arbitrariness of the virtual orbitals may be utilized profitably in such a way that the convergence may be improved in the perturbation theory and the configuration interaction calculation based on the Hartree-Fock equation. It is hoped that the discussion presented here will also have some pedagogical value in furthering a sound understanding of the nature of virtual orbitals.

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PHYSICAL REVIEW A VOLUME 1, NUMBER 5 MAY 1970

Induced Anisotropy and Light Scattering in Liquids[*]

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A weak depolarized Rayleigh wing has been observed for liquid xenon and for several liquids composed of spherical-top molecules. The intensity contours for these liquids decrease exponentially with increasing frequency shift. This behavior is similar to that predicted for spectra of collision-induced scattering from gases.

The existence of a continuous depolarized spectrum of scattered light centered at the exciting frequency has long been known[1] for liquids composed of anisotropic molecules. This spectrum, commonly called the "Rayleigh wing," is believed to arise from orientation fluctuations of individual molecules and has been the subject of many papers.[1,2] Depolarized scattering by liquids composed of spherical-top (tetrahedral) molecules has also been observed,[3] but is not well understood. Recently, Levine and Birnbaum[4] have discussed the scattering of light arising from the change in anisotropic polarizability produced in pairs of atoms or molecules during collision and have derived expressions for the intensity of the spectrum and the degree of depolarization. McTague and Birnbaum[5] have observed depolarized spectra of gaseous Ar and Kr at high pressure in general agreement with this theory, and they attribute the spectra to colliding pairs. Also, Thibeau and Oksengorn[6] have developed a theory based on the fluctuations of the internal field at each atom, which explains their observations on the depolarization of Rayleigh scattering in compressed Ar. We have observed depolarized spectra from liquid Xe, CCl_4, $SiCl_4$, $TiCl_4$, $SnCl_4$, $SnBr_4$, $C(CH_3)_4$, and $Si(CH_3)_4$. These spectra are all of very-low intensity; they have depolarization ratios of $\frac{3}{4}$ (for plane-polarized incident light); and they exhibit an exponential decrease in intensity with increasing frequency shift.

A He-Ne laser provided plane-polarized radiation of 50 mW power at 6328 Å. Reagent-grade liquids were filtered or vacuum distilled into glass Raman cells designed to minimize stray light. The cells were enclosed in a temperature-controlled metal block (±0.5°), and the liquids maintained at a temperature of 295°K, with the exception of $SnBr_4$ which was kept at 313°K. Research-grade Xe was liquefied and maintained at 164°K. Depolarized radiation scattered at an angle of 90° was selected by a polarizer placed between the sample and spectrometer. The scattered light was analyzed with a Spex 1400 double monochromator, the total instrumental width (laser plus spectrometer) being $1.7\ \text{cm}^{-1}$ for a slit width of 100 μm. A cooled photomultiplier tube (ITT-FW130) with a dark count of 2 to 3 per sec was used for detection. This was followed by photon-counting equipment and a chart recorder. The spectrometer-detector combination was calibrated for sensitivity to light of different polarization directions over the wavelength region 6000 – 7000 Å.

Depolarized spectra having a continuous distribution of intensity out to 50–100 cm^{-1}, with a maximum at the exciting frequency were observed for all the liquids studied. The spectra are all of very-low intensity. For example, for Xe, the total integrated intensity is $\sim 10^{-3}$ of that of the polarized Rayleigh-Brillouin triplet; moreover, this spectrum disappears in solid Xe. The relative intensi-

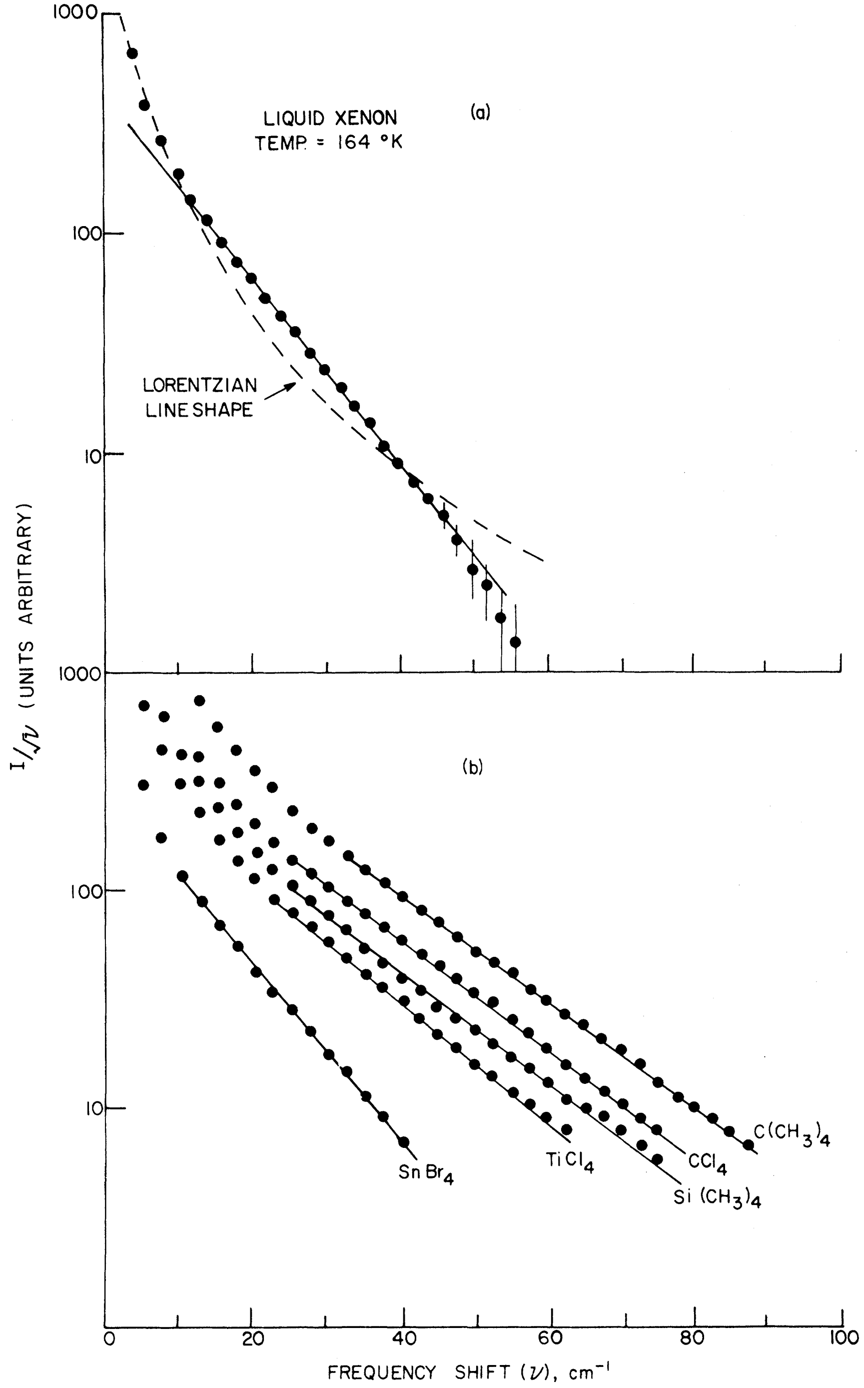

FIG. 1. Graphs of $I/\sqrt{\nu}$ versus frequency for the Rayleigh wings of (a) liquid Xe, and (b) liquids composed of spherical-top molecules. The solid circles represent experimental points; the solid straight lines through the points represent the frequency regions over which Eq. (1) appears to be obeyed. In (a), a comparison with the dashed line shows the departure of the wing from a Lorentzian line shape.

ties of the depolarized spectra were found to be: $CCl_4 = 1$; $Xe = 0.3$; $C(CH_3)_4$ and $Si(CH_3)_4 = 0.5$; $SiCl_4$, $TiCl_4$, $SnCl_4$, and $SnBr_4 \sim 1.2$. For comparison, the Rayleigh wing of CS_2 has an intensity of 20 on this scale, and extends to 250 cm^{-1}.

According to the theory of Levine and Birnbaum,[4] the intensity contour of the Rayleigh wing arising from collision-induced light scattering in gases is given approximately by

$$I(\nu) \propto \sqrt{\nu}\, e^{-\nu/\nu_0} .$$

Here, ν is the frequency shift and

$$\nu_0^{-1} = 2\pi\gamma_2^{-1}[m/kT)]^{1/2} ;$$

γ_2 is a constant, k is Boltzmann's constant, m is the reduced mass of a colliding pair, and T is the absolute temperature. We have analyzed the observed spectra using Eq. (1). Figure 1(a) is a graph of $\log_{10}(I/\sqrt{\nu})$ versus ν for liquid Xe. The experimental points fall on a straight line over most of the frequency range of the wing, in good agreement with the theory for gases. The slope of the graph gives a value of $\nu_0 = 10.5 \pm 0.5$ cm^{-1} for liquid Xe. A similar plot gives straight lines for the depolarized Rayleigh wings of the spherical-top molecules, as shown in Fig. 1(b). The slopes of these lines[7] were found to be roughly proportional to $[m/(kT)]^{1/2}$; the constant of proportionality γ_2^{-1}, which is a measure of the distance between two colliding molecules for maximum induced anisotropy, was determined to be 0.6 Å for the molecular liquids.

It is concluded that the theory of collision-induced light scattering in gases appears to explain the existence and shape of the depolarized Rayleigh wing for liquids composed of isotropic molecules. Preliminary observations in this laboratory indicate that scattering due to induced anisotropy may be of more general importance since a similar dependence [Eq. (1)] over a limited frequency range has been found for liquids composed of anisotropic molecules such as CS_2, C_6H_6, C_6D_6, C_6F_6, and $C_6H_5NO_2$.

We are grateful to Professor C. J. L. Lock of McMaster University for purifying the more reactive liquids investigated.

Note added in proof. A similar depolarized spectrum with exponential line shape has been observed in liquid argon (P. A. Fleury and J. P. McTague, Opt. Commun. 1, 164, 1969; J. P. McTague, P. A. Fleury, and D. B. Du Pré, Phys. Rev. 188, 303, 1969).

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[7] For CCl_4, the slope appears to be independent of temperature and scattering angle over the limited ranges investigated, 273–338 °K and 50–127 °K, respectively.

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Electron *g* Factors of Low-Lying Levels of Ce I †

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Electron *g* factors have been measured for 33 low-lying states of Ce I with the atomic-beam magnetic-resonance technique.

INTRODUCTION

The measurement of electron *g* factors to high precision provides quantitative evidence with which to judge the validity of theoretical atomic wave functions. Such measurements thus yield information that can be useful in guiding theoretical investigations of atomic states and their interactions.

The case of Ce I is very attractive experimentally. Forty-five odd-parity levels and two even-parity levels below 7000-cm^{-1} excitation energy, and with $J > 0$, have been identified in optical spec-