Journal of Molecular Liquids, 29 (1984) 37—43
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Submillimetre Laser Spectroscopy of Intensely Absorbing Liquids

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(Received 14 February 1984)

Abstract

The submillimetre spectra of several intensely absorbing liquids have been measured with a tunable submillimetre laser at several spot frequencies in the range from about 20 to 200cm^{-1}. The spot frequency measurements enable us to check the accuracy of broad-band power absorption spectra obtained by Michelson interferometry under a range of conditions and for several different types of heavily absorbing liquids, including aqueous solutions of current interest.

Introduction

We have recently devised a method[1-3] of measuring accurately the far infra-red power absorption coefficients ($\alpha(\bar{\nu})$/neper cm^{-1}) for intensely absorbing liquids. This method is based on the attenuation of the output submillimetre signal in a variable path length cell in which the thickness of liquid transversed by the beam is accurately defined. The measurement of this thickness is the limiting uncertainty in conventional far infra-red interferometry[4]. In this paper we illustrate the new method with results on intensely absorbing systems of interest, such as alkyl alcohol homologues[1,2], acetonitrile[5], aqueous solutions of biological and technological interest and for molecular liquids of

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0167-7322/84/$03.00

interest in testing experimentally the theory of molecular diffusion.

Experimental

The method for measuring power absorption coefficients by laser spectroscopy has been described fully elsewhere[2,3]. Briefly, a submillimetre cavity containing methanol vapour is pumped with CO_2 laser radiation from an Apollo Instruments tunable laser. This submillimetre laser radiation is detected using a Golay pneumatic cell and a lock-in amplifier. The number of spot frequencies available is illustrated in Fig.2 for CH_2Cl_2, which is a molecular liquid well-suited for spectroscopic study with a variety of methods. The output submillimetre radiation is collimated and may be used as a check for interferometric artifacts such as beam convergence effects. This is illustrated in this paper with reference to diphenyl methane, whose far infra-red power absorption is relatively weak compared with other samples described in this paper. The laser results are compared with broad-band far infra-red spectra obtained by conventional interferometry [6].

Results and Discussion

There has been a considerable amount of interest in the far infra-red properties of alkyl alcohols because of the challenge to interpretation provided by a combination of hydrogen-bonding and complex rototranslational molecular dynamics. Vij et al[1,2] have pointed out recently that it is pointless to theorize on such systems in the absence of accurate power absorption data in the far infra-red. Both the intensity and band-shape of the far infra-red broad-band absorption contain information on the molecular dynamics and interactions of these H-bonded systems. Therefore it is important to maximize ordinate accuracy (in the power absorption coefficient). The result of this exercise is illustrated for a series of alcohols in Fig.1 where the ordinate is power absorption coefficient, $\alpha(\bar{\nu})$ (in neper cm^{-1}), and the abscissa is $\bar{\nu}/cm^{-1}$. In general, the interferometric and laser results agree satisfactorily so that it will be possible in future to use the data with confidence for a theoretical analysis - probably by computer simulation[1].

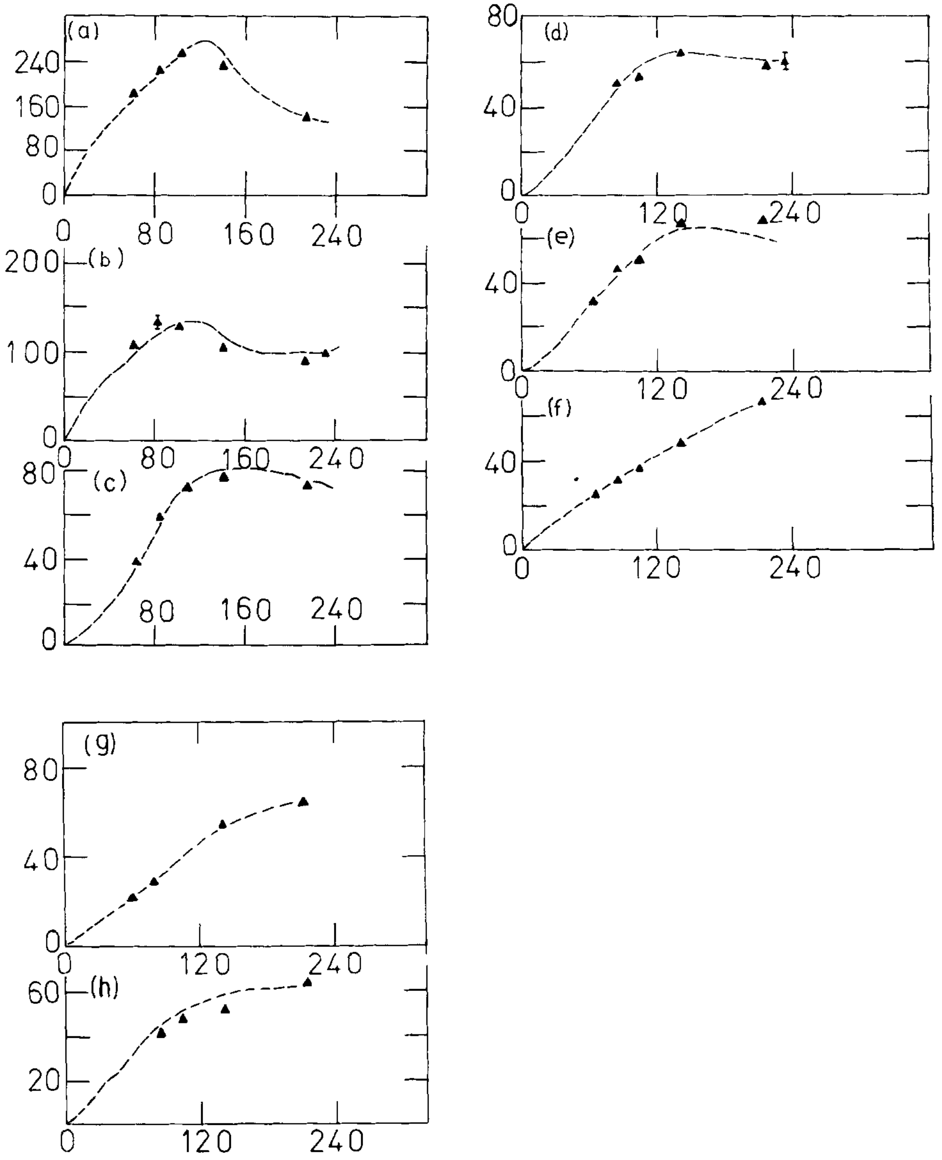


Fig.1: Interferometric (-----) and submillimetre laser (▲) power absorption coefficients ($\alpha(\bar{\nu})$/neper cm^{-1}) as a function of wavenumber ($\bar{\nu}$/cm^{-1}).

(a) methanol; (b) ethanol; (c) n-pentanol;
(d) n-hexanol; (e) n-heptanol; (f) 3-heptanol;
(g) 4-heptanol; (h) 5-methyl-2-hexanol.

The molecular liquids in Fig.2(a) CH_2Cl_2, (b) pyridine and (c) acetone, are ideal for fourth moment[7] and band-shape analysis. The results of molecular dynamics and theoretical investigations on CH_2Cl_2[8] and acetone[9] have been published elsewhere[10]. The power absorption coefficients of these liquids have been well-defined by interferometry[4] and this time the interferometric curves can be used as a check on the spurious noise level in the laser system. It is seen from Fig.2 (a) and Fig.2(c) that some laser points are anomalous, i.e. do not fit onto the broad-band background of the interferometric profile. This is attributed to power fluctuation in the CO_2 laser and polarization effects. In general, these anomalies appear with the weaker submillimetre lines.

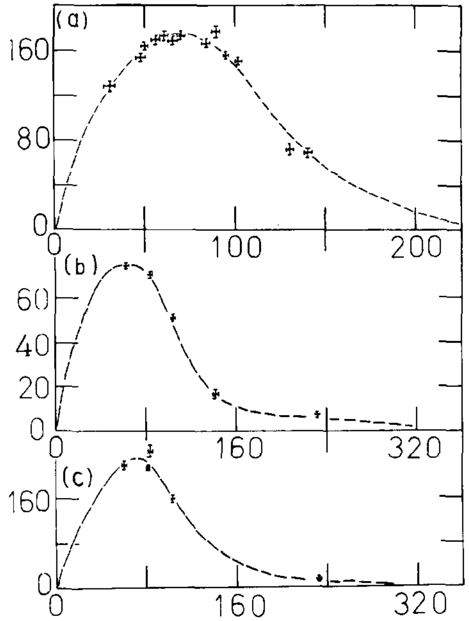


Fig.2: (a) dichloromethane; (b) pyridine; (c) acetone.

In Fig.3 we illustrate the results of this investigation for two intensely absorbing liquid systems: (a) acetonitrile and (b) water and a water/lycine saturated solution. It is particularly difficult to obtain $\alpha(\bar{\nu})$ by interferometry for these systems because of the heavy attenuation of the diffuse interferometric beam and consequent uncertainty in path-length definition. The comparison with the laser results in Fig.3 shows that there is considerable uncertainty in the interferometric data, hitherto thought of as a broad band. G.J. Evans has recently reported[5] a sharp dip in the acetonitrile laser spectrum at 84cm^{-1}, but we do not observe this feature. In order to clear up this uncertainty it would be useful to study acetonitrile in the far infra-red with a high resolution broad-band instrument such as the Bruker IFS 114.

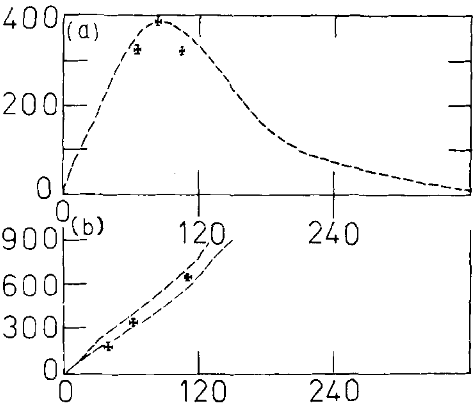
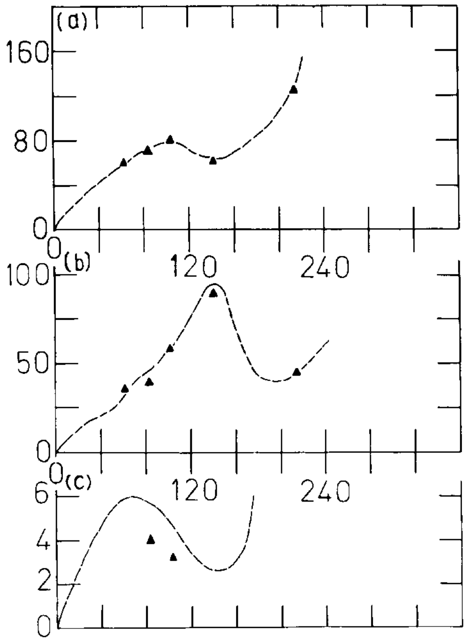


Fig.3: (a) acetonitrile;
(b) water (lower), aqueous lycine solution (upper).

Such a feature would be of fundamental interest. In Fig.3(b) we illustrate the usefulness of our method for the study of heavily absorbing species such as a saturated aqueous lycine solution. This is more heavily absorbing than water itself in the far infra-red.

In Fig.4 some laser and interferometric results are illustrated for aniline and N,N dimethyl aniline, in which significant electric field effects were detected by Evans et al[10] by interferometry. Again the two sets of data seem to agree satisfactorily. In Fig.4(c), on the other hand, there is a significant intensity difference between the interferometric and laser data for diphenyl methane, which is a weak absorber. This is attributed tentatively to beam convergence effects in the interferometry. Beam convergence effects increase in significance with sample path length.



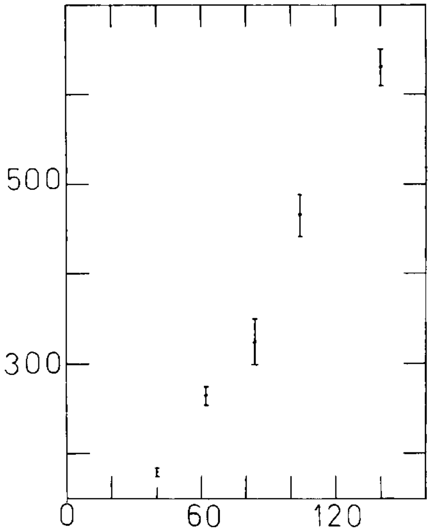


Fig.4: (a) aniline; (b) N,N dimethyl aniline;
(c) diphenylmethane.

Fig.5: Aqueous Ferromagnetic Suspension.

Finally, in Fig.5, we illustrate the use of submillimetre laser spectroscopy in detailing the far infra-red spectrum of an aqueous ferromagnetic suspension. This type of suspension has several technological applications and its submillimetre spectrum is an intensely absorbing rising continuum (Fig.5) similar to that of water itself, but less absorbing, in contrast to the lycine solution of **Fig**.4.

Acknowledgements

The Nuffield Foundation is thanked for the award of a bursary under its 'Small Grants' scheme. The University of Wales is thanked for a Fellowship to Myron W. Evans.

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