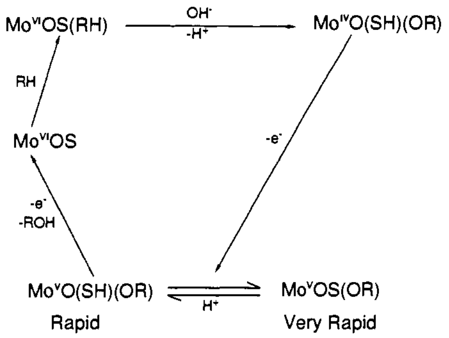
**Scheme II.** Proposed Catalytic Cycle for the Molybdenum Site in XnO



the minimal catalytic cycle at the Mo site of XnO (Scheme II). There is some uncertainty[11] as to whether the Very Rapid center is on the main catalytic pathway and detailed observations are substrate-dependent. However, given the simple acid–base relationship between the Mo$^{V}$OS( (Very Rapid) and Mo$^{V}$O(SH) (Rapid) found in the present work, and the possible presence of molybdenum-bound product OR modulating the system, a substrate dependence is unsurprising. The single equation in Scheme II describing the Mo$^{VI}$ to Mo$^{IV}$ redox event masks a number of primary steps. These include electron transfer from substrate to molybdenum, proton transfer from substrate to thio sulfur, and an apparent oxygen atom transfer from oxo ligand to substrate[4] with replacement of the former from water. While a specific mechanism for the electron–proton transfer is addressed in the present work, the existing analogue species containing quadridentate ligand L cannot probe potential oxygen atom transfer to substrate as a model substrate site is not available. Tridentate ligands that both allow observation of Mo$^{V}$OX and Mo$^{V}$O(XH) centers (X = O, S) and provide a model substrate site are currently under development.[81]

**Acknowledgment.** A.G.W. thanks the Australian Research Council for financial support. J.T.S. acknowledges support from NIH Grant GM 08347. Professor J. H. Enemark is thanked for stimulating discussion.

---

(81) Xiao, Z.; Laughlin, L.; Young, C. G.; Enemark, J. H.; Wedd, A. G. Work in progress.

# Nuclear Quadrupole Resonance Study of $^{51}$V in Metavanadates[†]

**D. Mao, P. J. Bray,* and G. L. Petersen**

*Contribution from the Department of Physics, Brown University, Providence, Rhode Island 02912.*

*Received November 23, 1990*

**Abstract:** Pure nuclear quadrupole resonance (NQR) studies of $^{51}$V in several metavanadates have been performed at both room temperature and liquid nitrogen temperature. Values of the quadrupole interaction parameters ($Q_{cc}$'s and $\eta$'s) in these compounds were obtained, which are more than an order of magnitude more accurate than those obtainable from NMR studies. Multiquantum transitions have been found in some cases. A sensitive NQR spectrometer was constructed for this study with a Robinson-type oscillator, a bi-symmetric square wave magnetic field modulator, and a data acquisition system based on an IBM PC/XT computer.

## Introduction

The interaction between a nucleus (spin 1 or greater) possessing an electrical quadrupole moment and the electric field gradient (EFG) at the nuclear site provides important information about the chemical bonding and environment of the atom containing the nucleus under investigation. It has been proven to be a valuable probe in the study of the structure and chemistry of solid materials.[1,2] A conventional way to obtain quadrupole interaction parameters is through comparison of experimental NMR spectra with computer-stimulated spectra that include the effects of the quadrupole interaction.[3-8] But the quadrupole interaction parameters obtained by this method are generally not of high accuracy because of the following: (1) the second-order NMR line shape of the central ($m = +{}^{1}/_{2} \leftrightarrow m = -{}^{1}/_{2}$) transition of half-integer spin nuclei is not very sensitive to changes in quadrupole interaction parmeters of as much as 5% or more;[8] (2) when the chemical shift interaction and the quadrupole interaction are both present and comparable in magnitude, the NMR line shapes are very complicated and difficult to analyze; (3) in the computer simulation of NMR line shapes, there is a possible systematic error present in the assumption that the principal axes of the chemical shift tensor and the EFG tensor coincide with each other, which is not necessarily true;[9] and (4) in the presence of large quadrupole interactions, the NMR spectra are usually too wide (say 200 kHz) to be excited homogeneously due to the limitation of the RF power of the pulsed NMR spectrometer. On the other hand, pure nuclear quadrupole resonance provides a direct and accurate method to measure the quadrupole interaction parameters. Recently, Bray and Gravina[10] have studied $^{11}$B and $^{10}$B NQR in crystalline and vitreous $B_2O_3$ and some borate compounds and glasses in the frequency region from 250 kHz to 2 MHz with a sensitive Robinson oscillator.[11] Their results show that $^{11}$B and $^{10}$B NQR spectroscopy can distinguish responses from different $BO_3$ structural units in borate crystals and glasses.

---

[†] Research supported by the National Science Foundation through NSF Grant No. DMR-8920532.

(1) Cohen, M. H. *Phys. Rev.* **1954**, *96*, 1278.
(2) Weiss, A. *Adv. Nucl. Quadrupole Reson.* **1972**, *1*, 1.
(3) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: London, 1961.
(4) Slichter, C. P. *Principles of Magnetic Resonance*; Harper and Row Publishers, Inc.: New York, 1963.
(5) Cohen, M. H.; Reif, F. *Solid State Physics*; Academic Press Inc.: New York, 1957; Vol. 5.
(6) Stauss, C. H. *J. Chem. Phys.* **1964**, *40*, 1988.
(7) Narita, K.; Umeda, J.; Kusumoto, H. *J. Chem. Phys.* **1966**, *44*, 2719.
(8) Taylor, P. C.; Baugher, J. F.; Kriz, H. M. *Chem. Rev.* **1975**, *75*(2), 203.
(9) Baugher, J. F.; Taylor, P. C.; Bray, P. J. *J. Chem. Phys.* **1969**, *50*(11), 4914.
(10) Bray, P. J.; Gravina, S. J. *Proc. XVth Int. Congr. Glass, Leningrad* **1989**, *1a*, 63.
(11) Robinson, F. N. H. *J. Phys. E: Sci. Instrum.* **1982**, *15*, 814.

0002-7863/91/1513-6812$02.50/0 © 1991 American Chemical Society

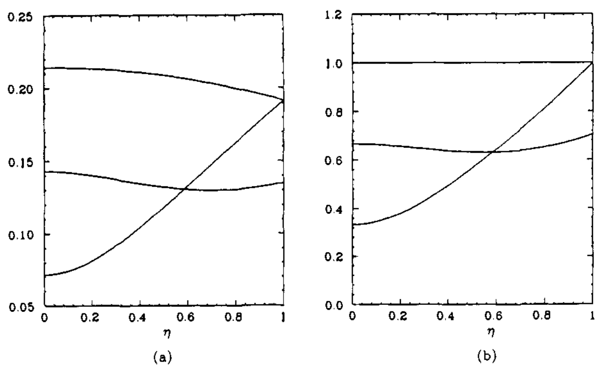


**Figure 1.** (a) NQR frequencies (in units of $Q_{cc}$) vs $\eta$ for spin $^7/_2$ nuclei; (b) normalized NQR frequencies with the highest frequency equal to 1.

$^{51}V$ has a natural abundance of 99.76% and a spin of $^7/_2$. Its quadrupole moment is about 1.46 times as large as that of $^{11}B$, favorable for NQR studies. The oxygen chemistry of vanadium can be quite different in various vanadium oxides and vanadates.[12] It should be interesting to explore the possibility of using $^{51}V$ NQR to study the environment of vanadium nuclei in vanadium-containing compounds. Here we present the results of a pure NQR study of $^{51}V$ in three metavanadate compounds $KVO_3$, $NH_4VO_3$, and $NaVO_3$.

## Theory

In the principal-axis system of the EFG tensor (whose components are $V_{xx}$, $V_{yy}$, and $V_{zz}$), the Hamiltonian for the quadrupole interaction can be written as[3]

$$H_Q = \frac{hQ_{cc}}{4I(2I-1)}\left[(3I_z^2 - I^2) + \frac{\eta}{2}(I_+^2 - I_-^2)\right]$$

where $Q_{cc} = eQV_{zz}$, $\eta = (V_{xx} - V_{yy})/V_{zz}$, $Q$ is the quadrupole moment of the nucleus, and $I$ is the spin. $Q_{cc}$, the quadrupole coupling constant, measures the strength of the quadrupole interaction. $\eta$, the asymmetry parameter, measures the departure from axial symmetry of the EFG tensor. Conventionally, $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, so $0 \leq \eta \leq 1$.

The secular equation for spin $^7/_2$ is given by[13]

$$E^4 - 42(1 + \eta^2/3)E^2 - 64(1 - \eta^2)E + 105(1 + \eta^2/3)^2 = 0$$

where the unit of $E$ is $hQ_{cc}/28$. A simple computer program was written to solve the equation numerically for 1000 values of $\eta$, and the results were tabulated to derive accurately the values of $Q_{cc}$ and $\eta$ from experimental data.

Transitions between the quadrupole energy levels are induced by applying a RF electromagnetic wave to the sample, which couples to the magnetic dipoles of the nuclei. The NQR frequencies for spin $^7/_2$ nuclei are plotted versus $\eta$ in Figure 1. Normally, three transitions are observable for spin $^7/_2$ nuclei, but in the case of large $\eta$, one or two more transitions (so called multiquantum transitions) are also observable.[1] These frequencies are simply the sum of two of the normal transition frequencies. Also shown in Figure 1 are the normalized frequencies (ratios of the transition frequencies with respect to the highest one). Note that there is a one-to-one correspondence between the value of $\eta$ and the normalized transition frequencies. This feature is used to determine the vaue of $\eta$ from the ratios of NQR frequencies measured experimentally. Once $\eta$ is obtained, the calculation of $Q_{cc}$ is straightforward.

## Experimental Section

The NQR spectrometer used in this study is a new version of the one constructed by Gravina.[14] A Robinson-type oscillator was built to operate in the frequency range from 200 kHz to 15 MHz. Only a few capacitors were adjusted from the original circuit. A new design is used for the bi-symmetric square wave magnetic field modulator.[15] The modulation field is adjustable from 10 to 200 G and the modulation frequency from 27 to 480 Hz. Most of the spectra in this study were obtained with a modulation field of 50 G and a modulation frequency of 133 Hz. The tank circuit consists of a 200 pf air-spaced variable capacitor and a sample coil 28 mm in diameter and 51 mm long, which is shielded in a brass can that is 3 in. in diameter. The capacitor is adapted to be able to rotate at liquid nitrogen temperature and it is driven by a 0.7 or 2 rpm motor through a chain of three 20:1 reducing gear boxes. The sample coil is placed perpendicular to the modulation coil to avoid pickup. The data acquisition system consists of an IBM PC/XT equipped with an inexpensive Lab Tender[16] data processing board, which has AD conversion and frequency counting functions. The RF output from the Robinson oscillator is converted to a TTL (a popular digital logic family) signal by a Matec 110 frequency source before being counted by the Lab Tender, which is TTL compatible. A PAR HR-8 lock-in samplifier was used to detect the NQR signal. A computer program in C language was written to control the frequency counting, AD conversion, data averaging, and display of data. With a frequency resolution of 10 Hz, the computer can accomplish one measurement within 0.18 s. The data smoothing function of the program plays the role of a low-pass digital filter, and the time constant of this filter has virtually no limitation. Typical time constants used in this study range from 600 to 5000 s. It has been found that the key factor in detecting the NQR signals is the proper RF level in the tank circuit. Briefly, the best signal-to-noise ratio is obtained when the RF level nearly saturates the resonances.

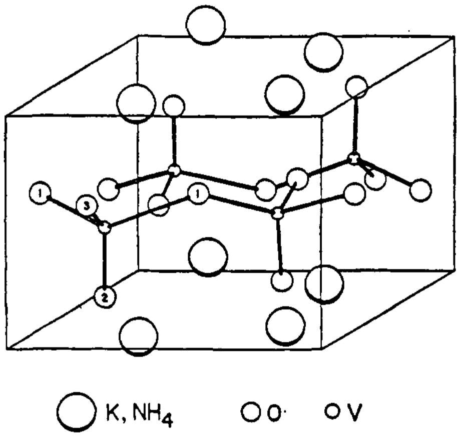


Figure 2. Unit cell for $KVO_3$ and $NH_4VO_3$: oxygens labeled 1 are bonded to two vanadium atoms, while oxygens labeled 2 and 3 are bonded to only one vanadium atom.

The metavanadate compounds studied in this study were reagent grade chemicals obtained commercially. Thirty-five grams of sample were employed for each compound in this study. Two or more measurements were performed on each sample to ensure reproducibility and accuracy. Experiments were carried out at both room temperature and liquid nitrogen temperature.

## Results and Discussion

Figure 2 shows the unit cell of $KVO_3$ and $NH_4VO_3$.[17] The basic vanadium–oxygen bonding unit is a distorted $VO_4$ tetrahedron. Both the V–O$^2$ and V–O$^3$ bond lengths are slightly shorter than the V–O$^1$ bond length. The crystal structure of $NaVO_3$ is slightly different. The main feature of its structure consists of chains of $VO_4$ tetrahedra. Because of the deviation from symmetry of the tetrahedron, fairly large asymmetry parameters can be expected for these units.

**$KVO_3$.** The NQR spectra of $KVO_3$ are shown in Figure 3. At 77 K, three resonances were found at 827.0 ± 0.3, 730.5 ± 0.3, and 553.0 ± 0.3 kHz, with a line width (full width at half height) of 11 ± 2, 16 ± 1, and 9 ± 1 kHz, respectively. The signal-to-noise ratios were between 40:1 and 100:1. The ratios of these frequencies

---

(12) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: New York, 1984; pp 565–569.

(13) Dehmelt, H. G.; Kruger, H. *Z. Phys.* **1951**, *130*, 385.

(14) Gravina, S. J. Ph.D. Thesis, Physics Department, Brown University, pp 75–98.

(15) Mao, D.; Bray, P. J.; Petersen, G. L. A Bi-symmetric Zeeman Modulator for NQR. To be published.

(16) Scientific Solutions, Inc., 6225 Cochran Road, Solon, Ohio 44139.

(17) Evans, H. T. *Z. Krist.* **1960**, *114*, 257.

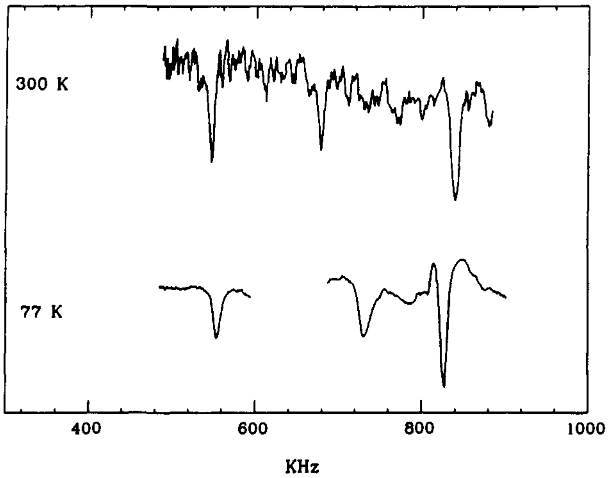


**Figure 3.** $^{51}$V NQR spectra in $KVO_3$: (a) at 300 K; (b) at 77 K.

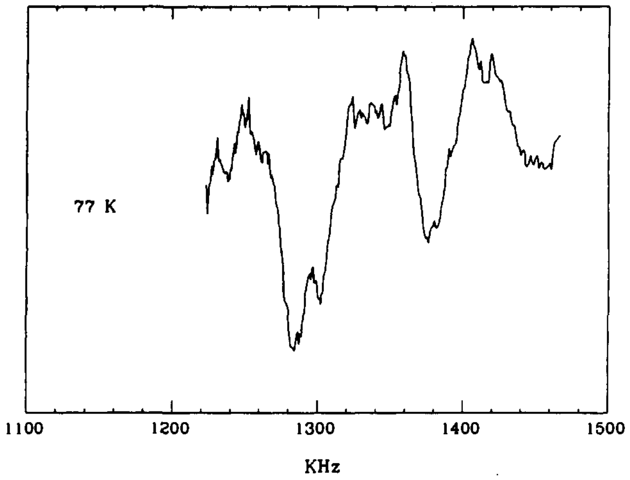


**Figure 4.** $^{51}$V NQR "mutiquantum transitions" in $KVO_3$ at 77 K.

**Table I.** NQR Lines (kHz) from $KVO_3$ at 300 K

| | $\pm 5/2 \leftrightarrow \pm 7/2$ | $\pm 1/2 \leftrightarrow \pm 3/2$ | $\pm 5/2 \leftrightarrow \pm 3/2$ |
|---|---|---|---|
| calcn | 839.6 ± 0.5 | 678.4 ± 0.8 | 547.1 ± 0.3 |
| exptl | 839.2 ± 0.3 | 678.0 ± 0.3 | 547.3 ± 0.3 |

were found to be 1.0000, 0.8833 ± 0.0006, and 0.6687 ± 0.0006. This set of ratios corresponds to the case for $\eta = 0.877$, which requires normalized transition frequencies at 1.0000, 0.8831, and 0.6687. Thus the quadrupole coupling parameters are determined to be as follows: $Q_{cc} = 4207 \pm 2$ kHz and $\eta = 0.877 \pm 0.001$.

At 300 K, resonances were found at 839.2 ± 0.3, 678.0 ± 0.3, and 547.3 ± 0.3 kHz, with line widths of 13 ± 2, 9 ± 2, and 7 ± 2 kHz, respectively. The signal-to-noise ratios were better than 6:1. The quadrupole interaction parameters were determined as follows: $Q_{cc} = 4201 \pm 2$ kHz and $\eta = 0.794 \pm 0.001$. Table I shows how well the calculated resonance frequencies fit the ones found experimentally.

It is worthwhile to notice that the asymmetry parameter changed by 10% when the sample was cooled from room temperature to liquid nitrogen temperature, while the quadrupole coupling constant remained almost the same. This would indicate that some type of phase transition probably occurred during cooling of the sample.

With $\eta$ as large as 0.794 and 0.877, one would expect to see the $|\Delta m| = 2$ multiquantum transitions. Indeed, two multiquantum transitions were found at 1284 and 1380 kHz at 77 K (see Figure 4), which were about twice as broad as the single-quantum transitions. The 1284-kHz line comes from the $\pm^1/_2 \leftrightarrow \pm^5/_2$ transitions, whose frequency is the sum of 730.5 kHz $(\pm^1/_2) \leftrightarrow \pm^3/_2)$ and 553.0 kHz $(\pm^3/_2 \leftrightarrow {}^5/_2)$. And the 1380-kHz line is the $\pm^3/_2 \leftrightarrow \pm^7/_2$ transition, the sum of 553.0 kHz $(\pm^3/_2 \leftrightarrow \pm^5/_2)$ and 827.0 kHz $(\pm^5/_2 \leftrightarrow \pm^7/_2)$. The transition $\pm^1/_2 \leftrightarrow \pm^7/_2$ was not seen because it is a $|\Delta m| = 3$ transition and the transition probability is very low.

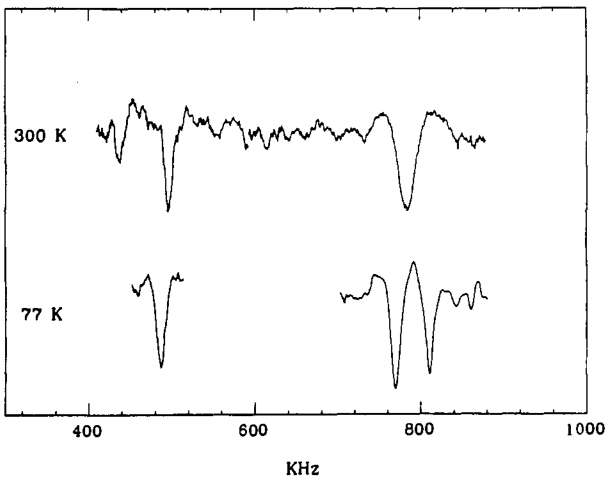


**Figure 5.** $^{51}$V NQR spectra in $NaVO_3$: (a) at 300 K; (b) at 77 K.

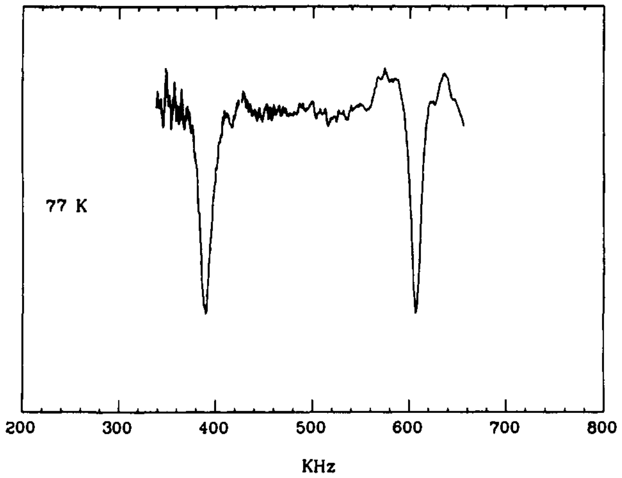


**Figure 6.** $^{51}$V NQR spectra in $NH_4VO_3$ at 77 K.

**$NaVO_3$.** The NQR spectra are shown in Figure 5. At 77 K, the frequency region from 300 to 900 kHz was swept and three resonances were found at 811.3 ± 0.3, 769.5 ± 0.3, and 486.7 ± 0.3 kHz. The ratios of these frequencies are 1.0000, 0.9484 ± 0.0006, and 0.6004 ± 0.0006. Strangely, there is no value of $\eta$ for which the three resonances are predicted. The puzzle can be solved if one recalls that $^{23}$Na is a spin $^3/_2$ nucleus which can give one NQR line. Thus two of the three lines are $^{51}$V lines and the other is the $^{23}$Na line. The grouping of the 811.3-kHz line with any of the other two would require another line to appear between 500 and 560 kHz, which is not the case. The choice left is to assign the 769.5- and 486.7-kHz lines to $^{51}$V nuclei and the 811.3-kHz line to $^{23}$Na. $Q_{cc} = 3725 \pm 2$ kHz and $\eta = 0.587 \pm 0.001$ would require the $^{51}$V resonances to be at 769.5 ± 0.5, 486.9 ± 0.3, and 486.4 ± 0.3. Obviously the line at 486.7 kHz is the superposition of two lines.

At 300 K, three resonances were found at 782.7 ± 0.5, 495.7 ± 0.5, and 436.5 ± 0.5 kHz. $Q_{cc}$ and $\eta$ are required to be 3745 ± 3 kHz and 0.489 ± 0.003, respectively. The 782.7-kHz line is unusually broad (21 kHz) compared with the other two lines (13 and 12 kHz). It is very likely that this line actually includes the $^{23}$Na line. If this is the case, the quadrupole parameters obtained for $^{51}$V will have slightly larger errors.

**$NH_4VO_3$.** At 77 K, two resonances were found at 606.3 ± 0.3 and 388.4 ± 0.5 kHz in the frequency region from 300 to 1050 kHz (see Figure 6). The line widths were 12 ± 1 and 13 ± 1 kHz. If the two observed lines were the lower frequency responses, the highest frequency line would be around 930 kHz. This region was searched and no resonance was found. It is unlikely that the

J. Am. Chem. Soc. **1991**, *113*, 6815–6822

**Table II.** $Q_{cc}$'s and $\eta$'s in Metavanadates

| | $Q_{cc}$, kHz [$\eta$] | | |
|---|---|---|---|
| | NMR (300 K) | NQR (300 K) | NQR (77 K) |
| $KVO_3$ | 4360 ± 60<br>[0.75 ± 0.10] | 4201 ± 2<br>[0.794 ± 0.001] | 4207 ± 2<br>[0.877 ± 0.001] |
| $NaVO_3$ | 3650 ± 60<br>[0.60 ± 0.10] | 3745 ± 3<br>[0.489 ± 0.003] | 3725 ± 2<br>[0.587 ± 0.001] |
| $NH_4VO_3$ | 2880 ± 60<br>[0.30 ± 0.10] | 2975 ± 20<br>[0.437 ± 0.020] | 2868 ± 5<br>[0.363 ± 0.013] |

highest frequency line could be missed because it is usually the easier one to detect. With these two lines as the two higher frequency responses, the quadrupole parameters are estimated to be $Q_{cc}$ = 2868 ± 5 kHz and $\eta$ = 0.363 ± 0.013. The third line is expected between 250 and 300 kHz. Attempts have been made to detect this line, but no obvious resonance was seen in the noisy spectra. It is believed that some modification of the Robinson oscillator must be made to reduce noises when operating below 300 kHz. The spectrum at 300 K was also taken. Only one line at 625 ± 1 kHz was detected with a decent signal-to-noise ratio. Two weak lines were found at 325 ± 5 and 400 ± 5 kHz. The quadrupole parameters would be 2975 ± 5 kHz for $Q_{cc}$ and 0.437 ± 0.02 for $\eta$.

Table II lists the quadrupole interaction parameters of $KVO_3$, $NaVO_3$, and $NH_4VO_3$ obtained in this work. These metavanadates were previously studied by Baugher et al. using CW NMR and computer simulation techniques.[9] The results from that NMR study are also listed for comparison. Baugher also estimated the components of the chemical shift tensors in these compounds to be on the order of several hundred ppm. These fairly large chemical shift effects caused the calculation of the quadrupole interaction parameters to be not very accurate. It is clear that the quadrupole interaction parameters obtained through NQR and more than an order of magnitude more accurate than those obtained through NMR.

## Conclusions

Pure $^{51}V$ NQR has been observed for $KVO_3$, $NaVO_3$, and $NH_4VO_3$ with decent signal-to-noise ratios (40 to 100 at 77 K and 6 to 8 at 300 K). The quadrupole interaction parameters obtained by this study are accurate to within 3 kHz for $Q_{cc}$'s and to within 0.001 for $\eta$'s in most cases. These accurate quadrupole coupling parameters are useful not only in that they give structural information by themselves but also in that they can facilitate the analysis of NMR spectra. For example, knowing the exact quadrupole interaction parameters, it would be easier to extract chemical shift parameters from the NMR spectra for quadrupolar nuclei.

The line width of $^{51}V$ NQR lines from the metavanadates studied vary from 7 to 16 kHz. The narrow line widths indicate that $^{51}V$ NQR spectroscopy can resolve vanadium sites which differ in their NQR frequencies by 20 kHz or less. In the case of large $\eta$, multiquantum transitions can be observed. These lines can be used to ensure the correct calculation of the quadrupole parameters.

The sensitivity of the Robinson-type oscillator degrades when operating below 300 kHz. Some modification is necessary.

---

# 2D NOESY Simulations of Amide Protons in Acetamido Sugars[†]

**Perseveranda Cagas, Kumaralal Kaluarachchi,[‡] and C. Allen Bush***

*Contribution from the Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, Maryland 21228.* *Received January 11, 1991*

**Abstract:** Because of the flexibility of most small peptides, quantitative simulation of amide proton nuclear Overhauser effects (NOE) by relaxation matrix methods which ignore internal motion are not thought to be generally useful. But NOE simulations for the carbon-bound protons of some complex oligosaccharides carried out as a function of geometry have produced an excellent fit to experimental data suggesting that these carbohydrates adopt relatively rigid conformations. Therefore we have devised a method for simulation of amide proton NOE and applied it to the amide protons of GlcNAc in some Lewis blood group oligosaccharides which have been proposed to adopt rigid single conformations. The quantitative simulation of amide proton NOE is complicated by chemical exchange with solvent, by the effects of rapid quadrupolar relaxation of $^{14}N$, and by dipolar relaxation of $^{14}N$. The effects of chemical exchange can be eliminated by choice of solvent pH and temperature, and quadrupolar effects can be shown to be small for this case. The influence of $^{14}N$ dipolar relaxation is significant but can be readily calculated and incorporated into existing schemes for relaxation matrix computation of NOE in carbohydrates. NOESY spectra are reported in $H_2O$ for two Lewis blood groups oligosaccharides, lacto-*N*-difucohexaose-1 and lacto-*N*-fucopentaose-1, with solvent suppression pulse sequences which have been used for peptides. Crosspeaks whose magnitudes depend on glycosidic dihedral angles are observed between the amide proton of GlcNAc and protons of the adjacent galactose residue. These values can be matched by simulations with the same model geometry deduced for these oligosaccharides from carbon-bound proton NOE supporting the rigid model hypothesis. Crosspeaks observed for the amide protons with protons in the same GlcNAc residue are sensitive to the orientation of the amide plane, and we propose slightly different dihedral angles for these two oligosaccharides. Vacuum ultraviolet circular dichroism spectra are reported on these human milk oligosaccharides which bear on the difference in the amide orientation in GlcNAc.

## Introduction

Some workers who have studied the conformation of complex carbohydrates in solution have proposed that oligosaccharides, in contrast to small peptides which generally demonstrate a substantial amount of internal motion, assume relatively rigid conformations determined largely by steric repulsion.[1-3] In our research group, we have attempted to devise rigorous tests of this hypothesis as applied to a series of blood group oligosaccharides. Our primary experimental technique has been quantitative

---

[†] Research Supported by NIH Grant GM-31449.

[‡] Present address: Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.

* Author to whom correspondence should be addressed.

(1) Bush, C. A.; Cagas, P. In *Advances in Biophysical Chemistry*; Bush, C. A., Ed.; JAI Press: CT, in press.

(2) Bush, C. A.; Yan, Z.-Y.; Rao, B. N. N. *J. Am. Chem. Soc.* **1986**, *108*, 6168–6173.

(3) Rao, B. N. N.; Dua, V. K.; Bush, C. A. *Biopolymers* **1985**, *24*, 2207–2229.