

Bromine dioxide, OBrO:
the rotational spectrum and molecular properties

Holger S. P. Müller, Charles E. Miller, and Edward A. Cohen
Jet Propulsion Laboratory, California Institute of Technology

Mail Stop 183-301

Pasadena, CA 91109-8099

received:

Abstract

The rotational spectrum of the **OBrO** radical has been observed in the gas phase over the solid products of the $\text{O} + \text{Br}_2$ reaction. Spectra have been measured for both 0^{79}BrO and 0^{81}BrO in their (000), (01 0), and (020) vibrational states in selected regions between 88 and 627 GHz spanning the quantum numbers $1 \leq N \leq 61$ and $0 \leq K_a \leq 14$. The spectra are well described by a **Hamiltonian** which includes centrifugal distortion effects for fine and **hyperfine** terms. The molecular structure and the harmonic force field have been derived, and they, as well as fine and hyperfine structure constants, are compared with data of related molecules and ESR data from **OBrO** isolated in cryogenic salt matrices.

minations of polyatomic bromine oxides in the gas phase. In this article the spectra of two OBrO isotopomers in the ground state as well as the first and second excited bending states are described in detail together with the fitting procedure. The derived spectroscopic constants and molecular properties are discussed.

II. EXPERIMENTAL SECTION

The measurements were done using a 1 m long, 7.3 cm in diameter, double-path, temperature controlled glass cell. Phase-locked klystrons operating near 100 GHz were used as sources. Diode detectors were used for fundamental frequencies, and a liquid He-cooled InSb hot electron bolometer was used to detect harmonics. Further details of the spectrometer are given in Refs. 16 and 17. The regions 405.0 -422.0 GHz and 423.9 -426.4 GHz were scanned in their entirety in order to facilitate the initial assignment process. Additional, selected measurements were done in the regions 398-432, 313-319, 88-96, and 626-627 GHz during the final stages of the analysis for the purpose of improving the precision of the derived molecular parameters.

The products of an O₂ discharge (- 6 Pa) and Br₂ (0.1 -0.4 Pa) were introduced into the absorption cell (T -250 K) *via* separate sidearm inlets under slow flow conditions. An unidentified bromine oxide was condensed on the cell walls. After the flows of O₂ and Br₂ were stopped, the solid produced a clean and stable source of gas phase OBrO. With well conditioned cell walls spectra could be recorded for an amount of time that was comparable to the deposition time, up to several hours.

($I(^{79}\text{Br}) = I(^{81}\text{Br}) \approx 3/2$). The strongest of the allowed transitions are described by $AF = AJ = AN$ and make up the majority of those observed. Thus, a typical rotational transition appears as a doublet of quartets.

Initial simulations of the spectra were made using values for the electron spin-rotation, spin-spin, and nuclear quadruple coupling constants derived from ESR measurements and structural parameters ($r_0 = 164.5$ pm and $\alpha_0 = 112.3^\circ$) and centrifugal distortion constants estimated from the related molecules OCIO ,²² $^{22}\text{SO}_2$,²⁴ 25 and SeO_2 .^{26,27}

The spectra were recorded near 410 GHz. In this part of the spectrum the strongest transitions are those with moderately high N (≈ 30) and $N - 2 \leq K_c \leq N$. These transitions have easily recognizable patterns for which all eight **hyperfine** components occur within 100 MHz. An example of one such group is shown in Fig. 2. Transitions having a certain value of $N - K_c$ have characteristic spacings of $-2C$ for high N and $K_c \approx N$, making the identification of a series of related transitions straightforward. Further assignments proceeded quickly from this point for both O^{79}BrO and O^{81}BrO . Eventually it was possible to assign rotational transitions for which **hyperfine** splittings of more than 1 GHz and fine structure splittings of up to 5 GHz were observed. Selected OBrO ground state transitions are given in Table I, with some statistical information **decribing** the observed transitions given in Table II.

A number of transitions for the $V_2 = 1$ vibrational state were identified based on the similarity of their patters with those of the ground state transitions, their relative intensity, and the consistency of the derived vibration-rotation interaction constants with those of OCIO ,²² $^{22}\text{SO}_2$,²⁵ and SeO_2 .²⁶ Finally, a substantial number of $V_2 = 2$ lines **could** also be assigned. The complete list of lines used in the **final** fit, their uncertainties, as well as their positions calculated from the final **fit** is available from

$$\begin{aligned}
 & H_{NKK}(N^2 N_a^3 S_a + N_a^3 S_a N^2)/2 + H_{KKN} N_a^4 N \cdot S + H_K N_a^5 S_a + \\
 & h_1^v N^2 (N_+^2 + N_-^2) N \cdot S + h_2^v N^2 (N_+^3 S_+ + N_-^3 S_-) + h_3^v (N_+^5 S_+ + N_-^5 S_-). \quad (5)
 \end{aligned}$$

The completeness of the above expression has not been addressed, but there appear to be no redundant terms. Since the data set does not contain enough information for the determination of all nine sextic spin-rotation constants, various combinations of parameters in the sextic Hamiltonian were used in trial fits of the data. The parameter set which gave the best fit consisted of the last four terms of Eq. 5.

Predictions and fittings were done with Pickett's programs SPCAT and SPFIT.³⁰ The uncertainties attributed to individual transitions were in general one tenth of the half-width; they were increased for lines with low signal-to-noise ratio or incompletely resolved lines. The uncertainties reflect a 2σ confidence level. Completely blended lines were fit as the intensity weighted average of their components. All parameters are positively defined, except for $D_J, D_{JK},$ and D_K .

For the $V_2=1$ state, changes $A^1 C_i$ from the ground state constants C_i^0 were defined as

$$A^1 C_i := C_i^1 - C_i^0, \quad (6)$$

where C_i^1 designates $V_2=1$ spectroscopic constants. For the $v_2=2$ state changes from the ground state were in general assumed to be twice as big as those from the $V_2=1$ state. For some constants it was necessary to introduce changes $A^2 C_i$ from the changes $A^1 C_j$ which were defined as

$$A^2 C_i := C_i^2 - C_i^0 - 2 \Delta^1 C_i, \quad (7)$$

where C_i^2 designates $V_2=2$ spectroscopic constants. The (000), (010), and (020) states for both isotopomers were fit simultaneously in a single calculation. Some high order parameters were common to both isotopomers or to different vibrational states. The ratios of some higher order hyperfine constants were fixed to the isotopic ratios determined for the Br nuclei in atomic beam experiments.³¹

Here $\langle u^2 \rangle$ and K are the zero-point mean square amplitude of the BrO bond and its perpendicular amplitude correction, respectively, calculated from the harmonic force field. The Morse anharmonicity constant $a = 1.976 \text{ \AA}^{-1}$ is taken from the BrO radical.² The initial r_e value is then used to refine the force field, and the procedure is repeated. In this model ground-state average and equilibrium bond angles are assumed to be equal. It has been shown for C₁₂O that the C1O bond length calculated according to Eq. 8 agrees very well with the value determined from equilibrium rotational constants.⁵ For OCIO, however, the bond length derived from Eq. 8 is -0,2 pm longer than the one determined from equilibrium rotational constants, and in Table VII it is shown that the equilibrium bond angle is about 0.08° smaller than the ground state average value. The OBrO equilibrium bond length has been calculated according to Eq. 8. The bond length and angle have been corrected by assuming similar deviations to those of OCIO. The resulting r_e structure given in Table VII.

The harmonic force field has been calculated using Christen's program NCA.³³ The input parameters are given in Table VIII. The ν_3 isotopic shifts were corrected for the differences between gas phase and argon matrix positions, - 3.4 cm⁻¹. Harmonic wavenumbers were estimated³⁴ using the OCIO values of $\omega/\nu_i = 1.02, 1.01, \text{ and } 1.02$ for $i = 1, 2, \text{ and } 3$.³⁵ The ground state quartic distortion constants and the inertial defect differences for $V_2 = 1$ and 2, obtained in the present study, were also used in the force field calculation.

The input data were weighted inversely to the squares of their attributed uncertainties: One hundred times the experimental values were used for the quartic distortion constants, 1 cm⁻¹ and 0.3 cm⁻¹ for the vibrational wavenumbers and isotopic shifts, respectively, and three times the experimental uncertainties were used for the inertial defect differences. The resulting force constants are given in Table IX together with values for related molecules. More than 99 % of the potential energy

compounds; these effects can be explained by bromine's smaller tendency to form double bonds which in general corresponds to a smaller degree of z-bonding.

As is expected the bond angles increase from OBrO to OCIO and from SeO₂ and SO₂. However, the angle increases from OCIO to SO₂, but it decreases from OBrO to SeO₂.

B. Electron spin-rotation coupling constants

As is shown in Table IV, the electron spin-rotation constants are large, and they are precisely determined. In Table XI the consistency of the constants is demonstrated by the fact that the $A_{ii}^e = \epsilon_{ii}/B_i$ are virtually identical for both O⁷⁹BrO and O⁸¹BrO.

The magnitude of the fine structure constants of radicals can be related to the fine structure intervals A of the atoms involved.^{39,40} The ratio between ⁷⁹Br and ³⁵Cl is 4.19.39 Because only about half of the spin-density is on the X atom for OXO (see next section) and because the fine structure interval for ¹⁶O is much smaller than those of ⁷⁹Br and ³⁵Cl, the ratios of the A_{ii}^e are smaller for $i = a$ and b , about 3.15, see Table XII. For the XO radicals **only** about one third of the spin-density is on the halogen,^{12,41} the ratio of the spin-orbit coupling constants is consequently even smaller, 3.02.

In general, the A rotational constant increases markedly upon excitation of the bending mode for a molecule with C_{2v} symmetry; even though the number of examples is rather limited it appears as if the absolute value of ϵ_{aa} usually increases as well.⁴⁰ The known examples include H₂O⁺ (²B₁),⁴² NH₂ (²B₁),⁴³ CH₂ (³B₁),⁴⁴ and NO₂ (²A₁).⁴⁵ However, the magnitude of ϵ_{aa} **decreases** upon excitation of V₂ for both OBrO and OCIO.²² In this context it is interesting to note that the bond angle in the first excited doublet state (²B₂) according to *ab initio* calculations is almost 30° smaller than in the ground

Since the electron spin-rotation constants are proportional to the rotational constants it is more appropriate to compare values of A_{ii}^e . These values are quite similar along the *a*- and *b*-axes for both OBrO and OC1O, for planar radicals with 2B_1 symmetry in the ground electronic state these components are expected to be the dominant ones.⁴⁰ Despite the differences in *n*-bonding between OBrO and OC1O, pointed out in the previous section, the ratios of A_{aa}^e and A_{bb}^e are very similar. Ideally, the *c*-component should be zero for the planar OBrO and OC1O radicals.⁴⁰ However, A_{cc}^e is small and negative for both molecules. This fact may be the result of higher order effects, such as spin-polarization or influences of multiple excitations.⁴⁰ Since these effects are dominant in determining the value of A_{cc}^e it should not be surprising that the relative values of the OBrO and OC1O constants do not follow the simple relationships exhibited by the *au*- and *bb*-components.

C. Spin-spin coupling constants

It is shown in Table V that the spin-spin coupling constants and most of their **quaric** distortion terms have been precisely determined. As is demonstrated in Table XI, the ${}^{79/81}\text{Br}$ isotopic ratios obtained for *al*, $T_{\alpha\sigma}$ and *T. are* in very good agreement with the ratio of the nuclear dipole constants of the Br atoms. The values from matrix ESR measurements are in good agreement with the present spin-spin coupling constants. The absolute values of a_f and T_{ii} from Ref. 6 are 3.0 to 7.2 % larger than those of the gas phase O^{79}BrO molecule.

The spin-spin coupling constants are commonly interpreted in terms of spin-density of the unpaired electron in the valence shell of a given nucleus by comparing them with the coupling constants of the atom. The isotropic coupling constant, or Fermi contact term, $a_f = 88.950$ (30) MHz for

well with the ratio of the nuclear quadruple constants of the Br atoms, as can be seen in Table XI. The diagonal elements of the quadruple tensor of matrix-isolated $O^{79}BrO$ from Ref. 6 deviate between less than 1 and -10 MHz from those of the free molecule.

In spite of the changes in π -bonding between $OBrO$ and $OCIO$, discussed above in the structure and force field section, the relative field gradients at the X nuclei, which are given in Table XIII, are very similar, particularly along the a-axis. Small differences occur along the c-axis; the relative changes are more pronounced along the *b*-axis because these components are rather small. Modified extended Hückel calculations yielded reasonable values for the quadruple coupling constants of $O^{79}BrO$: 360, -15, and -345 MHz for χ_{aa} , χ_{bb} , and χ_{cc} , respectively,⁵⁰ compared to experimental values of 356, 22, and -378 MHz. In Ref. 43 it was found that the calculated constants strongly depend on changes in the bond length, and they are affected to a lesser extent by changes in the bond angle; 162.5 pm and 117.6° were assumed for the $OBrO$ geometry.⁵⁰ Using our estimate of $r_e = 164.4$ pm and $\angle_e = 114.3^\circ$ and their calculated derivatives of the quadruple constants,⁵⁰ values of 351, 0, and -351 MHz are obtained, in better agreement with experiment.

E. Nuclear spin-rotation constants

The $^{79/81}Br$ isotopic ratios of $A_{ii}^n = C_{ii}/B_i$ agree well with the ratio of the magnetic dipole moments of the Br atoms, see Table XI.

Although the effects of the nuclear spin-rotation coupling are in general very small, the respective spectroscopic constants have been precisely determined for $OBrO$. Because the nuclear spin-rotation constants C_{ii} are proportional to the rotational constants B_i , one should compare, e. g., the

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$6_{6,1} - 5_{5,0}$				
7,7 -6,7	313939.875	60	21	
7,8 -6,7	313983.935	35	-26	
7,7 -6,6	313985.513	35	0	
7,6 -6,5	313990.516	35	2	
7,5 -6,4	314005.964	35	-7	
7,6 -6,6	314100.759	50	-15	
7,5 -6,5	314204.936	80	-7	
6,6 -5,6	316043.947	40	16	
6,5 -5,5	316231.612	40	-4	
6,5 -5,4	316325.339	40	3	
6,4 -5,3	316327.484	40	-1	
6,6 -5,5	316332.012	50	7	
6,7 -5,6	316337.083	50	-9	
6,4 -5,4	316347.164	70	4	

$O^{81}BrO$

$2_{2,1} - 1_{1,0}$				
3,3 -2,2	88860.912	35	9	
3,4 -2,3	88888.478	35	23	
2,2-1,2	90310.681	30	-27	
2,3-1,2	90550.750	30	-4	
$32_{2,31} - 31_{1,30}$				
32,33-31,32	424283.455	50	-2	
32,32-31,31	424286.881	50	11	
32,31-31,30	424289.731	50	21	
32,30-31,29	424291.737	50	-26	
33,31-32,30	424329.762	50	-9	
33,32-32,31	424334.074	50	3	
33,33-32,32	424337.151	50	5	
33,34-32,33	424340.981	50	-6	
$48_{2,47-47,46}$				
48,48-47,47	626252.640	150	-3	
48,47-47,46	626253.080	250	-64	

TABLE II: Number of rotational levels, fine, and hyperfine structure components, and range of N and K_a quantum numbers in the final fit of OBrO.

	ground state		$v_2 = 1$		$v_2 = 2$	
	O ⁷⁹ BrO	O ⁸¹ BrO	O ⁷⁹ BrO	O ⁸¹ BrO	O ⁷⁹ BrO	O ⁸¹ BrO
N_{rot}	82	92	41	40	15	17
N_{fs}	128	145	53	55	25	20
N_{hfs}	455	533	162	161	83	60
$N_{\text{min}} - N_{\text{max}}$	1 - 61	1 - 61	8 - 54	9 - 54	14 - 32	8 - 32
$K_{\text{min}} - K_{\text{max}}$	0 - 14	0 - 14	0 - 14	0 - 12	0 - 10	0 - 10

^a Numbers in parentheses are two standard deviations in units of the least significant figures. One entry for both 07%0 and O⁸¹BrO indicates common constants for both isotopomers.

^b See section IIIB.

TABLE V : Spin-spin, nuclear quadruple, and nuclear spin-rotation coupling constants' C of OBrO (MHz) in the (0,0,0) state and their changes A¹C in (0,1,0) state.^b

parameter C	O ⁷⁹ BrO	O ⁸¹ BrO	O ⁷⁹ BrO	O ⁸¹ BrO
	ground state		v ₂ = 1	
a_F	88.950 (30)	95.900 (32)	0.379 (121) ^c	0.408 (130) ^c
$a_F^J \cdot 103$	0.1262 (260) ^c	0.1360 (280) ^c		
$a_F^K \cdot 103$	-2.706 (276) ^c	-2.916 (298) ^c		
T_{aa}	-373.336 (47)	-402.452 (48)	-0.095 (78) ^c	-0.102 (84) ^c
$T_{aa}^J \cdot 103$	-0.211 (91) ^c	-0.227 (98) ^c		
$T_{aa}^K \cdot 10^3$	2.88 (42) ^c	3.11 (45) ^c		
T	-1189.804 (42)	-1282.545 (41)	0.942 (117) ^c	1.015 (126) ^c
$T^J \cdot 103$	0.979 (40) ^c	1.055 (43) ^c		
$T^K \cdot 103$	-46.38 (240) ^c	-49.99 (259) ^c		
Nuclear quadruple coupling constants				
χ_{aa}	356.221 (65)	297.587 (65)	0.354 (189) ^c	0.296 (158) ^c
x-	400.456 (95)	334.477 (92)	1.067 (260) ^c	0.892 (217) ^c
Nuclear Spin-Rotation Coupling Constants				
$C_{aa} \cdot 10^3$	160.12 (267)	167.52 (283)		
$C_{bb} \cdot 103$	41.58(172)	42.32 (192)		
$C_{cc} \cdot 10^3$	31.65(178)	31.89 (198)		

^cNumbers in parentheses are two standard deviations in units of the least significant figures. One entry for both O⁷⁹BrO and O⁸¹BrO indicates common constants for both isotopomers.

^bSee section IIIB. ^cIsotopic ratio fixed, see section IIIB.

TABLE VII: Structural parameters (pm, deg.) of OBrO and OCIO.

parameter	OBrO, exptl. ^a			<i>ab initio</i>		
	r_0	r_z	r_e^c	UMP2 ^c	CCSD(T) ^c	CCSD(T) ^d
r	164.91 (15)	164.968 (1)	164.4	164.0	165.0	166.0
α	114.44 (25)	114.429(1)	114.3	115.4	114.9	114.8

	OCIO, exptl.			<i>ab initio</i>	
r	147.49'	147.556'	146.984 ^f	148.5	
α	117.49'	117.485'	117.403 ^f	117.9	

^aThis work. ^bDerived from r_z , *see* text. ^c r_e parameters, AREP/TZ(2df) basis set, Ref. 21.

^d r_e parameters, TZ2P basis set, Ref. 11.

^eThis work, ground state rotational constants from Ref. 23. ^fRef. 22.

TABLE IX: Harmonic force constants (N m^{-1}) of OBrO and related molecules.

	OBrO ^a	OCIO ^b	SeO ₂ ^c	So* ^d
f_r	546.9	705.5	705.7	1064.3
f_α	102.6	138.2	135.7	169.7
f_{rr}	-5.0	-19.3	12.9	1.6
$f_{r\alpha}$	-6.1	1.8	13.8	25.2

^aThis work.

^bRef. 22.

^cRef. 36.

^dRef. 24.

TABLE XI: Isotopic ratios C^{79}/C^{81} of fine and hyperfine constants of OBrO.

C	observed	expected/theoretical ^a
A_{aa}^e ^b	0.999982 (10)	1.0
A_{bb}^e	1.000013(13)	1.0
A_{cc}^e	1.000057 (155)	1.0
a_{F_1}	0.927529 (440)	0.9276990 (2)
T_{aa}	0.927653 (161)	0.9276990 (2)
T_-	0.927690 (44)	0.9276990 (2)
χ_{aa}	1.19703 (34)	1.1970568(15)
χ_-	1.19726 (44)	1.1970568(15)
A_{aa}^n ^c	0.949 (24)	0.9276990 (2)
A_{bb}^n	0.983 (61)	0.9276990 (2)
A_{cc}^n	0.991 (84)	0.9276990 (2)

^a Neglecting vibrational effects.

^b $A_{ii}^e = \epsilon_{if}/B_f$.

^c $A_{ii}^n = C_{if}/B_f$.

TABLE XIII: Quadruple coupling constants (MHz) of $O^{79}BrO$ and $O^{35}ClO$ and relative field gradient at the X nucleus.

	$O^{79}BrO^a$	$O^{35}ClO^b$
χ_{aa}	356.221 (65)	-52,086 (102)
χ_{bb}	22.118 (53)	2.808 (66)
χ_{cc}	-378.339 (62)	49.278 (66)
f_a^c	0.4628	0.475
f_b^c	0.0287	-0.026
f_c^c	-0.4915	-0.449

^a This work. ^b Ref. 23. ^c $f_i = \chi_{ii}(OXO)/eQq_{n10}(X)$.

Figure Captions

Fig. 1. Detail of the rotational spectrum of a mixture of bromine oxides over a condensate at -7°C and *cu.* 1 Pa pressure. Some transitions are indicated: a) ^{81}BrO , $^2\Pi_{3/2}$, $33/2 - 31/2$; b) $^{79}\text{BrO}^{81}\text{Br}$, V_2 , $1, 26_6 - 25_5$; c) $^{81}\text{Br}_2\text{O}$, $93_{11} - 94_{10}$; d) $^{79}\text{BrO}^{81}\text{Br}$, $92_{11} - 93_{10}$; O^{81}BrO , $30_{10, 21} - 30_{10, 21}$, $J = 29.5$. Here BrO is about three orders of magnitude less abundant than Br_2O ; OBrO is inbetween.

FIG. 2. *The* $32_{1, 32} - 31_{0, 31}$ transition of O^{81}BrO in the ground vibrational state; the quantum numbers J, F of the lower state are indicated.

