

# NMR Shielding and the Periodic Table

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The concept of chemical periodicity is central to the study of chemistry (1, 2). As applied to the chemical elements, the term indicates the regular recurrence of particular types of chemical and/or physical properties as a function of some atomic parameter. No other generalization rivals the periodic table of the elements in its ability to systematize and rationalize known chemical facts or to predict new ones and suggest fruitful areas for further study (3). Chemical periodicity and the periodic table now find their natural interpretation in the detailed electronic structure of the atom. There are many properties of both elements and their compounds that exhibit periodicity based upon electron configuration. Properties such as ionization energies, affinity energies, oxidation states, and atomic and ionic radii may be singled out as being more important than others that may be considered as composite properties such as electronegativities, bond energies, and redox potentials (2).

The objective of this article is to find periodic, structurally significant observables that can be correlated to the nuclear shielding or alternatively to investigate whether chemical shift can be used to intensify the periodic disposition of valence electrons. The fundamental principles and concepts of periodicity in nuclear shielding are quite unfamiliar to most chemists and are essentially unknown to undergraduate chemistry students. There are, no doubt, many reasons for this lack of comprehension of the principles of nuclear shielding and its periodic properties, but one frequently cited reason is the need for a relatively sophisticated mathematical background (4, 5). Such a foundation is helpful, just as it is in all fields of science, but an understanding of the principles of nuclear shielding can be acquired by using commonly understood models or analogies.

## Atomic Nuclear Shielding

The origin of the shielding of a nucleus, which belongs to an isolated atom, is understood easily in qualitative terms (6). Since electrons are moving charges, they are subject to the laws of electromagnetic induction. The net effect of an external magnetic field is to superimpose, on the orbital motion of the electron, an extra motion of electron around the field axis that generates a local magnetic field at the nucleus opposing the applied external magnetic field (Fig. 1). Thus, the effective field  $B_{\text{eff}}$  at the nucleus will be

$$B_{\text{eff}} = B_0(1 - \sigma^d) \quad (1)$$

The nucleus is said to be shielded, the extent of diamagnetic shielding being given by the dimensionless shielding constant  $\sigma^d$ . The numerical sizes of the shielding constants of different atoms are related to the number of circulating electrons and, thus, increase rapidly and monotonically with the nuclear atomic number (Table 1). They vary from  $18 \times 10^{-6}$  for hydrogen to  $9894 \times 10^{-6}$  for thallium atoms and do not exhibit a periodic relationship as a function of the atomic number.

## Molecular Nuclear Shielding

In a molecule, the Larmor precession of the electron(s) of the observed nucleus about the field direction  $z$  is now im-

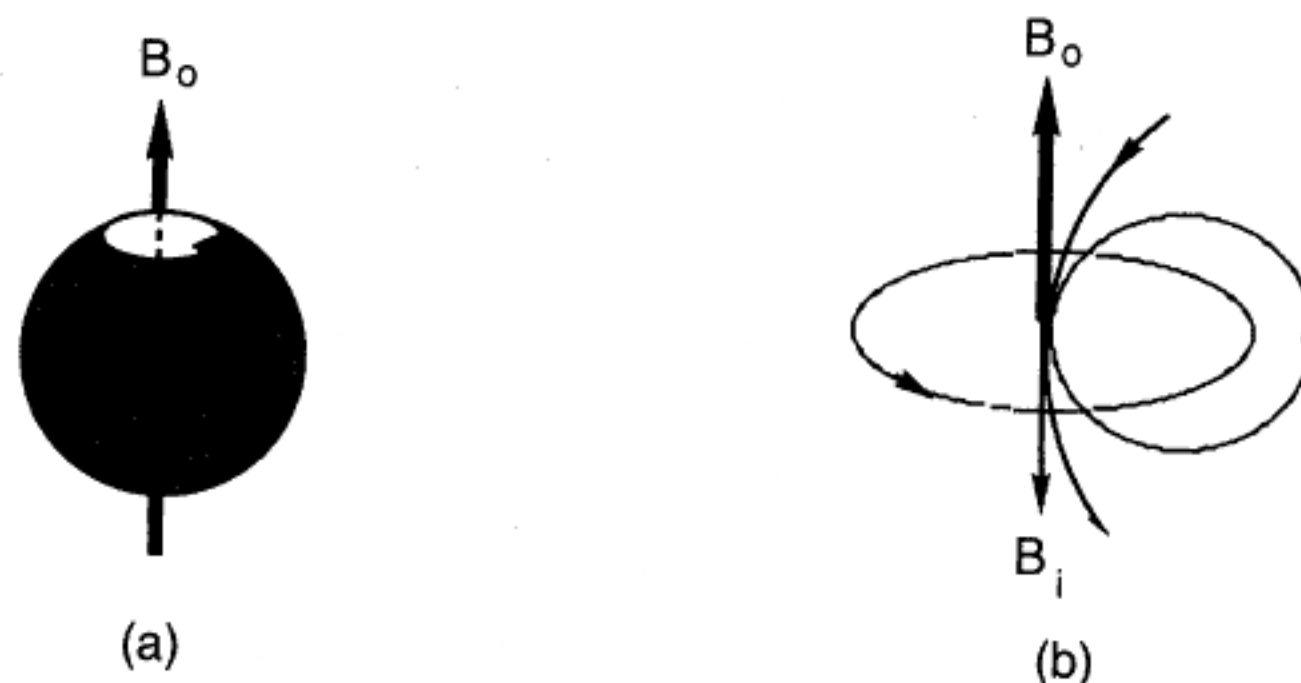


Figure 1. Electronic shielding (6). (a). Circulation of the electronic charge cloud under the influence of a magnetic field  $B_0$ . (b) The secondary magnetic field  $B_1$  produced by the precession. Note that the circulation is equivalent to electric currents  $i$  in the reverse direction.

ped by the presence of the other nuclei. The simple model of circular electron paths of (Fig. 1) is applicable only if the molecule can be so orientated that the nuclei and electrons have an arrangement that is axially symmetric along a line parallel to the  $z$  axis. For all other cases, and even for axially symmetric molecules, a second term is necessary to describe the hindering of electron circulation by the presence of the other nuclei. The resultant reduced circulation may be represented by a superposition of an atomic current in the opposite direction to that of the free atom (Fig. 2) (7). Because this second term corresponds to a magnetic moment opposing that of the diamagnetic term  $\sigma^d$ , it causes deshielding and it is customarily referred to as the paramagnetic term  $\sigma^p$ . (The expression paramagnetic is somewhat misleading because it represents a temperature independent paramagnetism that is entirely different in origin from the temperature-dependent paramagnetism of the electron spin). Thus, the shielding may be expressed as

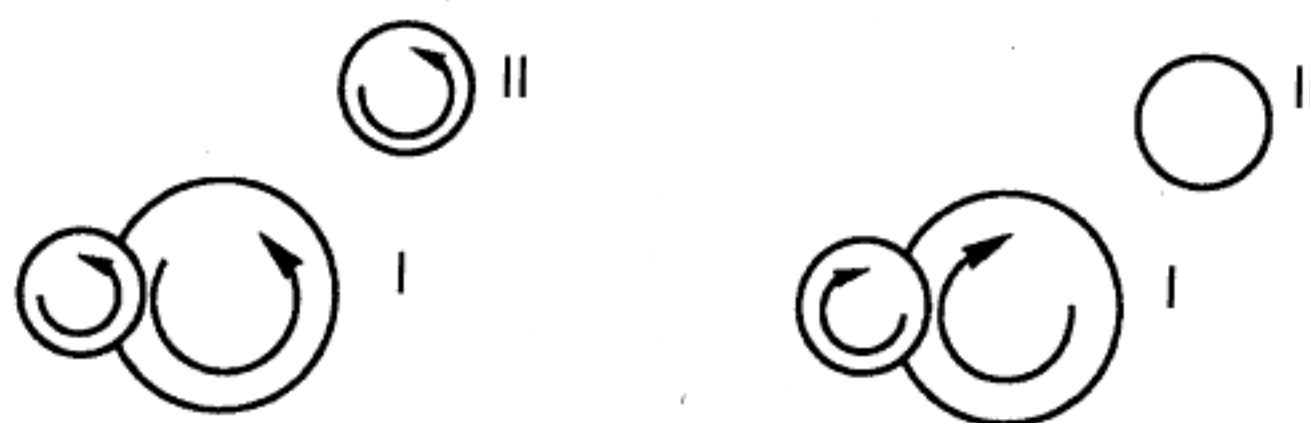


Figure 2. Molecular currents. (a) Local diamagnetic currents in a diatomic molecule I and atom II. (b) Local paramagnetic currents in molecule I only.

Table 1. Free Atom Values of Nuclear Shielding (6)

Atom	H	Li	C	N	O	F	Si	P
$\sigma^d/\text{ppm}$	17.8	101.5	260.7	325.5	395.1	470.7	874.1	961.1
Atom	Mn	Co	Se	Mo	Xe	Pt	Tl	Pb
$\sigma^d/\text{ppm}$	1942.1	2166.4	2998.4	4000.6	5642.3	9395.6	9894.2	10060.9



**Table 2. Some Contributions to Shielding (in ppm) for Carbon, Nitrogen and Oxygen (6)**

Molecule	Nucleus	$\sigma^d$	$\sigma^p$
CO	C	259.36	-206.24
	O	395.39	-367.39
H <sub>2</sub> CO	C	257.77	-208.24
	O	397.80	-651.47
HCN	C	259.08	-157.53
	N	326.70	-301.30

$$\sigma = \sigma^d + \sigma^p \quad (2)$$

where the diamagnetic term  $\sigma^d$  is of an origin similar to that of the free atom, and the paramagnetic term  $\sigma^p$  has the form

$$\sigma^p \propto -\langle r^{-3} \rangle_{2p} \frac{1}{\Delta E} \left[ Q_{AA} + \sum_{B \neq A} Q_{AB} \right] \quad (3)$$

The expression  $\langle 1/r^3 \rangle_{2p}$  is the average value of the inverse cube of the distance of the 2p electrons from the nucleus;  $\Delta E$  is the lowest excitation energy in the electronic spectrum of the compound concerned, and  $Q_{AA}$  and

$$\sum_{B \neq A} Q_{AB}$$

are defined in terms of the elements of the charge density and the bond order matrix and, thus, represent a measure of multiple bonding to the nucleus being studied. An expression analogous to eq 3 has been derived for d orbital shielding contributions.

How do excitation energies affect the shielding constant? As long as the molecule is unperturbed by a magnetic field this excited state orbital magnetism has no effect on the ground state molecule (8). Indeed, if NMR spectra could be obtained without placing the molecule in a magnetic field, then, electronic excitation energies would have no effect on the shieldings observed. However, the presence of the magnetic field creates a new electronic ground state for the molecule, similar to the old one, but with small amounts of (old) excited state character. The degree of mixing is inversely proportional to the energy separation between the ground and excited states. The reciprocal of the electronic excitation energy is, therefore, the weighting factor that determines the degree of excited state mixing.

### Shielding Ranges—Shielding Sensitivity

In NMR experiments we are concerned mainly with differences in shielding constants between atoms of the same nuclear species in different compounds rather than with absolute  $\sigma$  values. Such differences, which are very small fractions of the total shielding effect, may be estimated by the overall range of chemical shifts for a given nucleus which defines the shielding range or shielding sensitivity. Chemical shift measurements, of course, normally should be based on the resonance position of the bare nucleus (e.g.,  $H^+$  for  $^1H$  NMR or  $Li^{3+}$  for  $^6,7Li$  NMR) for which there is no shielding and, hence,  $\sigma = 0$ . Because these are quite impracticable standards, it is necessary to choose some reference substance, for each particular nucleus, as a secondary standard and to measure the resonance positions of the nucleus in different chemical species from this in parts per million as follows

$$\delta(\text{ppm}) = \frac{B_j - B_{\text{ref}}}{B_{\text{ref}}} 10^6 = (\sigma_{\text{ref}} - \sigma_j) \times 10^6 \quad (4)$$

where the factors  $B_j$  and  $\sigma_j$  refer to the effective field and shielding constant, respectively, for nucleus  $j$  ( $\sigma_{\text{ref}}$  is negligible compared to unity).

Although the absolute magnitudes of the diamagnetic and paramagnetic terms are comparable (Table 2), 90% of the variation in nuclear shielding that is manifested as a shielding range or shielding sensitivity is attributable to the variation in the orbital angular momentum of the valence electrons associated with the nucleus; this shielding variation is modelled in the paramagnetic term. Thus, the  $^{13}C$  shielding change in the  $\sigma^d$  term in CO, H<sub>2</sub>CO, and HCN is only 1.6 ppm, while the respective change in the  $\sigma^p$  term is 48.7 ppm (4, 5).

The relative importance in the variation of the  $\sigma^d$  and  $\sigma^p$  terms is illustrated nicely in  $^{19}F$  NMR. The  $^{19}F$  nucleus of the partly ionic molecule HF is strongly shielded relative to that in the nonionic molecule F<sub>2</sub> by 625 ppm. The simplest explanation of this shift would be in terms of the increase of electron density on the fluorine atom in the ionic compounds and the consequent increase in the diamagnetic term  $\sigma^d$ . This is qualitatively inadequate, however, because in going from F<sub>2</sub> to F<sup>-</sup> only a 2p electron is added. Further, the actual charge may be even smaller, since the other electrons move in expanded orbitals in the negative ion. The principal cause of shielding changes in these compounds is a variation in the paramagnetic term  $\sigma^p$ . In the spherically symmetrical fluoride ion F<sup>-</sup>, the paramagnetic contribution approaches zero; whereas, in a totally covalently bonded fluorine the deshielding contribution is at a maximum for this nucleus.

Equation 3 reveals three potential sources of variation for  $\sigma^p$  and, thus, shielding ranges, namely  $\langle r^{-3} \rangle_{np}$ , the mean excitation energy  $\Delta E$ , and the molecular orbital (MO) coefficients of the p (or d) orbitals. These parameters can be utilized to identify periodic properties in the ranges of the nuclear shielding.

### Periodicity in the Shielding Range and the Orbital-Size Factor

Jameson and Gutowsky (9) highlighted the significant role played by the  $\langle r^{-3} \rangle$  variable; that is, the inverse cube radius of the local valence electrons. It may be shown that the observed periodicity in the range of chemical shifts experienced by the different nuclei is correlated with the periodicity in free-atom  $\langle r^{-3} \rangle$  values for valence-shell p and d electrons (Fig. 3). In general, the larger values of  $\langle r^{-3} \rangle$  are those that are more susceptible to change giving rise to larger nuclear shielding ranges (10). The value of  $\langle r^{-3} \rangle$  is

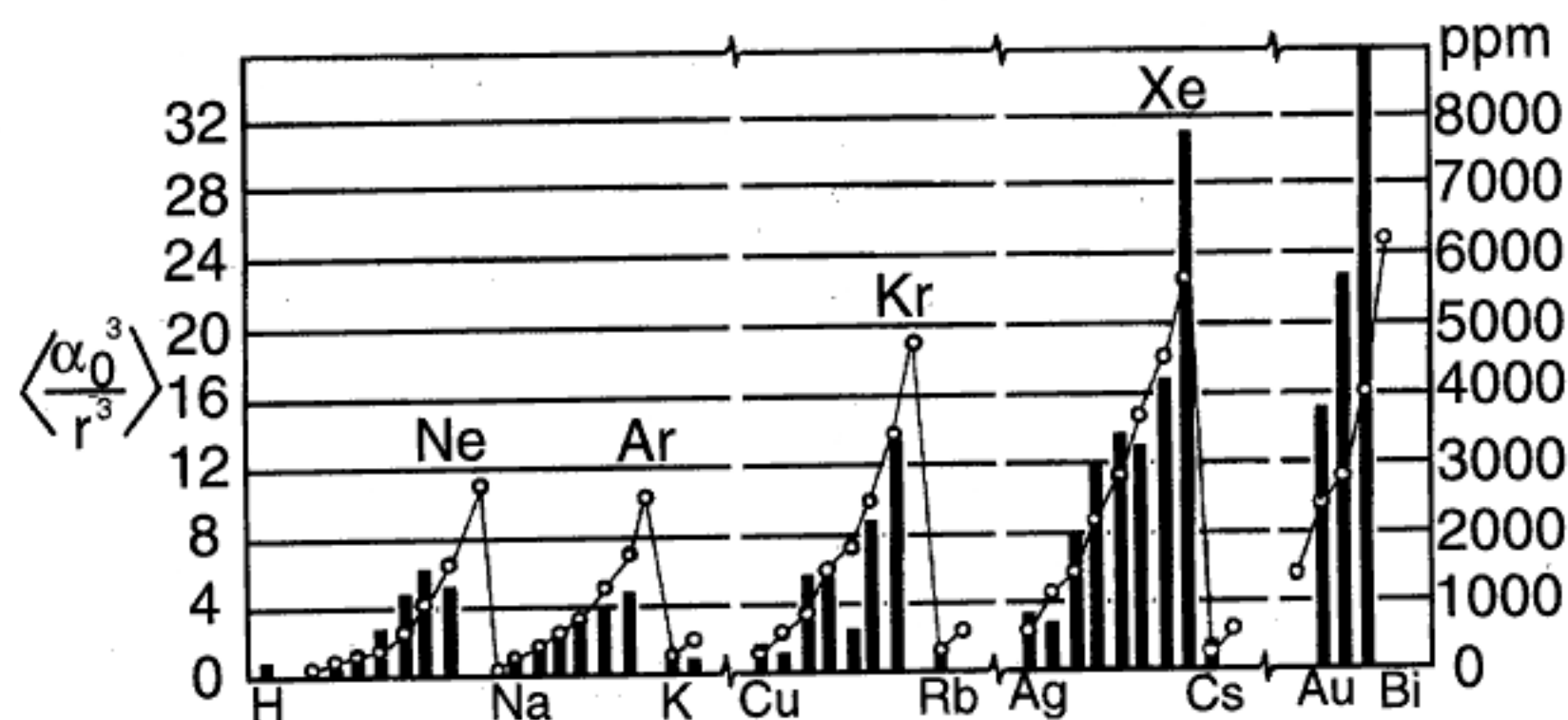


Figure 3. Experimental nuclear shielding ranges (ppm), denoted by vertical bars on the scale given to the right, of nuclei of main group and post-transition elements (9) (10). The  $\langle r^{-3} \rangle_{np}$  values (open circles) are shown, on the scale given to the left, as dimensionless ratios  $\langle \alpha_0^3 / r^3 \rangle_{np}$ , where  $\alpha_0$  is the atomic unit of length ( $\alpha_0 = 0.529 \text{ \AA}$ ).



related to the atomic number and to the position of the element in the periodic table. It is a maximum for the noble gases and drops to a minimum for each alkali metal (Fig. 3). Its variation with atomic number accounts for the fact that shielding ranges for corresponding elements in the first two rows of the periodic table are small but there are increases for the third and fourth rows.

From the above it is evident that the shielding ranges reveal broad patterns of periodicity despite wide differences in chemical structure. A more precise comparison, however, of shielding is that for compounds with analogous structure. These also appear to be scaled by ratios of  $\langle r^{-3} \rangle$  (10). For example, a plot of  $^{125}\text{Te}$  versus  $^{77}\text{Se}$  chemical shifts for analogous compounds gives a straight line with a slope of 1.8 that can be compared with 1.56 for the ratio of  $\langle r^{-3} \rangle_p$  for the free atoms. For  $^{51}\text{V}$  compared with  $^{41}\text{Ti}$  the scale factor is 1.33 for the shift ranges and 1.28 for  $\langle r^{-3} \rangle_d$ .

#### Shielding Range and Excitation Energy

$^{14,15}\text{N}$ ,  $^{17}\text{O}$ , and  $^{19}\text{F}$  have larger ranges than  $^{11}\text{B}$  and  $^{13}\text{C}$ , and a parallel situation occurs among the third row elements. These ranges reflect the presence of nonbonding electrons on N, O, and F. In general, these electrons give rise to low energy  $n \rightarrow \pi^*$  transitions and, thus, to large values of  $\sigma^p$  that cause nuclear deshielding. If the lone pairs are involved in bonding then this contribution to  $\sigma^p$  is removed and the nuclear shielding increases. Thus, the lone pair of electrons provide an extended range of nuclear shielding values.

The  $\sigma^p$  contribution to shielding ranges is particularly marked for transition metal complexes because the term  $\Delta E$  in eq 3 is usually dominated by the lowest electronic excitation energy. Ligand field theory shows this energy difference is often rather small (many solutions of transition metal ions are distinctively colored). Thus, it is not surprising that the relatively small ligand field splitting in the first transition series dramatically increases the ranges for these nuclei and may yield good  $\sigma^p / \Delta E^{-1}$  relationships.

#### Periodicity of Shielding and the Bond Multiplicity

It has already been emphasized that the atoms must possess valence p (or/and d) electrons for  $\sigma^p$  to be nonzero. The very small shielding ranges found for the elements of groups IA and IIB of the periodic table are principally due to the fact that, in addition to the unfavorable  $\langle r^{-3} \rangle_{np}$  term (Fig. 3), these atoms do not normally have valence p electrons and form mainly ionic compounds. Therefore, the

$$\left[ Q_{AA} + \sum_{B \neq A} Q_{AB} \right]$$

term and, consequently,  $\sigma^p$  do not contribute to the shielding of these nuclei. On the contrary, large shift ranges are observed for the nuclei of the elements of the groups IV–VI of the periodic table which undoubtedly reflects the readiness to form  $\pi$  bonds ( $\text{C}=\text{O}$ ,  $\text{C}=\text{C}$ ,  $\text{N}=\text{C}$ , etc). The very large shielding ranges observed for transition metal nuclei reflect the large coordination numbers, increased d-orbital participation and greater polarizability of the p and d orbitals.

#### Periodicity in the Shielding Range and the Oxidation-State

Without exception the atoms in their lowest oxidation states are the most highly shielded. The progression from

Table 3. Xenon-120 Chemical Shifts (4)

Compound	Xe	XeF <sub>2</sub>	XeF <sub>4</sub>	XeOF <sub>4</sub>	[XeO <sub>6</sub> ] <sup>4-</sup>
Oxidation Number	0	2	4	6	8
$\delta_{\text{Xe/ppm}}$	-5331	-1750	-253	0	+2077

high to low shielding with increase in oxidation state is fairly uniform (Table 3). Furthermore, the shielding sensitivity or shielding range of each atom species, expressed in parts per million per oxidation unit, coincides rather well with the total chemical shift range and slopes of  $\delta(\text{A})$  versus  $\delta(\text{B})$  plots for atoms A and B in identically or similarly bonded environments (8).

Qualitatively, the effect of oxidation on the parameters of eq 3 is rather obvious. The

$$\left[ Q_{AA} + \sum_{B \neq A} Q_{AB} \right]$$

factor is proportional to the number of electrons, and when this number is reduced through oxidation, the above factor also is reduced and consequently the  $\sigma^p$  term. However, the effect of oxidation on  $\sigma^p$  through the  $\langle 1/r^3 \rangle$  factor is more pronounced. Removal of electrons from the valence shell increases the effective nuclear charge experienced by those remaining and draws them closer to the nucleus. In the  $\langle 1/r^3 \rangle$  term even small contractions are cubed and transformed into the major factor that causes nuclear shielding to become uniformly lower (deshielding) with increase in oxidation state.

#### General Considerations—Selected Applications

$^1\text{H}$  is very probably the most important nucleus in NMR, however,  $^1\text{H}$  shifts have a very small range ( $\sim 20$  ppm with a few exceptions). This is mainly due to three factors. First, the total number of electrons in the vicinity of  $^1\text{H}$  is smaller than that of other nuclei so the magnitude of  $\sigma^p$  is smaller and consequently changes in  $\sigma^p$  from one nucleus site to another are very small. Second, the lowest excitation energy involved in  $^1\text{H}$  is of the type  $1s \rightarrow 2p$  that implies a large value of  $\Delta E$  in eq 3. Third, hydrogen atoms do not possess valence p electrons; therefore, the p orbital coefficient is zero. On the contrary the  $^{17}\text{O}$  nucleus, a representative nucleus of the VI group of the periodic table, indicates a shielding range  $>2000$  ppm (11). This is due to the large radial factor  $\langle r^{-3} \rangle_{2p}$  (Fig. 3), the presence of small excitation energies and multiple bonding for certain oxygen-containing functional groups. Thus, there is a clear-cut distinction between  $^{17}\text{O}$  resonances from alcohol and

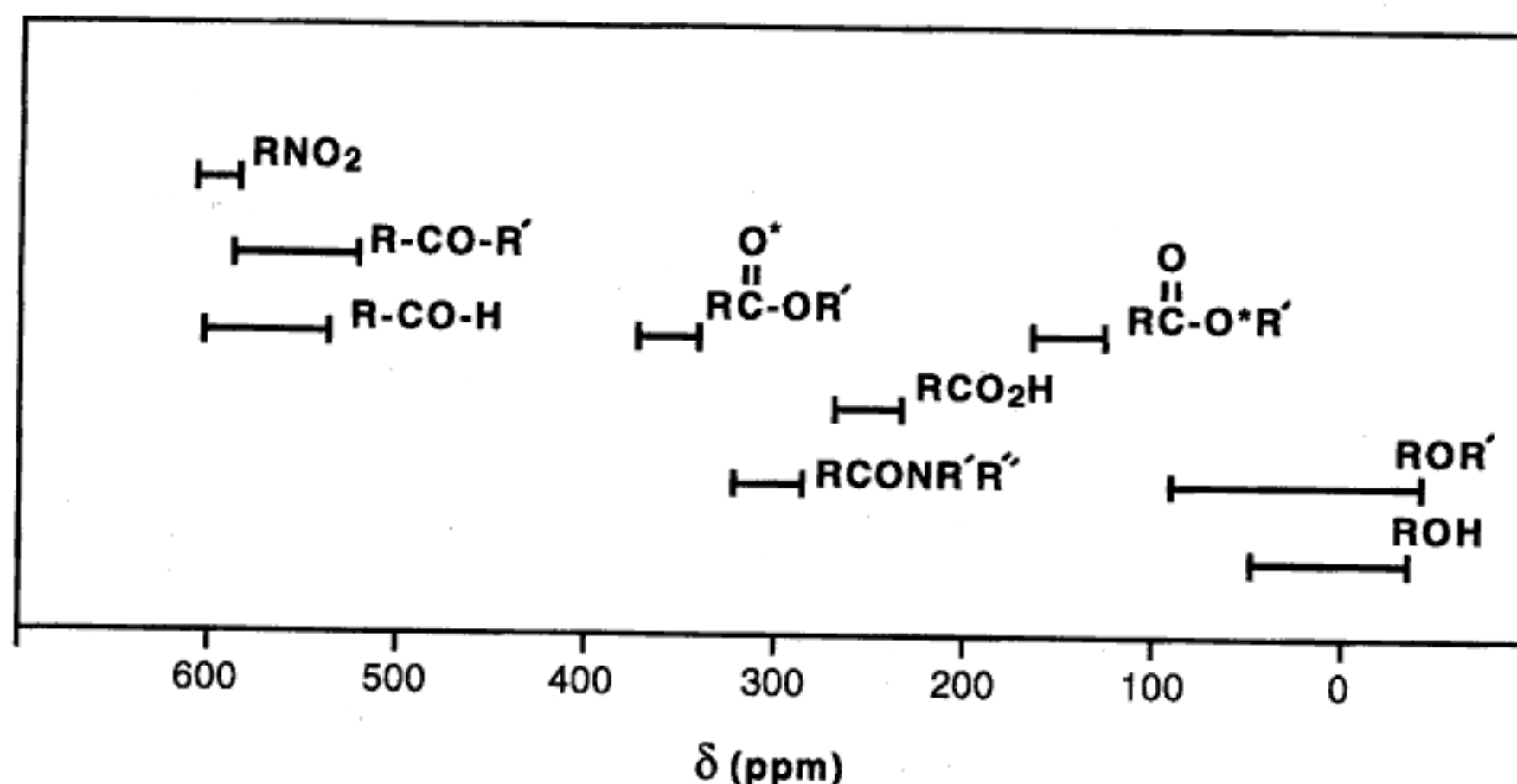
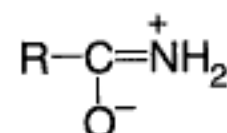


Figure 4.  $^{17}\text{O}$  shielding ranges (ppm) for different C–O bonds.



ether-type sites and those from C=O groups (Fig. 4). Aldehydes and ketones have a low-lying electronic state, resulting from an  $n \rightarrow \pi^*$  transition, and a  $\pi$ -bond order of about one. As anticipated the  $^{17}\text{O}$  in aldehydes and ketones is strongly deshielded ( $\delta = 600\text{--}500$  ppm) than the oxygen in alcohols. These values, however, are reduced substantially by attached oxygen- or nitrogen-containing substituents as in esters and amides (Fig. 4). This is presumably because of the participation of alternative resonance forms; for example,



for amides that reduce the  $\pi$ -bond order of the C–O bond and increase the energy of the  $n \rightarrow \pi^*$  transition and charge density at the oxygen atom ( $Q_{\text{AA}}$  term in eq 3) (11).

## Conclusion

A simple approach has been presented for correlating nuclear shielding with the periodic disposition of valence electrons and, thus, the position of the nucleus in the periodic table of elements. This approach may be suitable for presentation to introductory courses on nuclear magnetic resonance spectroscopy. Therefore, students will become familiar with nuclear shielding as something more than merely a set of useful empirical parameters (12, 13).

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## Literature Cited

- Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1985; Chapter 2.
- Day, Clyde M.; Selbin, J. *Theoretical Inorganic Chemistry*; Reinhold: London, 1965; London, 1965; Chapter 3.
- Seadorg, G. T. In *Collected Readings in Inorganic Chemistry*; Galloway, G., Ed.; Division of Chemical Education of the American Chemical Society: Easton, Pennsylvania, 1972; Vol. II, p 64.
- Webb, G. A. In *NMR and the Periodic Table*; Harris, R. K.; Mann, B. E., Eds.; Academic Press, 1978; Chapter 2.
- Webb, G. A. In *The Multinuclear Approach to NMR Spectroscopy*; Lambert, J. B.; Riddell, F. G., Eds.; D. Reidel: Dordrecht, 1983; Chapter 2.
- Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983.
- Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; Chapter 7.
- Kidd, R. G. *Ann. Rep. NMR Spectrosc.* **1991**, 23, 85.
- Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, 40, 1714.
- Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 3.
- Gerothanassis, I. P. In *Encyclopedia of NMR*; Grant, D. M.; Harris, R. K., Eds.; Wiley: Chichester, 1995, in press.
- Friedrich, E. C.; Runkle, K. G. *J. Chem. Educ.* **1984**, 61, 831.
- Friedrich, E. C.; Runkle, K. G. *J. Chem. Educ.* **1986**, 63, 127.

# Molecular Constants of Carbon Monoxide at $\nu = 0, 1, 2$ , and 3

## A Vibrational Spectroscopy Experiment in Physical Chemistry

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The vibrational–rotational spectrum of a diatomic molecule is treated in most laboratory-experiment textbooks (1, 2). The analysis usually refers to the fundamental absorption of the HCl molecule; the spectrum is analyzed to obtain the equilibrium rotational constant, the moment of inertia, and the internuclear distance. Parameters such as harmonic frequency, anharmonicity of the vibration, and centrifugal distortion are not obtained experimentally, but the students are usually encouraged to find the values in the literature. The first overtone of HCl was reported in undergraduate experiments using a conventional near-IR spectrophotometer. A partial set of constants is reported in each experiment (3–5).

In the Department of Chemistry at Baylor University there are two semesters of lecture and laboratory of physical chemistry. The second semester laboratory is mainly dedicated to lasers and molecular spectroscopy. The students (juniors and seniors) learn about rotational, vibrational, and electronic transitions in molecules, as well as the basic principles of laser action.

Before each experiment there is a 1-h discussion class dedicated to explaining the theory surrounding the experiments. Usually there are six experiments; each can be done in one afternoon. The experiments are done at least

every other week to let the students interpret the results and write the laboratory report.

One of the experiments deals with the vibrational–rotational transitions in carbon monoxide (6, 7). The advantage of using CO is that the fundamental and first overtone are around 2143 and 4259  $\text{cm}^{-1}$ , and the two regions can be covered with a standard FT IR. We have extended this experiment to study the vibrational–rotational transitions of the fundamental and the first and second overtones of CO. The experiment illustrates the decrease in absorption coefficient as a function of the excited vibrational quantum number and the magnitude of the changes in structural parameters, such as rotational constant, moment of inertia, and internuclear distance. The experiment also allows the students to obtain spectroscopic parameters, such as harmonic frequency, anharmonicity, rotation–vibration interaction constant, and centrifugal distortion.

## Experimental Procedure

For this experiment, two cells are used. One is a 38-mm-diameter, 10-cm-length, glass cell with sodium chloride windows. The other is a variable-path-length cell (8). This variable-path-length cell fits into the sample compartment of the spectrophotometer. It is also necessary to have a vacuum manifold like the one described in Shoemaker (1) to