

Variation of the Intensity of Infrared Bands of Chloroform and Acetone with Temperature

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Intensities of i.r. bands at 1213 cm^{-1} in chloroform (ν_4) and at 1087 cm^{-1} in acetone (ν_{22}) are measured at temperatures between 170 and 300 K using different spectrophotometers (one with pre-sample chopping). The chloroform band is approximately independent of temperature but the acetone band has a negative temperature coefficient. These results are independent of the type of spectrophotometer used. The implications of these results and related data in the literature are discussed in connection with the use of i.r. intensity measurements at different temperatures for the determination of thermodynamic parameters.

WE have reported¹⁻⁴ enthalpy (ΔH^0) and in some cases entropy (ΔS^0) differences between conformers in a variety of saturated and unsaturated carbonyl compounds. These determinations were based on the measurement of the intensity of i.r. bands at different temperatures using various methods and assumptions which have been set out in detail.³ The critical factor is often whether the absorption coefficients for two or more bands have the same temperature coefficient⁵ or a zero temperature coefficient.⁶ To some extent the validity of these assumptions may be tested. Nevertheless it is desirable to have a better understanding of the

factors which govern the variation of peak and integrated absorbance values with temperature.

A number of limited studies of intensity temperature coefficients of the i.r. spectra of organic molecules in the liquid phase have been reported;⁷⁻¹⁷ these have often related to neat liquids measured over a limited range of temperatures above ambient. The conclusion is^{12,14,18} that both peak and integrated absorbance values increase linearly with decreasing temperature, as the result of intermolecular interactions from collisional processes. The temperature coefficients appear to be very dependent upon the particular vibrational

¹ A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc. (B)*, 1969, 810.

² A. J. Bowles, W. O. George, and D. B. Cunliffe-Jones, *J. Chem. Soc. (B)*, 1970, 1070.

³ W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 400.

⁴ W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 1029.

⁵ S. Mizushima, T. Shimanouchi, K. Kuratani, and T. Miyazawa, *J. Amer. Chem. Soc.*, 1952, **74**, 1378.

⁶ K. O. Hartman, G. L. Carlson, E. R. Witkowski, and W. G. Fateley, *Spectrochim. Acta*, 1968, **24A**, 157.

⁷ E. J. Slowinski and G. C. Claver, *J. Optical Soc. Amer.*, 1955, **45**, 396.

⁸ R. A. Hughes, R. J. Martin, and N. D. Coggeshall, *J. Chem. Phys.*, 1956, **24**, 489.

⁹ U. Liddel and E. D. Becker, *J. Chem. Phys.*, 1956, **25**, 172.

¹⁰ G. Dijkstra, *Spectrochim. Acta*, 1957, **11**, 618.

¹¹ P. A. Bazhulin and V. N. Smirnov, *Optics and Spectroscopy*, 1959, **6**, 485.

¹² M. P. Lisitsa, V. P. Malinko, and I. N. Khalimonova, *Optics and Spectroscopy*, 1959, **7**, 386.

¹³ M. P. Lisitsa and Y. P. Tsyashchenko, *Optics and Spectroscopy*, 1960, **9**, 99.

¹⁴ M. P. Lisitsa and Y. P. Tsyashchenko, *Optics and Spectroscopy*, 1960, **9**, 229.

¹⁵ M. P. Lisitsa and I. N. Khalimonova, *Optics and Spectroscopy*, 1961, **11**, 179.

¹⁶ A. W. Baker, H. O. Kerlinger, and A. T. Shulgin, *Spectrochim. Acta*, 1964, **20**, 1467.

¹⁷ Y. E. Zabiyaikin and N. G. Bakhshiev, *Optics and Spectroscopy*, 1969, **26**, 38.

¹⁸ N. G. Bakhshiev and Y. E. Zabiyaikin, *Optics and Spectroscopy*, 1969, **27**, 221.

mode^{11,14,15} but, from the limited evidence available, similar results are obtained for solutions.¹⁷

The enthalpy and entropy difference measurements on the series of carbonyl compounds¹⁻⁴ were made in dilute solution in carbon disulphide over a range of temperatures from ambient to *ca.* 170 K; it therefore seemed appropriate to make careful measurements of the temperature coefficients of intensity of a few well-defined bands of organic compounds, for which conformational changes cannot occur, under these conditions. This also provided the opportunity to assess another factor which may lead to errors in quantitative measurements of this type, namely the radiation loss from the spectrometer detector to the sample when the former is at a higher temperature than the latter. Mierzecki¹⁹ has given a method for calculating the magnitude of this effect but the recent development of spectrometers in which the radiation is chopped before and after passage through the sample provides the means for a direct measurement of the effect.

EXPERIMENTAL

The spectra run on a Perkin-Elmer 457 i.r. spectrometer were obtained with the previously reported conditions.³ Measurements on a Perkin-Elmer 180 instrument, in which the radiation is chopped before and after passage through the sample, were also made at a resolution of *ca.* 2 cm⁻¹. Preliminary studies had shown that the peak and integrated absorbance values were substantially independent of resolving power under these conditions.

Analar reagent grade samples of chloroform and acetone were used as solutions in carbon disulphide at concentrations of *ca.* 0.2% v/v and 3.0% v/v respectively. The absorbance values at the band maxima and the integrated absorbances were measured from tangent base lines, a simple procedure in the absence of overlap with adjacent bands. A correction was applied for the change in density of the solvent with temperature.

RESULTS AND DISCUSSION

Chloroform.—Peak absorbance measurements on the 1213 cm⁻¹ (ν_4) band of chloroform are given in the Table. The intensity is substantially independent of temperature over the interval 170–300 K with, perhaps, a slight decrease at the extreme lower end of the range. The fact that this result is obtained on both instruments shows that there is no measurable error resulting from the detector reradiating to the sample in the case of the Perkin-Elmer 457 instrument. The integrated absorbance of this band is slightly temperature dependent and varies linearly over the range studied, decreasing by 6.5% over the interval 300–170 K. This decrease with decreasing temperature was anticipated in view of the substantial independence of peak height with temperature and the known decrease in half-width with decreasing temperature.

Acetone.—In contrast, the intensity of the 1087 cm⁻¹ (ν_{22}) band of acetone is markedly temperature dependent.

¹⁹ R. Mierzecki, *Acta Physica Polonica*, 1964, **25**, 813.

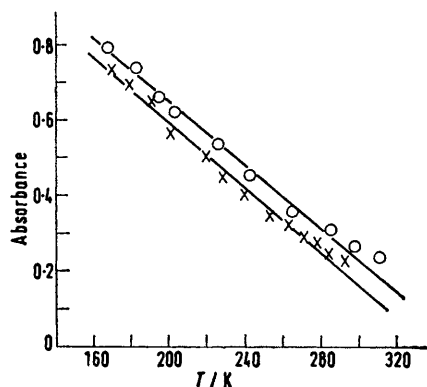
²⁰ E. D. Schmid, F. Langenbucher, and H. W. Wilson, *Spectrochim. Acta*, 1963, **19**, 835.

Peak absorbance values as a function of temperature are shown in the Figure. The photometric scales of the

Peak absorbance measurements on the 1213 cm⁻¹ band of chloroform in solution in carbon disulphide, at various temperatures

| Instrument | | | |
|------------|------------|--------|------------|
| PE 180 | | PE 457 | |
| T/K | Absorbance | T/K | Absorbance |
| 308 | 0.219 | 298 | 0.229 |
| 300 | 0.217 | 281 | 0.232 |
| 291 | 0.220 | 270 | 0.239 |
| 282 | 0.222 | 256 | 0.245 |
| 268 | 0.222 | 243 | 0.244 |
| 242 | 0.224 | 226 | 0.241 |
| 230 | 0.226 | 212 | 0.241 |
| 217 | 0.221 | 197 | 0.236 |
| 203 | 0.220 | 186 | 0.228 |
| 190 | 0.220 | 178 | 0.231 |
| 180 | 0.213 | | |
| 170 | 0.213 | | |

two spectrometers were not standardised and the work of Schmid *et al.*²⁰ and of Shimozawa and Wilson²¹ has shown that errors of up to 10% are to be expected when



Peak height, absorbance of the 1087 cm⁻¹ band (ν_{22}) in acetone at 3% v/v in 0.5 mm path length at different temperatures: ×, PE 457, ○, PE 180

both peak and integrated absorbance values from two instruments are compared, unless careful precautions are taken.²² For present purposes the slopes of the two lines are of primary interest and these are found to be -0.00397 ± 0.00013 K⁻¹ and -0.00421 ± 0.00013 K⁻¹ for the PE180 and PE457 instruments respectively. Hence the difference is not significant. This conclusion is also drawn from the integrated absorbance measurements. These vary linearly with temperature and the slopes are -0.00576 ± 0.00024 K⁻¹ and -0.00552 ± 0.00025 K⁻¹ for the PE180 and PE457 instruments respectively. Hence, radiation from the detector, at ambient temperature, to the cold sample produces a negligible error in the intensity measurements, even for temperature differences of 130 K.

This result is not surprising in the light of the calculations of Mierzecki.¹⁹ He tabulated values of the Planck

²¹ J. T. Shimozawa and M. K. Wilson, *Spectrochim. Acta*, 1966, **22**, 1591.

²² R. T. C. Brownlee, D. G. Cameron, B. Ternai, and R. D. Topsom, *Appl. Spectroscopy*, 1971, **25**, 564.

factor $\nu^3[\exp(h\nu/kT)]^{-1}$, which determines the energy transfer when there is a temperature difference between the cell and the detector, for various values of ν and T . With $T = 370$ K the emission reaches a maximum in the interval $\nu = 700\text{--}800$ cm^{-1} and it drops to *ca.* 600 cm^{-1} for $T = 300$ K and is lower in intensity by a factor of two. At $T = 300$ K the emission at 1200 cm^{-1} is smaller by a factor of two than at *ca.* 600 cm^{-1} . The emission from an absorbing species is dependent upon the absorbance being measured and Mierzecki has calculated the relevant corrections for a number of cases. For example, measurements on a bromobenzene solution at 370 K gave absorbance values of 0.304, 1.110, 1.240, and 0.608 respectively for the bands at 902, 1022, 1067, and 1445 cm^{-1} and the calculated corrections are 3, 8.5, 8.5, and 2.6%. This variation reflects both the change in ν and the absorbance of the band being measured. In the present work ν has been 1087 or 1213 cm^{-1} and T *ca.* 300 K and the absorbance of the bands measured has not exceeded 0.8 and has usually been appreciably smaller. In these circumstances the correction will never exceed about 2% and, as has been found, will not be observed when comparisons are made between measurements on instruments with single and double chopping systems. Hence, ΔH^0 and ΔS^0 measurements of the type recently reported¹⁻⁴ will not be in error on this account, although this might not be true if the temperature range used lay significantly above ambient.

General Implications.—The limitations imposed upon ΔH^0 and ΔS^0 measurements by the assumptions involved in the methods of Mizushima *et al.*⁵ and Hartman *et al.*⁶ are clearly more difficult to assess. The present results, although adding to the hitherto limited knowledge of the intensity temperature coefficients, are certainly too sparse for general conclusions to be drawn. The difference in behaviour between ν_4 of chloroform, whose intensity is substantially independent of temperature, and ν_{22} of acetone, for which the peak absorbance increases by a factor of three between ambient temperature and 175 K would, in itself, be of less significance if it were possible to discern correlations between groups of compounds or to understand the reason for the difference in temperature coefficients between the various modes of a particular molecule. Unfortunately this is not the case at present. One possibility is that the increase in intensity with decreasing temperature which we observe in acetone and generally in other carbonyl compounds^{3,4} is associated with components of the band arising from sum and difference combinations. These may be associated with upper torsional levels associated with the methyl groups. These torsions are normally anharmonic and the population of the torsional levels is markedly temperature dependent.

The results of Bazhulin and Smirnov¹¹ show that in the case of chloroform, measured as a neat liquid, the integrated intensity of ν_1 increases by the factor 1.97 for a decrease in temperature of 100 K whereas the corresponding figures for ν_5 and ν_4 are 1.17 and 1.00 respectively. These results were confirmed qualitatively

by Lisitsa and Tsyashchenko,¹⁴ although there are differences in their temperature coefficients. These latter workers also examined liquid bromoform¹³ and found that ν_4 has the largest temperature coefficient, approximately twice that of ν_1 and ν_5 . Hence, the corresponding vibrational modes in structurally similar molecules show differing behaviours. On the other hand Lisitsa and Khalimonova¹⁵ have found an identical behaviour in the case of the aromatic C-H stretching bands of chlorobenzene and bromobenzene. It is therefore impossible to generalise, although X-H stretching modes usually have appreciable temperature coefficients.^{8,9,16}

The only results previously reported for acetone are those of Bazhulin and Smirnov¹¹ for the neat liquid. Integrated intensity ratios were obtained for a temperature change of 100 K for $\nu_3(1.14)$, $\nu_{17}(1.28)$, $\nu_{18}(1.09)$, and $\nu_{22}(1.47)$. Thus, the four bands have significant and different temperature coefficients. The intensity ratio method for expressing the results is only useful for comparative purposes if the two temperatures are given. In the case of the Russian workers these appear to have been 293 and 193 K and the corresponding ratio or ν_{22} from the present measurements, in CS_2 solution, is 1.40.

The essential similarity in behaviour of ν_{22} for acetone as a neat liquid and in carbon disulphide solution is in line with the results of Zabyakin and Bakhshiev¹⁷ who studied carbon disulphide, chloroform, and carbon tetrachloride in a range of solvents and compared their results with published measurements on the neat liquids. Although the temperature coefficients are mildly solvent dependent there is an essential similarity between the two states and they conclude that if the change of intensity with temperature is the result of intermolecular interactions they must be of a universal type because they are clearly very similar for solute-solvent and solute-solute interactions. Lisitsa and her co-workers had previously suggested^{12,15} interactions of this type and had noted that they would be consistent both with the fact that there is no obvious correlation with the particular vibrational mode involved and the increasing magnitude of both the peak absorbance and integrated absorbance with decreasing temperature. This latter is a consequence of the fact that the average distance between molecules in the condensed (liquid) state increases with increasing temperature and leads to a corresponding decrease in the intermolecular interaction.²³ Attempts to advance a more detailed explanation along these lines and also to account for the fact that limited work on gaseous samples⁷ has shown that the absorption intensity increases with increasing temperature have met with limited success.¹⁸

It is therefore not surprising that calculations based on simple models have also been of very limited value. Brown,²⁴ assuming a statistical distribution of collisional perturbations in the liquid phase and a Lorentzian band shape, deduced that the intensity should vary as $T^{-\frac{1}{2}}$.

²³ V. N. Smirnov and P. A. Bazhulin, *Optics and Spectroscopy*, 1959, 7, 123.

This conclusion, which is not in line with the experimental evidence, has been criticised by Lisitsa and Tsyaschenko¹⁴ on the ground that Brown's theory requires that his parameter $A = \nu_{\frac{1}{2}} D_{\max} / 4$, where $\nu_{\frac{1}{2}}$ is the band half-width and D_{\max} is the peak absorbance, shall be independent of temperature. The Russian workers pointed out that there is reasonable experimental evidence to show that A often increases with increasing temperature. They also criticise the approach of Person²⁵ who considers the change of dielectric constant with temperature as a relevant factor. His treatment is based on Onsager's theory, describing the connection between the integrated absorption of a molecule in the gaseous and liquid phases, and this is not confirmed experimentally in many instances.

Despite the inadequacies and complications of these qualitative and quantitative approaches it is clear that a simple situation prevails in practice, namely that both the peak and integrated absorbance values vary linearly with temperature, although the magnitude of the effect may be small, as in the case of the ν_4 band of chloroform. Only in the special instance of liquids at higher temperatures is there some evidence for non-linearity.^{17,26,27} This simple behaviour undoubtedly accounts for the apparent success of ΔH^0 and ΔS^0 measurements in many instances.¹⁻⁴ The linear variation of integrated absorbance with temperature is more surprising because of the variation of band width with temperature, which is usually non-linear but is often quasi-linear over a restricted range.²⁸ The fact that a similar behaviour is observed for various vibrational modes of a wide range of molecules suggests that a universal factor, such as general intermolecular interactions, predominates. Nevertheless, factors of a specific character, such as solvent viscosity,²⁹ may contribute.

In conclusion, the simple linear relation between absorbance, both peak and integrated, and temperature,

²⁴ T. L. Brown, *J. Chem. Phys.*, 1956, **24**, 1281.

²⁵ W. B. Person, *J. Chem. Phys.*, 1958, **28**, 319.

²⁶ Y. E. Zabiyaikin and N. G. Bakhshiev, *Optics and Spectroscopy*, 1968, **25**, 29.

one which seems to be almost universal on the basis of what has been reported by various workers, should enable the methods of Mizushima *et al.*⁵ and Hartman *et al.*⁶ to be used in many instances. Unfortunately, it is not possible to predict in advance of experimental studies which systems are amenable to this approach. Substantial solvent effects appear to be absent and this facilitates measurements of the type used for the present work on a range of carbonyl compounds. The present study has demonstrated the soundness of solution measurements below ambient temperature, for ΔH^0 and ΔS^0 measurements, for the following reasons. (a) Although errors arise from radiation transfer between sample and detector, when the two are at different temperatures, these are smaller the lower the sample temperature. Experimental studies and semi-quantitative estimates have shown that they are negligible under the conditions used for the measurements on various carbonyl compounds. (b) The use of carbon disulphide solutions permits a wide temperature range below ambient to be used, thereby improving the precision of the ΔH^0 and ΔS^0 measurements. (c) The bands become sharper the lower the temperature and in some instances, where there is overlap, this leads to more precise values for the integrated areas. (d) Deviations from linearity between absorbance and temperature, which are likely to lead to difficulties in the determination of ΔH^0 and ΔS^0 , will only occur at elevated temperatures. (e) Problems with the volatility of sample and solvent do not arise.

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²⁷ Y. E. Zabiyaikin and N. G. Bakhshiev, *Optics and Spectroscopy*, 1968, **25**, 525.

²⁸ Y. E. Zabiyaikin and N. G. Bakhshiev, *Optics and Spectroscopy*, 1968, **24**, 539.

²⁹ A. V. Rakov, *Optics and Spectroscopy*, 1962, **13**, 208.