CALCULATED FUNDAMENTAL VIBRATIONAL FREQUENCIES OF ISOTOPICALLY SUBSTITUTED OZONE

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ABSTRACT. — The fundamental vibrational frequencies of eighteen distinct isotopically substituted ozones have been calculated.

Oxygen consists of three stable isotopes, oxygen—16, oxygen—17, and oxygen—18. As a result there exists the possibility of forming eighteen distinct isotopically substituted species of ozone. Nine species belong to the group C_{2v}. These are the bent X_3 or XY_2 molecules. The remaining nine species, the bent XXY or the bent XYZ molecules, belong to the lower symmetry group C_s.

Wilson's FG matrix method (Wilson, Decius, Cross, 1955) was used to calculate the vibrational frequencies for the isotopically substituted ozones. Explicit expressions for the F's and the G's used for the molecules belonging to the group C_{2v} are given by Nakamoto (1963; p. 264). Expressions for the F's and the G's used for the molecules belonging to the group C_s are given by Polo and Wilson (1954).

The structural parameters of ozone and the values of the potential constants used in the F matrix were taken as those determined by Pierce (1956). These values, as well as the values of the atomic masses used in the calculations, are listed in Table I.

The calculations of the G's, F's, and subsequent multiplications and solutions of the resultant secular equations were carried out on an IBM 1620 electronic computer. Twelve significant digits were carried in all calculations. The results of the calculations are listed in Table II.

DISCUSSION

The calculated frequencies in cm^{-1} agree well with those reported by Pierce (1956).

$^{16}O_3$ observed: 1110, 705, 1043; calculated: 1110.00, 704.99, 1042.99; ^{16}O ^{18}O ^{16}O reported by Pierce (1956): 1080, 697, 1008; calculated this work: 1079.91, 697.22, 1008.00; ^{16}O ^{16}O ^{18}O reported by Pierce (1956): 1095, 688, 1029; calculated this work: 1096.82, 688.23, 1028.45. The minor discrepancy observed in the last case represents less than 0.2% deviation.

A check on the accuracy of the vibrational frequency calculations is afforded by an application of the Sum Rule, (Wilson, Decius, Cross, 1955; p. 186) which states that for the case of ozone:

$$\sigma(^{16}O_3) + \sigma(^{18}O_3) - \sigma(^{16}O\ ^{16}O\ ^{18}O) - \sigma(^{16}O\ ^{18}O\ ^{18}O) = 0$$

and

$$\sigma(^{16}O_3) + \sigma(^{18}O_3) - \sigma(^{16}O\ ^{18}O\ ^{16}O) - \sigma(^{18}O\ ^{16}O\ ^{18}O) = 0$$

where σ represents the sum of the vibrational frequencies for the indicated species.

For the cases listed above agreement is about 0.2%, which is considered good since the Sum Rule takes no account of electrical anharmonicity and vibrational-rotational interactions.

TABLE I

Structural parameters and potential constants of ozone.

$0 - 0 - 0 = 116° 58'$
$0 - 0$ bond length $= d_o = 1.276$ Å
^{16}O mass $= 16$ amu
^{17}O mass $= 17.004533$ amu
^{18}O mass $= 18.00487$ amu
$f_d = 5.7007 \times 10^5$ dyne cm^{-1}
$f_{dd} = 1.5233 \times 10^5$ dyne cm^{-1}
$f/d_o^2 = 1.2847 \times 10^5$ dyne cm^{-1}
$f_d/d_o = 0.3324 \times 10^5$ dyne cm^{-1}

TABLE II

Vibrational frequencies of isotopically substituted ozone.

SPECIES	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
$^{16}O_3$	1110.00	704.99	1042.99
$^{17}O_3$	1076.72	683.85	1011.72
$^{18}O_3$	1046.38	664.58	983.21
$^{17}O\ ^{16}O\ ^{17}O$	1093.18	687.50	1030.36
$^{18}O\ ^{16}O\ ^{18}O$	1078.29	671.31	1019.05
$^{16}O\ ^{17}O\ ^{16}O$	1094.02	701.06	1024.58
$^{18}O\ ^{17}O\ ^{18}O$	1061.37	667.92	1000.20
$^{16}O\ ^{18}O\ ^{16}O$	1079.91	697.22	1008.00
$^{17}O\ ^{18}O\ ^{17}O$	1062.14	680.28	994.93
$^{17}O\ ^{16}O\ ^{18}O$	1086.37	679.42	1024.10
$^{16}O\ ^{17}O\ ^{18}O$	1080.42	684.57	1009.76
$^{16}O\ ^{18}O\ ^{17}O$	1071.80	688.77	1000.72
$^{16}O\ ^{16}O\ ^{17}O$	1102.34	696.27	1035.95
$^{16}O\ ^{16}O\ ^{18}O$	1096.82	688.23	1028.45
$^{16}O\ ^{17}O\ ^{17}O$	1086.13	692.48	1017.41
$^{17}O\ ^{17}O\ ^{18}O$	1069.69	675.90	1005.34
$^{16}O\ ^{18}O\ ^{18}O$	1065.91	680.98	992.94
$^{17}O\ ^{18}O\ ^{18}O$	1054.91	672.45	988.44

The low isotopic abundance of oxygen-17 and oxygen-18 probably precludes observations of infrared data on these isotopically substituted ozone species. Infrared data on oxygen-16 and oxygen-18 ozone species could be obtained from oxygen-18 enriched ozone.

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