the $N$ component and the properties of the neutral meson.

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# Six-Millimeter Spectra of OCS and N₂O†

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The $J=3\rightarrow4$ pure rotational transition of OCS and the $J=1\rightarrow2$ transition of $N_2O$ have been investigated. The molecules were in their normal isotopic abundances. The results are compared with those of previous investigators. Quadrupole hyperfine structure, $l$-type doubling, and Fermi resonance effects are analyzed.

## I. INTRODUCTION

BOTH the $J=3\rightarrow4$ pure rotational transition of the linear molecule OCS and the $J=1\rightarrow2$ rotational transition of the linear molecule $N_2O$ occur in the wavelength region around 6 mm. These spectra have been measured using the apparatus previously described.[1]

## II. CARBON OXYSULFIDE

The OCS molecule has been extensively investigated at wavelengths longer than 6 mm, and some work has been done at shorter wavelengths. The OCS was prepared by the action of $NH_4SCN$ on $H_2SO_4$ in water.[2] All OCS isotopic species were observed in their normal abundances. Ground-state lines were measured at $T=195°K$, and excited vibrational state lines were measured at room temperature. The pressure was kept at about $2\times10^{-3}$ mm Hg. Line positions were measured to an accuracy of $\pm0.1$ Mc/sec.

Table I presents the experimental results obtained. No attempt was made to measure intensities, the relative intensities only being used as an aid in identifying the lines.

Only two quadrupole hyperfine components due to the $O^{16}C^{12}S^{33}$ molecule were found. Using the value of the coupling constant $(eqQ)=-29.07\pm0.01$ Mc/sec obtained by Eshbach, Hillger, and Strandberg,[3] and the center of gravity $\nu_0=48,038.86$ Mc/sec, the calculated line positions agree almost exactly with those observed.

The calculated rotational constants and $l$-type doubling constant are shown in Table II. A value of $1.28\pm0.05$ kc/sec for $D_0$, the centrifugal distortion coefficient in the ground vibrational state of $O^{16}C^{12}S^{32}$, was used in the calculation. This value is obtained from the data of Johnson, Trambarulo, and Gordy.[4] Strandberg, Wentink, and Kyhl[5] obtained a value of $D_0$ in $O^{16}C^{12}S^{32}$ of $1.60\pm0.05$ kc/sec. The first value agrees very closely with the theoretically determined value. $D_v$ in excited vibrational states and in all isotopes was taken equal to $D_0$ in $O^{16}C^{12}S^{32}$. The values of $\alpha_1$ and $\alpha_2$ were obtained from the excited state data, corrections being made for Fermi resonance (see below). The value of $\alpha_3$ was obtained from an analysis of the frequency shifts for isotopic changes of the masses of each of the three atoms of OCS. Townes, Holden, and Merritt obtained the relationship[6]

$$\alpha_1+2\alpha_2+\alpha_3=0.00856B_0,$$

TABLE I. $J=3\rightarrow4$ rotational spectrum of OCS.

| Molecule | Vibrational state and F transition | Experimental frequency in Mc/sec | Previously determined frequency in Mc/sec | Calculated intensity[b] at 300°K in $10^{-6}$ cm⁻¹ |
|---|---|---|---|---|
| $O^{16}C^{12}S^{32}$ | 0 0 0 | 48,651.40 ±0.10 | 48,651.64 ±0.05[a] | 436 |
| | 1 0 0 | 48,506.24 | | 7.0 |
| | 0 1₁0 | 48,710.80 | | 34.9 |
| | 0 1₂0 | 48,761.55 | | 34.9 |
| | 0 2⁰0 | 48,801.08 | | 2.7 |
| | 0 2²0 | 48,819.92 | | 5.2 |
| $O^{16}C^{12}S^{34}$ | 0 0 0 | 47,462.20 | 47,462.40 ±0.05[a] | 17.8 |
| $O^{18}C^{13}S^{32}$ | 0 0 0 | 48,494.76 | | 4.7 |
| $O^{16}C^{12}S^{33}$ | 0 0 0 | | | |
| | 3/2→ 5/2<br>5/2→ 7/2 | 48,038.19 | | 1.0 |
| | 7/2→ 9/2<br>9/2→11/2 | 48,039.13 | | 1.8 |

[a] Strandberg, Wentink, and Kyhl, Phys. Rev. **75**, 270 (1948).
[b] Calculated using intensity relation of P. Kisliuk and C. H. Townes, J. Research Natl. Bur. Standards **44**, 611 (1950), $\Delta\nu=6$ Mc/sec, and the dipole moments given in R. G. Shulman and C. H. Townes, Phys. Rev. **77**, 500 (1950). Those moments not measured were taken equal to 0.7085 debye.

† Assisted by the ONR.
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[1] S. J. Tetenbaum, Phys. Rev. **86**, 440 (1952).
[2] Stock, Siecke, and Pohland, Ber. deut. chem. Ges. **57**, 719 (1924).

[3] Eshbach, Hillger, and Strandberg, Phys. Rev. **85**, 532 (1952).
[4] Johnson, Trambarulo, and Gordy, Phys. Rev. **84**, 1178 (1951).
[5] Strandberg, Wentink, and Kyhl, Phys. Rev. **75**, 270 (1949).
[6] Townes, Holden, and Merritt, Phys. Rev. **74**, 1113 (1948).

TABLE II. Rotational constants of OCS (all quantities in Mc/sec).

| Molecule | $B_0$ | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $q_l$ |
|---|---|---|---|---|---|
| $O^{16}C^{12}S^{32}$ | 6081.466±0.013 | 20.56±0.04[a] | $\begin{cases} -10.594\pm0.022 \\ -10.533\pm0.009 \end{cases}$[b] | 52.6[a] | 6.344±0.01$\overline{8}$ |
| $O^{16}C^{12}S^{33}$ | 6004.899±0.007 | | | | |
| $O^{16}C^{12}S^{34}$ | 5932.816±0.013 | | | | |
| $O^{16}C^{13}S^{32}$ | 6061.886±0.013 | | | | |

[a] Calculated using $\alpha_2 = -10.563 \pm 0.02$ Mc/sec.
[b] Upper value computed from (0 0 0) and (0 1¹0) vibrational states. Lower value computed from (0 0 0) and (0 2⁰0) vibrational states.

from which $\alpha_3$ can be computed. The $l$-type doubling constant $q_l$ agrees well with the theoretical value of 6.34 Mc/sec obtained by Nielsen.[7]

Fermi resonance perturbation effects have previously been detected in OCS[8] and discussed in greater detail in the molecule BrCN.[1] The $J=3\rightarrow4$ transition has been analyzed,[9] and the results are shown in Table III. The two levels which perturb each other are the (1 0⁰0) and (0 2⁰0) levels. The energy separation between these levels in their unperturbed states ($\delta$) can be obtained from the experimental infrared data of Bartunek and Barker.[10] (The $2_0$ and $2_2$ levels should be interchanged from the positions of Bartunek and Barker because Fermi resonance would push the $2_0$ level up and the level corresponding to $\omega_1$ down. This also necessitates a change in their value of $X_{ll}$.) Using their data, we get $\delta = 163.6$ cm⁻¹. The values of $\alpha_2$ obtained using different pairs of unperturbed vibrational state lines are unequal. This is due to the use of a first-order approximation formula relating the $B$'s and the $\alpha$'s. In the calculation of $\alpha_1$ an average value of $\alpha_2 = -10.563\pm0.02$ Mc/sec was used. The computed value of the interaction energy $W_{12}$ is 43.2 cm⁻¹. The correction to the rotational frequency due to Fermi resonance perturbations is given by $2(J+1)(B-B^0)$. For the interacting levels bracketed together in Table III the correction is 19.33 Mc/sec.

### III. NITROUS OXIDE

The molecule N₂O has a relatively small electric dipole moment, resulting in a rotational spectrum of small absolute intensity. Thus far, pure rotational transitions have been observed only in the ground vibrational state. This has precluded the observation of Fermi resonance and $l$-type doubling effects in the microwave data of N₂O, although an appreciable Fermi resonance effect has been found in the infrared spectrum.[11]

The microwave spectrum of N₂O was first observed by Coles, Elyash, and Gorman.[12] They studied the molecules $N^{14}N^{14}O^{16}$ and $N^{15}N^{14}O^{16}$ in the $J=0\rightarrow1$ pure

rotational transition. They also observed and analyzed the hyperfine structure due to the electric quadrupole moment of the $N^{14}$ nucleus. Since the two-quadrupole theory of Bardeen and Townes[13] had not yet been developed, they could only estimate the quadrupole coupling constant of the $N^{14}$ nucleus in the end position. The coupling constant for the central nitrogen was computed from the hyperfine structure of $N^{15}N^{14}O^{16}$.

The quadrupole hyperfine structure of $N^{14}N^{14}O^{16}$ in the $J=0\rightarrow1$ transition has also been investigated by Smith, Ring, Smith, and Gordy.[14] Using the previously determined value of $(eqQ)$ for central $N^{14}$, they determined the value of the end $N^{14}$ coupling constant so as to give the best fit with the two-quadrupole theory.[13] In their theoretical plot of this spectrum, the authors have left out a third line which belongs with the central group of the pattern.

The $J=3\rightarrow4$ and $J=4\rightarrow5$ spectra have been observed in $N^{14}N^{14}O^{16}$.[4] No hyperfine structure is mentioned in this paper.

The author has observed and analyzed the $J=1\rightarrow2$ rotational transition of $N^{14}N^{14}O^{16}$ in its ground state. Because there is quadrupole splitting of the $J=2$ level as well as of the $J=1$ level (as compared to only the $J=1$ level being split in the $J=0\rightarrow1$ transition), and also because the relative separation of the hyperfine components is only about one-half that in the lowest rotational transition, it is considerably more difficult to obtain accurate values of the quadrupole coupling constants.

At low pressures the absorption line was seen to consist of three separate components. The large central line was measured with the marker system. The relative positions and amplitudes of the three components were

TABLE III. Fermi resonance perturbations in the $J=3\rightarrow4$ transition of $O^{16}C^{12}S^{32}$.

| Vibrational state | Experimental $B$ value in Mc/sec[a] | Unperturbed $B$ value in Mc/sec[b] |
|---|---|---|
| 0 0 0 | 6081.466±0.013 | — |
| 0 1¹0 | 6092.060±0.018 | — |
| 0 2⁰0 | 6102.521±0.013 | — |
| 1 0⁰0 ⎫ | 6063.321±0.013 | 6060.906 |
| 0 2⁰0 ⎭ | 6100.176±0.013 | 6102.592 |

[a] Center of gravity used when $l$-type doubling present. $B_v$ calculated using $D_v = 1.28 \pm 0.05$ kc/sec for all vibrational states.
[b] Calculated using $\alpha_1 = 20.56$ Mc/sec and $\alpha_2 = -10.563$ Mc/sec.

[7] H. H. Nielsen, Phys. Rev. **78**, 296 (1950).
[8] W. Low and C. H. Townes, Phys. Rev. **79**, 244 (1950).
[9] I should like to thank Professor C. H. Townes for making available an unpublished analysis of Fermi resonance in linear triatomic molecules.
[10] P. F. Bartunek and E. F. Barker, Phys. Rev. **48**, 516 (1935).
[11] G. Herzberg and L. Herzberg, J. Chem. Phys. **18**, 1551 (1950).
[12] Coles, Elyash, and Gorman, Phys. Rev. **72**, 973 (1947).

[13] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).
[14] Smith, Ring, Smith, and Gordy, Phys. Rev. **73**, 633 (1948).

TABLE IV. The $J=1\rightarrow2$ transition of $N^{14}N^{14}O^{16}$.

| Transition $(F_{1i}, F_i \rightarrow F_{1f}, F_f)$[a] | Observed relative intensity | Calculated relative intensity[b] |
|---|---|---|
| (2,1→2,2), (2,3→2,2), (2,1→2,1),<br>(2,3→2,3), (2,2→2,2), (0,1→1,1),<br>(2,2→2,3), (0,1→1,2), (2,2→2,1),<br>(0,1→1,0) | 50,245.63±0.15 | 2 | 2 |
| (1,1→2,2), (2,3→3,3), (1,2→2,2),<br>(1,1→2,1), (2,2→3,3), (1,2→2,3),<br>(2,1→3,2), (2,3→3,4), (1,2→2,1),<br>(2,3→3,2), (1,0→2,1), (2,2→3,2),<br>(2,1→1,1), (2,1→1,2), (2,3→1,2),<br>(2,1→1,0), (2,2→1,1), (2,2→1,2) | 50,246.03±0.10 | 8 | 8.2 |
| (1,1→1,1), (1,2→1,1), (1,1→1,2),<br>(1,2→1,2), (1,0→1,1), (1,1→1,0) | 50,246.53±0.15 | 1 | 1 |

[a] Notation used is that of J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).
[b] Calculated assuming $|(eqQ)_{end}| \gg |(eqQ)_{center}|$.

TABLE V. Rotational constants of $N^{14}N^{14}O^{16}$.

| Spectrum | Center of gravity | $B_0$ in Mc/sec | $D_0$ in kc/sec |
|---|---|---|---|
| $J=0\rightarrow1$[a] | 25,123.25 | 12,561.64[b] | |
| $J=1\rightarrow2$[c] | 50,246.01 ±0.10 | 12,561.55 ±0.025[b] | |
| $J=3\rightarrow4$[d] | 100,491.76 ±0.25 | 12,561.65 ±0.025[b] | 5.67 ±0.05 |
| $J=4\rightarrow5$[d] | 125,613.68 ±0.30 | | |
| Vibrational bands<br>from 0.8 to 1.2$\mu$[e] | | 12,564.5[f] | 5.7[g] |
| Vibrational bands<br>near 4.5$\mu$[g] | | 12,565.3  ±4.5 | |

[a] Coles, Elyash, and Gorman, Phys. Rev. **72**, 973 (1947).
[b] Computed using $D_0=5.67$ kc/sec.
[c] Present work.
[d] Johnson, Trambarulo, and Gordy, Phys. Rev. **84**, 1178 (1951).
[e] G. Herzberg and L. Herzberg, J. Chem. Phys. **18**, 1551 (1950).
[f] $B_1=12,634.2$ Mc/sec.
[g] H. W. Thompson and R. L. Williams, Proc. Roy. Soc. (London) **A208**, 326 (1951).

interpolated from an enlarged photograph of the face of the cathode-ray oscilloscope. Frequency modulation sidebands were placed on the 3.5-cm klystron carrier,[1] and their frequency and amplitude were adjusted so

TABLE VI. Quadrupole coupling constant of the end $N^{14}$ in $N^{14}N^{14}O^{16}$.

| Transition | $(eqQ)$ in Mc/sec | Reference |
|---|---|---|
| $J=0\rightarrow1$ | $-0.78$[a] | b |
| $J=0\rightarrow1$ | $-1.03\pm0.10$ | c |
| $J=1\rightarrow2$ | $-1.05\pm0.20$ | |

[a] Calculated using the line frequencies of reference b and the two-quadrupole theory of J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).
[b] Coles, Elyash, and Gorman, Phys. Rev. **72**, 973 (1947).
[c] Smith, Ring, Smith, and Gordy, Phys. Rev. **73**, 633 (1948).

that the main marker and one sideband straddled the pattern on the scope. Table IV shows the results obtained. The total spread is 0.9±0.1 Mc/sec, and the relative spacing from the low frequency component to the high frequency one is 0.4±0.05 Mc/sec and 0.5±0.05 Mc/sec.

The observed frequencies and calculated rotational constants for the $J=1\rightarrow2$ transition and previously investigated rotational transitions are shown in Table V. The results of recent infrared investigations are also included. It is seen that our $B_0$ value is somewhat smaller than that obtained in other microwave transitions.

Table VI shows the calculated quadrupole coupling constant for the end $N^{14}$ nucleus and compares it with previously determined values. In all cases, the coupling of the central $N^{14}$ nucleus was taken equal to $-0.27$ Mc/sec, the value obtained by Coles, Elyash, and Gorman.[11] The coupling constant for the $J=1\rightarrow2$ transition has a much larger probable error than that calculated from the $J=0\rightarrow1$ transition, but it seems to be closer to the value given in footnote b.

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