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# Interpretation of Spectroscopic Changes upon Adduct Formation and Their Use To Determine *E* and *C* Parameters

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**Abstract:** Spectroscopic probes have been examined to determine whether the spectral shifts accompanying adduct formation are dominated by donor–acceptor interactions. New spectral acceptors which employ IR, NMR, or visible spectral shifts are established. Since the $C_A^*/E_A^*$ ratios for these spectral probes differ from those of acceptors whose spectral response is the change of their OH stretching frequency, these new spectral correlations greatly simplify the addition of new donors to the *E* and *C* database. Several spectral acceptors, reported to be useful indicators of donor strength, are shown to be insensitive to, or not dominated by, donor–acceptor interactions.

## Introduction

The recent extension of the electrostatic–covalent (E-C) approach[1]

$$-\Delta H = E_AE_B + C_AC_B + W \qquad (1)$$

to gas-phase, ion–molecule reactions[2] and to bond energies[3] has served to emphasize the importance of this quantitative application of the early Pauling[4] and Mulliken[5] bonding models to an immense area of chemistry. In this article, the role that such considerations play in the understanding of a variety of spectroscopic shifts is evaluated.

The finding of spectroscopic relations, dominated by bond energies, is very important not only to the expansion of the E-C approach to new areas of chemistry but also for the incorporation of new donors (bases), B, and acceptors (acids), A, into the E and C database. In order to add a new donor molecule, the enthalpy of reaction of this donor is measured toward four or more acceptors with known $E_A$ and $C_A$ parameters, and the four or more simultaneous equations are solved for $E_B$ and $C_B$. If a constant energy contribution to the measured enthalpy is present or suspected, *W* is also solved for a third unknown and more measurements are needed. Otherwise, *W* is set equal to zero. The effort expended to carry out calorimetric measurements to add a new donor or acceptor to the correlation is extensive.

Physicochemical properties, $\Delta\chi$, have been analyzed with the E-C approach.[1] For example, the spectral shifts, $\Delta\chi$, for a given acceptor bonding to donors with known $E_B$ and $C_B$ parameters are substituted into eq 2. The series of simultaneous equations

$$\Delta\chi = E_A^*E_B + C_A^*C_B + W^* \qquad (2)$$

are solved for $E_A^*$, $C_A^*$, and $W^*$. These values lead to the calculated $\Delta\chi$ by substituting them into eq 2 along with reported $E_B$ and $C_B$ enthalpy-based parameters. Thus, the fit of $\Delta\chi$ to eq 2 is a fit to enthalpy-based parameters. In treating spectral shifts, asterisks indicate the spectroscopic counterparts of the enthalpy parameters ($E_A$, $C_A$, and *W*) in eq 1 and are referred to as spectral acceptor parameters. Since $E_B$ and $C_B$ are the eq 1 donor parameters in units of (kilocalories mole$^{-1}$)$^{1/2}$, $E_A^*$ and $C_A^*$ also contain the pertinent conversion factors.

The existence of spectral correlations with the *E* and *C* parameters is of value in understanding the spectroscopy. They also provide additional simultaneous equations (eq 2) that can be employed in the determination of the $E_B$ and $C_B$ parameters for a new donor that is not part of the E and C database. Spectroscopic data are easier to measure than enthalpy changes accompanying adduct formation, so that valid spectral acceptor correlations facilitate the expansion of the database to new donors.

The value of the $C_A^*/E_A^*$ ratio of a spectroscopic correlation is very important when adding a *new* donor to the E and C database. If, for example, the $C_A^*/E_A^*$ ratio is the same for two or more spectral acceptors, the two or more equations are not independent, and only one of them is in effect providing any information to solve for the two unknowns, $E_B$ and $C_B$. When the $C_A^*/E_A^*$ ratios of the acids used to solve for $E_B$ and $C_B$ differ only slightly, small errors in the measured shifts lead to a shallow minimum and large errors in the values of $E_B$ and $C_B$ from the solution of the simultaneous equations. Thus, acids with a wide range of values for their $C_A^*/E_A^*$ and $C_A/E_A$ ratios are needed to determine $C_B$ and $E_B$.

The change in the OH stretching frequency of phenol upon complex formation is a well-established correlation[6] with $E_A^* = 167$, $C_A^* = 109$, $W^* = 205$, and a $C_A^*/E_A^*$ ratio of 0.65. Other alcohols give correlations with similar $C_A^*/E_A^*$ ratios. Thus, if a series of measurements is to be carried out to add a new donor to the E and C database, there is no point in measuring more than two or at most three OH frequency shifts. Spectral acceptors with different values of $C_A^*/E_A^*$ ratios and acceptors with different $C_A/E_A$ ratios are needed to accurately define the $E_B$ and $C_B$ values for a new donor.

In this article, we shall examine a series of spectral shifts with eq 2. In so doing, we gain an appreciation of the factors influencing the spectroscopy and evaluate the utility of various spectral measurements in determining $E_B$ and $C_B$ parameters for new donors. Such information is particularly essential for the interpretation of gas-phase ion–molecule reactions with the ECT approach.[2] Because of the limited range of the $C_A/E_A$ ratios found[2] for gas-phase ions, it is difficult to use only gas-phase data to characterize the properties of new donors. Gas-phase measurements can be used in conjunction[2,3] with spectral acceptors to add new donors to the E and C database.

## Results and Discussion

Spectral changes have been used to assess reactivity parameters and to provide experimental justification of Mulliken's charge-transfer model.[5] In order to assess the electrostatic–covalent bonding contribution to a spectral change, data are selected in which the nonspecific solvation contribution to the measured

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**Table I.** Experimental and Calculated $\Delta\nu_{OH}$ Values (cm$^{-1}$) for a Series of Adducts of Methanol and *tert*-Butyl Alcohol ($CCl_4$ Solvent)

| | $CH_3OH$ | | $(CH_3)_3COH$ | |
|---|---|---|---|---|
| donor | $\Delta\nu_{OH}$ (exptl)[a] | $\Delta\nu_{OH}$ (calcd)[b] | $\Delta\nu_{OH}$ (exptl)[c] | $\Delta\nu_{OH}$ (calcd)[d] |
| $O(C_2H_4)_2O$ | 126 (109) | (135) | 118 | 115 |
| $(C_2H_5)_2O$ | 150 (140) | 152 | 127 | 128 |
| $CH_3C(O)OC_2H_5$ | 83 (84) | 87 | 75 | 77 |
| $C_5H_5N$ | 286 (286) | 284 | 231 | 231 |
| $(C_2H_5)_3N$ | 429 (370) | (386) | | |
| $4\text{-}CH_3C_5H_4N$ | 304 (305) | 307 | | |
| $HCON(CH_3)_2$ | 160 (116) | (172) | 143 | 145 |
| $(CH_3)_2SO$ | 205 (199) | 205 | 181 | (172) |
| $[(CH_3)_2N]_3PO$ | 274 (269) | (265) | | |
| $(CH_3)_2CO$ | 115 (112) | 120 | 101 | 102 |
| $CH_3CN$ | 75.5 (81) | 70 | 63 | 63 |
| $CH_3C(O)N(CH_3)_2$ | 179 | (189) | 160 | 159 |
| $(CH_3)_2NCN$ | 117.5 | 115 | 101 | 100 |
| $ClCH_2CN$ | 48.5 | 47 | 44 | 45 |
| $(C_2H_5O)_3PO$ | 189 (189) | 185 | | |
| $C_6H_5CN$ | 72.5 | 76 | | |
| $(n\text{-}C_4H_7)_2O$ | 154 | (165) | | |
| $(CH_3)_2S$ | 137 | 133 | | |
| $(C_2H_5)_2S$ | 146 | 144 | | |
| $(CH_2)_4S$ | 154 | 157 | | |

[a] Values from ref 7; values in parentheses in the experimental data column are from ref 8. [b] Calculated using $E_A^* = 107.7$, $C_A^* = 70.0$, and $W^* = -155.8$. The % fit is 1.1, the $C_A/E_B$ range is 0.2–16.3, the value of $\Delta$ is 3 cm$^{-1}$, and the experimental error is 3.5 cm$^{-1}$. The values in parentheses under the $\Delta\nu_{OH}$(calcd) column are omitted from the fit. They are calculated from the $E_A^*$, $C_A$, and $W^*$ parameters obtained by fitting the rest of the data. [c] Data from ref 8. [d] Calculated using $E_A^* = 88.95$, $C_A^* = 54.54$, and $W^* = -121.0$. The value of $\Delta$ is 3 cm$^{-1}$, the experimental error is 3–5 cm$^{-1}$, the % fit is <1, and the $C_B/E_B$ range is 0.4–2. The value in parentheses is calculated from the resulting parameters, and this data point is omitted from the fit.

**Table II.** Criteria for Evaluating the Overall Quality of Fit

| criterion | excellent | good | acceptable | poor |
|---|---|---|---|---|
| $C_B/E_B$ range | ≥5.1 | 3–5 | 2 | 1 |
| $\Delta$/av exp error | 1 | 2 | 3 | 4 |
| % fit | 0–1.9 | 2–3.9 | 4–5 | >5 |

**Table III.** Change in C–I Stretching Frequencies $\nu$ (cm$^{-1}$) of Donor Adducts of ICN[a] and $IC_2I$ (1:1 Adducts)

| donor | $\Delta\nu_{ICN}$ (exptl)[a] | $\Delta\nu_{ICN}$ (calcd)[b] | donor | $\Delta\nu_{ICN}$ (exptl)[a] | $\Delta\nu_{ICN}$ (calcd)[b] |
|---|---|---|---|---|---|
| $(EtO)_3PO$ | 26.0 | 23.1 | $4\text{-}CH_3C_5H_4N$ | 61.5 | 63.5 |
| $CH_3C(O)CH_3$ | 18.0 | 23.4 | $(C_2H_5)_3N$ | 88.0 | 88.4 |
| $HC(O)N(CH_3)_2$ | 30.0 | 26.5 | $(CH_3)_3N$ | 96.0 | (86) |
| $(CH_3)_2SO$ | 32.0 | 30.0 | $(CH_2)_4O$ | 25.0 | (36.9)[d] |
| $(C_2H_5)_2O$ | 20.5 | (29.3)[d] | $CH_3CN$ | 17.0 | 14.6 |
| $O(C_2H_4)_2O$ | 17.0 | 24.4 | $(CH_2)_4SO$ | 34.0 | 32.7 |
| $C_5H_5N$ | 57.5 | 57.9 | $(C_2H_5)_2S$ | 59.0 | 55.6 |
| $3\text{-}ClC_5H_4N$ | 45.5 | (49.5)[e] | $3\text{-}CH_3C_6H_4N$ | 61.5 | (60.5)[e] |

| donor | $\Delta\nu_{IC_2I}$ (exptl)[a] | $\Delta\nu_{IC_2I}$ (calcd)[c] | donor | $\Delta\nu_{IC_2I}$ (exptl)[a] | $\Delta\nu_{IC_2I}$ (calcd)[c] |
|---|---|---|---|---|---|
| $(C_2H_5)_2O$ | 6.5 | 8.3 | $HCON(CH_3)_2$ | 12.5 | (6.7)[d] |
| $O(CH_2)_4O$ | 7 | 6.4 | $(C_2H_5)_2S$ | 18.5 | 18.5 |
| $(CH_3)_2CO$ | 7 | 6.0 | $4\text{-}CH_3C_5H_4N$ | 22 | 21.7 |
| $(CH_2)_4O$ | 9 | (11.2)[d] | $(C_2H_5)_3N$ | 31.5 | 31.5 |
| $3\text{-}CH_3C_5H_4N$ | 21.0 | (20.6)[e] | | | |

[a] Reference 9 and references therein. [b] Calculated with $E_A^* = 5.2$, $C_A^* = 15.0$, and $W^* = -4.6$. Data in $C_6H_6$. The value of $\Delta$ is 2.8 cm$^{-1}$. The % fit is 3.8, and the $C_B/E_B$ range is 0.38–16.3. [c] Calculated with $E^* = 2.10$, $C^* = 5.90$, and $W^* = -5.09$. Data in $CS_2$ solvent. The value of $\Delta$ is 0.6 cm$^{-1}$. The % fit is 1.8, and the $C_B/E_B$ range is 0.69–16.3. [d] The values in parentheses were omitted from the fit and were calculated from the resulting $E_A^*$, $C_A^*$, and $W^*$ spectral parameters. [e] Omitted from fit because its $E_B$ and $C_B$ parameters are tentative.

transition is absent or minor. This is accomplished by measuring the data in a nonpolar, noninteracting solvent or by using a model compound that does not interact with the donor solvent to subtract out the nonspecific solvation contribution. We shall proceed to evaluate donor–acceptor contributions to infrared spectral shifts, $^{19}F$ NMR chemical shifts, and changes in electronic transitions.

**Infrared Frequency Shifts.** In addition to the $E_A^*$, $C_A^*$, and $W^*$ parameters mentioned for phenol, analogous infrared frequency shift parameters have been reported[6] for substituted phenols, alcohols, and pyrrole. Recent data[7] enables the ECW analysis of OH frequency shifts for methanol in order to determine what factors influence its shift and determine whether the $C_A^*/E_A^*$ ratio is different from that of the aromatic alcohols. Table I gives the experimental frequency shifts and those calculated from the parameters $E_A^* = 107.7$, $C_A^* = 70.0$, and $W^* = 156$. Data from the most recent study[7] are listed and used in the data fit. Older reported data[8] are indicated in parentheses. The range of $C_B/E_B$ ratios is large (ranging from 0.2 to 16.3), indicating that a variety of donor types was employed in this study. The systems listed in parentheses under $\Delta\nu_{OH}$ (calcd) do not fit well. Most of these donors have different values reported for them in the literature. Purification of the donor- or concentration-dependent shifts may lead to problems with this data.

Because of small equilibrium constants and the asymmetry of many of the bands of the adducts, the frequency shifts are only accurate to 3–5 cm$^{-1}$. The average absolute difference between the calculated and experimental shifts is 3 cm$^{-1}$, which compares well with the experimental error. In addition, these data have an excellent response range (largest minus smallest value) of 260 cm$^{-1}$. One of the criteria used to judge the quality of this fit is called the percentage fit. For methanol, the *average absolute difference* in the calculated and experimental values, $\Delta$, is 3 cm$^{-1}$, and the shifts range over 260 cm$^{-1}$ (the calculated range is used). The percentage fit, %*F*, is given by

$$\%F = (\Delta/\text{response range})100 \qquad (3)$$

Thus, (3/260)100 is a fit of 1.1%. This percent fit is comparable to the enthalpy fit of ±0.2 kcal/mol for enthalpies that range up to 10 kcal/mol or a fit of ±0.3 kcal/mol for enthalpies that range from 15 to 30 kcal/mol. The above criteria indicate that the frequency shift is dominated by the donor–acceptor bond energy.

Three criteria should be used to judge the overall quality of the fit: (1) the range of $C_B/E_B$ values in the measured data; (2) ($\Delta$)/(average experimental error); and (3) the percentage fit. Table II gives the guidelines that have been successfully used in making judgements for spectral acceptors. Their usefulness will be shown with the ECW analyses that follow.

Before proceeding, two points concerning the percentage fit should be made. If the percentage fit is very poor and a large range of $C_B/E_B$ is used in the fit, the E*C*W* model has not failed, but the spectral shifts are not related to bond strengths. Experiments should be devised to investigate what factors other than bond strengths are controlling the shifts. The second point involves the situation in which the percentage fit is excellent but the $C_B/E_B$ range is fair to poor. This situation is illustrated by the data for *tert*-butyl alcohol OH shifts in Table I. The percentage fit is <1%, but the range of $C_B/E_B$ is only fair (0.4–2). In this case, estimated shifts should be calculated only for donors whose $C_B/E_B$ ratios fall within this limited range. Shifts for donors that lie outside the chosen range may or may not be controlled by bond strengths. The $C_A^*/E_A^*$ ratio for *tert*-butyl alcohol has a large uncertainty and provides uncertain information about the relative importance of covalent and electrostatic bonding. Additional measurements, using amines and sulfur donors, are needed to define the acid property more completely. In spite of this limitation, the E*C*W* analysis of *tert*-butyl alcohol shows that the spectral shift is dominated by the donor–acceptor bond strength for the donors studied and that the $E_A^*$, $C_A^*$, and $W^*$ parameters can be used to estimate the shifts for any donor in the E and C database whose $C_B/E_B$ ratio falls in the prescribed range.

A series of measurements involving the change in the I–C stretching frequencies of $IC{\equiv}N$ and $IC{\equiv}CI$ upon adduct for-

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(7) For more recent $CH_3OH$ data, see: Berthelot, M.; Grabowski, G.; Lawrence, C. *Spectrochim. Acta* **1985**, *41A*, 657. Berthelot, M.; Grabowski, G.; Lawrence, C. *J. Chim. Phys.* **1985**, *82*, 427.

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**Table IV.** ECW Fit of the $^{19}$F Chemical Shift Difference ($\Delta$, ppm) of 4-Fluorophenol and Its Adducts

| donor | $\Delta^{19}$F exptl[a] | $\Delta^{19}$F(I) calcd[b] | $\Delta^{19}$F(II) calcd[c] |
|---|---|---|---|
| $(C_2H_5)_3N$ | 2.66 | 2.76 | 2.64 |
| $C_5H_5N$ | 2.49 | 2.67 | 2.61 |
| $C_6H_5CN$ | 1.71 | 1.71 | 1.87 |
| $CH_3C(O)OC_2H_5$ | 1.85 | 1.66 | 1.82 |
| $CH_3C(O)N(CH_3)_2$ | 2.86 | 2.70 | 2.70 |
| $HC(O)N(CH_3)_2$ | 2.72 | 2.50 | 2.52 |
| $(CH_2)_4O$ | 2.00 | 2.06 | 2.13 |
| $O(C_2H_4)_2O$ | 1.45 | 2.07 | (2.15) |
| $(C_2H_5)_2O$ | 1.88 | 2.10 | (2.17) |
| $(C_2H_5)_2S$ | 1.10 | 0.81 | 1.02 |
| $(CH_3)_2SO$ | 2.71 | 2.82 | 2.79 |
| $[(CH_3)_2N]PO$ | 3.71 | 3.25 | (3.14) |

[a] Reference 10a. Reported experimental errors range from 0.02 to 0.06 and average 0.03 ppm. $(C_2H_5)_2O$, $(C_2H_5)_2S$, $O(CH_2CH_2)_2O$, and $C_6H_5CN$ have low $K$ values of 10 or less. [b] Calculated with $E_A{}^* = 1.29$, $C_A{}^* = 0.315$, and $W^* = -0.739$. The % fit is 9, and the $C_B/E_B$ range is 0.35–16.3. [c] Calculated with $E_A{}^* = 1.09$, $C_A{}^* = 0.242$, and $W^* = -0.192$. The % fit is 6, and the $C_B/E_B$ range is 0.35–16.3. The values in parentheses were omitted from the fit and were calculated from the resulting $E_A{}^*$ and $C_A{}^*$ spectral parameters.

mation have been reported.[9] The decrease observed upon adduct formation, $\Delta\nu_{CI}$, is expected from three center bond formation. The data and fits for ICN and $IC_2I$ are given in Table III. The value of $\Delta$ for ICN is 2.8 cm$^{-1}$ with a percentage fit of 3.8. An excellent range of donor $C_B/E_B$ values was selected. The percentage fit for $IC_2I$ is an excellent 1.8 with a $\Delta$ of 0.6 cm$^{-1}$. A wide range of $C_B/E_B$ values for the donors was employed in this system.

As in the case of methanol, the ECW analysis shows that donor–acceptor interactions dominate the IC frequency shift. Most significantly, the $C_A{}^*/E_A{}^*$ values of ICN and $IC_2I$ are 2.9 and 2.8, respectively, indicating a larger covalent contribution to the shift than that of methanol, whose $C_A{}^*/E_A{}^*$ ratio is 0.65. The $E_A{}^*$, $C_A{}^*$, and $W^*$ parameters for all three of the acids discussed above are recommended for estimating shifts for donors with known $E_B$ and $C_B$ values. Only donor types that are similar to those in the data fits should be used. These spectral acceptors will also find utility in determining the $E_B$ and $C_B$ parameters for new donors from measured shifts.

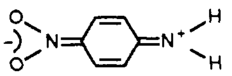
**$^{19}$F Chemical Shifts.** The $^{19}$F chemical shift of 4-fluorophenol changes upon adduct formation with donors. A very thorough experimental study of this system has been reported,[10] and the data are suggested as a scale of hydrogen-bond strength.[11] The results for all of the donors studied, which are in the E and C database, are listed in Table IV, and the fit of the entire data set is listed under $\Delta^{19}$F(I)calcd. The agreement between the calculated and observed shifts is poor, with a percentage fit of 9. The variation in the $C_B/E_B$ ratio of the donors studied is excellent, but $\Delta$ is more than 7 times the average experimental error.

The $^{19}$F NMR signal of the adduct is in fast exchange with that of the free acceptor in solution, yielding a mole fraction weighted average value for the peak position. Thus, $K$ must be known accurately to calculate the shift of the adduct or enough donor must be added to fully complex the acceptor so that none is left to exchange. Weak donors, with low adduct formation equilibrium constants, require large base concentrations to obtain the extent of complexation (75%) necessary to accurately determine $K$. Excess base can lead to nonspecific solvation of the adduct by aggregation of the donor around the polar adduct. The values of the chemical shift and $K$ are both influenced by nonspecific solvation. The poor fit of this system to E*C*W* leads us to conclude that factors other than those that influence hydrogen-bond strength make appreciable contributions to these measured $^{19}$F shifts.

In an attempt to determine whether nonspecific solvation is the only problem, the weak donors were omitted and the fit was rerun without much of an improvement. The best of several attempted data fits resulted when $[(CH_3)_2N]_3PO$ was omitted in addition to $(C_2H_5)_2O$ and $O(C_2H_4)_2O$. The column labeled $\Delta^{19}$F(II)calcd shows the results obtained when these donors are omitted from the fit. Dioxane and diethyl ether are weak donors, and the nonspecific solvation by the large amount of donor used in their studies may be the cause of their deviation. The donor $[(CH_3)_2N]_3PO$ is a strong donor, but problems are often encountered with it in spectral fits. Maybe the nitrogen lone pair also interacts with the acid when it is coordinated to the oxygen, leading to a large value for the experimental shift. Although the fit labeled $\Delta^{19}$F(II) looks improved, the response range of the shifts in the fit is considerably smaller (1.8 ppm), giving a poor percentage fit of 6.

This analysis of the $^{19}$F chemical shifts indicates that the trend in $\Delta^{19}$F is weakly correlated with the hydrogen-bonding strength, but contributions from other sources such as nonspecific solvation may make very important contributions to the chemical shift. The $E_A{}^*$, $C_B{}^*$, and $W^*$ parameters cannot be used with confidence to accurately calculate $^{19}$F chemical shifts using the $E_B$ and $C_B$ parameters in our extensive database. Furthermore, the $^{19}$F chemical shift is not recommended for determining the $C_B$ and $E_B$ parameters of new donors and is, at best, a rough scale of hydrogen-bond strength.

**Electronic Transitions.** The shift in the electronic transition of the solute 4-nitroaniline, in a basic solvent, is influenced by a hydrogen-bonding interaction involving the NH proton with basic donor solvents and by the nonspecific solvation of these adducts by the solvent.[11] The electronic transition occurs to a polar excited state of the form:



Polar solvents and hydrogen bonding of a donor to the NH hydrogen lower the energy of the excited state more than that of the ground state, decreasing the transition energy. The frequency for 4-nitroaniline is measured in the pure donor as solvent and is subtracted from that of *N,N*-diethyl-4-nitroaniline in the same donor solvent. This procedure is reported[11] to correct for the influence of nonspecific solvation by the donor solvent on the electronic transition, $\nu$, because the *N,N*-diethyl derivative cannot hydrogen bond to donor solvents. Thus, $\Delta\nu$ is *proposed* to give the shift due to the specific hydrogen-bonding interaction of the solvent to the NH group. The E*C*W* analysis of the shifts corrected in this manner is reported in Table V. The value of $\Delta$ is 0.03 kK (1 kK = 1000 cm$^{-1}$), and the percentage fit is 3.4. This is a good value, as is the 0.4–4 range of $C_B/E_B$ for the donors studied. The $W$ value of 3.97 kK (with $\Delta\nu$ given as $\nu$ for 4-nitroaniline minus $\nu$ for *N,N*-diethyl-4-nitroaniline) gives a positive $\Delta\nu$ contribution in the absence of hydrogen bonding. The difference in the electronic transition frequency of 4-nitroaniline and *N,N*-diethyl-4-nitroaniline in hexane is 3.6 kK, and this is a significant component of the constant $W^*$ value. The negative values for $E_A{}^*$ and $C_A{}^*$ make $\Delta\nu$ less than 3.97 kK when there is an acid–base contribution. The $C_A{}^*/E_A{}^*$ ratio for the hydrogen-bonding contribution is 0.18. The weak donors omitted from the fit do not fully complex the probe.[11b]

Table V also contains data for a similar experiment with 4-nitrophenol employing 4-nitroanisole to correct for nonspecific solvation. Hydrogen bonding and polar solvents stabilize the charge-separated form and decrease the transition energy. For nitrophenol, the $C_A{}^*/E_A{}^*$ ratio is 0.17, essentially the same ratio as that obtained for 4-nitroaniline. The percentage fit is 6.5, and the $C_B/E_B$ range of the donors studied is 2. These values are only in the poor/acceptable range. Use of this indicator is limited to a narrow range of donors.

Table V also gives the E*C*W* analyses of closely related spectral acceptors. When the hydrogen on the nitrogen of 4-

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**Table V.** Hydrogen Bonding Induced Shifts in the Electronic Transitions of 4-Nitroaniline, and N-Substituted 4-Nitroanilines, and 4-Nitrophenol (in kK)[a]

4-Nitroaniline[a]

| | $\nu$(*N*,*N*-diethyl-4-nitroaniline) | $\nu$(4-nitroaniline) | $\Delta\nu$ | $\Delta\nu$ (calcd)[b,f] | | $\nu$(*N*,*N*-diethyl-4-nitroaniline) | $\nu$(4-nitroaniline) | $\Delta\nu$ | $\Delta\nu$ (calcd)[b,f] |
|---|---|---|---|---|---|---|---|---|---|
| $CH_3C(O)OC_2H_5$ | 25.74 | 27.93 | 2.19 | 2.21 | $(C_2H_5O)_3PO$ | 25.19 | 26.49 | 1.30 | 1.33 |
| $(CH_3)_2CO$ | 25.22 | 27.32 | 2.10 | 2.05 | $CH_3C(O)N(CH_3)_2$ | 24.75 | 26.21 | 1.46 | 1.44 |
| $(CH_2)_5O$ | 25.74 | 27.82 | 2.08 | (1.98) | $(C_2H_5)_2O$ | 26.52 | 28.65 | 2.13 | (1.92) |
| $(CH_2)_4O$ | 25.61 | 27.59 | 1.98 | 1.98 | $OCH_2CH_2O$ | 25.77 | 28.25 | 2.48 | (1.93) |
| $C_5H_5N$ | 24.78 | 26.42 | 1.64 | 1.60 | hexane | 27.71 | 31.30 | 3.6 | (3.97) |
| $(C_2H_5)_3N$ | 27.14 | 28.77 | 1.63 | 1.65 | $(n\text{-}C_4H_9)_2O$ | 26.85 | 29.03 | 2.18 | (1.83) |
| $HC(O)N(CH_3)_2$ | 24.66 | 26.18 | 1.52 | 1.60 | $[(CH_3)_2N]_3PO$ | 24.75 | 25.45 | 0.70 | (1.07) |
| $(CH_3)_2SO$ | 24.30 | 25.71 | 1.41 | 1.36 | | | | | |

4-Nitrophenol[a]

| | $\nu$(4-nitroanisole) | $\nu$(4-nitrophenol) | $\Delta\nu$ | $\Delta\nu$ (calcd)[c,f] | | $\nu$(4-nitroanisole) | $\nu$(4-nitrophenol) | $\Delta\nu$ | $\Delta\nu$ (calcd)[c,f] |
|---|---|---|---|---|---|---|---|---|---|
| $(C_2H_5)_2O$ | 33.45 | 33.11 | −0.34 | −0.37 | $(EtO)_3PO$ | 32.41 | 31.70 | −0.71 | −0.73 |
| $CH_3C(O)OC_2H_5$ | 32.79 | 32.57 | −0.22 | −0.21 | $CH_3C(O)N(CH_3)_2$ | 31.90 | 31.25 | −0.65 | −0.66 |
| $(CH_2)_4O$ | 32.79 | 32.47 | −0.32 | −0.33 | $O(CH_2CH_2)_2O$ | 32.89 | 32.89 | 0 | (−0.37) |
| $C_5H_5N$ | 32.00 | 31.44 | −0.56 | −0.54 | $(n\text{-}C_4H_9)_2O$ | 33.56 | 33.17 | −0.39 | −0.43 |
| $HCON(CH_3)_2$ | 32.05 | 31.35 | −0.70 | −0.56 | $[(CH_3)_2N]_2PO$ | 31.90 | 30.67 | −1.23 | (−0.86) |
| $(CH_3)_2SO$ | 31.70 | 31.06 | −0.64 | −0.70 | hexane | 34.31 | 35.08 | +0.77 | (0.78) |

*N*-Methyl-4-nitroaniline[a]

| | $\nu$(*N*,*N*-diethyl-4-nitroaniline) | $\nu$(*N*-methyl-4-nitroaniline) | $\Delta\nu$ | $\Delta\nu$ (calcd)[d,f] | | $\nu$(*N*,*N*-diethyl-4-nitroaniline) | $\nu$(*N*-methyl-4-nitroaniline) | $\Delta\nu$ | $\Delta\nu$ (calcd)[d,f] |
|---|---|---|---|---|---|---|---|---|---|
| $(CH_3)_2CO$ | 25.22 | 26.28 | 1.06 | 1.08 | $CH_3C(O)N(CH_3)_2$ | 24.75 | 25.45 | 0.70 | 0.74 |
| $(CH_2)_4O$ | 25.61 | 26.60 | 0.99 | 1.00 | $(n\text{-}C_4H_9)_2O$ | 26.85 | 27.82 | 0.97 | 0.94 |
| $C_5H_5N$ | 24.78 | 25.48 | 0.70 | 0.72 | $(CH_2)_5O$ | 25.74 | 26.77 | 1.03 | 0.99 |
| $HC(O)N(CH_3)_2$ | 24.66 | 25.45 | 0.79 | 0.83 | $OCH_2CH_2O$ | 25.77 | 26.92 | 1.15 | (1.01) |
| $(CH_3)_2SO$ | 24.30 | 25.06 | 0.76 | 0.69 | $(C_2H_5)_2O$ | 26.52 | 27.66 | 1.14 | (0.99) |
| $(C_2H_5O)_3PO$ | 25.19 | 25.87 | 0.68 | 0.69 | $CH_3C(O)OC_2H_5$ | 25.74 | 26.81 | 1.07 | (1.19) |
| $[(CH_3)_2N]_3PO$ | 24.75 | 25.25 | 0.50 | 0.50 | $(CH_2)_4SO$ | 24.30 | 25.06 | 0.76 | (0.69) |

*N*-Ethyl-4-nitroaniline[a]

| | $\nu$(*N*,*N*-diethyl-4-nitroaniline) | $\nu$(*N*-ethyl-4-nitroaniline) | $\Delta\nu$ | $\Delta\nu$ (calcd)[e,f] | | $\nu$(*N*,*N*-diethyl-4-nitroaniline) | $\nu$(*N*-ethyl-4-nitroaniline) | $\Delta\nu$ | $\Delta\nu$ (calcd)[e,f] |
|---|---|---|---|---|---|---|---|---|---|
| $CH_3C(O)OC_2H_5$ | 25.74 | 26.77 | 1.03 | 1.07 | $(C_2H_5O)_3PO$ | 25.19 | 25.77 | 0.58 | 0.56 |
| $(CH_3)_2CO$ | 25.22 | 26.18 | 0.96 | 0.96 | $[(CH_3)_2N]_3PO$ | 24.75 | 25.06 | 0.31 | 0.36 |
| $(CH_2)_5O$ | 25.74 | 26.67 | 0.93 | 0.87 | $CH_3C(O)N(CH_3)_2$ | 24.75 | 25.35 | 0.60 | 0.61 |
| $(CH_2)_4O$ | 25.61 | 26.46 | 0.85 | 0.88 | $OCH_2CH_2O$ | 25.77 | 26.77 | 1.00 | (0.89) |
| $C_5H_5N$ | 24.78 | 25.38 | 0.60 | 0.60 | $(C_2H_5)_2O$ | 26.52 | 27.55 | 1.03 | (0.87) |
| $HC(O)N(CH_3)_2$ | 24.66 | 25.35 | 0.69 | 0.70 | $(n\text{-}C_4H_9)_2O$ | 26.85 | 27.78 | 0.93 | (0.81) |
| $(CH_3)_2SO$ | 24.30 | 24.91 | 0.61 | 0.56 | | | | | |

[a] $\Delta\nu$ is defined as $\nu$(4-nitroaniline or 4-nitrophenol) minus $\nu$(*N*,*N*-diethyl-4-nitroaniline or 4-nitroanisole). The units are kilokaysers, kK, where 1 kK = 1000 $cm^{-1}$. See ref 11. [b] Calculated with $E_A^* = -0.976$, $C_A^* = -0.180$, and $W^* = 3.97$. The % fit is 3.4, and the $C_B/E_B$ range is 0.38–4.3. [c] Calculated with $E_A^* = -0.569$, $C_A^* = -0.095$, and $W^* = 0.81$. The % fit is 6.5, and the $C_B/E_B$ range is 0.38–2.0. [d] Calculated with $E_A^* = -0.546$, $C_A^* = -0.147$, and $W^* = 2.22$. The % fit is 4.8, and the $C_B/E_B$ range is 0.38–2.0. [e] Calculated with $E_A^* = -0.561$, $C_A^* = -0.148$, and $W^* = 2.12$. The % fit is 3.8, and the $C_B/E_B$ range is 0.38–2.0. [f] The values in parentheses were omitted from the fit and were calculated from the resulting $E_A^*$, $C_A^*$, and $W$ spectral parameters.

nitroaniline is replaced with a methyl group, the $C_A^*/E_A^*$ ratio increases to 0.27. The hydrogen-bonding interaction of the NH proton on *N*-methyl-4-nitroaniline with the basic donor solvent has a larger covalent contribution to the shift than the two previous spectral systems. The analysis of *N*-ethyl-4-nitroaniline spectral shifts yields a similar $C_A^*/E_A^*$ of 0.26 for its hydrogen-bonding properties. However, in both cases, the percentage fit is only acceptable due to small response ranges, and the $C_B/E_B$ ranges are small (1.6). The shifts in the electronic transitions for these anilines are recommended for obtaining $C_B$ and $E_B$ parameters only for new bases whose $C_B/E_B$ values are in the narrow ranges used in the studies of the various indicators.

The $I_2$ molecule undergoes a blue shift of the visible band upon complexation to a Lewis base.[12] The bands are broad and difficult to resolve, but large shifts occur. Reported data, determined by curve resolution, are summarized in Table VI. The value of $\Delta$ is 6 $cm^{-1}$ (average experimental error is ~50 $cm^{-1}$), and the percentage fit is less than 1. Acetone does not fit well. Both n and $\pi$ complexes have been observed in the infrared of hydro-

**Table VI.** Blue Shifts in the Visible $I_2$ Transition ($cm^{-1}$) upon Adduct Formation

| donor | $\Delta\nu_{exptl}$ | $\Delta\nu_{calcd}$[d] | donor | $\Delta\nu_{exptl}$ | $\Delta\nu_{calcd}$[d] |
|---|---|---|---|---|---|
| $(CH_3)_2SO$[a] | 2950 | 2954 | $(CH_3)_2CO$[b,c] | 1850 | (2009) |
| $CH_3CN$[a] | 1550 | (1299) | $CH_3C(O)N(CH_3)_2$[b] | 2730 | 2725 |
| $O(C_2H_4)_2O$[a] | 2375 | (2172) | $CH_3CO(OC_2H_5)$[b] | 1570 | 1572 |
| $C_5H_5N$[c] | 4560 | 4545 | $CH_3C(O)OCH_3$[b] | 1550 | 1550 |
| $3\text{-}ClC_5H_4N$[c,e] | 3920 | 3922 | $3\text{-}CH_3C_5H_4N$[e] | 4730 | 4742 |

[a] Measured in this study. [b] Reference 12a. [c] Reference 12b. [d] Calculated with $E_A^* = 1085$, $C_A^* = 1093$, and $W^* = -1257$. The value of $\Delta$ is 6 $cm^{-1}$, the % fit is less than 1, and the $C_B/E_B$ range is 0.6–2.1. Data in heptane solvent. The values in parentheses were omitted from the fit and were calculated from the resulting $E_A^*$, $C_A^*$, and $W^*$ parameters. [e] $E_B = 1.75$ and $C_B = 3.00$ for $3\text{-}ClC_5H_4N$, and $E_B = 1.77$ and $C_B = 3.73$ for $3\text{-}CH_3C_5H_4N$ (Drago, R. S. Submitted for publication).

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(12) (a) Berthelot, M.; Helbert, M.; Laurence, C. *C. R. Acad. Sci. Ser.* **1982**, *295*, 1093. (b) Nicolet, P.; Laurence, C. *J. Chim. Phys.* **1983**, *80*, 677.

**Table VII.** Change in $J_{C^{13}\text{-}H}$ of Chloroform upon Hydrogen Bonding to Donors (Hz)

| donor | $\Delta J_{C^{13}\text{-}H}$- (exptl)$^{c}$ | $\Delta J_{C^{13}\text{-}H}$- (ECW)$^{a,d}$ | $\Delta J_{C^{13}\text{-}H}$- (EC)$^{b,d}$ |
|---|---|---|---|
| $C_5H_5N$ | 7.24 | (9.53) | (9.39) |
| $CH_3CN$ | 6.30 | 6.32 | 6.43 |
| $(CH_3)_2CO$ | 7.40 | 7.22 | 7.27 |
| $CH_3CON(CH_3)_2$ | 9.50 | 9.55 | 9.47 |
| $(C_2H_5)_2O$ | 7.20 | 7.79 | 7.80 |
| $(CH_2)_4O$ | 8.28 | 7.72 | 7.71 |
| $(CH_2)_4S$ | 4.27 | 4.35 | 4.46 |
| $(C_2H_5O)_3PO$ | 8.60 | (9.89) | (9.82) |
| 4-$CH_3C_5H_4N$ | 8.08 | (9.76) | (9.58) |
| *N*-MeIm | 8.50 | 8.53 | 8.39 |
| $EtC(CH_2O)_3P$ | 5.44 | 5.42 | 5.49 |

$^{a}$Calculated with $E_A^* = 3.74$, $C_A^* = 0.952$, and $W^* = -0.496$. Experimental error in $J$ is ±0.3 Hz, $\Delta J_{C^{13}\text{-}H}(AB) = 208.5$. The percentage fit is 3.7 with a value of 6.9 expected from the experimental error in $J$. The $C_B/E_B$ range is 0.43–15.6. $^{b}E_A^* = 3.55$, $C_A^* = 0.868$, and $W = 0$. The percentage fit is 3%. $^{c}$Measured by L. Chamusco, University of Florida. $^{d}$Data in parentheses were omitted from fit, and ECW was calculated from resulting acid parameters.

gen-bonding systems, and this could distort the band maxima and lead to a small net shift. The large concentration of polar base needed to give a reasonable complex peak for $CH_3CN$ may result in nonspecific solvation contributions.[13] In this data fit, any donor with a shift <1900 cm$^{-1}$ is assigned one-half the weight of other systems. The $C_A^*/E_A^*$ ratio is 1, which is considerably reduced from that of the $I_2$ enthalpy parameters ($C_A/E_A = 4$). The application of this probe should be limited to donors whose $C_B/E_B$ ratios fall in the range 0.6–2.1.

**Spectral Shifts of Chloroform.** The enthalpies of adduct formation for chloroform hydrogen bonding to various donors[14] are well behaved in the E–C analysis.[1] A variety of spectral changes accompany adduct formation. These changes include reports of proton[14] and $^{13}C$ chemical shifts,[15] $^{13}C$–H coupling constant[15] changes, and infrared chemical shifts.[15] For example, when chloroform hydrogen bonds to donor molecules, the NMR $C^{13}$–H coupling constant, $J_{C^{13}\text{-}H}$, increases. These spectral handles have resulted in chloroform being one of the earliest probes of donor strength reported in the literature.[16] Analysis of these data led to the conclusion[14] that these spectral shifts do not provide a reliable estimate of donor strength.

Table VII lists the $J_{C^{13}\text{-}H}$ values for a series of donor adducts measured in this study. These results differ considerably from those reported earlier. The literature results were obtained in a 1/9/1 chloroform/donor/cyclohexane mole ratio. As such, they contain contributions from specific and nonspecific solvation. Reported equilibrium constants also suggest that $CHCl_3$ may not be completely coordinated in some of these solvents. The values reported in this study are obtained by running different base concentrations in the solvent methylcyclohexane and solving for the equilibrium constant and the coupling constant using the fast-exchange approximation. A poor fit of the data results when the entire data set is analyzed by E*C*W*. We report an interpretation that assigns complications to pyridine and 4-methylpyridine. Small steric problems are apparently operative in triethyl phosphate. When these donors are omitted from the fit, the results in Table VII are obtained. A satisfactory fit is also obtained when $W^*$ is set equal to zero. The $W^* = 0$ fit is preferred as there is no theoretical necessity for a non-zero $W$ and the simpler interpretation is always preferred.[2]

**Table VIII.** Change in the C–D Stretching Frequency of Chloroform (cm$^{-1}$) upon Hydrogen Bonding to Donors

| donor | $\Delta\nu_{CD}$(exptl)$^{b}$ | $\Delta\nu_{CD}$(ECW)$^{a}$ |
|---|---|---|
| $C_5H_5N$ | 33.0 | (26.4) |
| $CH_3CON(CH_3)_2$ | 13.1 | 11.9 |
| $(C_2H_5)_2O$ | 9.5 | 11.2 |
| $(CH_2)_4O$ | 7.2 | (14.6) |
| $(CH_2)_4O$ | 7.2 | (14.6) |
| $(CH_2)_4S$ | 22.0 | 21.5 |
| $(C_2H_5)_2S$ | 20.3 | 20.2 |
| $(C_2H_5O)_3PO$ | 10.7 | 10.3 |
| $(C_2H_5)_3N$ | 79 | (41.2) |
| $C_5H_5NO$ | 19.0 | 19.7 |
| $CH_3C(O)OC_2H_5$ | ~5 | (4.9) |
| $(CH_3)_2CO$ | ~5 | (7.9) |
| $(CH_3)_2SO$ | 13.8 | 13.5 |

$^{a}$Calculated with $E_A^* = 5.98$, $C_A^* = 8.01$, and $W = -12.64$. The Δ is 0.8 cm$^{-1}$. The % fit is 6.1, and the $C_B/E_B$ range is 0.36–16.3. Experimental error is ±1 cm$^{-1}$. The values in parentheses were omitted from the fit and were calculated from these parameters. $^{b}$Measured by L. Chamusco, University of Florida.

**Table IX.** $\Delta\nu_{CO}$ (cm$^{-1}$) of Ethyl Acetate upon Adduct Formation with Various Lewis Acids

| Lewis acid | $\Delta\nu_{C=O}$(measd) | $\Delta\nu_{C=O}$(calcd)$^{a}$ |
|---|---|---|
| $I_2$ | 26 | 24 |
| ICl | 55 | 53 |
| $C_6H_5OH$ | 36 | 39 |
| $CF_3CH_2OH$ | 35 | 36 |
| $BF_3$ | 107 | 106 |
| $SbCl_5$ | 138 | 139 |

$^{a}$Calculated with $E_B^* = 13.4$, $C_B^* = 8.7$, and $W^* = -0.41$. The % fit is 1.5, the $C_A/E_A$ range is 0.47–4, and Δ is 1.7 cm$^{-1}$.

Table VIII lists the $\Delta\nu_{CD}$ infrared shifts for deuteriochloroform hydrogen bonding to a series of donors. The deuterio derivative is employed because most donors have CH stretching frequencies in the infrared that overlap those of chloroform. The results have been obtained by studying the shift as a function of base concentration and extrapolating to infinite dilution. The fit again is poor unless the donors whose values are indicated in parentheses are omitted. Pyridine and the amine donors exhibit large differences between the calculated and measured values, as was observed for the $\Delta J_{C^{13}\text{-}H}$ fit. Complications exist in the interaction of pyridine and amine donors with $CHCl_3$. The effects cause the frequency shifts of the amine donors to be too large and the coupling constants to be too small. These effects do not influence the fit of the enthalpy of formation of $CHCl_3$ adducts.[1] A double well may exist in the potential energy curve for this hydrogen-bonding interaction.

The low measured value for the THF adduct suggests some problems with the infrared spectrum, e.g., a shifted THF overtone peak being mistaken for CD. The E*C*W* analysis has indicated that, with the exception of pyridine and amine donors, $CHCl_3$ spectroscopy is dominated by bond-strength considerations. The % fit of 6.1 is poor because of a small response range (11.3 cm$^{-1}$). Band resolution makes the infrared correlation a problem with weak donors, i.e., with shifts <9 cm$^{-1}$. For donors of intermediate strength (10–25 cm$^{-1}$), $\Delta\nu_{CD}$ is recommended as a spectral acceptor probe.

**Spectral Donor Probes.** A spectral donor is defined as a donor molecule which, upon reaction with a series of acceptors, undergoes a spectral change that can be fit to E*C*W*, i.e., its spectral shift is related to the same factors that influence the bond strength of the interaction. Though it has often been assumed[17] that the shift in the infrared spectrum of a donor upon coordination is an indication of bond strength, there is little data available to test this assumption. The existence of such correlations would be of value in determining $E_A$ and $C_A$ values for acceptors that are not part of the E and C database. The most promising system is summarized in Table IX. These data involve the change in the C–O infrared stretching frequency of ethyl acetate upon complexation to various Lewis acids. Normal coordinate analysis indicates[18]

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(13) Vogel, G. C.; Searby, L. A. *Inorg. Chem.* **1973**, *12*, 936.

(14) Slejko, F. L.; Drago, R. S.; Brown, D. G. *J. Am. Chem. Soc.* **1972**, *94*, 9120.

(15) Lichter, R. L.; Roberts, J. D. *J. Phys. Chem.* **1970**, *74*, 912.

(16) Gordy, W.; Stanford, S. C. *J. Chem. Phys.* **1941**, *9*, 204.

(17) See, for example: Nakamoto, K. *Infrared Spectra of Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

(18) Brown, D. G.; Drago, R. S.; Bolles, T. F. *J. Am. Chem. Soc.* **1968**, *90*, 5706.

that the CO stretch is not extensively coupled to other vibrations in the molecule, and the coupling of the CO stretch with the donor–acceptor O–A bond stretching vibration is also expected to be minimal. Thus, the vibrational frequency shifts are expected to parallel force constant changes, simplifying their interpretation. Coordination of an acceptor to the carbonyl stabilizes the $CH_3C(O)OC_2H_5$ resonance form, decreasing the carbonyl CO bond order. The limited data available and the E*C*W* fit are reported in Table IX. Though limited by the number of acids in the correlation, the percentage fit (1.5%) and the range of $C_A/E_A$ values for the acceptors used are excellent.[19] This spectral donor probe has potential for determining $E_A$ and $C_A$ parameters for new acids that are not part of the E and C database, but it should be investigated further.

## Conclusion

In addition to reported correlations involving phenol, substituted phenols, pyrrole, trifluoroethanol, and hexafluoroisopropyl alcohol, several new spectral acceptors have been established in this work. Methanol and *tert*-butyl alcohol have $C_A{}^*/E_A{}^*$ ratios of 0.65 and 0.61, respectively, similar to those of the other alcohols. Their OH shifts with strong donors are not as large and the band not as broad as the phenols. This is an advantage for these alcohols because large shifts can overlap CH stretching vibrations.

The change in the IC stretching frequency when ICN and $I_2C_2$ form adducts is dominated by the strength of the bond formed during adduct formation. The $C_A{}^*/E_A{}^*$ ratios of these spectral probes are 2.9 and 2.8, respectively, which are larger than those of hydrogen-bonding acids. The larger $C_A{}^*/E_A{}^*$ ratios make these spectral acceptors valuable additional correlations for determining the $E_B$ and $C_B$ parameters for donors not in the E and C database. They should be applied to donors similar to those retained in the data fits.

The final recommended IR probe is the change in the CD stretching frequency of deuteriochloroform. The IR spectral acid has a $C_A{}^*/E_A{}^*$ ratio of 1.3 and is limited to donors of intermediate strength, that is, for $\Delta\nu_{CD}$ in the range of 10–25 cm$^{-1}$.

The red shift in the electronic spectrum of 4-nitroaniline, corrected for nonspecific solvation by *N,N*-diethyl-4-nitroaniline, correlates well with a $C_A{}^*/E_A{}^*$ ratio of 0.18. This spectral acceptor should not be used for weak donors or for donors with large alkyl groups that could have large negative entropies of adduct formation. These conditions lead to incomplete complexation of the acceptor probe and limit the utility of this probe for obtaining $C_B$ and $E_B$ parameters for new donors. The other spectral indicators given in Table V have severe limitations and are useful for obtaining $C_B$ and $E_B$ parameters for new bases whose $C_B/E_B$ ratios are in the narrow ranges employed in obtaining the $E_A{}^*$, $C_A{}^*$, and $W^*$ parameters for each indicator. The blue shift in the iodine molecule upon adduct formation is a viable spectral probe that is limited to donors with $C_B/E_B$ ratios of up to 2. The $C_A{}^*/E_A{}^*$ ratio for $I_2$ is 1.1, indicating considerably reduced covalent character compared to the iodine parameters for correlating enthalpies.

Spectral donor correlations are limited. The change in CO stretching frequency of ethyl acetate upon adduct formation appears to be dominated by bond-strength considerations. The number of acceptors used in the study is limited. This data can be used to confirm enthalpy data to establish $E_A$ and $C_A$ parameters for new acceptors that are not part of the E and C database. Studies of spectral donors are in a preliminary stage. Accordingly, only ethyl acetate is recommended as a spectral donor probe of donor–acceptor interactions, and this recommendation is tentative in view of the limited number of systems studied.

## Experimental Procedure

The data for spectral acceptors are fit to eq 2 to obtain $E_A{}^*$, $C_A{}^*$, and $W^*$ parameters using a previously reported[1,2] least-squares fitting program. Donors in the E-C correlation whose values are labeled tentative (i.e., determined from only 2 or 3 measurements) are not used. If a donor, whose $E_B$ and $C_B$ values are both smaller than those of another donor, is reported to cause a larger shift than the stronger donor, the system providing the better ovall fit is employed. If two fits involving each donor are comparable in Δ's but different, both values are employed in the fit that is reported. Any donor that misses by 3Δ is eliminated. Errors in literature data can arise from data recording, donor impurities, band overlap, etc. and have been labeled[11] spectral anomalies. If a given donor that misses by 2Δ is removed and the fit is drastically improved (e.g., twice as many donors are improved as are made worse), the donor is eliminated. Improvement is judged by considering the improvement in those donors where the difference in the calculated and experimental values is close to experimental error, e.g., in a fit where experimental error is 0.2, the change of a donor fit from 0.1 to 0.01 is not considered an improvement. Care must be taken when donors are excluded that limit the range of $C_B/E_B$. This could give a fit of data that is not dominated by bond strengths and, at best, limits the applicability of the resulting fit. The donor hexamethylphosphorotriamide often causes problems in spectral correlations. A probable cause involves simultaneous interaction of the probe with the oxygen and nitrogen lone pairs. This donor has been omitted from all data fits. All systems that have been eliminated from a data fit are indicated by putting the value in parentheses in the $\Delta\chi_{calcd}$ column. An analogous procedure is used for determining the $E_B{}^*$, $C_B{}^*$, and $W^*$ parameters for ethyl acetate.

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[19] The $C_A/E_A$ range for acceptors in general is smaller than that for donors due to fixing the $I_2$ parameters at $C_A = 2.00$ and $E_A = 0.50$. See ref 1.