Microwave spectrum and molecular structure of the carbon monoxide-hydrogen bromide molecular complex

(rotational spectrum/nozzle expansion/Fourier transform spectroscopy)

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Contributed by W. H. Flygare, June 17, 1980

ABSTRACT Rotational spectra have been assigned for five isotopic species of the OC $\cdots$ HBr hydrogen-bonded molecular complex by using pulsed microwave Fourier transform spectroscopy in a Fabry-Perot cavity and a pulsed supersonic nozzle as the molecular source. The rotational constants, centrifugal distortion constants, Br nuclear-quadrupole-coupling constants, and Br spin-rotation constants were determined and from them, the vibrationally averaged structure of OCHBr was derived. This structure is consistent with a linear geometry at equilibrium and an atomic arrangement as written above. The intermolecular potential binding CO to HBr is discussed.

A method for the measurement of the molecular properties of transient and other weakly bound molecular species has been developed by applying Fourier transform techniques in the microwave frequency range (1-4). The method combines the principles of the pulsed Fourier transform microwave technique, a Fabry-Perot cavity, and synchronization of the microwave pulse with a pulsed supersonic-nozzle beam of a gaseous mixture used to generate, in this case, weak van der Waals molecular complexes (5, 6).

In this paper, we report rotational assignments for five isotopic species of the weakly bound OCHBr molecular complex (7). The rotational spectrum of OCHBr was measured at 11-18 GHz. From the measured transition frequencies, the rotational constants, centrifugal distortion constants, Br nuclear-quadrupole-coupling constants, and Br spin-rotation constants were obtained and, by using these constants, the vibrationally averaged structure of OCHBr was derived. OCHBr is nearly linear. We also used the structure and spectroscopic constants of OCHBr to obtain information on the potential that binds CO to HBr. Finally, we compared OCHBr with the ArHBr (8) and KrHBr (8) van der Waals molecules and noted the similarities and differences.

EXPERIMENTAL

Apparatus. A microwave oscillator at frequency ν is phase stabilized to a harmonic of a lower frequency oscillator, which is monitored by using a frequency counter. The primary oscillator is then used to phase stabilize the local oscillator at a frequency of $\nu - 30$ MHz; this second oscillator is used in the subsequent superheterodyne detection of the signal. The primary microwave source at ν is then formed into a pulse by a switch, after which the pulse is impedance matched to a Fabry-Perot cavity. Maximum polarization of the gas is achieved after a $\pi/2$ pulse, $T_2 \gg t_p$, where T_2 is the polarization relaxation time, which is related to the low-power steady-state transition half-width at half-height by $\Delta\nu = 1/(2\pi T_2)$, and t_p is the microwave pulse length. After polarization

of a band of molecular frequencies centered at ν , the microwave pulse is switched off, and the pulse dissipates over a relaxation time of τ_c , the cavity relaxation time. We now require that the molecules maintain their coherent polarization for a period of time long relative to τ_c ; i.e., $T_2 \gg \tau_c$. The $T_2 \gg \tau_c$ requirement allows the original microwave pulse to die away before the coherent polarization is lost. After the microwave pulse has died away, the coherent emission from all polarized transitions is observed in the superheterodyne receiver as a beat between the field of the local oscillator and that of the coherent emission.

The molecular sample is a pulsed supersonic-nozzle beam. For noncondensable substances such as rare gas atoms, adiabatic expansion can cool the velocity distribution to 1-10 K. The pulsed gas adiabatically expands in and traverses through the Fabry-Perot cavity; its cold gas transit time through the region where the microwave field passes at right angles is ≈ 0.1 -1 ms. The microwave pulses are switched on shortly after the opening of the nozzle pulse, and the repeating transient emissions are digitized and averaged. Finally, the time-domain signal is Fourier transformed to give the spectrum. A complete description of the theory and the experimental details has been given (8, 9).

Measurements. The microwave spectrum of OCHBr was recorded by using the Fabry-Perot Fourier transform spectrometer (5, 6, 8). The OCHBr dimers were formed by pulsing a mixture of 4% CO and 4% HBr in Ar through a 0.5-mm supersonic nozzle into the cavity. The mixture was held at room temperature and 0.5-2.5 atm (1 atm = 1.013×10^5 Pa). Although the spectra could be observed by using mixtures of 4% HBr in CO, the signal-to-noise ratio steadily decreased as the CO concentration was increased from its optimum value (4%). We account for this phenomenon by noting that, because CO possesses rotational and vibrational degrees of freedom, it will be less efficient than Ar in cooling the expanding gas. It is also possible that higher order polymers of the type (CO) $_n$ HBr are forming at high CO concentrations. Another observation was that the strong spectrum of ArHBr (8), found by using a mixture of 4% HBr in Ar, completely disappeared when 4% CO was added, which indicates that the gas expansion products are not statistically distributed and that HBr shows a strong preference for binding to CO rather than to Ar.

Inside the Fabry-Perot cavity, the OCHBr molecules were polarized by a synchronous, near-resonant microwave pulse. After the microwave pulse dissipated, the coherent resonant emission from the dimers was detected by a superheterodyne receiver. These time-domain signals were digitized at 0.5-1 μ s per point and averaged. The final time-domain record was then Fourier transformed to give a 256-point frequency spectrum having a resolution of 3.9-1.9 kHz per point. The spectral lines exhibited the characteristic Doppler splitting (8, 10) and had half-widths at half-height of about 5 kHz. The measured transition frequencies for OCHBr are given in Table 1.

Table 1. Transition frequencies of OCHBr of different isotopic compositions

$J, F \rightarrow J', F'$			Frequency, MHz		Difference, kHz
			Observed	Calculated	
$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$					
4, 7/2	5, 7/2	11,405.9009	11,405.9004	0.5	
4, 9/2	5, 9/2	11,473.4238	11,473.4220	1.8	
4, 9/2	5, 11/2	11,501.6503	11,501.6509	-0.6	
4, 11/2	5, 13/2	11,501.6840	11,501.6836	0.4	
4, 7/2	5, 9/2	11,508.5002	11,508.4999	0.3	
4, 5/2	5, 7/2	11,508.6059	11,508.6072	-1.3	
5, 11/2	6, 11/2	13,778.5931	13,778.5946	-1.5	
5, 11/2	6, 13/2	13,802.2582	13,802.2588	-0.6	
5, 13/2	6, 15/2	13,802.2809	13,802.2797	1.2	
5, 9/2	6, 11/2	13,806.8251	13,806.8235	1.6	
5, 7/2	6, 9/2	13,806.8739	13,806.8771	-3.2	
5, 13/2	6, 13/2	13,904.7597	13,904.7589	0.8	
6, 13/2	7, 15/2	16,102.2774	16,102.2763	1.1	
6, 15/2	7, 17/2	16,102.2901	16,102.2906	-0.5	
6, 11/2	7, 13/2	16,105.5495	16,105.5491	0.4	
6, 9/2	7, 11/2	16,105.5791	16,105.5794	-0.3	
$^{16}\text{O}^{12}\text{CH}^{81}\text{Br}$					
4, 9/2	5, 9/2	11,405.5891	11,405.5868	2.3	
4, 9/2	5, 11/2	11,429.2595	11,429.2608	-1.3	
4, 11/2	5, 13/2	11,429.2858	11,429.2844	1.4	
4, 7/2	5, 9/2	11,435.0061	11,435.0057	0.4	
4, 5/2	5, 7/2	11,435.0782	11,435.0807	-2.5	
5, 11/2	6, 11/2	13,695.3905	13,695.3918	-1.3	
5, 11/2	6, 13/2	13,715.2369	13,715.2376	-0.7	
5, 13/2	6, 15/2	13,715.2539	13,715.2529	1.0	
5, 9/2	6, 11/2	13,719.0654	13,719.0658	-0.4	
5, 7/2	6, 9/2	13,719.1034	13,719.1030	0.4	
5, 13/2	6, 13/2	13,800.8563	13,800.8558	0.5	
6, 13/2	7, 15/2	16,000.6677	16,000.6669	0.8	
6, 15/2	6, 17/2				
6, 11/2	7, 13/2	16,003.4053	16,003.4060	-0.7	
6, 9/2	7, 11/2	16,003.4270	16,003.4268	0.2	
$^{16}\text{O}^{12}\text{C}^2\text{H}^{79}\text{Br}$					
5, 11/2	6, 13/2	13,841.2478	13,841.2480	-0.2	
5, 13/2	6, 15/2	13,841.2740	13,841.2729	1.1	
5, 9/2	6, 11/2	13,846.1110	13,846.1089	2.1	
5, 7/2	6, 9/2	13,846.1655	13,846.1685	-3.0	
6, 13/2	7, 15/2	16,147.8739	16,147.8736	0.3	
6, 15/2	7, 17/2	16,147.8895	16,147.8911	-1.6	
6, 11/2	7, 13/2	16,151.3577	16,151.3585	-0.8	
6, 9/2	7, 11/2	16,151.3937	16,151.3916	2.1	
$^{16}\text{O}^{13}\text{CH}^{79}\text{Br}$					
4, 9/2	5, 11/2	11,308.4323	11,308.4317	0.6	
4, 11/2	5, 13/2	11,308.4648	11,308.4652	-0.4	
4, 7/2	5, 9/2	11,315.2896	11,315.2894	0.2	
5, 11/2	6, 13/2	13,570.4216	13,570.4209	0.7	
5, 13/2	6, 15/2	13,570.4414	13,570.4424	-1.0	
5, 9/2	6, 11/2	13,574.9928	13,574.9915	1.3	
5, 7/2	6, 9/2	13,575.0442	13,575.0460	-1.8	
6, 13/2	7, 15/2	15,831.8325	15,831.8323	0.2	
6, 15/2	7, 17/2	15,831.8469	15,831.8471	-0.2	
6, 11/2	7, 13/2	15,835.1094	15,835.1093	0.1	
6, 9/2	7, 11/2	15,835.1401	15,835.1400	0.1	
$^{18}\text{O}^{12}\text{CH}^{79}\text{Br}$					
5, 11/2	6, 13/2	12,949.3497	12,949.3507	-1.0	
5, 13/2	6, 15/2	12,949.3780	12,949.3734	4.6	
5, 9/2	6, 11/2	12,953.9186	12,953.9153	3.3	
5, 7/2	6, 9/2	12,953.9712	12,953.9722	-1.0	
6, 13/2	7, 15/2	15,107.3457	15,107.3474	-1.7	
6, 15/2	7, 17/2	15,107.3581	15,107.3631	-5.0	
6, 11/2	7, 13/2	15,110.6152	15,110.6202	-5.0	
6, 9/2	7, 11/2	15,110.6544	15,110.6522	2.2	
7, 15/2	8, 17/2	17,264.8366	17,264.8338	2.8	
7, 17/2	8, 19/2	17,264.8464	17,264.8453	1.1	

Table 2. Spectroscopic constants of OCHBr

Isotopic composition	$\bar{B}_0$, MHz	D_J , kHz	χ_a , MHz	c , kHz
$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$	1150.51218 (14)	2.7034 (18)	409.7145 (42)	1.19 (15)
$^{16}\text{O}^{12}\text{CH}^{81}\text{Br}$	1143.23704 (14)	2.6709 (18)	342.2854 (56)	1.39 (16)
$^{16}\text{O}^{12}\text{C}^2\text{H}^{79}\text{Br}$	1153.75614 (45)	2.5145 (50)	437.12 (35)	2.60 (157)
$^{16}\text{O}^{13}\text{CH}^{79}\text{Br}$	1131.18609 (12)	2.6138 (14)	410.453 (89)	1.42 (51)
$^{18}\text{O}^{12}\text{CH}^{79}\text{Br}^*$	1079.41084 (48)	2.3460 (47)	410.44 (57)	—

* The gas mixture used to generate $^{18}\text{O}^{12}\text{CH}^{79}\text{Br}$ dimers was much less than optimum due to the small amount of $^{12}\text{C}^{18}\text{O}$ available, which resulted in weaker and broader lines. Consequently, the spin-rotation constant could not be obtained.

SPECTROSCOPIC CONSTANTS

Because of the extreme cooling caused by the supersonic-nozzle expansion, only rotational transitions in the ground vibrational and $K = 0$ rotational states were observed (Table 1). The data were fit by a nonlinear least-squares procedure involving diagonalization of the Hamiltonian matrix. A good fit to the measured transition frequencies was obtained by using the $K = 0$ symmetric top Hamiltonian, including Br nuclear-quadrupole coupling and the Br spin-rotation interaction, given by

$$\mathcal{H} = B_0 J^2 - D_J J^4 - \frac{1}{6} Q: \nabla E + c I: J, \quad [1]$$

where $\bar{B}_0 = 1/2(B_0 + C_0)$ is the rotational constant, D_J is the centrifugal distortion constant, c is the Br spin-rotation constant, and $I = 3/2$ is the Br nuclear spin. χ_a , the Br nuclear-quadrupole-coupling constant, is simply related to the matrix elements of the quadrupole Hamiltonian (11),

$$-\frac{1}{6} Q: \nabla E,$$

and is the parameter determined from the fit. The matrix elements of $\mathcal{H}$ were evaluated in the coupled basis given by $(J + F = E)$. Although both ArHBr and KrHBr show an effect due to centrifugal distortion, D_χ , of the Br nuclear-quadrupole-coupling constant, OCHBr did not. As has been shown for ArHBr (8), this centrifugal-distortion effect is proportional to θ^5 , where θ is the angle between HBr and the heavy-atom axis. Because the size of this angle in OCHBr is about half that in ArHBr, D_χ is estimated to be much less than 1 kHz and therefore lower than our limits of detection.

Table 3. Molecular properties of CO and HBr

	$\bar{B}_0$, MHz	r_0 , Å	χ_0 , MHz	c_0 , kHz
H^{79}Br	250,358.510*	1.42426†	532.30590‡	290.796‡
H^{81}Br	250,280.582*	1.42426†	444.68066‡	313.370‡
$^2\text{H}^{79}\text{Br}$	127,357.639*	1.42144†	530.6315§	145.82§
$^{12}\text{C}^{16}\text{O}$	57,635.971¶	1.13090	—	—
$^{13}\text{C}^{16}\text{O}$	55,099.748**	1.13084	—	—
$^{12}\text{C}^{18}\text{O}$	54,890.138**	1.13084	—	—

* See ref. 12.

† Calculated by using the data in ref. 12.

‡ See ref. 13.

§ See ref. 14.

¶ See ref. 15.

|| See ref. 16.

** Calculated by using the data in ref. 16.

FIG. 1. Coordinate system used in analysis of OCHBr.

The derived spectroscopic constants for OCHBr are given in Table 2. It is interesting to note that the rotational constant of $\text{OC}^2\text{H}^{79}\text{Br}$ is actually larger than that of OCH^{79}Br . This is the result of two competing effects: The increase in mass will tend to decrease the rotational constant, but this tendency is evidently more than compensated for by a decrease in the effective length of the hydrogen bond. This decrease in bond length is opposite to the effect of ^2H substitution in the rare gas-HBr analogues (8).

MOLECULAR STRUCTURE

We begin our treatment of the structure of OCHBr by making the simplifying assumption that complex formation does not affect the structural and electronic properties of free CO and free HBr. Thus, the O—C and H—Br lengths are given by their vibrationally averaged bond lengths, and the Br nuclear-quadrupole-coupling constant, χ_a , is related to the free HBr coupling constant, χ_0 , by

$$\chi_a = \frac{1}{2} \langle 3\cos^2\gamma - 1 \rangle \chi_0 \quad [2]$$

where γ is the angle between HBr and the a inertial axis of the complex. The molecular properties of free CO and HBr are given in Table 3. By using Eq. 2 and the data in Tables 2 and 3, we find γ to be $\approx 23^\circ$ (or 157°), which indicates that the structure is almost linear. Because we have isotopically modified OCHBr at all atomic positions, we can determine the gross molecular structure by considering a linear model and computing the substitution structure. If we use $^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$ as the parent molecule, we find $|Z_{\text{O}}| = 3.835 \text{ \AA}$, $|Z_{\text{C}}| = 2.748 \text{ \AA}$, and

Table 4. Results used in determination of the angle between r_{CO} and R_{cm}

ϕ	R_{CBr}			Avg. deviation $\times 10^4$
	$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$	$^{16}\text{O}^{13}\text{CH}^{79}\text{Br}$	$^{18}\text{O}^{12}\text{CH}^{79}\text{Br}$	
0	3.9172	3.9180	3.9160	7.1
2	3.9178	3.9185	3.9165	7.3
4	3.9193	3.9200	3.9181	6.9
6	3.9217	3.9224	3.9207	6.0
8	3.9252	3.9257	3.9243	5.1
10	3.9296	3.9299	3.9290	5.1
12	3.9349	3.9351	3.9346	1.8
14	3.9412	3.9411	3.9412	0.4
16	3.9484	3.9481	3.9489	2.9
18	3.9565	3.9559	3.9573	4.9
20	3.9655	3.9645	3.9668	8.0
22	3.9753	3.9741	3.9772	11.1
24	3.9861	3.9844	3.9885	14.4
26	3.9976	3.9956	4.0000	17.8
28	4.0100	4.0075	4.0137	22.0
30	4.0232	4.0202	4.0275	25.8
32	4.0371	4.0336	4.0422	30.4
34	4.0517	4.0477	4.0576	35.1
36	4.0671	4.0626	4.0737	39.3
38	4.0831	4.0780	4.0906	44.7
40	4.0998	4.0941	4.1082	50.0

$$^* \text{Avg. deviation} = \frac{1}{3} \sum_j \left| \frac{1}{3} \sum_i (R_{\text{CBr}})_i - (R_{\text{CBr}})_j \right|$$

Table 5. Structural parameters of OCHBr

Isotopic composition	$\theta, ^\circ$	$R_{\text{cm}}, \text{\AA}$	$R_{\text{CBr}}, \text{\AA}$
$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$	23.16	4.5469	3.9172
$^{16}\text{O}^{12}\text{CH}^{81}\text{Br}$	23.16	4.5472	3.9172
$^{16}\text{O}^{12}\text{C}^2\text{H}^{79}\text{Br}$	20.21	4.5231	3.8935
$^{16}\text{O}^{13}\text{CH}^{79}\text{Br}$	23.09	4.5252	3.9180
$^{18}\text{O}^{12}\text{CH}^{79}\text{Br}$	23.09	4.5779	3.9160

$|Z_{\text{Br}}| = 1.194 \text{ \AA}$ for the distance from the molecular center of mass to the atom in question. We choose the acute value of γ because the obtuse value requires the H atom to be a large distance from the center of mass, which is inconsistent with an increase in $\bar{B}_0$ on substitution of ^2H . The r_s bond length for CO, $1.087 \text{ \AA}$, is significantly shorter than the bond length of free CO, $1.131 \text{ \AA}$. This discrepancy arises, in part, from the fact that the vibrationally averaged structure of OCHBr is not totally linear, as was assumed above.

Further information on the structure of OCHBr is obtained by considering the coordinate system shown in Fig. 1. The coordinates describing the structure of OCHBr are R_{cm} , the distance between the centers of mass of the CO and HBr subunits, ϕ and θ , the angles this line makes with CO and HBr, respectively, and ζ , the angle between the plane containing O, C, and H and that containing C, H, and Br. Noting that the three heavy atoms lie in a plane and that the rotational constant is insensitive to the location of the H, we will assume that $\zeta = 0$ —i.e., that the molecule is planar. The measured rotational constant, $\bar{B}_0$, can be expressed in terms of a pseudodiatom rotational constant, B_D , calculated by assuming that the masses of the CO and the HBr are entirely located at their centers of mass and corrections for the sizes and orientation of the diatomic species. Expanding the rotational constant in the coordinates shown in Fig. 1, we find

$$\begin{aligned} \bar{B}_0 = B_0 \left\{ 1 - B_D \left[\frac{1}{2b_{\text{CO}}} (1 + \cos^2\phi) + \frac{1}{2b_{\text{HBr}}} (1 + \cos^2\theta) \right] \right. \\ \left. + B_D^2 \left[\frac{1}{2b_{\text{CO}}^2} (\cos^4\phi - \cos^2\phi \sin^2\phi + 1) \right. \right. \\ \left. \left. + \frac{1}{2b_{\text{HBr}}^2} (\cos^4\theta - \cos^2\theta \sin^2\theta + 1) + \frac{1}{b_{\text{CO}}b_{\text{HBr}}} \right. \right. \\ \left. \left. \times (\cos^2\phi \cos^2\theta + \cos\phi \sin\phi \cos\theta \sin\theta + 1) + \dots \right\} \quad [3] \end{aligned}$$

where b_{CO} and b_{HBr} are the rotational constants of free CO and free HBr, respectively. Hence, if ϕ , θ , and $\bar{B}_0$ are known, Eq. 3 can be solved for B_D and R_{cm} can be obtained by using

$$R_{\text{cm}} = \left(\frac{h}{8\pi^2 \mu_s B_D} \right)^{1/2} \quad [4]$$

where the reduced mass, μ_s , is given by

$$\mu_s = \frac{m_{\text{COM}} m_{\text{HBr}}}{m_{\text{CO}} + m_{\text{HBr}}} \quad [5]$$

θ can be determined by an analysis of the Br nuclear-quadrupole-coupling constant. The angle γ obtained by using Eq. 2

FIG. 2. Vibrationally averaged structure of $^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$.

Table 6. Measured and calculated Br spin-rotation constants of OCHBr

Isotopic composition	c, kHz	
	Measured	Calculated
$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$	1.19 (15)	1.23
$^{16}\text{O}^{12}\text{CH}^{81}\text{Br}$	1.39 (16)	1.32
$^{16}\text{O}^{12}\text{C}^2\text{H}^{79}\text{Br}$	2.60 (157)	1.24
$^{16}\text{O}^{13}\text{CH}^{79}\text{Br}$	1.42 (51)	1.21

is related to θ and the angle needed to diagonalize the moment of inertia tensor, α , by $\theta = \gamma - \alpha$. By using the coordinates shown in Fig. 1, we find

$$\alpha \approx B_D \left(\frac{1}{b_{\text{CO}}} \cos\phi \sin\theta - \frac{1}{b_{\text{HBr}}} \cos\theta \sin\theta \right) \times \left[1 + \frac{B_D}{b_{\text{CO}}} (1 - 2\cos^2\phi) + \frac{B_D}{b_{\text{HBr}}} (1 - 2\cos\theta) \right]. \quad [6]$$

Thus, α depends on B_D and θ , whereas we only know $\bar{B}_0$ and γ ; therefore, for all structure calculations, we made two iterations to obtain a consistent set of structural parameters. For the isotopes examined, CO lacks a quadrupolar nucleus. It is therefore difficult to assign a value for the angle, ϕ , that CO makes with the line connecting the centers of mass of CO and HBr. As a first approximation, we assume that isotopic substitution does not change the molecular structure. We then calculate R_{cm} as a function of ϕ for the various isotopes of OCHBr. As we know θ , ϕ , and R_{cm} , the distance from C to Br follows from geometry. The angle, ϕ , is then found such that R_{CBr} is not changed by isotopic substitution. The results of this calculation are shown in Table 4. If negative values of ϕ are used, the results of the calculation are the same because the rotational constant depends on the squares of the coordinates. The angle ($\sim 14^\circ$) determined in this manner should be considered an upper limit. As the mass of the isotope increases, the amplitude of the stretching vibration along the hydrogen bond, and thus the vibrationally averaged bond length, should decrease. It is evident that, if we constrain R_{CBr} to be too large, we are forced to compensate by using a larger value of ϕ . In summary, the angle that CO makes with R_{cm} is uncertain but very small. In our final structure calculation (Table 5), ϕ was assumed to be 0° . Fig. 2 shows our best estimate of the vibrationally average structure of $^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$.

The structures and rotational constants of OCHBr can be used to predict the magnitude of the Br spin-rotation constant in OCHBr. Assuming, once again, that complex formation does not affect the electronic distribution of HBr and noting that a diagonal component of the spin-rotation tensor is inversely proportional to the moment of inertia about that axis, we transform the free HBr spin-rotation tensor to the principal inertial axes of the complex to obtain

$$c = \frac{c_0 \bar{B}_0}{2b_{\text{HBr}}} (1 + \cos^2\gamma), \quad [7]$$

Table 7. Stretching force constants, frequencies, and Lennard-Jones parameters of OCHBr

Isotopic composition	μ_s , amu	k_s , mdyn $\text{\AA}^{-1}$	ν_s , cm^{-1}	r_e , $\text{\AA}$	ϵ , $(\text{cm}^{-1})^*$
$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$	20.73298	0.0330	51.9	4.5153	469
$^{16}\text{O}^{12}\text{CH}^{81}\text{Br}$	20.86500	0.0329	51.7	4.5154	469
$^{16}\text{O}^{12}\text{C}^2\text{H}^{79}\text{Br}$	20.80007	0.0363	54.4	4.5108	516
$^{16}\text{O}^{13}\text{CH}^{79}\text{Br}$	21.27824	0.0333	51.5	4.5168	474
$^{18}\text{O}^{12}\text{CH}^{79}\text{Br}$	21.81224	0.0329	50.6	4.5150	469

* For a fixed atomic arrangement, R_{cm} is changed by isotopic substitution; hence, these values are normalized to those of $^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$.

Table 8. Bending force constants and frequencies of OCHBr

Isotopic composition	μ_b , amu $\text{\AA}^2$	ν_b , cm^{-1}	k_b , mdyn $\text{\AA}$
$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$	3.11839	248	0.0113
$^{16}\text{O}^{12}\text{CH}^{81}\text{Br}$	3.11863	248	0.0113
$^{16}\text{O}^{12}\text{C}^2\text{H}^{79}\text{Br}$	3.92578	254	0.0150
$^{16}\text{O}^{13}\text{CH}^{79}\text{Br}$	3.22024	241	0.0110
$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$	3.16890	245	0.0112

where c_0 is the Br spin-rotation constant for free HBr. The predicted and measured values of c are given in Table 6. In all cases, they agree within experimental uncertainty.

INTERNAL DYNAMICS AND EQUILIBRIUM STRUCTURE

As shown above, the vibrationally averaged structure of OCHBr is almost linear. It is likely, as in the case of HCNHF (17), where l -type doubling was observed, that the equilibrium geometry of OCHBr is also linear. In this case, complex formation introduces five additional normal modes of vibration—two doubly degenerate bending modes and a symmetric stretching mode along the hydrogen bond.

By using the pseudodiatom model, we can relate the stretching frequency, ν_s , to the centrifugal distortion constant by $D_J = (4B_D^3/\nu_s^2)$, where $B_D = (h/8\pi^2\mu_s R_{cm}^2)$ and $\nu_s = (1/2\pi)(\sqrt{k_s/\mu_s})^{1/2}$, where k_s is the stretching force constant. By making the further assumption that the radial interaction can be described by the Lennard-Jones potential

$$V(R) = \epsilon \left[\left(\frac{R_e}{R} \right)^{12} - 2 \left(\frac{R_e}{R} \right)^6 \right], \quad [8]$$

where R_e is the equilibrium separation of the CO and HBr centers of mass and ϵ is the well depth, we can estimate the radial potential that binds CO to HBr. Expanding this potential in a Taylor series about $R = R_e$ gives

$$V(R) = -\epsilon + \frac{36\epsilon}{R_e^2} (R - R_e)^2 - \frac{252\epsilon}{R_e^3} (R - R_e)^3 + \dots \quad [9]$$

The harmonic force constant is related to the quadratic term of the potential by

$$\frac{1}{2} k_s = \frac{36\epsilon}{R_e^2} \quad [10]$$

where

$$R_e = \left(\frac{h}{8\pi^2\mu_s B_e} \right)^{1/2} \quad [11]$$

and the equilibrium rotational constant, B_e , is given by $B_D = B_e - 1/2\alpha_e$. If we assume that $\nu_e \approx \nu_s$, the vibration-rotation interaction constant, α_e , is related to the cubic term in the potential and is given by (8) $\alpha_e = (36B_e^2/\nu_s)$ or

$$B_D = B_e - \frac{18B_e^2}{\nu_s} \quad [12]$$

Hence, we can use D_J to determine ν_s and k_s , and then use Eqs. 10–12 to derive the radial well depth, ϵ , and the equilibrium separation, R_e . The radial potential parameters for OCHBr are given in Table 7.

For a linear-equilibrium geometry, the measured angle, θ , between HBr and R_{cm} results from an averaging over the two doubly degenerate bending modes that involve the hydrogen bond. In the case of HCNHF (17), where the harmonic force field was determined from an analysis of the vibrational satellites in its rotational spectrum, it was found that the amplitude

of the off-axis hydrogen motion was determined predominantly by the high-frequency bending mode involving the C—N—H angle. By analogy, we assume that the measured θ is a result of averaging solely over the corresponding mode in OCHBr. For a two-dimensional isotropic harmonic oscillator, the average angle, $\langle\beta^2\rangle$, (see Fig. 2) is given by

$$\langle\beta^2\rangle = \frac{\hbar}{2\pi\mu_b\nu_b}, \quad [13]$$

where ν_b is the bending frequency and is related to the bending force constant, k_b , by

$$\nu_b = \frac{1}{2\pi} \left(\frac{k_b}{\mu_b} \right)^{1/2}. \quad [14]$$

The bending reduced mass, μ_b , is taken to be (18)

$$\frac{1}{\mu_b} = \frac{1}{m_O r_{CO}^2} + \frac{1}{m_H r_{CH}^2} + \frac{1}{m_C} \left[\frac{1}{r_{CO}} + \frac{1}{r_{CH}} \right]^2. \quad [15]$$

The bending force constants and frequencies are given in Table 8. Unfortunately, we have no information about the normal mode that involves bending of the C—H—Br angle.

By examining Tables 7 and 8, we see that the force constants and potential parameters of $^{16}\text{O}^{12}\text{C}^2\text{H}^{79}\text{Br}$ are significantly different from those of the ^1H -containing species. This is due to the different vibrational averaging that the two isotopes experience. The bending vibrations of the species containing the heavier isotope will have smaller amplitudes (as measured by θ); thus, this species will, on average, sample nearer the bottom of the potential well. The net effect makes OC^2HBr appear to be more strongly bound than OCHBr.

DISCUSSION

These results indicate that OCHBr is bound by a linear hydrogen bond between C and Br. The atomic arrangement is

Table 9. Stretching force constants and well depths of $^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$, HCN---HF, ArHBr, and KrHBr

	ν_s, cm^{-1}	ϵ, cm^{-1}
$^{16}\text{O}^{12}\text{CH}^{79}\text{Br}$	52	469
HCN---HF*	197	2182
HCN---HF†	199	2272
ArHBr‡	22	89
KrHBr‡	23	165

* See ref. 17.

† Calculated by using the data in ref. 6 and the method given in this paper.

‡ See ref. 8.

consistent with electrostatic considerations based on the sign of the CO dipole moment (19). Comparison of the binding energies and stretching frequencies of OCHBr, HCN---HF (17), ArHBr (8), and KrHBr (8) (Table 9) shows that the OC---HBr bond is weak by normal hydrogen bond standards but strong relative to the analogous rare gas-HBr complexes. It is interesting to compare the values of ν_s and ϵ for HCN---HF as computed by the methods described above with those derived from microwave intensity measurements (17). The two methods yield the same results within the experimental uncertainty. Apparently, despite the approximations inherent in the pseudodiatomic model, the assumption of a Lennard-Jones radial potential works well in determining the strength of the hydrogen bonding interaction.

The support of the National Science Foundation is gratefully acknowledged.

1. Ekkers, J. & Flygare, W. H. (1976) *Rev. Sci. Instrum.* **47**, 448-454.
2. Flygare, W. H. & Schmalz, T. G. (1976) *Acc. Chem. Res.* **9**, 385-392.
3. Voss, H. L., Krajnovich, D., Hoke, W. E. & Flygare, W. H. (1978) *J. Chem. Phys.* **68**, 1439-1443.
4. Hoke, W. E., Voss, H. L., Campbell, E. J. & Flygare, W. H. (1978) *Chem. Phys. Lett.* **58**, 441-446.
5. Balle, T. J., Campbell, E. J., Keenan, M. R. & Flygare, W. H. (1979) *J. Chem. Phys.* **71**, 2723-2724.
6. Balle, T. J., Campbell, E. J., Keenan, M. R. & Flygare, W. H. (1980) *J. Chem. Phys.* **72**, 922-933.
7. Legon, A. C., Soper, P. D., Keenan, M. R., Minton, T. K., Balle, T. J. & Flygare, W. H. (1980) *J. Chem. Phys.* **73**, 583-584.
8. Keenan, M. R., Campbell, E. J., Balle, T. J., Buxton, L. W., Minton, T. K., Soper, P. D. & Flygare, W. H. (1980) *J. Chem. Phys.* **72**, 3070-3080.
9. Campbell, E. J., Buxton, L. W., Balle, T. J. & Flygare, W. H. (1980) *J. Chem. Phys.*, in press.
10. Campbell, E. J., Buxton, L. W., Keenan, M. R., Balle, T. J. & Flygare, W. H. (1980) *J. Chem. Phys.*, in press.
11. Townes, C. H. & Schawlow, A. L. (1955) *Microwave Spectroscopy* (McGraw-Hill, New York).
12. Delucia, F. C., Helminger, P. & Gordy, W. (1971) *Phys. Rev. A* **3**, 1849-1857.
13. Dabbousi, O. B., Meerts, W. L., Deleeuw, F. H. & Dymanus, A. (1973) *Chem. Phys.* **2**, 473-477.
14. van Dijk, F. A. & Dymanus, A. (1974) *Chem. Phys.* **6**, 474-478.
15. Helminger, P., Delucia, F. C. & Gordy, W. (1970) *Phys. Rev. Lett.* **25**, 1397-1399.
16. Watson, J. K. G. (1973) *J. Mol. Spectrosc.* **48**, 479-502.
17. Legon, A. C., Millen, D. J. & Rogers, S. C. (1980) *Proc. R. Soc. London Ser. A* **370**, 213-237.
18. Wilson, E. B., Decius, J. C. & Cross, P. (1955) *Molecular Vibrations* (McGraw-Hill, New York).
19. Rosenblum, B., Nethercot, A. H. & Townes, C. H. (1958) *Phys. Rev. A* **109**, 400-412.