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Microwave Spectroscopy of Isotopic Cyclobutene Ozonide as a Means of Quantification of Ozone Isotopomers

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The microwave spectrum of [2-^{18}O]cyclobutene ozonide, a new isotopomeric species, has been assigned and the absolute direction of the dipole moment has been determined. The aim of this investigation has been to determine symmetric/asymmetric isotopomer concentrations in an arbitrary ^{18}O-substituted ozone isotopomer mixture. The method we have used consists of transforming the ozone into cyclobutene ozonide and using intensities of rotational lines of these to quantify the composition of the original ozone isotopomer mixture. Such a method has been accomplished; unfortunately propagation of errors renders it difficult to obtain results of high accuracy. © 1994 Academic Press, Inc.

INTRODUCTION

In two previous papers (*1, 2*) we have reported on investigations of the mechanism of ozone formation using oxygen isotopes (^{18}O, which we shall refer to as Q in this paper) as probes. In order to assess abundances not only of the total amount of isotopomers of a certain mass (say 50) but also of the relative amounts of asymmetric and corresponding symmetric species (OOQ/OQO) we used high-resolution rotational spectroscopy in the microwave (MW) region. (These molecular species are formed, together with OOO, QQO, QOQ, and QQQ, when atomic oxygen reacts with (isotopic) molecular oxygen.)

MW spectroscopy has the advantage of making it straightforward to distinguish between absorption lines belonging to two isotopomers of equal mass. Furthermore only the *permanent dipole moment* and the temperature are needed in order to calculate the theoretical line intensities, assuming that higher order effects are negligible. This is unlike vibrational spectra where the theoretical linestrength depends on *dipole moment derivatives.* While the permanent dipole moment of, for example, QOO may be easily calculated from that of OOO—which is known with high precision—the same is much more difficult for the derivatives. However, MW has the drawback that the experimental line intensities do not provide sufficiently reliable measures of the concentrations. Even though the experimental value for the intensity of an absorption line of a certain molecular species can be assumed to be proportional to the partial pressure of this species in the cell, it depends in an unpredictable manner on the frequency at which the line is situated. This is a very unfortunate built-in deficiency that has to do with the way MW instruments are constructed. (See Appendix of (*2*) for further discussion of the problem.)

In our previous work we made two attempts, described in Refs. (*1, 2*), to get around these difficulties. In the first we depended on calibration mixtures that we assumed to be completely scrambled, an assumption we had no way of verifying. In the other we

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analyzed a large number (26) of different isotopomer mixtures in an attempt to assess pertinent specific line intensities by a least-squares procedure. Neither of the two approaches was entirely satisfactory.

The first method suffered from doubts raised by the finding of nonstatistical abundances of ozone isotopomers not only in the laboratory, but also in the stratosphere (see Mauersberger *et al.* (*3–5*), Abbas *et al.* (*6*), and Goldman *et al.* (*7*)).

The second method did not allow for an independent determination of the specific line intensities for the symmetric and asymmetric isotopomers of mass 50 and of 52. This was caused by inadequate variability in the relative abundances of these pairs in the 26 mixtures.

In the method presented here the ozone mixture to be analyzed is converted into cyclobutene ozonide by addition to cyclobutene. (Systematically cyclobutene ozonide is known as 2,3,7-trioxabicyclo[2.2.1.]heptane, henceforth CBO; see Fig. 1 for the formula and numbering). It is assumed that there is no appreciable kinetic isotope effect during the addition process, so that the isotopic composition of the mixture is conserved (the addition takes place in the liquid phase; see below for details). CBO is much more stable than ozone, so that the mixture may now be stored in the freezer for future analysis. It might seem that we have the same problem when we want to use MW to analyze the CBO mixture as we have for ozone. This is, however, not the case because there is an alternative route to preparing an oxygen-isotopomer mixture of cyclobutene ozonide, a route in which none of the species formed contain Q at position 7 (see Borseth *et al.* (*9*)). The two routes are shown in Fig. 1.

The alternative route starts from furan. Note that one of the oxygen atoms—that of furan—is then already present—this is the atom that ends up in position 7. Singlet dioxygen (singlet OO, OQ, and QQ in our case) is added to furan aided by a photoexcitation system and the intermediate cyclobutadiene ozonide is reduced chemically

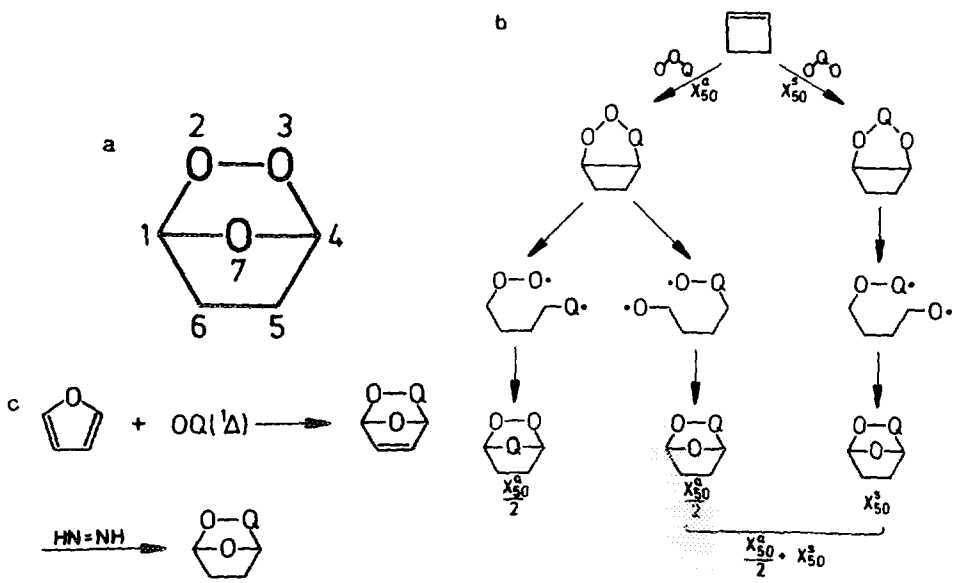

FIG. 1. (a) The numbering of cyclobutene ozonide (CBO). (b) The direct route to CBO via ozone and cyclobutene. (c) The route to CBO via furan.

(see Fig. 1). Since all the CBO species formed have O at the ether bridge and either OO, OQ, or QQ in the peroxide bridge, mass spectrometry can now be used to assess the amounts of the isotopomers in the mixture (see Quantification of Ozone Isotopomers, for details).

It was necessary to assign and measure the spectrum of [2-^{18}O]CBO. To obtain better rotational and centrifugal distortion constants for the parent species we also added a number of *Q* lines to the set of *R* lines measured by Borseth (*9*).

Measurement of the Stark effect of one R line of [2-^{18}O]CBO provided information about the absolute direction of the dipole moment.

EXPERIMENTAL DETAILS

Synthesis of Ozonide from Cyclobutene

Borseth *et al.* (*9*, *10*, and references therein) have given fairly complete descriptions of the synthesis (see also Fig. 1). We have modified the ozonization procedure, however, since we were dealing with small amounts of (expensive) isotopes.

Cyclobutene was obtained from commercially available bromocyclobutane by refluxing a solution of 2.0 g bromocyclobutane and 2.4 g KOH in 4.2 ml ethanol. The reflux condenser was connected to a CO_2(s)/ethanol cooling bath and swept with nitrogen in order to rinse out the last part of the (gaseous) sample.

While Borseth added (normal) ozone from an ozonizer to cyclobutene through a tube immersed into the cyclobutene dissolved in isopentane and cooled to −95°C, we instead added the ozone from the gas phase by letting small portions from the vacuum line become absorbed in the stirred solution as it was consumed. The consumption was followed on a sulfuric acid manometer. Even though the solution was kept cooled to −95°C throughout there were tiny explosions accompanied by blue

TABLE I

New Microwave Absorption Lines for CBO

$J'_{K'_{-1}\,K'_{+1}} \leftarrow J_{K_{-1}\,K_{+1}}$	Obs. Frequency/MHz	Obs.− Calc.
$17_{2\,16} \leftarrow 17_{0\,17}$	25246.628	−0.0101
$17_{1\,16} \leftarrow 17_{1\,17}$	25246.628	−0.0101
$18_{3\,16} \leftarrow 18_{1\,17}$	25089.770	0.0193
$18_{2\,16} \leftarrow 18_{2\,17}$	25089.770	0.0197
$19_{4\,16} \leftarrow 19_{2\,17}$	24902.737	0.0132
$19_{3\,16} \leftarrow 19_{3\,17}$	24902.737	0.0171
$20_{11\,10} \leftarrow 20_{9\,11}$	20265.430	−0.0132
$24_{9\,16} \leftarrow 24_{7\,17}$	23303.011	−0.0090
$24_{8\,16} \leftarrow 24_{8\,17}$	23276.998	−0.0462
$24_{13\,12} \leftarrow 24_{11\,13}$	24088.676	0.0118
$25_{9\,17} \leftarrow 25_{7\,18}$	24935.165	−0.0040
$25_{8\,17} \leftarrow 25_{8\,18}$	24926.405	−0.0728
$28_{11\,17} \leftarrow 28_{11\,18}$	22932.345	0.0218
$29_{12\,18} \leftarrow 29_{10\,19}$	25023.038	0.0432
$29_{13\,17} \leftarrow 29_{11\,18}$	22836.597	−0.0270
$29_{12\,17} \leftarrow 29_{12\,18}$	21636.169	0.0449
$38_{17\,21} \leftarrow 38_{17\,22}$	21881.335	0.0175
$40_{18\,22} \leftarrow 40_{18\,23}$	22351.702	−0.0200

lightning phenomena whenever a new portion of ozone was added. The amounts were never so large that a serious explosion took place, however, and in the end the yield of ozonide was acceptable. Presumably we were witnessing chemiluminescense phenomena due to gas-phase reaction between ozone and cyclobutene.

The isotopically substituted ozone was obtained by subjecting portions of 100 ml at 100 Torr of a dioxygen mixture of 25% O_2 and 75% Q_2 to a Tesla coil discharge as described previously (*1*).

The sample was analyzed by mass spectrometry (see below).

Synthesis of Ozonide from Furan

This synthesis proceeds in two steps. First, singlet dioxygen is added to furan to give an adduct (see Fig. 1). Next, this adduct is reduced by diazene to give CBO. The dioxygen sample was the same as above but it had been scrambled by subjecting it to the Tesla coil discharge for several hours.

The addition of dioxygen to furan was accomplished by illuminating the furan solution with a sodium lamp (150 W Phillips SON-T PLUS). The solution consisted of 0.34 g furan in 15 ml methylene chloride to which a solution of tetraphenylporphyrin (sensitizer) in methylene chloride was added.

Microwave and Mass Spectra

Microwave spectra were obtained at −20°C on our computer-assisted HP-MRR spectrometer. Results are found in the next section.

Mass spectrometric analysis was performed on a four-sector double focusing mass spectrometer (Jeol JMS-HX/HX110A). Results are found under Quantification of Ozone Isotopomers below. The abundances are given with a 1% relative uncertainty.

MICROWAVE SPECTRUM AND DIRECTION OF DIPOLE MOMENT

The set of microwave lines measured by Borseth *et al.* (*9*) was extended with a number of Q lines (see Table I), mostly to obtain more accurate centrifugal distortion constants and rotational constants. Furthermore the microwave spectrum of [2-^{18}O]CBO was assigned and measured (see Table II). The rotational and centrifugal distortion constants are collected in Table III.

Borseth *et al.* (*9*) have measured the dipole moment of CBO. They found $|\mu_a| = 2.856(4)$ D and $|\mu_c| = 0.075(4)$ D (μ_b is zero by symmetry). Since isotopic substitution leads to a slight rotation of the principal axis system, then the sign of μ_c relative to that of μ_a may be inferred. Table IV contains the results, assuming the same and the opposite sign for μ_c and μ_a (see Fig. 2).

Table V shows the calculated Stark displacements for the transition $4_{14} \leftarrow 3_{13}$ at three different field strengths assuming the two signs for μ_c (see Table IV). The table also shows the observed displacements. We conclude that μ_a and μ_c have the same sign.

QUANTIFICATION OF OZONE ISOTOPOMERS

The following description pertains to the quantification of OOQ and OQO and could in principle be applied to the pair QQO/QOQ. The symbol X^{a}_{50} denotes the

TABLE II

Measured Microwave Absorption Lines for [2-^{18}O]CBO

$J'_{K'_{-1}\,K'_{+1}} \leftarrow J_{K_{-1}\,K_{+1}}$	Obs. Frequency/MHz	Obs.– Calc.
$3_{0\,3} \leftarrow 2_{0\,2}$	18858.333	0.0068
$3_{1\,3} \leftarrow 2_{1\,2}$	18652.022	0.0163
$4_{0\,4} \leftarrow 3_{0\,3}$	24811.420	0.0347
$4_{1\,4} \leftarrow 3_{1\,3}$	24722.840	0.0301
$4_{2\,3} \leftarrow 3_{2\,2}$	25870.513	-0.0822
$17_{2\,16} \leftarrow 17_{0\,17}$	25135.243	0.0157
$17_{1\,16} \leftarrow 17_{1\,17}$	25135.243	0.0157
$18_{3\,16} \leftarrow 18_{1\,17}$	24963.191	0.0085
$18_{2\,16} \leftarrow 18_{2\,17}$	24963.191	0.0092
$19_{4\,16} \leftarrow 19_{2\,17}$	24757.742	-0.0202
$19_{3\,16} \leftarrow 19_{3\,17}$	24757.742	-0.0123
$23_{8\,16} \leftarrow 23_{6\,17}$	23469.054	0.1436
$23_{7\,16} \leftarrow 23_{7\,17}$	23457.071	-0.0802
$24_{8\,17} \leftarrow 24_{6\,18}$	25074.841	0.0141
$24_{7\,17} \leftarrow 24_{7\,18}$	25070.893	-0.0441
$24_{9\,16} \leftarrow 24_{7\,17}$	22989.323	-0.0041
$24_{8\,16} \leftarrow 24_{8\,17}$	22939.777	0.0157
$25_{9\,17} \leftarrow 25_{7\,18}$	24623.565	-0.0165
$25_{8\,17} \leftarrow 25_{8\,18}$	24606.087	-0.0283
$25_{13\,13} \leftarrow 25_{11\,14}$	23737.560	-0.0386
$27_{11\,17} \leftarrow 27_{9\,18}$	23518.619	-0.1608
$27_{14\,14} \leftarrow 27_{12\,15}$	25755.988	0.0468
$28_{11\,18} \leftarrow 28_{9\,19}$	25188.132	0.0099
$28_{10\,18} \leftarrow 28_{10\,19}$	25093.381	0.0349
$28_{12\,17} \leftarrow 28_{10\,18}$	22944.424	0.0492
$28_{11\,17} \leftarrow 28_{11\,18}$	22174.746	0.0357
$29_{13\,17} \leftarrow 29_{11\,18}$	22555.116	-0.0089
$29_{12\,17} \leftarrow 29_{12\,18}$	20437.225	0.0180
$31_{14\,18} \leftarrow 31_{12\,19}$	23633.429	-0.0056
$31_{13\,18} \leftarrow 31_{13\,19}$	21061.769	0.0099
$39_{17\,22} \leftarrow 39_{17\,23}$	22947.530	-0.0030
$43_{19\,24} \leftarrow 43_{19\,25}$	23513.372	0.0014

fraction of the total number of isotopomeric ozone molecules of molecular mass 50 that are asymmetric (OOQ), while X^{s}_{50} is the fraction that are symmetric. The symbols are introduced in Fig. 1.

The oxygen mixture used has been prepared with the aim of minimizing the amount of ozone species of masses 52 and 54. This is to minimize interferences from unwanted species in the MW spectra.

Mass Spectrometry

Table VI contains the composition of the original dioxygen mixture determined by mass spectrometry. The composition of the two samples of CBO (paths b and c of Fig. 1) is given in Table VII.

Microwave Spectrometry

Measurements have been performed under three different sets of circumstances referred to as cases a–c:

TABLE III

Rotational Constants and Centrifugal Distortion Constants in Watson's *A* Reduction, for CBO (Including Previous Measurements by Borseth *et al.* (*9*)) and [2-^{18}O]CBO

Constant	CBO	[2-^{18}O]-CBO
A/MHz	4199.6918(41)	4149.9502(72)
B/MHz	3588.0275(32)	3509.8476(42)
C/MHz	3066.1577(39)	2999.5952(35)
D_j/kHz	0.407(64)	(0.407)
D_{jk}/kHz	1.236(16)	1.140(18)
D_k/kHz	−1.079(37)	−0.952(30)
d_j/kHz	0.0087(14)	0.0115(19)
d_{jk}/kHz	0.6782(76)	0.6491(89)

Note. D_j for [2-^{18}O]CBO has been kept fixed at the value determined for CBO.

Case a: Spectral region around 25 782 MHz, 800 V Stark voltage.
Case b: Same spectral region, 1200 V Stark voltage.
Case c: Spectral region around 22 170 MHz, 800 V Stark voltage.

The aim of cases a and b was to elucidate the importance of the Stark voltage chosen.

Cases a and c likewise attempted to elucidate the importance of the spectral region selected, but also to obtain independent data. Each of the two spectral regions had to contain two spectral lines lying fairly close to each other (to ensure near-equal properties of the instrument at the two frequencies; see below) and at the same time belonging to the two species which we aimed to measure (superscripts (1) and (2); see Fig. 3).

TABLE IV

Dipole Components in the Principal Axis System (PAS) of the Parent Molecule (Assuming the Direction of the *a* Projection) According to Ref. (*9*)

Component	Parent	Subst. $\mu_c > 0$	Subst. $\mu_c < 0$
μ_a/D	2.856	2.848	2.848
μ_b/D	0.000	0.2159	0.2199
μ_c/D	±0.075	0.0084	−0.1415

Note. In the third and fourth columns the components relative to the PAS of [2-^{18}O]CBO, assuming a positive and a negative sign, respectively, for μ_c.

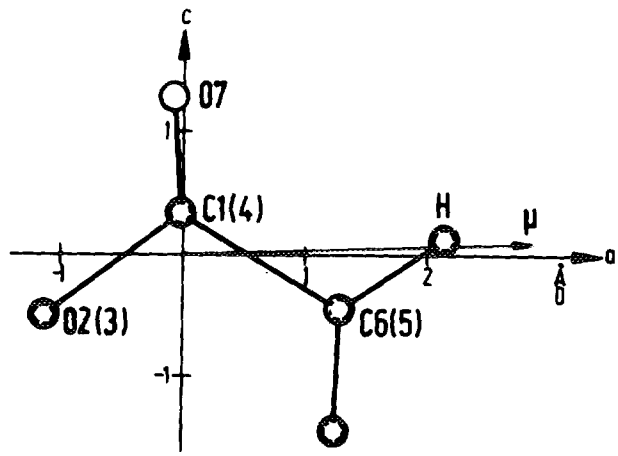

FIG. 2. The dipole vector of the parent species of CBO lies in the symmetry plane (*ac* plane). The direction of the projection of the dipole vector on the *a* axis has been assumed to have its negative end at the oxygen end of the molecule. Note that the units on the axes are distances in Ångstrom and dipole moment in Debye.

The measurement for case a is performed as follows:

1. The species obtained via the furan path (subscript FU) is introduced into the cell and its spectrum is recorded.
2. The species obtained via the CBO path (subscript CB) is introduced and its spectrum is similarly recorded.

The procedure is repeated for cases b and c.

Figure 3 contains the spectra obtained for cases a to c. Figure 3d identifies, in a schematic way, the intensities $I_{FU}^{(1)}, \ldots, I_{CB}^{(2)}$ measured in case c; similar identifications for cases a and b are implied. The following equations are assumed for the intensities:

TABLE V

Calculated and Observed Stark Displacements for $4_{14} \leftarrow 3_{13}$ of CBO

Field-strength/ (V cm^{-1})	M	$\Delta\nu$/MHz for $\mu_c > 0$	$\Delta\nu$/MHz for $\mu_c < 0$	$\Delta\nu$/MHz observed
300	0	−0.17	−0.17	.
–	1	0.26	0.49	.
–	2	1.54	2.40	1.2
–	3	3.68	5.44	3.4
400	0	−0.30	−0.29	.
–	1	0.47	0.86	.
–	2	2.74	4.18	2.35
–	3	6.53	9.35	.
800	0	−1.18	−1.17	.
–	1	1.86	3.30	1.80
–	2	10.93	15.20	.
–	3	25.93	32.63	.

Note. The first calculation assumes a positive value for μ_c, and the second a negative.

TABLE VI

Composition of the Basic, Unscrambled Dioxygen Mixture Used in All Experiments, Obtained by Mass Spectrometry and Expressed as Mole Percent

Species	% from MS
OO	72.20(72)
OQ	8.06(8)
QQ	21.71(22)
Total Q	23.76(24)

$$I_{FU}^{(1)} = X_{32} \cdot k^{(1)} \cdot k_{FU} \tag{1}$$

$$I_{FU}^{(2)} = X_{34} \cdot k^{(2)} \cdot k_{FU} \tag{2}$$

$$I_{CB}^{(1)} = X_{48} \cdot k^{(1)} \cdot k_{CB} \tag{3}$$

$$I_{CB}^{(2)} = (X^{s}_{50} + \tfrac{1}{2} X^{a}_{50}) \cdot k^{(2)} \cdot k_{CB}. \tag{4}$$

X_{32}, X_{34}, and X_{36} are the mole fractions of the dioxygen species in the scrambled dioxygen and X_{48} is that of normal ozone. X_{32} enters into the first equation because FU species (1) was obtained by addition of OO of mass 32 to furan, etc. As mentioned above, the mole fractions are assumed to be conserved during the chemical transformations and hence to be faithfully represented by the corresponding mole fractions of the final species. The factor $(X^{s}_{50} + \frac{1}{2} X^{a}_{50})$ in the last equation arises as described in Fig. 1.

$k^{(1)}$ and $k^{(2)}$ are line constants that are characteristic for the molecular species (1) or (2) and for the transition. They depend on the quantum numbers involved in the transition, on the frequency of the transition, on the Stark voltage to the extent that it influences the lineshape (as is actually observed in cases a and b; see Fig. 3), and on the temperature.

k_{FU} and k_{CB} are factors that are characteristic for the conditions prevailing during the measurement, in particular the filling pressure, and can be assumed to be equal for two lines that have been obtained in the same spectral run.

TABLE VII

Composition of the Two CBO Mixtures Obtained from Furan and from Cyclobutene (Fig. 1) and Measured by Mass Spectrometry

	CBO from furan			CBO from cyclobutene		
Mass	%	Species	Name	%	Species	Name
102	62.42(62)	OO	X_{32}	19.41(19)	OOO	X_{48}
104	28.01(28)	OQ	X_{34}	44.01(44)	OOQ,OQO	$X^{a}_{50} + X^{s}_{50}$
106	9.58(10)	QQ	X_{36}	15.39(15)	OQQ,QOQ	$X^{a}_{52} + X^{s}_{52}$
108	–	–	–	1.59(2)	QQQ	X_{54}

Note. "Species" is the oxygen species that went into the product observed at the mass peak. "Name" is name given (in the text) to the mole fraction of the same oxygen species, assuming conservation of abundances.

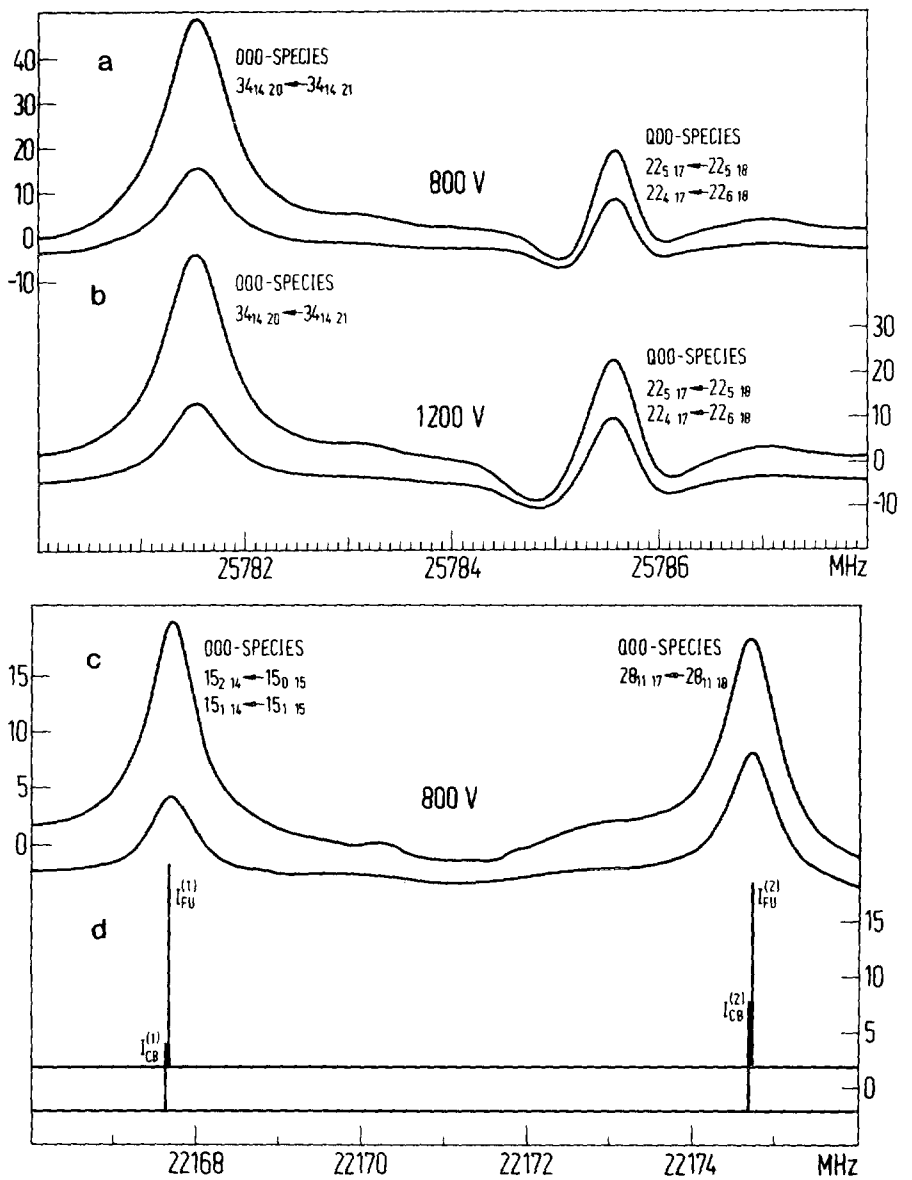

FIG. 3. The microwave lines used to assess the mole fractions. See text for an explanation. In (d) we identify the peak intensities used in the calculation for case (c). There are similar identifications for cases (a) and (b).

From Eqs. (1)–(4) we obtain

$$X^{s}_{50} + \frac{1}{2} X^{a}_{50} = \frac{I^{(1)}_{FU}}{I^{(1)}_{CB}} \cdot \frac{I^{(2)}_{CB}}{I^{(2)}_{FU}} \cdot \frac{X_{48} X_{32}}{X_{34}} . \tag{5}$$

Solving for the fractions X^{s}_{50} and X^{a}_{50} using the microwave results in conjunction

TABLE VIII

The Final Results for the Fractions X^{s}_{50} and X^{a}_{50} Obtained as Described in the Text

	Mole-% from cases a)–c)		
Fractions	% from a)	% from b)	% from c)
X^{a}_{50}	30.3(16)	30.0(16)	29.9(16)
X^{s}_{50}	13.7(14)	13.9(14)	14.1(14)
r_{50}	2.22(25)	2.16(25)	2.12(25)

Note. r_{50} denotes X^{a}_{50}/X^{s}_{50}.

with the MS results of Table VII, the results of Table VIII were obtained. Uncertainties are obtained by assuming 1% uncertainty for all measurements. Note the unfortunate propagation of errors; thus the crucial quantity r_{50} is uncertain by 12%.

A final remark concerns the actual intensity measurements. As is evident from Eq. (5) it is the two intensity ratios that contain the essential experimental information. Each ratio was determined by a least-squares procedure: The relevant part of the CB spectrum is multiplied by a factor and subtracted from the corresponding part of the FU spectrum; the factor, i.e., the wanted ratio, is determined so that the norm of the difference spectrum is minimized.

DISCUSSION

Anderson *et al.* (*11*) were the first who attempted to measure the relative abundance of the isotopomers OOQ and OQO, using infrared tunable diode laser spectroscopy and mass spectrometry simultaneously, in ozone mixtures prepared by electric discharge in dioxygen. In two ozone production experiments they found $r_{50} = 2.274(31)$ and $r_{50} = 2.187(22)$. Our result is similar, but we have much wider error limits.

The error limits given in Ref. (*11*) reflect the measurement errors only, but do not take into account the possibility of systematic errors, notably errors in line strength, when stating the uncertainty in r_{50} ($2 + R$ in their notation). The authors do address this problem. Assuming a realistic ±10% systematic error in the linestrength we obtain an error range of ±0.2 in both cases. The possibility of systematic errors has to do with (1) the use of very few lines, three for each species, and (2) the use of linestrengths which are based, among other things, on the assumption that the ozone isotopomers are distributed exactly 2:1 among asymmetric and symmetric.

We hope to publish the results of still another calibration method soon, using about 20 rotational lines for each species from the ozone rotational bands in the FAR IR, measured on the Bruker IFS120 HR FTIR spectrometer. After careful examination of the permanent dipole moment, considering also higher order effects, we obtain $r_{50} = 2.03 \pm 0.04$—a preliminary result. We hope to reduce the uncertainty further with new spectra.

The present method assumes that the reaction of cyclobutene with ozone proceeds without significant isotope effects, otherwise we could not trust the isotopic ratios to be preserved during reaction b of Fig. 1. This assumption is justified by the choice of a condensed reaction medium, where no statistical weight considerations apply (in gaseous symmetric ozone species every other rotational state is absent due to nuclear spin statistics). Presumably only mass-dependent isotope effects arise, and they are

expected to be small because we are dealing with only small relative mass changes (unlike H/D isotope effects).

It is perhaps worth noting that the trapping of ozone as ozonides of cyclic alkenes can also be applied when mass spectrometry is used as the analytical tool. (For this purpose cyclopentene would be a more convenient option. Noncyclic alkenes cannot be applied because the rearrangement process of the primary ozonides, via the so-called Criegee intermediates, to the secondary ozonides would mix the isotopes!) Trapping has the great advantage that the trapped ozone is no longer labile or explosive.

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