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Light scattering in gas mixtures: Evidence of fast and slow sound modes

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Campa and Cohen [Phys. Rev. A **39**, 4909 (1989)] have predicted that dilute, binary mixtures of gases with disparate masses should exhibit a (fast) sound mode whose velocity is considerably greater than expected on the basis of conventional hydrodynamic theory, and which should be observable via light-scattering experiments. Effects that are consistent with this prediction were observed in the Brillouin spectra of the H_2+Ar system, but were not detected for the case of CH_4+SF_6. Results for the SF_6+H_2 mixture demonstrate the existence of an analogous slow-mode contribution to the spectrum.

The suggestion[1] that a fast sound mode can exist in binary mixtures of noble-gas *liquids* when the two molecular species have widely different (i.e., disparate) masses has been confirmed by neutron-scattering experiments,[2] which are capable of probing the appropriate wave-vector regime. More recently[3] it has been proposed that the corresponding effect should also be present in binary mixtures of *gases* at low density and in the wave-vector regime accessible by light-scattering techniques. The Brillouin scattering experiments and calculations described in this paper provide evidence for the existence of a fast-mode contribution in the spectrum of H_2+Ar mixtures which, however, is difficult to detect. Spectra of CH_4+SF_6 as obtained under comparable conditions did not exhibit a similar behavior. By comparison, corresponding effects which can be identified with an analogous slow-mode contribution to the spectrum were found to be readily observable in the case of SF_6+H_2 mixtures.

The fast mode is interpreted[4] as one which propagates only in the lighter of the two species when the mole fraction of the heavier species is relatively low (≤ 0.3) and under conditions which conform to the approximate criterion $kl_1 \sim kl_2 \sim 1$, where l_1 is the mean free path for the lighter species, l_2 is the mean free path for the heavier species, and $k=2\pi/\Lambda$ is the wave number of the sound being probed. One thus envisions an experiment where the sample cell is first charged with a fixed number density of the lighter species which is high enough so that a well-defined Brillouin peak is observed in the scattered-light spectrum, and this spectrum is subsequently monitored as successive increments of the heavier species are added. Qualitatively, the predicted[3,4] behavior (for low concentrations of the heavier species) is that a spectral peak will persist at a position (frequency shift) which is *not* determined by the density of the mixture as normally expected, but which remains substantially unchanged. This is indicative of a *fast* sound mode which continues to propagate in the lighter species only. One expects, however, that the heavier species will contribute to the attenuation of this mode, so that the observed spectral feature will become broader and perhaps unrecognizable.

Given that the minimum value of the probed wavelength Λ in a Brillouin scattering experiment is ~ 250 nm (at a scattering angle of 180°), it turns out that the appropriate conditions can be satisfied for mixture pressures of order 10 bars or less, provided the mole fraction x_2 of the heavier species is kept sufficiently small. There is, however, the observational requirement that the permissible range of x_2 values be large enough so that the corresponding changes in the mean density of the mixture give rise to readily measurable changes in the characteristics of sound propagation that are normally expected for a mixture, e.g., the velocity. Otherwise, a possible fast-mode contribution to the spectrum would not be distinguishable from the (normal) contribution of the mixture. With the above constraint on Λ, this dictates that in most cases the partial pressure of the lighter species should be kept as low as possible while maintaining a readily detectable Brillouin signal.

In the theoretical formulation of the problem[3,4] the scattered light intensity is expressed as a sum of three contributions, the first two of which are associated respectively with the lighter and heavier species alone, while the third is a mixed term

$$I(k,\omega) \sim \alpha_1^2 x_1 S_{11}(k,\omega) + \alpha_2^2 x_2 S_{22}(k,\omega) + 2\alpha_1\alpha_2\sqrt{x_1 x_2}\, S_{12}(k,\omega)\,. \tag{1}$$

Here the S_{ij} are partial dynamic structure factors, α_i are molecular polarizabilities, the x_i are mole fractions, and k (as above) and ω are the probed wave number and angular frequency, respectively. Throughout the remainder of this paper we adhere to the convention established in this equation, whereby the subscripts 1 and 2 refer to the lighter and heavier species, respectively. It is clear from Eq. (1) that, for given x_i, the α_i values are important in determining which (if any) of the three contributions will dominate the spectrum. In particular (while recognizing that heavier molecules have generally higher polarizabilities), observation of the fast-mode associated with the first term is facilitated by an α_1 value that is at least comparable to α_2. The combination of H_2 and Ar, with a mass ratio of 1:20, represents a reasonable compromise in this respect ($\alpha_2/\alpha_1 \simeq 2$),[5] and it is this suggested[3] mixture that was chosen for initial investigations. As mentioned above, experiments were also performed with the mixtures CH_4+SF_6 and SF_6+H_2. In the latter case emphasis was placed on investigation of the slow-mode contribution corresponding to the second term in Eq. (1).

The spectra were obtained using incident radiation provided by an Ar^+ laser (Coherent Radiation Innova Model 90-5) operating in a single-cavity mode with a nominal wavelength (λ_0) of 514.5 nm and a power output in the range 300–500 mW. The spectrometer consisted of a scanning Fabry-Pérot interferometer (Burleigh Model RC-110), a cooled photomultiplier detector (ITT FW130), photon counting electronics, and a combined data-acquisition and Fabry-Pérot control system (Burleigh Model DAS-1). The scattered radiation was prefiltered (using a grating monochromator) to reject unwanted Raman radiation, and the spectra were obtained by a repetitive scanning process with accumulation times ranging from 5 to 24 h. All experiments were performed at room temperature (293 K) using a sample cell which permitted a choice between scattering angles (θ) of 157.5° and 22.5°. The former angle was used in most experiments and corresponds to a probed wavelength $\Lambda = 2\lambda_0/\sin(\theta/2) = 262$ nm. Pressures were measured via Bourdon-tube gauges with an estimated accuracy of ± 0.05 bar, and particular care was taken to ensure that all gases were properly mixed before the spectral accumulation process was begun.

As implied above, the criterion used to detect a fast-mode contribution to a given spectrum was to compare the frequency shift of the observed spectral peak with that determined from the well-known Brillouin equation, $\omega_B = 4\pi(v_s/\lambda_0)\sin(\theta/2)$, where the sound speed v_s for the mixture is calculated in the limit $k \rightarrow 0$ via the basic relation $v_s = (V_m/M\kappa_s)^{1/2}$. Here V_m is the molar volume of the mixture, M is the average molecular weight, and κ_s is the adiabatic compressibility. For mixtures of components with very different molecular weights, the largest correction to the ideal-gas value for the sound speed is due to the molecular weight of the mixture being different from that calculated on the basis of partial pressures. Consequently, the measured pressures were first used to calculate different mixture compositions (i.e., the x_i's) via the virial equation of state, with terms involving virial coefficients beyond the second being ignored. Second virial coefficients were calculated using the method of Hayden and O'Connell.[6] For each series of experiments (where different mixture compositions were obtained by incremental addition of one species to an initially pure sample of the other species), the molar volume of the initially pure component at the initial pressure was calculated first. The x_i's for subsequent mixture compositions were then determined subject to the constraint that the partial volume of the initial pure component maintain its original value. Sound speeds were calculated using the virial form,

$$v_s^2 = \frac{RT}{M}\left(1+\frac{Bp}{RT}\right)^2\left[1-R\left(1+\frac{p}{R}\frac{dB}{dT}\right)^2 \times\left(C_p^0-pT\frac{d^2B}{dT^2}\right)^{-1}\right]^{-1}, \tag{2}$$

where p is the (total) pressure, C_p^0 is the ideal-gas heat capacity, and B is the second virial coefficient for the mixture.

The values of kl_1 and kl_2, which are used to characterize the sample conditions, were calculated using the following expression[4] for the mean free paths in a binary mixture:

$$l_i^{-1} = \sqrt{2}\pi n_i\sigma_i^2+(1+m_i/m_j)^{1/2}\pi n_j\sigma_{ij}^2 . \tag{3}$$

Here n_i and n_j are the partial number densities, σ_i and σ_j are the hard-sphere diameters for the two species of mass m_i and m_j, and $\sigma_{ij} = (\sigma_i+\sigma_j)/2$.

H_2+Ar

Spectra for this mixture were obtained for three different base pressures p_1 of H_2. The σ values (in nm) that were used in the calculations were $\sigma_1 = 0.297$,

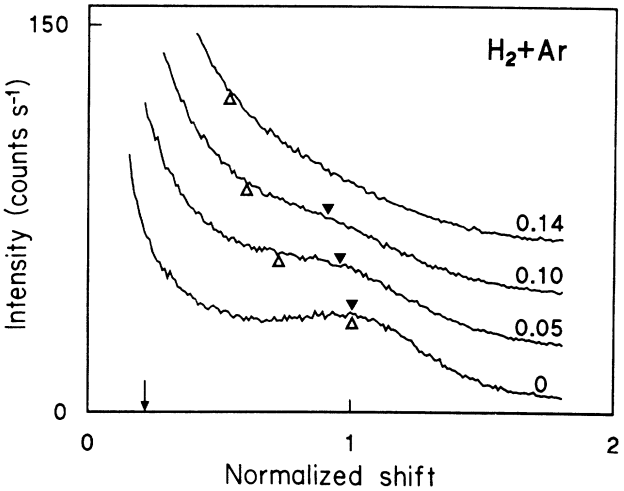

FIG. 1. Selected scattered-light spectra for mixtures of H_2 and Ar with a fixed H_2 partial pressure (p_1) of 6.3 bars, and fractional concentrations (x_2) of Ar as indicated. The central Rayleigh peak has been removed to permit stacking of the spectra on an appropriate scale. Only the (Stokes) region of downshifted frequencies is shown, with the frequency shifts normalized to unity at the position of the Brillouin peak for $x_2 = 0$. The solid triangles indicate the estimated peak positions of the observed Brillouin features, while the open triangles designate the normalized shifts that were calculated (see text) for $k \rightarrow 0$. The arrow indicates the position of the Brillouin peak for $x_2 = 1$. The scattering angle was 157.5°.

$\sigma_2 = 0.340$. The mixture conditions are listed as follows:

$$0 \leq x_2 \leq 0.25\,,\ 0.27 \geq kl_1 \geq 0.21\,,\ kl_2 \simeq 0.07\,,\ p_1 = 9.0 \text{ bars}\,,$$
$$0 \leq x_2 \leq 0.18\,,\ 0.32 \geq kl_1 \geq 0.27\,,\ kl_2 \simeq 0.09\,,\ p_1 = 7.7 \text{ bars}\,,$$
$$0 \leq x_2 \leq 0.17\,,\ 0.39 \geq kl_1 \geq 0.33\,,\ kl_2 \simeq 0.10\,,\ p_1 = 6.3 \text{ bars}\,.$$

Evidence of a fast-mode contribution to the spectrum in the lower part of the x_2 range was observed in all three cases. The best results were obtained for $p_1 = 6.3$ bars, and this case is shown in Fig. 1. Here it can be seen that, while a distinct spectral feature is identifiable only for $x_2 \leq 0.1$, it is nevertheless apparent that the peak position on the scale of normalized frequency shifts remains essentially unchanged with increasing x_2, and differs considerably from the calculated $(k \rightarrow 0)$ values as described above. This behavior is consistent with theoretical predictions.[3,4] The obvious difficulty experienced in detecting the fast-mode contribution as a well-defined spectral feature is most probably associated (i) with a relative polarizability α_2/α_1 that favors the dominance of the second and third terms in Eq. (1) and (ii) with the low absolute value of α_1 leading to low signal levels in the density range of interest. Investigations of the $CH_4 + SF_6$ mixture were undertaken with the latter point in mind.

$CH_4 + SF_6$

The polarizability[5] of CH_4 is approximately three times greater than that of H_2 so that lower p_1 values are accessible while maintaining a strong signal. The value[7,8] of α_1/α_2 for this mixture is very nearly the same as for the $H_2 + Ar$ case, while $m_2/m_1 = 9$ is lower by roughly a factor of 2. The hard-sphere diameters used in the calculations were (in nm) $\sigma_1 = 0.389$, $\sigma_2 = 0.468$. Spectra were recorded for two values of p_1 (in bars) as follows:

$$0 \leq x_2 \leq 0.27\,,\ 0.23 \geq kl_1 \geq 0.17\,,\ kl_2 \simeq 0.07\,,\ p_1 = 6.3 \text{ bars}$$
$$0 \leq x_2 \leq 0.30\,,\ 0.39 \geq kl_1 \geq 0.28\,,\ kl_2 \simeq 0.11\,,\ p_1 = 3.7 \text{ bars}\,.$$

It should be noted that conditions for the lower p_1 case are similar to those of Fig. 1 for $H_2 + Ar$. Nevertheless, no significant fast-mode contribution was detectable in either case; i.e., the observed frequency shifts of the spectral peak did not differ significantly from the values calculated for $k \rightarrow 0$. An understanding of this result must await future theoretical calculations: perhaps the mass ratio is too low for the effect to be observable.

$SF_6 + H_2$

This mixture, with $m_2/m_1 = 73$, was chosen for the investigation of a possible slow-mode contribution associated with the second term in Eq. (1). On intuitive grounds, this contribution was presumed to be observable in the same regime of kl_1 and kl_2 values as above, but with $x_1 \leq 0.3$. The mixture takes advantage of a large disparity in polarizability $(\alpha_2/\alpha_1 \simeq 6)$ which favors the dominance of the S_{22} term of Eq. (1). In fact, for the noted range of x_1 values, this large polarizability effect can be expected to reduce the contributions from the first and third terms of Eq. (1) to a negligible level. In other words, to a good approximation the experiment is sensitive to light scattering from the heavier species only, and any mode which propagates exclusively in this species should be identifiable without ambiguity as the only (shifted) feature in the spectrum. The wide separation between the Brillouin shifts for $x_2 = 1$ and $x_2 = 0$ is also of importance in this connection. The conditions for two separate experiments were as follows:

$$0 \leq x_1 \leq 0.50\,,\ 0.59 \geq kl_2 \geq 0.11\,,\ 1.2 \geq kl_1 \geq 0.66\,,\ p_2 = 1.7 \text{ bars}\,,$$
$$0 \leq x_1 \leq 0.84\,,\ 0.74 \geq kl_2 \geq 0.03\,,\ 1.3 \geq kl_1 \geq 0.23\,,\ p_2 = 1.3 \text{ bars}\,.$$

The first case is shown in Fig. 2 where it is clear that, although some broadening is evident, a distinct spectral feature persists over the complete range of x_1 values investigated. In view of the above comments, there can consequently be no doubt that a well-defined mode exists which propagates exclusively in the heavier species. Furthermore, the frequency shift of the peak is essentially independent of x_1, and a large discrepancy develops between the observed and calculated $(k \rightarrow 0)$ values of the shift at the upper limit of x_1. Although the theory[3,4] has not yet been applied to elucidating the properties of this (slow) mode, it can be assumed by analogy with the fast-mode predictions that qualitative agreement exists. It remains to be seen whether agreement is preserved in matters of detail.

Figure 3 represents a further investigation of this phenomenon with the principal differences being (i) that the scattering angle was changed from 157.5° to 22.5°, thereby probing a range of k values which is lower by a factor of ~ 4, and (ii) that a wider range of x_1 values was employed. Although the wave-vector regime is less favorable, it is nevertheless clear that the effect persists for low values of x_1, with the observed peak position conforming to the calculated $(k \rightarrow 0)$ value only at the upper limit of

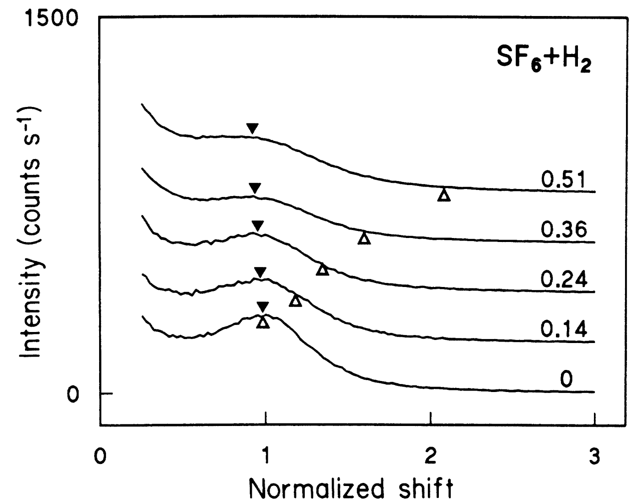

FIG. 2. Stokes spectra for SF_6+H_2 with a fixed SF_6 partial pressure (p_2) of 1.7 bars and fractional concentrations (x_1) of H_2 as listed. The scattering angle was 157.5°. The Brillouin peak for $x_1=1$ occurs at a normalized shift of 8.5. The triangular markers have the same meaning as in Fig. 1.

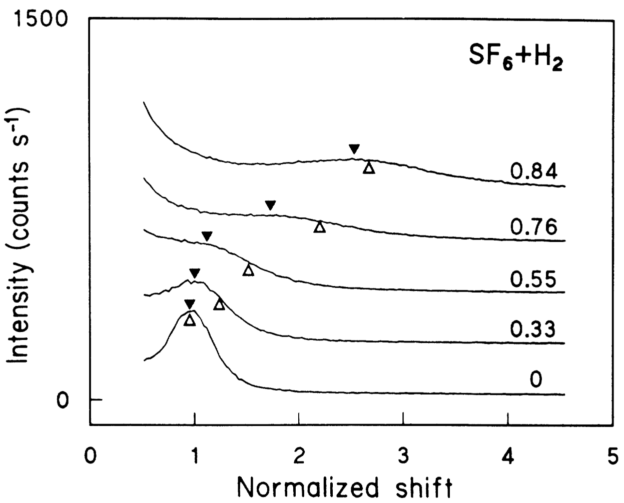

FIG. 3. Stokes spectra for the same mixture as in Fig. 2, but with $p_2=1.3$ bars and a scattering angle of 22.5°. The triangular markers have the same meaning as in Figs. 1 and 2.

x_1 where the third term in Eq. (1) begins to play a dominant role.

In brief, a fast-mode contribution to the light-scattering spectrum of H_2+Ar mixtures has been detected under conditions predicted by theory. The negative result obtained for CH_4+SF_6 mixtures raises the question of what is meant by *disparate* masses, i.e., what is the minimum value of m_2/m_1 required for the effect to be observable? One might also question whether the hard-sphere model of the theory is applicable for this mixture. An analogous slow-mode contribution to the spectrum of SF_6+H_2 mixtures has been clearly identified, and it is concluded that this mode is, in general, much more readily observed because of the highly favorable polarizability ratios that can be achieved for a variety of different mixtures.

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