THE SHAPES OF INFRARED ABSORPTION BANDS OF LIQUIDS[†]

R. P. YOUNG[‡] AND R. N. JONES[*]

Division of Chemistry, National Research Council of Canada, Ottawa, Canada

Received August 19, 1970

Contents

I. Introduction

Insight into the kinetics of molecular motion in liquids can be gained from an analysis of the shapes of the infrared absorption bands, and in this article we shall review recent work on this subject. The physicochemical implications will be considered in section III and we shall begin with an account of the experimental problems of measuring the reflection and transmission spectra of liquids in the mid-infrared (4000–200 cm^{-1}). The absorption bands of many liquids are very intense and the transmission must be measured through thin films. This causes distortions from interference effects within the films and from phase changes at the boundaries with the cell windows; in consequence the conventional techniques of quantitative infrared spectrophotometry based on the use of double beam spectrometers to compensate for cell boundary effects are not applicable. This has led many investigators to turn to methods based on interferometry, simple reflection, or attenuated total reflection (ATR).

The shapes of infrared absorption bands of liquids can be described quantitatively in several ways. There are purely statistical methods, based on moments analysis; these are empirical and invoke no preconceived physical theory. The simplest theoretical treatment leads to the prediction of a Lorentzian band contour, but the bands observed experimentally rarely conform to this and are better fitted by a Lorentz function subject to a Gauss perturbation. A new approach to the theoretical interpretation of the shapes of infrared absorption bands of liquids has been proposed by Gordon[1] and Shimizu[2] and extended by Bratoẑ and coworkers.[3,4] This work has established that the Fourier transform of the frequency spectrum yields a time correlation function from which the nature and rate of molecular reorientation in the liquid may be inferred. Some aspects of these studies have been reviewed by Ewing.[5]

In 1963 Seshadri and Jones[6] discussed the instrumental factors affecting the infrared band profile and outlined methods for recovering the true band shape from that observed experimentally. Since that time spectroscopists have enjoyed many technical advances. The availability of electronic computers has enormously simplified all aspects of data processing from the initial smoothing and calibration of the raw experimental data to sophisticated methods of band-shape analysis and curve fitting.[7,8] The attenuated total reflection method, originally proposed by Fahrenfort and Visser,[9,10] has been developed by Irons and Thompson[11] and by Crawford and coworkers[12–14] in studies of the principal absorption bands of several organic liquids.

An accurate determination of the band intensity, both as ordinate height and area, will usually be obtained concomitantly with the band shape. In this review our interests in the intensities will be secondary and we shall not probe into their physicochemical significance. At present, integrated area intensities of vibrational absorption bands can be interpreted explicitly only for nonoverlapping band systems of simple molecules in the vapor phase; this subject has been reviewed by Steele.[15] The intensities associated with the characteristic group frequency vibrations of larger molecules have diagnostic value in molecular structure determination, and this has been reviewed by Wexler.[16]

II. The Measurement of the Optical Constants

The optical behavior of any absorbing material with respect to monochromatic radiation is completely determined by its

---

[†] Published as Contribution No. 11803 from the Laboratories of the National Research Council of Canada.

[‡] NRCC Postdoctoral Fellow. Present address: Perkin-Elmer Limited, Beaconsfield, England.

[*] Author to whom correspondence should be addressed.

(1) R. G. Gordon, *J. Chem. Phys.*, **39**, 2788 (1963); **41**, 1819 (1964); 43, 1307 (1965).

(2) H. Shimizu, *ibid.*, 43, 2453 (1965); 48, 2494 (1968).

(3) S. Bratoẑ and J. Rios, *C. R. Acad. Sci., Ser. B*, **269**, 90 (1969).

(4) S. Bratoẑ, J. Rios, and Y. Guissani, *J. Chem. Phys.*, 52, 439 (1970).

(5) G. Ewing, *Accounts Chem. Res.*, 2, 168 (1969).

(6) K. S. Seshadri and R. N. Jones, *Spectrochim. Acta*, **19**, 1013 (1963).

(7) R. N. Jones, *Pure Appl. Chem.*, **18**, 303 (1969).

(8) R. N. Jones, *Appl. Opt.*, **8**, 597 (1969).

(9) J. Fahrenfort, *Spectrochim. Acta*, **17**, 698 (1961).

(10) J. Fahrenfort and W. M. Visser, *ibid.*, **18**, 1103 (1962).

(11) G. M. Irons and H. W. Thompson, *Proc. Roy. Soc., Ser. A*, **298**, 160 (1967).

(12) A. C. Gilby, J. Burr, and B. Crawford, *J. Phys. Chem.*, 70, 1520 (1966).

(13) A. C. Gilby, J. Burr, W. Krueger, and B. Crawford, *ibid.*, 70, 1525 (1966).

(14) A. A. Clifford and B. Crawford, *ibid.*, **70**, 1536 (1966).

(15) D. Steele, *Quart. Rev. Chem. Soc.*, **18**, 21 (1964).

(16) A. S. Wexler, *Appl. Spectrosc. Rev.*, **1**, 29 (1967).

optical constants; these are the *refractive index* (n) and the *absorption index* (k) which are the real and imaginary parts of the *complex refractive index* ($\hat{n}$).[17]

$$\hat{n} = n + ik \tag{1}$$

In conventional transmission spectrophotometry, the transmittance (T) is measured as the ratio of the transmitted to the incident intensity

$$T = I/I_0 \tag{2}$$

The absorbance (A) given by

$$A = \log (T^{-1}) \tag{3}$$

is related to the apparent absorption index (k_a) by

$$k_a = 2.30258A/4\pi\nu l \tag{4}$$

where ν is the wavenumber (cm^{-1}) and l the path length (cm). The relation between k and k_a will be discussed later and presents a major experimental problem.

The Napierian absorption coefficient (α), defined by the Lambert–Bouguer law

$$I = I_0 \exp(-\alpha l) \tag{5}$$

is related to k_a by

$$k_a = \alpha/4\pi\nu \tag{6}$$

The molar absorption coefficient (ϵ) is given by

$$\epsilon = A/cl \tag{7}$$

where c is the concentration (mol/dm^{-3}) of the absorbing species. As commonly used with solutions, Beer's law is assumed, so that A is constant and independent of c and l. When pure liquids or solids are involved the concentration is expressed as

$$c = 1000d/M \tag{8}$$

where d is the density (g cm^{-3}) and M is the gram molecular weight.

The *reflectance* (R) is measured as the ratio of the reflected to the incident intensity.

Current theoretical interest centers on the intense fundamental vibration bands of simple organic liquids such as C_6H_6, CCl_4, and CS_2. Even the weaker of these bands have k_{max} of the order of 0.1 and require a path length of approximately 10 μm for accurate transmission measurement. The stronger bands have $k_{max} \simeq 1.5$, and for these, film thicknesses of the order of 1 μm are needed. The construction of precision cells of known and uniform thickness with path lengths in the 1–10-μm range presents special difficulties.[18]

At path lengths less than 5 μm the apparent absorption is sensitive to the thickness because of *reflection loss distortion* within the film. This results from the phase change on reflection at the liquid–window interfaces; it is a function of the refractive index difference, the film thickness, and the absorption coefficient and becomes increasingly serious as the film thickness diminishes. The effect is complicated by the large changes in the refractive index that occur in traversing a strong absorption band. The calculations of Maeda and Schatz[19] for a number of experimentally reasonable situations predicted relative errors of 10–20% on this account. Young and Hannah[20] have noted that the peak wavenumber position may also be displaced. A separate source of error is the generation of interference fringes superimposed on the spectrum by multiple reflection within the film; this is more serious for somewhat thicker cells (10–100 μm) where the path length is comparable with the wavelength. A combination of the two effects can be termed *dispersion distortion* and because of it interest shifted to other ways of measuring the optical constants, not involving transmission through thin films. These are based on dispersion, simple reflection, and ATR.

A. METHODS BASED ON INTERFEROMETRIC DISPERSION

In 1958 Kagarise and Mayfield[21] demonstrated that refractive indices in the infrared could be obtained with a germanium interferometer. The condition for interference maxima is

$$2\,nl \cos \phi = N\lambda \tag{9}$$

where ϕ is the angle of incidence, λ the wavelength, and N the interference order. Usually ϕ is assumed to be zero and, provided l is known with sufficient accuracy, only the fringe order N need be evaluated. Kagarise[22] has described one method of doing this and applied it to several organic liquids, including CH_2Cl_2, CCl_4, CH_2I_2, and CS_2. From the refractive index he calculated absorption intensities of the main bands in the spectra of CCl_4 and CH_2I_2, and his values compare well with those obtained by transmission.[23] Similar measurements on CCl_4 were made by Maeda and Schatz[24] and on CH_2I_2 by Prichard and Orville-Thomas.[25] The method performs best on very strong bands and the accuracy is low if the bands are weak. Another limitation is that the calculations only yield the integrated absorption intensity; hence details about the optical constants in the peak absorption region are lacking. Nevertheless, interferometric dispersion has proved a valuable technique for calculating infrared absorption band intensities from refractive indices. Schatz[26] has studied the spectrum of C_6H_6 by this method and Vincent-Geisse and Ladd[27,28] have measured dispersion curves and computed intensity data for some dozen organic liquids. Orville-Thomas and coworkers have also examined halogen-substituted methanes and acetonitriles by this technique.[25,29–31]

---

[17] The symbolism and nomenclature of absorption spectrophotometry are still confused. In most respects ours conform with recent recommendations of IUPAC and are published in *Pure Appl. Chem.*, No. 1, **21** (1970); recommendations on terminology and symbolism for the complex refractive index are still pending.

[18] R. P. Young and R. N. Jones, *Can. J. Chem.*, **47**, 3463 (1969).

[19] S. Maeda and P. N. Schatz, *J. Chem. Phys.*, **35**, 1617 (1961).

[20] E. F. Young and R. W. Hannah in "Modern Aspects of Reflectance Spectroscopy," W. W. Wendlandt, Ed., Plenum Press, New York, N. Y., 1968, p 218.

[21] R. E. Kagarise and J. W. Mayfield, *J. Opt. Soc. Amer.*, **48**, 430 (1958).

[22] R. E. Kagarise, *ibid.*, **50**, 36 (1960).

[23] R. E. Kagarise, *J. Chem. Phys.*, **31**, 1258 (1959).

[24] S. Maeda and P. N. Schatz, *ibid.*, **36**, 571 (1962).

[25] W. H. Prichard and W. J. Orville-Thomas, *Trans. Faraday Soc.*, **59**, 2218 (1963).

[26] P. N. Schatz, *J. Chem. Phys.*, **32**, 894 (1960).

[27] J. Vincent-Geisse and J. A. Ladd, *Spectrochim. Acta*, **17**, 627 (1961).

[28] J. Vincent-Geisse, *J. Phys. Radium*, **26**, 289 (1965).

[29] W. H. Prichard and W. J. Orville-Thomas, *Trans. Faraday Soc.*, **61**, 1549 (1965).

[30] L. Nemes and W. J. Orville-Thomas, *ibid.*, **61**, 2612 (1965).

[31] H. Ratajczak and W. J. Orville-Thomas, *ibid.*, **61**, 2603 (1965).

B. METHODS BASED ON SIMPLE REFLECTION

The reflectance (R) of a material is related by the classical Fresnel equations[32] to the angle of incidence (θ) and the optical constants. If R is measured at two angles, two simultaneous equations can be set up and solved for n and k. This is the basis of the method of evaluating n and k proposed by Simon.[33] The need to measure θ accurately posed experimental difficulties and this approach did not receive very wide attention. Later Robinson and Price[34,35] pointed out that, provided the experimental data extend over the whole relevant absorption region, both n and k can be derived from a single reflection measurement. Their method depends on the fact that the phase shift on reflection θ_R is related to the observed reflectance by a Kramers–Kronig integral transform

$$\theta_R = -2\nu_0/\pi \int_0^\infty \frac{\ln|r|}{\nu^2 - \nu_0^2} d\nu + \pi \qquad (10)$$

where $|r|$ is the modulus of the amplitude of the observed reflection[36] and ν_0 is the band center.

The optical constants are obtained from known expressions relating each separately to $|r|$ and θ_R. Because the computations are complicated, some simplifying assumptions were introduced by Schatz and coworkers,[37] who used the method to derive optical constants from near-normal incidence reflection spectra of C_6H_6, $CHBr_3$, $CHCl_3$, CCl_4, and CS_2. They assumed that each vibrational transition could be represented by a damped harmonic oscillator, thereby implying that all the absorption bands are Lorentzian and can be specified by three parameters: the peak wavenumber, the band half-width, and the total intensity. The equations relating the n and k curves to these parameters are not complicated and it is not difficult to optimize the fit of the Lorentz bands to the observed reflection spectra. The results are in many cases in good agreement with earlier measurements from dispersion data, but a comparison of the curves shows that there is a failure to reproduce the shape of the reflection curve in the peak region. Subsequently these workers[38,39] reexamined the method of Robinson and Price and devised a means of calculating accurate n and k data from near-normal incidence reflection spectra without assuming the damped oscillator model. The data published by Barnes and Schatz[39] for CCl_4 and CS_2 are probably the most detailed liquid optical constant evaluations yet obtained by simple reflection. As they themselves indicate, the weakness of the method lies in the experimental difficulty of accurately measuring the reflectance in regions of low absorption, as in the wings of the bands; another difficulty is the extreme sensitivity of $\ln |r|$ to errors in small values of R. For this reason methods based on simple reflection lack the overall precision required for detailed band-shape analysis though they are convenient and useful for less exacting intensity studies and for deriving n and k in the region of the absorption maxima.

A similar experimental approach has been used by Vincent-Geisse and Cameo,[40,41] who have studied an extensive range of organic liquids by reflection spectrophotometry. Their emphasis has been predominantly on the refractive index curves and the integrated absorption intensities; absorption data on the wings have not generally been included. Their publications nevertheless contain much valuable intensity data which are usually in good agreement with other published values. Some results obtained by the simple reflection method are included in Table I. In the method developed by Libov and Bakhshiev the two values of R are obtained by reflection from two different window materials.[42]

C. METHODS BASED ON ATTENUATED TOTAL REFLECTION

The simple reflection method is suitable only for the most intense absorption bands and even for these it may yield imprecise results in the wings. An increase in sensitivity can be achieved if the liquid sample is in contact with a transparent material of high refractive index (n_w). This was recognized by Barnes and Schatz[39] who used an AgCl window ($n_w \simeq 2$) in their work on CCl_4 and CS_2. A further improvement results if the radiation strikes the reflecting surface obliquely. If $\sin\theta \geq n_s/n_w$ (n_s is the refractive index of the liquid), the reflection is total for nonabsorbing liquids. In regions of absorption the totality is attenuated by an amount dependent on n, k, and θ; by the choice of suitable incident angles conditions can be found for which R is extremely sensitive to small changes in n and k. This is the basis of the ATR method, originally proposed by Fahrenfort[9] and developed by Fahrenfort and Visser[10] for the determination of optical constants. In practice the radiation is directed onto the liquid film through a contacted layer of high refractive index material such as AgCl, germanium, or KRS-5. As with Simon's original reflection method,[33] it is necessary to make measurements at two angles so that n and k can be found by the solution of a pair of simultaneous equations for R in terms of n and k. A number of variants may be used as discussed by Fahrenfort;[32,43] these are mainly explicit expressions that apply to parallel and perpendicular plane-polarized radiation. The most detailed studies of optical-constant and band-shape measurements on liquids using the ATR technique have been made by Irons and Thompson[11] and by Crawford and coworkers.[12–14] These investigators have studied several organic liquids. Some typical results are shown in Table I and compared with those obtained by simple reflection.

Clifford and Crawford[14] pointed out that since the ATR method yields good n and k data throughout the absorption band, the observed intensity ordinates can be corrected for internal dielectric effects that may distort the vibrational spectra of liquids. By application of the Lorentz–Lorenz formula and Maxwell's equations they obtain a local susceptibility

---

(32) For succinct accounts of the relevant dispersion theory, see (a) J. Fahrenfort in "Infrared Spectroscopy and Molecular Structure," M. Davies, Ed., Elsevier, New York, N. Y., 1963, Chapter XI; (b) N. J. Harrick, "Internal Reflection Spectroscopy," Interscience, New York, N. Y., 1967, Chapters II and III.

(33) I. Simon, *J. Opt. Soc. Amer.*, **41**, 336 (1951).

(34) T. S. Robinson, *Proc. Phys. Soc., London, Sect. B*, **65**, 910 (1952).

(35) T. S. Robinson and W. C. Price, *ibid., Sect. B*, **66**, 969 (1953).

(36) The amplitude of the wave reflected from an absorbing medium is complex; the modulus $|r| = \sqrt{R}$; likewise $|t| = \sqrt{T}$ (*cf.* eq 13). Note also that both R and T are functions of the angle of polarization relative to the plane of incidence. For further elaboration see p 385 of ref 32a.

(37) P. N. Schatz, S. Maeda, J. L. Hollenberg, and D. A. Dows, *J. Chem. Phys.*, **34**, 175 (1961).

(38) P. N. Schatz, S. Maeda, and K. Kozima, *ibid.*, **38**, 2658 (1963).

(39) D. W. Barnes and P. N. Schatz, *ibid.*, **38**, 2662 (1963).

(40) M. Cameo, Thesis, University of Paris; *Th. Sc. Phys. Paris, Ser. A*, 4411, No. 5259 (1964).

(41) M. Cameo and J. Vincent-Geisse *C. R. Acad. Sci.*, **252**, 1579 (1961).

(42) V. S. Libov and N. G. Bakhshiev, *Opt. Spectrosc.* (*USSR*), **16**, 122 (1964).

(43) J. Fahrenfort in "Molecular Spectroscopy," Institute of Petroleum, London, 1968.

Table I

Selected Optical Constant Data for Organic Liquids[a]

Substance	ν_{max}, *cm*$^{-1}$	n_{min}	n_{max}	k_{max}	*Intensity (A), cm mol*$^{-1}$ × *10*^{6}	*Method*	*Ref*
CCl_4	786	0.465	1.753	1.48[b]	52.2	ATR	*c*
	763.5	1.481	2.250	1.27			
	786	0.465	1.721	1.349[b]	46.6	ATR	*d*
	762	1.557	2.252	0.915			
	784	0.49	1.63	1.28	63	Simple refl	*e*
	762	1.48	2.10	0.95			
	786	0.508	1.594	1.182[b]	46.0	Simple refl	*f*
	762	1.457	1.991	0.859			
CD_3I	656	1.488	1.517	0.032	0.53	ATR	*g*
	493	1.488	1.528	0.031	0.137	ATR	*g*
$CHBr_3$	1142.5			0.35	7.0	ATR	*c*
	656			1.11	18.9	ATR	*c*
	653.5	0.965	1.96	0.81	16.0	Simple refl	*e*
$CHCl_3$	1215			0.20	2.9	ATR	*c*
	757.5			1.46	30.0	ATR	*c*
	762	0.637	2.246	1.364	28.6	ATR	*d*
	755	0.74	2.23	1.22	33.0	Simple refl	*e*
sym-CH_2Br_2	1245			0.05	1.49	ATR	*c*
	1135			0.13	4.6	ATR	*c*
	713			0.50[b]	10.4	ATR	*c*
	701			0.33			
CH_3I	884	1.479	1.527	0.050	1.74	ATR	*h*
	522	1.472	1.526	0.053	0.38	ATR	*h*
CH_3NO_2	1557	0.98	1.60	0.60	35.0	Simple refl	*e*
CS_2	1510	0.730	2.663	1.472	74.1	ATR	*i*
	1504.5	0.81	2.20	1.20	84.0	Simple refl	*e*
	1508.5	0.697	2.307	1.314	77.1	Simple refl	*f*
	391	1.336	1.770	0.80	1.29	ATR	*c*
C_6F_6	1528	0.532	2.346	1.654	69.2	ATR	*j*
	1018	0.745	1.358	0.756[b]	48.6	ATR	*j*
	994	1.192	2.179	1.080			
	315	1.315	1.437	0.134	0.36	ATR	*j*
C_6H_5Br	733	1.19	1.78	0.65	12.5	Simple refl	*e*
$C_6H_5CH_3$	727	1.14	1.65	0.56	9.5	Simple refl	*e*
C_6H_5Cl	739	1.12	1.79	0.66	11.5	Simple refl	*e*
C_6H_5CN	727	1.20	1.61	0.42	9.0	Simple refl	*e*
C_6H_5F	750	1.03	1.73	0.70	10.0	Simple refl	*e*
C_6H_5I	729	1.33	1.81	0.52	13.5	Simple refl	*e*
$C_6H_5NH_2$	750	1.24	1.66	0.49	13.0	Simple refl	*e*
$C_6H_5OCH_3$	752	1.27	1.74	0.53	12.0	Simple refl	*e*
C_6H_6	1036	1.433	1.499	0.070	1.5	ATR	*c*
	1035	1.417	1.487	0.069	1.54	ATR	*d*
	673.5	0.777	2.161	1.55	14.6	ATR	*c*
	674.5	0.084	2.429	1.345	14.2	ATR	*d*
	670	0.825	1.91	1.02	14.5	Simple refl	*e*
$SiCl_4$	605.5	0.33	2.99	2.49	90.0	Simple refl	*e*

[a] This table is not exhaustive; some additional data are included in ref 11. [b] Overlapping doublet. [c] Irons and Thompson, ref 11. [d] Gilby, Burr, Krueger, and Crawford, ref 13. [e] Cameo, ref 40. [f] Barnes and Schatz, ref 39. [g] Fujiyama and Crawford, ref 48. [h] Favelukes, Clifford, and Crawford, ref 47. [i] W. C. Krueger, Ph.D. Thesis, University of Minnesota, 1966. [j] Fujiyama and Crawford, ref 46.

(C'') defined by eq 11; this varies with the wavenumber in a similar manner to k. From C'' a dielectrically corrected absorption ordinate (k_0) can be calculated.

$$C'' = \frac{9nk}{2\pi(n^2 - k^2 + 2) + 4n^2k^2} \qquad (11)$$

$$k_0 = 2\pi C'' \qquad (12)$$

Comparison of k and k_0 suggests that the bands may become significantly more symmetric and Lorentzian after this dielectric correction has been applied.

At present it is not clear, either experimentally or theoretically, if the transformation from k to k_0 is necessarily advantageous, and there are well-recognized limitations to the Lorentz model.[44,45] In some cases (*e.g.*, the 1528-cm^{-1} band of C_6F_6) the band is markedly asymmetric when plotted as k but it becomes symmetric and Lorentzian after transformation to k_0.[46] In other cases the effect of the transformation is

---

(44) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).

(45) N. G. Bakhshiev, O. P. Girin, and V. S. Libov, *Opt. Spectrosc. (USSR)*, **14**, 395 (1963).

(46) T. Fujiyama and B. Crawford, *J. Phys. Chem.*, **72**, 2174 (1968).

ambiguous; for the weaker bands of CH_3I, replacement of k by k_0 has no effect on the shape, though it diminishes the integrated intensity by more than 25%.[47,48] Further work is needed to establish whether or not this correction will necessarily lead to a fuller understanding of the significance of the dielectric effect in the liquid state. Crawford and collaborators are currently using these techniques to obtain optical constant data for a variety of liquids and are analyzing their results in terms of time correlation functions to gain information about the molecular motion in the liquid. Discussion of this aspect of their work will be deferred until we deal with band-shape analysis, and we shall first examine the ATR method in greater detail since it will undoubtedly play an important part in the future development of the subject.

The high sensitivity of the ATR method is achieved at some expense; one requirement is that the two angles of incidence be known to better than 10′ of arc and that the radiation beam striking the reflecting surface be collimated better than this. These exacting instrumental tolerances can be achieved with care, but the selection of the two optimal angles is more difficult. The best experimental angles of incidence can be computed and are usually just below and just above the critical angle. However, they vary considerably with k and therefore must be selected differently in the wings, on the steeper slopes, and around the peak of the band; for weak bands they may in some cases be separated by only a few degrees and $\mathrm{d}R/\mathrm{d}\theta$ can become extremely large.[43] If this is so, very small errors in the measurement of the angle can produce a large error in k. For strong bands the critical angle itself may change considerably in the region of the peak. It is often necessary to generate the n and k curves in several overlapping sections, measured at different angle pairs, and this may result in apparent discontinuities of the resultant n and k spectra.

Because of these exacting goniometric requirements large errors can occur if the radiation beam is not accurately collimated at the reflecting surface for all incident angles. The usual beam convergence with conventional infrared source optics is 8–10°, and some modification of the optical system must be made to reduce this. In the apparatus used by Irons and Thompson[11] the beam is collimated and the parallel beam directed normally on one face of a prism of highly refractive material cut in the form of an isosceles triangle; the reflecting liquid film is contacted with the prism base; prisms of AgCl, Ge, and KRS-5 are used. Crawford uses the hemicylinder optical system first described by Fahrenfort.[9] This only functions effectively if the beam is correctly focused at a prescribed distance in front of the hemicylinder, and this adjustment is critical. This is not the place to enter into further discussion of these optical alignment and focusing problems, but they do bear seriously on the duplication of measurements made in different laboratories and they take on increasing importance as more accurate n and k data are demanded to keep abreast of developments on the theoretical side.

D. THIN-FILM TRANSMISSION MEASUREMENTS

Notwithstanding these technical difficulties, the stimulating results flowing from the use of the ATR technique have prompted some authors to consider that ATR offers the only practical approach to the determination of precise absorption measurements for strongly absorbing liquids in the infrared.[49,50] Unquestionably, ATR is the most sensitive reflection-based technique and has the advantage of providing n and k values from two separate but interactive sets of experiments without resort to Kramers–Kronig transforms that necessitate the measurements covering the whole relevant spectral range. It would be premature, however, to assume that methods based on conventional transmission measurements must be summarily rejected. There are inherent advantages to the transmission approach if the problems associated with the construction of thin cells of known and reproducible path length can be overcome. The need for elaborate angle-measuring devices, along with the attendant problems of calibration and beam collimation, are eliminated and it becomes feasible to make the measurements on unmodified commercially available infrared spectrophotometers.

In addition to the purely technical problem of thin cell construction, the transmission method is beset by the need to correct for interference and reflection loss distortion within the film. It was first shown by Yasumi[51] that reflection loss distortion could significantly affect the apparent absorption intensity for transmission through films in the 1–5-μm thickness range.[52]

Maeda and Schatz[19] calculated the intensity errors for a range of Lorentzian bands under various experimental conditions, and later established a relationship between the true and apparent absorption curves in terms of a power series in l/λ, where l is the film thickness and λ the wavelength.[53] Their treatment was rigorous in the limiting case of zero thickness, but complicated correction terms were needed if l exceeded 0.5 μm. In the same paper they outlined a general method of calculating n and k from the transmission data. By analogy with eq 10, the phase shift on transmission, θ_T, can be related by eq 13 to the transmittance (T), where $|t|$

$$\theta_T = -2\nu_0/\pi \int_0^\infty \frac{n|t|}{\nu^2 - \nu_0^2}\mathrm{d}\nu + 2\pi\nu_0 l \qquad (13)$$

is the modulus of the amplitude of the observed transmission.[35] If T is known over the whole relevant spectral region, the integral can be evaluated at each wavenumber and the spectrum of θ_T determined. From the Fresnel-based equations relating T and θ_T to the optical constants, the latter may be obtained as the solution of two simultaneous equations.

---

(47) C. E. Favelukes, A. A. Clifford, and B. Crawford, *J. Phys. Chem.*, 72, 962 (1968).

(48) T. Fujiyama and B. Crawford, *ibid.*, 73, 4040 (1969).

(49) T. Fujiyama, J. Herrin, and B. Crawford, *Appl. Spectrosc.*, in press.

(50) P. A. Wilks, *ibid.*, 23, 63 (1969).

(51) Y. Yasumi, *Bull. Chem. Soc. Jap.*, 28, 489 (1955).

(52) The effects we are discussing are not relevant to measurements made on dilute solutions which constitute the bulk of contemporary quantitative infrared analysis. There it is customary for the path length to exceed 100 μm and to correct for gross reflections at the cell surfaces by placing a "matched" compensating cell containing the solvent in the reference path of the double-beam spectrophotometer. Only under exceptional conditions will the refractive index of the solvent and dilute solution differ sufficiently to influence the accuracy of the measurement, bearing in mind that the precision of the infrared spectrophotometers in current general use is rarely better than ±1% *T*. With newer infrared spectrometers now becoming available, especially when these are coupled with computer analysis of the digitally recorded data, it may be possible to improve the accuracy of the measurements to ±0.1% *T*. It could then become necessary to reexamine the use of the "matched" compensation cell technique, and possibly apply computed Fresnel corrections.

(53) S. Maeda, G. Thyagarajan, and P. N. Schatz, *J. Chem. Phys.*, 39, 3474 (1963).

This technique is analogous to Robinson and Price's reflection method[34,35] and was applied by Schatz and coworkers[54] to published data on the transmission of a solid film of CS_2 deposited on an AgCl plate.[55] Since the experimental data only covered a single absorption band, rather than the complete electromagnetic spectrum theoretically required by eq 13, the contribution of all other absorption was estimated. An empirical method was devised for this and it was possible to transpose the published absorption coefficient curve to corrected n and k spectra. The same type of calculation ought to be possible for liquids if suitable modifications are made for the effect of the second transparent window. However, applications of the Robinson and Price type of transmission technique have been thwarted by the difficulty of obtaining uniform liquid films in the range 0.5–5.0 μm. A cell suitable for this purpose has recently been designed in our laboratory[18] and its application is currently being investigated. Our method of calculation differs from that of Schatz and coworkers. Instead of relating the phase shift to the transmittance amplitude and solving two simultaneous equations for both optical constants, we currently use a Kramers–Kronig transform to derive n from k

$$n = 2/\pi \int_0^\infty \frac{\nu k}{\nu^2 - \nu_0^2} d\nu + \bar{n} \tag{14}$$

where $\bar{n}$ is a mean refractive index term for contributions from other bands. This can be estimated by extrapolation of the wings of the n–$\bar{n}$ spectrum or obtained experimentally by measuring the interference fringe spacings in the wings, using a thicker cell. An iterative procedure is used to obtain the reflection loss correction and the algorithm converges to a set of "true" n and k data that generate a computed k_a curve matching the experimental one. Provided the experimental conditions are suitably chosen, the reflection loss distortion is less than has been implied by previous workers, and the experimentally observed k_a curve obtained by application of eq 3 and 4 to the transmittance data is an adequate first approximation and can be refined in three or four cycles to a constant solution.

The effect of the reflection distortion on the peak height and integrated intensity are shown for some calculated curves in Figures 1 and 2. A window material of refractive index 1.5 is assumed (comparable with KBr), the film thickness range is 0.1–6.4 μm, and the peak height range is 0.1–1.5. The errors are expressed as percentages of the true values. It is seen that the integrated intensity errors do not exceed -3%, while the error in $k_{\max}$ ranges from -10 to 10%. These calculations presume that the mean refractive index of the liquid ($\bar{n}$) is 1.5 and the refractive index of the window material is about the same. This is an important consideration; if the index of the window material is increased to 2.0 (*cf.* AgCl), the errors in both $k_{\max}$ and the integrated intensity can exceed 20%. This is intuitively reasonable, since the greater the refractive index difference between the window and the liquid, the greater will be the proportion of reflected radiation.

Once the optical constants of a few standard bands can be unequivocally established, the peak transmittance at any film thickness can be computed using any window material of known refractive index. The mean thickness of any cell may then be determined by calibration with one of the standard liquids. Our calculations indicate that the transmission measurements are not significantly affected by a beam convergence of 8–10° or by a moderate degree of nonparallelism of the cell spacing. The situation differs from ATR in that the angles of incidence are always near zero. There remain problems associated with the evaluation of the mean refractive index in the absorbing region ($\bar{n}$ of eq 14), and at present it appears that k can be evaluated more precisely from the measured k_a than can n. For the purposes concerning us in the latter part of this paper, however, knowledge of k is the more important. Both for the ATR and transmission techniques it is necessary that electronic computing facilities be available and the data logging is much facilitated if the spectrophotometer is provided with digital readout on paper tape or magnetic tape.[7,56]

III. Band-Shape Analysis

The contours of the infrared absorption band envelopes of liquids can be discussed at two levels. First it may suffice to record the shape of the band in quantitative terms having a statistical though not necessarily an evident physical meaning. More fundamentally it is desirable to interpret such statistical parameters on a physicochemical basis.

A. STATISTICAL BAND-SHAPE MEASUREMENTS

Until recently it was considered that the significant information about an absorption band could be defined by three parameters: the peak wavenumber (ν_0), the peak height ($k_{\max}$), and the band width at half maximal intensity ($\Delta\nu_{1/2}$). If the band envelope can be specified by a Cauchy (*i.e.*, Lorentz) function[57] (eq 15) or by a Gauss function (eq 16), three parameters serve to define the intensity at all points on the curve

$$k_c(\nu) = \frac{a}{b_c^2 + (\nu - \nu_0)^2} \tag{15}$$

$$k_g(\nu) = \frac{a}{b_g^2} \exp\left(-\frac{\ln 2}{b_g^2}(\nu - \nu_0)^2\right) \tag{16}$$

where $a/b^2 = k_{\max}$ and $2b = \Delta\nu_{1/2}$.

For computational purposes it is convenient to generalize these equations in the form

$$k_c(\nu) = \frac{x_1}{1 + x_3^2(\nu - x_2)^2} \tag{17}$$

$$k_g(\nu) = x_1 \exp(-x_4^2(\nu - x_2)^2) \tag{18}$$

where x_1 is the peak height, x_2 the peak wavenumber, $x_3 = b_c^{-1}$, and $x_4^2 = (\ln 2)/b_g^2$.

Theoretical considerations[6] lead to the expectation that the bands of liquids are essentially Lorentzian; in practice, very few bands conform closely to this, and various Gaussian perturbations of the Cauchy profile have been suggested. These include the Voigt convolution[6,58] and the Cauchy–

---

(54) K. Kozima, W. Suëtaka, and P. N. Schatz, *J. Opt. Soc. Amer.*, **56**, 181 (1966).

(55) H. Yamada and W. B. Person, *J. Chem. Phys.*, **40**, 309 (1964).

(56) R. N. Jones, *J. Jap. Chem.*, **21**, 609 (1967).

(57) The term "Cauchy function" is preferable to "Lorentz function" when dealing with the purely statistical behavior of the band envelope since "Lorentz" implies that the band originates in a damped harmonic oscillator and so carries a physicochemical implication.

(58) W. Voigt, *Münch. Ber.*, 603 (1912).

Gauss product and sum functions[59–61] (eq 19 and 20). In eq

$$k_p(\nu) = x_1(1 + x_3^2(\nu - x_2)^2)^{-1} \exp(-x_4^2(\nu - x_2)^2) \quad (19)$$

$$k_s(\nu) = x_1(1 + x_3^2(\nu - x_2)^2)^{-1} + x_5 \exp(-x_4^2(\nu - x_2)^2) \quad (20)$$

20 x_1 is the peak height of the Cauchy component and x_5 is the peak height of the Gauss component.

Computer programs to optimize the fit of these functions to experimental curves are available[62] and by this means multiple overlapping band systems containing 15–20 components have been fitted within the noise level of the experimental spectrum.[7,59,60] Crawford and coworkers have used both a graphical[14] and a least-squares method[47] to check the validity of the Lorentz model with their ATR data for various liquids. In many cases the fit was acceptable, especially for dielectrically corrected curves, but they did not quantify the degree of misfit. Where the Lorentz model was grossly inapplicable they performed a Fourier transformation and examined the time correlation curves.

It is not reasonable to expect that all band profiles can be represented by such combinations of Cauchy and Gauss functions, and it is desirable to have a more general method to quantify the shape, preferably one independent of any specific mathematical model. For this purpose Jones and coworkers[63] have used the truncated moments of the absorption curve

$$\mu_r(j) = \frac{1}{b^r} \frac{\int_{-j}^{+j} (\nu - \nu_0)^r k \, d\nu}{\int_{-j}^{+j} k \, d\nu} \quad (21)$$

with $r = 2, 3, 4, \ldots$. Such moments are scaled in abscissal units of j, where $j = (\nu - \nu_0)/b$. These are dimensionless numbers, and all bands conforming to the same mathematical shape will possess identical moment characteristics irrespective of their peak height or half-band width. It is a property of Cauchy, Gauss, and all symmetric functions that the odd moments are zero. For asymmetric bands $\mu_3(j)$ and its variation with j are quantitative measures of the asymmetry. The values of $\mu_2(j)$ for the Cauchy and Gauss functions are shown in Figure 3. The truncated moments provide a graphical description of the accumulation of band area outward from the center. No attempt has yet been made to interpret these quantities in terms of molecular properties; nevertheless, they are most useful for quantifying subtle differences in band profiles and for relating unusual band shapes to different mathematical models. In this respect they are considerably more sensitive than time correlation functions. Jones and coworkers[6,63] have used them to describe bands in the spectra of anthracene, perylene, and *p*-chlorobenzonitrile. Shimozawa and Wilson[64] have calculated and discussed $\mu_2(j)$ and $\mu_4(j)$ for the C–H out-of-plane bending band of 1,2,4,5-tetrachlorobenzene which is highly symmetric, well isolated, and which it might be appropriate to consider as a possible intensity standard.

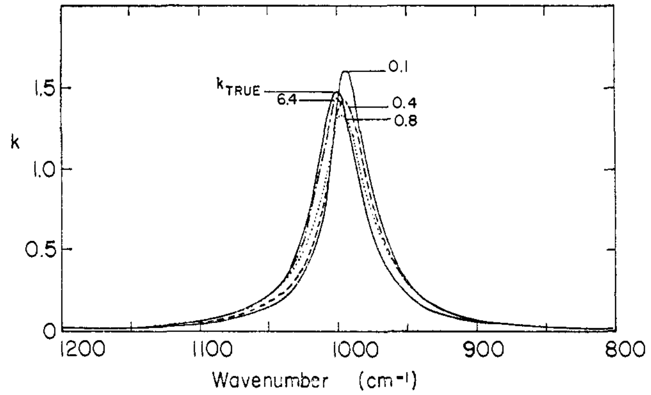

Figure 1. Effects of reflection loss distortion on a simulated Lorentzian absorption band. The refractive index of the window material is 1.5: $k_{max} = 1.5$, $\Delta\nu_{1/2} = 10$ cm^{-1}, $\nu_0 = 1000$ cm^{-1}; the cell thicknesses (μm) are indicated on the curves.

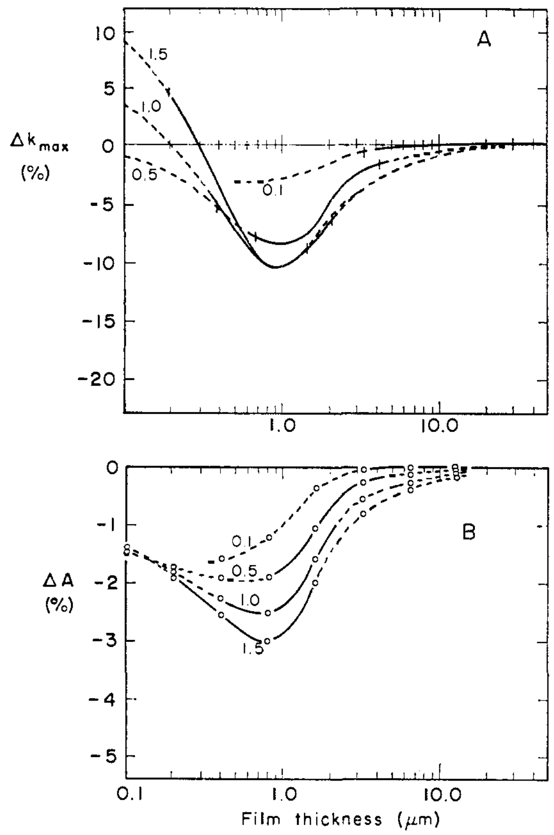

Figure 2. Reflection loss distortion errors at various film thicknesses and peak intensities: (A) error (%) in k_{max}, (B) error (%) in integrated absorption intensity. The values of k_{max} are indicated on the curves. Solid lines indicate experimentally attainable regions.

Figures 4 and 5 illustrate the use of truncated moments to quantify the interference and reflection loss distortion introduced in a Cauchy band when measured by transmission through films ranging in thickness from 0.1 to 6.4 μm, in a cell with windows of refractive index 1.5. These are computed curves generated by application of the Fresnel equations. The difference spectra ($k - k_a$) are shown in Figure 4, while $\mu_2(j)$ and $\mu_3(j)$ are given in Figure 5. The parameters of the model Cauchy curve were chosen to be comparable in intensity and half-band width with the strongest absorption

---

(59) J. Pitha and R. N. Jones, *Can. Spectrosc.*, **11**, 14 (1966).

(60) J. Pitha and R. N. Jones, *Can. J. Chem.*, **44**, 3031 (1966).

(61) J. Pitha and R. N. Jones, *ibid.*, **45**, 2347 (1967).

(62) R. N. Jones, *et al.*, *NRC* (*Nat. Res. Counc. Can.*) *Bull.*, No. 11 (1968); No. 12 (1968); No. 13 (1969).

(63) R. N. Jones, K. S. Seshadri, N. B. W. Jonathan, and J. W. Hopkins, *Can. J. Chem.*, **41**, 750 (1963).

(64) J. T. Shimozawa and M. K. Wilson, *Spectrochim. Acta*, **22**, 1591 (1966).

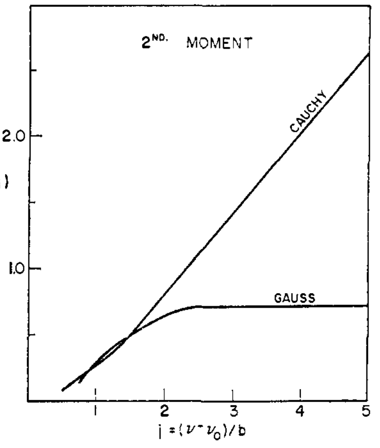

Figure 3. Truncated second moments of Cauchy and Gauss curves.

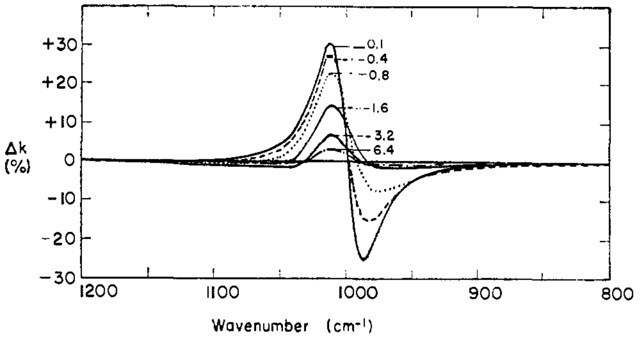

Figure 4. Difference curves ($k - k_a$ expressed as % k) for the curves of Figure 1; the cell thicknesses (μm) are indicated.

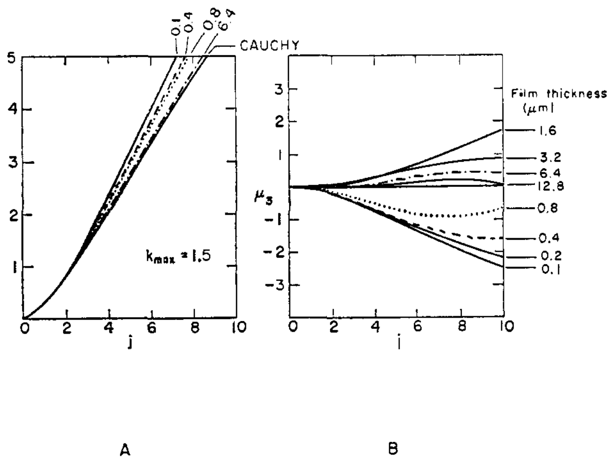

Figure 5. Second and third truncated moments of the curves of Figure 1.

bands of C_6H_6, C_6F_6, $CHCl_3$, and CS_2. It can be inferred from the $\mu_2(j)$ plots of Figure 5A that the reflection loss distortion does not seriously disturb the band shape, bearing in mind that the significant experimental thickness range is 0.5–5 μm. The distortion is only beginning to be appreciable beyond three half-band widths from the center. In considering the difference curves in Figure 4, it should be noted that although the positive and negative lobes may reach 20%, this, in itself, only indicates a wavenumber shift of the whole band, provided the two lobes are congruent. It represents the aspect of the distortion noted by Young and Hannah.[20] It is the behavior of $\mu_3(j)$ in Figure 5B that provides a sensitive and quantitative description of the change in magnitude and asymmetry of the apparent absorption curves as a function of the film thickness. This is seen to be highly complex especially in the thickness range between 0.4 and 1.6 μm.

The truncated second moment curves in Figure 6 illustrate the effect of introducing a Gauss perturbation into a Cauchy band, using the product and sum functions in Figures 6A and 6B, respectively. It is seen that the effect of small Gauss components is much greater for the product than the sum function. This is because the Gauss curve approaches zero intensity at about 3.5 half-widths from the peak; therefore any function that is multiplied by it will behave likewise. The Cauchy function on the other hand falls more slowly and the addition of Gauss components has a lesser effect on the total area. In fitting experimental curves with either type of Cauchy–Gauss function inspection of the truncated second moment plot is helpful in selecting appropriate input parameters for the curve fitting procedure.

B. FOURIER TRANSFORMATION—THE TIME CORRELATION FUNCTION

Molecules in the gas phase undergo free rotation between collisions, and information about the rotational energy levels is contained in the resolvable rotational fine structure. In liquids the situation is more complicated; the vibrational energy levels are usually diminished, producing the well-recognized negative solvent shift of the whole band system. The intermolecular potentials between neighboring molecules also damp the translational and rotational motions. The result is that the vibrational bands broaden, resolvable rotational fine structure is lost, and discrete rotational energy levels cease to exist. It has been shown, mainly by Gordon[1] and Shimizu,[2] that information about the nature of rotational and translational motion in the liquid is contained in the broadened wing contours of the vibration band. The Fourier transform of the infrared frequency spectrum yields a dipole correlation function ($\phi(t)$) that describes the averaged molecular reorientation over varying time intervals. This time correlation function constitutes the real part of the Fourier transform of the normalized frequency spectrum

$$\phi(t) = \frac{\int^{\text{band}} k(\nu) \cos 2\pi c(\nu - \nu_0)t \, d\nu}{\int^{\text{band}} k(\nu) \, d\nu} \tag{22}$$

where k is the absorption index, c the velocity of light, and t the time (sec) from any arbitrary starting time $t = 0$. For Lorentzian absorption $\phi(t)$ falls exponentially as a function of t, and a plot of log $\phi(t)$ against t is linear. This is a mathematical property of all Cauchy functions, and the rate of exponential decay (β) is directly proportional to the half-band width of the frequency curve

$$\phi(t) = \exp(-\beta t) \tag{23}$$

where $\beta = 2\pi c b_0$, in which b_0 is the semi-half-band width of the absorption curve (cm^{-1}) (eq 15). A Gauss frequency curve transforms to a Gauss time correlation function whose decay rate is directly proportional to the semi-half-band width of the frequency curve (eq 16). Representative time correlation curves for Cauchy and Gauss frequency curves are shown in Figure 7A.

To explain the meaning of the time correlation curve in physical terms, let us consider a vibrating dipole oriented in a specific direction in the liquid at an arbitrarily chosen starting time t_0. After progressively increasing time intervals the molecules will, on the average, reorient themselves, and our ability to predict the orientation of the selected dipole will decrease. During a brief initial period, free rotation, as in the gas, will determine the kinetics of the dipole rotation, and the accuracy of our statistical estimate of the directional change of our selected dipole will be governed by the inertial properties of the free molecule. After longer times the effects of disruptive collisions with neighboring molecules will take over and our prediction of the orientation of the selected dipole will be governed by molecular collision theory, as developed by Debye. On theoretical grounds, Shimizu has argued that in the initial period, before neighboring molecules have begun to affect the dipole, the time correlation function should follow a Gauss decay rate. Later, in the so-called Debye limit, the reorientation becomes essentially random and the orientation probability is characterized by an exponential decay constant and a Lorentzian frequency spectrum. Ewing has recently reviewed those aspects of this theory specifically concerned with simple systems such as hydrogen and methane dissolved in argon,[5] and the theory has been developed in more general terms for diatomic molecules by Bratož, Rios, and Guissani;[4] they have derived an expression which takes vibrational as well as rotational damping into consideration.

The form of the time correlation function observed experimentally is illustrated diagrammatically for log ϕ in Figure 7B. There is usually an initial bend or hump which later straightens into a linear slope. The hump corresponds to the Gauss part of the time correlation function and the linear part indicates where the Debye kinetics take over. Some examples of experimentally obtained curves for bands in the spectrum of methyl iodide, obtained by Crawford and coworkers,[47,48] are shown in Figure 8. From these data it is concluded that, on the average, methyl iodide molecules in the liquid state experience essentially free rotation over periods of about 0.2 psec, after which collision effects begin to randomize the motion and rotational diffusion sets in. For molecules of asymmetric shape it is possible to infer from the slopes of the correlation curves something about the relative tumbling motions about different rotational axes. Thus for C_6H_6 and C_6F_6 Fujiyama and Crawford[46] conclude that replacement of hydrogen by fluorine has little effect on the "spinning" of the molecules in the plane of the ring, but the facility to "flip" is diminished by a factor of 3. These effects are conveniently described in terms of rotational diffusion constants (D_x, D_y, D_z).

Cabana, Bardoux, and Chamberland[65] have made similar studies of CH_4 and CD_4 in the liquid state and in dilute solution in Ar, Kr, and Xe. Here also rotational diffusion predominates after about 0.2 psec and substitution of H by D slows the diffusion rates. Fujiyama and Crawford found this isotope effect also for CD_3I in comparison with CH_3I. Other solution studies have been made by Shimozawa and Wilson[64] and by Rothschild.[66]

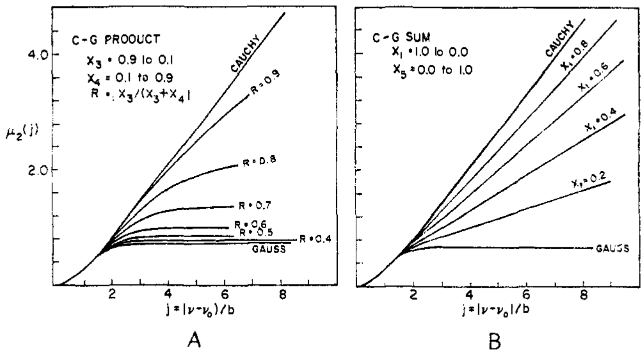

Figure 6. Second and third truncated moments of Cauchy–Gauss product and Cauchy–Gauss sum functions.

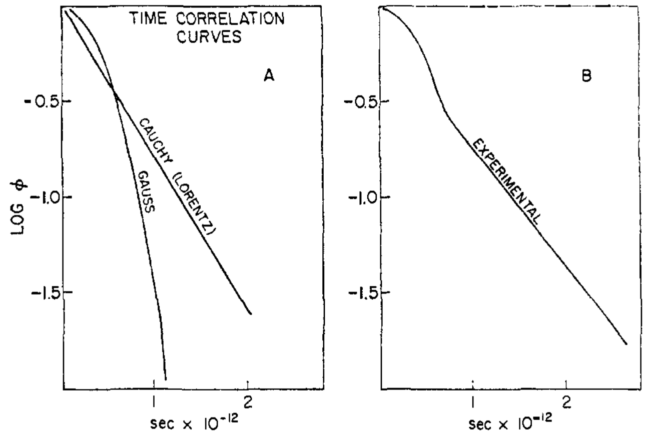

Figure 7. Time correlation curves (log ϕ): (A) Cauchy and Gauss absorption curves, (B) experimental curve (diagrammatic).

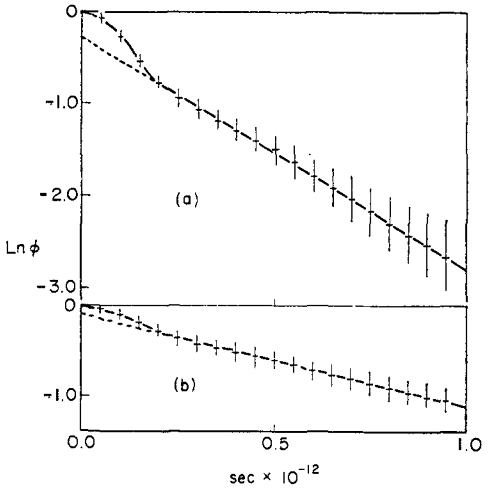

Figure 8. Time correlation curves (ln ϕ) for liquid methyl iodide: (a) perpendicular band at 884 cm^{-1}; (b) parallel band at 522 cm^{-1}. The vertical lines indicate the experimental uncertainty (from the data of Favelukes, Clifford, and Crawford.[47])

With hindsight it is not difficult to relate the kinetic picture derived from the time correlation curves with the observations on the Cauchy–Gauss sum function fits to the absorption bands. The sum of two Fourier transforms is identical with the Fourier transform of the sum of the two energy do-

---

[65] A. Cabana, R. Bardoux, and A. Chamberland, *Can. J. Chem.*, 47, 2915 (1969).

[66] W. G. Rothschild, *J. Chem. Phys.*, 49, 2250 (1968).

main component curves. The rotational diffusion is defined by the half-band width of the linear portion of the log ϕ–time correlation curve; this corresponds to the Cauchy component of the absorption band and can therefore be obtained from x_3 of eq 20 since $\beta = 2\pi c b_c = 2\pi c/x_3$. The time at which the rotational diffusion becomes the principle factor in the kinetics corresponds to the time on the correlation curve abscissa where the Gauss component falls to zero, and this may be related to the semi-half-band width (b_g) of the Gauss component of the sum curve in the energy spectrum. It is not appropriate to pursue these speculations further here, but an analysis of the shapes of time correlation curves of Cauchy–Gauss sum functions currently in progress in our laboratory is consistent with these concepts.

IV. Conclusion

The study of infrared band shapes of liquids and solutions is one facet of the developing interest of theoreticians in the nature of the liquid state. The concept of the time correlation function is being applied to other measurements of the properties of liquids, particularly proton magnetic resonance spectroscopy, electron spin resonance spectroscopy, neutron diffraction spectroscopy, and light scattering. It has had a major impact on the experimentalist by shifting his attention from the exact location of peak positions to the wing areas of the bands, and in so doing has generated a new set of technical problems. In some respects we appear to be entering a phase in the study of liquid-state physics comparable with that which revolutionized solid-state physics over a decade ago. The infrared spectroscopists have so far concentrated their attention on a few selected bands of simple molecules. It would clearly be of interest to organic chemists to have detailed knowledge of the manner in which more complex and asymmetric molecules tumble about in the liquid state; in particular one would like to be able to recognize under what conditions nonrandom factors prevail, as these could have important effects on liquid-state kinetics and on such properties as diffusion, viscous flow, and enzyme activity.

In a final word of caution it must be pointed out that in his preoccupation with optical constants and time correlation curves the infrared spectroscopist must not forget that the wings of infrared absorption bands are also influenced by factors of an entirely different nature. These include weak underlying combination bands, hot bands, and displaced bands arising from molecules containing nondominant isotopic species. As the precision of the measurements improve, these effects will take on increasing significance, and their contributions to the overall band shape will have to be assessed and, if necessary, corrected before attempts are made to relate the band contour to the internal structure of the liquid.

Even granted that the "true" kinetically significant band contour can be obtained, current emphasis on the reorientation mechanism as the exclusive band-broadening process may need reevaluation. The attribution of intermolecular interaction in liquid systems to reorientation originates with Sobelman[67] in 1953; it has the merit of presenting a mechanistic picture which can be readily grasped, since the rotational dynamics can be expressed with sufficient approximation in classical terms.[4] An opposite extreme is provided by the rotationally static "cavity" model of liquid systems proposed by Onsagar[44] and developed largely by Buckingham.[68] This has been most helpful in predicting and explaining the displacements of the whole band system (solvent shifts) in terms of the dielectric changes induced by neighboring molecules. It has been less informative about the effects on the band contours. The recent theory of Bratoz and coworkers achieves a formal synthesis of these diverse viewpoints; the Buckingham equations and the Gordon–Shimizu equations emerge as special cases.

We may well need to look to more sophisticated models of liquid systems later, but for the present, the experimental difficulties of generating meaningful spectra are a more serious limitation than inadequate theory and it is this aspect of the problem that we have wished to emphasize in this review.

Acknowledgment. In conclusion we wish to express our thanks to several people with whom we have had the benefit of stimulating discussions. These include H. J. Bernstein, S. Bratoz, A. Cabana, B. L. Crawford, T. Fujiyama, R. G. Gordon, W. J. Orville-Thomas, H. Shimizu, and Mme. J. Vincent-Geisse. We also wish to acknowledge the help of our colleagues in our own laboratory whose major contributions are acknowledged in the reference cited to their works; to these we would add D. Escolar and P. Neelakantan who have recently joined our group. With them we include also our able technicians R. Lauzon, Mrs. M. A. MacKenzie, and A. Nadeau.

---

(67) I. I. Sobelman, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **57**, 554 (1953).

(68) A. D. Buckingham, *Proc. Roy. Soc., Ser. A*, **248**, 169 (1958); **255**, 32 (1960); *Trans. Faraday Soc.*, **56**, 753 (1960).