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Light-scattering studies of chemical reactions: Theoretical and experimental aspects

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We report experimental results of Rayleigh-Brillouin light-scattering studies of fluids with chemical reaction processes. An adapted hydrodynamic model allows the description of the coupling between the chemical relaxation process and hydrodynamic sound and thermal modes.

I. INTRODUCTION

The quasielastic light-scattering (LS) technique is a powerful method for the study of the dynamics of gases and liquids.[1] This essentially nonperturbative method gives information about theoretical models, transport coefficients and thermodynamic coefficients of fluids.

Among the great variety of dynamic situations studied by the LS technique, we can quote, for example, effects of internal degrees of freedom of molecular gases,[2] relaxation of the stress tensor in supercooled liquids,[3] and disparate mass effects in gas mixtures.[4]

The study of chemical reactions by the LS technique was an important field of research that started at the end of the 1960s and continued to develop strongly until the end of the following decade. Unhappily, after considerable theoretical advances, experimental confirmation was poor and any clear result lay stagnant in the field.

Yeh and Keeler were one of the first groups to publish results in this area.[5] A few years after, Clarke *et al.*[6] obtained data in contradiction with those of the previous authors. This more complete study was effectuated with the two complementary LS techniques: light-beating spectroscopy and Fabry-Pérot interferometric methods. In a previous study, Alms *et al.*[7] also disagreed with Yeh and Keeler's data. Since these works appeared, we are unaware of other results in the field.

If we carefully analyze the previous experimental works, we note that the expected characteristic times are in general in the "blind zone" for the two techniques. This zone situated in the border of resolution of the two techniques corresponds roughly to the set of time values contained between 10^{-6} and 10^{-8} s. Long times are studied by light-beating spectroscopy and short times by Fabry-Pérot spectroscopy.[1(a),1(b),8] As far as we know there are no devices that resolve with enough confidence, by LS, the time scale of the blind zone.

From a theoretical point of view, the works of Blum and Salzburg,[9] Berne and Pecora,[1(a)] Lekkerkerker and Laidlaw,[10] and Ming-Nan Huang and Schwarz[11] are some of the more important models developed, from a hydrodynamical framework, for the study of coupling of the dynamics with chemical reaction.

We have considered with special attention a model developed by Allain and Lallemand,[12] devoted to "forced Rayleigh" scattering situations. Starting from this last model we developed a calculation adapted to the spontaneous Rayleigh scattering. It is clear that the major problem of this area of research is to obtain reliable experimental results.

In this paper we give results of Rayleigh-Brillouin LS studies of some simple chemical reactions in organic fluids. In fact, we study the simplest situation we can find that can be adapted to the experimental setup predicted by the numerical simulations developed with our theoretical model.[13]

Rayleigh-Brillouin LS simulations were done for cyclopentene, methylcyclohexane, crotonaldehyde, and acrolein. Those fluids were selected because, as said before, our numerical simulations had predicted significant effects of fluctuations of conformational equilibrium in ther scattered spectra.

Section II is devoted to a presentation of the theoretical model developed for the study of this kind of simulation. The experimental setup and the parameters needed for the numerical simulations of the theoretical spectra are presented in Sec. III. Results and discussion are given in Sec. IV.

II. HYDRODYNAMIC MODEL FOR CHEMICAL REACTION AND SCATTERED SPECTRA

We are interested in the chemical reactions that follow the equation of chemical equilibrium between two species A and B,

$$A \underset{K_B}{\overset{K_A}{\leftrightarrow}} B \ ,$$

where K_A and K_B are the rate constants at equilibrium that are related to the relaxation time of the rate equation by

$$\tau=(K_A+K_B)^{-1} \ .$$

Following Lamb[14] and Allain and Lallemand[12] we can define a change in the concentration fluctuating variable C due to the reaction

$$\frac{dC}{dt}=-\frac{\mathcal{A}}{\tau\left[\dfrac{\partial\mathcal{A}}{\partial C}\right]} \ ,$$

where $\mathcal{A}$ is the affinity that measures the departure of the system from equilibrium and is related to the chemical potential.

The set of thermodynamic variables and our model, defined by Mountain and Deutch[15] and modified by Allain and Lallemand[12] is defined by φ, C, P, and $\operatorname{div} V$ where

$$\varphi = \frac{C_P}{T_0} T - \frac{\alpha_T}{\rho_0} P ,$$

T, P, and C are the temperature, pressure, and concentration fluctuating variables, V is the mean velocity of particles, T_0 and ρ_0 are the temperature and density at equilibrium, α_T is the coefficient of thermal expansion, and C_P is the specific heat at constant pressure. The thermodynamic variables diagonalize the expression of the entropy production used in the theory of fluctuations and are useful for mode calculations.[15] Conservation equations of mass, moment, and energy combined with the entropy balance equation represent the set of four coupled equations that govern the dynamics of the fluid.[12,15]

The Fourier-Laplace transform of the linearized form of the hydrodynamic equations can be presented by a matrix equation

$$[M(q) + Iz] N(q,z) = N(q,0) . \tag{1}$$

$M(q)$ is the hydrodynamic matrix where elements depend on thermal and transport coefficients, I is the unit matrix, and $N(q,z)$ and $N(q,0)$ are column vectors that represent the dynamic variables and their initial conditions. q is the wave vector of the fluctuation under consideration and z is the complex frequency $i\omega$.

Expressions of matrix elements of the hydrodynamic matrix are

$$M_{11} = \frac{k_2 K_T}{C_P} + \left[\frac{\partial C}{\partial T} \right] \frac{1}{C_P \tau} \left[\left[\frac{\partial S}{\partial C} \right] T_0 + \left[\frac{\partial h}{\partial C} \right] \right] ,$$

$$M_{12} = k_2 + \left[\frac{\partial S}{\partial C} \right] \frac{1}{\tau} - \left[\frac{\partial h}{\partial C} \right] \frac{1}{\tau T_0} ,$$

$$M_{13} = k_1 \left[\frac{\partial \mathcal{A}}{\partial T} \right] + \frac{\alpha_T q^2 D_T}{\rho_0} ,$$

$$M_{14} = M_{24} = M_{41} = M_{42} = 0 ,$$

$$M_{21} = \frac{T_0}{C_P} \left[\frac{D K_T}{T_0} q^2 - \frac{1}{\tau} \left[\frac{\partial C}{\partial T} \right] \right] ,$$

$$M_{22} = D q^2 + \frac{1}{\tau} ,$$

$$M_{23} = \frac{K_P}{\rho_0} q^2 - \left[\frac{\partial C}{\partial P} \right] \frac{1}{\tau} + \frac{\alpha_T M_{21}}{\rho_0} ,$$

$$M_{31} = \frac{-1}{\left[\frac{\partial \rho}{\partial P} \right]} \left[\left[\frac{\partial \rho}{\partial S} \right] M_{11} + k_0 M_{21} \right] ,$$

$$M_{32} = \frac{-1}{\left[\frac{\partial \rho}{\partial P} \right]} \left\{ \left[\left[\frac{\partial S}{\partial C} \right] \frac{1}{\tau} + k_2 \right] + k_0 M_{22} \right\} ,$$

$$M_{33} = \frac{-1}{\left[\frac{\partial \rho}{\partial P} \right]} \left\{ \left[\left[\frac{\partial \mathcal{A}}{\partial T} \right] k_1 + \frac{q^2 \alpha_T}{\rho_0} D_T \right] - \left[\left[\frac{\partial C}{\partial P} \right] \frac{1}{\tau} - \frac{\alpha_T M_{21}}{\rho_0} - \frac{K_P}{P_0} q^2 \right] \right\} ,$$

$$M_{34} = \frac{\rho_0}{\left[\frac{\partial \rho}{\partial P} \right]} , \quad M_{43} = -\frac{q^2}{\rho_0} , \quad M_{44} = b q^2 ,$$

where K_T, S, h, and D_T are, respectively, the thermal diffusion ratio, the entropy, the enthalpy, and the thermal diffusivity coefficient which is defined as

$$D_T = \frac{\lambda}{\rho_0 C_P} .$$

K_P is the barodiffusion coefficient and D is the mutual diffusion coefficient. The coefficient b is defined by

$$b = \tfrac{4}{3} \eta_S + \eta_V ,$$

where η_S and η_V are the shear and volume viscosities of the fluid.

Expressions for k_0, k_1, and k_2 are

$$k_0 = \left[\frac{\partial \rho}{\partial C} \right] - \left[\frac{\partial \rho}{\partial S} \right] \left[\frac{\partial \mathcal{A}}{\partial T} \right] ,$$

$$k_1 = \frac{K_P}{P_0} q^2 - \frac{1}{\tau} \left[\frac{\partial C}{\partial P} \right] + \frac{\alpha_T M_{21}}{\rho_0} ,$$

$$k_2 = D q^2 \frac{K_T}{T_0} \left[\frac{\partial \mathcal{A}}{\partial C} \right] .$$

As we said before, the used variables diagonalize the entropy production and the probability distribution is Gaussian. Now it is easy to evaluate the mean values of the square of the fluctuations

$$|\varphi_0|^2 = k_B C_P , \quad |C_0|^2 = \frac{K_B T_0}{\left[\frac{\partial \mathcal{A}}{\partial C} \right]} , \quad \overline{|P_0|^2} = \frac{k_B T_0 \rho_0}{\chi_S} ,$$

where k_B is the Boltzmann constant and χ_S the adiabatic compressibility.

Fluctuating variables are coupled to the permittivity fluctuations by

$$\delta\varepsilon = \left[\frac{\partial \varepsilon}{\partial \varphi} \right] \varphi + \left[\frac{\partial \varepsilon}{\partial P} \right] P + \left[\frac{\partial \varepsilon}{\partial C} \right] C$$

and the scattered spectra are proportional to the correlation function of the permittivity. Partial derivatives of ε are evaluated with Clausius-Mossoti equation.[16]

With knowledge of the hydrodynamic matrix, a straightforward calculation based on the resolution of the matrix equation (1) gives the correlation functions appearing in the spectra.[1(a),1(c)] We have developed a simple FORTRAN program for numerical simulations.

III. EXPERIMENTAL SETUP AND AUXILIARY PARAMETERS

A. Experimental setup

A detailed description and a summary of the characteristics of the experimental setup is given elsewhere;[13,17] here we will describe only the essential aspects. A Spectra Physics laser Model No. 2020 delivers a stable monomode radiation for wavelengths of 5145, 4765, and 4579 Å with intensities up to 1 W. The laser beam is split in two parts. The first beam contains 90% of the intensity and is used for the LS study itself. The second beam with 10% of the intensity is used in the alignment of the optical system formed by the lens of the experimental setup and the Fabry-Pérot interferometer. The weak beam is also required in order to obtain and maintain the high resolution of the Fabry-Pérot interferometer.

The sample is placed in a test tube and put in the center of a cylindrical container that has four pairs of parallel faces in order to obtain a set of scattering angles. The angles, combined with the wavelengths of the laser beam, allow a variety of wave vectors defined by

$$q=\frac{4\pi n}{\lambda}\sin\frac{\theta}{2}\ ,$$

where n is the index of refraction of the medium, λ is the wavelength of the laser radiation, and θ is the scattering angle. The cylindrical container is filled with water in order to match the refraction index and ensure the thermal stability of the system.

The scattered spectra are analyzed by a double-pass planar Fabry-Pérot interferometer (DPPFP) scanned piezoelectrically and the parallelism is obtained and maintained by a home-built electronic system. The Fabry-Pérot interferometer free spectral range (FSR) can be modified in order to obtain the most favorable condition for each of the studied fluids. The FSR needed in this work are 14 500 7500, and 5000 MHz.

The scattered light is finally collected by a photomultiplier (PM) and stored in a multichannel analyzer (MCA). The information contained in the MCA can be stored in the memory of a computer for further process or drawn with an (x,t) plotter.

Optical devices are put on a marble table, which ensures insulation from mechanical vibrations. The experimental spectrum contains both the apparatus function and the Rayleigh-Brillouin spectrum. Theoretical simulations of Rayleigh-Brillouin spectra were convolved by the experimental apparatus function prior to comparison with experimental spectra. The study is planned for a temperature of $20.0\mp0.1\,^{\circ}$.

B. Choice of sample and parameters for the numerical simulation

We have studied four organic liquids in which very simple chemical reactions occur. For these fluids, there are available measurements of the relaxation time of chemical reactions at equilibrium, obtained by ultrasonic methods.[14] In order to avoid important problems of stray light in the Rayleigh line, which can be produced by the presence of dust, the sample is prepared by triple distillation and stored in a sealed test tube.

Cyclopentene is a test fluid because we can predict a Rayleigh-Brillouin spectrum that can be observed by our experimental devices. Nevertheless, relaxation times which can exist are so different from hydrodynamic times, at least at the temperature of 20 °C, that there aren't relaxational processes coupled with hydrodynamic modes. With this sample we can also check the capability of our experimental setup for the resolution of a Rayleigh-Brillouin spectrum of the organic fluids under consideration.

The other three fluids are methylcyclohexane, and two unsaturated aldehydes: crotonaldehyde and acrolein. Methylcyclohexane has two "chair" forms called equatorial and polar. In crotonaldehyde and acrolein there are *s-cis* and *s-trans* isomer forms in equilibrium. For those three samples our numerical simulation predicts an important coupling between usual hydrodynamic modes and chemical reaction.

Thermodynamic coefficients can be evaluated with the equation of state for hard-sphere fluids of Lebowitz[18] but some values are also directly available in the literature.[19–22] Values of the viscosity are available too,[23–25] and following Kor and Gerson[23] we suppose that the ratio of the shear and bulk viscosities η_S/η_V is constant for hard spheres.

Thermal conductivity is determined with an equation proposed by Beaton[26] for cycloalkanes and methylcycloalkanes or obtained in the literature.[27,28] All the parameters we needed are listed in Tables I and II. More details about parameters are given in Ref. 13.

TABLE I. Thermodynamic coefficients of studied fluids needed in the numerical simulation.

Fluid	C_P ($\mathrm{cm^2\,s^{-2}\,K^{-1}}$)	ρ_0 ($\mathrm{g\,cm^{-3}}$)	χ_S ($\mathrm{cm^2\,dyn^{-1}}$)
Cyclopentene	1.053×10^{7}	0.0771	92.149×10^{-12}
Methylcyclohexane	2.64×10^{7}	0.769	84.97×10^{-12}
Crotonaldehyde	4.35×10^{7}	0.840	67.596×10^{-12}
Acrolein	4.45×10^{7}	0.838	72.416×10^{-12}

TABLE II. Transport coefficients and relaxation time used in the numerical simulation of studied fluids.

Fluid	λ (10^{-4} g cm s^{-1} K^{-1})	η_S (10^3 p)	η_V (10^2 p)	τ (10^9 s)
Cyclopentene	1.425	3.25	4.817	
Methylcyclohexane	1.124	2.78	4.39	0.904
Crotonaldehyde	1.34	0.73	1.216	2.274
Acrolein	1.89	0.246	0.329	0.9047

IV. RESULTS AND DISCUSSION

All the experimental situations we have studied show a Rayleigh-Brillouin spectrum with widths bigger than the apparatus function. We can note that the triple distillation of the sample seems to ensure an absence of stray light. This preparation of the sample is very important in order to ensure reliability of the results. Only for acrolein is there a small amount extra light (but we will discuss this point later).

Figure 1 corresponds to the Rayleigh-Brillouin spectrum of cyclopentene and it can be seen that the theoretical simulation represented by the straight line and experimental points represented by dots are in good agreement. If we change the wave vector q from 2.013×10^5 cm^{-1} to 2.46×10^5 cm^{-1} we still have concordance between the two spectra as we can see in Fig. 2.

The calculated spectra do not change if we remove the chemical relaxation process. It is clear that in those spectra we do not detect any effect of a chemical reaction; there is no coupling of the hydrodynamic modes with any other process. We can also conclude that the thermodynamic and transport parameters used in the model simulation seem to correspond to the true physical situation.

The three other fluids we have studied are also quite correctly described by numerical simulations as we can see in Fig. 3 for methylcyclohexane, Fig. 4 for crotonaldehyde, and Fig. 5 for acrolein. For Figs. 4 and 5, Brillouin lines are crossed and the Brillouin line close to the Rayleigh line belongs to the previous one. That means that the quantity $\omega_B = qV$, which describes the Brillouin position, is bigger than half the FSR (overlapping orders).

In Fig. 5 we can observe a small difference at the top of the central line, between theoretical simulation and experimental spectra. That can be explained in the following manner. Acrolein is well known for its tendency to polymerize. In the sample, after distillation, we restore the initial composition with 3% of watter and some small amount of hydroquinone in order to avoid polymerization, nevertheless we have to consider the possibility of the presence of a small amount of polymers.

Taking that situation into account, we can assume that a small amount of polymers introduces in the sample some effects that are equivalent to the presence of dust. It is well known that dust produces stray light at the top of the Rayleigh line. The extra energy of the central line can be attributed reasonably to the presence of polymers of acrolein in the sample.

With the accordance between the theoretical calcula-

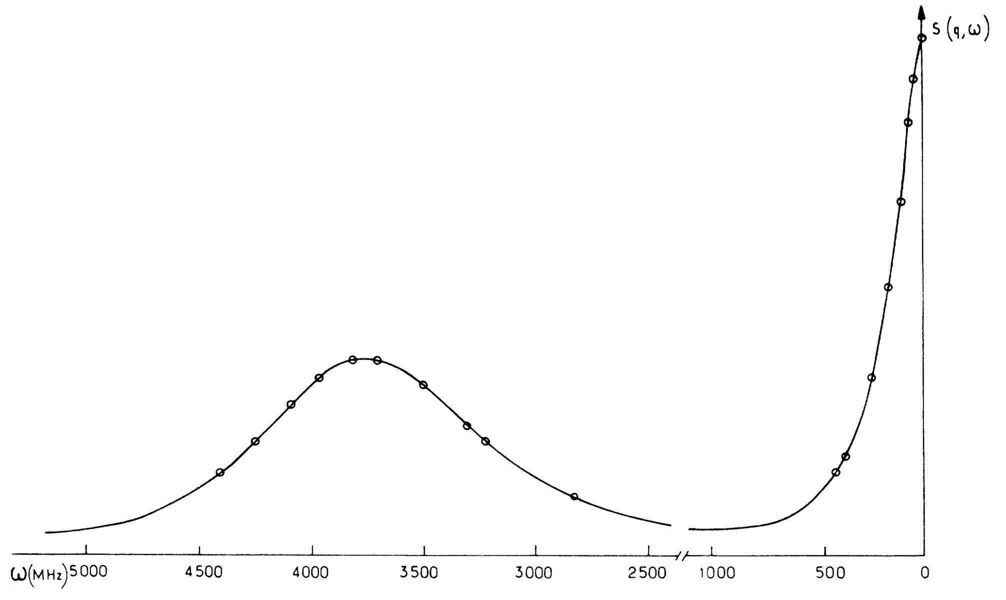

FIG. 1. Rayleigh-Brillouin spectrum of cyclopentene in a half FSR at 20 °C. $q = 2.013\times10^5$ cm^{-1}. ○○○, experimental spectrum; ——, convolved theoretical spectrum. Agreement between the two plots is very satisfactory in all the half FSR's but we report only a limited number of experimental points.

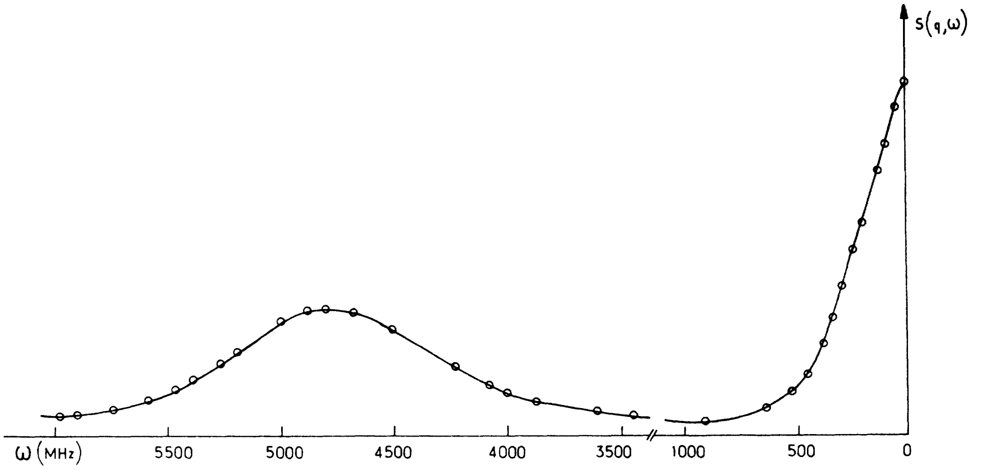

FIG. 2. Rayleigh-Brillouin spectra of cyclopentene. $q = 2.468 \times 10^5\ \mathrm{cm}^{-1}$; other conditions are the same as in Fig. 1.

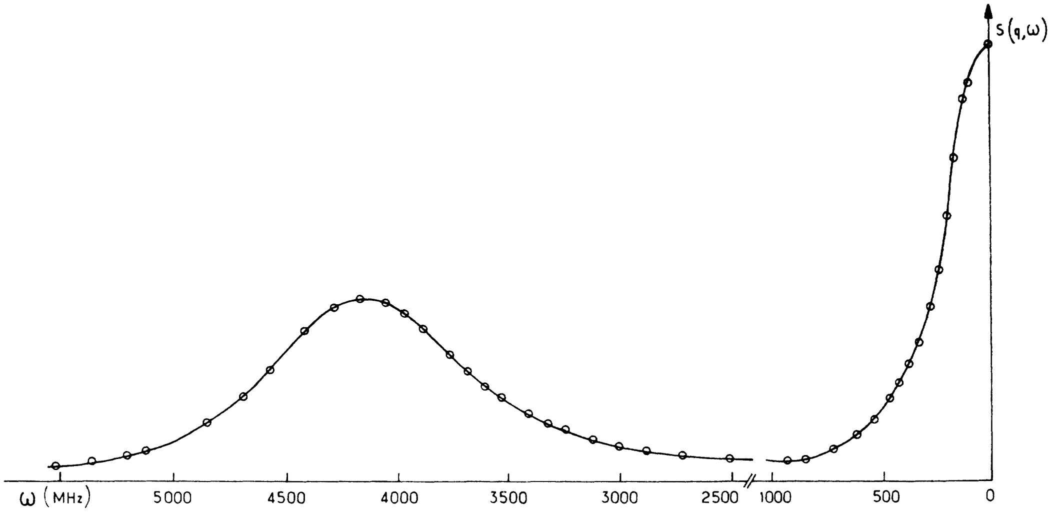

FIG. 3. Rayleigh-Brillouin spectra of methylcyclohexane. $q = 2.26 \times 10^5\ \mathrm{cm}^{-1}$. See Fig. 1 for more details.

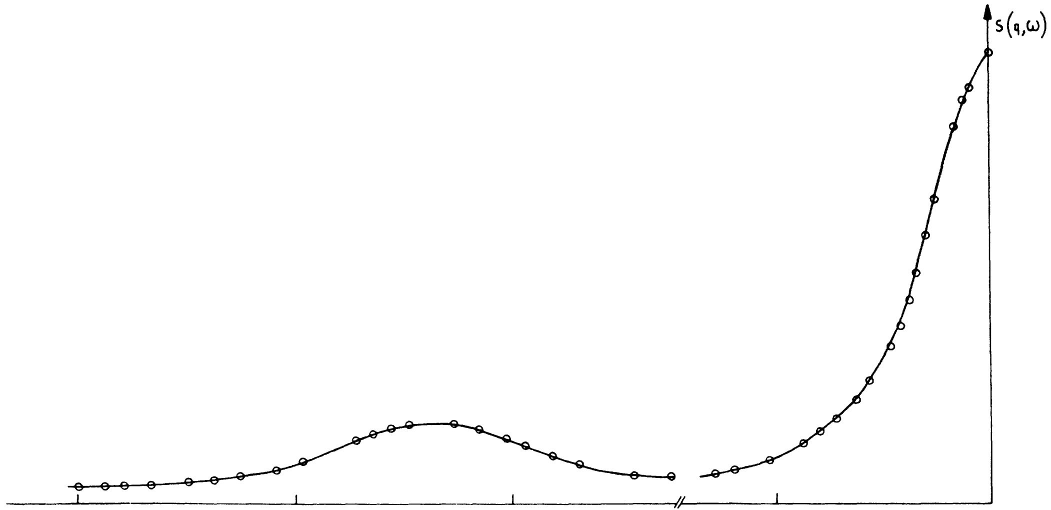

FIG. 4. Rayleigh-Brillouin spectra of crotonaldehyde. Brillouin lines are "crossed," see text. $q = 2.416 \times 10^5\ \mathrm{cm}^{-1}$. See Fig. 1 for more details.

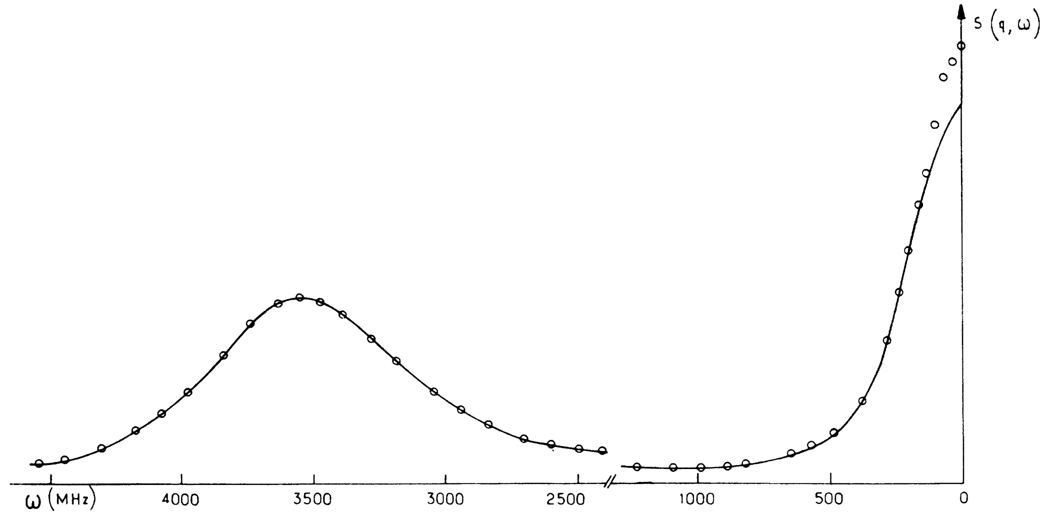

FIG. 5. Rayleigh-Brillouin spectra of acrolein. Brillouin lines are "crossed," see text. $q = 2.418 \times 10^5$ cm^{-1}. See Fig. 1 for more details.

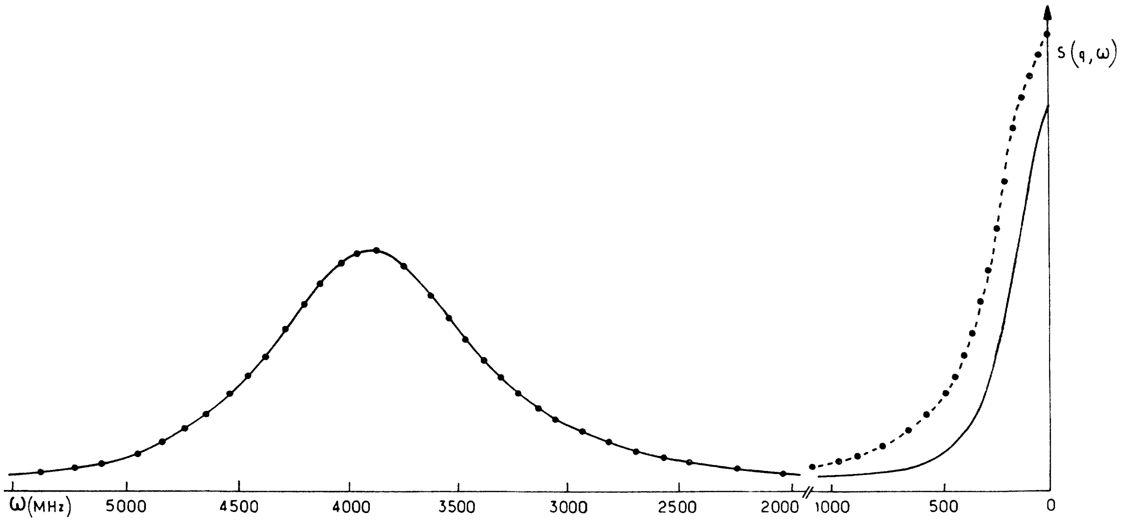

FIG. 6. Rayleigh-Brillouin spectra of methylcyclohexane $q = 2.013 \times 10^5$ cm^{-1}. ——, model without chemical relaxation; ○○○, model with chemical relaxation; — — —, experimental.

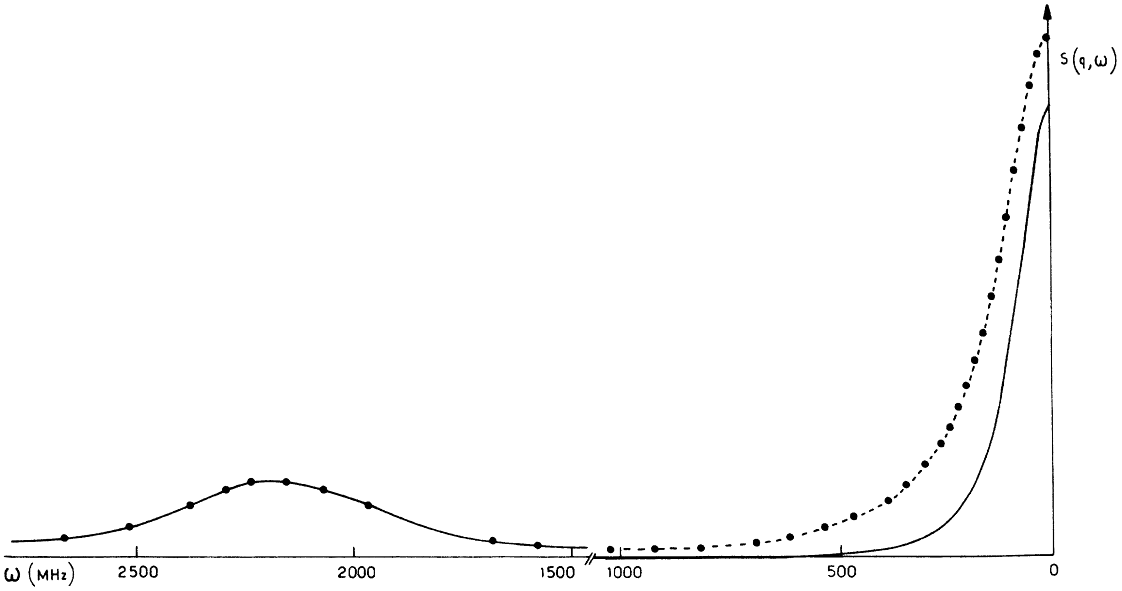

FIG. 7. Rayleigh-Brillouin spectra of crotonaldehyde. $q = 2.416 \times 10^5$ cm^{-1}. ——, model without chemical relaxation; ○○○○, model with chemical relaxation; — — —, experimental.

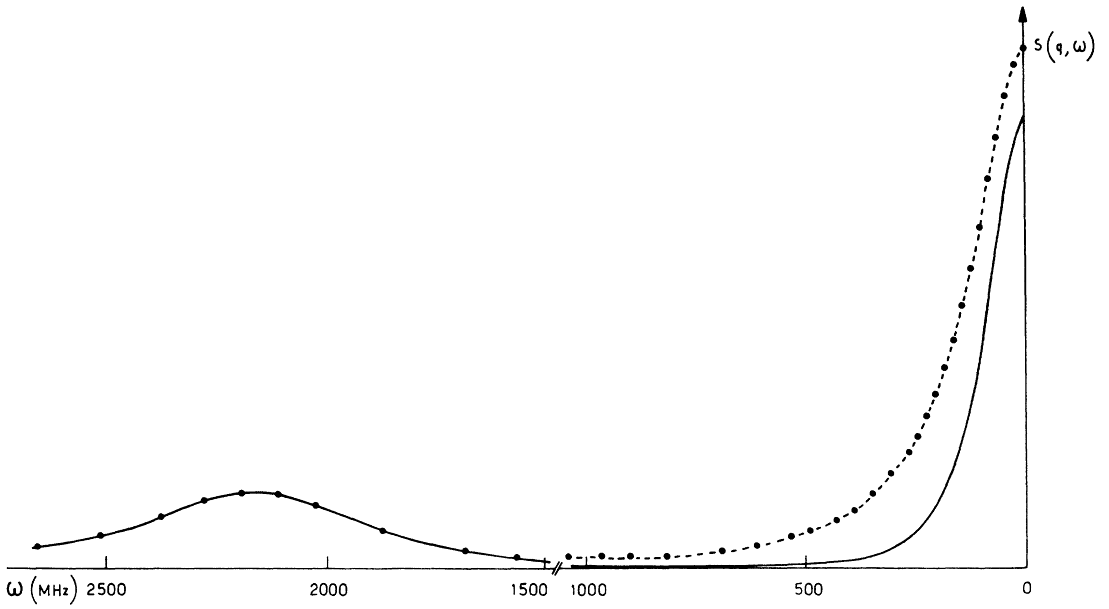

FIG. 8. Calculated Rayleigh-Brillouin spectra of acrolein. $q=3.416\times10^5$ cm^{-1}. ——, model without chemical relaxation; ○○○○, model with chemical relaxation; — — —, experimental.

tion and the experimental Rayleigh-Brillouin spectra we can evaluate the change due to the chemical reaction. For this purpose we represent in Figs. 6, 7, and 8 the spectra corresponding to calculations with the chemical reaction and the spectra calculated with a model in which we remove the chemical reaction effect.

There are important changes in the Rayleigh line in the three situations. As we said before there are no detectable changes if we do the same in the case of cyclopentene.

We have shown that Rayleigh-Brillouin spectra of cyclopentene, methylcyclohexane, crotonaldehyde, and acrolein are correctly described by the hydrodynamic theory of chemical reaction we use, and there are perturbations in the Rayleigh line of the last three components. We now describe the details of the physical information that we can obtain from those spectra.

1. Sound speed

From the position of the Brillouin line we can deduce the sound speed by the relation[14] $\omega_B=Vq$. In the Table III we have summarized the speed values for the studied components. It is interesting to note that the state equation of Lebowitz[18] for hard-sphere fluids leads to a calculated speed in agreement with our measured values and values given by other authors.[19–21]

2. Sound attenuation

The numerical simulation with or without the chemical reaction process does not show any change in the Brillouin width. This can be understood in the following way. Usually the sound attenuation has the form

$$\Gamma_B=\frac{q^2}{\rho_0}\left[\tfrac{4}{3}\eta_S+\eta_V+(\gamma-1)D_{\text{eff}}\right],$$

where D_{eff} is the effective diffusion coefficient that takes into account the relaxation, the thermal diffusivity, and the mutual diffusion terms. In liquids, the mutual diffusion contribution is negligible. Here γ is C_P/C_V.

Nevertheless, the viscosity term is dominant and in a numerical calculation for methylcyclohexane we can see that for the viscosity term we obtain a value of 6.5×10^{-2} cgs and for the diffusion term the value is 1.7×10^{-4} cgs. Otherwise it is clear that the relaxation term, with a contribution of 10^{-3} cgs, can have only a small effect in comparison with the viscosity term. Note that the viscosity contribution is dominated by the bulk viscosity term.

With viscosities given in Table II, obtained from literature, we have a good description of the Brillouin width at half height.

TABLE III. Comparison between the nonrelaxing ratio of intensities $R_{RB}|_{\text{NR}}$ and the relaxing ratio intensities $R_{RR}|_{\text{R}}$ obtained in this work. We also give the values of experimental sound speed.

	Methylcyclohexane	Crotonaldehyde	Acrolein	Cyclopente
$R_{RB}\|_{\text{NR}}$	0.31	0.29	0.26	0.30
$R_{RB}\|_{\text{R}}$	0.47	0.36	0.37	0.30
V_0 (cm s^{-1})	1.23×10^5	1.272×10^5	1.274×10^5	1.21×10^5

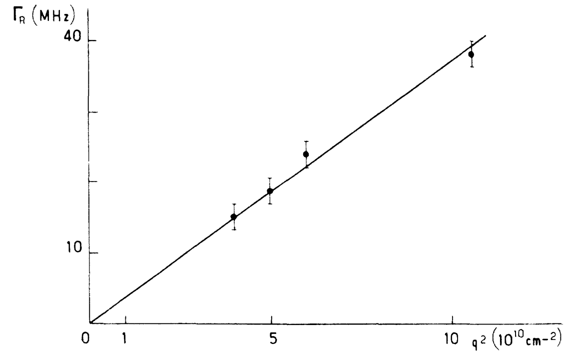

FIG. 9. Change of HWHH of the Rayleigh line of cyclopentene with q^2, the square of the wave vector. Points correspond to experimental results and the straight line corresponds to a plot of $D_T q^2$, where D_T is the calculated value of thermodiffusivity.

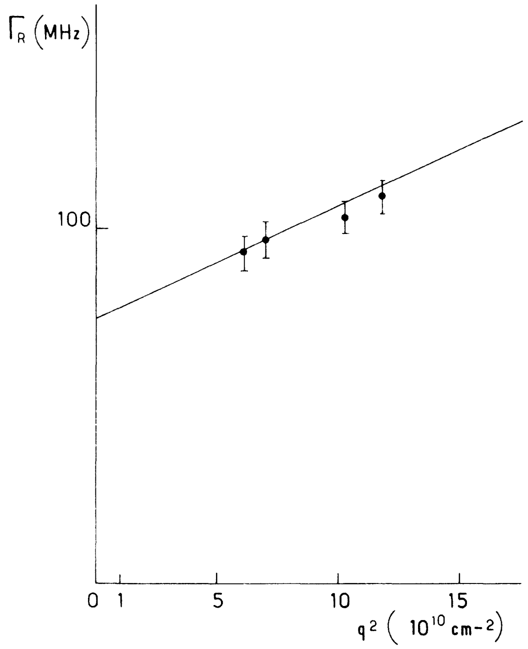

FIG. 11. Change of HWHH of crotonaldehyde with q^2, the square of the wave vector. For more details see Fig. 9.

3. *Width of the Rayleigh line*

The half width at half height (HWHH) of the central line is supposed to give information about the diffusion process and the chemical relaxation. In order to clarity the behavior of the HWHH we plot that quantity for different values of the wave vector q.

In Fig. 9 we plot Γ_R for different q values for cyclopentene and as expected we obtain a straight line that follows the equation $\Gamma_R = D_T q^2$. This result confirms that for this fluid, the diffusion process is uncoupled to the chemical relaxation process.

For Figs. 10, 11, and 12 the plot Γ_R versus q^2 is still a straight line but there is a finite value for the limit $q^2 = 0$, which means that the equation of this line has the form $\Gamma_C = D_T q^2 + \tau^{-1}$. Another important result is the agreement of the calculated thermal diffusivity D_T with the slope of lines reported in Figs. 10, 11, and 12.

The thermal diffusivity D_T is calculated with the pa-

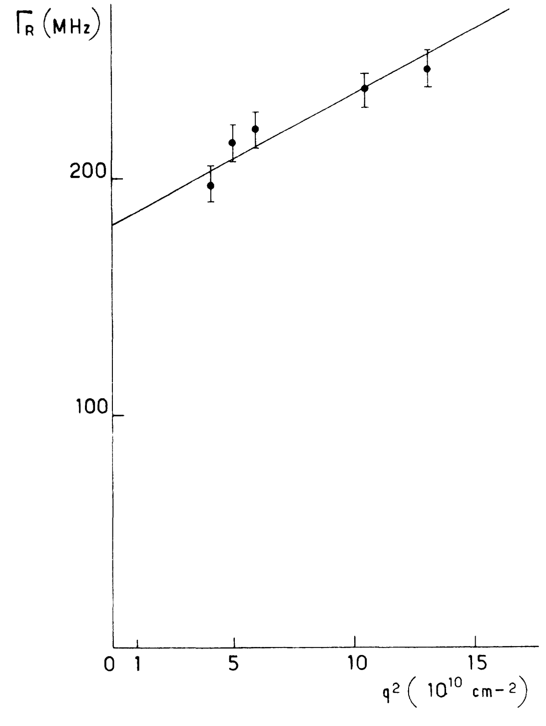

FIG. 10. Change of the HWHH of methylcyclohexane with q^2 the square of the wave vector. For more details see Fig. 9.

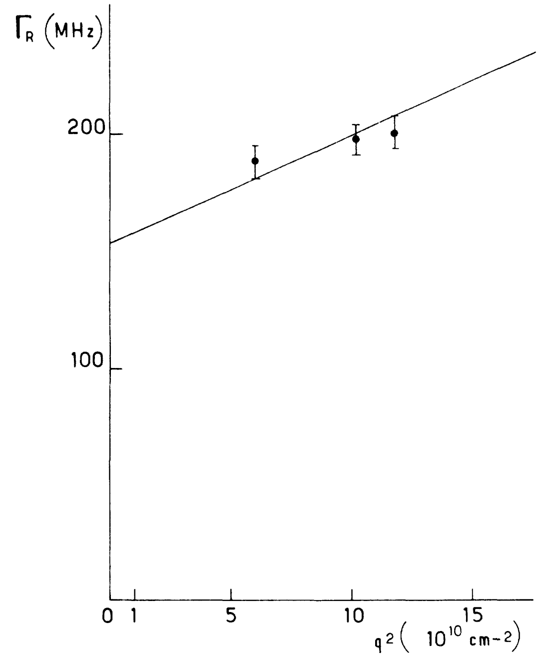

FIG. 12. Change of HWHH of acroleine with q^2, the square of the wave vector. For more details see Fig. 9.

rameters λ, ρ, and C_P given in Tables I and II. Relaxation times determined in Figs 10, 11, and 12 in the limit $q^2=0$ are in agreement with relaxation times obtained by ultrasonic techniques.[13,14]

4. *Rayleigh-Brillouin intensity ratio*

The ratio of Rayleigh line intensity (I_R) and Brillouin line intensity (I_B) defined as $R_{RB}=I_R/2I_B$ can give some information about the presence of a chemical reaction, because a change in R_{RB} is expected for an additional dynamical process in the fluid.[1] The additional process increases the energy of the central line and an increase of this ratio is expected for the spectra of fluids with dynamic coupling with a chemical reaction.

We have evaluated this ratio for the four fluids we have studied, and we compare the values with the calculation without the chemical reaction process. For cyclopentene the two determinations of R_{RB} leave, as expected, the same value; this fact confirms the absence of a chemical reaction. For the other three studied fluids there are detectable differences between the two values of R_{RB}. This fact can be considered as a confirmation that a chemical reaction effect exists in the spectra. The different values of R_{RB} are given in Table III and this situation appears clearly in the central lines of Figs. 7, 8, and 9.

This set of experimental results are, as far as we know, the first clear experimetal evidence of chemical reaction by LS techniques. As we said before, the studied physical situations are very simple and it will be useful to try to develop this method for more interesting systems such as solutions. It is not certain that the method can be adapted for more complicated physical situations.

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