A Nuclear Magnetic Resonance Study of the Effect of Hydrogen

Bonding and Protonation on Acetone[1a]

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With the aid of ^{13}C resonance and the ^{13}C satellites in ^1H resonance the following nmr parameters of acetone are obtained: carbonyl $\delta(^{13}C)$, methyl $\delta(^{13}C)$, $^1J_{CH}$ and $^4J_{HH}$. Measurements are reported for the solvent dependence of these quantities for acetone at various concentrations in water and for 20 mol % acetone in various concentration ratios of sulfuric acid–water. Both $^1J_{CH}$ and $^4J_{HH}$ increase due to hydrogen bonding of the carbonyl group with the solvent, and for the acidic solutions also due to protonation of the acetone molecule. The carbonyl ^{13}C is shifted to a lower field, while the methyl $\delta(^{13}C)$ remains almost constant. The iterative extended Hückel theory and the CNDO method are used for theoretical calculations of the changes in the acetone molecule. The direction and the order of magnitude of the changes in the chemical shifts are in general predicted very well; the results for the coupling constants are less satisfactory. Both for hydrogen bonding and for protonation there is an electron displacement away from the carbonyl carbon (which explains the shift of carbonyl $\delta(^{13}C)$ to a lower field qualitatively) and away from the methyl hydrogen atoms. The methyl carbon is hardly affected, which is in agreement with the near constancy of methyl $\delta(^{13}C)$.

Introduction

During the last decades nmr has appeared to be a powerful tool, not only for analytical purposes, but also for gaining insight into the structure of molecules. The chemical shifts and coupling constants provide valuable information about the electronic structure of the molecule and form an important test on the accuracy of the wave functions. Both chemical shifts and coupling constants are solvent dependent.[2] From these solvent shifts additional information can be obtained about possible solute–solvent interactions and accompanying electronic displacements.

In this paper a systematic study of some of the nmr parameters of acetone in various solvents is presented. From the proton spectrum the chemical shift of the methyl protons can be obtained. As 1.1% of all carbon atoms is a carbon-13 ($I = {}^1/_2$), two satellites with a spacing of $^1J_{CH}$ occur in the proton spectrum. With one methyl ^{12}C replaced by a ^{13}C the two methyl groups are no longer equivalent and each of the satellites is a quadruplet with an equal spacing of $^4J_{HH}$.[3] Furthermore, in ^{13}C resonance the chemical shifts of the methyl and carbonyl carbon atoms can be measured. Christ and Diehl[4] have obtained the chemical shift of the carbonyl oxygen by ^{17}O resonance (natural abundance 0.037%; $I = {}^5/_2$). More parameters exist, but the attention will be focused on the ones mentioned.

The chemical shifts as well as the coupling constants depend highly on the nature of the solvent.[3b-5] The carbonyl group is able to form H bonds with proton donating solvents, which causes electronic displacements in the molecule. In strongly acidic solutions even protonation of the acetone molecule occurs.[6] The chemical shift of the carbonyl proton can be measured at about $-60°$.[7] These effects are also apparent in other spectroscopic methods. In uv spectroscopy the n–π^* frequency of acetone and other ketones is well known to shift to higher values (blue shift) in solvents with increasing proton donating properties.[8,9] In acidic solutions, *e.g.*, more than 65 wt % sulfuric acid, the transition disappears gradually. From this a pK_a value of -7.2 has been established for acetone.[6] Furthermore, changes are found in the carbonyl stretching frequency $\nu_s(CO)$ in infrared and Raman spectroscopy.[10,11] $\nu_s(CO)$, and thus the strength of the CO bond, decreases with increasing H bonding. However, this effect is accompanied by an increase in strength of the CC and CH bonds.[11] A Raman study of acetone in sulfuric acid confirms the pK_a value of -7.2.[12]

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(2) P. Laszlo, "Progress in NMR Spectroscopy," J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Vol. III, 1967, p 231.

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Many of the properties mentioned depend on the polarity of the carbonyl group of the ketone under investigation. Several relations have been proposed, often assuming a nonpolar, nonpolarizable core of σ bonds and a polar carbonyl π bond. Nagakura[13] and Sidman[14] studied $\nu_{n \to \pi^*}$ and other electronic transitions in relation to the π bond polarity. Maciel[5,15] did the same for $\delta(^{13}C)$. Cook[16] established two linear relations between $\nu_s(CO)$ and the ionization potential I for conjugated and unconjugated carbonyl compounds, respectively. Figgis, Kidd and Nyholm[17] found a general linear relation between $\delta(^{17}O)$ and $\nu_{n \to \pi^*}$, which was extended to solvent effects on these two quantities by de Jeu.[18] Savitsky, Namikawa, and Zweifel[19] tried to correlate $\delta(^{13}C)$ and $\nu_{n \to \pi^*}$. However, in this case there is no strict linearity.[18] Finally, Ito, Inuzuka, and Imanishi[20] established a linear relation between the increase of $\nu_{n \to \pi^*}$ and the decrease of $\nu_s(CO)$ for ketones in various solvents.

General calculations on all valence electrons of a molecule with a carbonyl group, that in principle take all properties into consideration, are still rare. There are some notable nonempirical MO calculations on formaldehyde.[21] Contrary to general opinion about the carbonyl bond, a polar σ bond as well as a polar π bond is found. For a further discussion we refer the reader to the review paper by Berthier and Serré.[21] We used some semiempirical methods for all valence electrons in order to see if the qualitative predictions of the effects of H bonding and protonation on acetone are confirmed. The results of the Hückel-type method of Pople and Santry[22,23] and the extended Hückel theory of Hoffmann[24] are given elsewhere.[25] Here we restrict ourselves to the iterative extended Hückel method[26] and the CNDO method[27,28] (most simple SCF method for all valence electrons). These latter methods can be expected to give a reasonable account of the expected charge redistribution.

Experimental Section

The proton measurements were carried out on a Varian DA-60 spectrometer, equipped with an internal lock. The samples were in spinning Pyrex tubes of 5 mm outer diameter. All the reported values are averages of 6 to 12 spectra. For the acetone concentrations below 3 mol %, spectrum accumulation was applied using a Varian C-1024 time averaging computer.

The ^{13}C resonance was carried out on the same spectrometer provided with a 15.08-MHz transmitter, built in this laboratory. For detection the appropriate 60-MHz circuits were retuned at 15.08-MHz. The 5-MHz intermediate frequency (normally obtained by mixing the 60-MHz with a 55-MHz signal) was generated by mixing the 15.08-MHz with the signal from a 10.08-MHz oscillator. As an external reference about 50% carbonyl ^{13}C enriched acetic acid was used. The

reference was kept in a small concentric inner tube in the nonspinning 15-mm outer diameter sample tube. The necessary bulk susceptibility corrections were made. We observed 2-kHz side bands and suppressed the center 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.[29,30] The reported values are averages of six spectra, each consisting of a scan increase and decrease in order to avoid transient shifts.

The acetone was obtained from E. Merck AG (uvasol) and used without further purification. The water used was distilled several times. The sulfuric acid was 95.2% Baker Analyzed reagent from J. T. Baker Chemical Co.

Theoretical Section

A. Molecular Wave Functions. In the extended Hückel theory of Hoffmann[24] a Hückel matrix is constructed in an empirical way. The diagonal elements α_μ are taken as the negative valence state ionization potentials of the corresponding orbitals. The off-diagonal elements are approximated by

$$\beta_{\mu\nu} = 1.75 S_{\mu\nu}(\alpha_\mu + \alpha_\nu)/2 \tag{1}$$

Further, in solving the eigenvalue equations, overlap is taken into account. As the ionization potentials depend on the atomic charges,[31] the diagonal elements α_μ are a function of the charges too. We used

$$\alpha_\mu = \alpha_\mu{}^0 + \Delta\alpha q_A \tag{2}$$

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where μ refers to an AO χ_μ on atom A with excess charge q_A. In this iterative extended Hückel method (IEH) iterations are performed until the charges at the output do not differ more than about 0.001 au from the charges at the input.[26]

In the CNDO method[27,28] a Hartree–Fock matrix F is constructed with elements

$$F_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + \{(P_{AA} - Z_A) - \tfrac{1}{2}(P_{\mu\mu} - 1)\}\gamma_{AA} + \sum_{B(\neq A)} (P_{BB} - Z_B)\gamma_{AB} \quad (3)$$

$$F_{\mu\nu} = \beta_{AB}{}^0 S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \quad (\mu \text{ on A, } \nu \text{ on B}) \quad (4)$$

$P_{\mu\nu}$ is an element of the ordinary charge and bond order matrix; P_{AA} is the total electron density on atom A with core charge Z_A. For the Mulliken electronegativity $\tfrac{1}{2}(I_\mu + A_\mu)$, for $\beta_{AB}{}^0$, and for γ_{AB}, the average Coulomb integral between valence AO's on A and B, the CNDO/2 parametrization of Pople and Segal[28] is used. The calculation is considered to be self-consistent if the total energy agrees with that of the last iteration to within 10^{-5} au. Trial vectors are obtained from a Hückel-type calculation retaining only the first terms of eq 3 and 4. In solving the eigenvalue equations for F, overlap is ignored by setting $S_{\mu\nu} = \delta_{\mu\nu}$.

B. Coupling Constants. In the theory of nuclear spin–spin coupling of Pople and Santry[32,33] the Fermi contact contribution to the coupling constant is

$$J_{AB} = C_{AB}\, s_A{}^2(0) s_B{}^2(0) \pi_{s_A,s_B} \quad (5)$$

C_{AB} is a constant for a specific pair of nuclei AB; $s^2(0)$ is the density of the relevant s orbital at the nuclear position. Furthermore

$$\pi_{s_A,s_B} = -4 \sum_i^{occ} \sum_\alpha^{unocc} (\epsilon_a - \epsilon_i)^{-1} c_{is_A} c_{is_B} c_{as_A} c_{as_B} \quad (6)$$

is the atom–atom polarizability. For the CNDO method $(\epsilon_a - \epsilon_i)$ is replaced by $(\epsilon_a - \epsilon_i - \gamma_{ia})$, where γ_{ia} is the Coulomb integral between the MO's ψ_i and ψ_a. For $s^2(0)$ of carbon we used the atomic SCF value of 2.767 au.[32] For hydrogen 0.550 au was used which value is consistent with the orbital exponent of 1.2. In the derivation of eq 5 only one-center integrals are retained.

This type of theory of nuclear spin–spin coupling has been applied by various authors, using the Hückel-type theory of Pople and Santry[32–36] and the extended Hückel theory of Hoffmann.[37,38] A comparison between these two approaches has been made by de Jeu and Beneder.[39] CNDO calculations of coupling constants have been carried out by Ditchfield and Murrell.[40,41]

C. Chemical Shifts. For the calculation of the ^{13}C and ^{17}O screening constants we use the MO theory of localized contributions to the screening.[42–44] The most important approximations are the neglect of differential overlap and the neglect of electronic cur-

rents on neighbor atoms. The diamagnetic contribution to the screening of atom A is

$$\sigma_d = \frac{e^2}{3mc^2} \sum_\mu P_{\mu\mu}\langle r^{-1}\rangle_\mu \quad (7)$$

For a Slater-type orbital (STO) with exponent ζ_μ

$$\langle r^{-1}\rangle_\mu = \zeta_\mu/a_0 \quad (8)$$

In agreement with Pugmire and Grant[45] we take as our starting point for the paramagnetic contribution the formula of Karplus and Das.[43] Neglecting again differential overlap and the neighbor anisotropy term, we arrive at

$$\sigma_p = -\frac{2e^2\hbar^2}{3m^2c^2\Delta E} \left\{ \sum_{\mu = x,y,z} P_{\mu A\mu A} R_{\mu\mu} + \frac{1}{4} \sum_{\substack{\mu,\nu = x,y,z \\ (\mu \neq \nu)}} \sum_B P_{\mu A\nu B} P_{\nu A\mu B} - P_{\mu A\mu B} P_{\nu A\nu B})R_{\mu\nu} I_{\mu\nu} \right\} \quad (9)$$

The summation B runs over all atoms, including the atom A under investigation; the index μA refers to an STO χ_μ on A; ΔE is the average excitation energy. Furthermore the following substitutions are made for the radial integrals on one atom

$$R_{\mu\nu} = \langle R(\mu)|r^{-3}|R(\nu)\rangle = \frac{(\zeta_\mu\zeta_\nu)^{5/2}}{6a_0^3(\zeta_\mu + \zeta_\nu)^2} \quad (10)$$

$$I_{\mu\nu} = \langle R(\mu)|R(\nu)\rangle = \frac{32(\zeta_\mu\zeta_\nu)^{5/2}}{(\zeta_\mu + \zeta_\nu)^5} \quad (11)$$

$R(\mu)$ is the radial part of STO χ_μ. Using a simple Slater screening concept the exponent ζ_μ is defined, for instance, for a carbon atom by

$$\zeta_\mu = 3.25\beta - 0.35 \sum_{\nu(\neq\mu)}^A (q_\nu - 1) \quad (12)$$

q_ν is the electron density in STO χ_ν; β is a parameter describing the contraction of an STO in a molecule.[46]

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β is given the value 1.05 for a π electron and 1.15 for a σ electron.

Equation 9 for the paramagnetic screening reduces to the well-known formula of Karplus and Pople,[47] if all electron densities q_ν in eq 12 are equal. Then $R_{\mu\nu} = \langle r^{-3} \rangle$ and $I_{\mu\nu} = 1$. However, we shall not use these simplifications.

Table I: Parameters for the IEH calculations (eV)

|	H(1s)	C(2s)	C(2p)	O(2s)	O(2p)
$-\alpha°$	13.60	21.40	11.40	32.30	15.84
$-\Delta\alpha$	14.00	11.90	11.90	15.95	15.95

D. Numerical Evaluations. All overlap integrals were calculated using a basis of STO's, with exponents according to Slater's rules. For hydrogen we used $\zeta = 1.2$. In the IEH method where overlap is not ignored, solutions of the eigenvalue equations were obtained by the method of two successive diagonalizations. The necessary parameters are given in Table I. In this method the usual problem to obtain convergence was met and overcome by using in the successive iterations only a fraction of the charge predicted by the former iteration cycle. The diagonal elements are made consistent with the atomic charges as defined by Löwdin.[48] This does not automatically imply self-consistency for other charge definitions.[49] In the application to eq 9 the charge and bond order matrix over the orthogonal Löwdin orbitals is used; so eq 9 and the wave functions are consistent with each other with respect to the neglect of differential overlap. Nevertheless, the integrals $R_{\mu\nu}$ and $I_{\mu\nu}$ are calculated with the normal basis of STO's. In all the calculations, ΔE in eq 9 is chosen equal to 7 eV. A small increase that might be expected for H bonding[13] would not affect our conclusions seriously.

In the calculations, the experimental geometry used for acetone is $r_{CO} = 1.23$ Å, $r_{CC} = 1.56$ Å, and $r_{CH} = 1.09$ Å.[50] All the carbon atoms and the oxygen lie in one plane; $\angle CCC = 120°$. Each of the methyl groups can have a position with a CH bond eclipsed or staggered to the carbonyl bond (barrier 0.78 kcal mol^{-1}). For the calculations on acetone H-bonded to water the following model is used
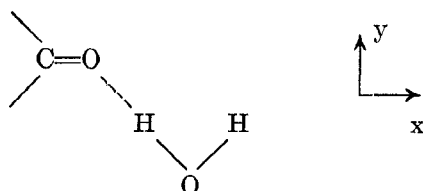
Thus the water molecule is put in the plane of the acetone skeleton and a linear H bond is assumed making an angle of 120° with the carbonyl bond. The water

geometry ($r_{OH} = 0.96$ Å, $\angle HCH = 105°$) is modified by taking in the H bond $r_{OH} = 1.05$ Å. Furthermore $r_{OO} = 2.50$ Å. These values give a minimum for the total energy of the acetone–water complex in a CNDO calculation.[51] For protonated acetone we used
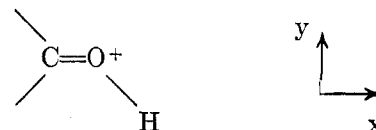
$r_{OH} = 0.985$ Å and $\angle COH = 120°$. Furthermore r_{CO} is increased from 1.23 Å to 1.27 Å. These values give an energy minimum for protonated formaldelyde in a nonempirical MO calculation by Ros.[52]

Results

The ^{17}O, ^{13}C, and ^1H chemical shifts of pure acetone, relative to some reference compound, are given in Table II. The methyl ^{13}C is much more shielded than the carbonyl ^{13}C. Without calculations on the reference

Table II: Experimental Chemical Shifts for Pure Acetone

Chemical shift		Relative to
Carbonyl ^{17}O	-572^a	Water
Carbonyl ^{13}C	-12.4	Carbon disulfide
Methyl ^{13}C	162.9	Carbon disulfide
Methyl ^1H	-2.03	TMS

^{a} Reference 4.

compounds, the only chemical shift accessible to numerical calculation is the difference between methyl and carbonyl ^{13}C. We shall denote this quantity by Δ.

In Figure 1 the concentration dependence is shown for the ^1H chemical shifts in acetone–water.[53,54] In Table III the same concentration dependence is given for $^1J_{CH}$, $^4J_{HH}$, carbonyl $\delta(^{13}C)$, and methyl $\delta(^{13}C)$ of acetone. The coupling constants increase with increasing H bonding (decreasing molar % acetone). The carbonyl ^{13}C is shifted to lower field (deshielded) with increasing H bonding, while the methyl ^{13}C is hardly affected. $\delta(^{17}O)$ data are given for the purpose of comparison; we see that the ^{17}O resonance shifts in the

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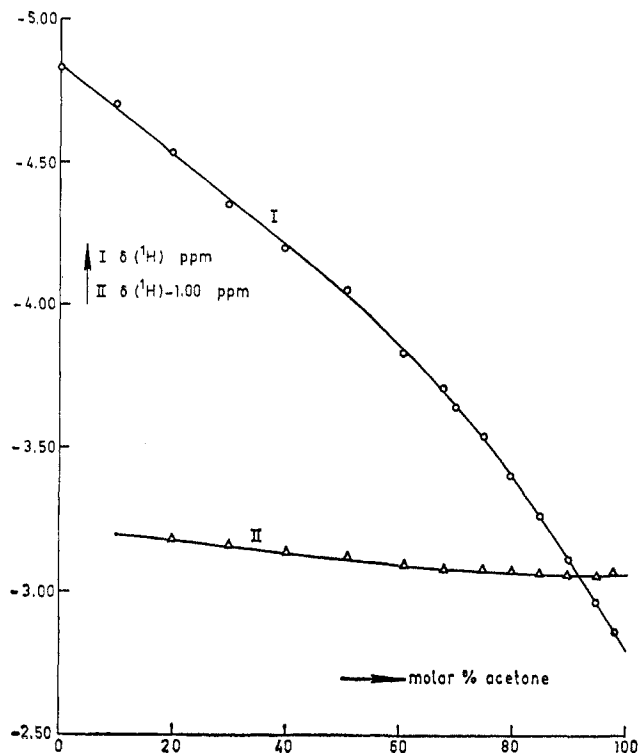(54) I. Satake, private communication.

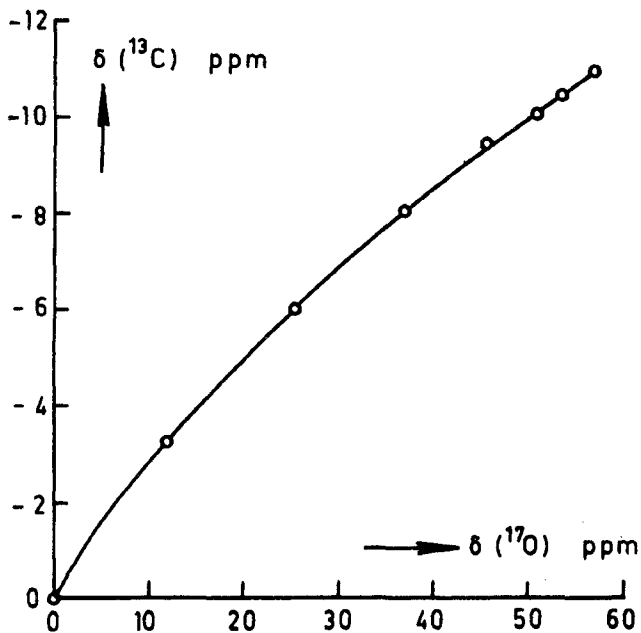Figure 1. Proton chemical shifts for acetone–water. I, water protons (ref 53); II, acetone protons (ref 54).

Figure 2. Carbonyl ^{13}C vs. ^{17}O chemical shift for acetone at various concentrations in water.

Figure 3. $^{1}J_{CH}$ and $^{4}J_{HH}$, vs. $\delta(^{13}CO)$ for acetone at various concentrations in water.

Figure 4. $^{1}J_{CH}$ vs. $\delta(^{13}CO)$ for 0.2 M acetone in various concentration ratios of sulfuric acid–water.
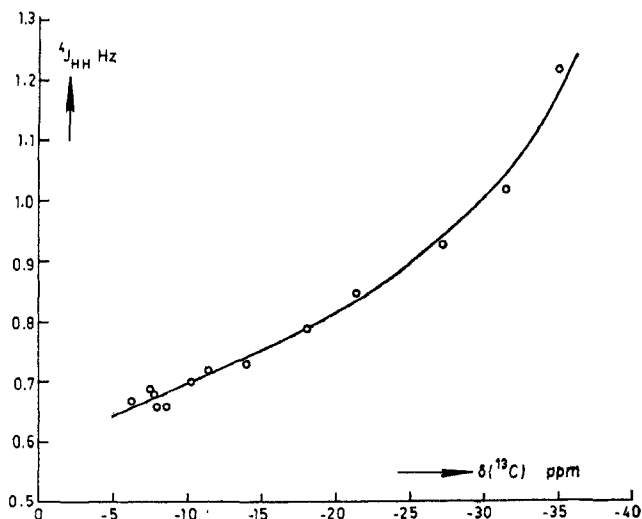
Figure 5. $^{4}J_{HH}$, vs. $\delta(^{13}CO)$ for 0.2 M acetone in various concentration ratios of sulfuric acid–water.

opposite direction as the carbonyl ^{13}C. From Figure 2 we see that the absolute changes in carbonyl $\delta(^{13}C)$ and $\delta(^{17}O)$ are not strictly linear with each other. In Figure 3 it is shown that within the experimental errors $^{1}J_{CH}$ and $^{4}J_{HH}$ vary linear with carbonyl $\delta(^{13}C)$.

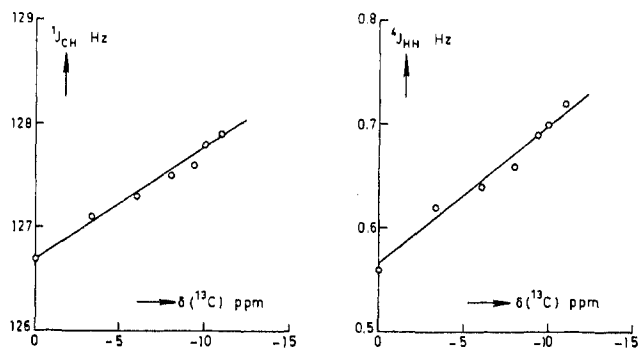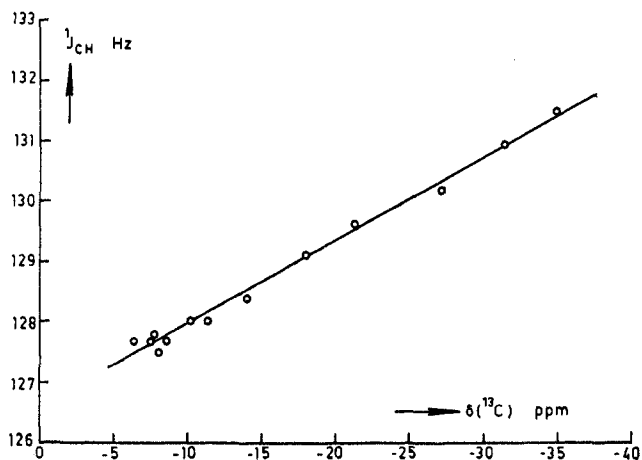In Table IV the same coupling constants and chemical shifts (except $\delta(^{17}O)$) are given for 20 mol % ace-

tone in various sulfuric acid–water concentration ratios. Thus the sulfuric acid concentration varies from 0 to 80 mol % in the total solution. The increase in $^{1}J_{CH}$ and $^{4}J_{HH}$ is now much more. The methyl ^{13}C chemical

Table III: Concentration Dependence of Coupling Constants (Hz) and ^{17}O and ^{13}C Chemical Shifts (ppm) for Acetone in Water

Mol % acetone	Coupling constants		Chemical shifts		
	$^1J_{CH}{}^a$	$^4J_{HH}{}^b$	Carbonyl $^{17}O{}^c$	Carbonyl $^{13}C{}^d$	Methyl $^{13}C{}^d$
100	126.7	0.56	0.0	0.0	0.0
65	127.1	0.62	12.0	−3.3	−0.4
35	127.3	0.64	25.5	−6.0	−0.4
20	127.5	0.66	37.1	−8.0	−0.6
10	127.6	0.69	45.7	−9.4	−0.9
5	127.8	0.70	51.1[e]	−10.0	−0.9
2.5	127.9	0.71	53.8[e]	−10.4	−1.3
1.0	127.8	0.71			
0.5	127.8	0.70			
0.2	127.9	0.72			
0	127.9[e]	0.72[e]	57.0[e]	−10.9[e]	−1.2[e]

[a] Standard deviation 0.05 Hz. [b] Standard deviation 0.005 Hz. [c] ± 1.0 ppm (ref 4). [d] Standard deviation 0.2 ppm. [e] Extrapolated from the higher concentrations.

Table IV: Coupling Constants (Hz) and Chemical Shifts (ppm) for 20 Mol % Acetone in Various Concentration Ratios of Sulfuric Acid–Water

Mol % sulfuric acid	Coupling constants		Chemical shifts			
	$^1J_{CH}{}^a$	$^4J_{HH}{}^b$	Carbonyl $^{13}C{}^c$	Methyl $^{13}C{}^c$	Methyl $^1H{}^d$	Solvent $^1H{}^e$
0	127.5	0.66	−8.0	−0.6	−2.24	−4.56
2	127.7	0.67	−6.3	−0.6	−2.29	−5.10
3	127.7	0.69	−7.5	−0.6		
6	127.7	0.66	−8.6	−0.5	−2.29	−6.23
8	127.8	0.68	−7.8	−0.5	−2.31	−7.13
12	128.0	0.70	−10.2	−0.5	−2.35	−8.19
16	128.0	0.72	−11.4	−0.5	−2.37	−8.40
23	128.4	0.73	−14.0	−0.5	−2.43	−9.86
32	129.1	0.79	−18.0	−0.1	−2.54	−11.00
40	129.7	0.85	−21.3	0.2	−2.68	−11.57
49	130.2	0.93	−27.1	0.8	−2.80	−12.02
55	130.9	1.02	−31.4	−0.7		
63	131.5	1.22	−35.0	−1.3	−2.96	−12.26

[a] Standard deviation 0.05 Hz; [b] Standard deviation 0.005 Hz. [c] Relative to pure acetone; standard deviation 0.5 ppm. [d] Relative to TMS; standard deviation 0.02 ppm. [e] Relative to TMS; standard deviation 0.1 ppm.

shift still does not change appreciably, while the carbonyl ^{13}C is shifted to a much lower field by protonation rather than by H bonding. The variations in $^1J_{CH}$ and carbonyl $\delta(^{13}C)$ are again linear with each other (Figure 4). For $^4J_{HH}$ a large deviation from linearity occurs (Figure 5).

The results of the theoretical calculations with aid of the methods described in the previous section, are given in the Tables V, VI and VII; H bonded refers to the calculation on acetone H bonded to water. In Table V the excess charges on the atoms are given, in Table VI the theoretical coupling constants together with the experimental values (when available), and in Table VII the diamagnetic and paramagnetic screening constants together with the values for Δ. All theoretical values are averages over the three rotational isomers.

Discussion

A. General Considerations. The two theoretical methods both reproduce the energetical order of the rotational isomers. The conformation with both methyl groups eclipsed to the CO bond is the most favorable; with both staggered is the least favorable. The expected polarity of the carbonyl group is also found in both methods, while the excess charges on the methyl carbon and hydrogen atoms are very slight (Table V). In the orbital populations (not given in the tables) the $2p_y$ lone pair on oxygen is clearly present; the 2s lone pair is more mixed up with the other AO's. From the $2p_x$ and $2p_z$ populations we learn that both the carbonyl σ and the carbonyl π bond are polar; in the IEH method the σ bond is more polar while in the CNDO method the π bond is the more polar.

Table V: Theoretical Excess Charges for Acetone (au)

| | | Carbonyl | | | Methyl | |
		H	O	C	C	H
IEH[a]	Pure		−0.240	0.093	0.003	0.024
	H-bonded		−0.190	0.144	0.014	0.030
	Protonated	0.240	0.022	0.281	0.059[b]	0.056[b]
CNDO	Pure		−0.263	0.251	−0.071	0.026
	H-bonded		−0.270	0.275	−0.074	0.033
	Protonated	0.268	−0.113	0.415	−0.090[b]	0.101[b]

[a] Löwdin charges (ref 48).   [b] There is a slight difference between the two methyl groups, which is disregarded here.

Table VI: Experimental and Theoretical Coupling Constants for Acetone (Hz)

		CC	CH	HCH	HCC	HCCC	HCCCH
Exptl	Pure	40.6[a]	126.8	−14.9[b]	−5.9[c]	2.2[d]	0.56[d]
	H-bonded		127.9				0.72
	Protonated		131.5				1.22
IEH	Pure	26.5	67.3	−21.3	−5.1	0.4	−0.1
	H-bonded	26.5	66.7	−21.1	−4.9	0.4	0.1
	Protonated	26.6	64.4	−20.2	−4.4	0.4	1.8
CNDO	Pure	11.2	55.6	0.4	0.1	1.2	−1.8
	H-bonded	10.8	54.8	0.3	0.3	1.0	−1.2
	Protonated	9.1	58.4	−0.1	0.8	0.8	−0.4

[a] F. J. Weigert and J. D. Roberts, private communication.   [b] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959); negative sign assumed in analogy with the same coupling in methane (ref 34).   [c] G. J. Karabatsos and C. E. Orzech, *J. Amer. Chem. Soc.*, **86**, 3574 (1964); negative sign assumed in analogy with the same coupling in acetaldehyde, E. Sackmann and H. Dreeskamp, *Spectrochim. Acta*, **21**, 2005 (1965).   [d] H. Dreeskamp, *Z. Phys. Chem.*, **59**, 321 (1968); W. H. de Jeu and H. Angad Gaur, *Mol. Phys.*, **16**, 205 (1969).

Table VII: ^{17}O and ^{13}C Screening Constants for Acetone (ppm)

| | | Carbonyl O | | Carbonyl C | | Methyl C | | Δ^a |
		σ_d	σ_p	σ_d	σ_p	σ_d	σ_p	
Exptl	Pure							175.3
	H-bonded							185.0
	Protonated							209.0
IEH	Pure	419.9	−1238.6	266.4	−526.2	268.8	−482.2	46.4
	H-bonded	418.7	−1190.2	265.8	−538.0	269.2	−485.5	55.9
	Protonated	414.1	−1176.1	264.5	−581.7	268.2	−499.7	85.7
CNDO	Pure	420.0	−1287.3	264.6	−580.1	269.7	−473.5	111.8
	H-bonded	419.9	−1253.5	264.4	−585.1	269.8	−473.5	117.0
	Protonated	416.2	−1128.2	263.3	−622.7	269.9	−478.9	150.6

[a] $\Delta = \delta(^{13}CH_3) - \delta(^{13}CO)$.

For H bonding and for protonation we notice a considerable decrease of charge on the carbonyl carbon (Table V). The oxygen atom is much less affected although some decrease of electron density is predicted in the case of protonation. For H bonding some charge is transferred to the water molecule.[51] Generally we see that there is a drift of electrons in the direction of the oxygen atom for H bonding and to the carbonyl proton for protonation. This is mainly at the expense of the carbonyl carbon. Furthermore, the methyl protons together lose some electrons while the methyl carbons are much less affected. These changes cause an increase in carbonyl π bond polarity; the polarity of the σ bond changes much less.

B. Coupling Constants. From Table VI we see that for pure acetone the sign and the order of magnitude of the directly bonded CC and CH coupling constants are rather well reproduced in both methods. As expected, the theoretical values are smaller than the experimental ones because of the fact that simple MO theory underestimates electron correlation.[55] Recent calculations[56] seem to indicate that the atomic SCF value we used for $s_C^2(0)$ is too low for molecules. Consequently, agreement in absolute magnitude with experiment is probably better than is apparent from Table VI. The CNDO method is not very successful for the prediction of the two-bond coupling constants. Probably the inclusion of the one-center exchange integrals (INDO method) is essential to get the negative value.[41,56] π-Electrons contributions which are not included in Table VI may be of importance for the long-range coupling constants. Using a valence bond formalism, Holmes and Kivelson[3a] calculated for acetone a π-electron contribution to $^4J_{HH}$ of -0.6 Hz. This value decreases in absolute magnitude with increasing π-bond polarity. In order to obtain the experimental value, we have to postulate a positive contribution through the σ bonds and/or through space[57] of $+1.2$ Hz. However, both calculations give a negative value. Nevertheless we may hope that the substituent effects can be predicted with more reliability.[34]

From Table VI we see that the increase in $^1J_{CH}$ for H-bond formation and for protonation is in general not reproduced by the calculations. However, the increase in $^1J_{CH}$ is qualitatively in accordance with the well-known theory in which it is emphasized that $^1J_{CH}$ in CH_3X is proportional to the amount of carbon s character in the CH bonds.[55,58] A change in electronegativity of X is supposed to cause a rehybridization of the carbon atom. With increasing electronegativity of X the CX bond becomes more polar (more p character), leaving more s character for the CH bonds; thus $^1J_{CH}$ increases. In our case the carbonyl group gets an increased electron attracting power when an H bond is formed and even more for protonation. This means an effective increase in electronegativity, and the increase in $^1J_{CH}$ is as expected.[3b] There are several ways to

obtain a quantitative estimate of the amount of s character from the calculations. Assuming that a transformation to highly localized MO's is possible, we can use the squares of the bond orders.[59] In this way we get CNDO values for the amount of carbon s character of 0.249 (pure acetone), 0.250 (acetone H bonded to water), and 0.260 (protonated acetone). So for H bonding a small and hardly significant increase of s character is found despite the predicted decrease of $^1J_{CH}$ (Table VI). For protonation the predicted increase of $^1J_{CH}$ is in agreement with the increase of carbon s character in the CH bonds.

For $^4J_{HH}$ the experimental increase when an H bond is formed and for protonation is relatively much more than for $^1J_{CH}$. As the π-bond polarity increases, we can expect a decrease in absolute magnitude of the π electron contribution to $^4J_{HH}$.[3a] The calculations also predict a change in positive direction for the contribution *via* the σ skeleton (Table VI). Thus the changes in both contributions reinforce each other to give the more positive value of $^4J_{HH}$. This is consistent with a simple MO picture of substituent effects on $^4J_{HH}$ in which a shift in positive direction is predicted when electrons are withdrawn from the central carbon atom.[60,61]

Laszlo[2] has expressed his doubt about the explanation given above. The main argument is that changes with solvent of $^4J_{HH}$ in monochloroacetone can be explained by a change in preference for eclipsed and staggered rotational isomers.[62] We know of no evidence to support this view in the case of acetone, as the energetical differences between the isomers are very slight. Moreover, both calculations on acetone give differences in the coupling constants of the different isomers that are less than 0.2 Hz. Only the π-electron contribution to $^4J_{HH}$ depends on the orientation of the methyl groups.

C. Chemical Shifts. Looking at the chemical shifts (Table II and VII) we see, as expected, that the major part of the difference in shielding between carbonyl and methyl ^{13}C arises from variations of σ_p. The CNDO method gives the right order of magnitude for Δ; the value of the IEH calculation is far too low. The shift to lower field of carbonyl $\delta(^{13}C)$ when an H bond is formed and for protonation is very well reproduced by the calculations. This is also true for the near constancy of methyl $\delta(^{13}C)$. So even the IEH method

(55) J. N. Murrell in "Progress in NMR Spectroscopy," J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., in press.

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(59) C. Trindle and O. Sinanoğlu, *J. Amer. Chem. Soc.,* **91,** 853 (1969).

(60) D. J. Sardella, *J. Mol. Spectrosc.,* **31,** 70 (1969).

(61) M. Barfield and B. Chakrabarti, *Chem. Rev.,* in press.

(62) K. Takahashi, *Bull. Chem. Soc. Jap.,* **37,** 291 (1964).

which gives a bad result for Δ reflects the changes rather well. For the carbonyl ^{17}O the experimental shift of 57.0 ppm to a higher field when an H bond is formed is also found in the calculations. Thus here we find a shift to a higher field despite the fact that no appreciable increase of the electron density on oxygen is predicted. Unfortunately, no experimental ^{17}O chemical shifts are available for protonated acetone.

A shift to a lower field is normal for H-bonded protons.[63] For the water protons in acetone–water we have two competing types of H bonds, water–acetone and water–water. The shift to a lower field with increasing water concentration (Figure 1) suggests that the H bonds water–water are stronger than water–acetone.[53] The near constancy of the acetone ^1H chemical shift when an H bond is formed is probably due to a cancellation of several factors. As in both calculations the charges on the methyl protons decrease when an H bond is formed (and even more for protonation), we can expect a decreased diamagnetic screening. This is more or less compensated by a greater neighbor anisotropy effect. For the acidic solutions the changes in the ^1H chemical shift of the solvent (Table IV) are more difficult to explain. We observe a weighted average of the protons in the species H_2SO_4, HSO_4^-, H_3O^+, H_2O, $(CH_3)_2CO^+H$, and higher order complexes.

The deviation from linearity in the relation between the changes in carbonyl $\delta(^{17}O)$ and $\delta(^{13}C)$ when an H

bond is formed (Figure 2) can be attributed to the fact that the carbon atom has an opportunity to compensate for the loss of electrons at the cost of the methyl groups. Therefore the change in $\delta(^{13}C)$ is not as rapid as in $\delta(^{17}O)$, whereby we get the curve. The linear relation between the changes in $^1J_{CH}$ and carbonyl $\delta(^{13}C)$ (Figures 3 and 4) can be understood by the direct way in which both depend on the increased electron attracting power of the carbonyl oxygen when an H bond is formed and for protonation. In the light of the more complicated mechanisms for $^4J_{HH}$ the linear relation between the changes in $^4J_{HH}$ and carbonyl $\delta(^{13}C)$ when an H bond is formed (Figure 3) must be more or less fortuitous. This is confirmed by the fact that this linearity does no longer hold in the case of protonation (Figure 5).

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On the Oxyiodine Radicals in Aqueous Solution

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The flash photolysis of IO_3^- and IO^- provides evidence for the following primary processes: $IO_3^- \xrightarrow{h\nu} IO_2 + O^-$ and $IO^- \xrightarrow{h\nu} I + O^-$. These are followed by secondary reactions involving the parent ions. O^- (or OH) reacts with IO_3^- and IO^- to yield IO_3 and IO, respectively; the rate constants of these reactions could be determined by studying the O_3^- decay in alkaline solutions containing O_2. IO_2 and I_2^- (produced from I in presence of I^-) react with IO_3^- and IO^-, respectively, to yield IO. The spectra and decay kinetics of the oxyiodine radicals were also studied by pulse radiolysis. The two techniques lead to the same conclusions.

The flash photolysis and pulse radiolysis techniques have yielded some basic information on the oxybromine radicals BrO_2 and BrO in solution.[1,2] The analogous chlorine radicals are well known. On the other hand, very little is known on the oxyiodine radicals. Such information is essential for understanding the photochemistry of the oxyiodine anions.

The oxybromine anions were shown to undergo two radical types of photo-dissociation to yield O^- and O atom, respectively, which can react with the parent

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