

Vibrational relaxation in condensed media

V. E. Pogorelov, A. I. Lizengevich, I. I. Kondilenko, and G. P. Buyan

T. G. Shevchenko Kiev State University
Usp. Fiz. Nauk 127, 683-704 (April 1979)

We review the literature on spectroscopic methods of studying processes of vibrational relaxation of molecules in condensed media; special attention is paid to liquids. We discuss the features and advantages of the following methods: spontaneous Raman scattering, picosecond spectroscopy, and active Raman spectroscopy. Comparison of the results obtained by the different methods yields detailed information on the course of relaxation processes.

PACS numbers: 07.65. - b, 06.60.Jn, 78.30.Cp

CONTENTS

1. Introduction	270
2. Distinguishing the contributions of orientational and vibrational relaxation in the contours of spontaneous Raman bands	270
3. Picosecond stimulated Raman spectroscopy	272
4. Picosecond active Raman spectroscopy	275
5. Mechanisms of vibrational relaxation	275
6. Results of studying the dynamics of vibrational relaxation	276
7. Conclusion	280
Bibliography	280

1. INTRODUCTION

The shape of the band contours in vibrational spectra of materials in the liquid phase and in molecular crystals is determined both by the orientational movement of the molecules and by the dynamics of relaxation of the energy of intramolecular vibrations. Many original and review studies¹⁻⁶ have been concerned with the effect of reorientation on the contours of bands in molecular spectra. This review aims to analyze the studies concerned with the contribution of intra- and intermolecular interactions to the component of the contour of the vibrational bands that does not depend on the orientational movement of the molecules.

Currently several methods exist of studying the dynamics of vibrational relaxation. Historically the first of these is the separation of the contributions of orientational and vibrational relaxation in the contours of the spontaneous Raman bands. The first studies were performed in the Institute of Physics of the Academy of Sciences of the USSR.⁷ However, all the potentialities of this method have emerged only with the application of lasers as the sources of the exciting radiation.⁸ Another method is based on coherent vibrational pumping of the medium through stimulated Raman scattering (SRS) of a high-power picosecond laser pulse. Then one applies another picosecond probe pulse to the medium and studies its anti-Stokes Raman scattering. By varying the delay time of the probe pumping pulse during the experiment, one can get information on the relaxation times of the vibrational energy in the medium.⁹⁻¹² Priority along this line of studying the dynamics of vibrational relaxation belongs to Alfano, Shapiro, Laubereau, Von der Linde, and Kaiser, whose studies were published in 1971. We should note that these studies were preceded by a theoretical study of the problem

by Akhmanov and his associates¹³⁻¹⁴ (1969) and by Bloembergen's group¹⁵ (1970). These studies treated the fundamental properties of Raman scattering under non-steady-state picosecond excitation.

Finally, the third method of studying the dynamics of vibrational relaxation is based on biharmonic picosecond resonance vibrational "pumping" of the medium with subsequent probing of this nonequilibrium, vibrationally excited medium with a picosecond pulse.¹⁶ Here also the dynamics of relaxation is studied with a time delay of the exciting pulse with respect to the pump pulse. This line has been developed successfully by the groups of S. A. Akhmanov (Moscow State University) and of Kaiser (Technische Universität, Munich). The latter two methods can be called picosecond SRS spectroscopy and picosecond active Raman spectroscopy, respectively.

2. SEPARATION OF THE CONTRIBUTIONS OF ORIENTATIONAL AND VIBRATIONAL RELAXATION IN THE CONTOURS OF SPONTANEOUS RAMAN BANDS

First we should note that one can distinguish the contributions of orientational and vibrational relaxation only in the contours of Raman bands. The point is that the Raman tensor is symmetric when far from electronic absorption bands. This means that one can distinguish the isotropic and anisotropic components in it. One can show² that the isotropic component of the scattering tensor is determined exclusively by intra- and intermolecular interactions. Within the framework of neglecting vibrational-rotational interactions, this component of the Raman tensor does not depend on the nature of the rotational motion of the molecules. Both intra- and intermolecular interactions and reorientation of the molecules contribute to the anisotropic com-

ponent of the Raman tensor.

The possibility of experimentally distinguishing the contribution of the orientations and interactions of the particles to the contours of the vibrational bands opens up broad potentialities of employing Raman spectroscopy for studying materials in a condensed phase. This potentiality is lacking in infrared (IR) absorption spectroscopy since a vector quantity, the dipole moment of the transition, is responsible for the parameters of the IR bands.

Following Ref. 2, we can write an expression for the intensity of the light scattered by a molecule as a function of the frequency in the form

$$J(\omega_s) = A(\omega_i - \Omega)^4 (2\pi)^{-4} \int_{-\infty}^{\infty} \langle [e^{(i)} \alpha(0) e^{(i)}] [e^{(s)} \alpha(t) e^{(s)}] \rangle_{or} \times \langle Q(0) Q(t) \rangle_{vib} \exp(i\omega_s t) dt. \quad (1)$$

Here A is a certain constant; ω_i , ω_s , $\epsilon^{(i)}$, and $\epsilon^{(s)}$ are respectively the frequencies and polarization vectors of the incident (i) and scattered (s) radiation; Ω is the frequency of the vibrational transition in the molecule; α is the component of the scattering tensor that depends only on the angular and electronic variables; and Q is the normal coordinate of the vibration:

$$Q(t) = U^{-1}(t) Q U(t),$$

$U(t)$ is the evolution operator (in the interaction representation) that corresponds to the intermolecular interaction potential; $\langle \dots \rangle_{vib}$ implies the quantum average $\text{Sp}[\rho_s Q(0) Q(t)]$ and averaging over the orientational-translational motion, which is treated classically in a liquid; and $\langle \dots \rangle_{or}$ implies averaging over the random reorientations of the particles.

In order to distinguish the contributions of orientational and vibrational relaxations from the recorded band contours, one employs the method of perpendicular experimental geometry, in which one studies the components of the scattered light $J_{\parallel}(\omega_s)$ with $\epsilon_s \parallel \epsilon_i$ and $J_{\perp}(\omega_s)$ with $\epsilon_s \perp \epsilon_i$. Here we have the following for an isotropic liquid:

$$g_v(t) = \langle Q(0) Q(t) \rangle_{vib} = \int_{-\infty}^{\infty} J_{vib}(\omega) e^{-i\omega t} d\omega = \int_{-\infty}^{\infty} \left[J_{\parallel}(\omega) - \frac{4}{3} J_{\perp}(\omega) \right] e^{-i\omega t} d\omega, \quad (2)$$

$$g_{or}(t) = \langle \alpha(0) \alpha(t) \rangle_{or} = \int_{-\infty}^{\infty} J_{\perp}(\omega) e^{-i\omega t} d\omega \langle Q(0) Q(t) \rangle_{vib}. \quad (3)$$

The correlation functions (2) and (3) are not normalized. In practice it is more convenient to use the normalized functions $G_v(t) = g_v(t)/g_v(0)$ and $G_{or}(t) = g_{or}(t)/g_{or}(0)$.

Let us list the approximations that we have used in deriving (1)–(3). The molecules scatter light independently. The frequency of the incident light is far from the frequencies of electronic transitions (non-resonance Raman scattering). The electronic, vibrational, and rotational movements in the molecule do not

interact. The trace of the scattering tensor differs from zero. The system of scattering molecules is isotropic. The possibility of "hot" transitions is ruled out in the experiment.

For experimental study of vibrational and orientational relaxation using Raman spectra, one employs the apparatus¹⁷ whose block diagram is shown in Fig. 1. A Raman band is recorded twice: first with an analyzer passing scattered light (with its electric vector polarized in the V plane perpendicular to the scattering plane), and then with an analyzer that passes light polarized in the H plane. Thus one records the intensities $J_{\perp V}^*$ and $J_{\perp H}^*$. The asterisks here indicate that these are experimentally observed contours.

The contour of the anisotropic component of the Raman band is

$$J_{anis}^* = J_{\perp H}^* - J_{\perp V}^* = J_{\perp H}^* - J_{\perp V}^*. \quad (4)$$

At the same time, in line with (2), the contour of the isotropic component is defined as

$$J_{is}^* = J_{\perp V}^* - \frac{4}{3} \frac{J_{\perp H}^*(\omega)}{k(\omega)}. \quad (5)$$

Here $k(\omega) = J_H(\omega)/J_V(\omega)$ is the polarizing action of the instrument. The contour of the isotropic component of the vibrational Raman band contains information on vibrational relaxation. The anisotropic contour contains information both on vibrational and rotational relaxation. In order to distinguish the vibrational and orientational contributions from the observed isotropic and anisotropic contours, we must rule out or reduce to a minimum the distorting effect of the spectral instrument. As we know,¹⁸ we can find the true contour of a Raman line by solving an integral equation in which two of the three functions are determined experimentally. One can apply computer Fourier analysis in solving this equation.^{19,20} This type of problem belongs to the incorrectly posed problems of mathematical physics.²¹ The trouble is that the relative error in assigning the two observed contours and the error of computation begin to rise with increasing frequency in the spectrum of Fourier harmonics of the observed contours. As we know, one can solve this type of incorrectly posed problems by using *a priori* information on the sought

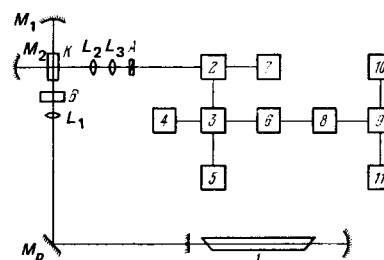


FIG. 1. Block diagram of the apparatus. 1—laser, 2—monochromator, 3—photomultiplier (with cryostat), 4—Photomultiplier power supply, 5—temperature-control device for the photocathode of the photomultiplier, 6—photon-flux meter (IPF-2), 7—recorder, 8—frequency meter F-5080, 9—transcriber F-5033, 10—punch PL-80, 11—printer.

function or on its Fourier transform. As the *a priori* information on the sought function, one can employ its property of going to zero at infinite distance from the center of gravity in such a way that the function and its square are integrable. In connection with the requirements imposed on the sought contour based on Plancherel's theorem (see Ref. 22), the weight of the higher frequencies in the Fourier transform of the true contour must be limited. That is, the amplitude of the Fourier harmonics must fall off with increasing frequency. The amplitude of the spectrum of the Fourier transforms of the observed contours comes rather close to its limiting value up to certain small frequencies. Hence, if we restrict the Fourier transformation to a certain frequency U_{\max}^{λ} , we conserve in practice the fundamental information on the details of the sought contour. However, here we perform a reduction to an instrument having an apparatus function of a certain finite width, rather than to an ideal spectral instrument. The limiting frequency U_{\max}^{λ} of the Fourier transformation employed in reconstructing the true contour of the Raman band contains information on the source data of the problem, namely on the frequency of the spectrum of Fourier components at which the noise signal begins to predominate. We can estimate the relationship between the limiting employed frequency of the Fourier transform of the true contour of the Raman band and the details of this contour resolvable through reduction by the relationship

$$\Delta\lambda_{\min} \sim \frac{2\pi}{U_{\max}^{\lambda}} \quad (6)$$

Here $\Delta\lambda_{\min}$ is the interval between just-resolvable details of the true contour. If we transform to wave numbers, then we have

$$\Delta\tilde{\nu}_{\min} \sim \frac{2\pi}{\lambda^2 U_{\max}^{\lambda}} \quad (7)$$

Thus we can obtain by reduction the contours of Raman bands having the same shape as would be recorded by a spectrometer having an effective apparatus function with a width of the order of $\Delta\tilde{\nu}_{\min}$. A test of this method of reduction of observed contours of Raman lines has shown its great effectiveness.

In order to determine the vibrational component $J_{\text{vib}}(\omega)$ of the Raman line from the observed contour $J_{\text{is}}^*(\lambda)$, one employs the above-described procedure to eliminate the observed contour $J_{\text{laser}}(\lambda)$ of the exciting laser line as recorded under the same conditions as for the contour $J_{\text{v}}^*(\lambda)$.

The problem of distinguishing the rotational contribution of the anisotropic component of the Raman band in the contour $J_{\text{anis}}^*(\lambda)$ is quite analogous, from the technical standpoint, to the problem of eliminating apparatus distortions. Actually the observed contour $J_{\text{anis}}^*(\lambda)$ is the convolution of the sought orientational contour $J_{\text{or}}(\lambda)$ with the observed contour $J_{\text{is}}^*(\lambda)$:

$$J_{\text{anis}}^*(\lambda) = \int_{-\infty}^{\infty} J_{\text{or}}(x) J_{\text{is}}^*(\lambda - x) dx \quad (8)$$

Upon solving this integral equation for $J_{\text{or}}(\lambda)$, one automatically eliminates the apparatus distortions, which exist to an equal extent in both the isotropic and the anisotropic contours (apart from a negligibly small difference in the distorting action of the instrument on the shape of the contours of the exciting line with differing polarizations). In view of the incorrect posing of the problem, we should note that here the contribution of vibrational relaxation is not fully eliminated from the anisotropic contour, but reduced to a certain minimum. The normalized correlation functions $G_{\text{anis}}^*(t)$, $G_{\text{is}}^*(t)$, and $G_{\text{laser}}(t)$, which are found from the contours $J_{\text{anis}}^*(\lambda)$, $J_{\text{is}}^*(\lambda)$, and $J_{\text{laser}}(\lambda)$ by a computer program for calculating direct Fourier transforms, show greater accuracy in this regard. The normalized vibrational-relaxation correlation function is found by

$$G_{\text{vib}}(t) = G_{\text{is}}^*(t) / G_{\text{laser}}(t) \quad (9)$$

and the orientational correlation function by

$$G_{\text{or}}(t) = \frac{G_{\text{anis}}^*(t)}{G_{\text{is}}^*(t)} \quad (10)$$

In these functions, at least for times that are not very large, the recording and calculation errors have less effect than in determining the shapes of the contours $J_{\text{vib}}(\omega)$ and $J_{\text{or}}(\omega)$.

Moreover, as a rule, one can extract information on the dynamics of relaxation processes from the contours $J_{\text{vib}}(\omega)$ and $J_{\text{or}}(\omega)$ by analyzing the dependence of a parameter of the shape of the contours (their width) on the conditions of experiment. The width of the contour of a spectral line, as usually measured at the half-height of the contour, i.e., near the center of gravity of the band, gives a picture of the relaxation after large time intervals. At the same time, the temporal autocorrelation functions allow one to trace the nature of the relaxation at each instant of time at intervals of the order of ten picoseconds. This is what determines the information content of the autocorrelation functions of molecular spectroscopy.

3. PICOSECOND STIMULATED RAMAN SPECTROSCOPY

In recent years the progress in the field of laser technique of generating ultrashort picosecond pulses has enabled direct measurements of the lifetime of short-lived states (including vibrational ones).^{9-12,23-27} The essence of this method consists in the following.

A short, high-power pulse of laser radiation of duration from 6 to 8 picoseconds is directed at the studied object. The stimulated Raman scattering of this radiation in the medium leads to population of the excited vibrational states. After a certain time (called the delay time and denoted as t_D), the object is irradiated with another short picosecond pulse obtained from the first one by frequency doubling. As a rule the probe pulse is several orders of magnitude weaker than the pump pulse. Therefore it is scattered spontaneously

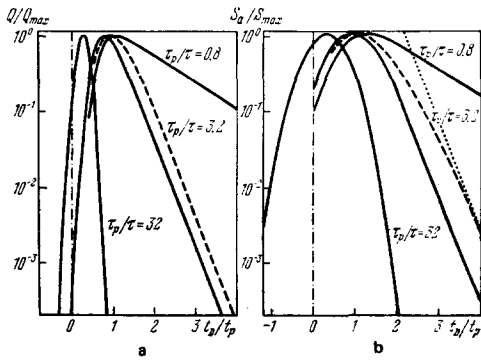


FIG. 2. Choice of conditions for measuring the lifetime of excited vibrational states: Q/Q_{\max} are the calculated values of the normalized vibrational amplitudes, t_D is the delay time between the pump and probe pulses, and τ_p is the duration of the pump pulse.

by the studied object. Owing to the high population of the excited vibrational state obtained with the pump pulse, the anti-Stokes component is enhanced in the scattering spectrum of the probe pulse. By varying the delay time between the probe pulse and the pump pulse, one can directly determine the vibrational relaxation time τ . In order to ensure reliable measurements, a certain relationship should obtain between the sought τ and the durations of the pump and probe pulses. Figure 2a⁹ shows the calculated vibrational amplitudes Q/Q_{\max} as a function of t_D/τ_p for three values of $\tau_p/\tau = 32$, 3.2, and 0.8. We see from Fig. 2a that the ratio Q/Q_{\max} strongly depends on the parameter τ_p/τ . The experimentally measured ratios S_a/S_{\max} of the signals at the frequency of the anti-Stokes scattering of the probe beam behave analogously (Fig. 2b). The anti-Stokes signal S_a turns out to decline exponentially with τ for small τ_p/τ , while directly following the vibrational-deexcitation time. Yet if the ratio τ_p/τ is large ($\tau_p/\tau = 32$ in Fig. 2), the contribution of τ to the dependence of Q/Q_{\max} or S_a/S_{\max} on t_D/τ_p is very small. In essence, the corresponding curves match the shape of the probe pulse. The shape of the picosecond pulse is very important in the experiments described. It is quite necessary to have the leading and trailing fronts of the probe pulse and the pump pulse as steep as possible. Hence a Gaussian shape of these pulses is preferable to a Lorentzian shape.⁹

We can note from Fig. 2b that it takes a certain time to establish vibrational excitation. Actually, the maximum of S_a is shifted away from the instant of applying the probe pulse.

Figure 3 shows the fundamental diagram of the apparatus.⁹ A Q-switched neodymium laser generates a single picosecond pulse at the frequency ω_1 . A second-harmonic generator doubles the frequency of the oscill-

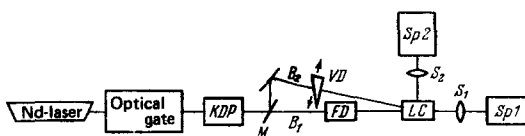


FIG. 3. Fundamental diagram of a picosecond experiment.

lations in this pulse. The radiation is then split in such a way that the beam B_1 at the frequency ω_1 traverses the fixed delay line FD and is directed onto the studied specimen LC generating stimulated Raman scattering in it. The beam B_2 at the frequency $2\omega_1$ through the regulated delay line VD is also incident on the specimen LC and yields spontaneous Raman scattering in it. Phased vibrations arise in the medium in the process of stimulated Raman scattering. The corresponding wave vectors must satisfy the following equation (Fig. 4):

$$\mathbf{k}_{\omega_1} - \mathbf{k}_s = \mathbf{k}_{\text{vib}}. \quad (11)$$

(Here \mathbf{k}_s is the wave vector of the Stokes component of the stimulated Raman scattering.) Upon interacting with these phased vibrations, the probe beam is scattered in such a way that one observes an especially intense coherent anti-Stokes signal S_a^c in a direction that satisfies the equation

$$\mathbf{k}_{2\omega_1} + \mathbf{k}_{\text{vib}} = \mathbf{k}_a. \quad (12)$$

In all other directions one also observes anti-Stokes spontaneous Raman signals, but they are of considerably smaller intensity. In Fig. 3 the spectrometer $Sp1$ establishes the anti-Stokes scattering in the direction of phase synchronization. As the phase grating established in the medium during stimulated Raman scattering breaks down, the signal S_a^c recorded by the spectrometer $Sp1$ declines. We shall denote the time for breakdown of phase synchronization of the vibrations, or the dephasing time, as τ .

By studying the relationship of the incoherent signal $S_a^{\text{inc}} = f(t_D/\tau_p)$ to the time in directions that do not satisfy the synchronization conditions (11) and (12), one can establish the time for vacating the excited vibrational state, or depopulation time τ' from the time decay of the signal S_a^{inc} .

The amplitude of the phased vibrations that have arisen during stimulated Raman scattering will decline with time owing to damping of the vibrations and decline in the number of vibrationally excited molecules¹²:

$$\frac{\partial Q}{\partial t} + \frac{Q}{2\tau} = \frac{i}{4m\omega_0} \left(\frac{\partial \alpha}{\partial Q} \right)_0 E_{L1} E_S^* (1 - 2n). \quad (13)$$

In this case, we have

$$\frac{\partial n}{\partial t} + \frac{n}{\tau'} = \frac{i}{8\hbar} \left(\frac{\partial \alpha}{\partial Q} \right)_0 (E_{L1} E_S^* Q^* - E_{L1}^* E_S Q). \quad (14)$$

Here m and ω_0 are the reduced mass and the frequency of the intramolecular vibration, n is the number of excited molecules per unit volume, E_{L1} is the intensity of the pump field, E_S is the field intensity of the Stokes wave, α is the polarizability of the molecules, Q is the

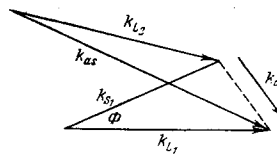


FIG. 4. On the determination of the direction of coherent scattering.

classical normal coordinate, and N is the number of molecules per unit volume.

The interaction of the excited molecules with the probe laser pulse gives rise to the incoherent anti-Stokes signal¹²

$$S^{\text{inc}}(t_D) = \frac{3\omega_a^2 N^2 A \Omega}{8\pi c^2 \rho} \left(\frac{\partial \alpha}{\partial Q} \right)^2 \int dz dt n(t, z) |E_{Lz}(t - t_D; z)|^2. \quad (15)$$

In Eq. (15) ω_a is the frequency of the anti-Stokes signal, ρ is the density, A is the cross-section of the beam, and Ω is the solid angle that characterizes the detector for the scattered radiation.

For coherent scattering we have⁹

$$S^c(t_D) = \left(\frac{2\pi\omega_a^2}{c^2 k_a} \right)^2 N^2 \left(\frac{\partial \alpha}{\partial Q} \right)^2 \left[\frac{\sin(I\Delta k/2)}{I\Delta k/2} \right]^2 I^2 \int Q^2(t + t_D) |E_{Lz}(t)|^2 dt. \quad (16)$$

Here k_a is the wave vector of the anti-Stokes scattering.

The expressions (15) and (16) have been employed¹³ for comparing the results of theory and experiment. The substances 1,1,1-trichloroethane and ethyl alcohol were studied in the experiment (Figs. 5 and 6). We should note the good agreement of theory and experiment.

Table I gives the results of direct measurements of the dephasing time τ and the depopulation time τ' that have been obtained by methods of picosecond spectroscopy up to the time of writing this review. In analyzing the data presented in the table, attention is called to the qualitative difference in the estimates of τ for liquid nitrogen. The authors of the later study²⁵ demonstrate that the elevated values of τ in Ref. 26 are erroneous, owing to an incorrect choice of the parameters of the probe pulse.

We noted earlier that one can estimate the vibrational relaxation time τ_{vib} from the isotropic contours of spontaneous Raman lines. Comparison of these times with the dephasing time τ shows that their values are close to the latter in three out of four measurements. The values of τ and τ_{vib} diverge only in the case of calcite. In Ref. 9 the agreement of τ and τ_{vib} is considered to be a "successful case in which the width of the spontaneous Raman lines is apparently determined by the dephasing time."

Generally both processes contribute to the width of the isotropic Raman bands, both the decline with time of the phase correlation of the intramolecular vibrations and the decay of the vibrational excitation. The direct

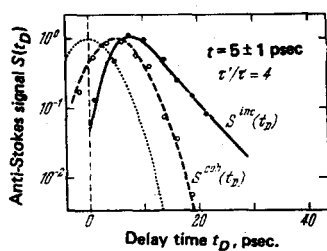


FIG. 5. Decay of the coherent and incoherent anti-Stokes scattering in 1,1,1-trichloroethane (frequency 2939 cm^{-1}). Dots: experiment; curves: calculation; dotted curve: pump pulse.

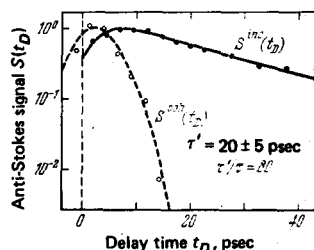


FIG. 6. Decay of the coherent and incoherent anti-Stokes scattering in ethyl alcohol. Frequency 2938 cm^{-1} . Dots: experiment; curves: calculation.

measurements discussed in this paper of the dephasing times τ and depopulation times τ' show that, as a rule, $\tau \ll \tau'$. Thus, for CH_2Cl_2 we have $\tau'/\tau = 4$, for $\text{C}_2\text{H}_5\text{OH}$ $\tau'/\tau = 80$, and for liquid nitrogen²⁸ $\tau'/\tau \approx 8.7 \times 10^5$. That is, the dephasing of the vibrations occurs considerably faster than the decay of the excited vibrational state. Hence the contribution of phase-correlation processes to the width of the spontaneous Raman scattering prevails over the contribution of the factors that determine the lifetime of the molecules in the excited vibrational state.

In analyzing the causes of the dephasing of the intramolecular vibrations, we can assume a substantial role in this process of orientational thermal disordering of the molecules. In this case correlation must exist between the dephasing time τ and the orientational relaxation time of the molecules. Studies on liquid nitrogen have been undertaken to elucidate this situation. The dephasing time has been established as $\tau = 75 \pm 8$ psec by picosecond spectroscopic methods.²⁵ Study of the anisotropic component of the spontaneous Raman scattering by using temporal angular autocorrelation functions shows that the correlation time of the orientational relaxation of the molecules in liquid nitrogen amounts to 0.6 picosecond²⁹ in the pure liquid and 0.8 picosecond in the inert solvent SF_6 .³⁰ We can assume it is firmly established that orientational relaxation does not affect the phase correlation of the intramolecular vibrations.

Picosecond spectroscopy allows us to study directly the nature of nonequilibrium relaxation processes and the kinetics of quantum states. In obtaining the spectral band contours, the measurement is performed on the equilibrium medium and one actually extracts information on the fluctuations (of density, orientations, etc.) in the system. The relationship between the charac-

TABLE I.

Substance	$\tau, 10^{-12}$ sec (from spontaneous Raman scattering)	$\tau, 10^{-12}$ sec	$\tau', 10^{-12}$ sec	Reference
Ethyl alcohol, 2928 cm^{-1}	0.26		20 ± 5 28 ± 14	24 27
1,1,1-trichloroethane	1.1	1.3 ± 0.6	5.0 ± 1	24
Diamond, $T = 77^\circ \text{K}$, 1333 cm^{-1}	3.5	3.4 ± 0.3		10
$T = 295^\circ \text{K}$	3.2-2.5	2.0 ± 0.3		10
Carbon tetrachloride, 459 cm^{-1}	4.0 ± 0.5	4.0 ± 0.5		9
Calcite, $T = 297^\circ \text{K}$	3.6-4.8	8.5 ± 2		11
$T = 100^\circ \text{K}$	7.7	19.1 ± 4		11
Nitrogen (liquid), 1332 cm^{-1}	80^{28}	$600-5000^{25}$	6.5×10^7	26

teristics of a dissipative process and the equilibrium fluctuations in the medium is established by the fluctuation-dissipation theorem. In comparing the correlation functions reconstructed from the band contour and the relaxation functions of picosecond spectroscopy, one must determine exactly the processes to which they (the correlation functions) refer. Thus, the contour correlation functions contain information on all the types of processes that lead to broadening (phase mismatch, resonance exchange of vibrational quanta, population relaxation, etc.). The direct measurements of the picosecond technique yield the relaxation functions of the phases and populations separately. The deviation of the correlation and relaxation times for the stated functions is natural.

Let us indicate another point to be taken into account in comparing the data of the two methods. The fluctuation-dissipation theorem is valid for small perturbations of a system, i.e., for weak departures from equilibrium. In picosecond experiments, the population inversion of levels can be very substantial, so that the process will be nonlinear in the thermodynamic parameters.³¹ Here the nonequilibrium relaxation functions and the equilibrium correlation functions can have different forms.

4. PICOSECOND ACTIVE RAMAN SPECTROSCOPY

In recent years another highly effective method of getting information on vibrational relaxation of molecules has been progressing vigorously: active Raman spectroscopy (ARS). In contrast to the traditional methods of studying equilibrium thermal excitations, this method uses tunable lasers to carry out effective excitation and phasing of intramolecular vibrations in large volumes. In order to do this, the ARS method, employs biharmonic laser pumping. One directs radiation into the studied medium with the frequencies ω_1 and ω_2 such that $\omega_1 - \omega_2 \approx \Omega$, where Ω is the frequency of a vibrational transition. Thus the beating of the light waves resonates owing to the coupling of the electronic and nuclear excitation with the elementary oscillators¹⁶

$$\frac{d^2 Q}{dt^2} + 2\Gamma \frac{dQ}{dt} + \Omega^2 Q = \frac{1}{2M} \left(\frac{\partial \alpha_{ij}}{\partial Q} \right)_0 E_i^{(1)} E_j^{(2)} e^{-i(\omega_1 - \omega_2)t}. \quad (17)$$

In Eq. (17), Q is the normal coordinate of the corresponding vibration, $E^{(1)}$ and $E^{(2)}$ are the amplitudes of the pump wave fields at the frequencies ω_1 and ω_2 , respectively, $(\partial \alpha_{ij} / \partial Q)_0$ is the derivative of the electronic polarizability of the molecules with respect to the nuclear coordinate, 2Γ is the decay constant of the vibration, and M is the reduced mass of the molecule.

The difference between the ARS method and the method of picosecond spectroscopy consists in the fact that in the former method the intensities of the pump field in the process of "preparing" the medium are not large. They do not reach the levels required for stimulated Raman scattering of radiation in the medium. At the same time, the population of the excited vibrational states in the ARS method substantially exceeds the equilibrium thermal value. In picosecond spectroscopy

one can study relaxation of vibrational excitation only for transitions manifested in stimulated Raman spectra. In the ARS method, by scanning $\omega_1 - \omega_2$, one can populate practically any vibrational levels of the studied system. The phased vibrations in the "prepared" medium are probed by the "probe" beam of frequency ω . Here the wave vectors $k_{1,2}$ of the pump, k of the probe wave, and k_c and k_s of the scattered radiation are interrelated by:

$$k_1 - k_2 = k - k_c \quad (\text{Stokes scattering}), \quad (18)$$

$$k_1 - k_2 = k_s - k \quad (\text{anti-Stokes scattering}). \quad (19)$$

In the ARS method, just as in picosecond spectroscopy, the scattering indicatrix is substantially anisotropic. The maximum scattering intensity of the probe beam is observed in the synchronization directions of (18) and (19).

By employing picosecond pulses in active Raman spectroscopy, one can measure relaxation times of vibrational processes in condensed media directly. Just as in the method discussed above, one can measure the dephasing times of the molecular vibrations in the synchronization direction in such an experiment. In all other directions, measurements of incoherent anti-Stokes scattering yield the decay times of the vibrational excitations, or depopulation times.

5. MECHANISMS OF VIBRATIONAL RELAXATION

The difficulty of creating a general theory of the contours of spectral lines has been discussed repeatedly (see, e.g., Ref. 32). Construction of a theory of the shape of vibrational bands of liquids is also complicated by the fact that simple model concepts of the nature of the movement of the particles are unsuitable in this case (e.g., rectilinear trajectories, as is assumed for gases). However, the molecules in liquids lack rotational transitions, i.e., the bands lack rotational structure. As is shown in Chap. 2, this allows us to reconstruct the correlation functions of vibrational processes from the band contour. The latter circumstance facilitates the theoretical treatment of the problem.

We can classify the relaxation processes of vibrational states into adiabatic and nonadiabatic. The former include perturbations that don't give rise to transition of the molecules to another energy level (shift of a level, phase mismatch). The latter gives rise to changes in the states of the molecules (relaxation of energy into the dissipative degrees of freedom, resonance exchange of vibrational quanta between identical molecules in pure materials). Let us discuss how these processes are manifested in the discussed experiments.

The contours of spectral bands are shaped by all the stated processes. Picosecond spectroscopy allows us to gain separate information on the breakdown of phase synchronization and on population relaxation in a system. Here the possibility of such a separation involves the large difference in the relaxation times of these

processes. The breakdown of phase synchronization of the vibrations of the molecules in the medium stems from the adiabatic dephasing and resonance exchange of vibrational quanta. The property of the phase-difference operator of commuting with the operator for the number of quanta is a system of two oscillators³³ implies that resonance exchange does not alter the phase difference of this pair. However, one loses information here on the initial phase of the vibrations. That is, these molecules become incoherent with the remaining oscillators of the medium and with the probe light pulse. Thus picosecond spectroscopy does not allow separate study of processes of adiabatic dephasing and resonance exchange in pure liquids. We should note that this fact is not always clearly formulated in the literature, and people identify a measured time for breakdown of synchronization with the adiabatic dephasing time.

We can distinguish two formulations of the problem for describing vibrational relaxation processes. One of these adopts the aim of describing the kinetics of population of the vibrational levels in the system of molecules. That is, one studies energy relaxation in the system. In order to do this, one constructs the kinetic equations for the population numbers in some way. In this approach one must relinquish exact accounting for resonance-exchange events, while phenomenologically introducing a variable vibrational temperature. Usually the result obtained here is an exponential or almost exponential kinetics of relaxation of the total vibrational energy. Rather complete reviews on this topic are to be found in Refs. 34-38.

In the other formulation of the problem, one treats the model of a molecule in a thermostat. For simplicity we approximate the molecule by a harmonic oscillator, and the thermostat amounts to a system having a continuous or discrete energy spectrum. The interaction potential of the molecule with the thermostat is a stochastic quantity that approximates actual intermolecular bonds. This approach allows us to estimate the lifetime of individual molecules in excited states. It is of importance in problems of studying contours and of breakdown of phase synchronization owing to nonadiabatic processes in picosecond experiments. The studies on this level differ in their fundamental method of constructing the relaxation equation.

One of the most fruitful methods is that of projection operators.³⁷⁻³⁹ This method has been applied to the problem of vibrational relaxation of molecules in liquids by Diestler and Wilson,⁴⁰ Yul'met'ev,⁴¹ and Wang.⁴²

The latter two studies relate the vibrational-relaxation parameters to the characteristics of the mobility of the molecules in the liquid—the pulse relaxation time and the diffusion coefficient.

Morawitz and Eisenthal⁴³ have employed the Van Hove approach to constructing the fundamental kinetic equation.

The theories of vibrational relaxation of molecules in liquids are reviewed in Ref. 44.

In studying relaxation processes, most studies have

paid major attention to obtaining the long-period asymptotics of the relaxation functions (the correlations). Yet it is of independent interest to study their behavior at short periods. The topicality of the problem is evident from the fact that the derivatives of the correlation functions at the zero point give the moments of the spectral distribution

$$I_n = \text{Re} \left[(-i)^n \frac{d^n}{dt^n} G(t) \Big|_{t=0} \right]. \quad (20)$$

We should say that extrapolation of the results for long times (e.g., the traditional result $\exp(-\alpha t)$) yield an unsatisfactory result in the neighborhood of $t=0$, since it yields divergent moments (the first derivative has a discontinuity at zero).

The behavior of the correlation function in the neighborhood of the origin has been studied in Refs. 45 and 46. The result is presented in the form of a power series in t in which the coefficients are the moments of corresponding order of the spectral distribution.

These studies on the formulation of the problem border on the statistical theories of the contour of spectral lines.³²

Let us point out several papers that discuss the limitations of the approaches applied in the given set of problems.

Reference 47 analyzes the applicability of the fundamental kinetic equation for describing vibrational relaxation; it is shown to hold only in the approximation of first order in the interaction potential of the molecules.

Zwanzig⁴⁸ has discussed the assumptions of the model of isolated binary collisions in liquids. He points out that the collisions of molecules in liquids are so frequent that the inequality $\omega_0 \gg 1/\tau$ (ω_0 is the vibration frequency of the oscillator, and τ is the time between collisions) loses validity. That is, the model becomes invalid. An attempt to account for interference of two subsequent collisions in vibrational relaxation has been undertaken.⁴⁹

References 50 and 51 analyze the validity of exponential curves for describing relaxations, and have pointed out certain assumptions that yield exponential laws.

In summarizing this section, we should say that, while a satisfactory theory of vibrational relaxation exists for gases, the problem for liquids is far from complete solution.

6. RESULTS OF STUDYING THE DYNAMICS OF VIBRATIONAL RELAXATION

The parameters of the band contours in molecular spectra contain essential information on the mechanism of vibrational relaxation and on the properties of the energy levels between which the transition occurs. Often the very same vibrational levels combine in the Raman and in the infrared (IR) absorption spectra. Yet the mechanisms of these phenomena differ. Thus, the parameters of the Raman lines are determined by a second-order tensor, which can be either isotropic or

anisotropic. In the former case, sharply polarized lines appear in the Raman spectrum, and depolarized lines in the latter case. The anisotropy of the Raman tensor gives rise to the sensitivity of the width of the depolarized lines to the conditions of reorientation of the molecules.^{52,53} The isotropic component of the Raman tensor is invariant to rotation of the coordinate axes. Hence the contours of the sharply polarized lines in Raman spectra should not depend on the nature of the orientational movement of the molecules.

In IR spectra the characteristics of the absorption bands are always determined by an anisotropic quantity: the derivative of the dipole moment with respect to the normal coordinate. Hence the width of any band in IR absorption spectra can be sensitive to the reorientation conditions of the molecules.

The opinion has existed in the literature for a long time that the width of bands in IR absorption spectra is practically fully determined by the stochastic reorientations of the molecules.⁵⁴⁻⁵⁶ The contribution to shaping of the contour of vibrational bands by other processes, including vibrational relaxation, has been assumed negligibly small. Hence we could conclude that the isotropic component of a Raman band, which does not depend on orientational relaxation, should have a contour of vanishingly small width. However, in actual experiment the contours of sharply polarized Raman lines ($\rho \leq 0.02$) have a finite, reliably recordable width (to an accuracy of 5-10%). This means that the contribution of effects not involving orientational relaxation to the contours of vibrational bands is substantial. One can select molecules (e.g., those of C_{2v} and C_{3v} symmetry) whose vibrations are manifested simultaneously in infrared absorption and in Raman spectra. In this case the contours of the sharply polarized Raman lines (isotropic scattering) are fully determined by vibrational relaxation processes, while, in addition, the orientational movement of the molecules exerts an effect on the contours of the IR absorption bands. Comparison of the parameters of the band contours in the Raman and IR absorption spectra corresponding to the very same molecular vibration enables one to estimate the contribution of vibrational relaxation to the contour of the IR band.⁵⁷ The comparison performed in Refs. 58 and 59 has shown that one can estimate the characteristics of the rotational Brownian movement such as the orientational relaxation time τ_{or} of the molecules by equating the parameters of the contours of IR bands and the corresponding sharply-polarized Raman lines. The agreement of the values of τ_{or} with the orientational relaxation time of the molecular dipoles obtained from the frequency-dependence of the tangent of the dielectric-loss angle^{60,61} indicates that the width of the sharply polarized Raman lines is determined by the same relaxation time of the vibrational excitation of the molecules for the Raman and IR absorption spectra. A considerable number of experimental studies have been concerned with studying the mechanism of vibrational relaxation in a condensed phase.

References 62-64 have studied experimentally the concentration behavior of the isotropic contours of

Raman bands. They have established that vibrational relaxation occurs more slowly in solutions than in the pure liquids. We should note that inert solvents were chosen in the solutions given in Table II. The same concentration variations were observed for the vibrational relaxation times at the frequency 992 cm^{-1} [the $\nu_2(a_{1g})$ vibration] in liquid benzene dissolved in deuterobenzene. Here they observed an increase in the relaxation time from 2.4×10^{-12} sec (pure C_6H_6) to 3.3×10^{-12} sec (solution in C_6D_6).

References 62, 65-68 have studied the effect of temperature on vibrational relaxation. Here the nature of the temperature variations differs for different molecules. Thus, at constant pressure an increase in the temperature of liquid benzene, toluene, chlorobenzene, chloroform, nitrobenzene, nitromethane,^{62,68} and tricyclooctane⁶⁷ increases the rate of vibrational relaxation. The temperature broadening of the isotropic components of Raman bands observed in the Raman spectra of polyatomic molecules in the liquid phase can involve a dissipative process. Similar effects have been established experimentally⁶⁹⁻⁷¹ and theoretically^{72,73} in isotropic scattering in solids. In the latter case people have associated the temperature-broadening of the Raman bands with a decay mechanism of scattering of optical phonons by acoustic and optical phonons. The lifetime of the scattered phonons is diminished thereby. Understandably, phonon decay is out of the question in a liquid. Nevertheless, the rich (for polyatomic molecules) spectrum of high-frequency intramolecular and low-frequency intermolecular vibrations enables the decay of vibrational excitation of the molecule with subsequent transfer of the excitation energy to the translational degrees of freedom. This mechanism becomes more important as the interaction of vibrations and intra- and intermolecular anharmonicity become more effective. In line with calculations,^{68,74} a decrease in the lifetime of the excited vibrational state should alter the scattering power of the molecules, i.e., alter the integral intensity of the line in the Raman spectrum. Actually the quantum theory of interaction of radiation with matter⁷⁵ implies that the probability of Raman scattering depends on the width of the vibrational levels between which the transition occurs. Hence, if the assumption holds that the width of the excited vibrational level determines the width of

TABLE II.

Substance	Solvent	ν_{vib}	Concentration, mole/mole	$\tau \cdot 10^{12}$, sec	References
CH_3NO_2	CCl_4	917	Pure	2.53	62
			1:1	2.79	
			1:2	3.54	
			1:4	4.42	
			1:8	5.31	
C_6H_5Cl	CCl_4	1002	Pure	3.32	
			1:2	6.63	
			1:16	7.58	
CH_3I	CS_2	2941	Pure	2.20	
			1%	2.70	
				2.30	
CD_3I	CS_2	2130	Pure	3.60	64
			1%	2.40	
				3.60	
				4.40	
		938	Pure	2.80	
			1%	6.60	
				2.90	
		493	Pure	2.90	
			1%	4.40	

the isotropic scattering band or the vibrational relaxation time calculated from this width, then it is expedient to adduce the stated theory for explaining the correlation between the temperature variations of the integral intensity and of the width of the Raman line. According to Ref. 75, the integral intensity J_{∞} of a Raman line is determined by the relationship

$$J_{\infty} = a_0 J_{exc} A(\omega_B, \omega_p, M_{II}, M_{k1}, \dots) F_k(t) B(T). \quad (21)$$

In this formula a_0 is a combination of constants, J_{exc} is the intensity of the exciting radiation. A is a function that is determined by the spectrum of the exciting and scattered radiations and certain intramolecular parameters, and $B(T)$ is a temperature factor.^{76,77} The function $F_k(t)$ determines the relationship of the intensity of the Raman lines to the width of the corresponding vibrational levels. One can show⁷⁴ that $J_{\infty} \sim q_k^{-1}$, where q_k is the width of the excited vibrational level that participates in the Raman-scattering event. This conclusion satisfactorily describes quantitatively the correlation of the temperature variations of the integral intensity and of the width of the polarized Raman lines (Table III).

Comparison of the concentration variations of the scattering power of molecules and the width of the corresponding polarized Raman lines also shows the correctness of the calculations given in Ref. 74 (Table IV).

For small molecules such as CH_3I , we should note that the rate of vibrational relaxation, and hence also the width of the isotropic scattering bands, declines with increasing temperature.^{65,66} We can trace in the data of Table V the variation in the vibrational relaxation time for the vibration $\nu_3(A_1)$ at 524 cm^{-1} of CH_3I . Reference 66 presents the following arguments to explain this temperature-dependence. The kinetic energy of the particles rises with increasing temperature. Hence the molecules approach considerably more closely in collisions than at low temperatures. We can treat this as a decrease in the effective radius of the molecules, and hence, an increase in the mean free path. The effect can be considerable with packings as dense as in liquids. References 78 and 79 have studied vibrational relaxation of diatomic molecules in the gas, liquid, and solid phases. They established that the vibrational relaxation time in the liquid and solid phases substantially involves the mean intermolecular dis-

TABLE III. Comparison of the temperature variations of the integral intensity and the width of polarized lines.

Object	$\nu_{\text{vib}}, \text{cm}^{-1}$	$t, ^\circ\text{C}$	δ, cm^{-1}	J_{∞}, calc' relative units	J_{∞}, exp' relative units
Toluene	1004	30	1.6	100	100
		40	1.6	94	94
		50	1.7	87	93
		60	1.7	84	92
		70	1.8	78	91
		80	1.9	73	88
		95	2.0	68	81
Chlorobenzene	1002	30	1.6	100	100
		40	1.6	93	92
		50	1.7	86	85
		60	1.7	80	78
		70	1.8	74	76
		80	1.9	68	72
		95	2.1	63	67

TABLE IV. Comparison of the concentration variations of the integral intensity and width of polarized lines.

Object	$\nu_{\text{vib}}, \text{cm}^{-1}$	C, mole/mole	δ, cm^{-1}	J_{∞}, calc' relative units	J_{∞}, exp' relative units
Nitromethane	917	Pure	2.1	100	100
		1:0.4	2.07	102	118
		1:0.8	1.95	108	112
		1:1	1.9	111	118
		0.5:1	1.5	140	128
		0.25:1	1.2	175	148

tance: $\tau \sim N^{-1/3}$, where N is the particle-density factor.

Besides other factors, the vibrational relaxation time is also determined by the possible transfer of energy of vibrational motion to neighboring molecules (vibrational exchange). Evidently, the contribution of this factor to the width of the isotropic scattering bands will depend on the nature of the intermolecular interaction. We can naturally expect that this interaction will contribute more to the width of the polarized Raman bands as its energy increases. In order to test this hypothesis, studies^{80,81} have been undertaken of the effect of hydrogen-bonding and dipole-dipole interaction on the width of polarized Raman lines.

The objects of study chosen for elucidating the role of hydrogen-bonding⁸¹ were solutions of acetone in water, methanol, carbon tetrachloride, and benzene. As we know from the literature, the depolarized Raman bands of acetone are narrowed when acetone is dissolved in water or methanol.⁸² One can explain this fact by accounting for the formation of a strong hydrogen bond between the molecules of acetone and the stated solvents. This same study⁸² implies that the depolarized lines are broadened upon dissolving $(\text{CH}_3)_2\text{CO}$ in CCl_4 and C_6H_6 . This indicates an increase in the orientational mobility of the acetone molecules, which in turn can involve decreased interactions of the acetone molecules with one another. Table VI gives the concentration variations of the width of the polarized lines of acetone in the stated solvents. This table implies that in all cases the formation of a hydrogen bond enhances the rate of vibrational relaxation, while the breaking of an H -bond diminishes it.

The effect of dipole-dipole interaction on the width of the polarized lines in Raman spectra has been studied in Ref. 81. For preparing the solutions, liquids were chosen that were transparent in the visible and had the following properties:

- a) a dipole moment of the molecules of 3–4 Debyes;
- b) intense polarized lines in the Raman spectra that correspond to characteristic vibrations of individual groups and bonds of the carriers of the molecular dipole moment;
- c) contours of the studied lines that do not overlap

TABLE V.

$T, ^\circ\text{K}$	196	209	228	242	239	298
$\tau_{\text{vib}}, 10^{-12} \text{ sec}$	1.82	1.92	1.91	2.08	2.18	2.31

TABLE VI.

Vibration frequency, cm^{-1}	Vibration	Acetone concentration, mole/mole	Width of the Raman line of $(\text{CH}_3)_2\text{CO}$, cm^{-1}			
			in H_2O	in CH_3OH	in CCl_4	in C_6H_6
787	C—C	Pure	10.4 ± 0.1	10.4 ± 0.1		10.4 ± 0.1
		4:1		10.7 ± 0.3		
		2:1	13.4 ± 0.6			10.2 ± 0.5
		1:1	14.6 ± 0.2	13.8 ± 0.4		10.4 ± 0.3
		1:2	13.8 ± 0.4	14.0 ± 0.3		10.6 ± 1.0
		1:4	13.5 ± 0.1	15.4 ± 1.4		
2922	C—H	Pure	15.5 ± 0.5	15.5 ± 0.5	15.5 ± 0.5	15.5 ± 0.5
		4:1		16.2 ± 0.1		
		2:1	16.6			14.8 ± 0.3
		1:1	16.9		14.9 ± 0.3	15.0 ± 0.8
		1:2	17.7		14.1 ± 1.0	14.7 ± 0.1
		1:4	17.7		13.7 ± 0.3	
		1:8	17.5		—	

with other Raman lines.

Table VII gives the experimental results of studying the concentration-dependence of the width of the polarized bands of nitrobenzene in various solvents. The nitrobenzene bands at frequencies 1345 and 1004 cm^{-1} belong respectively to the symmetric stretching vibration of the NO_2 group and the breathing vibration of the benzene ring. Upon dissolving nitrobenzene in such polar solvents as nitromethane, acetonitrile, and benzonitrile, one observes a considerable narrowing of the contour of the line belonging to the vibration of the NO_2 group. Solution of nitrobenzene in the neutral CCl_4 leads to an even greater narrowing of the 1345 cm^{-1} band.

The chosen polar solvents have approximately the same dielectric constant as nitrobenzene, while the dipole moments of their molecules are close to that of the $\text{C}_6\text{H}_5\text{NO}_2$ molecule. For these reasons we can assume that the decreased width of the nitrobenzene line does not stem from a change in the macroscopic properties of the medium in going from pure nitrobenzene to the solution. As we know, the molecules of acetonitrile and benzonitrile are dimerized in the pure liquid.^{83,84} The authors of Ref. 85 view nitromethane as an unassociated liquid.

The experiment of Ref. 81 implies that the polarized line due to the symmetric vibration of the NO_2 group in the nitrobenzene molecule is essentially uniformly narrowed in neutral CCl_4 and in the varyingly associated polar nitromethane, benzonitrile, and acetonitrile.

TABLE VII. Width of nitrobenzene lines in different solvents.

Frequency of vibrations cm^{-1}	Degree of depolarization	Nitrobenzene concentration, mole/mole	Width, cm^{-1}			
			In carbon tetrachloride ($\mu=0$)	In acetonitrile ($\mu=3.94$)	In nitromethane ($\mu=3.49$)	In benzonitrile ($\mu=4.05$)
1345	0.19	100%	7.2 ± 0.1	7.2 ± 0.1	7.2 ± 0.1	7.2 ± 0.1
		4:1	6.8 ± 0.1	7.2 ± 0.1	7.3 ± 0.1	7.0 ± 0.1
		1:2	6.2 ± 0.1	7.2 ± 0.1	7.2 ± 0.1	6.7 ± 0.1
		1:8	5.6 ± 0.1	7.0 ± 0.1	6.8 ± 0.1	6.1 ± 0.1
		1:16	5.3 ± 0.1	6.4 ± 0.1	6.3 ± 0.1	5.9 ± 0.1
		1:24	5.0 ± 0.1	6.1 ± 0.1	6.0 ± 0.1	5.8 ± 0.1
		1:48	4.8 ± 0.1	6.1 ± 0.1	6.0 ± 0.1	5.3 ± 0.1
		1:64	4.7 ± 0.1	5.7 ± 0.1	5.8 ± 0.1	5.1 ± 0.1
		1:96	4.6 ± 0.1	5.3 ± 0.1	5.6 ± 0.1	
		100%	2.2 ± 0.1	2.2 ± 0.1	2.2 ± 0.1	2.2 ± 0.1
		4:1	1.7 ± 0.1	2.1 ± 0.1	2.0 ± 0.1	
		1:2	1.7 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	
		1:8	1.1 ± 0.1	1.9 ± 0.1	1.9 ± 0.1	
		1:12	1.1 ± 0.1	1.9 ± 0.1	1.9 ± 0.1	
1:16	0.9 ± 0.1	1.9 ± 0.1	1.9 ± 0.1			
1:24	0.9 ± 0.1	1.9 ± 0.1	1.8 ± 0.1			
1004	0.11	100%				
		4:1				
		1:2				
		1:8				
		1:12				
		1:16				
		1:24				

trile. Apparently this fact indicates a resonance mechanism of broadening of this line in pure nitrobenzene. The narrowing of the lines in a neutral solvent can arise from a decreased dipole-dipole interaction energy between the molecules. This leads to impairment of the conditions for resonance exchange of vibrational energy between the molecules of the same type. In the polar solvents one observes experimentally a more smooth narrowing of the nitrobenzene lines of frequency 1345 cm^{-1} than in neutral CCl_4 . Here the least amount of narrowing as compared with the neutral solvent occurs in the binary mixture nitrobenzene-nitromethane. Considering that the CH_3NO_2 molecules are not associated, we can calculate the variation in distance between the $\text{C}_6\text{H}_5\text{NO}_2$ molecules upon diluting the solutions. Figure 7 shows the relation of the width of the 1345- cm^{-1} line to the distance between the molecules for binary mixtures of $\text{C}_6\text{H}_5\text{NO}_2$ in CCl_4 and of $\text{C}_6\text{H}_5\text{NO}_2$ in CH_3NO_2 . For identical distances between the nitrobenzene molecules, we see that the line is wider in the polar solvent. We can treat this as an effect of dipole-dipole interaction on the life time of the excited vibrational state. Since the dipole moment of the nitrobenzene molecule is localized in the NO_2 group, which directly participates in the dipole-dipole interaction, the line involving vibration of this group should be especially sensitive to this interaction. This is what one observed experimentally.

Valiev⁸⁶⁻⁸⁸ has performed a theoretical analysis of the mechanism of production of the band contours of isotropic Raman scattering in dipole liquids. The fundamental results of these studies amount to the following. The exchange interaction of the molecules in the liquid leads to transfer of vibrational excitation energy into translational Brownian movement. The dipole-dipole interaction also leads to dissipation of vibrational excitation energy, and here the time-dependence of the dipole-dipole interaction⁸⁶ arises from the rotational and translational diffusion of the particles. Upon assuming these diffusions to be independent, we can assume their contributions to dissipation to be additive. Dipole-dipole interaction affects the probability of only those transitions that are manifested only in the IR absorption spectra.

One can get interesting information on the process of vibrational relaxation by comparing the parameters of the fundamental Raman bands and of their overtones.⁸⁹⁻⁹¹ If we consider dephasing to be the fundamental mechanism of contour formation, then the width of the over-

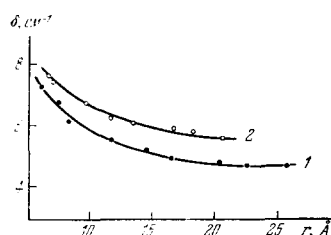


FIG. 7. Relationship of the width of the line $\nu=1345 \text{ cm}^{-1}$ to the distance between the nitrobenzene molecules in CCl_4 (1) and in CH_3NO_2 (2).

tone bands of isotropic Raman scattering should be proportional to the number of the excited level. However, experiment with the first overtone bands diverges from the expected ratio $\beta=2$ of the widths of the overtone and fundamental bands, namely,⁹⁰ one finds $\beta=6.2$ for ν_2 of C_6H_6 , $\beta=2.9$ for ν_6 , $\beta=1.9$ for ν_{11} , etc. Hence we see that phase relaxation cannot explain the mechanism of contour formation in this case. The need is evident of accounting for other factors in the process of vibrational relaxation.

Thus far we have been analyzing the results of studies that employed the traditional method of studying the parameters of vibrational spectra. Recently the method of picosecond spectroscopy has been applied to study the time dynamics and pathways of decay of intramolecular vibrational excitations.^{27,92} In this experiment the pump pulse gives rise to stimulated Raman scattering in ethyl alcohol at the frequency of the CH vibration at 2928 cm^{-1} . One can fix three bands in this region in spontaneous Stokes scattering: 2877 , 2928 , and 2972 cm^{-1} (Fig. 8a). In stimulated Raman scattering only the single mode 2928 cm^{-1} is populated. In the picosecond experiment, anti-Stokes scattering was observed with the appearance of three bands (Fig. 8b). This indicates a rapid redistribution of energy among the stretching CH vibrations in the 2900-cm^{-1} region. The picosecond experiment revealed two more bands of frequencies 1400 and 1456 cm^{-1} in anti-Stokes scattering. Here the spontaneous Raman spectrum showed two bands in this region at frequencies 1456 and 1485 cm^{-1} . In the anti-Stokes spectrum of the picosecond experiment, we can note that the spontaneous scattering spectrum contains one common band of frequency 1456 cm^{-1} and two different ones. Here the new frequency in the anti-Stokes spectrum is shifted toward lower frequencies with respect to the common band. The authors of Ref. 81 propose this treatment of the anti-Stokes spectrum.

The 2900-cm^{-1} region contains the fundamental frequency of the stretching vibration of the CH group at 2928 cm^{-1} and the overtone of the bending vibration of this group at frequency 2930 cm^{-1} . Owing to resonance, the level $\nu=2$ of the bending vibration of the CH group becomes populated. Generally speaking, the 2900-cm^{-1} region contains the frequencies of the over-

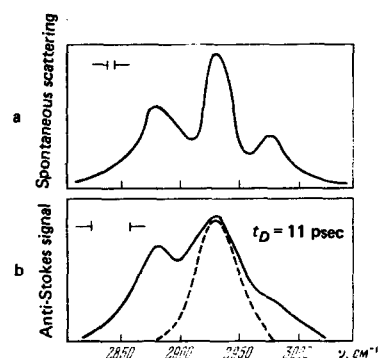


FIG. 8. a) Spontaneous Raman spectrum (Stokes region) in CH_3CH_2OH . b) Spectrum of the anti-Stokes scattering of the probe pulse in the same medium. The dotted line shows the mode active in Raman scattering.

tones of several bending vibrations of the CH group: two non-degenerate (2930 and 2750 cm^{-1}) and one triply degenerate (2870 cm^{-1}) vibration. The resonance population of the level $\nu=2$ of the vibration of frequency 2930 cm^{-1} leads also to population of the two other excited vibrational states of the CH bond by redistributing energy between the bending vibrations of the CH bond. Subsequently the vibrational state 2870 cm^{-1} decays so that the transitions $\nu=2 \rightarrow \nu=1$ and $\nu=1 \rightarrow \nu=0$ occur. The former transition yields a band that is new as compared with the spontaneous scattering spectrum. This transition is practically unobservable in the spontaneous scattering spectrum owing to the small population of the $\nu=2$ level. The latter transition yields a band that matches the spontaneous scattering spectrum. Study of the dependence of the intensity of the incoherent anti-Stokes signal on the delay time t_D allows us to estimate the times for population and decay of the two states $\nu=2$ and $\nu=1$. They proved to be 22 ± 5 and 40 picoseconds respectively. The shorter lifetime of the $\nu=2$ state is quite natural and arises from the possible transfer of vibrational energy to other states. Thus picosecond spectroscopy opens up completely new potentialities for studying intramolecular transfer of vibrational energy.

Phenomena analogous to those discovered^{27,92} in ethyl alcohol have been observed⁹³ in a mixture of the two liquids CH_2Cl_2 and CD_3OD .

7. CONCLUSION

The material presented above indicates the great potentialities of modern Raman spectroscopy in the field of studying the dynamics of decay of intramolecular vibrational excitations. Interesting results have been obtained here by direct measurement of relaxation times by the methods of picosecond Raman spectroscopy and active picosecond Raman spectroscopy. At the same time, the traditional methods, which are based on studying the shape of the isotropic scattering bands, allow one to determine the vibrational relaxation times, to study the factors that affect the dynamics of relaxation processes, and to calculate the time correlation functions of vibrational relaxation.

The possibility of separate study of vibrational and orientational relaxation from spontaneous laser Raman spectra and of direct determination of vibrational relaxation times by methods of picosecond spectroscopy allow us to expect substantial progress in understanding the mechanisms of molecular vibrational relaxation.

¹M. O. Bulanin and N. D. Orlova, in *Spektroskopiya vzaimodesistvuyushchikh molekul* (Spectroscopy of Interacting Molecules), Izd-vo LGU, L., 1970, p. 55.

²L. A. Nafie and W. L. Petitcolas, *J. Chem. Phys.* **57**, 3145 (1972).

³K. A. Valtev and E. N. Ivanov, *Usp. Fiz. Nauk* **109**, 31 (1973) [*Sov. Phys. Usp.* **16**, 1 (1973)].

⁴R. G. Gordon, *J. Chem. Phys.* **43**, 1307 (1965).

⁵R. G. Gordon, *Adv. Mag. Resonance* **3**, 1 (1968).

- ⁶L. A. Marabella, Appl. Spectrosc. Rev. 7, 313 (1973).
- ⁷N. V. Zubova, N. V. Shalomeeva, and M. M. Sushchinskiĭ, Preprint of the Institute of Physics of the Academy of Sciences of the USSR No. 198, Moscow, 1968.
- ⁸F. J. Bartoli and T. A. Litovitz, J. Chem. Phys. 56, 404, 413 (1972).
- ⁹D. Von der Linde, A. Laubereau, and W. Kaiser, Phys. Rev. Lett. 26, 954 (1971).
- ¹⁰A. Laubereau, D. Von der Linde, and W. Kaiser, *ibid.* 27, 802 (1971).
- ¹¹R. R. Alfano and S. L. Shapiro, *ibid.* 26, 1247 (1971).
- ¹²A. Laubereau, D. Von der Linde, and W. Kaiser, *ibid.* 28, 1162 (1972).
- ¹³S. A. Akhmanov, Mater. Res. Bull. 4, 455 (1969).
- ¹⁴S. A. Akhmanov, K. N. Drabovich, A. P. Sukhorukov, and A. S. Chirkin, Zh. Eksp. Teor. Fiz. 59, 485 (1970) [Sov. Phys. JETP 32, 266 (1971)].
- ¹⁵R. L. Carman, F. Shimizu, C. S. Wang, and N. Bloembergen, Phys. Rev. A 2, 60 (1970).
- ¹⁶S. A. Akhmanov and N. I. Koroteev, Zh. Eksp. Teor. Fiz. 67, 1306 (1974) [Sov. Phys. JETP 40, 650 (1975)].
- ¹⁷A. E. Boldeskul, S. S. Es'man, and V. E. Potorelov, Opt. Spektrosk. 37, 912 (1974) [Opt. Spectrosc. (USSR) 37, 521 (1974)].
- ¹⁸M. M. Sushchinskiĭ, Zh. Eksp. Teor. Fiz. 25, 87 (1953).
- ¹⁹A. E. Boldeskul, G. P. Buyan, I. I. Kondilenko, V. N. Novichenko, and V. E. Pogorelov, Opt. Spektrosk. 31, 579 (1971) [Opt. Spectrosc. (USSR) 31, 306 (1971)].
- ²⁰S. G. Petrash, Tr. Fiz. Inst. Akad. Nauk SSSR 27, 3 (1964).
- ²¹V. F. Turchin, V. P. Kozlov, and M. S. Kalkevich, Usp. Fiz. Nauk 102, 345 (1970) [Sov. Phys. Usp. 13, 681 (1971)].
- ²²R. W. Hamming, Numerical Methods for Scientists and Engineers, McGraw-Hill, New York, 1962 (Russ. Transl., Nauka, M., 1973).
- ²³P. M. Rentzepis, Chem. Phys. Lett. 3, 717 (1969).
- ²⁴A. Laubereau, D. Von der Linde, and W. Kaiser, Phys. Rev. Lett. 28, 1162 (1972).
- ²⁵A. Laubereau, Chem. Phys. Lett. 27, 600 (1974).
- ²⁶R. R. Alfano and S. L. Shapiro, in Phonons, ed. M. A. Nusimovici, Flammarion, Paris, 1971, p. 190.
- ²⁷R. R. Alfano and S. L. Shapiro, Phys. Rev. Lett. 29, 1655 (1972).
- ²⁸M. Scotto, J. Chem. Phys. 49, 5362 (1968).
- ²⁹R. G. Gordon, *ibid.* 42, 3958 (1965).
- ³⁰V. Le Duff, J. Chem. Phys. 59, 1984 (1973).
- ³¹A. I. Lizengevich, Ukr. Fiz. Zh. 23, 810 (1978).
- ³²I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Fizmatgiz, M., 1963 (Engl. Transl., Pergamon, Oxford, New York, 1972).
- ³³P. Carruthers and M. Nieto, Rev. Mod. Phys. 40, 411 (1968).
- ³⁴B. F. Gordiets, A. I. Osipov, E. V. Stupochenko, and A. A. Shelepin, Usp. Fiz. Nauk 108, 655 (1972) [Sov. Phys. Usp. 15, 759 (1973)].
- ³⁵E. V. Stupochnko, S. A. Losev, and A. I. Osipov, Relaxatsionnye protsessy v udarnykh volnakh (Relaxation Processes in Shock Waves, Nauka, M., 1965 (Engl. Transl., Relaxation in Shock Waves, Springer-Verlag, New York, 1967)).
- ³⁶S. Ormonde, Rev. Mod. Phys. 47, 193 (1975).
- ³⁷R. Zwanzig, J. Chem. Phys. 33, 1338 (1960).
- ³⁸H. Mori, Prog. Theor. Phys. 33, 423 (1965).
- ³⁹H. Mori, *ibid.* 34, 339 (1965).
- ⁴⁰D. J. Diestler and R. S. Wilson, J. Chem. Phys. 62, 1572 (1972).
- ⁴¹R. M. Yul'met'ev, Ukr. Fiz. Zh. 21, 1761 (1976).
- ⁴²C. H. Wang, Mol. Phys. 33, 207 (1977).
- ⁴³H. Morawitz and K. B. Eisenthal, J. Chem. Phys. 55, 887 (1971).
- ⁴⁴S. H. Lin, Ann. Rev. Phys. Chem. 25, 39 (1974).
- ⁴⁵A. I. Lizengevich and V. E. Pogorelov, in Fizika zhidkogo sostoyaniya (Physics of the Liquid State), Vishcha shkola, Kiev, 1978, p. 51.
- ⁴⁶S. Bratos and E. Marechal, Phys. Rev. A 4, 1078 (1971).
- ⁴⁷S. H. Lin, J. Chem. Phys. 61, 3810 (1974).
- ⁴⁸R. Zwanzig, *ibid.* 34, 1931 (1961).
- ⁴⁹H. K. Shin and J. Keizer, Chem. Phys. Lett. 27, 611 (1974).
- ⁵⁰I. Procaccia and R. D. Levine, J. Chem. Phys. 63, 4261 (1975).
- ⁵¹R. I. Cukier and J. T. Hynes, *ibid.* 64, 2674 (1976).
- ⁵²I. I. Sobel'man, Tr. Fiz. Inst. Akad. Nauk SSSR 9, 313 (1958).
- ⁵³A. V. Rakov, Tr. Fiz. Inst. Akad. Nauk SSSR 27, 111 (1964).
- ⁵⁴R. G. Gordon, J. Chem. Phys. 44, 1830 (1966).
- ⁵⁵C. E. Tavalukes, A. A. Clifford, and B. Crawford, J. Phys. Chem. 72, 962 (1968).
- ⁵⁶W. G. Rothschild, J. Chem. Phys. 53, 3265 (1970).
- ⁵⁷K. A. Valiev, in Optika i spektroskopiya, T. 2: Molekulyarnaya spektroskopiya (Optics and Spectroscopy), Izd-vo AN SSSR, L., 1963.
- ⁵⁸G. P. Buyan, I. I. Kondilenko, and V. E. Pogorelov, Opt. Spektrosk. 27, 248 (1969) [Opt. Spectrosc. (USSR) 27, 132 (1969)].
- ⁵⁹A. E. Boldeskul and V. E. Pogorelov, *ibid.* 28, 462 (1970) [Opt. Spectrosc. (USSR) 28, 248 (1970)].
- ⁶⁰J. G. Powler, J. Chem. Phys. 21, 633 (1953).
- ⁶¹V. L. Litvinov, Vestn. Leningr. Univ. Fiz. Khim. 22, 19 (1957).
- ⁶²I. I. Kondilenko, V. E. Pogorelov, and Khun' Khué, Opt. Spektrosk. 28, 580 (1970) [Opt. Spectrosc. (USSR) 28, 367 (1970)].
- ⁶³J. E. Griffithz, M. Clerc, and P. M. Rentzepis, J. Chem. Phys. 60, 3824 (1974).
- ⁶⁴H. S. Goldberg and P. S. Pershan, *ibid.* 58, 3816 (1973).
- ⁶⁵R. B. Wright, M. Schwartz, and C. H. Wang, *ibid.*, p. 5125.
- ⁶⁶J. H. Campbell, J. E. Fisher, and J. Jonas, J. Chem. Phys. 61, 346 (1974).
- ⁶⁷F. G. Baglin, R. B. Tomas, and G. N. Fickes, *ibid.* 60, 2475 (1974).
- ⁶⁸I. I. Kondilenko, V. E. Pogorelov, and Khun' Khué, Opt. Spektrosk. 31, 380 (1971) [Opt. Spectrosc. (USSR) 31, 203 (1971)].
- ⁶⁹K. Park, Phys. Lett. 22, 39 (1966).
- ⁷⁰K. Park, Phys. Lett. A 25, 490 (1967).
- ⁷¹V. E. Pogorelov, E. I. Pisanko, and A. E. Boldeskul, in Abstracts of Papers at the 11th European Congress on Molecular Spectroscopy, Tallin, 1973, p. 234.
- ⁷²R. A. Cowley, J. Phys. Lett. (Paris) 26, 659 (1965).
- ⁷³V. I. Vettegren' and V. A. Kosobukin, Opt. Spektrosk. 31, 589 (1971) [Opt. Spectrosc. (USSR) 31, 311 (1971)].
- ⁷⁴G. P. Buyan, V. N. Leshchenko, and V. E. Pogorelov, *ibid.* 43, 573 (1977) [Opt. Spectrosc. (USSR) 43, 338 (1977)].
- ⁷⁵M. M. Sushcheinskiĭ, Spektry kombinatsionnogo rasseyaniya molekul i kristallov (Raman Spectra of Molecules and Crystals), Nauka, M., 1969 (Engl. Transl., Israel Program for Scientific Translations, New York, 1972).
- ⁷⁶G. S. Landsberg and L. I. Mandelstam, Z. Phys. 60, 364 (1930).
- ⁷⁷I. E. Tamm, *ibid.*, p. 345.
- ⁷⁸M. M. Audibert, R. Vilaseck, J. Lukasik, and J. Ducuing, Chem. Phys. Lett. 37, 408 (1976).
- ⁷⁹C. Delalande and G. M. Gale, *ibid.* 50, 339 (1977).
- ⁸⁰I. I. Kondilenko, V. E. Pogorelov, and Khun' Khué, Opt. Spektrosk. 26, 956 (1969) [Opt. Spectrosc. (USSR) 26, 518 (1969)].
- ⁸¹A. E. Boldeskul, I. I. Kondilenko, V. E. Pogorelov, and Khun' Khué, *ibid.* 29, 270 (1970) [Opt. Spectrosc. (USSR) 29, 142 (1970)].
- ⁸²A. K. Atakhodzhaev, *ibid.* 16, 1024 (1964) [Opt. Spectrosc. (USSR) 16, 553 (1964)].
- ⁸³E. L. Zhukova, *ibid.* 4, 750 (1958).
- ⁸⁴W. Dannhauser and A. F. Flueckinder, J. Phys. Chem. 68, 1814 (1964).
- ⁸⁵Yu. Ya. Fialkov and Yu. Ya. Borovkov, Zh. Fiz. Khim. 40, 371 (1966).

- ⁸⁶K. A. Valiev, Zh. Eksp. Teor. Fiz. 40, 1832 (1961) [Sov. Phys. JETP 13, 1287 (1961)].
- ⁸⁷K. A. Valiev, Opt. Spektrosk. 11, 465 (1961) [Opt. Spectrosc. (USSR) 11, 253 (1961)].
- ⁸⁸K. A. Valiev and L. D. Ėskin, *ibid.* 12, 758 (1962) [Opt. Spectrosc. (USSR) 12, 429 (1962)].
- ⁸⁹R. Arndt and J. Yarwood, Chem. Phys. Lett. 45, 155 (1977).
- ⁹⁰V. E. Pogorelov and G. I. Salivon, in Teoreticheskaya spektroskopiya (Theoretical Spectroscopy), Nauka, M., 1977, p. 99.
- ⁹¹P. A. Madden and R. M. Lynden-Bell, Chem. Phys. Lett. 38, 163 (1976).
- ⁹²A. Laubereau, G. Kehl, and W. Kaiser, Opt. Commun. 11, 74 (1974).
- ⁹³V. Kaizer, Kvantovaya Elektron. (Moscow) 1, No. 9, 2036 (1974) [Sov. J. Quantum Electron. 4, 1131 (1975)].

Translated by M. V. King