

# INFRARED INTENSITIES IN CONDENSED PHASES

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## INTRODUCTION

In this paper we wish to bring together, not a total review of all the work which has been done on liquid-phase infrared intensities, but rather a review of the development of our own studies and interpretations in this area. We choose this approach partly because reasonably recent overall reviews of the quite large amount of work done on liquid-phase infrared intensities can be found elsewhere<sup>1</sup> and chiefly because the present position with regard to such studies, as we see it, can be set forth most economically if we confine ourselves to the work of our own laboratory.

Our interest, like that of other workers, arose from previous work on gas-phase intensities<sup>2</sup> and the interesting molecular information deducible from such measurements. In the gas-phase, one can measure the Beer-Lambert law parameter  $\alpha$ :

$$\ln(I_0/I) = \alpha l \quad (1)$$

where  $I_0$  and  $I$  are the incident and transmitted intensities and  $l$  is the cell thickness or optical path length; and one can integrate this parameter over a band to obtain an integrated intensity directly related to a molecular property:

$$\Gamma_i = (1/c_m) \int \alpha d \ln \nu = (N\pi/3c^2 \nu_i) (\partial p/\partial Q_i)^2 \quad (2)$$

where  $c_m$  is the molar concentration of the gas and  $(\partial p/\partial Q_i)$  is the molecular dipole-moment change with the normal coordinate  $Q_i$ ; the other symbols have their usual meaning.

## THE EXPERIMENTAL TECHNIQUE

To extend such studies into the liquid phase requires, first, a method of experimental study capable of inspiring confidence, and second, a similarly convincing theoretical model giving some such relation as equation (2). In this paper we do not wish to stress the experimental methods; after reviewing and studying the various techniques which had been used, we adopted as our choice the ATR method developed by Fahrenfort<sup>3</sup>. Its greatest advantage in our opinion is that it enables us to deal cleanly with the fact that a liquid, in contrast to a gas, has *two* optical constants which affect its light transmission: refractive index in the usual sense, and absorption. We write these combined constants in the form of a complex refractive index

$$\hat{n} = n + ik \quad (3)$$

and we refer to  $n$  as the refractive index and to  $k$  as the extinction coefficient.

The relation to the usual Lambert-law parameter is

$$\alpha = 4\pi\omega k \tag{4}$$

where  $\omega$  is the wave-number of the radiation *in vacuo*.

In the ATR method the situation depicted in *Figure 1* is set up: incident light being sent through a transparent medium of high refractive index,  $n_1$ ,

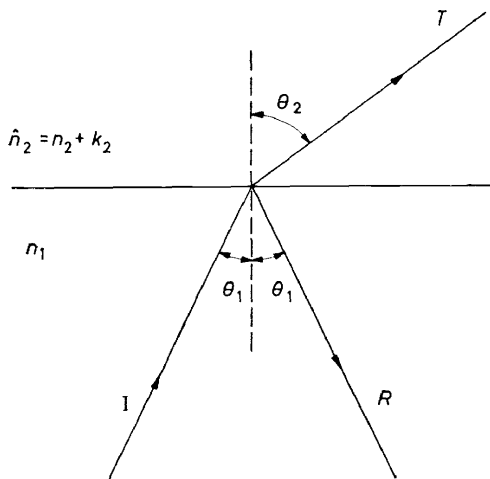


Figure 1. Optical path of rays at interface

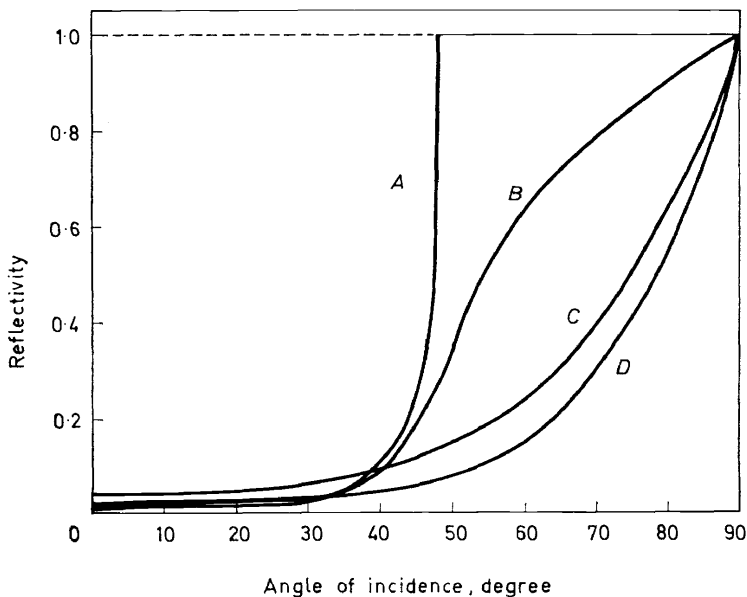


Figure 2. Reflectivity against angle of incidence. All curves refer to  $n_2 = 1.45$ , Curves A and B refer to internal reflection,  $n_1 = 1.95$ ; for A,  $k_2 = 0$ , for B,  $k_2 = 0.35$ . Curves C and D refer to external reflection,  $n_1 = 1.0$ ; for C,  $k_2 = 0.35$ , for D,  $k_2 = 0$

such as KRS-5 or germanium is reflected from the interface of that medium with the liquid sample whose complex refractive index is  $\hat{n}_2$ . As is well known and as is shown in *Figure 2*, the reflectance varies with the angle of incidence,  $\theta$ ; where the second medium is transparent there exists a critical angle,  $\theta_c$ , above which total reflection occurs; if the liquid absorbs, this total reflection is attenuated. At any angle, for an absorbing liquid, the reflectance is affected both by the refractive index  $n_2$  and by the extinction coefficient  $k_2$ , the former dominating at low angles and the latter at high angles of incidence. Spectra run in this way, giving for a fixed chosen angle reflectance as a function of frequency, can be very useful in ways similar to conventional infrared absorption spectra<sup>4</sup>.

In our application for determining liquid optical constants, we run the reflectance spectrum at two or more angles; thus at each frequency we have the data needed to determine<sup>5</sup> simultaneously *both* constants  $n_2$  and  $k_2$ . We cannot too strongly reiterate the importance of thus having *both* constants available; it has enabled us to use the relations between these two, such as the Kramers-Kronig relation, to check the quality of our data rather than to complete information needed; it has freed us from relying on models such as the classical damped harmonic oscillator and thus permitted us to examine other models in the interpretation of our data<sup>2, 3</sup>.

### FIRST SIMPLE INTERPRETATIONS

Our initial efforts, having available an experimental technique in which we had confidence, were directed towards certain well-known bands which had been studied by others—the 670  $\text{cm}^{-1}$  and 1035  $\text{cm}^{-1}$  bands of benzene, the 760  $\text{cm}^{-1}$  band of chloroform, and the 770  $\text{cm}^{-1}$  doublet of carbon tetrachloride<sup>6</sup>. Having these data, we were then at the point where we wished to interpret them; and for this one needs to construct models which may be tested.

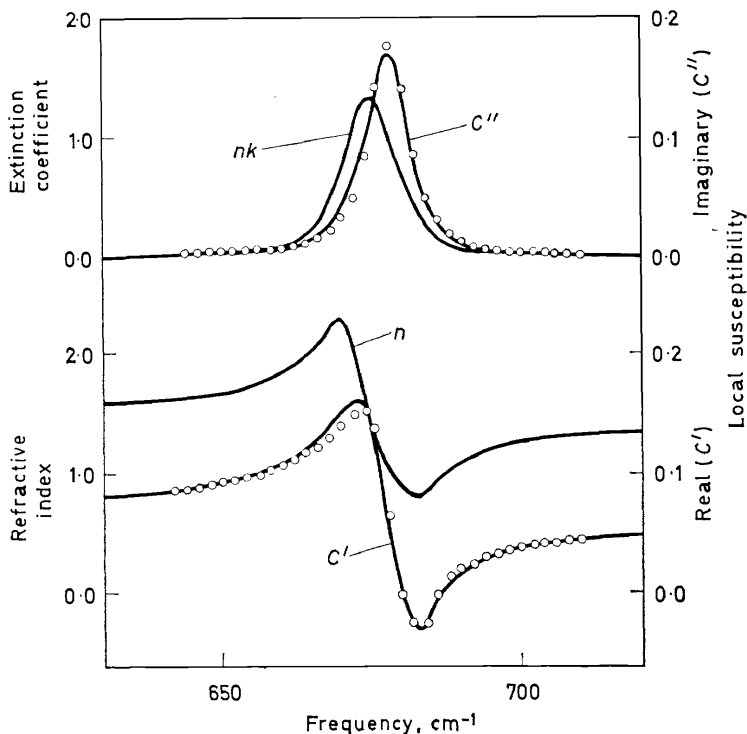
If we confine ourselves to molecular liquids, not too strongly associated (as we do in this review), the question of interpretation can be separated into two parts. First, the general non-specific effect of the liquid-phase environment on the individual molecule—the *dielectric effect*—must be taken into account. There has been much discussion as to the proper way to do this; let us simply say that to date we have been reasonably happy with the first approximation which is represented by the Lorentz-Lorenz correction<sup>7</sup>. We do not feel that it is absolutely 'correct'; all we wish to report is that so far the dielectric correction made in this way has been apparently good enough to permit us to proceed to further interpretation. Later, we may wish to attempt to improve the Lorentz-Lorenz model, and possession of both  $n$  and  $k$  at each frequency would permit such work. We stress that we have found it important and indeed essential, for achieving any understanding of the intermolecular effects, to be able to make the dielectric correction in a point-by-point manner at each frequency.

The Lorentz-Lorenz model allows us to compute the 'local susceptibility' relating the polarization of the dielectric to the *local* field felt by the molecule; we have denoted this local susceptibility by  $\hat{C}$  ( $= C' + iC''$ ), calculating it from the macroscopic or observed complex susceptibility (which can of

BRYCE CRAWFORD, Jr., A. C. GILBY, A. A. CLIFFORD and T. FUJIYAMA  
 course be calculated from  $n$  and  $k$ ) by the equation

$$(1/\hat{C}) = C 1/\hat{\chi} - (4\pi/3). \quad (5)$$

As the curves in *Figure 3* show for the benzene 670  $\text{cm}^{-1}$  band, the real and



*Figure 3.* Optical constants  $n$  and  $k$  and local susceptibilities  $C'$  and  $C''$  for the 670  $\text{cm}^{-1}$  band of benzene. The circles are calculated points from the VVW model

imaginary parts  $C'$  and  $C''$  are very much of the nature of  $n$  and  $k$  respectively, and can be thought of as 'dielectrically corrected' values for these constants. Indeed a simple scale adjustment to  $C''$  gives a 'corrected extinction coefficient',  $k_0$ , which can be directly compared to  $k$ .

Application of the dielectric correction permits one to progress to the chemically more interesting *second part* of interpretation; how does the molecule respond to the local field it feels? We seek the analogue of equation (2) which for a gas-phase molecule relates its electromagnetic interaction to molecular properties; but while the gas-phase molecular model underlying that equation is quite straightforward, the appropriate model for the liquid-phase molecule is not so apparent. As a simple one to try for the 'well-known' bands, we considered the Lorentz collision model of an oscillator whose resonance response to the field was damped by collisions with neighbours. In the modified form due to Van Vleck and Weisskopf, this model gives the

response function, in terms of the local susceptibility,

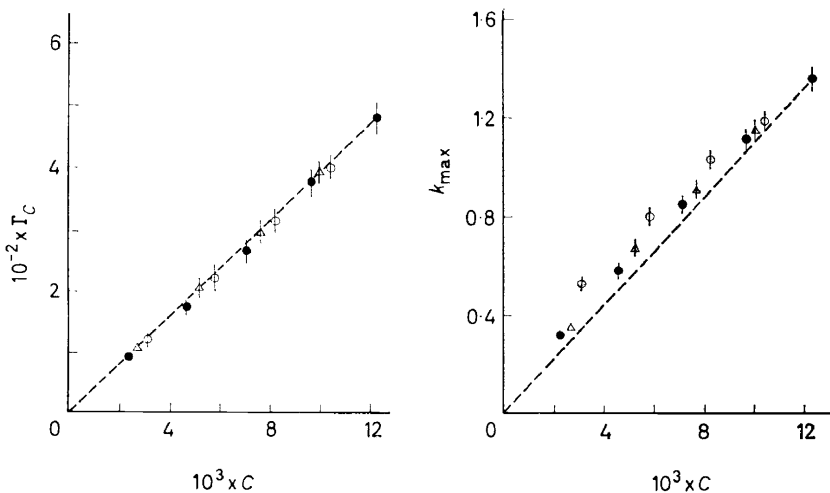
$$\hat{C} = S \left[ \frac{\omega_0 - i\gamma}{(\omega_0 - \omega) - i\gamma} + \frac{\omega_0 + i\gamma}{(\omega_0 + \omega) + i\gamma} \right] \quad (6)$$

where  $S$  is the oscillator strength factor,  $\omega_0$  is the oscillator frequency expressed as a wavenumber,  $\omega$  the vacuum wavenumber of the radiation, and  $\gamma$  the damping constant which is related to the collision frequency or relaxation time.  $S$  is related to the transition dipole-moment element<sup>7</sup>. This function also produces the *Lorentzian shape* for the extinction coefficient through an absorption band.

In this first application of this simple model to the 'well-known' bands we were pleased and a bit surprised to find that they fit rather well; for the benzene 670  $\text{cm}^{-1}$  band *Figure 3* shows how the points calculated from the VVW model lie well along the observed curves for  $C'$  and  $C''$ .

### SOME SOLUTION APPLICATIONS

Encouraged by the way in which these shapes of well-known bands conformed to a comfortably simple model, we next sought to examine the application of this (LL + VVW) model to solutions, and to find what if any intensity quantity actually obeyed Beer's law. To this end we examined solutions of benzene, chloroform, carbon tetrachloride, and carbon disulphide in each other and in acetone<sup>8</sup>. *Figure 4* shows the Beer's-law plots for the chloroform 760  $\text{cm}^{-1}$  band in benzene, carbon disulphide, and acetone; it is apparent that the usual intensity parameter  $k_{\text{max}}$ , the extinction coefficient at the band maximum, does not follow Beer's law, while the integrated intensity (based on  $C''$  or  $k_0$ ) does. We found also that the (LL + VVW) model fits rather well; particularly notable was the effect of the dielectric



*Figure 4.* Beer's-law plots for the 760  $\text{cm}^{-1}$   $\text{CHCl}_3$  band in benzene (solid circles),  $\text{CS}_2$  (open circles), and acetone (triangles). Left side, integrated intensity  $T_C$ ; right side, peak extinction coefficients  $k_{\text{max}}$ . Vertical lines indicate standard error

correction in changing the rather highly asymmetric carbon disulphide band into a pleasingly symmetric Lorentzian shape.

### MOLECULAR MOTIONS IN LIQUIDS

In spite of such successes, we felt it unlikely that *all* bands would conform to the Lorentzian shape when the dielectric correction was made; and in view of the previous interpretations of certain methyl halide bands in terms of persistence of rotation in the condensed phase, these seemed good examples to study. Accordingly we examined<sup>9, 10</sup> the  $\nu_3(a_1)$  parallel and  $\nu_6(e)$  perpendicular bands of  $\text{CH}_3\text{I}$  at 520 and 885  $\text{cm}^{-1}$  and of  $\text{CD}_3\text{I}$  at 492 and 656  $\text{cm}^{-1}$ . As we had hoped, significant deviations from the Lorentzian shape did occur, and more noticeably in the perpendicular bands. The deviations which were most clearly shown and most valuable in further interpretation were those *in the wings of the bands*—precisely those portions where our method gives its most accurate values.

In seeking a better description of the molecular motion, which would clarify the deviation from the simple random collision of the VVW model, we made use of the time-correlation function as recently discussed by Gordon<sup>11</sup>. This function  $a(t)$ , may be calculated by the Fourier inversion of a spectral density for which we take the dielectrically corrected  $C''$  or  $k_0$  in a rather simplified pictorial way,  $a(t)$  may be thought of as giving an average value for the cosine of the angle between the transition-moment

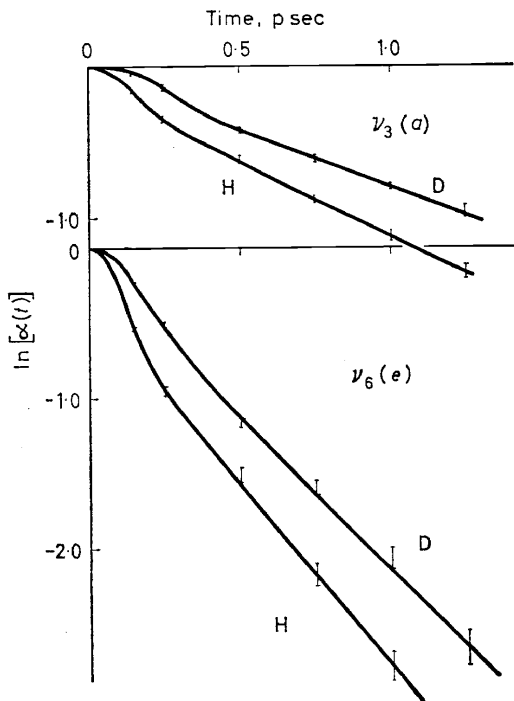


Figure 5. Time-correlation function for methyl iodide bands. Upper half, parallel bands  $\nu_3(a_1)$ ; lower half, perpendicular bands  $\nu_6(e)$ . H and D refer to  $\text{CH}_3\text{I}$  and  $\text{CD}_3\text{I}$  respectively

vector at a given moment and the same vector  $t$  seconds later. It thus describes the averaged rotational motion of the molecule. *Figure 5* shows these time-correlation functions for the four bands studied. If the rotational motion is purely stochastic (as would be implied by the collision model) these functions should fall off strictly exponentially with time, and the logarithmic plots of *Figure 5* would give straight lines. We see that indeed the longer-time correlations are stochastic, but that the shorter-time parts of the curves (which are largely determined by points from the wings of the bands) exhibit non-random implications.

In order to characterize the rotational motion of these methyl halides further, we used our data to calculate, according to the equations of Favro<sup>12</sup>, the rotational diffusion constants  $D_z$  about the symmetry axis and  $D_x$  about an axis perpendicular to it. These values are given in *Table 1*. It is beyond

*Table 1.* Rotational diffusion constants for methyl iodides

	CH <sub>3</sub> I	CD <sub>3</sub> I
$D_z$	1.94	1.71
$D_x$	0.48	0.33

our purpose here to interpret these values, but they suffice to show that such quantitative characterization of rotational motion in liquids can be determined from infrared optical constants sufficiently carefully determined and corrected for the dielectric effect.

### INTEGRATED INTENSITIES

In seeking to understand and to demonstrate the information which integrated intensities from liquid-phase spectra might give, we were helped by the suggestion from Prof. W. Person that C<sub>6</sub>F<sub>6</sub> might provide a good example. Its gas-phase spectra and integrated intensities had been studied, and there were reasons to suggest that, aside from the dielectric effect, the liquid-phase intensities should be the same (except for band-shape factors) as those of the gas-phase; i.e., that intermolecular force or 'chemical' effects should be negligible. Accordingly we studied the 1527 cm<sup>-1</sup> strong band, the 1020-993 cm<sup>-1</sup> doublet, and the 315 cm<sup>-1</sup> weak band<sup>10</sup>.

*Figure 6* shows the uncorrected  $n$  and  $k$  (continuous line) and dielectrically corrected  $k_0$  (broken line) of the 1527 cm<sup>-1</sup> band as functions of frequency. We can see the decrease in intensity on the lower frequency side and the increase in intensity on the higher frequency side following the elimination of the dielectric field effect, resulting in the removal of the asymmetry observed in the  $k$  curve, in the frequency shift of the absorption maximum to the higher frequency, and in the decrease of the integrated intensity. The resultant  $k_0$  curve becomes fairly symmetric in shape and is fitted well by the VVW model.

The most striking effect of the dielectric field on the intensity curve of the absorption band is illustrated in *Figure 7*. The intensity of the lower-frequency band of the Fermi-doublet at 1020 and 993 cm<sup>-1</sup> is seen to be stronger in the  $k$  curve (continuous line), while in the  $k_0$  curve the reverse situation

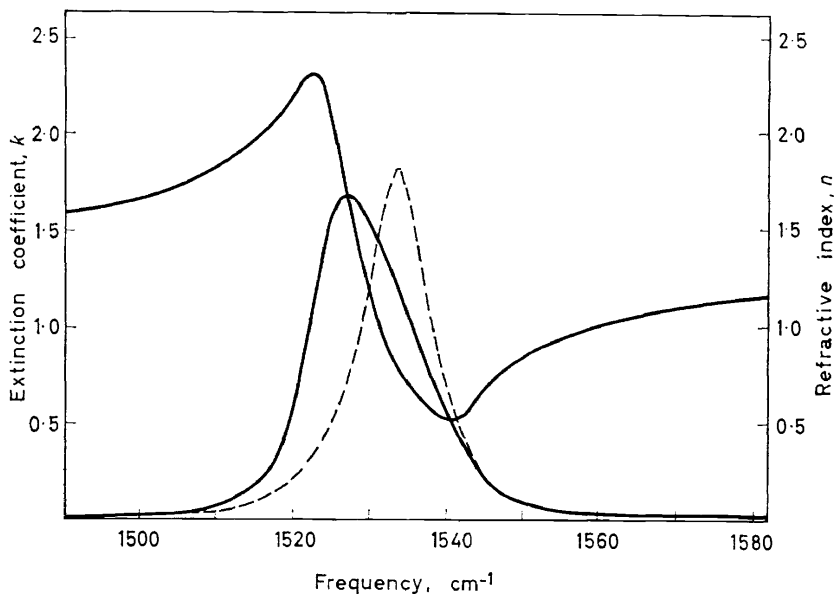


Figure 6. Uncorrected  $n$  and  $k$  (solid curves) and corrected  $k_0$  (broken curve) for  $1527\text{ cm}^{-1}$  band of hexafluorobenzene

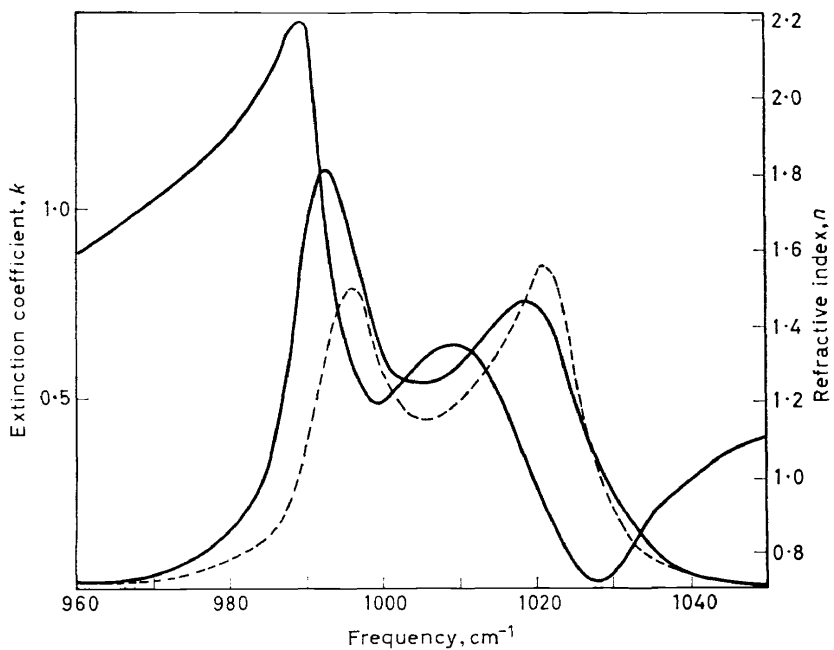


Figure 7. Uncorrected  $n$  and  $k$  (solid curves) and corrected  $k_0$  (broken curve) for  $990\text{--}1020\text{ cm}^{-1}$  doublet of hexafluorobenzene

holds, as it does in the gas phase. The result lends strong support to the application of the Lorentz-Lorenz field in the evaluation of the local field.

These examples show clearly the general nature of the dielectric field effect in 'distorting' the absorption spectrum: the increase of the extinction coefficients in one region and the decrease in another region, due to the fact that the refractive index of a substance varies rapidly in the neighbourhood of an absorption band; where the refractive index is large the observed extinction coefficient is larger than the 'true' extinction coefficient and vice versa. In the case of weak bands the dielectric-field effect is comparatively small because the oscillation in the refractive index is smaller for a weaker band. In fact, the intensity changes due to the dielectric field were observed to be rather small for the weak band at  $315\text{ cm}^{-1}$ .

The end effect to the integrated intensity, however, always tends to increase the apparent value. In *Table 2* the final integrated intensities of liquid hexafluorobenzene are compared with those of the gas-phase<sup>13</sup>. We

*Table 2.* Integrated intensities for  $\text{C}_6\text{F}_6$ , in darks

<i>Frequency</i>	<i>Liquid</i>		<i>Gas</i>
990	$\Gamma_k$	$48,596 \pm 3500$	—
1020	$\Gamma_{k0}$	$39,705$	$40,800 \pm 3000$
1527	$\Gamma_k$	$69,216 \pm 3000$	—
	$\Gamma_{k0}$	$56,175$	$54,600 \pm 4000$
315	$\Gamma_k$	$356 \pm 30$	—
	$\Gamma_{k0}$	$298$	$326$

see the amazingly good agreement between the gas-phase data and the liquid-phase data corrected for the dielectric field effect. In this table,  $\Gamma_k$  are based on the uncorrected  $k$  value;  $\Gamma_{k0}$  on the corrected ones.

### INTERMOLECULAR FORCES

Our observation that the integrated intensity of the  $760\text{ cm}^{-1}$  band of chloroform showed no 'solvent effect' enhancement in acetone solution (as indeed is shown by the straight-line behaviour in *Figure 4*) led us to realize that such data could be used to determine the local effects of intermolecular forces on the different parts of a molecule. This band involves motions perpendicular to the symmetry axis, and hence perpendicular to the line of the hydrogen bond formed with the acetone molecule, and for this reason is not sensitive to the solvent. The parallel vibrations, on the other hand, as of course had been previously observed, do show considerable intensity enhancement as between gas or inert-solution spectra and acetone-solution spectra.

We have therefore studied the parallel bands of chloroform and chloroform-d in the pure relatively unassociated liquid and in acetone solution; and we have found, as expected, great enhancement of the CH stretching vibration intensity and lesser enhancements of the other parallel bands. While it goes beyond our purpose here to give a full discussion of these results (to be published elsewhere<sup>10</sup>), it has been possible to make the dielectric correction and, using normal-coordinate analysis, to deduce from the intensities and their enhancements the different effects of the intermolecular force on the

different bonds of the chloroform molecule. The dipole-moment derivative with respect to the CH bond symmetry coordinate, for example, is more strongly affected than that with respect to the other two  $a_1$  symmetry coordinates.

### SUMMARY

Our studies have led us to believe that much of the difficulty in the observation of liquid-phase intensities, and likewise in the interpretation of both intensities and band shapes, lies in insufficient attention to the effects of the dielectric constant and its oscillation through the band. We have found that if both  $n$  and  $k$  are obtained as accurately as possible at every point in a band, it is possible to apply an appropriate point-by-point correction. The simple Lorentz-Lorenz approximation seems to be amazingly good at least for the class of liquids we have studied. In this way we have been able in appropriate examples studied to date to achieve some satisfactory understanding of band shapes, of the rotational motion of molecules in liquids, of the relation of integrated intensities between gas and liquid phases, and of the localized effects of intermolecular forces.

*We acknowledge with appreciation the contributions of other members of our laboratory group to the work reported here, particularly John Burr and W. T. Krueger. We profited also from discussion with Dr. J. Bass and Mr. R. Frech, and particularly Prof. J. Overend. Prof. W. Person pointed out to us the advantages of hexafluorobenzene as a molecule to study. Finally, we are most grateful to the National Science Foundation for its financial support of this programme.*

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