

On the relationship between carbon-13 and oxygen-17 carbonyl chemical shifts and $n \rightarrow \pi^*$ transition energies†

by W. H. DE JEU‡

Laboratorium voor Technische Natuurkunde, Technische Hogeschool,
Delft, the Netherlands

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Literature data for $\delta(^{13}\text{C})$, $\delta(^{17}\text{O})$ and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$ for carbonyl groups in various compounds are reviewed. In a wide variety of carbonyl compounds there is a linear relation between $\delta(^{17}\text{O})$ and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$. However, deviations from this general relationship occur for a group of ketones. The explanation is found in differences in electron-donating properties of the substituents at the carbonyl group, which cause changes in the electron density and in the polarity of the carbonyl group.

Measurements are reported for the concentration dependence of the three quantities for acetone in water. Here the variations of $\delta(^{13}\text{C})$ and $\delta(^{17}\text{O})$ can be explained by the changes in carbonyl polarity due to hydrogen bonding. For $\lambda_{\text{max}}^{n \rightarrow \pi^*}$ the blue shift due to hydrogen bond formation is dominant over the influence of changing carbonyl polarity. The relation between $\delta(^{17}\text{O})$ and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$ is strictly linear; for $\delta(^{13}\text{C})$ and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$ small deviations from linearity occur.

1. INTRODUCTION

Carbonyl groups have been the subject of much research using various spectroscopic techniques. Correlations between the results of the different methods have received less attention. Ito *et al.* [1, 2] established a linear relation between solvent effects on the $n \rightarrow \pi^*$ U.V.-adsorption and on the I.R. CO-band frequencies for various ketones. ^{17}O chemical shifts for a wide variety of carbonyl compounds were correlated with the $n \rightarrow \pi^*$ transition energies by Figgis *et al.* [3]. Savitsky *et al.* [4] did the same for ^{13}C carbonyl chemical shifts and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$ for ketones. Maciel *et al.* [5, 6] considered the question of an approximate linear relationship between $\delta(^{13}\text{C})$ and $\delta(^{17}\text{O})$; this is interesting because of the theoretical discussion of this relation in terms of π -bond and σ -bond polarity [7].

In this paper we discuss literature values of $\delta(^{13}\text{C})$, $\delta(^{17}\text{O})$ and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$, first for a wide variety of carbonyl compounds, then for simple ketones. Next we consider hydrogen bonding solvent effects on the same quantities with acetone as a model compound.

2. EXPERIMENTAL

The ^{13}C resonance was performed on a Varian DA-60 spectrometer, provided with a 15.08 MHz transmitter built in this laboratory. A 40 MHz probe was modified for use at 15.08 MHz. For detection of the signal the appropriate 60 MHz circuits were retuned to 15.08 MHz. The 5 MHz intermediate frequency, normally

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‡ Present address: School of Molecular Sciences, University of Sussex, Brighton, England.

obtained by mixing the 60 MHz with a 55 MHz signal, was now generated by mixing 15.08 MHz with the signal from a 10.08 MHz oscillator.

As an external reference we used about 50 per cent carbonyl ^{13}C enriched acetic acid. The reference was kept in a small concentric inner tube in the 15 mm outer diameter sample tube. The necessary bulk susceptibility corrections were made. We observed 2 kHz side-bands, and suppressed the centre-band. Calibration was performed by sweeping from the first lower to the first upper side-band and counting the 4 kHz separation accurately. The spectra were obtained using the adiabatic rapid passage technique.

The u.v. spectra were taken on a Cary-15 spectrometer. The optical path length was usually 0.1 mm, but 1 mm or 10 mm for the lower concentrations.

The acetone was obtained from E. Merck AG (uvasol), and used without further purification. The water was distilled several times.

3. THEORETICAL

Simple LCAO-MO theory of the chemical shift has been formulated by several authors [8-10]. For second-row elements the paramagnetic term is dominant [10]. The shift measured in the liquid state is a rotational average of the three main diagonal elements of the σ tensor. For the paramagnetic contribution this can be written as:

$$\sigma_p^A = -\frac{2e^2\hbar^2}{3m^2c^2\Delta E} \langle r^{-3} \rangle_{2p} \sum_B Q_{AB} \quad (1)$$

where A is the nucleus under investigation; the summation B runs over all atoms including A. $\langle r^{-3} \rangle_{2p}$ is the average value of r^{-3} for a $2p$ orbital. Furthermore

$$\begin{aligned} Q_{AB} = & \delta_{AB}(P_{xAxB} + P_{yAyB} + P_{zAzB}) \\ & - \frac{1}{2}(P_{yAyB}P_{zAzB} + P_{zAzB}P_{xAxB} + P_{xAxB}P_{yAyB}) \\ & + \frac{1}{2}(P_{yAzB}P_{zAyB} + P_{zAxB}P_{xAzB} + P_{xAyB}P_{yAxB}), \end{aligned} \quad (2)$$

δ_{AB} is the Kronecker delta; the P 's are the charge-density and bond-order matrix elements for the unperturbed wave functions. For the approximations involved in the derivation of (1) see [9]. A feature of the derivation of (1) is the introduction of an average excitation energy ΔE , defined for this case by:

$$\frac{\langle 0 | \mathcal{H}^2 | 0 \rangle}{\Delta E} = \sum_{n(\neq 0)} \frac{\langle 0 | \mathcal{H} | n \rangle \langle n | \mathcal{H} | 0 \rangle}{E_n - E_0}. \quad (3)$$

So the numerical value to be chosen for ΔE is a weighted average over the excited states.

Returning to carbonyl compounds an important contribution to ΔE will be supplied by the low-lying $n \rightarrow \pi^*$ transition (see figure 1). The energy of this transition is about 5 eV. Various authors have discussed changes in $\delta(^{13}\text{C})$ in terms of equation (1) using some additional approximations: Maciel [7] investigated the dependence of σ_p^A on the π -bond polarity, using a core of localized σ bonds and a constant value of ΔE . Savitsky *et al.* [4] discussed changes in ΔE , estimated from changes in $\lambda_{\text{max}}^{n \rightarrow \pi^*}$, but kept all other factors constant. From the work of Nagakura [11] it is known that the increase of ΔE in polar or hydrogen bonding solvents (and thus the decrease of $\lambda_{\text{max}}^{n \rightarrow \pi^*}$) is related to the π -bond polarity. So a

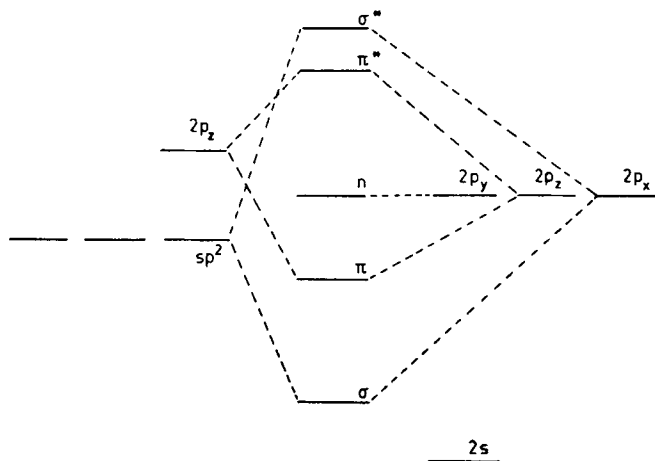


Figure 1. Schematic MO diagram for the carbonyl group of a ketone.

complete discussion should include both effects. Work along that line has been done by Rotlevi [12].

All the treatments discussed so far use a non-polar non-polarizable core of σ bonds and a polar π bond. It is very doubtful if this separation is valid. Calculations that take all valence electrons into consideration disagree with the idea of a non-polar carbonyl σ bond [13, 14].

4. RESULTS AND DISCUSSION

4.1. The carbonyl group in various organic compounds

Figgis *et al.* [3] established for general carbonyl compounds a linear relation between the $\delta(^{17}\text{O})$ data of Christ *et al.* [15] and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$. The ^{17}O resonance shifts to higher field with decreasing $\lambda_{\text{max}}^{n \rightarrow \pi^*}$. The relation holds for a wide range of about 600 p.p.m. and 200 nm. However, one should realize that this is a general trend and that relatively small changes in $\delta(^{17}\text{O})$ and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$ for a specific class of related compounds do not necessarily confirm this general pattern.

Savitsky *et al.* [4] established two approximate linear relations between $\delta(^{13}\text{C})$ and $\lambda_{\text{max}}^{n \rightarrow \pi^*}$ for cyclic and acyclic ketones. Here the ^{13}C resonance shifts to lower field with increasing $\lambda_{\text{max}}^{n \rightarrow \pi^*}$. In order to test the connection between the various relations we compared $\delta(^{17}\text{O})$ [15] and $\delta(^{13}\text{C})$ data [16] for a wide variety of carbonyl compounds. The conclusion is that for these two quantities no general relationship applies, although there is a very rough trend to proportionality. However, for the relatively small group of simple aldehydes and ketones there is an approximate linear relation between $\delta(^{13}\text{C})$ and $\delta(^{17}\text{O})$ with a negative slope (figure 2). Combination of figure 2 and the results of Savitsky *et al.* just mentioned, gives for ketones a rough trend of the ^{17}O resonance shifting to higher field with increasing $\lambda_{\text{max}}^{n \rightarrow \pi^*}$. This is opposite to the general trend between these two quantities mentioned earlier.

In order to find an explanation we notice that different substituents R can have different electron-donating properties with respect to the carbonyl group (inductive

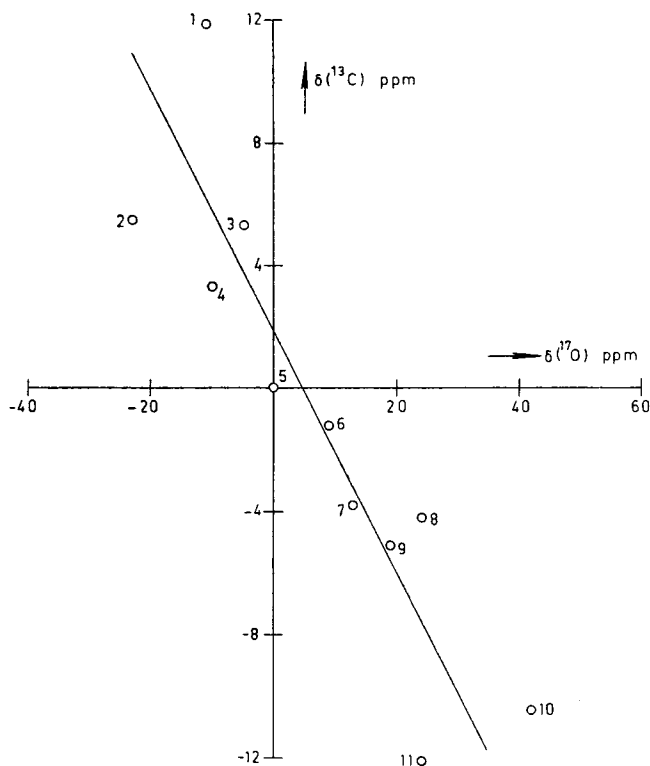


Figure 2. Carbonyl ^{13}C and ^{17}O chemical shifts for some aldehydes and ketones relative to acetone; 1, $\text{CH}_2=\text{CHCO}\cdot\text{H}$; 2, $\text{CH}_3\text{CO}\cdot\text{H}$; 3, $\text{CH}_3\text{CO}\cdot\text{CH}_2\text{Cl}$; 4, $\text{CH}_3\text{CH}_2\text{CO}\cdot\text{H}$; 5, $(\text{CH}_3)_2\text{CO}$; 6, $\text{CH}_3\text{CO}\cdot\text{C}_2\text{H}_5$; 7, cyclohexanone; 8, $(\text{C}_2\text{H}_5)_2\text{CO}$; 9, $\text{CH}_3\text{CO}\cdot\text{i-C}_3\text{H}_7$; 10, $(\text{i-C}_3\text{H}_7)_2\text{CO}$; 11, cyclopentanone.

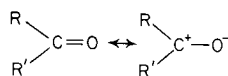
and mesomeric effects). We can split up the result of changing one substituent for another in the following way:

(1) We can get a resulting increase of electron density both on the carbonyl carbon and oxygen:



Now both the ^{17}O and the ^{13}C resonance shift to a higher field. The energy-level for the n orbital (figure 1) is raised due to the enhanced electron density on oxygen. The level of the π^* orbital is even more raised due to the enhanced electron density on both oxygen and carbon; consequently $\lambda_{\text{max}}^{n \rightarrow \pi^*}$ decreases. To explain the general trend for a wide variety of carbonyl compounds we have to accept that this is the dominant effect.

(2) The enhanced electron density in the carbonyl group is not necessarily distributed equally between the carbon and oxygen. This gives rise to changes in the polarity of the carbonyl group:



Increasing polarity gives a shift to higher field for δ(¹⁷O) and to lower field for δ(¹³C) (compare figure 2). Again the *n* level will be raised due to enhanced electron density on oxygen. But now the *π** level will be hardly affected, as enhanced electron density on oxygen is accompanied by decreased electron density on carbon. Consequently λ_{max}^{*n*→*π**} increases. This effect is clearly dominant for the group of ketones and explains the various relations qualitatively.

It is clear that simple interpretations in terms of *π*-bond polarity or changes in Δ*E* are not very useful. In order to gain further insight in the various relations we shall now turn to the effects of solvents on the three quantities.

4.2. Solvent effects on the carbonyl group of acetone

We have chosen acetone as a model compound because there is much data available on this ketone. As is well known the three quantities are influenced by hydrogen bonding in various proton-donating solvents. Unfortunately comparison of literature data is difficult because of the use of different concentrations. Data of Hayes and Timmons [17] for λ_{max}^{*n*→*π**} in various solvents are for dilute acetone of unknown concentrations. δ(¹⁷O) data of Christ and Diehl [18] are for 1 : 1 volume ratios. Maciel and Natterstad [5] have given δ(¹³C) values for 1 : 5 molar ratios. Dilution curves for δ(¹³C) of acetone in various solvents have been given by Natterstad [19]. He compared δ(¹³C) extrapolated to infinite dilution with λ_{max}^{*n*→*π**}. δ(¹³C) shifts to lower field with decreasing λ_{max}^{*n*→*π**}. We tried to extrapolate the available δ(¹⁷O) data to infinite dilution, but this introduced large errors.

In order to get better values we determined the concentration dependence of δ(¹³C) and λ_{max}^{*n*→*π**} for acetone in water. Accurate δ(¹⁷O) data are available for this system [18]. The results are given in the table and figures 3 and 4. Again there are approximate linear relations with the ¹⁷O resonance shifting to lower field and the ¹³C resonance shifting to higher field with increasing λ_{max}^{*n*→*π**}. The negative slope in the relation between δ(¹³C) and δ(¹⁷O) confirms a polarity effect. However, the direction of the changes in λ_{max}^{*n*→*π**} is now just opposite to that in the previous section. The explanation is that although the *n* level is raised by

Volume per cent acetone	Molar per cent acetone	δ(¹³ C)† p.p.m.	δ(¹⁷ O)‡ p.p.m.	λ _{max} ^{<i>n</i>→<i>π</i>*} † nm
100	100	0.0	0.0	274.9
88.3	65	-3.4	12.0	272.7
70.1	35	-6.1	25.5	270.4
50.4	20	-8.0	37.1	267.9
31.1	10	-9.4	45.7	266.0
17.6	5	-10.1	51.1§	265.1
9.3	2.5	-10.5	53.8§	264.7
0	0	-10.9§	57.0§	264.3§

† This work; accuracy about 0.4 p.p.m. and 0.5 nm.

‡ Reference [18]; accuracy about 1.0 p.p.m.

§ Extrapolated from the higher concentrations.

Acetone in water.

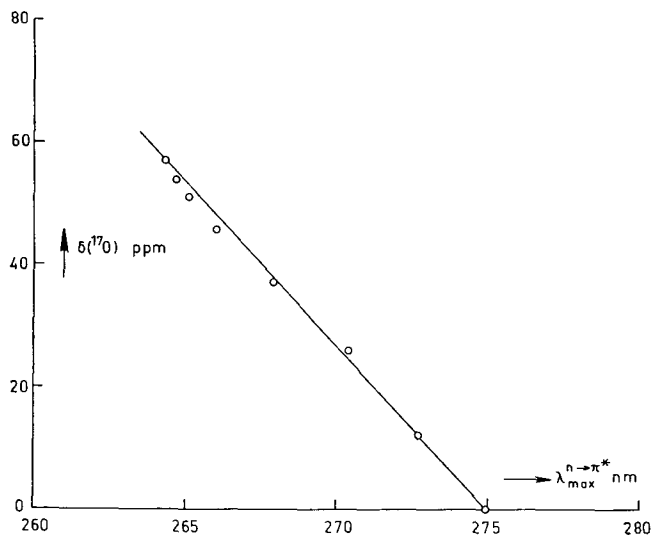


Figure 3. $\delta(^{17}\text{O})$ versus $\lambda_{\max}^{n \rightarrow \pi^*}$ for acetone in water.

increasing electron density on the oxygen atom with increasing polarity, this effect is more than compensated by the lowering of the n level when a hydrogen bond is formed. The π^* level is much less affected by hydrogen bonding. This causes the well-known blue shift in $\lambda_{\max}^{n \rightarrow \pi^*}$.

Finally, we see that there is a strict linearity between the changes in $\delta(^{17}\text{O})$ and $\lambda_{\max}^{n \rightarrow \pi^*}$ (figure 3). For the changes in $\delta(^{13}\text{C})$ and $\lambda_{\max}^{n \rightarrow \pi^*}$ there is no such linearity (figure 4), as also found by Natterstad [19]. These deviations from linearity indicate that the carbonyl carbon is able to compensate for the influence of the hydrogen bond at the cost of the methyl groups. This idea is supported by the observation of changes in the directly bonded $^{13}\text{C}^1\text{H}$ coupling constant [20].

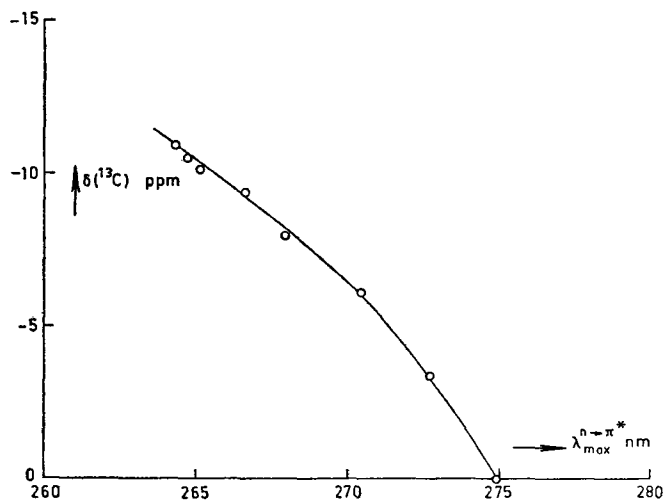


Figure 4. $\delta(^{13}\text{C})$ versus $\lambda_{\max}^{n \rightarrow \pi^*}$ for acetone in water.

Consequently, the relation between the changes in $\delta(^{17}\text{O})$ and $\delta(^{13}\text{C})$ of acetone is also not strictly linear. The observation of such a linearity by Natterstad [19] (also cited in [6]) is probably due to the very limited range of solvents studied.

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