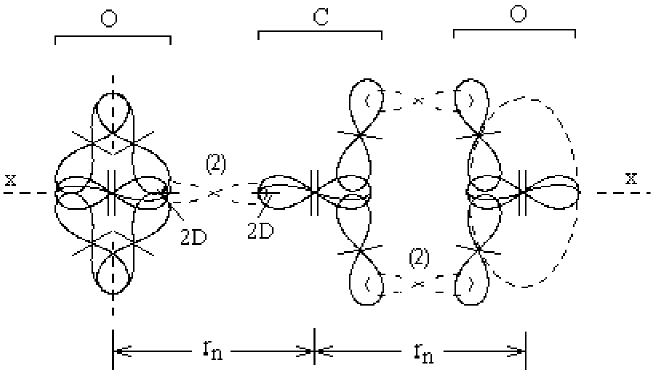

Fig. 9.65 Single view of CO_2 molecule Note: The two proton pairs in the left side of the drawing with two bonding orbits are similar as these in the right side but rotated at 90 deg. So only the projection of one of two bonding orbits is visible in the left side

If the view is rotated at 90 deg around *xx* axis, the left hand side will be interchanged with the right hand one. The molecule is twisted due to the proton twisting, but this is not shown in the drawing.

CO_2 molecule exhibits both types of above discussed vibrations contributing respectively to the following two types of spectra:

Case (a) Pure R and P branches only, the middle of the gap between them is at 2350 cm^{-1}

Case (b) R and P branch with very strong Q branch at 664 cm^{-1}.

Case (a) is related with linear vibrations, while case (b) with quasirotational motion. The latter is a result of molecular bending. Such conditions are possible due to the large length to width ratio of the molecular dimensions (a similar reason for Q branches in H_2 ortho-II molecule, see §9.9.4) The QM model for case (a) is known as antisymmetric stretch (top), and for case (b) as asymmetric stretch (bend). Their spectrum are shown respectively in Fig. 9.66 and Fig. 9.67.

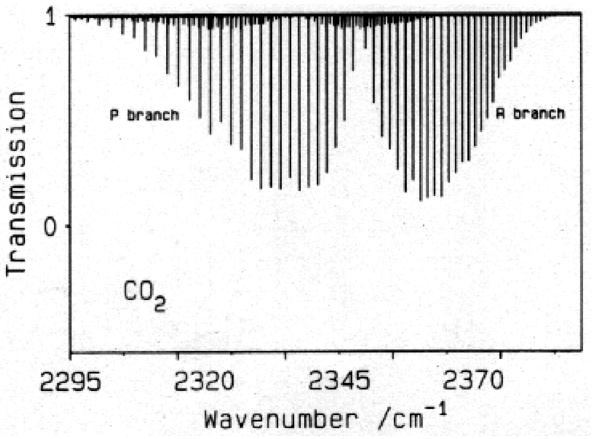

Fig. 9.66
Antisymmetric stretching fundamental band of CO_2

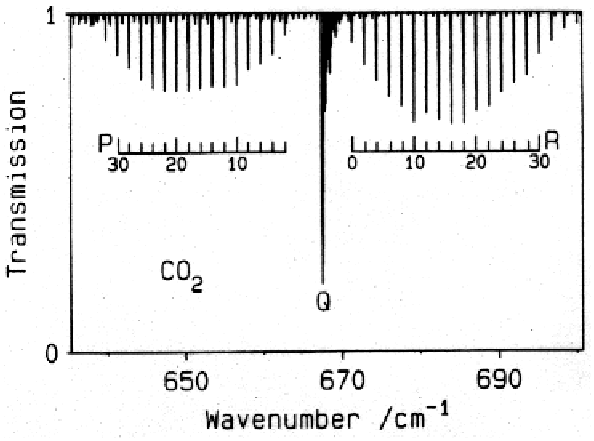

Fig.9.67
Bending fundamental band of CO_2

9.20. Water molecule

Figure 9.68 shows the configuration of the water molecule in one projection. The equatorial GBclp bonded deuteron are not shown in this projection.

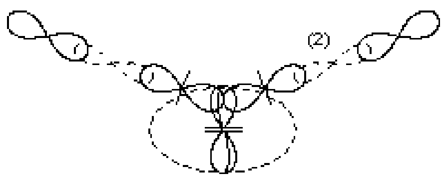

Fig. 9.68
Water molecule

The configuration of H_2O shows a large angular freedom of the oxygen protons. In the solid phase this angle is self adjusted in order to match the convenient crystal configuration.