Collision-Induced Light Scattering in Gaseous Helium

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We have measured the collision-induced light-scattering spectrum of gaseous helium at $T = 298$ K for densities between 46 and 366 amagats to obtain the two-body spectrum in the frequency range 10 to 250 cm^{-1}. The comparison between the dipole-induced-dipole theoretical values of the two-body spectral moments and the experimental values show large discrepancies.

In this Letter we report the first observation of collision-induced light scattering (CILS) in gaseous helium together with the determination of the two-body spectrum in the region up to 250 cm^{-1} and the measurement of the absolute values of its spectral moments. The comparison between the experimental values of the moments and the ones calculated in the dipole–induced-dipole (DID) approximation for the pair polarizability shows a large discrepancy, demonstrating the inadequacy of this model for gaseous He at room temperature.

The spectral distribution of CILS in gaseous systems at room temperature has been the object of numerous investigations since the first experiment was performed by McTague and Birnbaum.[1] In particular, gaseous argon has been extensively studied by various authors[2] and its two-body spectrum determined[3] up to 400 cm^{-1} in order to derive detailed information about the scattering mechanism, i.e., the collision-induced polarizability anisotropy $\beta(r)$.[4] An important result of the most recent investigation on argon[3] was to recognize that together with the DID and overlap terms other intermediate-range effects are significant.[4] There is no doubt, however, that to gain insight into the mechanism contributing to $\beta(r)$, it is important to study CILS in helium since first-principles calculations of the pair polarizability anisotropy are available.[5-7] Nevertheless, up to now only one experiment has been reported[8] for He with the vapor at 4.2 K, from which no information on the two-body contribution could be derived[9] as the spectrum at that temperature is not purely two-body in nature.

The problem which has prevented various investigators from even trying to detect the two-body spectrum of He is the difficulty in detecting the extremely low intensity of the depolarized spectrum. An estimate of the integrated intensity can be obtained if one assumes a model for the collision-induced pair anisotropy $\beta(r)$. Assuming the DID model, i.e., $\beta(r) = 6\alpha_0^2 r^{-3}$, where α_0 is the polarizability of the single atom and r the interatomic distance, we obtain the following for the ratio between the two-body integrated intensities of He and Ar[10,11]:

$$\frac{\varphi_0^{(2)}(\mathrm{He})}{\varphi_0^{(2)}(\mathrm{Ar})} = \frac{\alpha_0^4(\mathrm{He})}{\alpha_0^4(\mathrm{Ar})}\left(\frac{\sigma_{\mathrm{Ar}}}{\sigma_{\mathrm{He}}}\right)^3 \frac{I(T_{\mathrm{He}}^*)}{I(T_{\mathrm{Ar}}^*)}. \quad (1)$$

Here $\varphi_0^{(z)}$ is the zeroth moment of the two-body spectrum, which is proportional to the integrated intensity of the two-body spectrum,

$$I(T^*) = \int_0^\infty x^{-4} \exp(-U/kT)\, dx, \quad (2)$$

where U is the Lennard-Jones pair potential (L-J), T is the absolute temperature, $T^* = kT/\epsilon$ is the reduced temperature, and σ and ϵ are the pair potential parameters. Using the following values of the quantities[12] we find that the ratio in Eq. (1) equals 0.7×10^{-3}: $\alpha_0(\mathrm{Ar}) = 1.642$ Å^3, $\alpha_0(\mathrm{He}) = 0.207$ Å^3, $\sigma_{\mathrm{Ar}} = 3.405$ Å, $\sigma_{\mathrm{He}} = 2.57$ Å, $\epsilon_{\mathrm{Ar}} = 119.8$ K, $\epsilon_{\mathrm{He}} = 10.8$ K, $T = 298$ K, $I(T_{\mathrm{Ar}}^*) = 0.472$, and $I(T_{\mathrm{He}}^*) = 0.562$. This means roughly that if for Ar at 10 amagats the intensity at a frequency near the exciting line is of the order of 1.0 count/sec for an ~5-W argon-ion laser, for helium one should expect a depolarized scattered intensity around the same frequency of the order of $\sim 10^{-3}$ counts/sec. This is enormously small in comparison with the dark-current noise of the best available photomultiplier which is of the order of 0.8 count/sec.

Although the preceding estimate indicates the difficulty of measuring the two-body contribution to the CILS spectrum of helium, we have been able to accomplish this by using extremely long integration times and working at high densities. With regard to the second point an inspection of what one can expect for the shapes of the quadratic and cubic density contributions to the depolarized spectrum of helium at $T = 298$ K shows that this spectrum is dominated by the contribution of the two-body collisions up to very high density. This can be deduced by calculating the integrated intensities $\varphi_0^{(2)}$, $\varphi_0^{(3)}$ and decay constants Δ_2, Δ_3 of an exponentiallike spectrum for both quadratic and cubic contributions, respectively, within the DID approximation by means of the expressions given by Barocchi, Neri, and Zoppi[13]

and using the L-J potential with the parameters given above. We then obtain $\Delta_2 = 58.4\ \mathrm{cm}^{-1}$, $\Delta_3 = 0.37\ \mathrm{cm}^{-1}$, and $\varphi_0^{(2)} = 2.75 \times 10^{-2}\ \text{Å}^9$, $\varphi_0^{(3)} = -9.19\ \text{Å}^{12}$ which indicate that up to very high density the cubic contribution to the spectrum for He at $T = 298$ K should be confined to within the first 7 cm^{-1}.

The above-mentioned consideration gave us confidence in the feasibility of the experiment. The experimental apparatus and procedure has already been described in detail,[9] although it is important to emphasize its great overall stability for periods of several days. This stability permitted the detection of signals the order of 200 times smaller than the dark current of our photomultiplier (0.8 count/sec).

The helium gas contained impurities of only a few parts per million. A spectroscopic search for impurities was performed by us on a sample at 1000 bars and neither N_2 nor O_2 could be detected by their vibrational lines. This, together with the comparison between the signal around the maximum of the pure rotational bands of N_2 and O_2, which we measured in pure N_2 and O_2, and the intensity of He at 100 bars, indicated that these impurities could contribute at most 5% of the observed spectrum at the pressure of He.

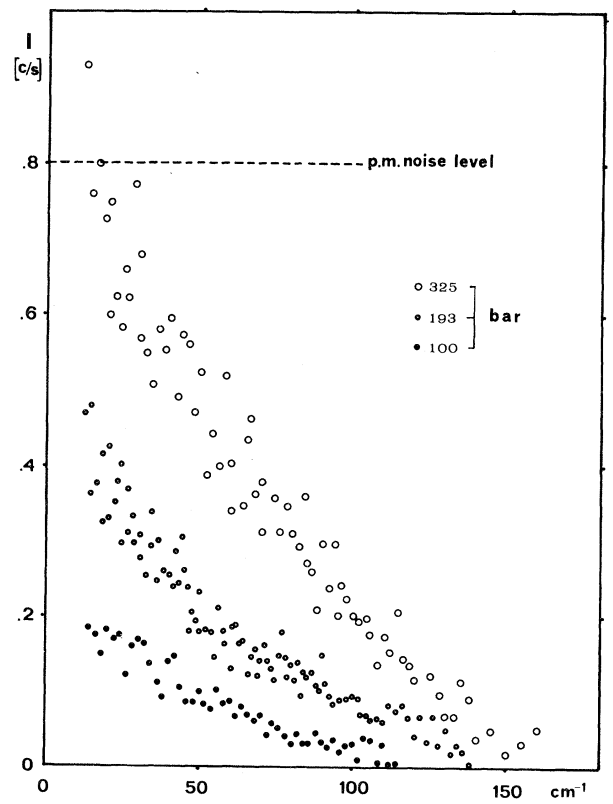

FIG. 1. Three typical CILS spectra of He at different densities; the intensity I is given in counts per second.

Figure 1 shows typical depolarized spectra of He at three different densities. The level of the dark current of the photomultiplier which is also shown is considerably greater than the depolarized scattering except at the lowest frequencies and highest densities.

The behavior of the depolarized intensity versus density ρ is shown in Fig. 2, where $I_{xy}(\omega)/\rho$ is given for $\omega = 30\ \mathrm{cm}^{-1}$. Similar behavior has been found for frequencies between 10 and 250 cm^{-1}. From Fig. 2 it is clear that the data show only a quadratic dependence of the intensity versus ρ in the overall density range 46 to 366 amagats. This is in agreement with the qualitative prediction made in the preceding section.

From the data we have derived, by means of a least-squares fitting procedure, the two-body spectrum $I_{xy}^{(2)}(\omega)$ which is plotted in Fig. 3 for the frequency range 10–250 cm^{-1}. Similar to the case of argon, the spectrum cannot be represented by a single exponential, although the shapes in the two cases are quite different.

By means of the absolute intensity calibration of the spectrum with the $S(1)$ line of H_2 as a standard[2,9] we have derived the absolute values of the first three even moments of the two-body spectrum. Table I gives the values of those experi-

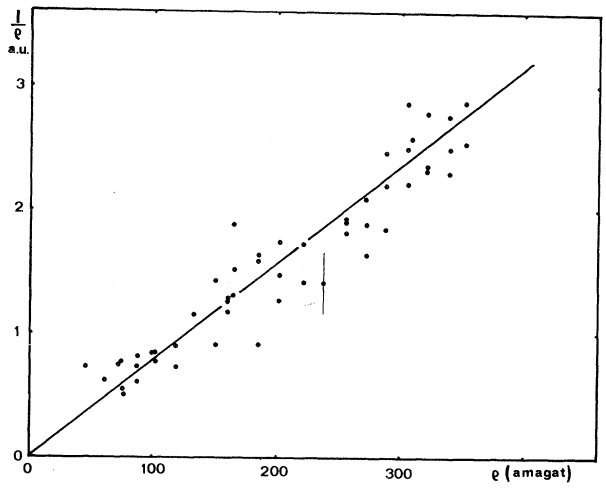

FIG. 2. Behavior of the depolarized intensity $I_{xy}(\omega)/\rho$ of He at $\omega = 30\ \mathrm{cm}^{-1}$. The dots are the experimental data, while the line represents a least-squares fit to the data points; a typical error is also given.

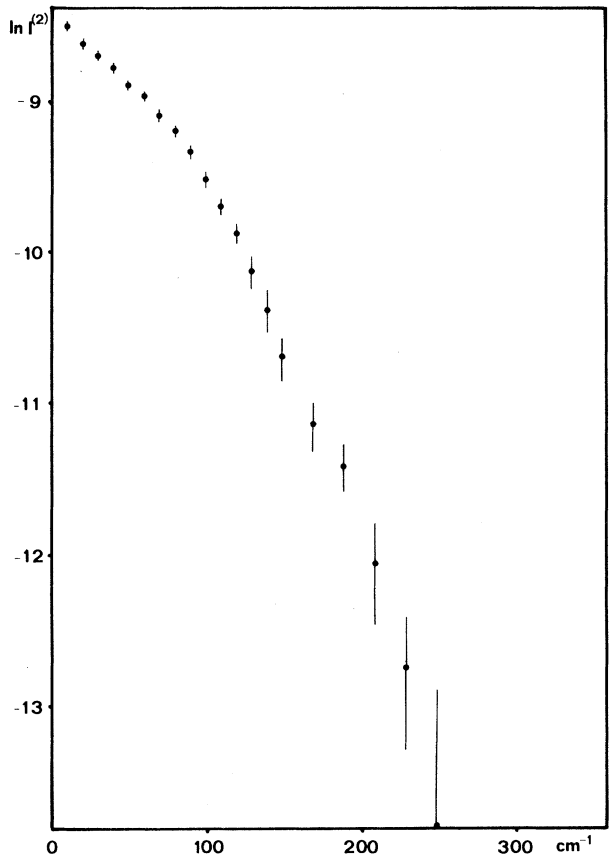

FIG. 3. Behavior of the two-body spectrum $I_{xy}^{(2)}(\omega)$ of He (logarithmic plot).

mental moments together with the values we have calculated identifying $\beta(r)$ with the leading term of the DID approximation[14] and using the Lennard-Jones potential. (The contribution of the second term in the classical DID expansion to the zeroth moment is less than 1% of the value of the first; this is why only the leading term has been retained.)

The comparison of the calculated and experimental values of the moments in Table I dramatically shows the insufficiency of the point-dipole approximation for the pair polarizability. The discrepancy is so large that it clearly cannot be resolved with a slight change in the pair potential, which could be plausible for He. The comparison shows also that the light-scattering mechanism, similar to the case of argon,[4] must be ascribed to a polarizability anisotropy which besides the DID and overlap terms has a positive intermediate-range term. In the case of helium the effect of the non-DID terms, which are shorter range than r^{-3}, is amplified with respect to the case of

TABLE I. Experimental and theoretical values of the moments of the two-body spectrum of He.

Moment	Experiment	Theory
$\varphi_0^{(2)}\times 10^2$ (Å^9)	4.71±0.47	2.75
$\varphi_2^{(2)}\times 10^{-24}$ (Å^9/sec^2)	8.9±2.7	6.66
$\varphi_4^{(2)}\times 10^{-52}$ (Å^9/sec^4)	0.64±0.32	1.85

argon because the experiment has been performed at a reduced temperature $T_{He}^* = 27.6$ which yields a much larger interparticle penetration during a He-He collision than for an Ar-Ar collision for which $T_{Ar}^* = 2.487$.

Theoretical calculation of the behavior of the pair-polarizability anisotropy of He at short range ($r \leq \sigma$) have been performed both from *ab initio* calculations[5,6] and with a local polarizability density model of the atom.[7] Those calculations predict a short-range contribution to the polarizability anisotropy which is negative in sign in strong disagreement with our experimental results. An empirical behavior for the pair-polarizability anisotropy of He can now be derived with a method similar to the one adopted for Ar (Ref. 4); this lengthy calculation is now in progress in our laboratory.

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Theory of Atomic Motion in a Resonant Electromagnetic Wave

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A new theory of atomic motion in a resonant standing or traveling electromagnetic wave is presented. It is shown that, when effects of spontaneous emission are negligible, the motion of a two-level atom in the resonant radiation is determined by two noninterfering wave functions, each of which satisfied a time-dependent Schrödinger equation with time-independent potential energy. An experiment is proposed to test the theory.

There has been renewed interest in recent years in the theory of atomic motion in resonant and near-resonant electromagnetic waves. This interest was initiated by the development of high-power tunable lasers, and interest has continued because of possible application of the theory to problems of laser isotope separation,[1-4] atomic trapping and cooling,[4-7] neutral-atom acceleration,[8-9] and atomic-beam–deflection spectroscopy.[10-12]

An atom illuminated by resonant radiation experiences at least two types of radiation force: a force associated with spontaneous emission, and a force due to interaction of the induced atomic dipole moment with the amplitude gradient of the applied field. The radiation pressure associated with spontaneous emission has been extensively investigated both theoretically[4,6] and experimentally,[1,12,13] and will not be discussed in this Letter. A theory of the induced-dipole force has been developed by Ashkin for the case where the atomic response may be described by a polarizability,[6] and a certain off-resonance focusing effect associated with this force has recently been detected experimentally.[14] A description of the atomic response in terms of a polarizability also involves spontaneous emission to the extent that it is spontaneous decay that causes atomic relaxation to the near–steady-state condition described by a polarizability. If the atom-field interaction is brief (less than a natural lifetime), a theory based on the steady-state polarizability is no longer appropriate, and, in general, Schrödinger's equation must be solved to determine the atomic response. In this case, effects of spontaneous emission are negligible.

The purpose of this Letter is (1) to present a new theory of atomic motion in a resonant electromagnetic wave, applicable when effects of spontaneous emission are negligible, and (2) to propose an experimental test of the new theory.

The Hamiltonian for an atom in a classically prescribed electromagnetic field, in the dipole approximation, takes the form

$$H = P^2/2M + H_0 - \vec{\mu}\cdot\vec{E}(\vec{R}, t), \tag{1}$$

where $P^2/2M$ is the kinetic energy associated with the center-of-mass momentum $\vec{P}$, H_0 is the Hamiltonian for the internal motion of the atom, $\vec{\mu}$ is the dipole-moment operator, and $\vec{E}(\vec{R}, t)$ is the electric field evaluated at the center-of-mass position $\vec{R}$. Consider first the motion of a two-level atom with energy levels E_1 and E_2 in a monochromatic standing wave $\vec{E}(\vec{x}, t) = \hat{\epsilon}\mathcal{E}(\vec{x})\cos\omega t$. Here the amplitude $\mathcal{E}(\vec{x})$ will be a solution of the time-independent wave equation $\nabla^2\mathcal{E} + (\omega/c)^2\mathcal{E} = 0$, but is otherwise arbitrary. Let $\psi_1(\vec{x})$ and $\psi_2(\vec{x})$ be the amplitudes for the atom to be located at position $\vec{x}$ and occupy energy levels E_1 and E_2, respectively. Then it follows from Eq. (1) that the Schrödinger equation for the two-component wave function is

$$\begin{aligned} i\hbar\frac{\partial\psi_1}{\partial t} &= -\frac{\hbar^2}{2M}\nabla^2\psi_1 + E_1\psi_1 - \mu\mathcal{E}(\vec{x})\cos\omega t\,\psi_2, \\ i\hbar\frac{\partial\psi_2}{\partial t} &= -\frac{\hbar^2}{2M}\nabla^2\psi_2 + E_2\psi_2 - \mu\mathcal{E}(\vec{x})\cos\omega t\,\psi_1, \end{aligned} \tag{2}$$

where $\mu = \langle 1 | \vec{\mu}\cdot\hat{\epsilon} | 2\rangle$ is the transition dipole moment. In the case of exact resonance, $\omega = (E_2$