

Lawrence Berkeley National Laboratory

Recent Work

Title

OBSERVATION OF CHEMICAL SHIFTS OF O17 NUCLEI IN VARIOUS CHEMICAL ENVIRONMENT

Permalink

<https://escholarship.org/uc/item/5ds9f9k1>

Authors

Weaver, H.E. (Varian Associates)

Tolbert, B.M.

LaForce, R.C.

Publication Date

1955-06-01

UCRL3054
UNCLASSIFIED

UNIVERSITY OF
CALIFORNIA

*Radiation
Laboratory*

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Observation of Chemical Shifts of O^{17} Nuclei
in Various Chemical Environments

by

H. E. Weaver
 Varian Associates
 Palo Alto, California

B. M. Tolbert and R. C. La Force
 Radiation Laboratory and Chemistry Dept.
 University of California
 Berkeley, California

JUN 1955

The dependence of the measured value of the gyromagnetic ratio of any nucleus upon the chemical environment of the nucleus is well known. To date a great deal of experimental data has been collected on chemical shifts of the more abundant nuclei that possess relatively strong nuclear magnetic moments. Observed chemical shifts arise from the fact that the value of the magnetic field at the nucleus is altered by the circulation of the molecular electrons induced through the application of a magnetic field, H_0 . The effect of the circulation of these electrons is such as to tend to shield the nucleus from the applied field and is proportional to that field. Dickinson⁽¹⁾ has made theoretical estimates of the magnitude of the diamagnetic effect to be expected for neutral atoms. For O^{17} , as a neutral atom, the diamagnetic shielding amounts to about 0.12%⁽¹⁾ of the applied field. Hence, the larger the magnetic field necessary for resonance, at a constant frequency, the larger is the diamagnetic shielding at the nucleus. Ramsey⁽²⁾ has shown that when the nucleus is not in a chemical environment associated with a neutral atom or monatomic ionic state, the shielding consists of essentially two parts; viz., a diamagnetic term and a term arising from second order induced paramagnetism. Saika and Slichter⁽³⁾ have applied this concept to an analysis of the fluorine magnetic resonant shifts in molecules. The resultant variation of the resonant frequency of a nuclear species is therefore a useful measurement in the study of the nature of the chemical bond. The observation of this variation by n-m-r has made it a valuable analytical tool in many chemical problems. The implication of the

(1) W. C. Dickinson, Phys. Rev. 82, 567 (1950)

(2) N. F. Ramsey, Phys. Rev. 86, 243 (1952)

(3) A. Saika and C. P. Slichter, Journ. of Chem. Phys. 32, 26 (1954)

observed shifts of O^{17} in the light of existing theories is reserved for a later time, but a few pertinent experimental features should be mentioned here.

Alder and Yu⁽⁴⁾ in their measurement of $\mu(O^{17})$ reported observing chemical shifts of the order of 1/4000 for O^{17} resonance in acetic acid relative to water. The very low abundance (.04%) of the O^{17} isotope and the resulting limitations in signal-to-noise of their apparatus were large factors which, until just recently, discouraged a more comprehensive study of chemical shifts associated with the O^{17} nuclear resonance.

Employing a Varian V-4200 Spectrometer and associated twelve-inch magnet system, n-m-r signals of O^{17} in water may be obtained with an amplitude up to 50 times that of the random noise. This value of S/N is sufficient to permit observation of resonances in a wide variety of compounds with much lower oxygen content, without artificial enrichment. With few exceptions, the natural thermal relaxation time (T_1) of the O^{17} nucleus was sufficiently short as to provide the experimental conditions necessary for "slow-passage"⁽⁵⁾ observation of the resonance and it was not necessary to add paramagnetic ions to the solutions to enhance the return to thermal equilibrium of the nuclear Zeeman levels. On the average, the line width of the O^{17} resonances was observed to be of the order of 3/10 of a gauss. The dispersion mode⁽⁴⁾ was employed for the reason that the optimum value of the rf field, H_1 , need not be so exactly chosen for maximum signal. The output signal was displayed on a strip chart recorder as the first harmonic of the dispersion mode and in this case was 80 cps.

Of the liquids thus far studied none has yielded an O^{17} resonance which occurs at a higher field (and hence greater relative diamagnetic shielding) than that of water. For this reason, the water signal was taken as reference and all measurements are relative to this compound. The accuracy of the results is no better than 1/10 of a gauss and in some cases is worse, depending upon the signal-to-noise.

(4) F. Alder and F. C. Yu, Phys.Rev. 81, 1067 (1951)

(5) F. Bloch, Phys.Rev. 70, 460 (1950)

The vertical scale of the table is in gauss, where these values have been reduced to a resonant field of 10,000 gauss (measurements were performed at 11.5 kilogauss) in order that a comparison may be easily made of the chemical shifts of N^{14} (see preceding letter) in those cases where a nitrogen-oxygen bond is involved.

In the tabulated series of chemical shifts, of particular interest are the two O^{17} signals of ethyl nitrate which occurred in an intensity ratio of roughly 1:2. These signals may be associated respectively with the oxygen in the C-O-N and $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{array}$ bonds of the ethyl nitrate molecule and provide a rather graphic illustration of the magnetic non-equivalence of these two types of bond situations of the oxygen atom.

The relative shifts of the O^{17} resonance in NO_3^- and NO_2^- are also particularly interesting, since these shifts may be readily compared with the N^{14} data (see preceding letter, Klein et al.) The direction of the relative shift for N^{14} and O^{17} is indicative of the magnetic behavior of the electrons involved in the bonding of the ion. The fact that the magnitude of the relative shift for N^{14} and O^{17} in the NO_3^- and NO_2^- is identical, within the experimental error, is probably coincidental and a more detailed theoretical picture is necessary before any significance may be attached to this result.

The fact that the oxygen resonance in water occurs at the highest field relative to all other bond situations thus far observed may lend itself to interpretation in light of the mechanism proposed by Saika and Slichter. As a result of the partial ionic character of the O-H bonds, the valence electrons of the oxygen atom probably form a system of high symmetry and under this condition of high symmetry, a lower amount of second order paramagnetic and a higher amount of diamagnetic shielding would result, thus placing the resonance at the highest relative field. This interpretation is consistent with, for example, the occurrence of the O^{17} resonance in H_2O_2 .

The above tabulation is admittedly very sketchy and a more detailed investigation is planned with a better coordination of n-m-r results from other nuclei. (e.g., H^1 ,

C^{13} , and N^{14} with O^{17}) in the same molecule. In the case of O^{17} of natural abundance, one is unfortunately limited to liquids of low molecular weight and to solids of very high solubility. Enrichment, where feasible, will, of course, alleviate somewhat this restriction.

The authors wish to express their appreciation of Professor M. Calvin's interest in this work. Thanks are also due to Dr. Malcolm Thaine of the Radiation Laboratories of the University of California.

Figure Caption: Fig. 1. Tabulation of the chemical shifts taken relative to water is in gauss. The brackets to the left of the vertical listing indicates those compounds in which a double resonance was observed. The dashed bracket indicates that the measurement was hampered by very low S/N for this compound.

