

*Synthetic Fuels
and Combustion*

CHIGIER

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SYNTHETIC FUELS AND COMBUSTION

Progress in Energy and Combustion Science

VOLUME 3

Edited by

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VOLUME 3



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FOREWORD

Progress in Energy and Combustion Science was originally planned as a series of books with each volume devoted to a specific topic. Volume 1 was devoted to Pollution Formation and Destruction in Flames and the leading authorities in this field were invited to prepare their contributions for the volume that would initiate the series. Because the whole volume was planned from the outset, it provided a coherent set of contributions, which was linked together by a general Introduction. The subsequent decision to publish *Progress in Energy and Combustion Science* as a quarterly review journal required the setting up of a production schedule which became dependent upon the flow of articles from authors invited to make contributions. This did not allow subsequent volumes to have the same degree of coherence as was achieved in Volume 1. All the authors are recognized experts in their fields, on the basis of their current active research and writing. Articles will thus reflect the topics that are of current importance but which are also expected to remain significant.

The energy crisis in the early 1970s diverted scientists and engineers to seeking alternate sources of energy. It was generally recognized that the supply of fossil fuels was limited and insufficient to meet world requirements. Nuclear power became an established form of generation of electricity and major research programs have been initiated in solar and geothermal energy and wind and wave power generation. In parallel with these efforts there has been a major upsurge in activity in the field of energy conservation and pollution control. Combustion science and engineering have become revitalized as a result of the special role that can be played by improving energy and combustion efficiencies. Fossil fuels have become more precious and expensive and, as the scarcity of these fuels increases, greater emphasis will be placed on conservation and development of systems with high energy efficiency. The requirement to use lower grade and alternate fuels is also posing new and difficult problems for designers of combustion systems. The continued interest in improving the quality of the environment has also led to more stringent demands on the reduction of emission of pollutants. The net result of these economic, political and technological pressures has been a major upsurge in activity in the fields of combustion science and engineering. The large-scale increase in research and publication in the general field of energy has resulted in a much greater emphasis on combustion science in articles published in *Progress in Energy and Combustion Science*.

The present volume contains articles on synthetic fuels, combustion of oil and coal and production of synthetic fuels by gasification. New developments in instrumentation and techniques for making measurements in flames are discussed. Special problems, arising from the use of future fuels in automobiles, are presented in a separate article. The general background to nonelectrical uses of geothermal energy is also included in this volume. Authors have been selected from university, industry and government research establishments.

1978

NORMAN A. CHIGIER

THE USE OF LASER RAMAN DIAGNOSTICS IN FLOW FIELDS AND COMBUSTION

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NOTATION

A	amplitude of incident electric field
A_{nm}	Einstein's transition probability in emission
B	rotational constant
B_{nm}	Einstein's transition probability in absorption
c	velocity of light
D	rotational constant
d	degeneracy
e	electron charge
E	energy or electric vector of incident radiation (see text)
$F(J)$	rotational term value
$G(v)$	vibrational term value
G	gain
h	Planck's constant
i	current
I	scattered intensity or moment of inertia (see text)
I_{abs}^{nm}	energy absorbed per second
I_{em}^{nm}	energy emitted by a source per second
J	rotational quantum number
k	Boltzmann constant
l	absorbing or emitting path length
K	constant
m	mass
M	transition moment
n	principal quantum number, index of refraction or number (see text)
N	number of molecules or noise (see text)
P	dipole moment (induced), power, or pressure (see text)
Q	partition function
R	Rydberg constant also resistance (see text)
R^{nm}	matrix element of the electric dipole moment
S	signal
S_{ph}	phototube sensitivity
T	temperature
t	time
v	velocity or vibrational quantum number (see text)
V_s	signal voltage
W_o	radius
χ	Raman susceptibility
x_e	quadratic coefficient of the term value
y_e	cubic coefficient of the term value
Z	atomic number
α	polarizability
α'	derivative of isotropic part of the polarizability tensor
α_e	constant for vibrating rotator
α_λ	absorbance
β_e	constant for vibrating rotator
γ'	derivative of anisotropic part of the polarizability tensor
Γ_R	Raman line-width
η	efficiency
η_q	quantum efficiency
λ	wavelength
Λ	angular momentum
ν	wavenumber
ν'	frequency
ρ	depolarization ratio or density (see text)
σ	scattering cross-section
τ	spectral transmittance
ψ	wave function amplitude
Ψ	wave function
Ω	solid angle
ω	frequency
μ	reduced mass

Subscripts

a	absorbing (pressure P_a)
b	background, or broadening (pressure P_b)
d	dark
e	equilibrium
J	rotational level J
k	k energy level or state
m	m energy level or state
n	n energy level or state
o	ground level, incident or optical (see text)
q	quantum
r	rotational
s	s energy level or signal (see text)
v	vibrational
x	x component
y	y component

Superscripts

'	upper level
"	lower level

1. INTRODUCTION

The search for new and improved diagnostic techniques applicable to fluid dynamics and combustion research has been an ongoing task for many years. The aim has been the development of techniques, which could provide all or most of the necessary information, nonintrusively, instantaneously, accurately and if possible remotely. The techniques should be of sufficient sensitivity and resolution capability to provide an accurate pointwise space and time history of a given flowfield. Furthermore a system which is cost-effective is certainly preferred.

The developments in laser technologies of the last decade resulted in an unprecedented period of growth of new diagnostic techniques, applicable to flowfields. The application of lasers to previously well-known diagnostic methods, which could not be applied to fluid dynamics, due to the inadequacy of the heretofore available light sources, received a new impetus. The desire to perform the measurements nonintrusively suggests immediately optical diagnostic techniques.

Optical flowfield diagnostic techniques can roughly be divided along two lines—qualitative and the quantitative techniques. On the one hand are the visualization techniques (qualitative); on the other, the data acquisition techniques (quantitative). The shadowgraph, schlieren interferometer and the—only recently made possible by the laser—holograph, are part of the former, scattering absorption and emission techniques belong to the latter. They are capable of describing a given flowfield completely. One may argue that the visualization methods are also capable of yielding quantitative data. This is quite true. However, the

necessary highly sophisticated processing equipment and the achievable results are not always commensurable.

In evaluating a particular technique, one must always keep in mind several of the criteria which contribute to an effective measurement. Some of the criteria one should consider in evaluating a particular technique are as mentioned above: (a) the nonintrusiveness; (b) the specificity; (c) the sensitivity; (d) S/N ratios; (e) accuracy; (f) space resolution; (g) time resolution; (h) the calibration methods available; (i) the degree of difficulty of the technique; and (j) the cost effectiveness.

The in-depth discussion of each of the above criteria is outside the scope of this work. A vast literature too numerous to list exists dealing with these problems extensively. As indicated above, the emergence of the laser gave great impetus to the development of optical diagnostic techniques specifically for fluid dynamic problems, and adaptation of known technologies to the specific diagnostics of flowfield phenomena. The techniques of interest are based essentially upon interaction of photons with particles. The interactions of interest used to a major or minor extent for flowfield diagnostic purposes are: Mie³ scattering, absorption,⁴ chemiluminescence,^{5,6} Rayleigh,^{7,8} Raman,⁹⁻²⁵ resonance Raman,²⁶ and coherent anti-Stokes Raman scattering known as CARS.^{27,28} The theoretical background of most of the above scattering phenomena are different and require generally different analytical treatment. They all, however, can be characterized by a common convenient parameter known as the equivalent scattering cross-section in units cm²/steradian. This parameter, besides being a strong function of the phenomenon itself, depends among others on the character of the scattering particle and the frequency of the illuminating light. These scattering cross-sections vary over an extremely large range. Typically, the scattering cross-section for Mie scattering is in the range of 10⁻⁸ cm²/sr, for absorption and fluorescence of the order of 10⁻²⁰ cm²/sr, for Rayleigh of the order of 10⁻²⁷ cm²/sr and Raman of the order of 10⁻³⁰ cm²/sr. The resonance Raman and CARS may have a scattering cross-section of up to six orders of magnitude higher than the spontaneous vibrational Raman. It is obvious that a technique with the larger equivalent scattering cross-section is to be preferred over the ones with smaller cross-sections. This, however, would be a great simplification of the problem at hand since it involves only one of the characteristic parameters. As indicated above, a number of criteria have to be met in performing a particular measurement in a particular situation. Some of these techniques are limited in sensitivity (small scattering cross-section) but are capable of spatial and time resolution (Raman). Others may be more sensitive but are incapable of spatial or time resolution. Information concerning space resolution using absorption diagnostics may be obtained after considerable accumulation of absorption data and sophisticated computational processing of the same. The other above-mentioned

scattering phenomena except the Mie scattering are generally superior as far as sensitivity is concerned relative to Raman but have other disadvantages which limit their usefulness.

It would be presumptuous and essentially impossible in the context of a single article to attempt to discuss the whole range of modern diagnostic methods in fluid dynamics and combustion utilizing lasers. Instead, an attempt will be made to discuss one group of techniques, which are believed to be of major importance in the diagnostics of flowfields and combustion²⁹ and which were made possible by the emergence of the laser. These are the laser Raman scattering techniques which in conjunction with LDV are believed to be capable of providing the researcher with a tool to measure most of the desired variables which, in conjunction with other parameters, may be used to completely describe a flowfield and may provide an insight into some of the phenomena which are difficult or inaccessible using standard conventional means.

As is well-known, the acquisition of information concerning local density, local specie concentration, local velocity, or local temperature in a flowfield is always of utmost importance. The Raman diagnostic technique provides a unique method of achieving most of the above, instantaneously, simultaneously and remotely without the use of flow disturbing probes. The last in itself is of major importance since the data thus obtained can be considered free of distortion and inaccuracies generally attributable to intrusive probes.

After a short elementary review of radiation and infrared spectroscopy based on Herzberg²¹ and Mansel and Davies³² the theory of Raman scattering and its relation to infrared spectroscopy is discussed. Some remarks concerning other diagnostic methods are made. Flow parameters obtainable and techniques applicable towards their measurement are indicated. The acquisition of the same flow parameters by the use of Raman scattering is presented. The lasers suitable for this purpose, as well as the data acquisition, processing and recording equipment necessary is discussed at large. Finally some specific experimental arrangements and some specific experimental results are presented.

2. FUNDAMENTALS OF RADIATION AND SPECTROSCOPY

It has long been recognized that the ensemble of wavelengths emitted or absorbed by any substance is determined by the atoms or molecules it contains. The theory of molecular spectra has been treated in many books too numerous to list here. In addition there are several national and international journals of spectroscopy published periodically.³⁰⁻³¹ It is, however, believed that a short introduction into the field of spectroscopy, and particularly into the field of the Raman spectroscopy, of a tutorial nature, could be of some value to researchers who are outside the circle of spectroscopists and who would still like to take

advantage of the latest developments in this particular field and the special features it possesses.

In connection with the above, for the sake of clarity, a distinction must be made between the applications spectroscopists make of the spectra they obtain and the use intended in this work for those spectra. Again, in describing the use spectroscopists make of the spectra, this topic can only be dealt with in very broad terms. In general, it can only be said that molecular spectra provide the physicist and chemist with one of the most important tools used in the understanding of molecular structures. From the given spectra, the various vibrational, rotational and electronic energy levels of a given molecule can be determined. The motions of the electrons provide information on the chemical valences. The vibrational frequencies provide information of the interatomic forces, and it is also possible to determine with great accuracy the energies of dissociation. The rotational frequencies, on the other hand, provide extremely accurate values of the internuclear distances. Both the vibrational and rotational spectra provide detailed information on the thermodynamic quantities and information concerning the nature of gases, liquids and solids. This is only a very small indication of the knowledge one is able to obtain from the molecular spectra. In recent years, a whole new field of astrophysics emerged. It is possible from the spectra to obtain not only information about the structure of distant planets, but also their composition and chemical changes going on in these planets.

Niels Bohr suggested that an atom or molecule cannot exist in states having any arbitrary energy, but only in certain discrete energy states called stationary states. These are selected according to certain rules from a continuous range of classically possible states. According to Bohr, electromagnetic radiation is not emitted while an electron is orbiting around the nucleus (as it should according to classical electrodynamics), but only when the electron is going from an energy level E_1 to another energy level E_2 . The energy emitted is in the form of a photon of energy,

$$E_1 - E_2 = h\nu' = h\nu c \quad (1)$$

This is Bohr's frequency condition. The wave number of the emitted or absorbed radiation becomes

$$\nu = \frac{E_1}{hc} - \frac{E_2}{hc} \quad (2)$$

which becomes

$$\nu = RZ^2 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad n_1 > n_2 \quad (3)$$

where $R = R'/hc = 2\pi^2\mu e^4/ch^3$ is the Rydberg constant, and n_1 and n_2 are the principal quantum numbers of the two energy states concerned. It should be noted here that the spectrum thus obtained is the so-called line spectrum of atoms in contrast to band spectra of molecules. The essential point of the Bohr theory, that is, the discrete stationary energy states, is retained in wave mechanics. While the Bohr theory

starts out from classical laws of motion and by means of certain quantum conditions selects only some of the possible orbits, wave mechanics, by using the fundamental idea of De Broglie which states that the motion of any corpuscle of matter is associated with a wave motion of wavelength,

$$\lambda = \frac{h}{mv} \quad (4)$$

becomes more comprehensive and agrees quantitatively with experiments while the values calculated by Bohr's theory do not. The governing wave equation for the nonrelativistic case is, according to Schrödinger

$$-\frac{h^2}{8\pi^2} \sum_k \frac{1}{m_k} \left(\frac{\partial^2 \Psi}{\partial x_k^2} + \frac{\partial^2 \Psi}{\partial y_k^2} + \frac{\partial^2 \Psi}{\partial z_k^2} \right) + V\Psi = i \frac{h}{2\pi} \frac{\partial \Psi}{\partial t}, \quad (5)$$

where $\Psi = \psi e^{-2\pi i \nu' t}$.

A solution for a single particle could be obtained by solving Schrödinger's wave equation which, in terms of its amplitude of the wave motion, ψ is given by

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0, \quad (6)$$

and which, in case of multiple particles, becomes

$$\sum_k \frac{1}{m_k} \left(\frac{\partial^2 \psi}{\partial x_k^2} + \frac{\partial^2 \psi}{\partial y_k^2} + \frac{\partial^2 \psi}{\partial z_k^2} \right) + \frac{8\pi^2}{h^2} (E - V)\psi = 0. \quad (7)$$

The complete solution of the Schrödinger equation yields not only the eigenvalues, that is, the energy values of E of the stationary state, but also the corresponding eigenfunctions $\Psi = \psi \exp[-2\pi i(E/h)t]$ where $(E/h) = \nu'$. Frequently, there are several different eigenfunctions associated with one and the same eigenvalue. In that case, we have a degenerate state. The degeneracy is d -fold if there are d linearly independent eigenfunctions for a given eigenvalue. These d eigenfunctions are not uniquely determined by the wave equation, since any linear combination of the eigenfunctions belongs to the same eigenvalue.

If the interaction with an electromagnetic field is introduced into the Schrödinger equation of an atomic system, it is found that a non-zero probability arises of finding the system in a state E_n , if originally it was in a state E_m and if radiation of wave number $\nu = [E_n - E_m]/hc$ is present. If $E_n < E_m$ radiation of this wave number is emitted, on the other hand, $E_n > E_m$ radiation of this wave number is absorbed by the atomic system.

The intensity of a spectral line in emission I_{em}^{nm} is defined²¹ as the energy emitted by the source per second. If there are N_n atoms in the initial state and if A_{nm} is the fraction of atoms in the initial state carrying out the transition to m per second, then

$$I_{em}^{nm} = N_n h \nu_{nm} A_{nm} \quad (8)$$

where A_{nm} is the Einstein transition probability of spontaneous emission which is related in the case of dipole radiation to the matrix element as follows:

$$A_{nm} = \frac{64\pi^4 \nu^3}{3h} |R^{nm}|^2 \quad (9)$$

then the intensity becomes

$$I_{em}^{nm} = \frac{64\pi^4 \nu^4 c N_n}{3} |R^{nm}|^2 \quad (10)$$

where

$$R^{nm} = \int \psi_n^* M \psi_m d\tau. \quad (11)$$

If the vector quantity R^{nm} , the matrix element of the electric dipole moment, differs from zero for two states n and m , the two states combine with each other with a certain probability of emission or absorption of radiation. If it is zero, the transition under consideration is forbidden as a dipole transition. It does follow certain selection rules as, for example, the selection rule in the case of a one-electron system, $\Delta l = \pm 1$.

In the case of absorption, the intensity is given by

$$I_{abs}^{nm} = \rho_{nm} N_m B_{mn} \Delta x h c \nu_{nm}. \quad (12)$$

If $I_o^{nm} = e \rho_{nm}$ is the intensity of the incident radiation, eqn. (12) can be written as

$$I_{abs}^{nm} = I_o^{nm} N_m B_{mn} h \nu_{nm} \Delta x \quad (13)$$

where N_m is the number of atoms in the initial lower state m and B_m is the Einstein transition probability of absorption,

$$B_{mn} = \frac{8\pi^3}{3h^2 c} |R^{nm}|^2 \quad (14)$$

this implies that

$$B_{nm} = \frac{1}{8\pi h c \nu_{nm}^3} A_{nm}. \quad (15)$$

Thus,

$$I_{abs}^{nm} \sim \nu_{nm} |R^{nm}|^2 \quad (16)$$

and

$$I_{em}^{nm} \sim \nu_{nm}^4 |R^{nm}|^2.$$

Absorption is thus proportional to the frequency, whereas emission is proportional to the fourth power of the frequency.

It should be noted that eqns. (9) and (14) are valid in the case of transitions between non-degenerate levels only. In case of transition between two degenerate levels of degeneracy d_n and d_m those equations should be replaced by the following:

$$A_{nm} = \frac{64\pi^4 \nu_{nm}^3 \sum |R^{n_i m_i}|^2}{3h d_n} \quad (17)$$

$$B_{nm} = \frac{8\pi^3 \sum |R^{n_i m_i}|^2}{3h^2 c d_m} \quad (18)$$

and eqn. (15) appropriately by

$$B_{nm} = \frac{1}{8\pi h c \nu_{nm}^3} \frac{d_n}{d_m} A_{nm}. \quad (19)$$

As indicated above, eqn. (2), the wave numbers are expressed in terms of the differences between energy states of the atom, which in turn are identified with the orbits of the electrons in the atom. These orbits are associated with the quantum numbers n and l and are

responsible for the so-called line spectra. In addition to the line spectra due to emission of radiation by atoms, there is another type of spectrum due to radiation by molecules, the so-called band spectrum. A band is characterized by a head, either on the violet or red side, the lines there being usually so close as to be indistinguishable and becoming more widely spaced and fainter towards the tail end. Heavy molecules have their bands more closely spaced than light molecules. It must also be noted here that a third kind of spectrum is observed, that is, a continuous spectrum. Two types of continuous spectra can be distinguished. The first obtained from liquids and solids as a result of very close packing of the atoms and the interaction of the atoms and molecules with each other. This kind of continuous spectrum is more a result of the resolving power of the spectrographs and also, what is more important, the doppler broadening of the spectral lines. The second kind, the so-called "continuous term" spectrum is a result of dissociation (molecules) and/or ionization (atoms). With the usual zero-point of the energy scale ($n = \infty$), all stable discrete quantum states of an atom with one outer electron have negative energy values. A positive value of energy E corresponds to an electron which moves in a hyperbolic orbit about the nucleus. It, of course, goes only once through such an orbit. The energy can assume all positive values of E . Therefore, from the limit $E = 0$ of a discrete energy spectrum of an atom, there is a continuous region of possible energy values, the so-called "continuous term spectrum". Figure 1 presents a simplified energy level diagram of hydrogen where the above is indicated. Included in the figure is a circular Bohr orbit diagram for hydrogen showing the Lyman, Balmer and Paschen series.

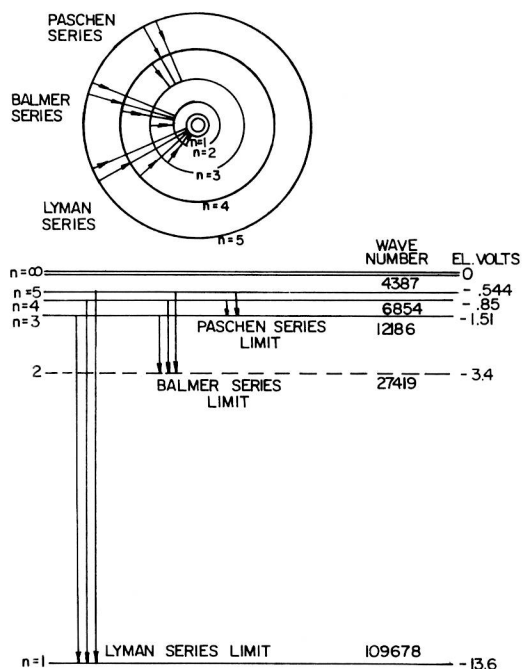


FIG. 1. The Bohr orbits of hydrogen and energy level diagram.

As indicated above, the term "band spectrum" is used to designate a spectrum originating from emission or absorption of molecules. As such, it must be distinguished from a line spectrum which is the designation of a spectrum originating in the atom. The optical radiant energy identified with molecular spectra is distributed over a very wide range of frequencies, extending from the ultraviolet to the microwave region.

The essential difference between atomic and molecular spectra is that the atomic spectra are completely explained by the quantized changes in the energy associated with the outer electronic structure, whereas the molecular spectra include not only this energy but also contributions of energy associated with the vibrations of the component atoms relative to each other and the rotation of the molecule as a whole about an axis through the center of gravity. The total internal energy of the system may be represented by the sum of all the above-mentioned contributions,

$$E_{tot} = E_e + E_v + E_r \quad (20)$$

which, in terms of the wave number units (term values), can be written as

$$T = T_e + G + F. \quad (21)$$

The development of the quantum theoretical explanation of the features of molecular spectra is generally started with diatomic molecules. This introduces a relatively greater degree of simplicity because one is dealing with a two-body problem. Furthermore, the full details of diatomic spectra are frequently completely observable, whereas the complexity of the spectra of polyatomic molecules is, in general, so great that details are resolved only in relatively few instances, usually where symmetry considerations permit simplification of the model. Generally, the features of polyatomic molecules are explained by extending the concepts of diatomic molecules.

The simplest model of a diatomic molecule is thought of as a dumbbell structure, the two atoms rigidly joined by a line, with an axis of rotation perpendicular to the line joining the nuclei, at the center of mass of the two atoms (Fig. 2). The solution of

the Schrödinger equation appropriate to the problem results in the following energy eigenvalues:

$$E_{rot} = \frac{h^2 J(J+1)}{8\pi^2 \mu r^2} = \frac{h^2 J(J+1)}{8\pi^2 I} \quad (22)$$

$$\frac{E_{rot}}{hc} = F(J) = BJ(J+1) \quad (23)$$

where $B = (h/8\pi^2 cI)$ is called the rotational constant; μ = the reduced mass $= (m_1 m_2 / m_1 + m_2)$; I = the moment of inertia and J = the rotational quantum number related to the total angular momentum M of the electrons in an atom, by $M = \sqrt{J(J+1)} (h/2\pi) \approx J(h/2\pi)$. Thus, J gives approximately the angular momentum in units of $h/2\pi$. Each rotational energy state is characterized by one of these J values, which can take on a series of integers from 0, 1, 2, ... The quantum mechanics leads to a selection rule for transition between energy states

$$\Delta J = \pm 1. \quad (24)$$

These transitions account for the spectral lines whose wave number is given by

$$v = F(J+1) - F(J) = 2B(J+1) \quad (25)$$

leading to a series of equidistant lines, which are observed in the far infrared region. The actual frequency of rotation of the rigid rotator is given by

$$v_{rot} = c2B[J(J+1)]^{1/2} \approx c2BJ. \quad (26)$$

Since, in actuality, the molecules are not strictly rigid, eqn. (23) for the rotational term values is generally modified to

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 \quad (27)$$

where $D = (4B^3/\omega^2)$ is always very small and for the present applications, insignificant, particularly at low rotational quantum numbers.

The same dumbbell model considered as an harmonic oscillator would result in

$$v_{osc} = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \quad (28)$$

where μ is the reduced mass defined previously. Again, a solution of Schrödinger's equation results in the vibrational energy states,

$$E(v) = h v_{osc} (v + \frac{1}{2}) \quad (29)$$

where v is the vibrational quantum number which takes on integral values 0, 1, 2, ... and again the selection rules for permitted energy transitions are

$$\Delta v = \pm 1. \quad (30)$$

In terms of energy term values, eqn. (29) can be written

$$G(v) = \frac{E(v)}{hc} = \frac{v_{osc}}{c} (v + \frac{1}{2}) = \omega (v + \frac{1}{2}). \quad (31)$$

Since emission and absorption of radiation takes place as a result of a transition from a higher to a lower state, or from a lower to a higher state, the wave number of

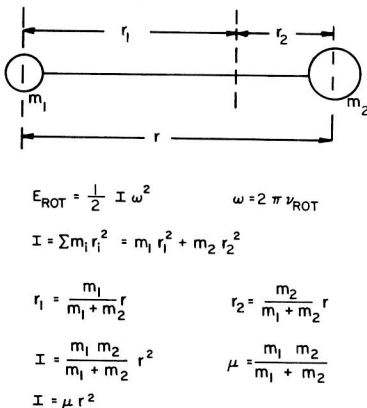


FIG. 2. The dumbbell model of the rigid rotator.

the emitted or absorbed radiation is given by

$$\nu = \frac{E(v')}{hc} - \frac{E(v'')}{hc} = G(v') - G(v'') = G(v+1) - G(v) = \omega \quad (32)$$

As in the case of the rotational term values, the expression for the vibrational term values must be modified to correct for the assumption of an harmonic oscillator. In fact, the finer details of the spectra can only be accounted for if the molecule is considered as an anharmonic oscillator. For small anharmonicities, which is generally the case, the term values are given by

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 \quad (33)$$

instead of by eqn. (31).

The zero point energy is obtained from eqn. (33) by setting $v = 0$; thus,

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + \frac{1}{8}\omega_e y_e + \dots \quad (34)$$

If the energy levels are referred to this lowest level as zero, then using eqns. (33) and (34),

$$G_0(v) = \omega_0 v - \omega_0 x_0 v^2 + \omega_0 y_0 v^3 + \dots \quad (35)$$

where

$$\begin{aligned} \omega_0 &= \omega_e - \omega_e x_e + \frac{3}{4}\omega_e y_e + \dots \\ \omega_0 x_0 &= \omega_e x_e - \frac{3}{2}\omega_e y_e + \dots \\ \omega_0 y_0 &= \omega_e y_e + \dots \end{aligned}$$

In both eqns. (33) and (34), $\omega_e \gg \omega_e x_e$ and $\omega_e x_e \gg \omega_e y_e$.

One important feature must be pointed out. Whereas the selection rule for the non-rigid rotator remained the same as for the rigid rotator, $\Delta J = \pm 1$, the selection rule for the anharmonic oscillator is changed. $\Delta\omega$ can now assume, besides the values of ± 1 , which give the most intense transitions, also values of $\pm 2, \pm 3$, but with rapidly decreasing intensity.

The combined effect of these modifications results in the term values for the vibrating rotator,

$$T = G(v) + F(J) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \dots + B_v J(J+1) - D_v J^2(J+1)^2 + \dots \quad (36)$$

where $B_v = B_e - \alpha_e(v + \frac{1}{2}) + \dots$ with $\alpha_e \ll B_e$, because change in internuclear distance during the vibration is small compared to the internuclear distance itself, and $D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots$ with $\beta_e \ll D_e$ on the same grounds as α_e . In this context, B_v and D_v signify the rotational constants for the vibrating rotator, the subscript v to be distinguished from the vibrational quantum numbers v . If a particular vibrational transition from v_1 to v_2 is considered, then according to eqn. (34), neglecting the rotational constant D_v , the wave numbers become

$$\nu = \nu_0 + B'_v J'(J'+1) - B''_v J''(J''+1) \quad (37)$$

where $\nu_0 = G(v') - G(v'')$ is the wave number of the pure vibrational transition neglecting rotation ($J' = J'' = 0$). If, in eqn. (37) $\Delta J = 1$ and $\Delta J = -1$, and the interaction between rotation and vibration is

neglected, then $B'_v = B''_v = B$ and eqn. (37) result in

$$\nu_R = \nu_0 + 2B + 2BJ \quad J = 0, 1, \dots \quad (38)$$

$$\nu_P = \nu_0 - 2BJ \quad J = 1, 2, \dots \quad (39)$$

These last two equations represent two series of lines called the R and P branches, respectively. In the above, the effect of the electrons surrounding the nuclei on the angular momentum has been neglected. If the angular momentum of the electrons about the internuclear axis is designated by $\Lambda = \lambda(h/2\pi)$, where λ is the quantum number of this angular momentum, then for $\lambda = 0$, we get $\Delta J = \pm 1$ as in (38) and (39). If, however, $\lambda \neq 0$, then $\Delta J = \pm 1$ and for $\Delta J = 0$, we obtain

$$\nu_q = \nu_0 + F'(J) - F''(J) \quad (40)$$

called the Q -branch.

As indicated previously, eqn. (21), the total energy of a system of molecules in terms of its term values consists of the term values of eqn. (36) and a term T_e representing the electronic transition. Thus,

$$\nu = (T'_e - T''_e) + (G' - G'') + (F' - F'') \quad (41)$$

is the wave number of the given system.

3. THE RAMAN EFFECT

The Raman effect is the phenomenon of light scattering from a material medium, whereby the light undergoes a wavelength change and the scattering molecules an energy change in the scattering process. The Raman scattered light has no phase relationship with the incident radiation. The phenomenon was predicted in 1923 by Smekal and experimentally observed in 1928 by Raman and Krishnan, in liquids and solids, and by Landsberg and Mandelstam in crystals. The Raman shifts correspond to energy differences between discrete stationary states of the scattering system. Classically, the Raman effect can be described as the modulation of the scattered light by the internal motions of the scattering molecules. In this kind of analogy, the Raman lines would correspond to the side bands, and the Rayleigh light to the carrier frequency. This, of course, would result in the Stokes and anti-Stokes lines having the same intensity, which is not the case. Quantum-theoretically, the incident photons collide elastically or inelastically with the molecules to give Rayleigh and Raman lines, respectively, with the inelastic process much less probable than the elastic. When an inelastic collision occurs with the incident photon furnishing energy to the molecule raising it to a higher energy level, the scattered photon being of lower energy, gives rise to the Stokes line. If the scattering molecule gives up energy to the impinging photon and moves to a lower energy state, the scattered photon gives rise to the anti-Stokes line. Since the anti-Stokes line must originate in molecules of higher energy level, which are less abundant at normal temperatures, the anti-Stokes lines would be expected to be much weaker than the Stokes lines. The process of light scattering can thus be visualized, as the absorption of an incident photon of

energy E by a molecule of a given initial state, raising the molecule to a "virtual" state, from which it immediately returns to a final stationary state emitting a photon of the difference energy between the two states and incident energy E . The process is illustrated in Fig. 3.

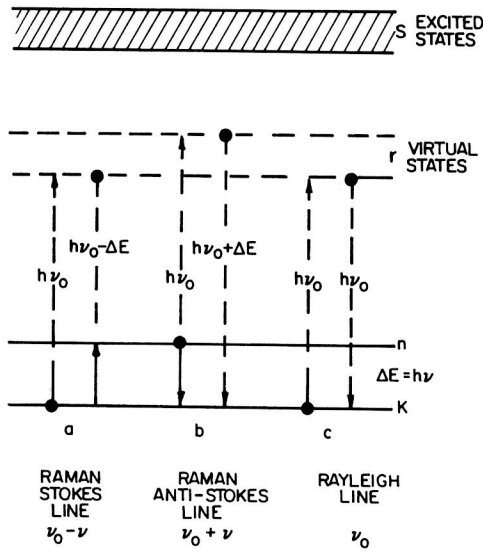


FIG. 3. Schematic energy level diagram.

The rotational Raman spectrum is governed by a selection rule which is different than the selection rule for the infrared spectrum as expressed in eqn. (24); namely,

$$\Delta J = 0, \pm 2. \quad (42)$$

When molecules with different J values are present, the rotational Raman spectrum consists of a number of lines. $\Delta J = 0$ corresponds to the undisplaced line. The transition $J \rightarrow J+2$ results in a shift to longer wavelength (Stokes lines) and the transition $J+2 \rightarrow J$ results in a shift to shorter wavelength (anti-Stokes lines). Using eqn. (23), the magnitude of the frequency shift can be found,

$$\Delta\nu = F(J+2) - F(J) = B(J+2)(J+3) - BJ(J+1) = 4B(J+\frac{3}{2}). \quad (43)$$

Equation (43) represents a series of equidistant Raman lines on either side of the undisplaced line. These small Raman displacements can, therefore, be identified as the rotational Raman spectrum.

It is found that in the case of a harmonic oscillator, the same selection rule holds for the Raman as for the infrared spectrum,

$$\Delta v = \pm 1. \quad (44)$$

Thus, a transition can take place only to the adjacent vibrational state. The frequency shift using eqn. (31) becomes

$$|\Delta\nu| = G(v+1) - G(v) = \omega \quad (45)$$

this shift occurring to either side of the illuminating radiation frequency.

A comparison of eqns. (32) and (45) reveals a very important relationship between the infrared and Raman spectra. It is seen that the infrared vibrational frequencies agree exactly with the Raman frequency shifts. This can be seen in Table 1,²¹ where a number of infrared frequencies and Raman displacements have been tabulated for several molecules for which both spectra have been observed. The Raman spectra can, therefore, be regarded as an infrared spectrum shifted into the visible or ultraviolet region.

TABLE 1. Infrared and Raman displacements of some diatomic molecules²¹

Gas	Raman displacement $\Delta\nu$ (cm ⁻¹)	Infrared ν_0 cm ⁻¹
HCl	2886	2885.9
HBr	2558	2559.3
NO	1877	1875.9
CO	2145	2143.2
H ₂	4160.2	—
N ₂	2330.7	—
O ₂	1554.7	—
Cl ₂	556	—

The selection rules for the Raman spectrum of the anharmonic oscillator are the same as those for the anharmonic oscillator of the infrared spectrum. Therefore, the Raman shifts can be represented by the same equations as the frequency of the anharmonic oscillator.

As in the case of the infrared spectrum, the Raman spectrum of the vibrating rotator, governed by the vibrational selection rules, $\Delta v = \pm 1$ and rotational selection rules, $\Delta J = 0, \pm 2$, consists of three branches, the S -branch, Q -branch, and O -branch. Their equations can be obtained from

$$\Delta\nu = \Delta\nu_0 + B'_v J'(J'+1) - B''_v J''(J''+1) \quad (46)$$

analogous to eqn. (37) for the infrared spectrum, by substituting $J' = J'' + 2$ (S -branch), $J' = J'' - 2$ (O -branch) and $J' = J''$ (Q -branch) and using $J' = J$.

$$(\Delta\nu)_S = \Delta\nu_0 + 6B'_v + (5B'_v - B''_v)J + (B'_v - B''_v)J^2 \quad (47)$$

$$J = 0, 1, \dots$$

$$(\Delta\nu)_O = \Delta\nu_0 + 2B'_v - (3B'_v + B''_v)J + (B'_v - B''_v)J^2 \quad (48)$$

$$J = 2, 3, \dots$$

$$(\Delta\nu)_Q = \Delta\nu_0 + (B'_v - B''_v)J + (B'_v - B''_v)J^2 \quad (49)$$

$$J = 0, 1, \dots$$

For the $0 \rightarrow 1$ vibrational transition, the difference between B'_v and B''_v is very small. The lines of the Q -branch are, therefore, very close to each other and are usually not resolved, giving rise to an intense line. The S - and O -branches are much weaker since their lines are not superimposed. The above are similar to the R and P branches of the infrared spectrum.

As mentioned previously, the Raman displacements of some molecules can be regarded as the infrared vibrational lines shifted into the visible or ultraviolet region. This should not be regarded as a general

law governing the relation between the Raman spectrum and infrared spectrum, or vice-versa. It should be noted that not all Raman active molecules are infrared active, and not all infrared active molecules are Raman active. The infrared and Raman activity are dependent on the structure and symmetry of the given molecule. Since in unsymmetrical molecules every normal vibration is associated with a change of the dipole moment, all normal vibrations of such molecules are infrared active. Symmetrical molecules, on the other hand, may have vibrations during which a change of the dipole moment is zero, and therefore, those molecules are infrared inactive.

At this point a few words should be said about the classification of molecules into groups. Molecules are classified according to the relative values of their three moments of inertia. Those possessing three different moments of inertia are referred to as asymmetric top. If all three moments of inertia are equal, the molecule is called a spherical top, and if only two moments are equal but the third is different, the molecule is referred to as a symmetric top. These may be further divided into prolate for which $I_A < I_B = I_C$ and oblate for which $I_A > I_B = I_C$. If $I_A = 0$, the molecule is a linear molecule, which is a special case of a prolate symmetric top. The linear molecules may have a center of inversion and it is referred to as $D_{\infty h}$ point group, and a molecule that does not have a center of inversion is referred to as belonging to point group $C_{\infty v}$.

Molecules having a center of inversion do not have a permanent dipole moment and therefore do not have a pure rotational spectrum. The same is true for spherical top molecules. The asymmetric top molecules, whose moments of inertia are all different, do possess a pure rotational spectrum. However, all molecules except spherical tops, irrespective of their symmetry, do have a rotational Raman spectrum.

In the case of Raman spectra, the amplitude of the dipole moment induced by the incident radiation must change during the vibration considered. According to the polarizability theory,²²⁻²³ the amplitude of the induced dipole moment is given by

$$|\bar{P}| = \hat{\alpha}|E| \quad (50)$$

where $\hat{\alpha}$ is the polarizability and E the electric vector of the incident radiation of frequency ν . In an unsymmetrical molecule, during all normal vibrations, a periodic change of the polarizability takes place. The induced dipole moment changes and the molecules are, therefore, Raman active. For symmetrical molecules this is not always the case although it is possible for a linear symmetrical molecule to be infrared inactive and Raman active. It should be noted here that all homonuclear diatomic molecules like O_2 , H_2 , N_2 , ... are infrared inactive while they are all Raman active. This is a result of the fact that the dipole moment and its change are zero for homonuclear diatomic molecules, whereas the polarizability, its change and the resulting amplitude change in the induced dipole moment do not vanish. This de-

scription of the Raman and infrared activity of the molecules is of a very elementary nature. For a detailed treatment of the subject refs. 8, 21, 22, 23, and 32 should be consulted.

4. LINE INTENSITIES OF ROTATIONAL AND VIBRATIONAL RAMAN SPECTRA

In the foregoing, some fundamental relations of molecular infrared and Raman spectra as well as the relations between those spectra, the selection rules for rotational and vibrational lines of both have been discussed. One of the fundamental measurable quantities of interest for the applications considered is the intensity of the given line both in the infrared and Raman spectra. As indicated previously, the intensity of a spectral line depends on the number of molecules in a given state. For a theoretical determination of the intensity of a given line, it is necessary to know the distribution of the molecules in the various initial states and the transition probabilities.²¹ Since most infrared and Raman spectra are observed under conditions of thermal equilibrium, the distribution of the molecules over the different quantum states in thermal equilibrium need be considered. According to the Maxwell-Boltzmann distribution, the number of molecules in each of the vibrational states is proportional to

$$N_v \sim e^{-\frac{E}{kT}} = e^{-\frac{G_o(v)hc}{kT}}. \quad (51)$$

Thus, the exponential gives the relative numbers of molecules in the different vibrational levels. In order to obtain the number of molecules in a particular energy level referred to the total number of molecules N , the state sum or partition function

$$Q_v = 1 + \exp\left[-\frac{G_o(1)hc}{kT}\right] + \exp\left[-\frac{G_o(2)hc}{kT}\right] + \dots \quad (52)$$

must be utilized.

The number of molecules in the state v is, therefore,

$$N_v = \frac{N}{Q_v} \exp[-G_o(v)hc/kT]. \quad (53)$$

Evaluation of eqn. (53) can be most tedious. Since successive terms in eqn. (53) decrease very rapidly and in most cases the exponential terms in eqn. (52) are small compared to unity, eqn. (53) can be written as

$$N_v = N \exp[-G_o(v)hc/kT]. \quad (54)$$

Figures 4, 5 and 6 indicate the population density of some molecules in the various vibrational states as a function of temperature. Again, here it is quite evident why at normal temperatures (300° K) the ratio of the Stokes to Anti-Stokes line intensities are so high. In the case of the thermal distribution of the rotational levels of the vibrational transitions, the problem is somewhat more complicated. It is not given by the Boltzmann factor $\exp(-E/kT)$ as above. According to the quantum theory each state of an atomic system with a total angular momentum J consists of $(2J+1)$ levels which