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THE LIGHT AS A TOOL TO UNRAVEL
THE STRUCTURE OF MOLECULES

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1 Introduction

The purpose of this article is to outline the present role of molecular spectroscopy in the understanding and describing the physics of molecules. This article is not aimed at the specialist but at scientists and technologists who wish to have an idea on i) what kinds of information on matter can be derived from spectroscopy and ii) what is the present state of the art at the level of information we can derive from such physical technique. Necessarily we will gloss over many details and mathematical developments, but will try to mention the basic concepts and discuss the lines of thoughts developed by spectroscopy; with the aid of a few examples, we'll give an idea of how far one can go in the understanding of a few natural phenomena and in exploring the world of molecule and their behavior as described

by spectroscopy. Moreover, when possible, indications of the applications already in use and possible potential applications for future technology will be mentioned.

Only a few techniques at present allow the curious researcher to reach the description of a molecule and of its properties at a spatial resolution of a few tenths of a nanometer (i.e. on the Angstrom scale $= 10^{-8}$cm.) On the other hand the development of a successful and useful Science requires a deep and detailed knowledge on the nature, shape (architecture and symmetry), dimensions, movements and behavior of molecules as isolated entities (as, for instance, in the gas phase) or in condensed phases (e.g. liquid, solution and solids). Such curiosity is justified by the fact that the macroscopic properties of materials which make them useful depend on the properties of the molecules the materials are made of and how they are assembled in a supermolecular organization.

Few are the physical techniques which provide the way to determine the structure and properties at the Angstroms scale; indeed one thing is to derive an "overall" or "average" macroscopic physical quantity which is related to an ensemble of molecules (e.g. thermodynamic quantities, mechanical or electrical properties etc) and one thing is to be able to measure atomic distances (with the accuracy of 10^{-3}A), bond angles, electronic densities, atomic charges and electronic mobility between atoms within each molecule (intramolecular) and between atoms belonging to the neighboring molecules (intermolecular).

At present the frequencies of molecular rotations, frequencies and amplitudes of atomic vibrations, electrical dipole moments, atomic electrical charges, atomic masses, nuclear and electronic spins etc. can be easily obtained and used for the deep understanding of the physics of natural phenomena.

For many years the direct vision of the extremely small world has been obtained by various kinds of microscopic techniques where nature appears directly at the human eye. With the traditional optical microscope objects with dimension of a few micrometers (1μm $= 10^{-6}$cm) can be easily seen and characterized; next objects of ~ 1 micron could be explored with a variety of electronic microscopies. The

direct observation of single molecules and/or atoms remained an un-thinkable dream for many years until 1986 (Nobel prize to E. Ruska, G. Binning and H. Roher) which saw the birth of two new techniques namely Scanning Tunnelling Microscopy (STM) and Atomic Force Microscopy (AFM) which were later implemented in various ways.

The mystery of the "invisible molecules" was broken by AFM and STM which provide the way to see single atoms and single molecules deposited on a solid surface and allow to unravel in detail their structure and organization and even some of their overall molecular motions [1] (figs. 1.1, 1.2). At present single atoms or molecules can be held by special tweezers and can be moved from one place into another one, at the molecular scale, in the specimen under study (fig. 1.3).

The knowledge of geometry and shape of molecules throughout many years has been based mostly on the detailed information derived from solid (crystalline) samples with X ray crystallography; this technique works best when atoms (or molecules) are organized in a periodic lattice of a given symmetry. The periodicity of the electronic distribution can be probed by the diffraction of the X ray radiation and molecular and crystal structures obtained (fig. 1.4). Interatomic distances in a non periodic assembly of molecules (gases, liquids and amorphous solids) could be reached also by electron diffraction (fig. 1.5).

The purpose of this paper is to provide a quick overall analysis of the possibility of probing the world of molecules by vibrational spectroscopy. We shall first outline the basic physical principles and will later indicate the recent developments which witness the renaissance of this technique.

2 Molecular Mechanics

Let a suitably chosen set of N atoms somehow approach each other and develop some kind of directional interactions which stick them together to form an aggregate of atoms called "molecule". Since atoms are made up of positive (nuclei) and negative (electrons) electrical charges the kind of repulsive and attractive interactions which
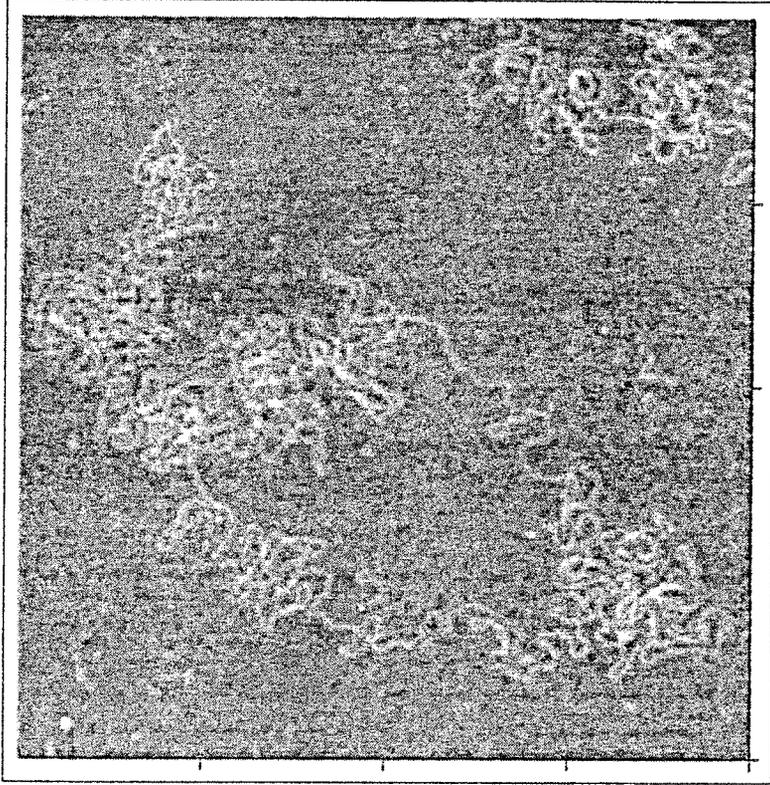
Figure 1.1: NM105 lambda DNA imaged dry on poly-L-lysine mica, by AFM technique. Scan size 900×900 nm [2]. Courtesy of: Dr. R.M. Henderson Department of Pharmacology Tennis Court Road, Cambridge, UK CB2 1QJ.

take place are essentially of electrostatic nature. Let $V(\{r_i\})$ be the total potential energy of the systems which changes when nuclear coordinates $\{r_i\}$ are changed. Physics tells us that the final shape of such object consisting of N electrically interacting atoms ($i = 1, \ldots, N$) corresponds to the minimum potential energy (equilibrium) structure, that is for a given choice of $\{r_i\} = \{r_i^0\}$, such that $\nabla V = 0$.

Let us consider, for sake of simplicity, a heteronuclear diatomic molecule A-B where atoms A and B (with atomic masses m_A and m_B respectively) lie at a distance r. Let us describe in a classical way, without any recourse yet to quantum mechanics, the process of formation of the molecule: when atoms A and B are approached from an
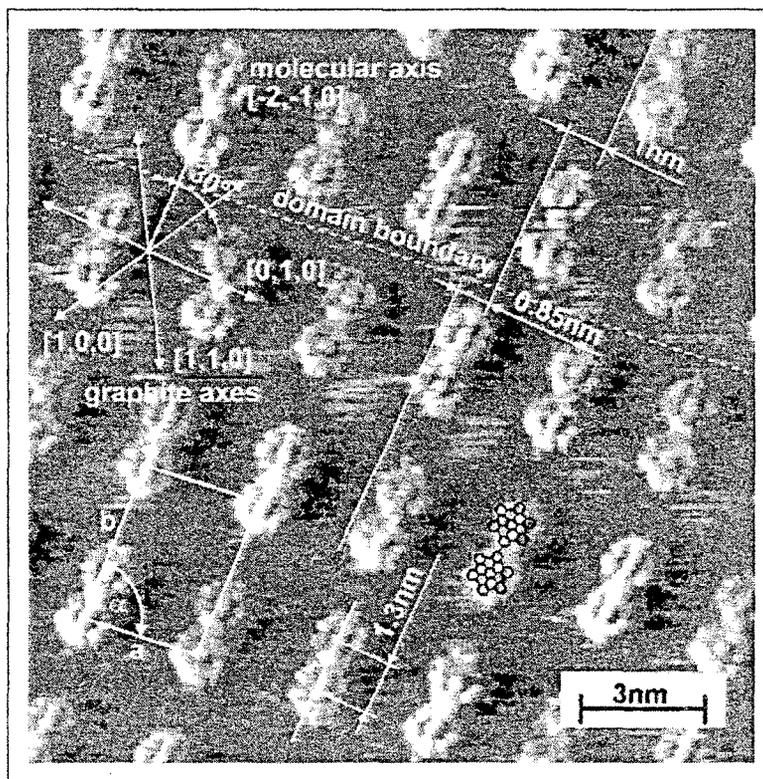
Figure 1.2: STM image of polycyclic aromatic molecules (Bishexa-peri-hexabenzocoronenyl) deposited on the basal plane of a graphite crystal. From ref. [3].

infinite distance they start interacting and attractive and repulsive forces are developed; we can sketch a potential energy curve $V(r)$ (fig. 2.1).

At $r = r^0$ a repulsive force originating by the interaction of the positive nuclear charges is exactly balanced by attractive forces between nuclei and electrons in such a way that atoms are bounded together in a stable atomic arrangement, i.e. a chemical bond is formed. The chemical bond is than formed when $\frac{dV}{dr} = 0$. From $V(r)$ of fig. 2.1 we derive additional interesting information. Classically the molecule is at rest at $r = r^0$, if an increasing amount of energy is provided the molecule start oscillating with amplitudes of vibration asymmetrically increasing at either sides of $r = r^0$: as a consequence, the av-
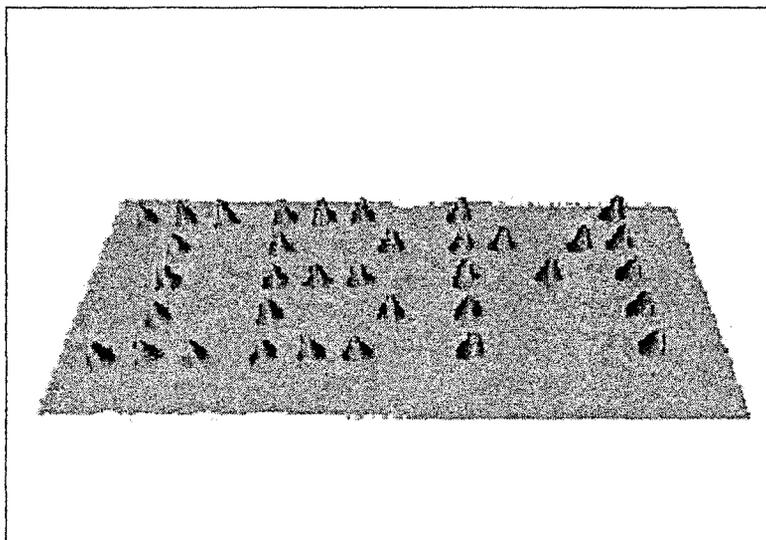
Figure 1.3: STM image of Xenon atoms on the (110) surface of a pure
Nickel crystal. The IBM acronym has been obtained by displacing the Xe
atoms on the surface with the STM tip. From ref. [4].

erage bond distance increases (thermal expansion). When $\Delta E = D^0$
is provided (D^0 = dissociation energy) $r = \infty$ is reached. It has to
be noticed that D^0 is qualitatively a measure of the reactivity of the
systems, i.e. on how easy is to make chemistry with the system.

The exact knowledge of the intramolecular potential still escapes
any human possibility and recourse is made to i) various "empirical"
models more or less successful, ii) an approximate (but at present
quite reliable) description from quantum mechanics.

Let $V(r)$ be the molecular potential energy function for the diat-
omic molecule A–B under study. We know very little of such a func-
tion for any molecule. We only know for sure that i) such function has
an absolute minimum at $r = r^0$, ii) has an asymmetrical shape with
a steep increase at $r < r^0$ (due to very strong repulsive forces when
atom A approaches atom B) and iii) at $r > r^0$ it reaches an asymp-
totic limit at $r = \infty$. We can than define $D^0 = V(\infty) - V(r^0)$, which
corresponds to the energy required for separating the two atoms at
infinite. Both r^0 and D^0 can be measured experimentally with great
accuracy.
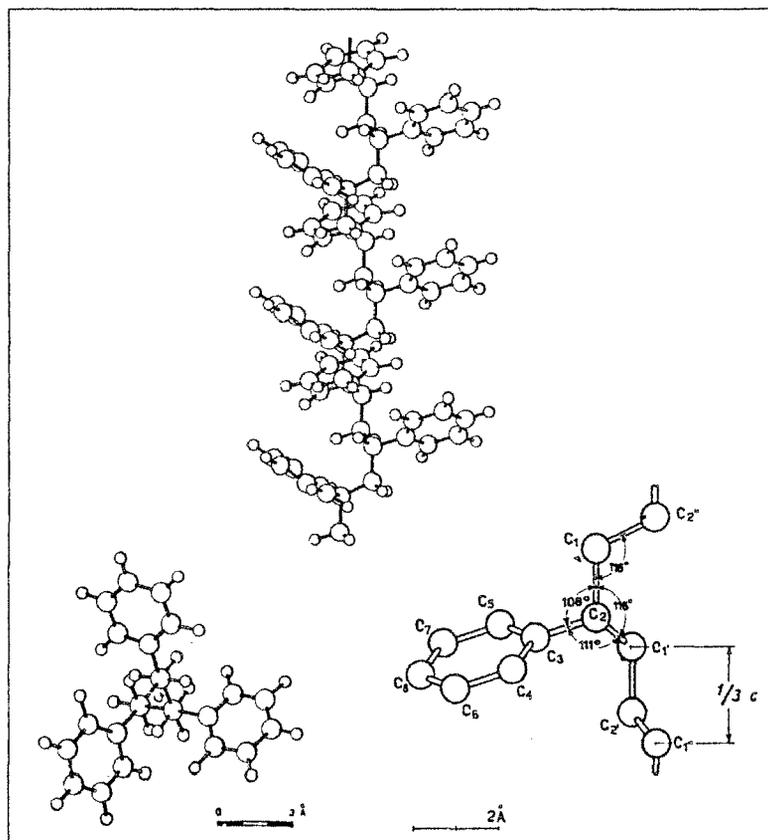
Figure 1.4: Structure of a chain of crystalline isotactic poly-styrene as obtained by X-rays diffraction. From ref. [5].

The first attempt to describe with an analytical function the intramolecular potential is a classical one which tries to write a potential function with parameters which can be derived, for a given molecule, from some experimental data (i.e. equilibrium geometry, dissociation energy, ...) [8, 9].

The classical approach briefly mentioned above cannot account for the electronic and dynamical properties of a real molecule. A quantum mechanical treatment has to be developed. As a consequence the internal energy associated to a molecule becomes quantized and several electronic states can be predicted at different energies, each state describing the system with specific electronic structure,
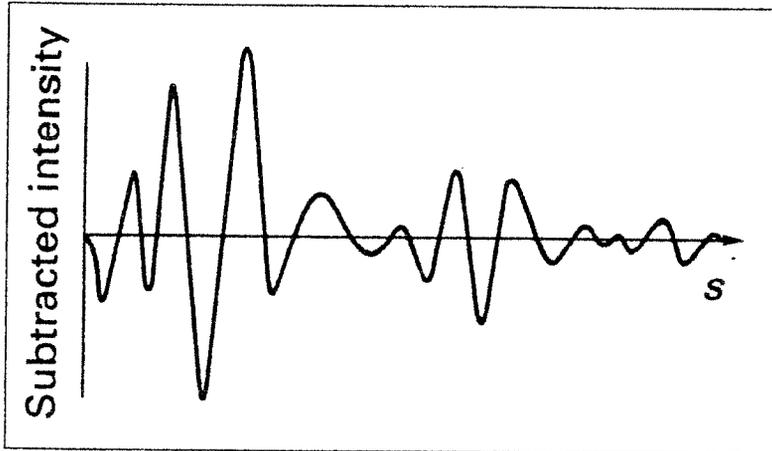
Figure 1.5: Electron diffraction pattern of a gaseous sample. Electron scattering intensity is plotted versus $s = 4\pi/\lambda \sin\theta$, θ = scattering angle. The diffraction pattern gives the distances between all possible pairs of atoms in the molecule. From ref. [6].
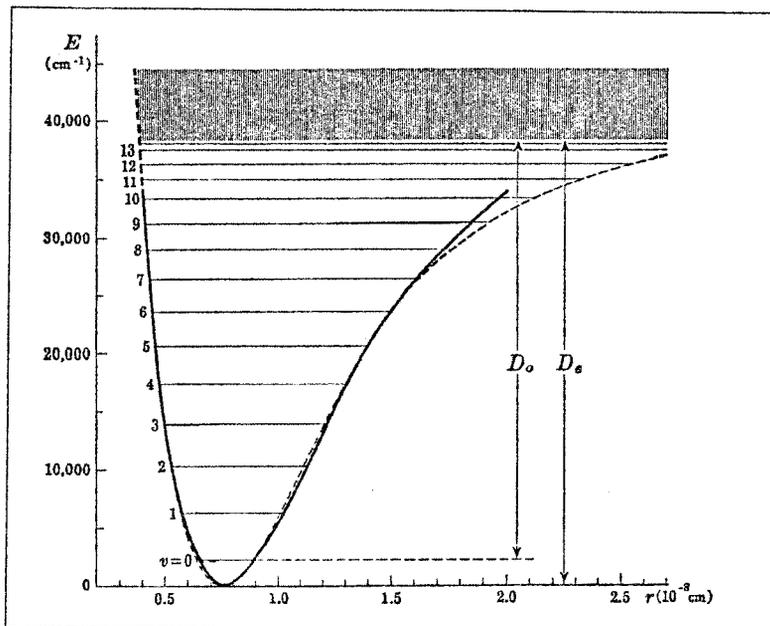
Figure 2.1: Scheme of a potential energy curve $V(r)$ of a diatomic molecule showing the most physically relevant quantities: r^0, D^0 and the quantized vibrational energies (from ref. [7, page 99]).

i.e. with a specific distribution of the electronic density in the bonds connecting the atoms. For each electronic state it is possible to obtain a specific intramolecular potential which depends on the peculiar electronic structure of the state considered and which allows to obtain with well defined interatomic distances and physical properties (fig. 2.2).
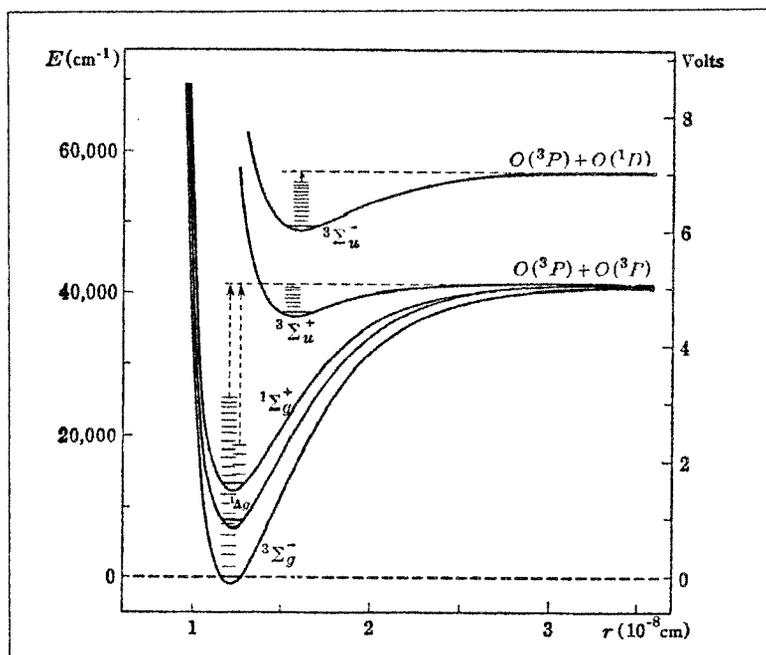
Figure 2.2: Intramolecular potential energy function associated to some of the electronic quantum states (with their vibrational states) of the O_2 molecule. The greek capital letters Σ and Δ with subscripts u or g and superscript $+$ or $-$ identify the symmetry of the wave-function associated to each state, the superscripts 1 and 3 indicate the multiplicity of spin state ($2S + 1$). From ref. [7, page 446].

In simple words each electronic quantum state describes an object (molecule) with a given shape. The structure, energies and symmetries of the manifold of electronic states of a molecule determines properties (or phenomena) which can be obtained by providing (= absorption) or removing (= emission) a precisely defined (and experimentally measured) energy. The lowest energy state in generally labelled as "ground state".

A molecule thus formed in any of its electronic quantum states is an object which in free space can perform translations, rotations and vibrations that can be described first with the rules of classical mechanics, then (when necessary) recourse is made to quantum mechanics.

If we wish to describe the motions of the molecule in terms of a laboratory fixed cartesian reference system we need $3N$ coordinates. If the molecule is considered as a rigid body the translational motion can be described by following the displacements of its center of mass with three instantaneous coordinates T_X, T_Y and T_Z. Three rotational coordinates (R_X, R_Y and R_Z) which describes rotational displacements around its 3 principal axis of inertia are required to treat the rotational motions of this rigid body. Moreover, when one consider that atoms can perform vibrational motions (during which the relative distances change) $3N - 6$ vibrational coordinates ($3N - 5$ for a linear molecule) are necessary for describing the instantaneous position in space of atoms which are performing some kind of (purely vibrational) periodic oscillations around the equilibrium positions r_i^0.

3 Rotational and Vibrational Motions of a Diatomic Molecule

The first step in the description of the rotational motion of the molecule can be easily obtained by describing with classical mechanics the rotation of a rigid body, i.e. by assuming that the interatomic bonds are held rigidly fixed [7]. For sake of simplicity let us consider a rigid diatomic molecule (dumbbell) where atoms with masses m_A and m_B lie at a fixed equilibrium distance r^0 (fig. 3.1).
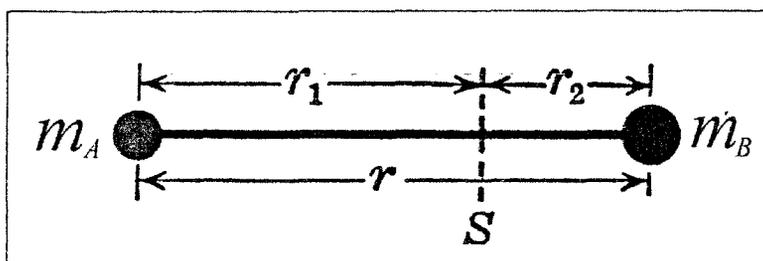
Figure 3.1: Model of a diatomic molecule with a rigid bond interconnecting atoms A and B with masses m_A and m_A.

The classical dynamical quantities associated to the molecular rotation of rigid rotor are the following :

- moment of inertia:

$$I = \sum_i m_i r_i^2 = \left(\frac{m_A m_B}{m_A + m_B}\right)(r^0)^2 = \mu(r^0)^2, \qquad (3.1)$$

- angular velocity:

$$w = 2\pi \nu_{rot}, \qquad (3.2)$$

where ν_{rot} is the rotational frequency (cycles per sec = Hz)

- angular momentum:

$$P = Iw, \qquad (3.3)$$

- classical rotational energy:

$$E = \frac{P^2}{2I}. \qquad (3.4)$$

While the classical energy is directly related to its angular velocity with no restriction on its actual values, quantization yields selected and discrete energy values

$$E(J) = \frac{h^2 J(J+1)}{8\pi^2 \mu(r^0)^2} = \frac{h^2 J(J+1)}{8\pi^2 I}, \qquad (3.5)$$

where h is the Planck's constant (6.6231×10^{-27} erg sec) and $J = 1, 2, 3, \ldots$ is the rotational quantum number associated to discrete values of the angular momentum. It follows from quantum mechanics that the rotational energies of the diatomic molecule A–B considered as a rigid rotor are discrete with values increasing quadratically with J. It follows also that the molecule can rotate only with certain rotational frequencies. From the allowed angular velocities:

$$w = \frac{h}{2\pi I}\sqrt{J(J+1)} \qquad (3.6)$$

from eq. (3.6) one derives the values for the rotational frequencies

$$\nu_{rot} = \frac{h}{4\pi^2 I}\sqrt{J(J+1)}. \tag{3.7}$$

Traditionally rotational frequencies are measured in Herz (cycles/sec = Hz). We can re-express the rotational energy $E(J)$ of eq. (3.5) in cm^{-1} by dividing by hc. Eq. (3.5) then becomes:

$$F(J)(\text{cm}^{-1}) = \frac{E(J)}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = BJ(J+1), \tag{3.8}$$

where:

$$B = \frac{h}{8\pi^2 cI} \tag{3.9}$$

is the called "rotational constant" and is the quantity which is measured experimentally from rotational spectrum.

The second step is to remove the restriction of rigidity of the bond. This requires the knowledge of $V(r)$. As previously discussed this is not an easy problem since sometimes a reasonable approximation to the "true" potential is sufficient for explaining some physical phenomena, in other cases the approximation to the true potential has to be strongly pushed further thus making the problem still more complex.

For treating molecular vibrations our lack of knowledge can be practically overcome by expanding $V(r)$ in a Taylor series about the equilibrium position at $r = r^0$:

$$V(r) = V^0 + \left(\frac{dV}{dr}\right)_0 (r - r^0) + \frac{1}{2}\left(\frac{d^2V}{dr^2}\right)_0 (r - r^0)^2 + \cdots \tag{3.10}$$

In eq. (3.10) V^0 can be removed by a suitable shift of the energy scale, $\left(\frac{dV}{dr}\right)_0 = 0$ by definition of r^0; we decide to truncate the expansion at the second order term and neglect the higher order terms. This is a strong approximation meaning that we restrict our analysis of the physical phenomena which are determined by very small displacement along r about r^0 and neglect to know the potential at large displacements from r^0.

We are then left with:

$$V(r) = \frac{1}{2}\left(\frac{d^2V}{dr^2}\right)_0 (r - r^0)^2 = \frac{1}{2}k(r - r^0)^2 \qquad (3.11)$$

which describes a parabolic potential with curvature k. We are then describing the molecule as an harmonic oscillator with reduced mass $\mu = \frac{m_A m_B}{m_A + m_B}$, with spring constant k and oscillating periodically with frequency

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}. \qquad (3.12)$$

In practice the model of the harmonic oscillator can be accepted since the atomic vibrational amplitudes are extremely small ($\sim 10^{-10}$ cm) and the anharmonic terms can, in a first approximation, be neglected.

Attention should be paid to the curious consequences in the physics (or chemistry) by the model of the molecule introduced with the approximations accepted for describing $V(r)$ (eq. (3.11)). We have accounted for the non-rigidity of the bond and allow a vibrational motion about the equilibrium position of the parabolic potential; however we have given up to the concept of D^0 because the molecule cannot be dissociated, i.e. no chemistry can exist.

As a consequence of having removed the rigidity of the diatomic molecule the dynamical problem becomes more complex since coupling between rotations and vibrations takes place and centrifugal distortions of a rotating harmonic oscillator have to be accounted for. In simple words we can easily understand that if a non rigid diatomic molecule performs very fast rotations in space (as an example for the molecule H-Cl $\nu_{osc} \sim 3 \times 10^{12}$ cycles per second) about its principal axis of inertia centrifugal forces are activated which increase the distance r between the two atoms thus stretching the spring connecting the bonds. Elegant theories and clever experiments have been developed for accounting in great details of such physical phenomena which, however, are outside the scope of this paper. For an extensive review of the basic theories see ref. [7].

As already stated if the rigidity of the interatomic bond is relaxed vibrational energies can be defined; assuming a harmonic oscillator

the potential and kinetic energies are given respectively as:

$$2V = k(r - r^0)^2 \tag{3.13}$$

$$2T = \mu \left(\frac{d(r - r^0)}{dt} \right)^2 \tag{3.14}$$

the quantized vibrational energies turn out to be

$$E(v) = \left(v + \frac{1}{2} \right) h\nu_{osc} \tag{3.15}$$

where v is the vibrational quantum number ($v = 0, 1, 2, 3, \ldots$) and ν_{osc} is the classical vibrational frequency already defined in eq. (3.12). It follows that the quantized vibrational energy levels of a diatomic molecule A-B taken as harmonic oscillator are equally spaced of a quantity $h\nu_{osc}$ and the amount of energy to be given in absorption (or emitted by emission) when the system changes vibrational states from v to $v' = v + 1$ (or $v' = v - 1$) is $\Delta E = h\nu_{osc}$.

Traditionally the vibrational frequencies are expressed in $\omega = \frac{\nu_{osc}}{c}$ (cm^{-1}) (c = velocity of light in cm/sec; further division of the members of eq. (3.15) by hc gives the usual expression of the vibrational energy, namely:

$$\frac{E(v)}{hc} = G(v) = \omega \left(v + \frac{1}{2} \right). \tag{3.16}$$

Let us select from the electromagnetic spectrum a certain range of energies $E(\nu) = h\nu$ which may interact with our diatomic molecule and possibly excite rotations and/or vibrations. In this chapter we purposely neglect to mention any technical concepts (sources, dispersing devices, optics, detectors, recorders etc.) which strongly depend on the frequencies (or wavelength) of the light beam considered.

Let $\mathbf{E} = \mathbf{E}^0 \cos(2\pi\nu t)$ describe the electrical component of the light beam which is impinging on our diatomic molecule and is perturbing its environment. The only possibility for a vibrating molecule to "perceive" the oscillating electrical field of the light beam is that its electronic distribution is such that it develops an oscillating (or rotating) molecular electric dipole moment μ. In such a case, classically,
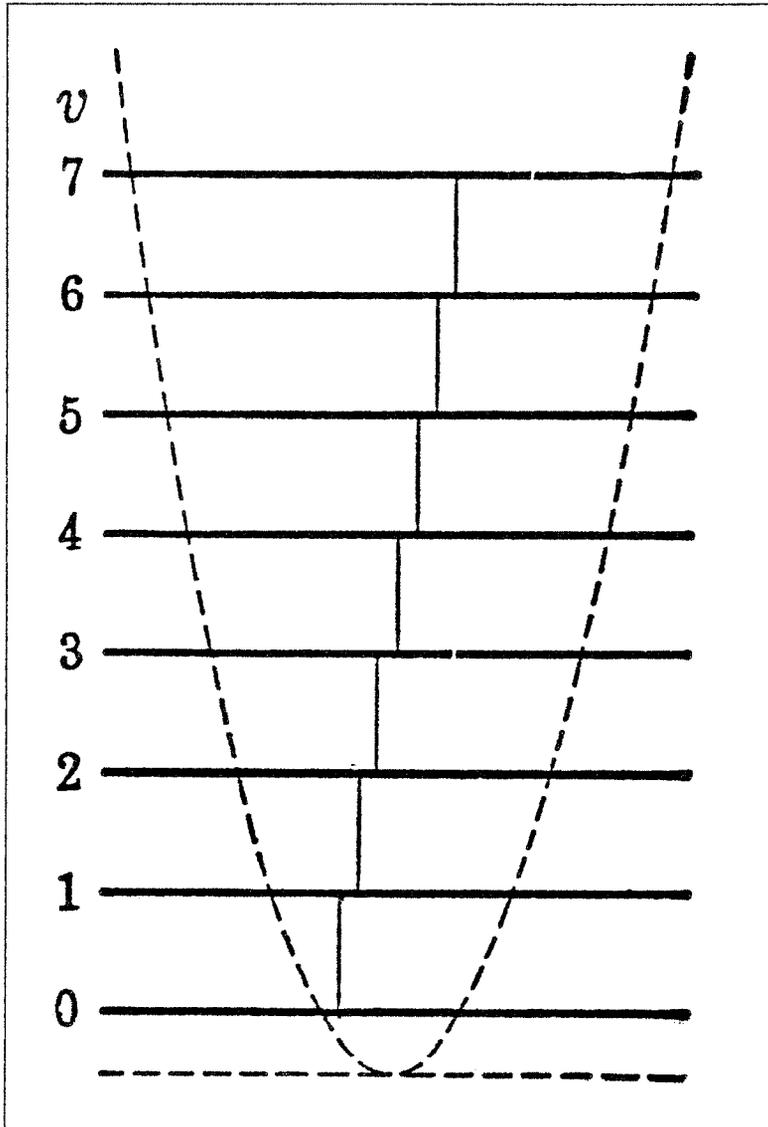
Figure 3.2: Vibrational levels of a harmonic oscillator . The dotted curve represents the harmonic potential energy (ordinate) as a function of interatomic distance r (abscissa). The equally spaced full lines with the corresponding vibrational quantum numbers v on the left represent the energy levels. The vertical segments indicate the transitions of one vibrational quantum. From ref. [7, pag. 75].

the oscillating electrical field of the light interacts with the molecular dipole: when conditions for mechanical resonance are verified the energy of the beam of light is transferred to the molecule.

The view of quantum mechanics is that the only energies which can be provided by the light beam to the molecule are those clearly defined by precise conditions of quantization (see eqs. (3.8) and (3.16)) and by selection rules. For a polar diatomic molecule the transitions allowed by selection rules between rotational quantum states are $\Delta J = \pm 1$. When light is absorbed in the pure rotational spectrum $\Delta J = +1$; from eq. (3.8) it follows that the energy absorbed turns out to be:

$$
\begin{aligned}
\omega &= F(J^{\text{upper}}) - F(J^{\text{lower}}) \\
&= B(J+1)((J+1)+1) - BJ(J+1) = 2BJ(J+1).
\end{aligned}
\tag{3.17}
$$

From eq. (3.17) we derive that the absorption spectrum associated to the pure rotations of a diatomic molecule is predicted to occur (and indeed observed) in the microwave range as a series of lines with a distance of $2B$ (here centrifugal distortions are neglected). If the frequencies of these absorption lines are accurately measured an accurate value of B is obtained; from eqs. (3.9) and (3.1) the unknown interatomic distance for the diatomic molecule A–B in a given electronic state is accurately measured with an accuracy of a few thousands of A [10].

Analogous procedure can be applied for the prediction of the absorption spectrum of the diatomic molecule A–B taken as harmonic oscillator. Vibrational selection rules are: $\Delta v = \pm 1$; for the absorption spectrum $\Delta v = +1$, thus:

$$
G(v^{\text{upper}}) - G(v^{\text{lower}}) = G(v+1) - G(v) = \omega,
\tag{3.18}
$$

which tells us that the frequency of the absorbed light is equal to the oscillation frequency of the harmonic oscillator and the absorption spectrum (generally in the infrared range) consists essentially of a single strong absorption band as indeed observed. From the observed frequency using eq. (3.12), once the atomic masses are known, the unknown force constant of the bond connecting the two atoms can be calculated. Tables of bond force constants (see table 3.1) of very
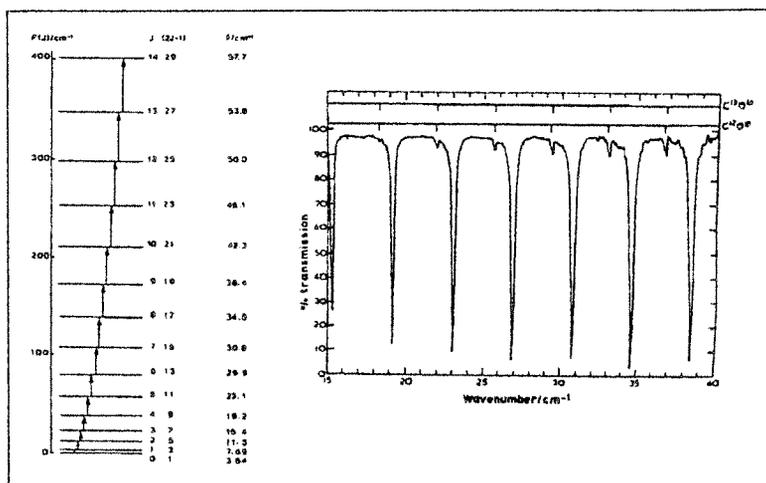
Figure 3.3: Rotational levels and rotational spectrum of the diatomic molecole CO.

many diatomic molecules have been obtained and from the analysis and comparison of the data a lot of chemistry (and physics) on the bond properties has been derived.

The last relevant observation refers to the quantized vibrational energies; from eq. (3.16) and fig. 2.1 it is apparent that the lowest vibrational energy level (zero point energy) does not coincide with the lowest energy minimum of the potential energy function. One has then to distinguish between equilibrium bond length (r^e) and r^0 (the average interatomic distance of an oscillators with $E^{vib} = E(v = 0)$). Any elaboration on this interesting issue is beyond the scope of this paper (see ref. [7]).

4 Moving Towards Larger and Structurally More Complex Systems. The Case of Polyatomic Molecules

Let us move from a very simple diatomic molecule and proceed toward more realistic molecular systems made up by several atoms (or very many, like a polymer or a protein!) of different type which take up in space a complicated structure.

Regarding the rotational motion of gaseous polyatomic molecules (when they can exist in the gas phase) the concepts just sketched for a

molecule	ν (cm^{-1})	k (mdynes/A)	r^0 (A)
HF	4138.5	9.66	0.927
HCl	2990.6	5.16	1.274
HBr	2649.7	4.12	1.414
HI	2309.5	3.14	1.609
CO	2169.7	19.02	1.130
NO	1904.0	15.95	1.151
ICl	384.2	2.38	2.321

Table 3.1: Vibrational frequencies (ν), Bond force constants (k), internuclear distances (r^0) for a set of diatomic molecules. From ref. [11].

diatomic molecule can be extended to the study of the accurate shape and geometry of polyatomic molecules in the gas phase. Instead of only one moment of inertia we have to consider the three principal moments of inertia I_A, I_B and I_C and derive energy levels and selection rules for such complex rotating systems [10, 12].

From rotational spectroscopy, geometries, bond distances and bond angles have been determined with great accuracy and have allowed to develop the basic correlations between molecular structure and physical and/or chemical properties.

The treatment of the vibrational dynamics of polyatomic molecules is an intriguing problem which has kept busy for a long time many workers, including the author of this chapter and many of his collaborators. Essentially one has to develop first the classical dynamics of a set of N "electrically" interacting atoms which make up an object whose shape is that at the "equilibrium" described by the absolute minimum of a multidimensional potential energy function.

Let $\{x_i\}$, $i = 1, \ldots, 3N$ be the set of instantaneous cartesian coordinates of the $3N$ atoms of the vibrating molecule and let $\{x_i^0 = 0\}$ be the corresponding equilibrium coordinates when the molecule is at rest (at the equilibrium). $\{x_i\}$ describe nuclear vibrational displacements from equilibrium, that is the potential minimum is taken as origin of our reference system. Moreover, the reference system is chosen in such a way that it translate and rotates with the molecule:

C_4H_4O				C_{2v}
r_s	Å	θ_s	deg	
O-C(2)	1.3621 (30)	C(2')-O-C(2)	106.55 (20)	
C(2)-C(3)	1.3609 (30)	O-C(2)-C(3)	110.7 (2)	
C(3)-C(3')	1.4309 (30)	C(2)-C(3)-C(3')	106.05 (20)	
C(2)-H(2)	1.0750 (50)	O-C(2)-H(2)	115.9 (5)	
C(3)-H(3)	1.0768 (50)	C(3')-C(3)-H(3)	128.0 (5)	

Atom	a_i [Å]	b_i [Å]
O	-1.1338	0
C(2)	-0.3193	±1.0918
C(3)	0.9885	±0.7155
H(2)	-0.8132	±2.0466
H(3)	1.8376	±1.3777

Bak, B., Christensen, D., Dixon, W. B., Hansen-Nygaard, L., Rastrup-Andersen, J., Schottländer, M.: J. Mol. Spectry. 9 (1962) 124.

MW: Nösberger, P., Bauder, A., Günthard, Hs. H.: Chem. Phys. 1 (1973) 418.

MW: Bak, B., Hansen, L., Rastrup-Andersen, J.: Discussions Faraday Soc. 19 (1955) 30.
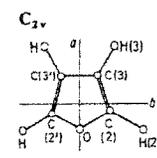
Figure 4.1: Geometrical parameter of a polyatomic molecule (C_4H_4O) as determined from its rotational spectrum observed in the microwave region of the electromagnetic spectrum. From ref. [13].

for this reason the coordinates $\{x_i\}$ are not independent. They must satisfy the 6 Eckart-Sayvetz [14] conditions, in order to allow a separation of the vibrational and rotational problem.

Just like in the case of diatomic molecule (eq. (3.10)) the generally unknown vibrational potential energy function can be approximated by the following Taylor expansion about the equilibrium structure

$$2V = 2V_0 + 2 \sum_i \left(\frac{\partial V}{\partial x_i}\right)^0 x_i + \sum_{ij} \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)^0 x_i x_j + \cdots \qquad (4.1)$$

The zero-th order term is removed by a suitable shift of the energy axis, the first order terms vanish, since the origin coincides with the equilibrium geometry*, the second order terms defines a quadratic potential. Again for most of the cases of chemical interest the expansion is truncated at the second order. The analysis of higher order terms goes beyond the scope of this paper.

The truncation at the second order implies that the restoring forces are assumed to be linear with displacements from the equilibrium,

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*Since the $\{x_i\}$ coordinates are not independent, due to Eckart-Sayvez conditions, the fact that linear terms in eq. (4.1) are zero is not immediate. It can be easily demonstrated (see for instance ref. [15, Appendix II]).

thus describing the polyatomic molecule as a set of N masses connected by elastic springs which can perform only harmonic oscillations.

For a complete discussion see, for instance, refs. [15, 16].

The kinetic energy of our system can be written as:

$$2T = \sum_i m_i \left(\frac{\partial x_i}{\partial t}\right)^2 . \tag{4.2}$$

For sake of conciseness we can rewrite eqs. (4.1) and (4.2) in matrix notation as:

$$2V = \mathbf{x}' \mathbf{F}_x \mathbf{x} \tag{4.3}$$

and

$$2T = \left(\frac{d\mathbf{x}}{dt}\right)' \mathbf{M} \left(\frac{d\mathbf{x}}{dt}\right), \tag{4.4}$$

where ' is the symbol of transposition, $f_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)^0$ are the elements of the force constant matrix and $\mathbf{M}$ is the $(3N \times 3N)$ diagonal matrix of the atomic masses.

A set of $3N$ equation of the motion (one for each cartesian degree of freedom) can be obtained when kinetic energy (eq. (4.4)) and potential energy (eq. (4.3)) are introduced into Lagrange equations. The equations obtained can be described as a set of $3N$ coupled harmonic oscillators. Solutions are in the form:

$$x_i^j = L_{ij} \cos \sqrt{\lambda_j} t, \tag{4.5}$$

where λ_j are called "frequency parameters" and define the frequency of oscillation of the atoms during the j-th normal modes Q_j. During a given vibrational normal mode Q_j all atoms move in phase with frequency ω_j (in cm^{-1}) $= \sqrt{\frac{\lambda_j}{4\pi^2 c^2}}$ and with amplitude L_j. λ_j and L_j can be calculated by solving the secular equation

$$\mathbf{M}^{-1} \mathbf{F}_x \mathbf{L}_x = \mathbf{L}_x \Lambda, \tag{4.6}$$

where Λ is the diagonal matrix of the $3N$ λ_j parameters. For a polyatomic molecule 6 of the λ_j vanish because of the Eckart conditions:

they indeed corresponds to 3 rigid translations and 3 rigid rotations of the molecule. Thus $3N - 6$ λ_j are non vanishing and refer to the $3N - 6$ normal modes Q_j of the molecule. Depending on the shape of the molecule (symmetry) some of the non vanishing λ_j may turn out to be equal (degenerate modes: doublets, triplets and even quintuplets for very high symmetrical molecules, e.g. fullerene).

The relation between cartesian displacements and normal modes is as follows:

$$\mathbf{x} = \mathbf{L}_x \mathbf{Q}. \tag{4.7}$$

The matrix $\mathbf{L}_x$ cannot be described as an orthogonal transformation because $\mathbf{M}^{-1}\mathbf{F}_x$ is not symmetrical. The normalization condition for the eigenvector matrix is chosen as:

$$\mathbf{L}_x \mathbf{L}_x' = \mathbf{M}^{-1}, \tag{4.8}$$

which allows to write both kinetic and potential vibrational energies in diagonal form:

$$2T = \left(\frac{dQ}{dt}\right)' \left(\frac{dQ}{dt}\right), \tag{4.9}$$

$$2V = \mathbf{Q}' \Lambda \mathbf{Q}. \tag{4.10}$$

The important information derived from eqs. (4.9) and (4.10) is that normal modes can be described as uncoupled simple harmonic oscillators.

At this point quantum mechanics (see, for instance ref 17) must be introduced : the molecule is now a set of $3N - 6$ simple harmonic oscillators. The associated Schrodinger equation gives rise to $3N - 6$ sets of vibrational levels, one for each Q_j:

$$E^{\text{vib}} = \sum_j E_j(v) = \sum_j \left(v + \frac{1}{2}\right) h\nu_j = \sum_j \left(v + \frac{1}{2}\right) hc\omega_j. \tag{4.11}$$

Application of the same selection rules as in the case of a diatomic molecule taken as harmonic oscillator allows to predict that the

vibrational absorption spectrum of a polyatomic molecule consists of a set of absorption bands each one corresponding to the transition between adjacent vibrational levels $v_j \longrightarrow v_j + 1$ (fundamental transitions) for each normal mode.

In reality the observed experimental spectrum of a polyatomic molecule i) may show less that $3N - 6$ fundamental transitions, ii) may show many additional bands not predicted by the theory of harmonic oscillations and iii) the observed bands can be strong, weak and very weak.

Case i) is accounted for if the point symmetry of the molecule (in its equilibrium geometry) is identified: in this case group theory applies [15, 18, 19, 20] and symmetry considerations allow to derive selection rules for vibrational transitions (see below).

Case ii) is due to the fact that in reality higher order terms in the expression of the molecular potential should be included [12, 15]; the anharmonicity of the potential produces transitions to quantum states with $\Delta v = 2, 3, 4, 5$ which generate strong or weak bands throughout the energy range of the vibrational spectrum.

Case iii) is associated to the fact that molecules are build up by nuclei and electrons which determine the charge distribution in molecules at rest and during vibrational modes. The electron charge distribution and its mobility are the ingredients determining (for a thorough discussion see refs. [21, 22, 23]) the vibrational absorption intensities (this applies also to the case of the rotational lines in rotational spectroscopy in the microwave region) and the Raman scattering factors.

It is conceptually very pleasing to realize that, if the molecule (in its equilibrium structure) has a symmetric shape, Group Theory helps a lot in the prediction of the spectra and of the related properties [15, 18, 19, 20]. Each molecule can be classified as belonging to a given point group. The vibrational displacements of the molecule expressed in cartesian coordinates form the basis of a reducible representation of the point group. The linear transformation (eq. (4.7)) carries to the normal coordinates Q_j which form a basis for the irreducible representation of the point group. With the help of Wigner's operator it is then possible to predict the structure of the irreducible

representation, i.e. how many times a given irreducible representation (symmetry species) appears in the full representation for the molecule considered. We can then assign all the $3N - 6$ Q_j and the 6 non vibrational degrees of freedom (3 translations and 3 rotations) to the various irreducible representations. When group theory is applied to the quantum treatment of vibrational problem it becomes possible to predict whether a given quantum transition can occur when light is impinging on the molecule [15]. For this reason some quantum transitions will be observed in the spectra (spectroscopic activity) and some will not (inactive transitions).

On the other hand, the matching of the theoretical predictions of group theory with the experimental vibrational spectra is a formidable tool for deriving the shape of the molecule (see, for instance, ref. [24]).

5   The Molecular Force Field

In principle eq. (4.6) can be easily applied to calculate molecular vibrational frequencies and the corresponding normal modes; in practice while atomic masses (matrix M) are known almost nothing is known for the force constant matrix F_x. In eq. (4.6) one would need to know all the elements of each of the $3N \times 3N$ force constant tensor. This difficulty has never been overcome by any researcher and smart tricks and models needed to be developed for deriving relevant information on the molecules from the infrared absorption spectrum which, as of today, is extremely easy to be obtained by the moderns instruments in this field.

The first important advancement in the field has been the definition of a new set of vibrational coordinates which have been suggested by the feeling chemists have on molecules as objects held together by directional forces developed along the chemical bonds. In 1940 the russian school of Elishevich [25] and in 1941 Wilson [26, 15] have defined sets of chemical "internal" displacement coordinates (generally labelled by R) by suitably making linear combinations of the cartesian displacements. The Wilson's new coordinates are called : a) Bond stretching, b) angle bending, c) out of plane deformation and d)

torsion.
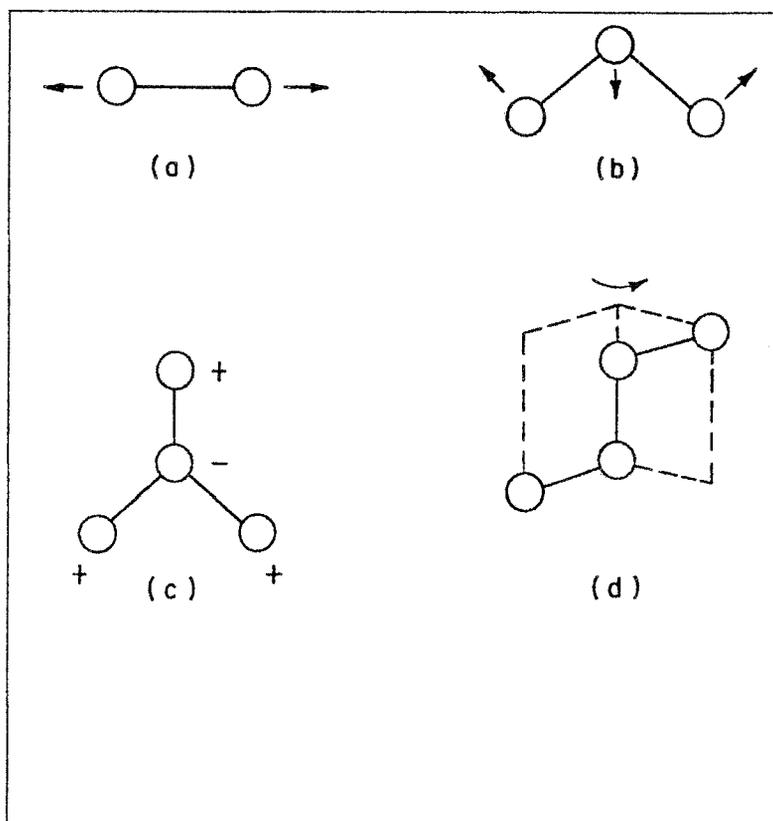
Figure 5.1: Definition of the internal vibrational displacement coordinates.

Let

$$\mathbf{R} = \mathbf{B}\mathbf{x} \tag{5.1}$$

be the linear transformation between $3N$ cartesian and $3N - 6$ internal vibrational displacement coordinates. Let us also assume for simplicity that we are dealing with a non redundant set of R's (i.e. the number of internal coordinates is indeed $3N - 6$).

The vibrational potential can be written in terms of R's as

$$2V = \mathbf{R}'\mathbf{F}_R\mathbf{R} \tag{5.2}$$

and the kinetic energy as

$$2T = \left(\frac{dR}{dt}\right)' (G_R)^{-1} \left(\frac{dR}{dt}\right),$$ (5.3)

where

$$G_R = BM^{-1}B'$$ (5.4)

is the inverse of the metrical tensor in the internal coordinate space R, which can be calculated easily because atomic masses and the geometry of the molecule are known.

The eigenvalue equation (eq. (4.6)) in internal coordinates becomes

$$G_R F_R L_R = L_R \Lambda$$ (5.5)

and can be solved once the elements $f_{ij} = \left(\frac{\partial^2 V}{\partial R_i \partial R_j}\right)_{eq}$ are known.

The great contribution by Wilson has been to provide us with a tool to learn chemistry from a vibrational spectrum since he is aiming at the molecular properties which are involved in the normal modes of vibrations. Diagonal terms f_{ii} are the elastic constants of springs which "replace" the chemical bonds or springs which describe the elastic reactions to the opening (closing) of bond angles and torsional angles.

The important concept which makes the dynamical problem of a molecule different from the dynamical problem of a strictly mechanical model is the following. In a purely spring-and-balls model only the diagonal elements f_{ii} of the F_R matrix must have non zero (and positive) values and all off-diagonal terms f_{ij} must be zero since mechanical springs do not affect each other during vibration. For an object held together by electrons and nuclei electrons are mobile throughout the whole molecule and change their distribution when bond stretchings and angle bendings or torsions are excited. The cross terms f_{ij} thus acquire a great importance since they tell us to what extent electrons are fluctuating across the molecule during each internal coordinate displacement.

Because their importance in chemistry and physics many and great efforts have been made in the past 50 years to calculate the force

constants f_{ij} from the experimentally observed spectra. Conceptually in eq. (5.5) G (from geometry and atomic masses) and Λ (from the experimental spectrum) are the known parameters which should allow to calculate the elements of the matrix F_R. 50 years of work are not many in such a field since spectra had to be recorded and analyzed and then the calculation of force constants had to be faced. The problem which needed to be overcome is that the number of independent force constants is, in general, larger than the number of experimental frequencies. Several methods have been proposed : the most relevant are: i) the use of spectra of the isotopic derivatives of a given molecule which, by definition, possess all an identical F_R matrix (see, for instance refs. [27] and [28]) ; ii) least squares refinement of force constants over the spectroscopic data of many chemically similar molecules (see for instance refs. [28, 29, 30]), iii) use of the data from vibro-rotational and rotational analysis such as centrifugal distortions etc (see for instance ref. [29]).

Empirical force constants from spectra of many classes of molecules are presently available; thanks to the computational facilities now available also on personal computers, the prediction of the vibrational frequencies and of the vibrational displacements of a given molecule (by eq. 34) is a routine work even for very large molecules, i.e. for molecules made up by very many atoms in a complex molecular structure (e.g. ref. [31]). Comparison of the calculated and experimental vibrational frequencies can provide chemists or physicists with information on the molecular structure.

6   Further Use of Molecular Dynamics: Chemical Analysis

We have already given a physical meaning and discussed the use of three of the terms (G, F and Λ) appearing in eq. (5.5). The last term which can be calculated is the matrix of the eigenvectors L_R which do provide extremely useful information in many practical applications of vibrational spectroscopy. Associated to the eigenvalue λ_j one calculates the eigenvector $(L_R)_j$ which describes the vibrational displacements in terms of the Wilson's internal coordinates R. From eqs. (4.7) and (5.1), and by a proper definition of the generalized in-

verse of the matrix **B** [32], it is possible to write

$$L_x = B^{-1}L_R \tag{6.1}$$

i.e. a linear transformation between the calculated displacements in internal coordinates and the corresponding ones in the cartesian space. In this way all normal modes of a given molecule can be visualized and, if needed, used as input of a computer program which displays the wiggling of molecules in tri-dimensions. From the example given in fig. 6.1 we can directly make some interesting observations:

In fig. 6.1 one notices that some of the normal modes imply displacements "localized" on a given bond while the other parts of the molecule practically remain at rest; some other modes, instead, involve the motions of all the atoms and they are said to be "delocalized" or "collective". Many bonds show localized vibrations at a more or less specific frequencies which are then taken as characteristic and typical of the existence of that particular bond. In other words it has been observed in many correlative studies (theoretical and experimental) that the so called chemical functional groups show characteristic frequencies in infrared. For example functional groups such as C–H, CH_2, CH_3, OH, NH, NH_2, C=N, C=O, C–Cl, C–Br, C–F, C–I, C–O–C, COOH, NO_2 and many others show characteristic group frequencies, related to normal modes well localized on the functional group.

It has been then easy to discover that the vibrational experimental spectrum provides characteristic signals for the identification of the existence of these functional groups in the molecule under study. It follows that each molecule shows its vibrational "fingerprint" in the vibrational spectrum; the "fingerprint" is so specific and characteristic of the molecule that a chemical diagnosis can be easily carried out, i.e. the chemical composition of the sample studied can be "read" from the experimental vibrational spectrum (fig. 6.2)

The use of vibrational group frequencies has become a widespread technique [34] of chemical characterization of practically all substances, from gases to biological materials, in all phases, from specimens in the most awkward physical situations (high and low temperature, solid, liquid, gases, macrosample or microscopic samples, from surfaces to aerosols etc.). Technology and engineering have developed
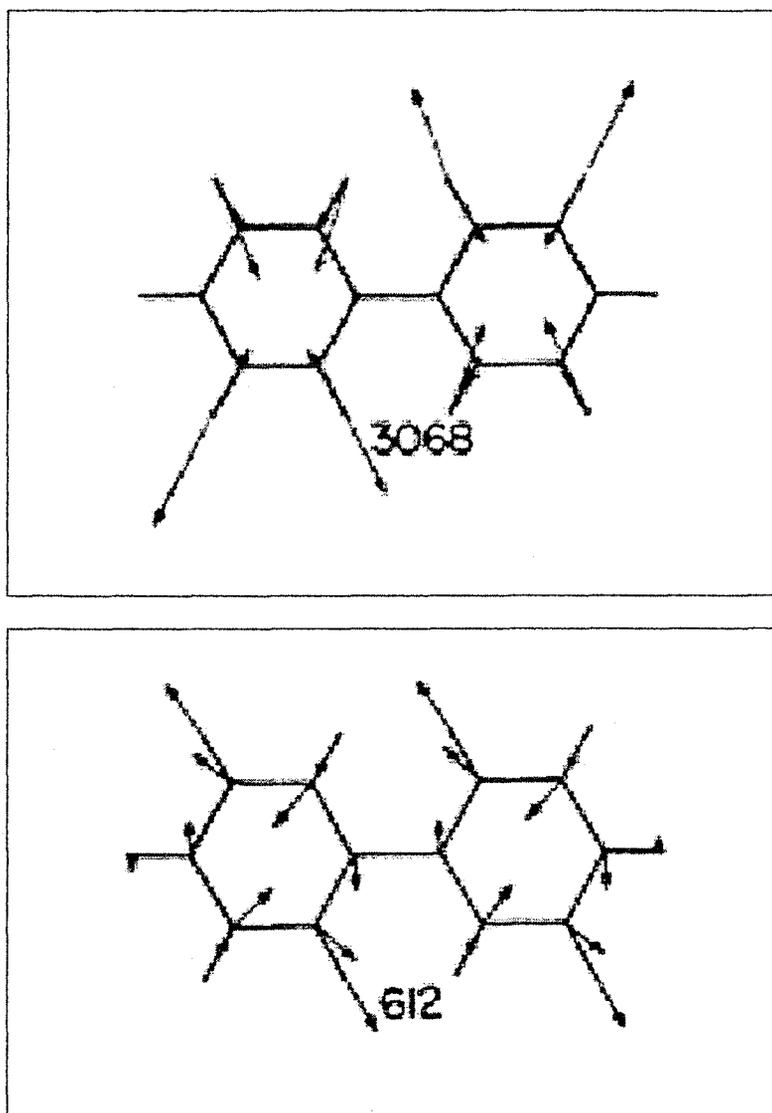
Figure 6.1: Vibrational displacements of biphenyl associated to: a "localized" normal mode (up) and a "collective" normal mode (down). The force field has been refined by least squares over many isotopic derivatives of this molecule (ref. [33]). Arrows indicate the trajectory followed by each atom during one fourth of a complete oscillation. (The scale of displacements is arbitrarily chosen).
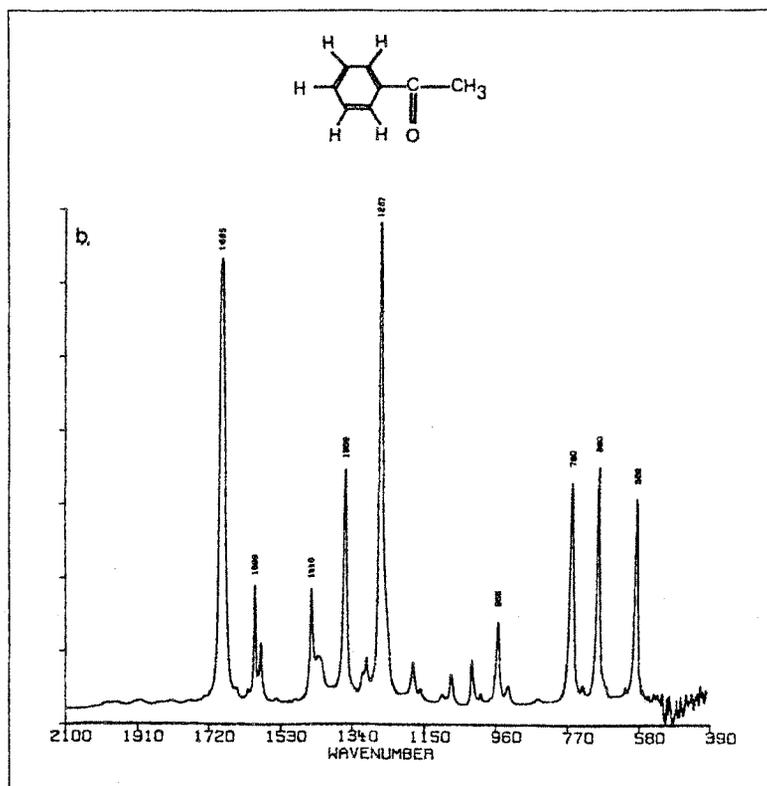
Figure 6.2: Observed infrared absorption spectrum of a supposedly un-
known material. The identification of the characteristic group frequen-
cies as indicated leads to the identification of the molecule: acetophen-
one, with chemical formula drawn on the bottom of the figure.

very sensitive, very fast (up to fsec) and super-automatic spectromet-
ers and Fourier transform interferometers.

At present every research laboratory at universities and in indus-
tries which deals with any sort of materials has more than one ma-
chine which allows the recording of the vibrational spectra. The list
of field where vibrations are routinely used can be very long; we just
name a few as examples: organic chemistry, pharmaceutical chem-
istry, plastic industry, paint industry, forensic laboratories, biolo-
gical laboratories in hospitals, geology, mining, coal industry, food
industry, electronic industry, industry of semiconductors, etc.

7   Vibrational Infrared and Raman Spectroscopy

For the everyday user there are two most relevant ways to obtain experimentally the vibrational spectra. These two ways have been exploited by technology and very sophisticated instruments have been developed and are commercially available.

7.1   Absorption Spectroscopy in the Infrared

The basic concepts have been already presented above in this article with eq. (3.18) for the diatomic molecule and eq. (4.11) for the polyatomic molecules taken as harmonic oscillators. Let us first remind the basic common relation $E = h\nu$ (where h is the Planck constant and ν is the oscillation frequency of the electric field associated to the light wave). The energy required for a one-quantum vibrational transition from $v = 0$ and $v = 1$ as given in eqs. (3.18) and (4.11) are usually in a frequency range from approximately 5000 to 5 cm^{-1} (i.e. with wavelength from 2 to 200 μm); thus fundamental vibrational transitions can be observed by irradiating the sample with infrared light.

Sources of infrared radiation, dispersive systems and detectors are available for exploring the whole frequency range and spectra are recorded in all possible modern ways with spectra plotted usually as absorption intensities vs. wavenumbers in cm^{-1}. Three are the observables which can be read on a spectrum, namely i) peak frequencies, ii) integrated band intensities and iii) band shapes. In the discussion which follows band shapes are neglected.

Very much has been already said in this paper on vibrational frequencies which are related to the dynamics, chemical structure and shape of the molecules. Let us quickly mention the relevance of the study of vibrational infrared intensities in order to derive further very relevant information of the electrical properties of molecules. This field of study is relatively recent and relatively few groups (including that of the author of this paper) have tackled in depth the theory and the experiments related to vibrational intensities [21, 22, 23]).

The distribution of electrons in any molecule determines their electrical properties. Depending on the equilibrium geometry the mo-
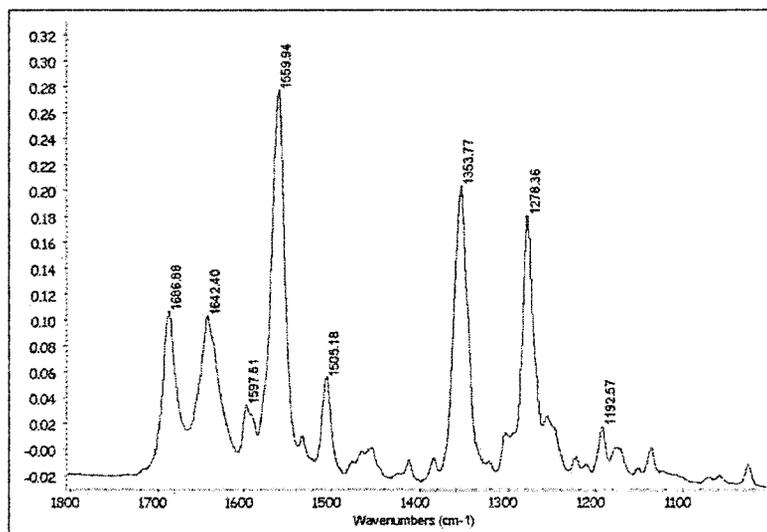
Figure 7.1: Infrared spectrum of a substituted perylene molecule $(C_{34}H_{28}N_2O_2)$.

lecule may possess a permanent dipole moment μ (polar molecules) or may have $\mu = 0$ (apolar molecules). During a given normal mode of vibration $\frac{\partial \mu}{\partial Q_i}$ may $= 0$ or $\neq 0$ depending on the geometrical changes induced by the vibration. For a one quantum quantum transition in vibrational absorption the intensity of the band (obtained from its integrated area) in the infrared is:

$$A_i = \text{const} \left| \frac{\partial \mu}{\partial Q_i} \right|^2 \qquad (7.1)$$

Again it is useful to express $\frac{\partial \mu}{\partial Q_i}$ in terms of the internal coordinates previously defined:

$$\frac{\partial \mu}{\partial Q_i} = \sum_t \frac{\partial \mu}{\partial R_t} (L_R)_{ti} \qquad (7.2)$$

The L_{ti} are defined in eq. (5.5). $\frac{\partial \mu}{\partial Q_i}$ are experimental quantities which can be measured in the spectra once the fundamental vibrations ($\Delta v = +1$) have been identified. Our group in Milano has paid a great attention to the study of vibrational intensity and has contributed to the development of a model which provides molecular parameters

from which again a lot of chemistry and physics can be learned for the interpretation of other phenomena.

The model consists in decomposing the molecular dipole moment μ into atomic quantities [35, 22, 23]. At any instant during the vibration

$$\mu = \sum_\alpha q_\alpha r_\alpha \qquad (7.3)$$

where q_α is the charge on atom α and may change during the vibration. Then the infrared intensities can be expressed as a function of the parameters q_α^0 and $\left(\frac{\partial q_\alpha}{\partial R_t}\right)^0$

$$\frac{\partial \mu}{\partial Q_i} = f\left(q_\alpha^0, \frac{\partial q_\alpha}{\partial R_t}, L_{ti}\right). \qquad (7.4)$$

Eq. (7.4) indicates that, once the dynamical problem of the molecules has been solved, from the experimentally measured infrared absorption intensities it is possible to calculate equilibrium atomic charges and charge fluxes. They tell us how much of the electronic charge is localized as a point charge on each vibrating atom and how much of the charge fluctuates along the bonds when the internal coordinate R_t is vibrating during the normal mode Q_i. These information are indeed nonnegligeable in molecular physics or in chemistry and are easily derived from the vibrational absorption spectra.

The model (Equilibrium Charges and Charge Fluxes) has been applied to many molecules (from small gas phase molecules to macromolecules) and is the basis for a further modern development of vibrational spectroscopy in material science [36, 37, 38].

7.2 Raman Scattering

Information on vibrational transitions can be obtained with a fully independent optical technique which has been discovered by Raman [39]. When a light beam (generally in the visible region of the electromagnetic spectrum) of frequency ν_0 goes through a substance in any phase the sample scatters light. If the scattered light is collected at a given angle and analyzed with a spectrometer one finds that a

component at frequency v_0 is strongly scattered (elastically scattered, Rayleigh radiation) and at either side of v_0 additional frequency components (anelastic, Raman scattering) are found at $v_0 \pm v_j$, where j corresponds to the normal mode frequencies of the molecule in the sample analyzed. It is thus possible also from the Raman effect to derive information on the normal modes of vibration of a given molecule [7, 12, 15, 40].
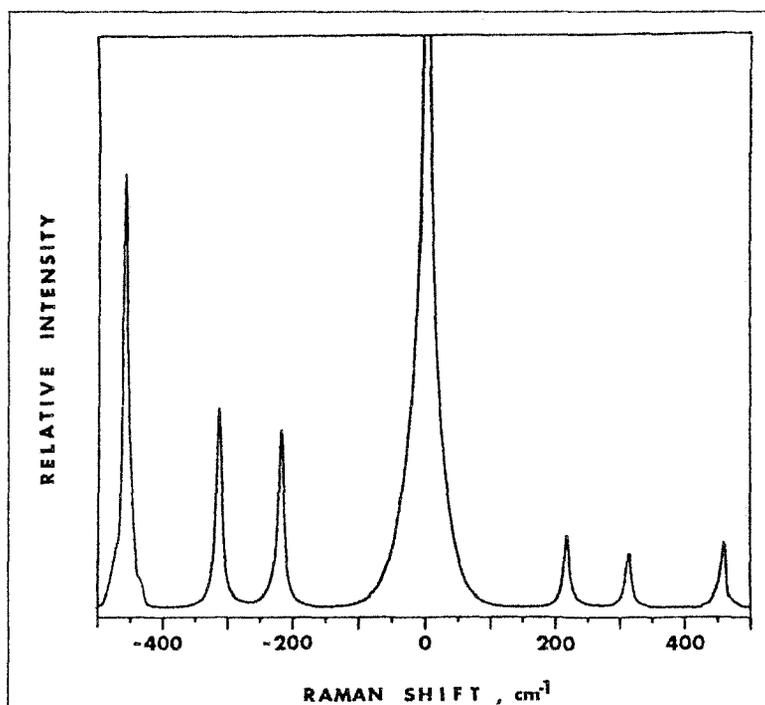
Figure 7.2: Raman spectrum of CCl_4. The Rayleigh line at 0 cm^{-1} in the Raman shift scale, Stokes (left side, negative Raman shifts) and Anti Stokes (right side, positive Raman shifts) can be clearly identified.

Like in the case of infrared some of the vibrational transitions may be observed in the Raman spectrum while other may be silent. This again depends on the symmetry of the molecule and selection rules can be easily predicted from group theory.

Raman scattering originates from the polarizability α of the molecule. When a molecule is immersed in a light beam in the visible region (high frequencies i.e. high energy) the electrical perturbation
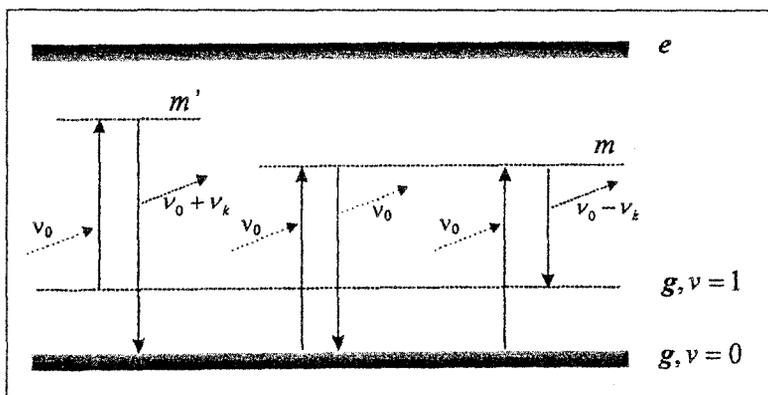
Figure 7.3: Description of the Raman effect with a simple scheme of the molecular energy levels involved.

by the oscillating electric field induces a periodic polarization of the molecule which is performing its lower frequency normal vibrations. The superposition of these two oscillating phenomena generates both Rayleigh and Raman scattering.

The changes of molecular polarizations $\frac{\partial \alpha}{\partial Q_i}$ of the various normal modes can be measured from the Raman intensities in a way parallel to what has been discussed above for the dipole moment derivatives in the infrared absorption. Because of the tensorial nature of $\frac{\partial \alpha}{\partial Q_i}$ the intensity of the Raman scattered radiation depends on the state of polarization of the exciting laser line and from the polarization of the scattered beam. On the other hand, experiments performed in different scattering geometries and polarization may allow to obtain values of each element of the tensor $\frac{\partial \alpha}{\partial Q_i}$.

On the experimental side we have to mention that while the Raman effect was discovered more than 70 years ago the lack of flexible technology kept its use away from laboratories and was reserved only for brave researchers in basic science. The coming of lasers has immediately revived Raman spectroscopy up to the point, today, to be strong rival of infrared spectroscopy. Lasers emit highly monochromatic light in a wide range of frequencies in the visible region, with a polarized beam and with powers which may range from watts to nanowatts. The sampling is easy and the collection and detection of the light is not a problem.

8   The Role of Quantum Chemistry

For many years the dream of theoretical chemists and physicists to apply quantum theories to molecules has been hindered by the mathematical and computational complexity of the problems which would have required the use of large and fast computers. Computers adequate to the demands of quantum chemistry have not been available for many years and problems have been solved using extremely approximated methods which yielded sometimes questionable and unsatisfactory results which have been the subject of interesting discussion. At present computational facilities are at hand in almost every laboratory and even personal computers can perform Quantum Chemical calculations of molecular properties which are very nicely approaching the reality as seen from experiments.

Conceptually (see for instance refs. [17] and [41]) molecular orbital quantum chemical computing program approximate the molecular orbitals ψ_i in the frame of the MO = LCAO model, by a linear combination of atomic orbitals ϕ_n

$$\psi_i = \sum_n c_i^n \phi_n \qquad (8.1)$$

where the coefficients are calculated by minimization of the energy. At present many *ab initio* computing programs are available, each one offering various options for the choice and extension of the basis set of atomic orbitals. For the *ab initio* calculation of ground state vibrational properties (i.e. intramolecular potential energy, infrared and Raman spectra and related quantities) the Hartree-Fock Self Consistent Field [41] approximation is widely used. However also electron correlation energies can be introduced for improving the predictive capabilities of such calculations.

More recently a new approach to the resolution of the molecular Shroedinger equation has been proposed, based on Density Functional Theory [42]. Calculations in this frame (which contains empirical functions for the description of electron correlation) give rise in many cases to better results in the prediction of vibrational spectra (especially for the values of transitions frequency) and are now well accepted in the community of theoretical spectroscopists.

For each molecule chemists aim at obtaining *ab initio* minimum energy, equilibrium geometry, vibrational force constants and wave-numbers, electronic charge densities and atomic charges, dipole moments and polarizabilities. *Ab initio* infrared and Raman spectra (frequencies and intensities) can be calculated and comparisons with the experimental data are becoming extremely satisfactory. The reliability of the calculations is in many cases so high that the calculated data can be considered as really predictive of spectroscopic properties which may have not yet been obtained from experiments. Good *ab initio* calculations can be carried out on large molecular systems (of the order of 10^2 atoms) with long computing time (also of the order of one month), but affordable and worth while to be done for the information they can provide.

The experience and the satisfactory results collected by my group in Milano [38, 43] have given us the necessary motivations for tackling complex systems made up by with very many atoms [44, 45]. Calculations have also open a new and systematic way to the interpretation of the vibrational spectra of specific classes of molecules, with peculiar electronic structure and properties, which are at present the center of interest for future technology based on molecular materials.

9 Applications

The combination of infrared and Raman spectroscopy can be used without much theoretical reasoning and is presently being exploited routinely in all research laboratories which need to determine qualitatively and quantitatively the existence of certain chemical compounds in a given sample. Thus basic, applied and industrial material science needs the support of both spectroscopies. This need has pushed instrument manufacturers to develop high tech instruments which provide very accurate data in short times. All chemical laboratories at present do have on their benches at least a simple infrared spectrometer for the diagnosis of the material they are producing. Biochemistry, biotechnology and even medical sciences today use vibrational spectroscopy for the diagnosis of the biological specimen or tissue or cell or even organs they are working on. Responses some-

times are required immediately and technology is at present meeting these requirements. Industry uses vibrational spectra for characterization of their materials, for checking and certifying the nature and the purity of their products. Forensic sciences, insurances, police etc identify and certify their specimens with the vibrational spectra. All these studies are based mostly on the use of the spectroscopic correlations of group frequencies as discussed above (Section 6).

On the other hand, basis science (theory and experiments) dwell on the molecular properties (shape, structure, electronic distribution, dipole moments, polarizabilities, atomic charges, charge fluxes, anharmonicity, centrifugal distortion, Fermi resonances, Coriolis coupling, mean square amplitudes of vibration etc) in order to understand the physics of many phenomena which depend on the behavior of molecules: i) as isolated entities (gas phase, isolated in inert matrices or in interstellar spaces) , ii) as supermolecular aggregates (disordered clusters, nano-objects, tri-dimensional crystals) and iii) as disordered objects as liquid, amorphous phases, solutions.

10   Faster and Smaller

The two coordinates which determine the technological applications of a certain technique are time and space. Experimental scientists and instrument manufacturers have joined their hands for pushing spectroscopy into great adventures in time and space. In order to keep informed the reader interested in the last developments of Infrared and Raman vibrational spectroscopy it is worth while mentioning the latest technological achievements (as for year 2000) which open enormous new fields in chemistry, molecular physics and materials science in general with a fallout of knowledge useful in other fields of frontier science.

First we consider the time. Chemists know that a given material, i.e. a given molecule, may be stable for long or short times. Some materials last long and remain unaltered after centuries, while other may be stable only for a few days or a few hours, minutes, seconds, ... milli-, nano-, pico-seconds.

The application of the principles discussed in this paper depend

on the level of technological development. Only a few years ago the recording of a good spectrum with a spectrometer required approximately one hour. The discovery of Fourier Transform interferometers pushed the time for recording to 1-2 seconds, thus opening great new sectors of science. In year 2000 technology has just presented commercially affordable instruments which push the limit to nano, pico and even femto-second. This means one can record a vibrational spectrum in such a short time to follow the elementary steps of formation of a molecule during the almost instantaneous chemical act. Quite often chemists know the ingredients of the reaction and the products at the end of the chemical process; what is happening in the flask is left to a sort of clever imagination. The black box of chemical reaction mechanism is being open and the knowledge of the elementary steps occurring in such a short time is at present becoming affordable. Similar important phenomena can be explored in biochemistry and biophysics, in electronic science, semiconductors etc.

Space is the second relevant variable in recording the spectra. Samples may be available in great quantities, but most of the time the amount of material available for any kind of spectroscopic analysis is very small. Sampling techniques for recording the spectra of minute samples have been always the problems for many experimental spectroscopists. In the past few years the recording of infrared and Raman spectra of samples at the microscopic scale became possible. Spectrometers or interferometers coupled with suitable microscopes allowed to focus at a given spot at the micron scale and get the spectrum of it. Thus micro-impurities in semiconductors or optical devices, components in mixtures and powders (even of Leonardo Da Vinci paintings! See, for example ref. [45]), cells in biological samples etc. could be examined. However, the barrier of the limiting size related to the diffraction limit could not be overcome. In year 2000 using techniques closely related to AFM and STM techniques (see section 1) the limit of 1 micron has been overcome with "near field" techniques attained by pushing the light into a cone with an aperture diameter of a few nanometers and approaching the sample to a few nanometers from the tip of the cone. At present one can map the molecular distribution

on a given surface reaching almost the resolution of a few molecules. The field of biology and material science will greatly benefit of such new techniques which allow the researcher to focus at a "molecular" site of a few nanometers where he wants to recognize the chemical nature and eventually its chemical evolution with time.

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