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Citation: The Journal of Chemical Physics **109**, 7169 (1998); doi: 10.1063/1.477354 View online: http://dx.doi.org/10.1063/1.477354 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/109/17?ver=pdfcov Published by the AIP Publishing

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Microwave spectroscopy of the NBr radical in the $X^{3}\Sigma^{-}$ state

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(Received 15 June 1998; accepted 29 July 1998)

The microwave spectrum of the NBr radical in the $X^{3}\Sigma^{-}$ ground electronic state has been observed by a source modulated spectrometer. The NBr radical was generated in a free space cell by a dc glow discharge in a mixture of N₂, Br₂, and He. The spectrum with three spin components of both two isotopomers, N⁷⁹Br and N⁸¹Br, was observed. The spectrum showed complicated splitting by the hyperfine interactions due to both bromine and nitrogen nuclei. The molecular constants including the magnetic hyperfine and nuclear quadrupolar hyperfine interaction constants were determined by analyzing the observed spectrum. The spin density of the unpaired electrons was estimated from the observed hyperfine coupling constants to be 73.4% and 22.4% on the nitrogen and the bromine atoms, respectively. © *1998 American Institute of Physics*. [S0021-9606(98)01141-6]

I. INTRODUCTION

The nitrogen monohalides NX (X=F, Cl, Br, and I), which are iso(valence)electronic with O₂, have the $X^{3}\Sigma^{-}$ ground electronic state and the two low-lying electronically excited states, $a^{1}\Delta$ and $b^{1}\Sigma^{+}$. These molecules have extensively been studied through their electronic transitions. High resolution spectroscopic studies of these molecules, however, were reported only for fluoride¹⁻⁸ and chloride⁹⁻¹³ $(X^{3}\Sigma^{-}, a^{1}\Delta, b^{1}\Sigma^{+})$. Since the NX radical has two atoms with nonzero nuclear spins, its rotational spectrum shows complicated structure by the fine and the hyperfine interactions. The information concerning the distribution of unpaired electrons will be obtained through the analysis of the hyperfine splittings.

The spectrum of NBr was first reported by Elliott¹⁴ in 1938. He photographed an orange flame produced by admitting molecular bromine into a stream of active nitrogen and observed banded structures. He analyzed the vibrational structure of the emission spectrum and attributed it to a transition between two unknown electronic states of NBr on the basis of the vibrational frequency and its isotope effect as well as of a detrimental effect of added oxygen on the production of the orange bands. This emission band was later assigned to the ${}^{1}\Sigma^{+}-{}^{3}\Sigma^{-}$ transition.¹⁵

Up to the present time the electronic transitions of NBr $(a \ ^{1}\Delta - X \ ^{3}\Sigma^{-} \text{ and } b \ ^{1}\Sigma^{+} - X \ ^{3}\Sigma^{-})$ have been studied both in the gas phase $^{14-16}$ and in rare gas matrices. ¹⁷ These studies revealed the energy intervals of the b-X and the a-X states, vibrational frequencies in these electronic states and radiative lifetimes in the upper states. The vibrational fundamental of NBr in the ground state was observed in an inert rigid matrix ¹⁸ and corresponded well with that from the electronic spectrum. There is no infrared study in the gas phase yet.

Though the extensive spectroscopic studies have been carried out, the data on the rotational energy structure of NBr

are scarce. Milton *et al.*¹⁵ observed the rotationally resolved spectrum of NBr produced by the same method as that used by Elliott. They assigned the spectrum to the $b^{-1}\Sigma^+ - X^{-3}\Sigma^$ transition from the rotational analysis by the combination differences for the upper and lower electronic states of individual bands. Although only the transitions terminating on the F_1 spin component (J=N+1) of the $X^{-3}\Sigma^-$ state (${}^{Q}P$ and ${}^{S}R$ branches) were observed, they succeeded in deriving two probable sets of the rotational (B), the spin-spin (λ) and the spin-rotation (γ) constants in the ground state as well as the rotational constant in the excited state.

More recently Pritt *et al.* reported on the low-resolution, visible and near-infrared transitions of NBr generated in the $F/Br+HN_3$ flame.¹⁶ This method of production populated the lower vibrational levels of NBr ($b^{1}\Sigma^{+}$) and thus allowed them to detect the 0–0 band. They compared the observed low-resolution spectrum with the synthesized one and found a good fit for a second set of the molecular constants reported by Milton *et al.*¹⁵ Subsequently Pritt¹⁹ observed rotationally resolved emission spectra of the 0–0 band of the $b^{1}\Sigma^{+}-X^{3}\Sigma^{-}$ transition in NBr produced by the reaction of atomic fluorine with molecular bromine and hydrogen azide. He observed weaker ${}^{O}P$ and ${}^{Q}R$ branches besides the ${}^{Q}P$ and ${}^{S}R$ branches observed by Milton *et al.*¹⁵ and obtained the



FIG. 1. A typical spectral line of $N^{81}Br$ in the 378.68 GHz region, N=14 - 13 and J=15-14. The vertical lines in the lower part of the figure show the calculated hyperfine components.

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TABLE I. Observed rotational transitions of the N⁷⁹Br radical(MHz).

N′	J'	F'1	Fı	N″	J″	<i>F</i> ₁ "	<i>F</i> ″	$ u_{\rm obs}$	v _{o-c}	wt
8	8	6.5	5.5	7	7	5.5	4.5		0.000	1.003
8	8	6.5	6.5	7	7	5.5	5.5	214007.843	-0.009	1.00"
8	8	0.5	1.5	7	7	5.5	0.5			
8	8	7.5	0.5 7.5	7	7	0.5	5.5			
8	8	7.5	7.5	/	/	0.5	0.5			
8	8	7.5	8.5	/	,	0.5 7 -	7.5	214012.000	-0.018	1.00 ^a
8	8	8.5	7.5	7	7	7.5	6.5			
8	8	8.5	8.5	/	7	7.5	7.5			
8	8	8.5	9.5	7	7	/.5	8.5			
8	8	9.5	8.5	7	7	8.5	1.5	014014 671	0.000	1 004
8	8	9.5	9.5	7	7	8.5	8.5	214014.071	0.008	1.00-
8	8	9.5	1q.5	7	/	8.5	9.5	004646 281	0.000	1.00
8	9	7.5	0.5	/	8	6.5	5.5	224646.381	-0.002	1.00
8	9	7.5	7.5	7	8	6.5	6.5	224648.359	0.045	1.00
8	9	7.5	8.5	7	8	6.5	7.5	224649.968	-0.015	1.00 ^a
8	9	8.5	7.5	7	8	7.5	6.5)		
8	9	9.5	8.5	7	8	8.5	7.5	224650.924	0.048	1.00
8	9	8.5	8.5	7	8	7.5	7.5	224651.879	0.027	1.00
8	9	9.5	9.5	7	8	8.5	8.5	224652.765	0.004	1.00
8	9	8.5	9.5	7	8	7.5	8.5	224653.875	-0.025	0.33ª
8	9	10.5	9.5	7	8	9.5	8.5)	0.020	0.00
8	9	9.5	10.5	7	8	8.5	9.5	224654.635	0.028	1.00
8	9	10.5	10.5	7	8	9.5	9.5	224655.936	-0.016	1.00
8	9	10.5	11.5	7	8	9.5	10.5	224657.723	-0.013	1.00
9	10	8.5	7.5	8	9	7.5	6.5	250291.344	-0.001	1.00
9	10	8.5	8.5	8	9	7.5	7.5	250293.041	-0.015	1.00
9	10	8.5	9.5	8	9	7.5	8.5	250204 521	-0.028	0.503
9	10	9.5	8.5	8	9	8.5	7.5	230294.331	-0.028	0.50
9	10	10.5	9.5	8	9	9.5	8.5	250295.657	0.057	b
9	10	9.5	9.5	8	9	8.5	8.5	250296.331	0.079	b
9	10	9.5	10.5	8	9	8.5	9.5	050007.006	0.046	a.b
9	10	10.5	10.5	8	9	9.5	9.5	250297.520	-0.246	
9	10	10.5	11.5	8	9	9.5	10.5	1	0.004	ab
9	10	11.5	10.5	8	9	10.5	9.5	<i>250298.182</i>	0.084	4,0
9	10	11.5	11.5	8	9	10.5	10.5	250300.079	-0.032	1.00
9	10	11.5	12.5	8	9	10.5	11.5	250301.649	-0.038	1.00
10	9	10.5	11.5	9	8	9.5	10.5	256935.696	0.001	1.00
10	9	9.5	10.5	9	8	8.5	9.5	0.0000.000	0.005	0.001
10	9	10.5	10.5	9	8	9.5	9.5	250937.080	0.085	0.33-
10	9	10.5	9.5	9	8	9.5	8.5		0.004	1 003
10	9	9.5	9.5	9	8	8.5	8.5	256938.690	-0.004	1.00*
10	9	7.5	8.5	9	8	6.5	7.5	1		
10	9	9.5	8.5	9	8	8.5	7.5	256940.212	-0.021	1.00"
10	9	7.5	7.5	9	8	6.5	6.5	1		
10	9	8.5	8.5	9	8	7.5	7.5	256941.512	0.052	0.50ª
10	9	8.5	7.5	9	8	7.5	6.5	1		
10	9	8.5	6.5	9	8	6.5	5.5	256943.211	-0.030	0.50ª
10	10	8.5	7.5	9	9	7.5	6.5	í í		
10	10	8.5	8.5	9	9	7.5	7.5	267480.032	0.010	1.00ª
10	10	8.5	9.5	9	9	7.5	8.5			
10	10	95	85	9	9	8 5	7.5	Ś		
10	10	9.5	9.5	9	9	8.5	8.5			
10	10	9.5	10.5	9	9	8.5	9.5			
10	10	10.5	95	9	9	95	8.5	267482.532	-0.036	0.17 ^a
10	10	10.5	10.5	ģ	9	95	9.5			
10	10	10.5	11.5	ó	o o	9.5	10.5	}		
10	10	11.5	10.5	9	9	10.5	10.5	Ś		
10	10	11.5	11 4	9 0	9	10.5	7.5 10 5	267484 293	-0.051	0 338
10	10	11.5	175	7 0	7	10.5	10.5	1 201.104.200	0.001	0.55
14	10	11.5	14.3	7 12	9 10	10.5	11.3	267577 214	-0.060	1 00
14	13	14.3	13.3	15	12	13.3	14.5	307327.214	-0.000	1.00
14	13	13.3	14.5	13	12	12.5	13.5	367528.205	0.042	0.50 ^a
14	13	14.5	14.5	13	12	13.3	13.3	<		
14	15	13.5	13.5	15	12	12.5	12.5	367529.218	-0.009	1.00 ^a
14	13	14.5	13.3	15	12	13.5	12.5	<		
14	13	12.5	13.5	13	12	11.5	12.5	367530.073	0.001	1.00 ^a
14	13	13.5	12.5	13	12	12.5	11.5)		

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TABLE I. (Continued).

N'	J'	F'_1	F/	N″	J″	F_1''	<i>F</i> ″	$\nu_{\rm obs}$	ν_{o-c}	wt
14	13	11.5	12.5	13	12	10.5	11.5	267520.052	0.016	1 003
14	13	12.5	12.5	13	12	11.5	11.5	307330.933	0.010	1.00
14	13	11.5	11.5	13	12	10.5	10.5	367531 065	-0.010	1.008
14	13	12.5	11.5	13	12	11.5	10.5	507551.905	-0.010	1.00
14	13	11.5	10.5	13	12	10.5	9.5	367532.974	0.031	1.00
14	14	12.5	11.5	13	13	11.5	10.5			
14	14	12.5	12.5	13	13	11.5	11.5	374352.507	-0.070	0.33ª
14	14	12.5	13.5	13	13	11.5	12.5			
14	14	13.5	12.5	13	13	12.5	11.5			
14	14	13.5	13.5	13	13	12.5	12.5			
14	14	13.5	14.5	13	13	12.5	13.5	274252 905	0.020	0 178
14	14	14.5	13.5	13	13	13.5	12.5	374353.805	-0.038	0.17*
14	14	14.5	14.5	13	13	13.5	13.5			
14	14	14.5	15.5	13	13	13.5	14.5			
14	14	15.5	14.5	13	13	14.5	13.5			
14	14	15.5	15.5	13	13	14.5	14.5	374354.899	0.070	0.33 ^a
14	14	15.5	16.5	13	13	14.5	15.5			
14	15	13.5	12.5	13	14	12.5	11.5	380053.652	-0.035	1.00
14	15	13.5	13.5	13	14	12.5	12.5	380054.590	-0.035	1.00
14	15	13.5	14.5	13	14	12.5	13.5	380055 506	0.008	1.00a
14	15	14.5	13.5	13	14	13.5	12.5 🕽	500055.500	0.000	1.00
14	15	14.5	14.5	13	14	13.5	13.5	380056 453	-0.003	1 00ª
14	15	15.5	14.5	13	14	14.5	13.5)	566656.455	0.005	1.00
14	15	14.5	15.5	13	14	13.5	14.5	380057 383	0.037	0.504
14	15	15.5	15.5	13	14	14.5	14.5	500057.505	0.057	0.50
14	15	15.5	16.5	13	14	14.5	15.5	380058 108	0.015	1 00 ^a
14	15	16.5	15.5	13	14	15.5	14.5	500050.100	0.015	1.00
14	15	16.5	16.5	13	14	15.5	15.5	380058.907	0.018	1.00
14	15	16.5	17.5	13	14	15.5	16.5	380059.758	0.030	1.00

^aUnresolved line. The calculated frequencies were obtained by averaging the frequencies of each component weighted to their relative intensities. ^bDisturbed line. Not included in the analysis.

rotational and the fine structure constants of NBr in the $X^{3}\Sigma^{-}$ state: $B_{0}=0.4529 \text{ cm}^{-1}$, $\lambda = 12.38 \text{ cm}^{-1}$ and $\gamma = -0.023 \text{ cm}^{-1}$.

In the present study, we have observed the pure rotational spectrum of $N^{79}Br$ and $N^{81}Br$ in the electronic ground state and determined their precise molecular constants: the rotational and the centrifugal distortion constants, the spinspin and the spin-orbit interaction constants, and the hyperfine coupling constants for the N and Br nuclei.

II. EXPERIMENT

The measurement was carried out using a sourcemodulated microwave spectrometer²⁰ with a 2 m free space discharge cell in the frequency region from 213 GHz to 381 GHz.

The NBr radical was generated in the cell by a dc glow discharge in a mixture of N₂, Br₂, and He. The optimum condition was 5–10 mTorr of Br₂, 15–20 mTorr of N₂, and 30–40 mTorr of He with the discharge current of 300–400 mA. The cell was cooled to about 0 °C, for bromine vapor condensed below this temperature. We first searched for the N=8-7, J=8-7 transition (F_2 spin component) which was expected to appear around 217.2 GHz from the molecular constants reported by Pritt.¹⁹ As the predicted frequency seemed to have relatively large uncertainty, we needed to scan a wide region centering at the predicted frequency. As soon as we started the observation, we found four strong

paramagnetic lines around the frequency region just below 217.1 GHz. These lines became much stronger when O_2 gas was introduced into the cell, and we supposed that this spectrum was due to an oxygen-containing radical, BrO. Since this spectrum of BrO was strong even when only a small amount of O_2 remained in the cell, we had to be careful not to leak air. As we proceeded to search toward the lower frequency side from the predicted region, we found three paramagnetic lines with a few MHz intervals around 214.0 GHz. The central line had intensity twice as strong as the other two lines and it apparently gained its intensity from the overlapping of two lines. We thought that these lines were split by the hyperfine interaction due to the bromine nucleus.

If these lines were to be ascribed to the NBr radical, an almost equally intense spectrum should appear for another bromine isotopomer at the corresponding frequency, since bromine has two isotopes (⁷⁹Br and ⁸¹Br) with nearly equal natural abundance. We calculated the frequency from the ratio of the reduced masses of N⁷⁹Br and N⁸¹Br and found four paramagnetic lines with almost the same intensity as the previous ones at the calculated frequency (about 213.2 GHz). Thus the spectrum at the higher frequency was definitely due to N⁷⁹Br and that at the lower frequency was due to N⁸¹Br. By using these frequencies, other F_2 transitions were predicted and observed.

We searched then for the N=9-8, J=10-9 transition (F_1 spin component). The frequency of the F_1 component

TABLE II. Observed rotational transitions of the $N^{81}\mbox{Br}$ radical (MHz).

N'	1'	F'	F,	N″	I "	F″	F"	1 7 -	77	sut
	J	r ₁	1.1	14	J	r 1	I '	⊭obs	<i>v</i> _{o-c}	wi
8	8	7.5	6.5	7	7	6.5	5.5		0.000	0.001
8	8	7.5	7.5	7	7	6.5 6.5	6.5 7.5	213216.717	-0.088	0.33*
0 8	0 8	7.5	8.5 7 5	7	7	0.5	65			
8	8	8.5	8.5	7	7	7.5	7.5	213218.082	0.089	0.33ª
8	8	8.5	9.5	7	7	7.5	8.5			
8	8	9.5	8.5	7	7	8.5	7.5)		
8	8	9.5	9.5	7	7	8.5	8.5	213220.952	-0.014	1.00 ^a
8	8	9.5	10.5	7	7	8.5	9.5)		
8	9	7.5	6.5	7	8	6.5	5.5	223852.705	0.019	1.00
8	9	7.5	7.5	7	8	6.5	6.5	223854.609	-0.009	1.00
8	9	7.5	8.5	7	8	6.5	7.5	223856.415	0.003	1.00 ^a
8	9	8.3	1.3	7	8	1.5	0.5			
0 8	9	8. <i>3</i> 9.5	8.5	7	0 8	7.5	7.5	223858.227	-0.022	1.00 ^a
8	9	85	9.5	7	8	75	85			_
8	9	9.5	9.5	7	8	8.5	8.5	223860.084	-0.026	1.00 ^a
8	9	9.5	10.5	7	8	8.5	9.5	0000001 704	0.014	1 003
8	9	10.5	9.5	7	8	9.5	8.5	223861.704	0.014	1.00"
8	9	10.5	10.5	7	8	9.5	9.5	223863.389	-0.015	1.00
8	9	10.5	11.5	7	8	9.5	10.5	223865.170	-0.019	1.00
9	10	8.5	7.5	8	9	7.5	6.5	249402.061	-0.010	1.00
9	10	8.5	8.5	8	9	7.5	7.5	249403.830	0.045	1.00
9	10	8.5	9.5	8	9	7.5	8.5	249405.409	0.006	1.00 ^a
9	10	9.5	8.5	8	9	8.5	7.5			
9	10	9.5	9.5	8 9	9	8.5	8.3 8.5	249407.166	0.004	1.00 ^a
9	10	95	10.5	8	9	9.5	0.5 9.5			
9	10	10.5	10.5	8	9	9.5	9.5	249408.861	0.052	1.00 ^a
9	10	10.5	11.5	8	9	9.5	10.5			
9	10	11.5	10.5	8	9	10.5	9.5	249410.317	0.009	1.00*
9	10	11.5	11.5	8	9	10.5	10.5	249411.844	0.003	1.00
9	10	11.5	12.5	8	9	10.5	11.5	249413.392	-0.026	1.00
10	9	10.5	10.5	9	8	9.5	9.5	255943.165	0.052	1.00
10	9	9.5	9.5	9	8	8.5	8.5	255944.101	-0.030	1.00
10	9	8.5	9.5	9	8	7.5	8.5	255944.837	-0.050	0.50 ^a
10	9	10.5	9.5	9	8	9.5	8.5			
10	9	95	85	9	8	8.5	7.5	255945.920	0.033	0.50 ^a
10	9	8.5	8.5	9	8	7.5	7.5	255946.602	0.001	1.00
10	9	7.5	7.5	9	8	6.5	6.5	255947.447	0.015	1.00
10	9	8.5	7.5	9	8	7.5	6.5	255040 106	0.019	1.002
10	9	7.5	6.5	9	8	6.5	5.5	255949.100	-0.018	1.00-
10	10	8.5	7.5	9	9	7.5	6.5			
10	10	8.5	8.5	9	9	7.5	7.5	266487.017	0.039	0.33 ^a
10	10	8.5	9.5	9	9	7.5	8.5			
10	10	9.5	8.5	9	9	8.5	7.5			4 0 0 0
10	10	9.5	9.5	9	9	8.5	8.5	266489.423	0.014	1.00"
10	10	9.5	10.5	9	9	8.5 0.5	9.5			
10	10	10.5	9.5	9	9	9.5	0.5	266/90 133	0.013	1 008
10	10	10.5	11.5	9	9	9.5	10.5	200490.133	0.015	1.00
10	10	11.5	10.5	9	9	10.5	9.5			
10	10	11.5	11.5	9	9	10.5	10.5	266492.091	-0.006	1.00 ^a
10	10	11.5	12.5	9	9	10.5	11.5			
14	13	14.5	15.5	13	12	13.5	14.5	366127.506	-0.063	1.00
14	13	13.5	14.5	13	12	12.5	13.5	366128 447	0.002	1 00ª
14	13	14.5	14.5	13	12	13.5	13.5		0.002	1.00
14	13	13.5	13.5	13	12	12.5	12.5	366129.497	0.017	1.00 ^a
14	13	14.5	13.5	13	12	13.5	12.5			
14	13	12.5	15.5	15	12	11.5	12.5	366130.290	0.003	1.00 ^a
14	13	13.5	12.5	13	12	12.5	11.5			
14	13	12.5	12.5	13	12	11.5	11.5	366131.176	0.008	1.00 ^a
14	13	11.5	11.5	13	12	10.5	10.5			
14	13	12.5	11.5	13	12	11.5	10.5	366132.206	0.010	1.00 ^a
14	13	11.5	10.5	13	12	10.5	9.5	366133.263	0.035	1.00

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TABLE II. (Continued).

N'	J'	<i>F</i> ' ₁	F٢	N″	J″	F_1''	<i>F</i> ″	$\nu_{\rm obs}$	v _{o-c}	wt	
14	14	12.5	11.5	13	13	11.5	10.5)			
14	14	12.5	12.5	13	13	11.5	11.5	372963.543	-0.034	0.33 ^a	
14	14	12.5	13.5	13	13	11.5	12.5)			
14	14	13.5	12.5	13	13	12.5	11.5)			
14	14	13.5	13.5	13	13	12.5	12.5				
14	14	13.5	14.5	13	13	12.5	13.5	272064 060	0.045	0 178	
14	14	14.5	13.5	13	13	13.5	12.5	372904.900	-0.045	0.17*	
14	14	14.5	14.5	13	13	13.5	13.5				
14	14	14.5	15.5	13	13	13.5	14.5)			
14	14	15.5	14.5	13	13	14.5	13.5)			
14	14	15.5	15.5	13	13	14.5	14.5	372966.253	0.002	1.00 ^a	
14	14	15.5	16.5	13	13	14.5	15.5)			
14	15	13.5	12.5	13	14	12.5	11.5	378676.228	-0.037	1.00	
14	15	13.5	13.5	13	14	12.5	12.5	378677.171	-0.036	1.00	
14	15	13.5	14.5	13	14	12.5	13.5	279679 157	0.000	1 008	
14	15	14.5	13.5	13	14	13.5	12.5	3/80/8.15/	0.006	1.00"	
14	15	14.5	14.5	13	14	13.5	13.5	279670 202	0.014	1 008	
14	15	15.5	14.5	13	14	14.5	13.5	378079.303	-0.014	1.00"	
14	15	14.5	15.5	13	14	13.5	14.5	279690.216	0.007	1 008	
14	15	15.5	15.5	13	14	14.5	14.5	378080.210	0.007	1.00-	
14	15	15.5	16.5	13	14	14.5	15.5	279601 196	0.022	0.501	
14	15	16.5	15.5	13	14	15.5	14.5	<i>j 3/8081.180</i>	0.032	0.50*	
14	15	16.5	16.5	13	14	15.5	15.5	378682.043	0.024	1.00	
14	15	16.5	17.5	13	14	15.5	16.5	378682.895	0.035	1.00	

^aUnresolved line. The calculated frequencies were obtained by averaging the frequencies of each component weighted to their relative intensities.

was dependent on the spin-spin and spin-rotation interaction constants. As these constants had been determined with marginal uncertainties, the prediction of the transition frequency was rather crude. We observed nine paramagnetic lines around 250.3 GHz and assigned these lines to the spectrum of N⁷⁹Br. The corresponding transition of N⁸¹Br was found around 249.4 GHz. By using these data, the molecular constants were refined to make the prediction more reliable. Other transitions of the F_1 and F_3 spin components were thus easily detected. In contrast to the F_2 component the spectrum of the F_1 and F_3 spin components showed splitting into many hyperfine components due to both the nitrogen and bromine nuclei. Figure 1 shows the N = 14 - 13, J = 15-14 transition of N⁸¹Br. Finally, fine and hyperfine components of the rotational transitions of N=8-7, N=9-8, N =10-9 and N=14-13 were observed for both bromine isotopomers. Tables I and II list the transition frequencies observed in the present study.

III. ANALYSIS

The Hamiltonian used in the present analysis is given as follows:

$$H = H_{\rm rot} + H_{\rm ss} + H_{\rm sr} + H_{\rm hfs}(N) + H_{\rm hfs}(Br), \qquad (1)$$

where $H_{\rm rot}$ represents the rotational energy of the molecule, $H_{\rm ss}$ the spin-spin interaction, $H_{\rm sr}$ the spin-rotation interaction, $H_{\rm hfs}(N)$ the hyperfine interaction of the nitrogen nucleus, and $H_{\rm hfs}(Br)$ the hyperfine interaction of the bromine nucleus including the nuclear spin-rotation interaction. The coupling scheme of the angular momenta based on the Hund's case b_{β} basis is written as $\mathbf{J}=\mathbf{N}+\mathbf{S}$, $\mathbf{F}_1=\mathbf{J}+\mathbf{I}(Br)$, $\mathbf{F}=\mathbf{F}_1+\mathbf{I}(N)$ with the standard notation for the angular momenta. The nuclear spin of both the ⁷⁹Br and ⁸¹Br nuclei is 3/2, and that of the ¹⁴N nucleus is 1. The matrix elements of the Hamiltonian were given by Yamada *et al.*⁹ The energy matrix was numerically diagonalized and used in a least-squares analysis.

The preliminary values of the rotational, centrifugal distortion and fine structure constants were first determined from the data obtained by averaging the frequencies of the hyperfine components. These parameters were used as initial parameters in the subsequent analysis. The Br hyperfine coupling constants b(Br), c(Br), and eQq(Br) were estimated from those of BrO (Ref. 21) and the ratio of the chlorine hyperfine constants of NCl to those of ClO.²² The nitrogen hyperfine constants of NCl were used as the initial values of the b(N), c(N), and eQq(N). As shown in Tables I and II, many hyperfine components were not resolved. For these transitions the frequencies were calculated by averaging those of component lines weighted in proportion to their relative intensities. Table III lists the molecular constants obtained by the least squares fit to the microwave transitions, together with the constants reported by Pritt.¹⁹ The nitrogen eQq constant was found to be smaller than its standard deviation and was thus fixed to zero in the analysis. The standard deviations of the fit were 30 and 29 kHz, respectively, for N⁷⁹Br and N⁸¹Br.

IV. DISCUSSION

Molecular constants including the hyperfine constants of NBr in the $X^{3}\Sigma^{-}$ ground state have precisely been obtained for the first time. As shown in Table III, the molecular constants reported by Pritt differ from those determined in the present work by more than their standard deviations. In his

TABLE III. Molecular constants of NBr (MHz).^a

	N ⁷⁹ Br	N ⁸¹ Br	Pritt ^b
$\overline{B_0}$	13380.46783(83)	13330.79426(64)	13580(110)
D_0	0.0226722(26)	0.0225004(20)	
λ	346635.8(17)	346642.8(15)	371100(3300)
λ_D	-2.6980(11)	-2.68803(90)	
γ	-517.100(48)	-515.244(42)	-690(540)
b(Br)	80.60(23)	86.63(27)	
c(Br)	-274.7(14)	-296.9(19)	
eQq(Br)	505.9(57)	428.6(50)	
$C_{\rm I}({\rm Br})$	0.0631(86)	0.0735(81)	
b(N)	42.01(26)	42.02(23)	
$c(\mathbf{N})$	-61.1(16)	-61.9(16)	

^aValues in parentheses denote one standard deviations in units of the last digits.

^bReference 19.

work the branches terminating on the F_2 spin component were not observed, which might explain the difference. From the observed B_0 and D_0 constants, the frequencies of the fundamental N–Br stretching vibration for N⁷⁹Br and N⁸¹Br were estimated to be 686 and 685 cm⁻¹, respectively, using the relation, $D = 4B^3/\omega^2$. These frequencies agree with those reported by Milton *et al.*¹⁵ (691.75 and 690.45 cm⁻¹), which confirms their assignment of the lower state of the electronic transition to the ground state.

The equilibrium bond length is estimated from the isotopically invariant Dunham constant U_{01} . This constant can be estimated from the ground state rotational constants of two isoptopic species, provided that the anharmonicity in the vibrational potential function negligibly affects the lowerorder Dunham constants. The equilibrium bond length is calculated to be 1.77799(11) Å, the uncertainty being three standard deviations.

Fermi contact interaction arises when an unpaired electron resides on the nucleus with nuclear spin. This interaction thus results from the *s*-character of the unpaired electron. The contact value $b_F = b + c/3$ is calculated to be -10.97 (52) MHz in N⁷⁹Br. The negative interaction constant reflects the spin-polarization. If this value is compared with the atomic value of 32 070 MHz for the ⁷⁹Br atom,²³ the *s*-character is only 0.034%, which shows that the orbital of the unpaired electron is not mixed with *s*-orbital. The same is true also for nitrogen with the *s*-character of 1.20%.

Using the hyperfine interaction constants, we have estimated the spin density of the unpaired electron. Although $g_s g_N \beta \beta_N \langle 1/r^3 \rangle$ cannot be calculated directly from hyperfine constants obtained, it is estimated from the hyperfine constant *c* by assuming the angular part $\langle 3 \cos^2 \theta - 1 \rangle_s$ to be -2/5. Through the comparison with the corresponding atomic value (⁷⁹Br: 2044 MHz, N: 138.8 MHz),²³ the spin density in N⁷⁹Br is calculated to be 22.4% and 73.4% on the bromine and the nitrogen nuclei, respectively. First column of Table IV shows the spin density on the halogen atom of the NX and OX (X = Cl and Br) molecules in the $X^3\Sigma^-$ state. As seen in the table, the spin density of NBr is nearly the same as that of the NCl radical,⁹ but the bromide has slightly larger spin density than the chloride. This tendency

TABLE IV. Spin density and π electron transfer (Δ_p) .

	Spin density(%) on halogen	Backdonation Δ_p	Reference
N ³⁵ Cl	21.9	0.44	9
N ⁷⁹ Br	22.4	0.45	This work
O ³⁵ Cl	35.1	0.35	22
O ⁷⁹ Br	36.7	0.37	24

is also valid in the oxygen compounds, CIO (Ref. 22) and BrO. 24

The electron configuration of NBr in the $X^{3}\Sigma^{-}$ state is $1\sigma^{2}2\sigma^{2}...10\sigma^{2}4\pi^{4}5\pi^{2}$. If we assume that the 4π and 5π orbitals are expressed by a linear combination of the 2p orbital of the nitrogen atom and the 4p orbital of the bromine atom, the π electrons transferred from Br to N (back donation) are given by $\Delta_{p} = (4-n)\rho$, where *n* represents the number of electrons that occupy the 5π orbital and ρ represents the spin density on the Br atom. The amount of Δ_{p} is calculated to be 0.45 for N⁷⁹Br(transfer from Br to N). The backdonated π electron Δ_{p} in NBr is compared in Table IV with the values for N³⁵Cl, ³⁵ClO, and ⁷⁹BrO. The values of Δ_{p} in the nitrogen compounds are slightly larger than those in the oxygen compounds.

In a diatomic molecule, the quadrupole coupling eQq is related to the electronegativity difference of the two atoms. Table V lists eQq(Br) of four second-row bromides (⁷⁹Br). The entry eQq(corr) denotes the value corrected for the transfer of π electrons described above. Since the transfer of one π -electron corresponds to the correction of -eQq/2, the correction is made by adding $-(\Delta_p/2)$ (eQq_{410}) to the observed eQq value. In Fig. 2, observed and corrected values are plotted against the electronegativity difference. The solid curve represents the empirical relation proposed by Gordy and Cook.²⁷ The corrected values can be fitted by shifting down the curve slightly. This relation is similar to the case of the second-row chlorides.⁹

It is thought that the observed spin-spin constant in a molecule bearing a heavy atom is dominated by the second-order spin-orbit contribution. The main second-order contribution comes from the $b^{1}\Sigma^{+}$ electronic state, the lowest state among many states capable of interaction. Lefebvre-Brion and Field²⁸ have presented a method to estimate this contribution,

TABLE V. Bromine ($^{79}\mathrm{Br})$ nuclear quadrupole coupling constant of XBr (MHz).

Molecule	eQq	eQq(corr)	$\Delta\chi^{ m a}$
BBr ^b NBr OBr ^c FBr ^d	133.2 505.9 650.0 1086.9	677.6 791.3	-0.8 0.2 0.7 1.2

^aElectronegativity difference, $\chi(X) - \chi(Br)$.

^bReference 25.

^cReference 21. ^dReference 26.



FIG. 2. Relation between the electronegativity difference of two constituent atoms and eQq values. The open circles represent the observed values and the closed circles the values corrected for the backdonation. The solid line shows the empirical relation.

$$\lambda^{\text{SO}} = [\langle {}^{3}\Sigma_{0}^{-} | H^{\text{SO}} | {}^{1}\Sigma_{0}^{+} \rangle]^{2} / 2[E({}^{1}\Sigma^{+}) - E({}^{3}\Sigma_{0}^{-})] \simeq [C_{\text{N}}^{2}\zeta_{\text{N}}(p) + C_{\text{Br}}^{2}\zeta_{\text{Br}}(p)]^{2} / 2[E({}^{1}\Sigma^{+}) - E({}^{3}\Sigma_{1}^{-})],$$
(2)

$$E(^{1}\Sigma^{+}) - E(^{3}\Sigma^{-}_{1}) = E(^{1}\Sigma^{+}) - E(^{3}\Sigma^{-}_{0}) - 2\lambda_{obs}, \qquad (3)$$

where H^{SO} is the spin-orbit interaction Hamiltonian, C_X is the atomic orbital mixing coefficient, and $\zeta_X(p)$ is the atomic spin-orbit value. We use the spin density on N and Br atoms, namely, 0.734 and 0.224, as C_N^2 and C_{Br}^2 , respectively. The ${}^{1}\Sigma^{+} - {}^{3}\Sigma_0^{-}$ energy interval is 14787.3 cm⁻¹ from Ref. 16 and $\zeta_N(p)=73.3$ cm⁻¹ from Ref. 28. Two different values of $\zeta_{Br}(p)$ for ⁷⁹Br are listed in Ref. 28, 2457 cm⁻¹ and 2215 cm⁻¹, from which λ^{SO} is calculated to be 371 GHz for the former and 307 GHz for the latter. The observed λ value (347 GHz) is intermediate between the two calculated values.

As Endo *et al.*^{9,29} have pointed out, the Br nuclear spinrotation interaction may be estimated from an approximate formula,

$$C_{\rm I}/\gamma = |a/A_{\rm SO}|. \tag{4}$$

For N⁷⁹Br, A_{SO} is estimated to be 550 or 604 cm⁻¹ from the relation $A_{SO} = C_N^2 \zeta_N + C_{Br}^2 \zeta_{Br}$, as discussed above and the atomic value of *a* is taken to be 2044 MHz.²³ The calculated value of C_I was 64.1 or 58.4 kHz, which was well compared with the observed value, 63.1 kHz.

ACKNOWLEDGMENTS

The present study was supported by a Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture (Nos. 07217209, 07454150, 07740456, and 08740457).

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