The Rotational Spectra, Molecular Structure, Dipole Moment, and Hyperfine Constants of HOBr and DOBr

YOSHINORI KOGA, HARUTOSHI TAKEO, SHIGEO KONDO,
MASAAKI SUGIE, AND CHI MATSUMURA

National Chemical Laboratory for Industry, Tsukuba, Ibaraki, 305 Japan

AND

G. A. MCRAE[1] AND E. A. COHEN[2]

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

Pure rotational spectra of the ^{79}Br and ^{81}Br isotopic species of gaseous hypobromous acid, HOBr and DOBr, as well the $v_3 = 1$ excited state of HOBr have been observed and analyzed. Structural parameters have been derived from the ground state rotational constants. The permanent molecular dipole moment of DOBr and the bromine nuclear quadrupole coupling and spin rotation constants of all the species have been determined. © 1989 Academic Press, Inc.

INTRODUCTION

Although the hypohalous acids, HOX (X = halogen), have been well studied in aqueous solution and their infrared spectra have been studied using matrix isolation techniques (*1–3*), gas-phase spectra have been observed in the infrared and microwave regions only for HOCl (*4–17*) and HOF (*18–21*). No gas-phase rotational or vibrational spectra of either HOBr or HOI have so far been reported.

We have observed the vibration–rotation and pure rotation spectra of hypobromous acid. This paper reports the results of the analysis of the rotational spectra of HOBr and DOBr in selected regions between 8 and 787 GHz. Analyses of the infrared vibration–rotation spectra will appear in subsequent publications.

The experiments were performed by groups at the National Chemical Laboratory for Industry, NCLI, and the Jet Propulsion Laboratory, JPL, using somewhat different techniques for synthesis and several spectrometers. HOBr was initially synthesized and its infrared and microwave spectra assigned at NCLI. The JPL measurements have been used to confirm and supplement the initial observations at NCLI by providing millimeter and submillimeter data as well as some high-resolution infrared data. Near the conclusion of this work, a number of additional lines were measured at high sensitivity using the millimeter spectrometer at the Institute for Molecular Science, IMS.

The analysis of the pure rotational spectrum and its Stark effect has yielded rotational, centrifugal distortion, and bromine hyperfine constants for the four normal and deuterated species as well as the electric dipole moment for $DO^{79}Br$. A molecular structure has been derived from the ground state rotational constants and its relationship to the equilibrium structure is briefly discussed.

EXPERIMENTAL DETAILS

The initial microwave study at NCLI was done using a conventional Stark modulation spectrometer with a 1.5-m X-band stainless steel waveguide cell. Various computer-controlled sources were used to cover the 8–85 GHz region. Further microwave spectra, below 500 GHz, were observed with the modified commercial Stark modulated microwave spectrometer at JPL (22). Spectra above 600 GHz were obtained with the JPL far infrared (FIR) laser sideband spectrometer (23) using a 1.5-m glass cell. FIR frequencies were measured with respect to well predicted lines of HNO_3 (24). The IMS spectrometer has been described by Endo and Hirota (25) and was used with a 3-m glass cell.

HOBr was synthesized by reacting bromine with water in the presence of HgO using procedures similar to those used in the production of HOCl (11, 26). It was necessary to maintain a continuous slow flow of the gas through the sample cells at pressures of 10–100 mTorr. At NCLI this was done by flowing bromine and water vapors through a 400-mm-long by 15-mm-diameter pyrex glass tube packed loosely with yellow HgO. This reaction produced a sufficient concentration of HOBr for both the infrared and microwave spectra to be readily observed at room temperature. At JPL, the HOBr was produced by reacting an excess of liquid bromine with approximately 5 cm^3 of a slurry of yellow HgO in water. The sample was degassed, excess bromine was removed by pumping on the reaction tube at $-20°C$, and HOBr production was checked by monitoring a microwave transition which had been previously measured at NCLI. With the reaction tube at $-20°C$ a relatively constant flow of HOBr could be maintained for several hours. This same procedure was used at IMS with freshly ground red rather than yellow HgO. The longer absorption path and very clean cell used at IMS allowed very slow flow, low pressure (10-mTorr) conditions to be employed. Under these conditions, a single synthesis would provide enough HOBr for several days of measurements.

ANALYSIS OF THE SPECTRA

The ground state rotational constants were initially estimated from conventional combination differences in the infrared spectrum of the ν_1 band. After these constants were obtained, the spectrum was predicted and a careful search for a-type R-branch transitions was made. However, no absorptions assignable to these transitions were found. Later, the a dipole component was found to be very small. The search in the frequency region 26.5 to 50 GHz yielded several equal-intensity doublet transitions. From the predictions these were tentatively assigned to various high-J b-type transitions whose splittings were due to the bromine quadrupole coupling. Using these transitions to obtain an improved set of molecular constants, the millimeter- and submillimeter-wave spectra were predicted. In the absence of low-frequency a-type transitions, the

millimeter and submillimeter spectra of HOBr and DOBr are required to uniquely determine the ground state rotational constants. A small number of these predicted transitions with lower J were measured in order to remove correlations among the rotational and centrifugal distortion constants and to determine the hyperfine constants and dipole moment. The assignments of the high-J b-type transitions were later confirmed by a frequency fit that included many lower-J transitions for which the quadrupole splitting gave definite assignments. Finally a considerable number of weaker $\Delta F \neq \Delta J$ transitions for all species as well as higher-K_a transitions for DOBr were detected. The observed rotational transitions are listed in Tables I–IV for $HO^{79}Br$, $HO^{81}Br$, $DO^{79}Br$, and $DO^{81}Br$ respectively. Several low-J transitions of the $v_3 = 1$ excited state of HOBr have also been observed and are listed in Table V.

The data were fit with an S-reduction rotational Hamiltonian in a I^r prolate representation (27) including an exact treatment of the nuclear quadrupole and spin–rotation hyperfine splittings. However, d_2 is determinable only for DOBr. For HOBr the $K_a = 2 \leftarrow 1$ transitions appear in the millimeter region at such high J that it is not possible to decorrelate D_K from other higher-order constants without extensive additional measurements. Consequently, the value for D_K has been taken from a preliminary analysis of the high-resolution spectrum of the v_1 band. The choice of sextic terms is not necessarily unique, but has little influence on the determination of the lower-order parameters. Although the magnitude of H_{KJ} is expected to lie between those of H_{JK} and H_K, it was excluded from the deuterated species fits because it was slightly smaller than its uncertainty. The remaining sextic constants are highly correlated with H_{KJ} and may show significant change with the inclusion of data which would allow its determination. The constant h_3 is not determinable from the present data.

Several $\Delta F \neq \Delta J$ transitions have been observed and provide precise determination of the hyperfine constants for all species. In the final fit only lines measured with a single spectrometer were included for any given hyperfine pattern. Table VI lists all the determined parameters in the form in which they are used by the fitting program.

The excited state has been fitted by allowing only the rotational and quadrupole coupling constants to vary while the remaining parameters are fixed at their ground state values. The results are given in Table VII.

The coefficients of the P_a^{2n} operators show a remarkable similarity to those of HOCl. A comparison of all the constants through the quartics is given in Table VIII. It is noteworthy that α_3^4 is also almost the same in HOBr as it is in HOCl, 876 vs 895 MHz (13).

MOLECULAR STRUCTURE

Although it may seem that the presence of two bromine isotopes would allow r_0 structures to be separately determined for both the deuterated and normal species, the effect of the bromine substitution is too small for this to be done with any precision. Instead, Kraitchman's equations were used to determine the substitution coordinates of the H and Br atoms. The oxygen was not substituted. Its position was calculated from either first or second moment conditions. The results are quite consistent among the four possible sets of three molecules used to determine the structure. These are

TABLE I

Observed HO ^{79}Br Transitions[a]

$J K_a K_c F'_+$	$J K_a K_c F''_+$	Frequency	Unc	O-C	Wt	O-C
6 1 6 6	7 0 7 7	454294.169	30	-3		
6 1 6 7	7 0 7 8	454298.259	30	-25		
6 1 6 5	7 0 7 6	454308.422	30	8		
6 1 6 8	7 0 7 9	454312.268	30	-22		
7 1 7 9	8 0 8 9	432446.564	30	20		
7 1 7 7	8 0 8 8	432661.482	30	25		
7 1 7 8	8 0 8 9	432665.005	30	2		
7 1 7 6	8 0 8 7	432671.612	30	15		
7 1 7 9	8 0 8 10	432674.925	30	-15		
7 1 7 8	8 0 8 8	432706.245	30	9		
7 1 7 7	8 0 8 7	432890.871	30	16		
9 1 9 10	8 0 8 9	787242.548	100	-97		
9 1 9 11	8 0 8 10	787247.878	100	-207	556	-94
9 1 9 9	8 0 8 8	787247.878	100	48	444	-94
9 1 9 8	8 0 8 7	787253.410	100	192		
10 1 10 12	11 0 11 12	366974.481	30	-39		
10 1 10 11	11 0 11 11	367229.355	30	-38		
10 1 10 10	11 0 11 10	367426.065	30	-40		
10 1 10 10	11 0 11 11	367196.522	30	-15		
10 1 10 11	11 0 11 12	367198.790	30	-10		
10 1 10 9	11 0 11 10	367200.638	30	-11		
10 1 10 12	11 0 11 13	367202.725	30	-18		
11 1 11 11	12 0 12 12	345189.004	30	20		
11 1 11 12	12 0 12 13	345190.970	30	14		
11 1 11 10	12 0 12 11	345192.008	30	-49		
11 1 11 13	12 0 12 14	345193.967	30	104		
11 1 11 13	12 0 12 13	344965.698	30	1		
11 1 11 12	12 0 12 12	345219.267	30	85		
11 1 11 11	12 0 12 11	345418.610	30	-1		
13 1 12 14	13 0 13 14	611770.230	100	247	519	-65
13 1 12 13	13 0 13 13	611770.230	100	-402	481	-65
13 1 12 15	13 0 13 15	611776.368	100	344	558	66
13 1 12 12	13 0 13 12	611776.368	100	-285	442	66
15 1 15 15	16 0 16 16	256252.470	50	-30		
15 1 15 14	16 0 16 15	256253.212	50	-35		
15 1 15 16	16 0 16 17	256253.676	50	-38		
15 1 15 17	16 0 16 18	256254.281	50	-16		
21 1 21 20	22 0 22 21	120234.230	50	-45		
21 1 21 21	22 0 22 22	120234.814	50	-52	476	-5
21 1 21 23	22 0 22 24	120234.814	50	37	524	-5
21 1 21 22	22 0 22 23	120235.564	50	23		
23 1 23	24 0 24	74233.280	100	60		
24 1 24	25 0 25	51113.730	100	116		
25 1 25	26 0 26	27916.290	500	-262		
28 0 28 29	27 1 27 28	18703.738	20	-16		
28 0 28 28	27 1 27 27	18704.175	20	7		
28 0 28 30	27 1 27 29	18705.062	20	1		
28 0 28 27	27 1 27 26	18705.266	20	-24		
29 0 29 30	28 1 28 29	42124.997	20	2		
29 0 29 29	28 1 28 28	42125.397	20	19		
29 0 29 31	28 1 28 30	42126.368	20	11		
29 0 29 28	28 1 28 27	42126.552	20	-2		
29 1 28 30	29 0 29 30	645436.136	100	41	509	-18
29 1 28 29	29 0 29 29	645436.136	100	-79	491	-18
29 1 28 28	29 0 29 28	645439.309	100	-5	474	18
29 1 28 31	29 0 29 31	645439.309	100	39	526	18
30 0 30	29 1 29	65618.900	500	-43		
31 0 31	30 1 30	89182.460	500	-13		
38 0 38 39	37 1 37 38	255965.250	50	94	520	-1
38 0 38 38	37 1 37 37	255965.250	50	-104	480	-1
38 0 38 40	37 1 37 39	255966.795	50	-7	506	-5
38 0 38 37	37 1 37 36	255966.795	50	-2	494	-5

a. $F_+ = F + \frac{1}{2}$. Frequency given in MHz. Experimental uncertainty (Unc) and observed – calculated(O–C) given in kHz. Wt is the relative weight of a blended line. The second O–C heading refers to the positions of blended features. If no F_+ is given, the line is treated as a blend of all hyperfine components and the single O-C refers to the unsplit line.

TABLE II

Observed HO^{81}Br Transitions[a]

$JK_aK_cF'_+$				$JK_aK_cF''_+$				Frequency	Unc	O-C	Wt	O-C
6 1	6	6	7 0	7	7			454989.687	30	9		
6 1	6	7	7 0	7	8			454993.117	30	34		
6 1	6	5	7 0	7	6			455001.585	30	-9		
6 1	6	8	7 0	7	9			455004.747	30	-15		
7 1	7	7	8 0	8	8			433453.000	30	6		
7 1	7	8	8 0	8	9			433455.919	30	-11		
7 1	7	6	8 0	8	7			433461.473	30	-12		
7 1	7	9	8 0	8	10			433464.212	30	2		
7 1	7	8	8 0	8	8			433490.518	30	1		
7 1	7	7	8 0	8	7			433644.723	30	9		
9 1	9	10	8 0	8	9			786507.018	100	8		
9 1	9	11	8 0	8	10			786511.508	100	-53	556	43
9 1	9	9	8 0	8	8			786511.508	100	164	444	43
9 1	9	8	8 0	8	7			786515.782	100	-55		
10 1	10	10	11 0	11	11			368281.532	30	-5		
10 1	10	11	11 0	11	12			368283.396	30	-10		
10 1	10	9	11 0	11	10			368284.969	30	-23		
10 1	10	12	11 0	11	13			368286.661	30	-19		
10 1	10	12	11 0	11	12			368096.192	30	-13		
10 1	10	11	11 0	11	11			368309.117	30	-19		
10 1	10	10	11 0	11	10			368473.422	30	-18		
11 1	11	13	12 0	12	13			346187.099	30	18		
11 1	11	11	12 0	12	12			346373.452	30	-8		
11 1	11	12	12 0	12	13			346375.111	30	25		
11 1	11	10	12 0	12	11			346376.090	30	43		
11 1	11	13	12 0	12	14			346377.515	30	19		
11 1	11	12	12 0	12	12			346398.852	30	1		
11 1	11	11	12 0	12	11			346565.445	30	19		
13 1	12	14	13 0	13	14			611736.533	100	301	519	36
13 1	12	13	13 0	13	13			611736.533	100	-250	481	36
13 1	12	15	13 0	13	15			611741.476	100	205	558	-36
13 1	12	12	13 0	13	12			611741.476	100	-340	442	-36
15 1	15	15	16 0	16	16			257842.547	50	-13		
15 1	15	14	16 0	16	15			257843.187	50	-16		
15 1	15	16	16 0	16	17			257843.469	50	-87		
15 1	15	17	16 0	16	18			257844.025	50	-0		
21 1	21	20	22 0	22	21			122454.066	50	4		
21 1	21	23	22 0	22	24			122454.477	50	46	476	-10
21 1	21	21	22 0	22	22			122454.477	50	-62	524	-10
21 1	21	22	22 0	22	23			122455.143	50	57		
23 1	23		24 0	24				76668.000	100	87		
24 1	24		25 0	25				53656.870	100	167		
25 1	25	24	26 0	26	25			30568.030	20	2		
25 1	25	27	26 0	26	28			30568.231	20	-1		
25 1	25	25	26 0	26	26			30568.835	20	-4		
25 1	25	26	26 0	26	27			30569.222	20	-4		
28 0	28	29	27 1	27	28			15832.331	20	-3		
28 0	28	28	27 1	27	27			15832.667	20	4		
28 0	28	30	27 1	27	29			15833.507	20	66	527	-2
28 0	28	27	27 1	27	26			15833.507	20	-77	473	-2
29 0	29		28 1	28				39143.800	100	70		
30 0	30		29 1	29				62525.840	100	-29		
31 0	31		30 1	30				85978.020	100	73		
42 0	42	43	41 1	41	42			348113.051	30	56	506	2
42 0	42	42	41 1	41	41			348113.051	30	-53	494	2
42 0	42	44	41 1	41	43			348114.378	30	-50	518	-3
42 0	42	41	41 1	41	40			348114.378	30	47	482	-3

a. See footnote to Table I.

shown in Table IX. Extra significant figures are kept in the table to show the internal consistency among the individual calculations. The r_s type structure of HOBr is $r_{O-Br} = 1.834$ Å, $r_{O-H} = 0.961$ Å, and $\angle$H–O–Br = 102.3°. The number of significant figures here reflects where differences from the equilibrium structure are expected to be significant.

KOGA ET AL.

TABLE III

Observed DO ^{79}Br Transitions ^{a}

$JK_aK_cF'_+$	$JK_aK_cF''_+$	Frequency	Unc	O-C	Wt	O-C
1 1 1 2	0 0 0 2	340076.582	30	52		
1 1 1 3	0 0 0 2	340188.270	30	-28		
1 1 1 1	0 0 0 2	340277.178	30	-40		
1 1 0 2	1 0 1 2	320628.005	50	-12		
1 1 0 3	1 0 1 2	320744.922	50	42		
1 1 0 1	1 0 1 2	320837.837	50	-23		
1 1 0 2	1 0 1 3	320856.379	50	-40		
1 1 0 3	1 0 1 3	320973.266	50	-16		
1 1 0 2	1 0 1 1	321038.711	50	5		
1 1 0 1	1 0 1 1	321248.561	200	12		
2 1 1 4	2 0 2 3	321014.591	50	-16		
2 1 1 3	2 0 2 3	321126.700	50	10		
2 1 1 4	2 0 2 4	321242.761	50	-39		
3 1 3 5	4 0 4 5	241359.181	50	6		
3 1 3 3	4 0 4 4	241531.814	50	-7		
3 1 3 4	4 0 4 5	241533.034	50	29		
3 1 3 2	4 0 4 3	241587.025	50	261	302	-22
3 1 3 5	4 0 4 6	241587.025	50	-144	699	-22
3 1 3 4	4 0 4 4	241612.812	50	23		
3 1 3 3	4 0 4 3	241760.461	50	53		
6 1 6 5	5 0 5 5	434705.089	30	48		
6 1 6 6	5 0 5 6	434855.496	30	-13		
6 1 6 7	5 0 5 6	434906.286	30	-7		
6 1 6 6	5 0 5 5	434919.953	30	156	414	-1
6 1 6 8	5 0 5 7	434919.953	30	-111	587	-1
6 1 6 5	5 0 5 4	434933.629	30	4		
6 1 6 7	5 0 5 7	435134.189	30	-30		
7 1 6 8	7 0 7 8	325030.958	50	10		
7 1 6 7	7 0 7 7	325033.922	70	11		
7 1 6 9	7 0 7 9	325045.644	500	-73		Blended
7 1 6 6	7 0 7 6	325048.742	70	-5		
11 1 11	12 0 12	76027.490	350	-465		
12 1 12	13 0 13	54697.090	350	-258		
13 1 13	14 0 14	33232.250	100	9		
14 1 14	15 0 15	11635.370	100	31		
15 1 14 14	15 0 15 15	339188.438	30	-3		
15 1 14 17	15 0 15 16	339189.638	30	-27		
15 1 14 15	15 0 15 16	339389.160	30	-44		
15 1 14 16	15 0 15 16	339411.618	30	11		
15 1 14 15	15 0 15 15	339412.162	30	43		
15 1 14 17	15 0 15 17	339417.137	30	12		
15 1 14 14	15 0 15 14	339417.625	30	15		
15 1 14 16	15 0 15 15	339434.519	30	-4		
15 1 14 16	15 0 15 17	339639.109	30	42		
15 1 14 15	15 0 15 14	339641.310	30	22		
16 0 16	15 1 15	10090.470	100	-11		
17 0 17	16 1 16	31942.180	100	2		
17 1 16 18	17 0 17 18	344675.164	50	198	514	4
17 1 16 17	17 0 17 17	344675.164	50	-201	486	4
17 1 16 19	17 0 17 19	344680.066	50	164	543	-1
17 1 16 16	17 0 17 16	344680.066	50	-198	457	-1

a. See footnote to Table I.

Although not a true r_s structure, the O–H bond length and H–O–Br bond angle are very close to those of the HOCl substitution structure (16). For HOCl the most significant change between the substitution and equilibrium structures was in the length of the O–Cl bond. Because of the similarity of the molecular parameters of HOBr and HOCl, the equilibrium O–Br length may be 0.005–0.006 Å shorter than the value given above. More detailed discussion of the equilibrium structure will be given in forthcoming publications on the infrared spectra.

TABLE III—*Continued*

$JK_aK_cF'_+$	$JK_aK_cF''_+$	Frequency	Unc	O-C	Wt	O-C
18 0 18	17 1 17	53916.660	100	118		
18 1 17 19	18 0 18 19	347569.579	30	161	514	-12
18 1 17 18	18 0 18 18	347569.579	30	-195	486	-12
18 1 17 20	18 0 18 20	347574.252	30	117	541	-29
18 1 17 17	18 0 18 17	347574.252	30	-200	459	-29
19 0 19	18 1 18	76009.890	350	-309		
20 1 19 21	20 0 20 21	353897.605	30	136	512	-7
20 1 19 20	20 0 20 20	353897.605	30	-156	488	-7
20 1 19 22	20 0 20 22	353901.979	30	126	537	13
20 1 19 19	20 0 20 19	353901.979	30	-118	463	13
26 1 25 26	26 0 26 26	377415.725	30	-103	491	-11
26 1 25 27	26 0 26 27	377415.725	30	77	510	-11
26 1 25 25	26 0 26 25	377419.556	30	-62	472	-4
26 1 25 28	26 0 26 28	377419.556	30	48	528	-4
26 2 25	27 1 26	376222.689	50	49		
27 2 26	28 1 27	352507.962	50	-43		
30 2 28 30	31 1 31 31	439602.614	30	18	492	-25
30 2 28 31	31 1 31 32	439602.614	30	-67	508	-25
30 2 28 29	31 1 31 30	439608.038	30	42	476	10
30 2 28 32	31 1 31 33	439608.038	30	-19	524	10
31 0 31 32	30 1 30 31	348997.604	30	175	508	9
31 0 31 31	30 1 30 30	348997.604	30	-162	492	9
31 0 31 33	30 1 30 32	348998.949	30	67	524	-10
31 0 31 30	30 1 30 29	348998.949	30	-94	476	-10
35 1 34 36	35 0 35 36	426795.688	50	55	508	5
35 1 34 35	35 0 35 35	426795.688	50	-45	493	5
35 1 34 37	35 0 35 37	426799.310	50	5	521	7
35 1 34 34	35 0 35 34	426799.310	50	10	479	7
35 2 33 35	36 1 36 36	374894.556	30	43	493	14
35 2 33 36	36 1 36 37	374894.556	30	-14	507	14
35 2 33 37	36 1 36 38	374899.525	30	-37	521	-9
35 2 33 34	36 1 36 35	374899.525	30	22	479	-9
36 2 34 36	37 1 37 37	362807.592	30	40	493	13
36 2 34 37	37 1 37 38	362807.592	30	-13	507	13
36 2 34 35	37 1 37 36	362812.528	30	36	480	5
36 2 34 38	37 1 37 39	362812.528	30	-23	520	5
37 2 35 37	38 1 38 38	351021.225	30	28	493	2
37 2 35 38	38 1 38 39	351021.225	30	-22	507	2
37 2 35 36	38 1 38 37	351026.140	30	46	480	14
37 2 35 39	38 1 38 40	351026.140	30	-16	520	14
38 2 36 38	39 1 39 39	339542.264	50	-7	494	-31
38 2 36 39	39 1 39 40	339542.264	50	-54	507	-31
38 2 36 37	39 1 39 38	339547.120	50	-12	481	-45
38 2 36 40	39 1 39 41	339547.120	50	-76	519	-45
56 1 55 57	55 2 54 56	360812.874	30	29	499	14
56 1 55 56	55 2 54 55	360812.874	30	-2	501	14
56 1 55 55	55 2 54 54	360814.487	30	95	487	-14
56 1 55 58	55 2 54 57	360814.487	30	-117	514	-14
58 3 56	59 2 57	373497.961	30	1		
59 3 57	60 2 58	349436.411	30	-1		

Dipole Moment Measurement

The dipole moment was determined for DO^{79}Br from the Stark effects of two transitions: the $J = 2_{11}-2_{02}$, $F = \frac{7}{2}-\frac{7}{2}$ and the $J = 1_{10}-1_{01}$, $F = \frac{5}{2}-\frac{5}{2}$. The Stark shifts were calculated from the differences in the standard second-order Stark energy expressions for the two levels involved in the transitions. The direction cosine matrix elements were calculated in the basis that diagonalized the complete Hamiltonian.

The dipole moment was first determined by a least-squares fit of the shifts of all the M_F components for both transitions at a fixed field of 15.05 kV/cm to the squares of both μ_a and μ_b. This resulted in a very small negative value for μ_a^2. Consequently

KOGA ET AL.

TABLE IV

Observed DO^{81}Br Transitions[a]

J	K_a	K_c	F'_+	J	K_a	K_c	F''_+	Frequency	Unc	O-C	Wt	O-C
1	1	1	2	0	0	0	2	340044.026	30	-4		
1	1	1	3	0	0	0	2	340137.359	30	-45		
1	1	1	1	0	0	0	2	340211.583	30	-65		
1	1	0	2	1	0	1	2	320711.813	50	10		
1	1	0	3	1	0	1	2	320809.437	50	-7		
1	1	0	1	1	0	1	2	320887.114	50	33		
1	1	0	2	1	0	1	3	320902.540	50	27		
1	1	0	3	1	0	1	3	321000.126	50	-28		
1	1	0	1	1	0	1	1	321230.231	100	59		
2	1	1	4	2	0	2	3	321082.149	50	-61		
2	1	1	3	2	0	2	3	321175.665	50	-23		
2	1	1	2	2	0	2	2	321244.724	50	14		
3	1	3	5	4	0	4	5	241792.829	50	68		
3	1	3	3	4	0	4	4	241936.922	50	6		
3	1	3	4	4	0	4	5	241937.898	50	33		
3	1	3	2	4	0	4	3	241983.077	50	308	302	56
3	1	3	5	4	0	4	6	241983.077	50	-52	698	56
3	1	3	4	4	0	4	4	242004.704	50	75		
6	1	6	5	5	0	5	5	434280.042	30	21		
6	1	6	6	5	0	5	6	434405.672	30	15		
6	1	6	7	5	0	5	6	434448.210	30	24		
6	1	6	6	5	0	5	5	434459.608	30	134	414	2
6	1	6	8	5	0	5	7	434459.608	30	-91	586	2
6	1	6	5	5	0	5	4	434471.007	30	10		
6	1	6	7	5	0	5	7	434638.459	30	-29		
7	1	6	8	7	0	7	8	325033.226	70	-2		
7	1	6	7	7	0	7	7	325035.709	50	5		
7	1	6	9	7	0	7	9	325045.644	500	67	Blended	
7	1	6	6	7	0	7	6	325048.097	70	6		
11	1	11		12	0	12		77211.490	200	-167		
12	1	12		13	0	13		55984.300	100	-44		
13	1	13		14	0	14		34623.620	100	28		
14	1	14		15	0	15		13131.820	200	-242		
15	1	14	14	15	0	15	15	339094.117	30	-28		
15	1	14	17	15	0	15	16	339095.514	30	-52		
15	1	14	15	15	0	15	16	339261.831	30	15		
15	1	14	16	15	0	15	16	339280.769	30	29		
15	1	14	15	15	0	15	15	339281.173	30	13		
15	1	14	17	15	0	15	17	339285.398	30	36		
15	1	14	14	15	0	15	14	339285.735	30	-6		
15	1	14	16	15	0	15	15	339300.072	30	-13		
15	1	14	16	15	0	15	17	339470.516	30	-21		
15	1	14	15	15	0	15	14	339472.784	30	28		
16	0	16		15	1	15		8487.440	100	20		
16	1	15	17	16	0	16	17	341801.873	30	17		
16	1	15	16	16	0	16	16	341802.231	30	8		
16	1	15	18	16	0	16	18	341806.399	50	187	546	41
16	1	15	15	16	0	16	15	341806.399	50	-134	454	41
17	0	17		16	1	16		30231.850	100	-13		
18	0	18		17	1	17		52098.110	100	-2		

a. See footnote to Table I.

μ_a was fixed to zero and only μ_b was fitted. The uncertainty was determined by fixing μ_a to different values until an unacceptable reproduction of the spectrum was obtained. The data and the results of the calculation are given in Table X. The a dipole component connects several levels which are very close in energy. This gives rise to very large second order Stark coefficients for μ_a. Thus, the absence of any observable contribution from μ_a allows a very low limit to be put on its magnitude. The dipole moment lies along the b axis and has a magnitude of 1.384(10) D. The magnitude along the a axis

TABLE IV—*Continued*

$JK_aK_cF'_+$	$JK_aK_cF''_+$	Frequency	Unc	O-C	Wt	O-C
19 0 19	18 1 18	74082.890	100	39		
20 1 19 21	20 0 20 21	353629.621	30	107	512	-6
20 1 19 20	20 0 20 20	353629.621	30	-126	488	-6
20 1 19 22	20 0 20 22	353633.255	30	64	486	-23
20 1 19 19	20 0 20 19	353633.255	30	-105	514	-23
26 1 25 26	26 0 26 26	376918.386	30	-66	490	3
26 1 25 27	26 0 26 27	376918.386	30	69	510	3
26 1 25 25	26 0 26 25	376921.568	30	-37	472	-13
26 1 25 28	26 0 26 28	376921.568	30	8	528	-13
26 2 25	27 1 26	379225.081	30	-23		
27 2 26	28 1 27	355634.735	30	19		
31 0 31 32	30 1 30 31	345724.932	30	129	508	2
31 0 31 31	30 1 30 30	345724.932	30	-128	492	2
31 0 31 33	30 1 30 32	345726.076	30	27	524	-2
31 0 31 30	30 1 30 29	345726.076	30	-33	476	-2
35 2 33 35	36 1 36 36	376994.495	30	35	493	4
35 2 33 36	36 1 36 37	376994.495	30	-26	507	4
35 2 33 34	36 1 36 35	376998.658	30	42	479	-4
35 2 33 37	36 1 36 38	376998.658	30	-46	521	-4
36 2 34 36	37 1 37 37	364913.497	30	40	493	10
36 2 34 37	37 1 37 38	364913.497	30	-19	507	10
36 2 34 35	37 1 37 36	364917.616	30	47	480	-1
36 2 34 38	37 1 37 39	364917.616	30	-45	520	-1
37 2 35 37	38 1 38 38	353129.277	30	41	493	13
37 2 35 38	38 1 38 39	353129.277	30	-16	507	13
37 2 35 36	38 1 38 37	353133.355	30	44	480	-6
37 2 35 39	38 1 38 40	353133.355	30	-53	520	-6
38 2 36 38	39 1 39 39	341648.537	50	18	494	-10
38 2 36 39	39 1 39 40	341648.537	50	-38	506	-10
38 2 36 37	39 1 39 38	341652.590	50	26	481	-26
38 2 36 40	39 1 39 41	341652.590	50	-75	519	-26
39 1 38 40	39 0 39 40	453518.498	30	16	506	-3
39 1 38 39	39 0 39 39	453518.498	30	-22	494	-3
39 1 38 38	39 0 39 38	453521.541	30	65	481	5
39 1 38 41	39 0 39 41	453521.541	30	-51	519	5
56 1 55 56	55 2 54 55	353864.058	30	-4	496	-10
56 1 55 57	55 2 54 56	353864.058	30	-16	504	-10
56 1 55 55	55 2 54 54	353865.460	30	164	487	14
56 1 55 58	55 2 54 57	353865.460	30	-128	513	14
57 1 56 57	56 2 55 56	380665.973	30	17	486	8
57 1 56 58	56 2 55 57	380665.973	30	0	514	8
57 1 56 56	56 2 55 55	380667.338	30	137	487	-16
57 1 56 59	56 2 55 58	380667.338	30	-161	513	-16
58 3 56	59 2 57	380116.077	30	2		
59 1 58 59	58 2 57 58	434494.079	30	-21	496	-33
59 1 58 60	58 2 57 59	434494.079	30	-46	504	-33
59 1 58 58	58 2 57 57	434495.555	30	194	488	36
59 1 58 61	58 2 57 60	434495.555	30	-116	512	36
59 3 57	60 2 58	356212.399	30	-2		

is less than 0.010 D. Because of the slight rotation of axes between HOBr and DOBr, μ_a in HOBr may be as large as 0.05 D.

Effective bond moments for the O–D and O–Br bonds may be calculated using the dipole moment derived above and the structure determined in the previous section. These are 1.41 D and 0.39 D, respectively, with the Br and D atoms both being positive. A similar calculation may be done for HOCl using the dipole moment from Ref. (*14*), the substitution structure from Ref. (*16*), and the change in μ_a on deuteration from Ref. (*6*). It is the change of μ_a on deuteration which determines the relative direction of μ_a and μ_b. The HOCl calculation then gives 1.52 D for the O–H bond

TABLE V

Observed HOBr $v_3 = 1$ Transitions[a]

$J\,K_a\,K_c\,F'_+$	$J\,K_a\,K_c\,F''_+$	HO^{79}Br Frequency	O-C	HO^{81}Br Frequency	O-C
6 1 6 5	7 0 7 6	454734.433	58		
6 1 6 6	7 0 7 7	454720.221	7		
6 1 6 7	7 0 7 8	454724.300	-12		
6 1 6 8	7 0 7 9	454738.217	-20		
7 1 7 6	8 0 8 7	433273.362	-156	434054.381	0
7 1 7 7	8 0 8 8	433263.458	17	434045.889	-5
7 1 7 8	8 0 8 9	433266.993	19	434048.826	3
7 1 7 9	8 0 8 10	433276.912	64	434057.101	2
10 1 10 9	11 0 11 10	368333.810	35	369405.684	0
10 1 10 10	11 0 11 11	368329.700	1	369402.225	0
10 1 10 11	11 0 11 12	368331.953	-1	369404.100	11
10 1 10 12	11 0 11 13	368335.880	19	369407.356	-12
11 1 11 10	12 0 12 11	346503.357	8	347673.727	7
11 1 11 11	12 0 12 12	346500.288	-19	347671.127	0
11 1 11 12	12 0 12 13	346502.248	-24	347672.739	-11
11 1 11 13	12 0 12 14	346505.148	-1	347675.166	1

a. See footnote to Table I. Unc = 30 kHz for all lines.

moment and a very small value of 0.02 D for that of O–Cl. The difference between the O–Br and O–Cl bond moments is similar to, but somewhat smaller than the 0.53 D difference observed in both of the pairs BrF, ClF (28, 29) and BrO, ClO (30, 31).

TABLE VI

Ground State Parameters for HOBr and DOBr

Parameter/MHz	HO^{79}Br	HO^{81}Br	DO^{79}Br	DO^{81}Br
A	613677.34(100)[a]	613673.62(100)[a]	330577.9434(206)	330573.4045(140)
B	10576.60290(145)	10530.42754(144)	9937.14648(116)	9891.72822(97)
C	10383.05728(181)	10338.55141(172)	9630.63100(97)	9587.96056(97)
D_J	0.0128520(54)	0.0127530(56)	0.01064491(260)	0.01054950(147)
D_{JK}	0.74938(35)	0.74517(34)	0.434603(184)	0.431130(102)
D_K	135.30(100)[b]	135.30(100)[b]	41.8592(296)	41.8588(149)
$d_1 \times 10^3$	-0.21402(42)	-0.21053(40)	-0.312987(189)	-0.309146(98)
$d_2 \times 10^4$			-0.27969(111)	-0.27263(66)
$H_J \times 10^8$			-0.782(194)	-0.613(54)
$H_{JK} \times 10^5$	0.3091(293)	0.31(fixed)	0.0459(231)	0.0713(56)
H_K			0.0480(55)	0.04393(128)
$h_1 \times 10^9$			0.164(64)	0.172(58)
$h_2 \times 10^9$			0.077(95)	0.157(42)
$\frac{3}{2}\chi_{aa}$	1373.495(86)	1147.330(92)	1369.328(64)	1143.794(66)
$\frac{1}{4}(\chi_{bb} - \chi_{cc})$	4.4631(193)	3.7260(197)	5.0891(160)	4.2591(159)
$C_{aa} - \frac{1}{2}(C_{bb} + C_{cc})$	-0.008(61)	-0.094(65)	-0.0402(155)	-0.0290(156)
$\frac{1}{2}(C_{bb} + C_{cc})$	0.05827(117)	0.06194(121)	0.05514(81)	0.05808(81)
$\frac{1}{4}(C_{bb} - C_{cc})$	0.001261(270)	0.00104(38)	0.00125(57)	0.00157(56)
R.M.S $\times 10^3$	59	38	76	49

a. The uncertainty reflects that of D_k. The uncertainty in $A - D_k$ is 0.03 MHz.
b. From the infrared spectrum.

TABLE VII

$v_3 = 1$ Parameters for HOBr

Parameter/MHz	$v_3 = 1$	Δ_{1-0}	$v_3 = 1$	Δ_{1-0}
	HO^{79}Br		HO^{81}Br	
A	612801.52(106)	-875.82(106)	612797.12(121)	-876.49(121)
B	10490.041(27)	-86.562(27)	10444.341(48)	-86.086(48)
C	10297.641(42)	-85.417(42)	10253.557(75)	-84.994(75)
$\frac{3}{2}\chi_{aa}$	1367.3(32)	-6.2(32)	1145.5(50)	-1.8(50)
$\frac{1}{4}(\chi_{bb} - \chi_{cc})$	4.478(53)	0.015(53)	3.701(64)	-0.025(64)
R.M.S $\times 10^3$	47		6	

HYPERFINE CONSTANTS

The measurement of a significant number of $\Delta F \neq \Delta J$ transitions for all isotopic species has allowed the determination of a very precise set of nuclear spin rotation and quadrupole coupling constants for all four species. The internal consistency of the hyperfine parameters is, in fact, better than the quoted uncertainties seem to indicate. This is due to the fact that errors arising from lineshape and baseline effects tend to be the same for a single hyperfine pattern. This cancellation of errors in the determination of the hyperfine constants is not accounted for in the global fit, which treats all assigned uncertainties as uncorrelated. The parameters used in the fitting have been previously listed in Table VI and the individual diagonal components of the quadrupole coupling and nuclear spin rotation tensors are given in Table XI.

The quadrupole coupling is very similar to that observed in HOCl with the ^{79}Br/^{35}Cl χ_{cc} ratio of -7.475 being close to the -7.014 ratio of the atomic quadrupole couplings (32). Almost the same ratios are observed for the related molecules BrF, ClF (28, 29) and BrO, ClO (33, 34), these being -7.455 and -7.402, respectively.

There are apparent H–D isotope shifts in the values of χ_{cc} of 136 and 112 kHz for the ^{79}Br and ^{81}Br isotopes. The ratio of these shifts, 1.21, is consistent with the observed ^{79}Br/^{81}Br χ_{cc} ratio of 1.19713 in these compounds.

TABLE VIII

HOBr and HOCl Parameter Comparison

Parameter/MHz	HO^{79}Br	HO^{35}Cl^a	DO^{79}Br	DO^{35}Cl^b
A	613677.34(100)	613483.882(56)	330577.9434(206)	331338.764(114)
B	10576.60290(145)	15116.7899(10)	9937.14648(116)	14298.5405(78)
C	10383.05728(181)	14725.7769(12)	9630.63100(97)	13675.3910(79)
D_J	0.0128520(54)	0.0268885(32)	0.01064491(260)	0.0222427(330)
D_{JK}	0.74938(35)	1.25142(24)	0.434603(184)	0.77494(153)
D_K	135.30(100)	130.1899(256)	41.8592(296)	39.6826(863)
$d_1 \times 10^3$	-0.21402(42)	-0.63516(77)	-0.312987(189)	-0.91411(330)
$d_2 \times 10^4$	$\cdots$	-0.5612(115)	-0.27969(111)	-1.0288(366)

a. From Reference 14
b. From Reference 16

TABLE IX

HOBr Structure Determination

Species used for structure	O-Br/Å	O-H/Å	∠H-O-Br/°
O position from a and b moments of reference species			
1-16-79, 1-16-81, 2-16-79	1.83415	0.9613	102.33
1-16-81, 1-16-79, 2-16-81	1.83414	0.9613	102.33
2-16-79, 2-16-81, 1-16-79	1.83417	0.9609	102.35
2-16-81, 2-16-79, 1-16-81	1.83417	0.9609	102.35
O position from center of mass conditions of reference species			
1-16-79, 1-16-81, 2-16-79	1.8328	0.9616	102.41
1-16-81, 1-16-79, 2-16-81	1.8328	0.9616	102.41
2-16-79, 2-16-81, 1-16-79	1.8329	0.9622	102.37
2-16-81, 2-16-79, 1-16-81	1.8329	0.9622	102.37

Extra digits are carried in the parameters to demonstrate the internal consistency. Equilibrium bond lengths may differ by several mÅ and the angle by several tenths of a degree. See text.

The angle between the O–Br bond and the principal axis of the quadrupole tensor may be determined by considering the observed changes in the coupling constants upon deuteration. In the inertial principal axis system of HOBr, the quadrupole tensor has a small off-diagonal term, χ_{ab}. Except for the small, axis-independent isotope shift discussed above, the quadrupole tensors in the HOBr and DOBr principal axis systems are related by

$$T^{-1} \begin{pmatrix} \chi_{aa} & \chi_{ab} & 0 \\ \chi_{ab} & \chi_{bb} & 0 \\ 0 & 0 & \chi_{cc} \end{pmatrix}_H T = \begin{pmatrix} \chi_{aa} & \chi_{ab} & 0 \\ \chi_{ab} & \chi_{bb} & 0 \\ 0 & 0 & \chi_{cc} \end{pmatrix}_{Dc}$$

where T is the unitary transformation for the axis rotation caused by isotopic substitution. The H and D subscripts refer to $HO^{79}Br$ or $DO^{79}Br$ values. In order for the relationship above to satisfy the requirement that the quadrupole tensor be traceless,

TABLE X

DOBr Dipole Moment

J_{KaKc}	F	M_F	Stark Shift/MHz at $E^2 = 15.05(kV/cm)^2$	Observed Shift[a]	Calc. Shift
$1_{10}-1_{01}$	2.5-2.5	2.5-2.5	$3088. \mu_a^2 + 6.973 \mu_b^2$	13.32(16)	13.34
		1.5-1.5	$1641. \mu_a^2 + 4.719 \mu_b^2$	9.08(16)	9.03
$2_{11}-2_{02}$	3.5-3.5	3.5-3.5	$459.8 \mu_a^2 + 8.138 \mu_b^2$	15.49(8)	15.59
		2.5-2.5	$264.7 \mu_a^2 + 5.532 \mu_b^2$	10.67(16)	10.60
		1.5-1.5	$134.6 \mu_a^2 + 3.795 \mu_b^2$	7.35(16)	7.27

$$\{\mu_a, \mu_b\} = \{0.000(10), 1.384(10)\} \text{ D}$$

a. Numbers in parentheses are estimated errors in units of the least significant figures.

TABLE XI

Hyperfine Constants

	HO^{79}Br	HO^{81}Br	DO^{79}Br	DO^{81}Br
χ_{aa}/MHz	915.663(57)	764.887(61)	912.885(43)	762.529(44)
χ_{bb}/MHz	−448.905(48)	−374.991(50)	−446.264(39)	−372.746(39)
χ_{cc}/MHz	−466.758(48)	−389.895(61)	−466.622(39)	−389.783(39)
C_{aa}/kHz	50.(60)	−32.(65)	15.(16)	29.(16)
C_{bb}/kHz	60.8(14)	64.0(13)	57.6(14)	61.2(14)
C_{cc}/kHz	55.8(14)	59.9(13)	52.6(14)	54.9(14)
$\Lambda_{aa} \times 10^{-6}$	0.039(48)	−0.023(47)	0.022(23)	0.039(22)
$\Lambda_{bb} \times 10^{-6}$	2.73(6)	2.68(5)	2.75(7)	2.73(6)
$\Lambda_{cc} \times 10^{-6}$	2.55(6)	2.55(6)	2.60(7)	2.52(6)

the values of $(\chi_{gg})_{Dc}$ of the right hand side of the equation are those given in Table XI for DO^{79}Br multiplied by the ratio $(\chi_{cc})_H/(\chi_{cc})_D$. Thus,

$$(\chi_{ab})_H = \frac{(\chi_{aa} - \chi_{bb})_{Dc} - (\chi_{aa} - \chi_{bb})_H \cos(2\theta)}{2 \sin(2\theta)}.$$

Using the rotation angle of 1.744° determined from the structure in Table IX, it is found that $|\chi_{ab}|$ in the HO^{79}Br principal axis system is 20.4(24) MHz. Here the uncertainty includes the uncertainty in the measurement of the diagonal quadrupole components as well as an estimate of 0.05° for the uncertainty in the angle. To transform to the principal axes of the quadrupole tensor one must rotate the inertial axes by 0.86(15)° toward the O–Br bond. From the structural calculation, the angle between the a principal axis and the O–Br bond is 2.01(2)°. Thus, the quadrupole a principal axis makes an angle of 1.15(17)° with the O–Br bond.

Although the assumption that χ_{aa} and χ_{bb} individually scale as χ_{cc} may not be entirely valid, large isotope shifts are required of χ_{aa} and χ_{bb} to reconcile the observed couplings with a principal quadrupole axis along the O–Br bond. If it is assumed that the α quadrupole principal axis is along the O–Br bond and the β axis is perpendicular to it in the molecular plane, then $\chi_{\alpha\alpha}$ = 917.34 and 918.76 MHz and $\chi_{\beta\beta}$ = −450.58 and −452.14 MHz for HO^{79}Br and DO^{79}Br, respectively. The change in $\chi_{\alpha\alpha}$ on deuteration would be nearly as large as that observed in HBr (35, 36) and of opposite sign. Moreover, the changes in both $\chi_{\alpha\alpha}$ and $\chi_{\beta\beta}$ are an order of magnitude greater than that observed for χ_{cc}. These seem too large to be attributable to a single H–D substitution at a site one atom removed from the coupling nucleus.

The change in quadrupole coupling constant with excitation of the O–Br stretching mode is quite small compared with its uncertainty, but it is consistent with the changes observed in the excited vibrational state of BrF (28).

The nuclear spin rotation coupling is at first surprising in that the element containing the largest rotational constant is too small to be reliably determined. If one uses the constants

$$\Lambda_{xx} = C_{xx}/B_x g_I,$$

where B_x is the appropriate rotational constant and g_I is the nuclear g factor, then a very consistent result is obtained for Λ_{bb} and Λ_{cc} for all four species. These values are shown in Table XI and may be compared with a value of 3.4×10^{-6} for BrF (28). The values of Λ_{aa} show considerable scatter with respect to their small magnitudes, but the results are consistent among all the isotopic species in setting an upper limit of approximately 100 times smaller than the other two diagonal components. This should provide useful information on the symmetry and location of the excited electronic states and will provide a useful check on calculations of excited state wave functions.

CONCLUSION

The ground state rotational parameters of HOBr and DOBr have been determined with high precision. These, as well as the structural parameters determined from them, show great similarities to those of HOCl. Several transitions of the $v_3 = 1$ state have been fitted to a set of rotational and quadrupole coupling constants for the two normal species. Finally, the nuclear quadrupole and spin rotation couplings have been well determined.

REFERENCES

1. J. A. GOLEB, H. H. CLAASSEN, M. H. STUDIER, AND E. H. APPELMAN, *Spectrochim. Acta Part A* **28**, 65–67 (1972).
2. I. SCHWAGER AND A. ARKELL, *J. Amer. Chem. Soc.* **89**, 6006–6008 (1967).
3. N. WALKER, D. E. TEVAULT, AND R. R. SMARDZEWSKI, *J. Chem. Phys.* **69**, 564–568 (1978).
4. K. HEDBURG AND R. M. BADGER, *J. Chem. Phys.* **19**, 508–509 (1951).
5. R. A. ASHBY, *J. Mol. Spectrosc.* **23**, 439–447 (1967).
6. D. C. LINDSEY, D. G. LISTER, AND D. J. MILLEN, *Chem. Commun.* 950–951 (1969).
7. D. G. LISTER AND D. J. MILLEN, *Trans. Faraday Soc.* **67**, 601–604 (1971).
8. M. SUZUKI AND A. GUARNIERI, *Z. Naturforsch. A* **30**, 497–505 (1975).
9. A. M. MIRRI, F. SCAPPINI, AND G. CAZZOLI, *J. Mol. Spectrosc.* **38**, 218–227 (1971).
10. R. A. ASHBY, *J. Mol. Spectrosc.* **40**, 639–640 (1971).
11. J. S. WELLS, R. L. SAMS, AND W. J. LAFFERTY, *J. Mol. Spectrosc.* **77**, 349–364 (1979).
12. R. L. SAMS AND W. B. OLSON, *J. Mol. Spectrosc.* **84**, 113–123 (1980).
13. W. J. LAFFERTY AND W. B. OLSON, *J. Mol. Spectrosc.* **120**, 359–373 (1986).
14. H. E. GILLIS SINGBEIL, W. D. ANDERSON, R. W. DAVIS, M. C. L. GERRY, E. A. COHEN, H. M. PICKETT, F. J. LOVAS, AND R. D. SUENRAM, *J. Mol. Spectrosc.* **103**, 466–485 (1984).
15. C. M. DEELY AND I. M. MILLS, *J. Mol. Spectrosc.* **114**, 368–376 (1985).
16. W. D. ANDERSON, M. C. L. GERRY, AND R. W. DAVIS, *J. Mol. Spectrosc.* **115**, 117–130 (1986).
17. C. M. DEELY, *J. Mol. Spectrosc.* **122**, 481–489 (1987).
18. H. KIM, E. F. PEARSON, AND E. H. APPLEMAN, *J. Chem. Phys.* **56**, 1–3 (1972).
19. E. F. PEARSON AND H. KIM, *J. Chem. Phys.* **57**, 4230–4233 (1972).

20. S. L. ROCK, E. F. PEARSON, E. H. APPLEMAN, C. L. NORRIS, and W. H. FLYGARE, *J. Chem. Phys.* **59,** 3940–3945 (1972).
21. H. BÜRGER, G. PAWELKE, A. RAHNER, E. H. APPLEMAN, AND I. M. MILLS, *J. Mol. Spectrosc.* **128,** 278–287 (1988).
22. E. A. COHEN AND H. M. PICKETT, *J. Mol. Spectrosc.* **93,** 83–100 (1982).
23. J. FARHOOMAND, G. A. BLAKE, M. A. FRERKING, and H. M. PICKETT, *J. Appl. Phys.* **57,** 1763–1766 (1985).
24. H. M. PICKETT AND R. L. POYNTER, *Appl. Opt.* **24,** 2235–2240 (1985).
25. Y. ENDO AND E. HIROTA, *J. Chem. Phys.* **86,** 4319–4326 (1987).
26. M. NAKATA, M. SUGIE, H. TAKEO, C. MATSUMURA, T. FUKUYAMA, AND K. KUCHITSU, *J. Mol. Spectrosc.* **86,** 241–249 (1981).
27. J. K. G. WATSON, *J. Mol. Spectrosc.* **65,** 123–133 (1977).
28. K. P. R. NAIR, J. HOEFT, AND E. TIEMANN, *J. Mol. Spectrosc.* **78,** 506–513 (1979).
29. R. E. DAVIS AND J. S. MUENTER, *J. Chem. Phys.* **57,** 2836–2838 (1972).
30. T. AMANO, A. YOSHINAGA, AND E. HIROTA, *J. Mol. Spectrosc.* **44,** 594–598 (1972).
31. T. AMANO, S. SAITO, E. HIROTA, Y. MORINO, D. R. JOHNSON, AND F. X. POWELL, *J. Mol. Spectrosc.* **27,** 275–289 (1972).
32. W. GORDY AND R. L. COOK, *in* "Techniques of Chemistry" (A. Weissberger, Ed.), Vol. 18, p. 737, New York, 1984.
33. E. A. COHEN, H. M. PICKETT, AND M. GELLER, *J. Mol. Spectrosc.* **106,** 430–435 (1984).
34. E. A. COHEN, H. M. PICKETT, AND M. GELLER, *J. Mol. Spectrosc.* **87,** 459–470 (1981).
35. O. B. DABBOUSI, W. L. MEERTS, F. H. DE LEEUW, AND A. DYMANUS, *Chem. Phys.* **2,** 473–477 (1973).
36. F. A. VANDIJK AND A. DYMANUS, *Chem. Phys.* **6,** 474–478 (1974).