shown differences of 0.2 volt for these lines. Similarly no measurable differences were found for the $L\alpha_1$ and $L\beta_1$ lines from U^{235} and U^{238} in U_3O_8. The increased width of these lines raises the limit of an observable effect to 0.4 volt. It appears that present x-ray spectroscopic techniques lack the resolution to detect nuclear isotopic influences on these x-ray levels. However, it may still be possible that somewhere in the isotopic chart a radical change in nuclear "volume," for example, may yet allow a measurable x-ray isotopic effect. It also appears of interest to make precision wavelength measurements of x-rays emitted in radioactive decay to see whether their energies really differ from x-rays produced in the conventional manner.

The authors wish to express their appreciation to Mr. Don J. Leffler, who helped much with the taking of the data. One of us (G. L. R.) wishes to acknowledge discussions with J. R. McNally, Jr., and W. Peed of the Oak Ridge National Laboratory. These discussions have stimulated this work.

PHYSICAL REVIEW VOLUME 92, NUMBER 6 DECEMBER 15, 1953

One-to-Two Millimeter Wave Spectroscopy. III. NO and DI†

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(Received September 14, 1953)

Pure rotational transitions of $N^{14}O^{16}$ and DI^{127} have been measured in the one-to-two millimeter wave region. For NO the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition in the $^2\pi_{\frac{1}{2}}$ electronic ground state was observed. The transition reveals a Λ doublet with separation $\Delta\nu_{dc}=355.1$ Mc/sec. Each component of the Λ doublet is further split into five hyperfine components as a result of the nuclear magnetic coupling of N^{14}. Nuclear quadrupole coupling of N^{14} was found to be small in comparison with the magnetic interaction. Analysis of the data yields $B_0=50818.0$ Mc/sec, $r_0=1.1540$ A, $\mathrm{B}_e=51084.8$ Mc/sec, and $\mathrm{r}_e=1.1510$ A for the $^2\Pi_{\frac{1}{2}}$ state. For DI^{127} the following information was obtained: $B_0=97\ 537.2$ Mc/sec, $r_0=1.6165$ A, and $eQq(I^{127})=1823\pm1$ Mc/sec. Nuclear magnetic interactions of I^{127} were also detected and analyzed.

INTRODUCTION

The opening up of the one-to-two millimeter wave region[1] has made it possible to study with the high precision of microwave methods the pure rotational spectra of such light diatomic molecules as NO and the deuterium halides, which, because of their small moments of inertia, were previously inaccessible to microwave spectroscopists. Results on NO and DI are reported here. We are searching for the lines of DBr and hope to measure DCl also.

NITRIC OXIDE

The electronic ground state of NO is $^2\Pi_{\frac{1}{2}}$, but only 120 cm^{-1} above lies the $^2\Pi_{\frac{3}{2}}$ state, also appreciably populated at room temperature. We have investigated the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ rotational transition of molecules in the $^2\Pi_{\frac{1}{2}}$ state. Because of the cancellation of the orbital and spin magnetic moments the $^2\Pi_{\frac{1}{2}}$ state is supposedly nonmagnetic. Nevertheless, widely spaced magnetic hyperfine structure was found. Table I gives the pattern of 10 lines which were observed. Figure 1 shows the lower frequency group of five as they appeared on the cathode-ray scope.

Without nuclear interaction the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition would be expected to have two components because of Λ doubling. Nuclear interaction with N^{14} would split each component of the doublet into five components, as observed. Each hyperfine multiple was found to fit an equation of the form

$$E=P\{F(F+1)-J(J+1)-I(I+1)\}+R\{(3/4)C(C+1)-J(J+1)I(I+1)\},$$

with $C=F(F+1)-J(J+1)-I(I+1)$, derived by Dr.

TABLE I. Observed and calculated components of the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition, $^2\pi_{\frac{1}{2}}$ state, of $N^{14}O^{16}$.

Transition $F\rightarrow F'$	Frequency (Mc/sec) Observed	Calculated[a]	Relative intensity Observed	Calculated
Lower frequency group of Λ doublet $\nu_0{}^c=150\ 195.49$ Mc/sec				
$\frac{3}{2}\rightarrow 5/2$	150,176.54	150,176.52	100	100
$\frac{1}{2}\rightarrow\frac{3}{2}$	150,198.85	150,198.85	35	37.1
$\frac{3}{2}\rightarrow\frac{3}{2}$	150,218.89	150,218.89	30	29.6
$\frac{1}{2}\rightarrow\frac{1}{2}$	150,225.75	150,225.80	30	29.6
$\frac{3}{2}\rightarrow\frac{1}{2}$	150,245.69	150,245.70	5	3.7
Upper frequency group of Λ doublet $\nu_0{}^d=150\ 550.60$ Mc/sec				
$\frac{3}{2}\rightarrow\frac{1}{2}$	150,375.48	150,375.47	5	3.7
$\frac{3}{2}\rightarrow\frac{3}{2}$	150,439.22	150,439.21	30	29.6
$\frac{3}{2}\rightarrow 5/2$	150,546.50	150,546.46	100	100
$\frac{1}{2}\rightarrow\frac{1}{2}$	150,580.70	150,580.64	30	29.6
$\frac{1}{2}\rightarrow\frac{3}{2}$	150,644.37	150,644.32	40	37.7

[a] See reference 2.

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† This research was supported by the United States Air Force under a contract monitored by the Office of Scientific Research, Air Research and Development Command.

* Shell Oil Company Fellow.

[1] W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953).

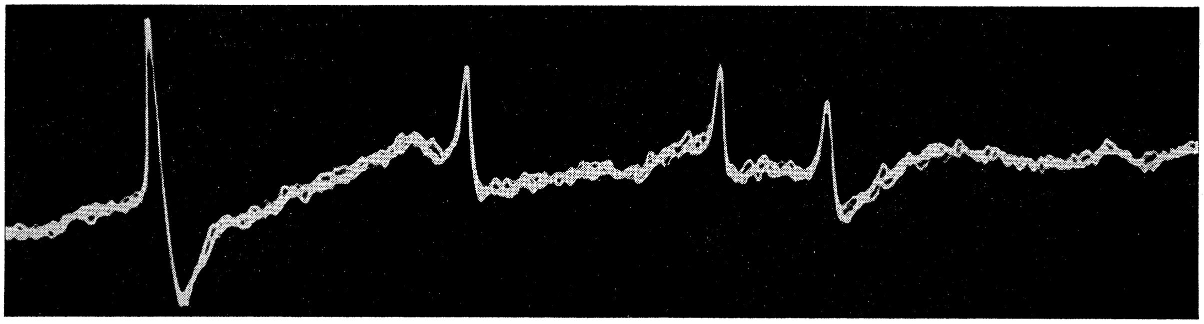

FIG. 1. Cathode-ray display of the magnetic hyperfine structure of the lower frequency component of the Λ doublet in the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition, ${}^2\pi_{\frac{1}{2}}$ state, of $N^{14}O^{16}$. For frequencies see Table I.

M. Mizushima[2] of this laboratory. The parameters P and R have different values for the different levels and for the different Λ sublevels. The term in P results from the magnetic interactions and is of the form previously derived by Frosch and Foley[3] if

$$P=\{a\mp b(2J+1)\}/J(J+1),$$

in which a and b are constants, with the minus sign used for the c component and the plus sign for the d component of the Λ doublets. However, the P in Mizushima's formula includes, in addition, a small term to account for interaction of the $J=\frac{3}{2}$ level with the ${}^2\Pi_{\frac{3}{2}}$ electronic state. A fitting of the data[2] requires that $a=23.15$ and $b=14.07$ Mc/sec. The term in R results from nuclear quadrupole interaction. It is zero for the $J=\frac{1}{2}$ state, and in the $J=\frac{3}{2}$ state R has the values[2] 0.77 Mc/sec and 0.035 Mc/sec for the c and d components, respectively. The rather large and somewhat complicated quadrupole coupling term results mainly from the odd electron. Details will be given in a theoretical paper by Mizushima[2] to follow. In Table I the observed frequencies are compared with those calculated from the above formula.

The electronic coupling in NO is intermediate between Hund's case (a) and (b). The energy levels have been worked out by Van Vleck.[4] If we neglect centrifugal distortion (which cannot be evaluated from the one transition observed) and the structure already mentioned, the rotational lines are given by the formula

$$\nu_0{}^i=2B_{\mathrm{eff}}{}^i(J+1)=2B_0{}^i\left(1-\frac{B_0{}^i}{A}\cdots\right)(J+1),$$

where $J=\frac{1}{2}, \frac{3}{2}, 5/2, \cdots$, and i designates the particular component, c or d, of the Λ doublet. The $D_J=0.53\times10^{-6}$ cm^{-1} for the ${}^2\Pi_{\frac{1}{2}}$ state obtained by Gillette and Eyster[5] from high J transitions in infrared vibration-rotation spectra indicates that centrifugal distortion shifts the $\frac{1}{2}\rightarrow\frac{3}{2}$ transition only about 0.4 Mc/sec, which is the order of our experimental error. For the ${}^2\Pi_{\frac{1}{2}}$ state, the doublet separation has been shown by Van Vleck[4] to be directly proportional to J. It can be expressed approximately by

$$\Delta\nu_{dc}=2p(J+\tfrac{1}{2}).$$

Our measurement gives $\Delta\nu_{dc}=355.1$ Mc/sec, and with $J=\frac{1}{2}$ it is seen from the formula that $p=355.1$ Mc/sec. If it is assumed that the upper and lower components $\nu_0{}^c$ and $\nu_0{}^d$ of the Λ doublet are equally displaced from the hypothetical unsplit line, the latter has the frequency $\nu_0=(\nu_0{}^c+\nu_0{}^d)/2=150373.04$ Mc/sec, and $(B_0)_{eff}$ as determined with this frequency is 50124.4 Mc/sec or 1.67198 cm^{-1}. (Compare with Gillette and Eyster's[5] infrared value of 1.6696 cm^{-1}.) With $A=124.2$ cm^{-1} from other sources,[5] this gives $B_0=50818.0$ Mc/sec. This value of B_0 yields for the internuclear distance the value $r_0=1.1540$ A for the ${}^2\Pi_{\frac{1}{2}}$ state, and with $\alpha=0.0178$ cm^{-1} from infrared data[5] it yields the values $B_e=51084.8$ Mc/sec and $\gamma_e=1.1510$ A. The results are summarized in Table II.

DEUTERIUM IODIDE

The $J=0\rightarrow1$ rotational transition of DI has been measured with high precision. The lines were readily observed on the cathode-ray scope with a video-type spectrometer having a wide band amplifier. Figure 2 shows the medium strength $F=5/2\rightarrow5/2$ line.

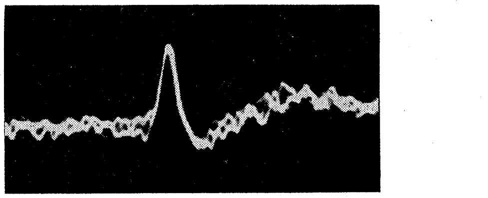

FIG. 2. Cathode-ray display of the medium strength $F=5/2\rightarrow5/2$ component of the $J=0\rightarrow1$ transition of DI^{127} at 1.5-millimeter wavelength.

The nuclear hyperfine pattern of $I^{127}(I=5/2)$ is particularly simple for the $J=0\rightarrow1$ transition since it con-

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[2] M. Mizushima (to be published).

[3] R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

[4] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929); R. S. Mulliken and A. Cristy, Phys. Rev. **38**, 87 (1931). For convenient summary see G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 227.

[5] R. H. Gillette and E. H. Eyster, Phys. Rev. **56**, 1113 (1939).

sists of only three lines. Nevertheless, quadrupole coupling theory, even with second-order effects included, did not entirely account for the observed line spacings. It was found that the deviation could be explained as the nuclear magnetic interaction of I^{127} as given by

$$E=\tfrac{1}{2}C[F(F+1)-J(J+1)-I(I+1)],$$

with $C=0.14$ Mc/sec. (Compare with NO above, $a=23$ Mc/sec.) The molecular magnetic moment required to account for this coupling probably results from the molecular rotation. Table III gives a comparison of the observed frequencies with those calculated by use of the quadrupole coupling as $eQq=1823$ Mc/sec and the magnetic-coupling constant for I^{127} as 0.07 Mc/sec. Although the magnetic displacements in all cases are less than one megacycle, they are well outside the limits of error in the measurement of the relative differences in the frequencies of the lines.

TABLE II. Constants of $N^{14}O^{16}$ in the $^2\Pi_{\frac{1}{2}}$ state.

$$\Delta\nu_{cd}=355.1\text{ Mc/sec},\quad p=355.1\text{ Mc/sec}$$
$$(B_0)_{eff}=50\,124.3\text{ Mc/sec}=1.67198\text{ cm}^{-1}$$
$$B_0=50\,818.0\text{ Mc/sec}=1.69512\text{ cm}^{-1}$$
$$B_e=51\,084.8\text{ Mc/sec}=1.70402\text{ cm}^{-1}$$
$$I_0=16.5082\times10^{-40}\text{ g cm}^2,\quad I_e=16.4219\times10^{-40}\text{ g cm}^2$$
$$r_0=1.1540\text{ A},\quad r_e=1.1510\text{ A}$$

Table IV summarizes the information obtained for the DI molecule. In calculation of B_0 we have used $D_J=1.5$ Mc/sec, as obtained from the formula $D_J=4B^3/\omega^2$.

TABLE III. Observed and calculated frequencies of DI^{127}. $J=0\rightarrow1$, $\nu_0=195\,068.15\pm0.30$ Mc/sec.

Transition $F-F'$	Quadrupole splitting (Mc/sec) 1st order	Quadrupole splitting (Mc/sec) 2nd order	Magnetic splitting (Mc/sec)	Calculated[a] frequency (Mc/sec)	Observed frequency (Mc/sec)
$5/2\rightarrow5/2$	−291.68	0.09	−0.16	194,776.40	194,776.40 ±0.30
$5/2\rightarrow7/2$	91.15	0.07	0.38	195,159.75	195,159.68 ±0.30
$5/2\rightarrow3/2$	225.22	0.18	−0.56	195,322.99	195,323.02 ±0.30

[a] Calculated with the constants given in Table IV.

TABLE IV. Molecular constants of DI^{127}.

$eQq(I^{127})=1823\pm1$ Mc/sec	$C(I^{127})=0.14$ Mc/sec
$B_0=97\,537.2$ Mc/sec	$r_0=1.6165$ A

The nuclear quadrupole coupling in atomic iodine has now been measured by Jaccarino, King, and Stroke[6] as 1146.215 Mc/sec. If one assumes that the effects of bond orbital hybridization are negligible, the nuclear quadrupole coupling should give a measure of the ionic character of the bond. In this case,[7]

$$\text{Ionic character}=1-\frac{\text{mol }eQq}{2\times\text{atomic }eQq}\approx\frac{x_A-x_B}{2}.$$

The electronegativity difference between I and H is 0.4, and from the above rule a coupling of

$$2290[1-(x_A-x_B)/2]=1832\text{ Mc/sec}$$

is expected, as compared with the observed value of 1823 Mc/sec.

While these results were being prepared for publication, the note by Klein and Nethercot[8] appeared, giving results on DI. Their measurements agree with ours within their specified limits of error which, however, are some 30 times as large as our own. C. M. Johnson informs us that he is also making measurements on NO.

We wish to thank Dr. W. C. King for assistance with experimental work and Dr. M. Mizushima for helpful discussions.

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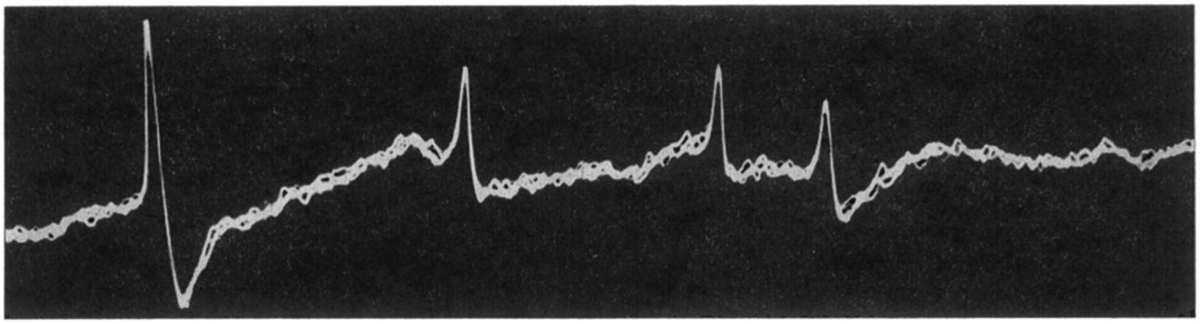
[6] Jaccarino, King, and Stroke (private communication).

[7] W. Gordy, J. Chem. Phys. **19**, 792 (1951).

[8] J. A. Klein and A. H. Nethercot, Jr., Phys. Rev. **91**, 1018 (1953).



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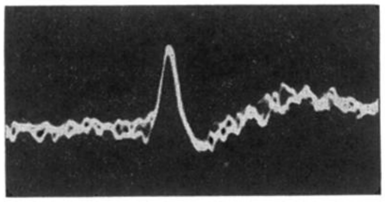

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