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## Introduction

As the density of a gas increases, free rotation of the molecules is gradually transformed into rotational diffusion of the molecular orientation. After ‘unfreezing’, rotational motion in molecular crystals also transforms into rotational diffusion. Although a phenomenological description of rotational diffusion with the Debye theory [1] is universal, the gas-like and solid-like mechanisms are different in essence. In a dense gas the change of molecular orientation results from a sequence of short free rotations interrupted by collisions [2]. In contrast, reorientation in solids results from jumps between various directions defined by a crystal structure, and in these orientational ‘sites’ libration occurs during intervals between jumps. We consider these mechanisms to be competing models of molecular rotation in liquids. The only way to discriminate between them is to compare the theory with experiment, which is mainly spectroscopic.

Line-shape analysis of the absorption or scattering spectra supplies us with normalized contours  $G_\ell(\omega)$  which are the spectra of orientational correlation functions  $K_\ell = \langle P_\ell[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ . The full set of averaged Legendre polynomials unambiguously defines the orientational relaxation of a linear or spherical rotator whose molecular axis is directed along the unit vector  $\mathbf{u}(t)$ . Unfortunately, only the lowest few  $K_\ell$  are available from spectroscopic investigation. The infrared (IR) rotovibrational spectroscopy of polar molecules gives us  $G_1(\omega - \omega_v)$  which is composed of some rotational branches around vibrational frequency  $\omega_v$ . In the case of a linear molecule such as CO the P- and R-branches in the rare gas spectrum transform into a single Q-branch in the liquid phase which is forbidden for the free rotator (Fig. 0.1). This effect, known as a rotational structure collapse [3, 4], is the spectral manifestation of the transition from free rotation to rotational diffusion. The collapsed line is progressively narrowed as the density increases. The anisotropic

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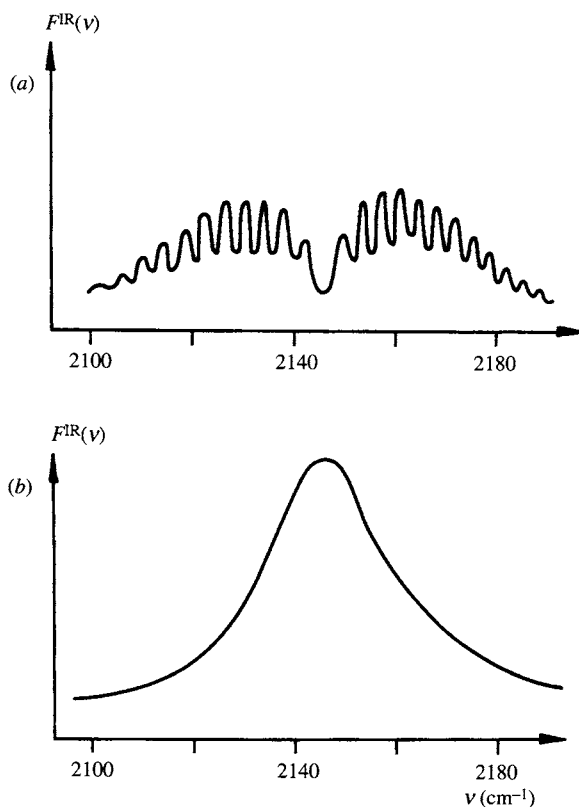
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Fig. 0.1. Infrared absorption spectrum of CO in gas (a) and liquid (b) at 80 K [6].

Raman scattering spectrum  $G_2(\omega - \omega_v)$  undergoes a spectral collapse of the same kind. The spectrum of the gaseous linear rotator is composed of three branches whose rotational structure becomes unresolved at relatively low pressure (Fig. 0.2). With further increase of pressure it is reduced to a single quasi-Lorentzian Q-branch which, in the liquid phase, is much narrower than the spectrum before collapse (Fig. 0.3). Similar information is available from the pure rotational spectra found from the Rayleigh scattering contour  $G_2(\omega)$  or from the light absorption coefficient in the far infrared (FIR) region which is proportional to  $\omega G_1(\omega)$ . The dielectric data commonly used to determine Debye's relaxation time  $\tau_D = \int_0^\infty K_1(t) dt = \pi G_1(0)$  supplement the spectroscopic information.

Since the mechanics of a rotator is set by two canonical variables  $\mathbf{u}$

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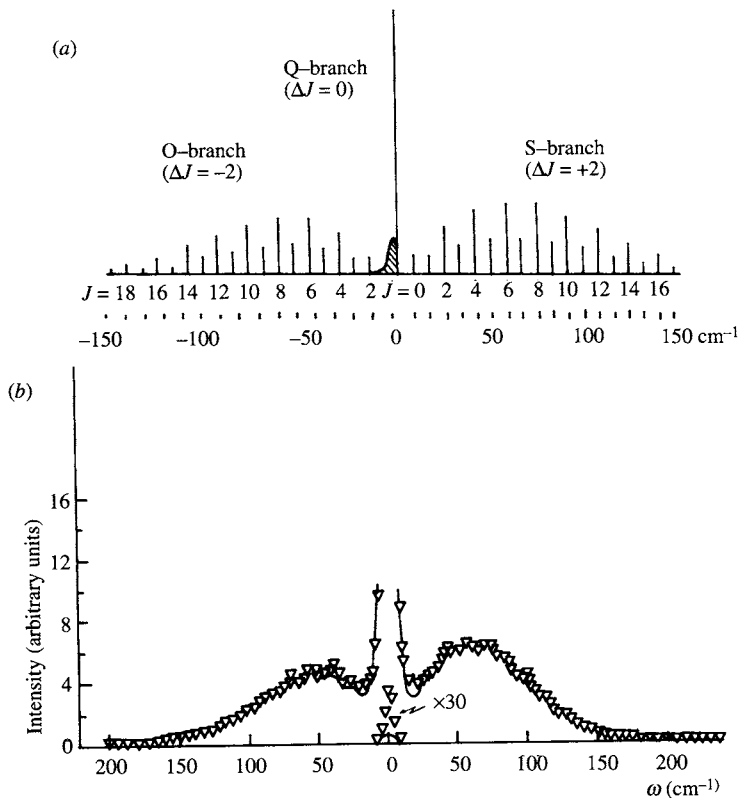


Fig. 0.2. (a) The 'comb' spectrum of N<sub>2</sub> considered as a quantum rotator. The envelope of the rotational structure of the Q-branch slightly split by the rotovibrational interaction is shaded. (b) The depolarized rotovibrational spectrum of N<sub>2</sub> at corpuscular density  $n = 92$  amagat,  $T = 296$  K and pressure  $p = 100$  atm. The central peak, reported in a reduced ( $\times 30$ ) scale is due to a polarized component [5]: ( $\nabla$ ) experimental; (—) best fit.

(axis) and  $\mathbf{J}$  (angular momentum), the rotational relaxation presented by  $K_J(t) = \langle \mathbf{J}(t)\mathbf{J}(0) \rangle$  and its spectrum  $g(\omega)$  must be studied together with  $K_\ell(t)$  and  $G_\ell(\omega)$ . The periphery of  $G_\ell(\omega)$  gives direct but difficult to obtain information about the far wings of  $g(\omega)$ . More frequently NMR data are used to find  $\tau_J = \int_0^\infty K_J(t) dt = \pi g(0)$  from both longitudinal and transverse relaxation times determined by spin-rotation interaction [7]. The relaxation of the rotational energy  $E \propto J^2$  is also of great importance. Its kinetics is characterized by the correlation function  $K_E(t) = \langle J^2(t)J^2(0) \rangle$  but only  $\tau_E = \int_0^\infty K_E(t) dt = \pi g_E(0)$  has been

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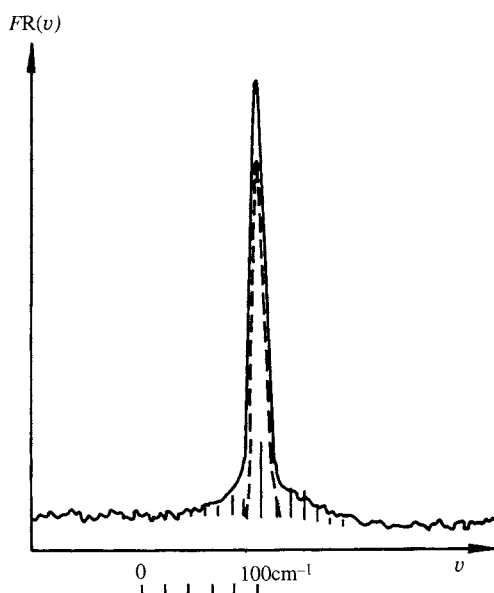
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Fig. 0.3. Raman spectrum of liquid oxygen [6]. The positions of the free rotator's  $j$ -components are shown by vertical lines and the isotropic scattering contour is presented by the dashed line.

measured, by acoustic methods. A relative quantity  $\tau_E/\tau_J$  characterizes the strength and adiabaticity of collisions. In principle the far wings of  $g_E(\omega)$  may be seen in the periphery of the isotropic Raman spectrum  $G_0(\omega) = (1/\pi) \int_0^\infty K_0(t) dt$ , when broadened mainly by rotational energy relaxation. Unfortunately such work has not yet been reported.

Since the information about all  $G_\ell(\omega)$  and especially about  $g(\omega)$  and  $g_E(\omega)$  is never complete, the importance of models capable of predicting them is greatly enhanced. The more developed gas-like models consider  $J$  to be a classical variable. They are appropriate at relatively large pressures when the rotational structure of the branches is smoothed. One of the best models is Gordon's impact theory of rotational and orientational relaxation [2, 8]. The impact theory implies that collisions are instantaneous and retard the molecular rotation by changing both the molecular orientation and the angular momentum. If collisions are adiabatic they do not change  $J^2$  but simply turn  $\mathbf{J}$  and  $\mathbf{n}$  (Gordon's  $m$ -diffusion model). However, the overwhelming majority of molecules (excluding hydrogen) undergo non-adiabatic collisions which change both the direction and

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magnitude of  $J$  but do not change a molecule's orientation (Gordon's ' $J$ -diffusion model'). The change in angular velocity, proportional to  $J$ , results in frequency exchange in each spectral branch, while the change in direction of rotation causes an exchange between the branches. To the extent that the collisions conserve the phase of rotation, the related radiation is only frequency modulated. Since the modulation is not accompanied by rotational dephasing, it must result in spectral narrowing after collapse. The averaging and narrowing of absorption and scattering spectra in the  $J$ -diffusion model amount to a direct analogue of the motional narrowing in NMR discovered earlier [9]. The residual width of the absorption spectra is obviously the rate of the Debye 'rotational diffusion', which decreases as the collision frequency increases.

The chapters in this book are arranged in accordance with both logical expediency and the authors' intention to complicate the problem gradually. We start from rotational (angular momentum) relaxation (Chapter 1), which does not change as radically with pressure as orientational relaxation (Chapter 2). Our main achievement is the utilization (through integral equations of impact theory) of the Keilson–Storer kernel originally proposed to describe the translational velocity distribution after collision [10]. It implies that collisions are purely non-adiabatic but makes it possible to solve exactly the Feller integral equation describing  $J$ -diffusion. The 'extended diffusion' model and the 'Langevin model' of rotation widely used in the literature were found to be opposite particular cases for strong and weak collisions respectively. Although in this book we consider primarily impact theories, non-model methods such as memory function formalism (the Mori chain) and perturbation theory (cumulant expansion) are also used to account for finite collision times. These methods as well as very fresh and disputable ideas (like non-Poissonian collisional statistics) are exploited to calculate  $K_J(t)$  outside the binary collision approximation, where it is expected to be of alternating sign, as MD simulations of the liquid show.

The perturbation theory presented in Chapter 2 implies that orientational relaxation is slower than rotational relaxation and considers the angular displacement during a free rotation to be a small parameter. Considering  $J(t)$  as a random time-dependent perturbation, it describes the orientational relaxation as a molecular response to it. Frequent and small chaotic turns constitute the rotational diffusion which is shown to be an equivalent representation of the process. The turns may proceed via free paths or via sudden jumps from one orientation to another. The phenomenological picture of rotational diffusion is compatible with both

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models. However, they are not equivalent because the original jumping theory completely ignores rotational relaxation and the very existence of angular momentum [11]. This is a significant demerit since the orientational relaxation time  $\tau_{\theta,\ell} = \int_0^\infty K_\ell(t) dt = \pi G_\ell(0)$  is usually plotted against  $\tau_J$ . This plot is a way to check the famous Hubbard relation [12] derived in the lowest order of perturbation theory

$$\tau_{\theta,\ell} \cdot \tau_J = I/\ell (\ell + 1) kT$$

( $I$  is the moment of inertia,  $T$  is the temperature). To introduce  $\tau_J$  into a jump-wise model (at least semiquantitatively) it is necessary to consider the dynamics of above-barrier rotation. As soon as this is done the model becomes self-consistent and also leads to the Hubbard relation in Debye's limit.

Although long-time Debye relaxation proceeds exponentially, short-time deviations are detectable which represent inertial effects (free rotation between collisions) as well as interparticle interaction during collisions. In Debye's limit the spectra have already collapsed and their Lorentzian centre has a width proportional to the rotational diffusion coefficient. In fact this result is model-independent. Only shape analysis of the far wings can discriminate between different models of molecular reorientation and explain the high-frequency peculiarities of IR and FIR spectra (like Poley absorption). In the conclusion of Chapter 2 we attract the readers' attention to the solution of the inverse problem which is the extraction of the angular momentum correlation function from optical spectra of liquids.

Chapter 3 is devoted to pressure transformation of the unresolved isotropic Raman scattering spectrum which consists of a single Q-branch much narrower than other branches (shaded in Fig. 0.2(a)). Therefore rotational collapse of the Q-branch is accomplished much earlier than that of the IR spectrum as a whole (e.g. in the gas phase). Attention is concentrated on the isotropic Q-branch of  $N_2$ , which is significantly narrowed before the broadening produced by weak vibrational dephasing becomes dominant. It is remarkable that isotropic Q-branch collapse is indifferent to orientational relaxation. It is affected solely by rotational energy relaxation. This is an exceptional case of pure frequency modulation similar to the Dicke effect in atomic spectroscopy [13]. The only difference is that the frequency in the Q-branch is quadratic in  $J$  whereas in the Doppler contour it is linear in translational velocity  $v$ . Consequently the rotational frequency modulation is not Gaussian but is still Markovian and therefore subject to the impact theory. The Keilson–

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Storer model used in this theory enables us to describe classically the spectral collapse of the Q-branch for any strength of collisions. The theory generates the canonical relation between the width of the Raman spectrum and the rate of rotational relaxation measured by NMR or acoustic methods. At medium pressures the impact theory overlaps with the non-model perturbation theory which extends the relation to the region where the binary approximation is invalid. The employment of this relation has become a routine procedure which puts in order numerous experimental data from different methods. At low densities it permits us to estimate, roughly, the strength of collisions.

The quantum theory of spectral collapse presented in Chapter 4 aims at even lower gas densities where the Stark or Zeeman multiplets of atomic spectra as well as the rotational structure of all the branches of absorption or Raman spectra are well resolved. The evolution of basic ideas of line broadening and interference (spectral exchange) is reviewed. Adiabatic and non-adiabatic spectral broadening are described in the frame of binary non-Markovian theory and compared with the impact approximation. The conditions for spectral collapse and subsequent narrowing of the spectra are analysed for the simplest examples, which model typical situations in atomic and molecular spectroscopy. Special attention is paid to collapse of the isotropic Raman spectrum. Quantum theory, based on first principles, attempts to predict the  $j$ -dependence of the widths of the rotational component as well as the envelope of the unresolved and then collapsed spectrum (Fig. 0.4).

This theory presented in Chapter 4 is applied to the nitrogen–argon mixture in Chapter 5. It is chosen as an example since the inter-molecular interaction in this system is well known and the cross-section of rotational energy relaxation is measured in the bulk and in molecular beam experiments. The semiclassical versions of infinite order sudden and centrifugal sudden approximations are used to calculate the impact operator which is bilinear in the scattering matrix and responsible for both isotropic Q-branch collapse and rotational energy relaxation. The theory fits well all experimental data over a wide range of temperatures, especially when the small adiabatic corrections to the quantum J-diffusion model are taken into account. In the conclusion of Chapter 5 the phenomenological approach to Q-branch collapse, based on the widely used semi-empirical ‘fitting laws’, is discussed and applied to pure nitrogen.

The orientational relaxation, considered in Chapters 6 and 7, is a more complex problem. The impact theory is the only model capable of tracing the transition from quasi-free rotation in the rare gas to

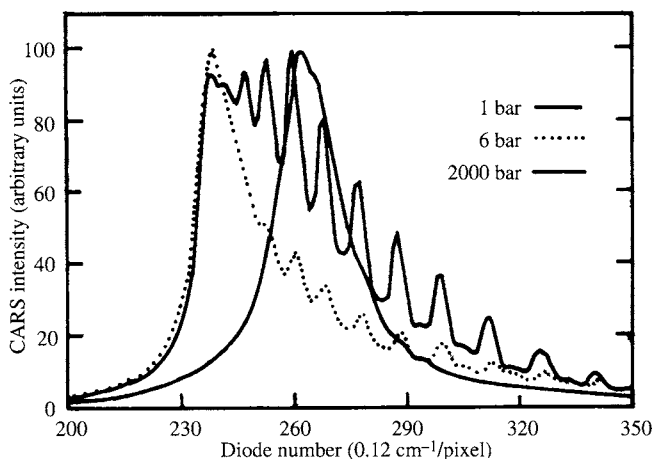


Fig. 0.4. Experimental nitrogen Q-branch of coherent anti-Stokes Raman scattering spectrum (CARS) measured at 700 K and different pressures [14].

rotational diffusion in dense media. In principle it may describe the gradual transformation of multi-branched spectra shown in Fig. 0.1(a) and Fig. 0.2(b) to a single Q-branch which arises from collapse and turns into a narrow line similar to that shown in Fig. 0.1(b) and Fig. 0.3. Classical impact theory presented in Chapter 6 ignores the quantum structure of rotational branches but is the simplest model that one can use to link the opposite cases of gases and liquids. Even in this approximation the problem is so complicated that it may be solved analytically solely in the limits of strong and weak collisions. The difference between them is clearly seen when  $\tau_{\theta,\ell}$  is plotted against  $\tau_J$ . In dense media one obtains the universal Hubbard dependence which is linear in a log plot. At lower pressures it declines from linearity and splits into two branches corresponding to strong and weak collisions which set upper and lower bounds for collisions of arbitrary strength. Rotation is quasi-free when the experimental points are located in this corridor and hindered if they fit the Hubbard relation. The only disadvantage is that the impact theory, being binary, is unlikely to be valid in very dense gas and liquid regions.

The fluctuating cage model presented in Chapter 7 is an alternative. The idea came from comparison of the different kinds of absorption spectra of HCl found in liquid solutions (Fig. 0.5). In SF<sub>6</sub> as a solvent the rotational structure of the infrared absorption spectrum of HCl is well resolved [15, 16], while in liquid He it is not resolved but has



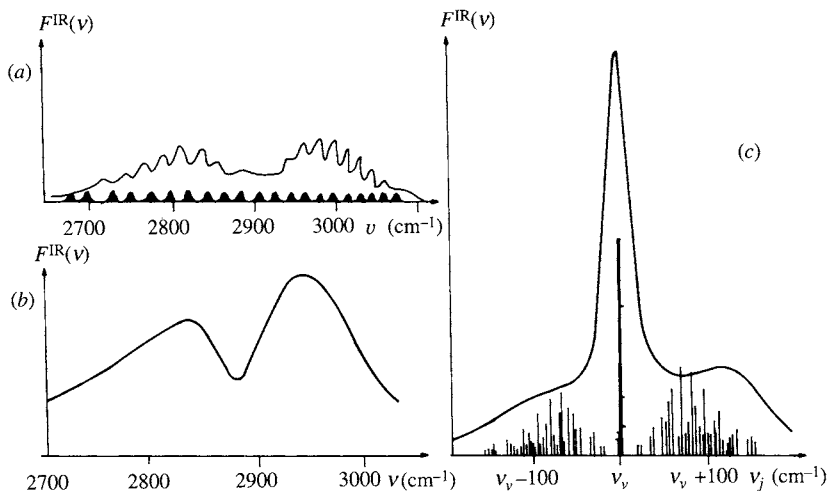


Fig. 0.5. IR absorption spectra of HCl in different liquid solvents: (a) in SF<sub>6</sub> [16] (the triangles mark the positions of the rotational components in the resolved spectrum of the rarefied gas); (b) in He [15]; (c) in CCl<sub>4</sub> (the vertical lines mark the frequencies  $\nu_j$  and the intensities of the Stark components of the linear rotator spectrum split by the electrical field of the cage)[17].

pronounced P- and R-branches (Fig. 0.5(a),(b)). Clearly the rotation may be either quantized or classical, but is practically free in these media. This observation might be a physical reason to explore the gaseous impact theory for describing the double-branch spectrum and to expect the appearance of a single Q-branch after (and as a result of) its collapse. However, in CCl<sub>4</sub> and many other solvents the spectrum consists not of two nor of one but of three branches simultaneously (Fig. 0.5(c)). Since the existence of such a triplet is absolutely excluded by the impact theory, it indicates the dubious impact origin of a doublet also. It is more likely that a molecule trapped in the cage rotates in the permanent random field created by surrounding solvent particles.

The envelope of the Stark structure of the rotator in a constant orienting field, calculated quantum-mechanically in [17], roughly reproduces the shape of the triplet (Fig. 0.5(c)). The appearance of the Q-branch in the linear rotator spectrum indicates that the axis is partially fixed, i.e. some molecules perform librations of small amplitude around the field. Only molecules with high enough rotational energy overcome the barrier created by the field. They rotate with the frequencies observed in the

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far wings of the P- and R-branches. It is well known that the orienting field in the centre of a spherical cell is zero but increases towards its border [6]. Thermal motion of the molecule between the borders as well as random temporal deformations of the cell modulate the value and direction of the field. In other words, the orienting field appears at any distortion of the spherical symmetry of the rotator's neighbourhood and changes randomly with time [18]. The importance of this mechanism depends on dielectric properties of the solution. One would expect the highly polar hydrogen halides to induce a particularly strong orienting field, which must be larger for solvent molecules of higher polarizability. From this point of view it is even more surprising that in He the axis of HCl is not fixed at all (Fig. 0.5(b)) and in SF<sub>6</sub> the rotation is even as free as in the gas phase (Fig. 0.5(a)). To explain this paradox, we have developed an original theory of rotation in the fluctuating cell [19]. The oriented field is assumed to change randomly and instantaneously and its successive values form the Markovian chain. The theory is first reviewed and is formalized, as is its impact alternative. This shows that free rotation in a liquid does not consist of free paths as in gas, but occurs in a permanent random field when it is small or changes so rapidly that it practically averages itself. This conclusion is confirmed by evidence that the rotational structure in SF<sub>6</sub> is better resolved at higher temperatures, when thermal motion is faster.

This brief discussion of the physical meaning and mutual correspondence of different models and theories of rotational motion is intended as a guide for those who do not intend to examine the book systematically. Setting forth the material consistently, one cannot avoid certain formalisms peculiar to angular momentum theories. We hope, however, that a detailed commentary will enable readers to form a clear notion of the most important assumptions and results without referring to proofs.

The authors are happy to acknowledge the help and support of those people and institutions who assisted in fulfilling the task of writing this book. The present English edition includes numerous original results obtained by the authors in cooperation with their graduate students and coworkers after publication of the Russian version of the book in 1982. We appreciate very much their collaboration and the important role of the seminar of the Theoretical Chemistry Laboratory in the Institute of Chemical Kinetics and Combustion of the Russian Academy, where most of them work.

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