Influence of Aprotic Solvents on the O–D Stretching Band of Methan[^{2}H]ol

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The O–D stretching band of methan[^{2}H]ol has been observed for 0.4M-solutions in 55 aprotic solvents, including hydrocarbons, halogeno-compounds, nitro-compounds, nitriles, ethers, ketones, esters, amines, and amides. Values of ν_{OD} for monomeric methan[^{2}H]ol have been measured as precisely as possible. Various discrepancies with earlier work are noted. The values of ν_{OD} are discussed in terms of solvent Lewis basicity, and revised values of Koppel and Palm's solvent parameter B are tabulated. Oligomer formation and the occurrence of anomalous bands in the case of certain solvents are also discussed. A more limited study was made of the O–D stretching band of t-butyl [^{2}H]alcohol.

In 1939—1941 Gordy and Stanford[1] measured the O–D stretching frequency of monomeric methan[^{2}H]ol in a variety of aprotic media and recommended using the solvent-induced shift as an approximately quantitative measure of Lewis basicity. Their results and related studies with other hydrogen-bond donor groups have been reviewed by Arnett.[2] More recently Kagiya, Sumida, and Inoue[3] have carried out more accurate and extensive work on methan[^{2}H]ol. They have suggested using the shift, $\Delta\nu_{OD}$ (cm^{-1}), relative to benzene as a measure of solvent Lewis basicity. Koppel and Palm[4] have selected the frequency for methan[^{2}H]ol in the gas phase as a more logical origin for such a scale, and have defined a Lewis basicity parameter B through equation (i), where ν^0_{OD} and ν_{OD} refer to the gas phase and a given solvent, respectively.

$$B = \nu^0_{OD} - \nu_{OD} \qquad \text{(i)}$$

Koppel and Palm[4] have made extensive use of B and parameters measuring other aspects of solvent–solute interaction for the correlation analysis of solvent effects. Chapman, Shorter, and their colleagues[5] have used $\Delta\nu_{OD}$ or B in correlating the rate coefficients for the reaction of diazodiphenylmethane with benzoic acid in aprotic solvents. In the course of this work ν_{OD} values were measured for various solvents not previously studied and measurements for other solvents have been repeated. Discrepancies with earlier work and various difficulties encountered indicated that careful examination of the O–D stretching band of methan[^{2}H]ol in a wide range of solvents was desirable. We now present the results of our study involving a wide range of aprotic solvents, including hydrocarbons, halogeno-compounds, nitro-compounds, nitriles, ethers, ketones, esters, amines, and amides. A more limited study was made of the O–D stretching bond of t-butyl [^{2}H]alcohol.

EXPERIMENTAL

Methan[^{2}H]ol and t-butyl [^{2}H]alcohol of isotopic enrichment 99% were used without further purification.

Solvents.—Good commercial samples were thoroughly purified by standard procedures.[6] These involved preliminary treatment (when necessary to remove expected acidic or basic impurities, peroxides, *etc.*), thorough drying ($CaCl_2$, K_2CO_3, Na, molecular sieve, *etc.* as appropriate), and fractional distillation (taking a narrow cut, and under reduced pressure if necessary). A few solvents were available as spectroscopic or other *puriss.* grade and were used without further purification. All solvents were examined by g.l.c. and with only rare exceptions were of purity 99.5%, and often >99.8%. No solvent of purity <99% was ever accepted. As far as possible the water content was measured by Karl Fischer titration[7] or g.l.c., and was usually *ca.* 0.02% w/v or less.

Spectroscopic Procedure.—The instrument used was a Unicam SP 100 i.r. spectrophotometer, with SP 130 grating monochromator, and the normal scan rate was 20 cm^{-1} min^{-1}. Solutions of methan[^{2}H]ol (0.4M) were examined in the wavenumber range 2 350—2 750 cm^{-1} in sealed cells of nominal thickness 0.2 mm, fitted with potassium bromide windows. The exact thickness of each cell was determined interferometrically. A variable path-length cell containing the pure solvent was placed in the reference beam of the instrument, the path-length being adjusted to compensate exactly for solvent absorption in the sample beam.

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[1] W. Gordy, *J. Chem. Phys.*, 1939, **7**, 93; 1941, **9**, 215; W. Gordy and S. C. Stanford, *ibid.*, 1940, **8**, 170; 1941, **9**, 204.

[2] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 223.

[3] T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Japan*, 1968, **41**, 767.

[4] I. A. Koppel and V. A. Palm, 'Advances in Linear Free Energy Relationships,' N. B. Chapman and J. Shorter, Plenum, London, 1972, ch. 5.

[5] (*a*) N. B. Chapman, M. R. J. Dack, and J. Shorter, *J. Chem. Soc.* (*B*), 1971, 834; (*b*) N. B. Chapman, M. R. J. Dack, D. J. Newman, J. Shorter, and R. Wilkinson, *J.C.S. Perkin II*, 1974, 962.

[6] J A. Riddick and W. B. Bunger, ' Techniques of Chemistry, vol. II, Organic Solvents,' ed. A. Weissberger, Wiley, New York, 3rd edn., 1970.

[7] W. Seaman, W. H. McComas, and G. A. Allen, *Analyt. Chem.*, 1949, **21**, 510.

The wavenumber of the maximum of the ν_{OD} band was measured with reference to the vibration–rotation spectrum of hydrogen bromide as a wavenumber calibration standard.[8] Under the conditions used, wavenumber accuracy and reproducibility were deemed to be better than ± 1 cm^{-1}. The position of the maximum of a sharp ν_{OD} peak could be measured with a precision of better than ± 2 cm^{-1}; for broader bands the precision was about ± 3 cm^{-1}.

The procedure for t-butyl [^{2}H]alcohol was similar. Some studies of 0.04M-solutions were made, by using a cell of 1 mm path-length.

RESULTS AND DISCUSSION

The original spectra for all systems studied are available as Supplementary Publication No. SUP 21 824 (111 pp., 2 microfiches).†

Before discussing our main results, the ν_{OD} values for 0.4M-solutions of methan[^{2}H]ol in 55 aprotic solvents, we dispose of several lesser matters.

Gordy and Stanford[1] chose methan[^{2}H]ol rather than methanol because many solvents of interest have absorption bands close to the ν_{OH} region, whereas few solvents absorb near ν_{OD}. This objection to methanol would be less serious in relation to a modern high-resolution spectrophotometer. Nevertheless the ν_{OD} region is less prone to interference by solvent absorptions and the preference for methan[^{2}H]ol is still justified, although precise measurements of ν_{OH} for methanol in certain solvents have been reported.[9]

Gordy and Stanford[1] used various concentrations of methan[^{2}H]ol, but Kagiya, Sumida, and Inoue[3] favoured 0.4M for the determination of $\Delta\nu_{OD}$, because ' the position of the O–D vibrational band was not clear when the concentration of methanol-d$_1$ was lower than 0.4M '. Our own results for this concentration in a number of solvents showed the presence of considerable quantities of oligomers in equilibrium with monomeric methan[^{2}H]ol. In such cases it was thought that the slightly overlapping oligomer bands might exert a small influence on the apparent position of ν_{OD} for the monomer. We therefore carried out certain experiments using 0.04M-solutions, in which the proportion of oligomers would be greatly reduced. However only very small shifts ($\leqslant 2$ cm^{-1}) occurred as between 0.4 and 0.04M in most cases, and where a significant effect was observed (3 or 4 cm^{-1}) this could not always be clearly related to the relative reduction in oligomer. For example, benzonitrile and nitrobenzene showed dilution shifts of $+4$ cm^{-1}, whereas cyclohexane and benzene showed only $+2$ cm^{-1}. Oligomer formation is, however, much more pronounced in the latter solvents than in the former. At concentrations greater than 0.4M the relative concentration of oligomer is often inconveniently high. At lower concentrations it becomes necessary to use thicker cells. Greater solvent absorption is then accompanied by a deterioration in the signal-to-noise ratio and a loss of precision in ν_{OD}. On the whole it seemed best to follow Kagiya, Sumida, and Inoue[3] in using 0.4M-solutions.

A further subsidiary investigation involved the use of t-butyl [^{2}H]alcohol. It was hoped that this might show a rather better defined ν_{OD} band than methan[^{2}H]ol because of steric hindrance reducing the tendency to form oligomers. Measurements were made on 0.4M-solutions of t-butyl [^{2}H]alcohol in twelve solvents. In the event, t-butyl [^{2}H]alcohol did indeed show a reduced half-band width for the ν_{OD} band in most solvents, but only rarely did this reduction exceed 20% of the half-band width for methan[^{2}H]ol. Furthermore, a plot of ν_{OD} values for t-butyl [^{2}H]alcohol (Table 1) *versus* the corresponding values for methan[^{2}H]ol (Table 2) showed a good linear relationship, with a gradient of

TABLE 1

Values of ν_{OD} for 0.4M-t-butyl [^{2}H]alcohol in aprotic solvents

Solvent	ν_{OD}/cm^{-1}
n-Hexane	2 673.5 ± 1
Cyclohexane	2 671 ± 2
Benzene	2 651 ± 1
Carbon tetrachloride	2 669 ± 1
Chlorobenzene	2 657 ± 1
Nitrobenzene	2 642 ± 1½
Benzonitrile	2 615 ± 1½
Dioxan	2 585 ± 1
Diethyl ketone	2 612 ± 1½
Ethyl acetate	2 618 ± 1
NN-Dimethylacetamide	2 546 ± 2
Dimethyl sulphoxide	2 544 ± 2

TABLE 2

Values of ν_{OD} for 0.4M-methan[^{2}H]ol in aprotic solvents and values of the Lewis basicity parameter, *B*

Solvent	ν_{OD} (present work)/cm^{-1}	ν_{OD} (Kagiya *et al.*)/cm^{-1}	*B* * (present work)/cm^{-1}
Hydrocarbons			
n-Hexane	2 696 ± 2	2 667	24
Cyclohexane	2 695 ± 3		25
Benzene	2 668 ± 1	2 668	52
Toluene	2 666 ± 1½	2 666	54
o-Xylene	2 661 ± 1½		59
m-Xylene	2 661 ± 1½		59
p-Xylene	2 662 ± 1½		58
Mesitylene	2 658 ± 1½		62
Halogeno-compounds			
Carbon tetrachloride	2 689 ± 1	2 689	31
Chloroform	2 681 ± 1½	2 685	39
Methylene chloride	2 677 ± 1½	2 680	43
Ethylene dichloride	2 671 ± 1½	2 666	49
Fluorobenzene	2 686 ± 2		34
Chlorobenzene	2 675 ± 1	2 670	45
Bromobenzene	2 671 ± 1½	2 669	49
Iodobenzene	2 667 ± 1½		53
o-Dichlorobenzene	2 677 ± 1½	2 679	43
m-Dichlorobenzene	2 678 ± 1½	2 683	42
Nitriles			
Acetonitrile	2 617 ± 1½	2 619	103
Benzonitrile	2 623 ± 2	2 630	97
Nitro-compounds			
Nitromethane	2 661 ± 1½	2 662	59
Nitrobenzene	2 657 ± 2	2 647	53

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† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue.

[8] ' Tables of Wave Numbers for the Calibration of Infra-Red Spectrometers,' Parts I and II, Butterworths (for I.U.P.A.C.), London, 1961.

[9] L. J. Bellamy, K. J. Morgan, and R. J. Pace, *Spectrochim. Acta*, 1966, **22**, 535.

TABLE 2 (*Continued*)

Solvent	ν_{OD} (present work)/ $\mathrm{cm^{-1}}$	ν_{OD} (Kagiya *et al.*)/ $\mathrm{cm^{-1}}$	B * (present wolk)/ $\mathrm{cm^{-1}}$
Ethers			
Di-isopropyl ether	2 586 ± 2	2 593	134
Di-n-butyl ether	2 591 ± 1½		129
Tetrahydrofuran	2 575 ± 2	2 578	145
1,4-Dioxan	2 592 ± 1½	2 591	128
Cineole(1,8-Epoxy-*p*-menthane)	2 565 ± 1½		155
Diphenyl ether	2 663 ± 2		57
Anisole	2 630 ± 2 2 659 ± 2	2 642	75 †
Phenetole	2 628 ± 2 2 660 ± 2	2 643	76 †
Ketones			
Acetone	2 597 ± 3	2 604 (2 596) ‡	123
Ethyl methyl ketone	2 611 ± 3	2 611	109
Diethyl ketone	2 620 ± 3	2 612 (2 619) ‡	100
Methyl n-propyl ketone	2 609 ± 3		111
Methyl isopropyl ketone	2 618 ± 3		102
Methyl n-butyl ketone	2 609 ± 3		111
Methyl t-butyl ketone	2 623 ± 2		97
Di-isopropyl ketone	2 628 ± 2		92
Cyclopentanone	2 596 ± 3		124
Cyclohexanone	2 588 ± 3	2 602 (2 587) ‡	132
Acetophenone	2 612 ± 3 (2 601) ‡	2 612 (2 592) ‡	108
Esters			
Methyl acetate	2 632 ± 2	2 632	88
Ethyl acetate	2 631 ± 2	2 629	89
Diethyl carbonate	2 635 ± 1½		85
Amines			
Triethylamine	2 406 ± 3	2 430	314
Piperidine	2 421 ± 2 2 438 ± 2	2 428	290 †
Aniline	2 511 ± 2	2 510	209
N-Methylaniline	2 536 ± 2	2 517	184
Pyridine	2 442 ± 2 2 478 ± 3	2 500	260 †
2-Picoline	2 435 ± 4 2 466 ± 4	2 485	270 †
3-Picoline	2 441 ± 4 2 472 ± 4		264 †
4-Picoline	2 440 ± 3 2 470 ± 3	2 508	265 †
Amides			
NN-Dimethylformamide	2 554 ± 3	2 561	166
NN-Dimethylacetamide	2 542 ± 3	2 555	178
Sulphoxide			
Dimethyl sulphoxide	2 528 ± 2	2 527	192

* For gas-phase CH_3OD, ν_{OD} is taken as 2 720 $\mathrm{cm^{-1}}$.[10]
† Mean. ‡ See text.

0.802, a correlation coefficient of 0.998, and a standard deviation of the estimate of 2.8 $\mathrm{cm^{-1}}$. Thus there would be no advantage in using ν_{OD} for t-butyl [^{2}H]alcohol for establishing a scale of Lewis basicity.

The O–D *Stretching Band for* 0.4M-*Solutions of Methan*[^{2}H]*ol in Aprotic Solvents.*—The values of ν_{OD} are shown in Table 2, together with the data of Kagiya, Sumida, and Inoue[3] and values of the Lewis basicity parameter B calculated from the results of the present work. Selected spectra are shown.

Hydrocarbons. Cyclohexane and hexane (spectrum 1) show a very weak monomer peak at *ca.* 2 696 $\mathrm{cm^{-1}}$, the highest value of ν_{OD} we observed, which is appropriate for what are obviously the least basic solvents used (*cf.* 2 720 for gaseous methan[^{2}H]ol[10]). There is a very strong oligomer band at *ca.* 2 490 $\mathrm{cm^{-1}}$ and the shape of the band envelope suggests that the predominant species may be trimer. We cannot detect the band at 2 667 reported by Kagiya *et. al.*[3] Koppel and Palm[4] have already pointed out that the apparent occurrence of monomer band at *ca.* 2 667 for both benzene and hexane is anomalous.

Our values of ν_{OD} for benzene (spectrum 2) and toluene agree closely with Kagiya's, and are *ca.* 30 $\mathrm{cm^{-1}}$ lower than for the saturated hydrocarbons, clearly showing the π-donor properties of the aromatic solvents. There is a marked oligomer band at *ca.* 2 580 $\mathrm{cm^{-1}}$, possibly due to dimer. For benzene there are shoulders at lower frequencies which may well be due to trimer and tetramer. In the case of toluene, dimer and trimer appear to be present in comparable amounts. Methylation of the aromatic ring clearly enhances the π-donor properties in accord with the electron-repelling effect of the methyl group, but no definite pattern for the isomeric xylenes can be discerned. Successive methylation appears slightly to favour higher oligomer formation at the expense of monomer and dimer (spectrum 3).

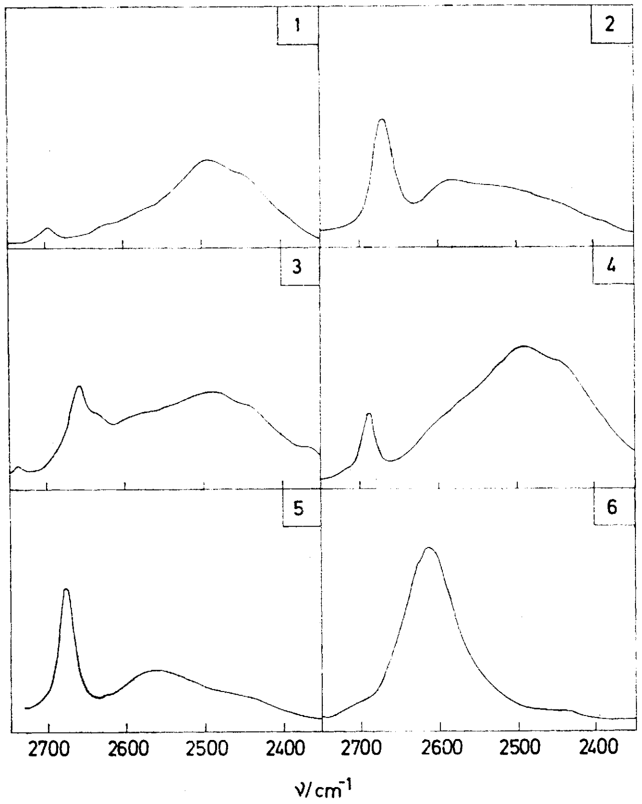

FIGURE 1 Spectra of methan[^{2}H]ol in various solvents (cell path 0.19 mm except where otherwise indicated): 1, n-hexane (0.17 mm); 2, benzene; 3, mesitylene; 4, carbon tetrachloride; 5, chloroform; 6, acetonitrile

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[10] G. Herzberg, ' Infrared and Raman Spectra of Polyatomic Molecules,' van Nostrand, Princeton, New Jersey, 1945, p. 335.

Halogeno-compounds. In the aliphatic chloro-compounds (spectra 4 and 5) the monomer peak is sharp. There is good agreement with Kagiya *et al.* for carbon tetrachloride but there are small discrepancies for the other chlorinated solvents. The pattern of ν_{OD} values is rational. Chlorine atoms are centres for Lewis basicity, but within a given molecule each tends to reduce the effect of the others through electrical induction. The mutual interference decreases as the number of chlorine atoms decreases and their distance apart increases. In carbon tetrachloride there is a strong oligomer band at *ca.* 2 490, approximately as in the aliphatic hydrocarbons, and possibly due to trimer.[11] In the other aliphatic chloro-compounds the monomer peak is much more intense and the oligomer band, much reduced in intensity, is at *ca.* 2 570, and possibly due to dimer (*cf.* the aromatic hydrocarbons). It may be that the weak hydrogen-bond donor properties associated with H and Cl on the same carbon atom reduce the tendency of the methan[^{2}H]ol to polymerise.

With the halogenobenzenes there is the possibility of π-donor or σ-donor Lewis basicity. For these, ν_{OD} would be in the same frequency region. The results appear to be in better accord with the π-donor effect. The values of ν_{OD} are higher than for benzene, in the order $F > Cl > Br > I \sim H$. This accords with the view that the electron-attracting properties of the halogens make the π-electrons less available than in benzene, and the order corresponds to that of decreasing electronegativity of the halogens. σ-Donor properties would probably give a different order for the ν_{OD} values (*cf.* the hydrogen-bonding properties of the fluorine atom). A second chlorine atom on the ring appears to weaken the π-donor properties only slightly.

The monomer peak in fluorobenzene is of rather low intensity and there is a pronounced oligomer peak at *ca.* 2 545 cm^{-1}. With the other halogenobenzenes the monomer peak is more intense, and the oligomer band is at *ca.* 2 570 and rather flat. Fluorobenzene thus appears to be less able than the other compounds to inhibit oligomer formation.

Nitriles. There is a discrepancy of 7 cm^{-1} between our value and Kagiya's for benzonitrile, but there is good agreement for acetonitrile (spectrum 6). In both the aliphatic and the aromatic solvent ν_{OD} is undoubtedly governed by the π-donor properties of the CN group; the frequency is far too low for the π-donor properties of the benzene ring. No oligomer can be detected in acetonitrile and there are only slight signs of any in benzonitrile.

Nitro-compounds. There is a discrepancy of 10 cm^{-1} between our value and Kagiya's value for nitrobenzene but there is good agreement for nitromethane (spectrum 7). There is a difference of only 4 cm^{-1} between the two nitro-compounds, and undoubtedly we are observing the donor properties of the nitro-group itself in both cases. The π-donor properties of the benzene ring are evidently weakened to the point of extinction by the electron-attracting nitro-group. There are slight signs of oligomer bands at *ca.* 2 560 and 2 470 cm^{-1}. For nitromethane there is apparently a weak band at 2 725, but we are unable to give any interpretation of this (*cf.* similar examples below).

Ethers. With the aliphatic and cyclic ethers (spectrum 8) we come to substances considerably more basic than other solvents discussed so far. For di-isopropyl ether there is a small discrepancy with Kagiya's value. There are only slight signs of oligomer formation. The secondary ether appears to be slightly more basic than the primary ethers, which is in accord with the normal inductive affect of alkyl groups,[12] while linking the ends of the alkyl groups together in the cyclic ether tetrahydrofuran increases the basicity, presumably by reducing steric hindrance (*cf.* Taft's E_s values for cyclic groups [12]). The inductive effect of the second oxygen atom reduces the basicity of dioxan with respect to tetrahydrofuran, while cineole (1,8-epoxy-*p*-menthane) as a cyclic tertiary ether combines all the factors enhancing basicity. In dioxan there is an anomalous but quite definite band at 2 695 (*cf.* nitromethane above).

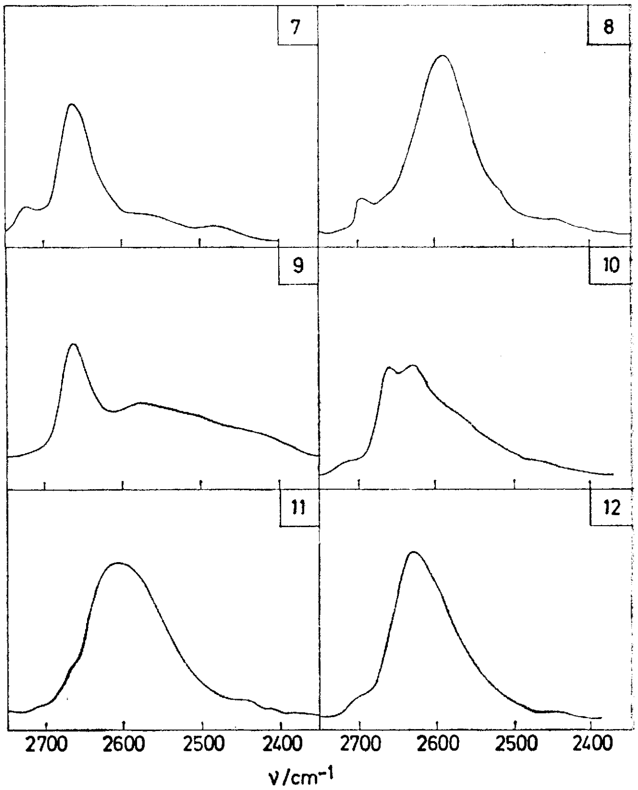

FIGURE 2 As Figure 1: 7, nitromethane; 8, dioxan (0.17 mm); 9, diphenyl ether (0.20 mm); 10, anisole; 11, acetophenone; 12, methyl acetate

The behaviour of diphenyl ether (spectrum 9) is very different from that of the above ethers, and seems to be characteristic of a substituted benzene. The monomer peak is at 2 663 (*cf.* aromatic hydrocarbons) and there are clear oligomer bands. We are probably observing the π-donor properties of the rings (but see below).

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[11] C. Duboc, *Spectrochim. Acta*, 1974, **30***A*, 441.

[12] R. W. Taft, 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

The mixed ethers anisole (spectrum 10) and phenetole show highly individual behaviour. What appears to be the monomer band is a doublet, with two peaks about 30 cm^{-1} apart, and of comparable intensity in the case of anisole, while the peak at lower wavenumber is slightly more intense in the case of phenetole. The frequency recorded by Kagiya is approximately the mean value of the two components in each case. It seems possible that here we are seeing comparable π- and σ-donor basicities. The higher frequency (*ca.* 2 660) would correspond to π-donor interaction with the methan[^{2}H]ol (as in diphenyl ether), while the lower (*ca.* 2 630) would correspond to σ-donor interaction, weakened relative to an aliphatic ether by delocalisation of the oxygen lone-pair electrons into the aromatic ring. (For diphenyl ether, σ-donor interaction would probably give a band even higher than 2 630 which would then overlap with the π-donor band. It is possible therefore, that both σ- and π-donor effects occur in the case of diphenyl ether.) Anisole and phenetole both show signs of oligomers, probably mainly dimer.

Ketones. In the aliphatic and cyclic ketones the O–D band of methan[^{2}H]ol is usually rather broad, and the exact position of the maximum is less certain than with many other solvents. In the case of acetone, diethyl ketone, and cyclohexanone there are discrepancies between our values of ν_{OD} and those of Kagiya, Sumida, and Inoue,[3] but in a recent redetermination Professor Kagiya [13] has found values (in parentheses) in closer agreement with ours. There are no signs of oligomer bands. The ν_{OD} values for the ten ketones present a rational pattern, although this is somewhat surprising.[5b] In the alkyl methyl ketones branching at the α-carbon atom decreases basicity. Diethyl ketone and di-isopropyl ketone show behaviour consistent with this but lengthening the alkyl chain beyond two carbon atoms has almost no effect. The dominating structural influence on the basicity of the carbonyl group appears to be α-CH hyperconjugation. The basicity of the cyclic ketones is enhanced by a diminished steric effect.[12]

With acetophenone (spectrum 11) we have had difficulty in obtaining a definitive result. Our value now agrees closely with that of Kagiya *et. al.*[3] However at an earlier stage we obtained 2 601 cm^{-1}, and in a redetermination Professor Kagiya [13] found 2 592 cm^{-1}. Acetophenone may possibly contain some interfering impurity. However the sample used by us most recently satisfies our normal criteria of purity. The spectra giving the low values show a rather broad, flat and unsymmetrical ν_{OD} band, while the spectrum giving our higher value has a more symmetrical and not so broad band. Accordingly we accept the value of 2 612 cm^{-1}. Certainly ν_{OD} is under the influence of the basicity of the carbonyl group rather than the aromatic ring. The enhanced basicity of acetophenone compared with that of methyl t-butyl ketone establishes the importance of conjugative interaction for acetophenone (*cf.* hyperconjugation above).

Esters. In esters there are two possible types of basic centre, ' carbonyl ' and ' ethereal ' oxygen. The corresponding centres in ketones and ethers are of roughly comparable basicity, and nothing in our results for esters (*e.g.* spectrum 12) suggests any preference of methan[^{2}H]ol for one centre rather than the other. Measurements of ν_{CO} for esters dissolved in alcohols indicate hydrogen-bonding to carbonyl oxygen,[14] but the situation for the ethereal oxygen is not clear.

ν_{OD} Values are slightly higher for esters than for most ketones or ethers, indicating that one oxygen reduces the Lewis basicity of the other. It is surprising that ν_{OD} for diethyl carbonate is so close to the values for the alkyl acetates.

Amines. Here we encounter considerable complexity in the ν_{OD} band (spectra 13—16) and in several cases very large discrepancies between our results and those of Kagiya *et al.*[3] In piperidine, pyridine, and all the picolines the ν_{OD} band is a doublet. In the case of piperidine, for which the absorption is extremely weak, influence on the ν_{OD} band must be due to the σ-donor properties of the nitrogen atom and we cannot explain why this should cause splitting.

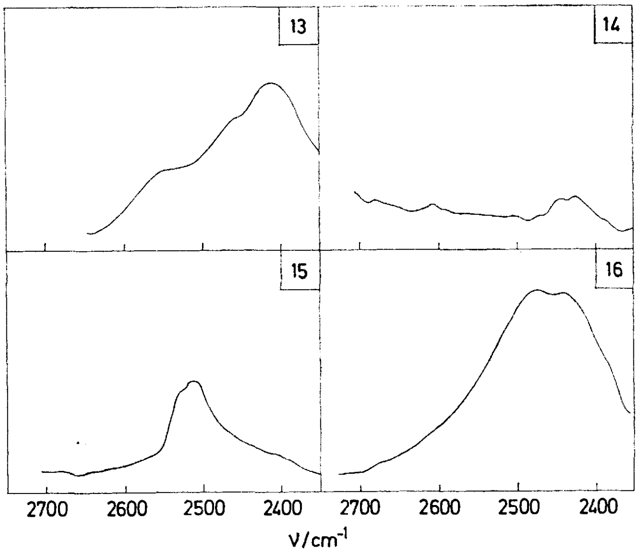

FIGURE 3 As Figure 1: 13 triethylamine; 14, piperidine (0.20 mm); 15, aniline (0.18 mm); 16, 4-picoline (0.18 mm)

While a π-donor effect might occur with pyridines (for which the absorption is very strong), it can hardly be supposed that it would be discerned at such a low frequency in comparison with substituted benzenes, or differ by only a little from the σ-donor effect of the nitrogen atom. Aniline is almost the weakest Lewis base of the amines studied, but, surprisingly, the basicity is apparently further reduced by *N*-methyl substitution; *cf.* the acid–base behaviour of these amines in water. Triethylamine is the strongest Lewis base. There is

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[13] T. Kagiya, personal communication.

[14] L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, 1959, **55**, 14; H. Minato, *Bull. Chem. Soc. Japan*, 1963, **36**, 1020.

little discrimination to be discerned in the basic properties of the picolines.

Amides and Sulphoxide. The ν_{OD} bands in these very basic solvents are broad. In the case of the amides there are discrepancies with Kagiya's values. The effective basic centre in the amides is probably the oxygen atom but there is current controversy about the structure of protonated amides.[15]

We are grateful for correspondence with Professor T. Kagiya, Kyoto University.

[5/2115 *Received, 29th October,* 1975]

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[15] M. Liler, *J.C.S. Perkin II*, 1974, 71.