The pure rotational spectrum of the ZnBr radical ($X^2\Sigma^+$): Trends in the zinc halide series

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ABSTRACT

The pure rotational spectrum of ZnBr ($X^2\Sigma^+$) has been recorded in the frequency range 259–310 GHz using millimeter-wave direct absorption techniques. This study is the first quantitative spectroscopic investigation of this free radical. ZnBr was synthesized in a DC discharge by the reaction of zinc vapor in argon with one of three reagents: BrCH₃, Br₂CH₂, or Br₂. Eight rotational transitions were measured for six isotopologues (⁶⁴Zn⁷⁹Br, ⁶⁴Zn⁸¹Br, ⁶⁶Zn⁷⁹Br, ⁶⁶Zn⁸¹Br, ⁶⁸Zn⁷⁹Br, and ⁶⁸Zn⁸¹Br), all of which exhibited spin-rotation interactions. Furthermore, transitions originating in the $v = 1$ through 3 excited vibrational states were obtained for certain isotopologues. Five rotational transitions were also recorded for ⁶⁷Zn⁷⁹Br, in which hyperfine splittings were observed arising from the ⁶⁷Zn nucleus ($I = 5/2$). The spectra were analyzed using a Hund's case ($b_{\beta J}$) Hamiltonian, and rotational, spin-rotation, and ⁶⁷Zn magnetic hyperfine constants were determined. Equilibrium parameters were also derived for the ⁶⁴Zn⁷⁹Br, ⁶⁴Zn⁸¹Br, ⁶⁶Zn⁷⁹Br, and ⁶⁶Zn⁸¹Br isotopologues, including the vibrational constant, $\omega_e = 286\text{ cm}^{-1}$. The equilibrium bond length was derived to be $r_e = 2.268\,48(90)\text{ \AA}$. Analysis of the ⁶⁷Zn hyperfine parameters suggest a decrease in ionic character in ZnBr from the other known zinc halides, ZnF and ZnCl.

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I. INTRODUCTION

Simple zinc halide molecules have been widely used in chemistry for decades.¹ These species have played a major role in organic synthesis and catalysis. For example, ZnCl₂ has been used to moderate aldol condensation reactions² and in the selective reduction of many alkyl halides,³ while ZnF₂ has been employed to generate other zinc synthetic agents.⁴ ZnBr₂ has been found to be an effective catalyst in the syntheses of styrene carbonate,⁵ epoxides,⁶ and ynones.⁷ In addition, this compound has a wide application in the construction of batteries, both for large-scale (flowing electrolyte, 50 kW-H) and small-scale (nonflow electrolyte, <5 kW-H) systems.^{8–12}

Because of these applications, there have been various studies attempting to characterize the fundamental properties of simple zinc halide systems, both experimentally and theoretically. Various electronic transitions have been recorded for ZnCl, including the $A^2\Pi-X^2\Sigma$, $C^2\Pi-X^2\Sigma$ and

$E^2\Sigma-X^2\Sigma$ bands, establishing vibrational constants for ground and several excited states.^{13,14} ZnCl has also been investigated via pure rotational spectroscopy in its $X^2\Sigma$ state¹⁵ and has been the focus of theoretical studies^{16,17} in which the dipole moment, dissociation energies, and other molecular properties were computed. ZnF has been the subject of both ESR/matrix¹⁸ and pure rotational measurements,¹⁹ as well as theory.¹⁶ The spectroscopic constants of ZnCl and ZnF are now well-determined, including the ⁶⁷Zn magnetic hyperfine parameters.

In contrast, little spectroscopic data currently exists for the next member in the series: ZnBr. There were various reports of the observation of electronic bands due to this molecule, as summarized by Gosavi *et al.*,²⁰ who conducted the first quantitative analysis of the $^2\Pi-X^2\Sigma$ transition of ZnBr. These authors established an equilibrium vibrational frequency (ω_e) for the $^2\Pi$ and $X^2\Sigma$ states of 358 and 319 cm⁻¹, respectively. A Raman spectrum was subsequently measured for this radical in a krypton matrix, also establishing the

ground state vibrational frequency of 198 cm^{-1} .²¹ The disagreement between the matrix and gas phase vibrational values prompted computational studies of ZnBr by Bowmaker and Schwerdtfeger²² and Liao *et al.*;²³ these authors derived a fundamental vibrational frequency near $\sim 230\text{ cm}^{-1}$, in disagreement with both experimental results. Very recently, further theoretical studies of ZnBr were performed using *ab initio* complete active space self-consistent field (CASSCF) methods by El Moussaoui and Korek²⁴ and El Moussaoui *et al.*²⁵ These studies produced the most reliable theoretical parameters for zinc bromide to date, estimating $\omega_e \sim 267\text{ cm}^{-1}$ and $r_e \sim 2.341\text{ \AA}$. El Moussaoui and Korek²⁴ also established the presence of 19 low-lying doublet and quartet states for the radical. Despite the computational interest, however, no spectroscopic work has been further conducted for ZnBr.

Here we present the first high-resolution spectroscopic study of ZnBr in its $X^2\Sigma^+$ state. The millimeter-wave spectrum of this free radical was recorded in the frequency range 259–310 GHz using direct absorption methods. Seven different isotopologues were studied in their $v = 0$ state, and several in the $v = 1$ –3 excited states. Rotation and spin-rotation constants were determined for these species, as well as the ^{67}Zn magnetic hyperfine parameters for $^{67}\text{Zn}^{79}\text{Br}$. Equilibrium parameters were also established for the four most abundant isotopologues. This work significantly extends the characterization of 3d-bromide species, which has been limited to microwave/millimeter-wave measurements of ScBr,²⁶ CuBr,^{27,28} and NiBr,²⁹ and rotationally resolved optical work for ScBr,³⁰ TiBr,³¹ and NiBr.³² It also allows direct comparison of chemical trends within the halide group, complementing our previous studies of ZnCl and ZnF. In this paper, we present our results, spectroscopic analysis, and interpretation of molecular parameters for ZnBr.

II. EXPERIMENTAL

The pure rotational spectra of ZnBr ($X^2\Sigma^+$) were recorded using one of the direct absorption spectrometers of the Ziurys group.³³ Briefly, the radiation source, covering the range 65–850 GHz, consists of various Gunn oscillator and varactor multiplier combinations. One linear polarization is produced by the source. The radiation is launched from a feed-horn/lens assembly, passed through a polarizing grid, and is directed quasi-optically into a 1/2 m long cylindrical reaction chamber, sealed at both ends with Teflon lenses. A Broida-type oven is attached to the cell for metal vaporization. A rooftop mirror, located at the end of the cell, reflects the radiation back through the chamber, rotating the polarization by 90° . The grid then reflects the radiation into the detector, a helium-cooled, hot electron bolometer. Phase-sensitive detection is implemented by frequency modulation of the source. Signals are collected at twice the modulation frequency, which produces a second-derivative line shape.

ZnBr was synthesized in a DC discharge by the reaction of zinc vapor, produced by the Broida-type oven, with

either BrCH_3 , Br_2CH_2 , or Br_2 diluted in an argon carrier gas. Less than 1 mTorr of reactant gas was flowed over top the oven and mixed with ~ 15 mTorr of argon, flowed up from the bottom of the oven, to entrain the metal vapor. Increasing the amount of reactant gas reduced the signals, particularly with Br_2 . Additional argon (~ 20 mTorr) was also streamed around the two Teflon lenses to prevent coating by the metal vapor. A DC discharge current of 0.85–1 amp was optimal for molecule production. The zinc and bromine isotopologues of ZnBr were observed in their natural abundances of ^{64}Zn : ^{66}Zn : ^{67}Zn : ^{68}Zn = 48.6 : 27.9 : 4.1 : 18.8 and ^{79}Br : ^{81}Br = 50.7 : 49.3.

Transition frequencies were determined from 5 MHz wide scans, centered on individual lines. Typically, 10 averaged scans (5 ascending in frequency, 5 descending) were required for an adequate signal-to-noise ratio. About 20–40 scan averages were needed to measure the ^{67}Zn hyperfine lines. The estimated experimental accuracy is $\pm 50\text{ kHz}$.

III. RESULTS

The spectrum of ZnBr was found in the course of searching for another molecule. Scanning a 30 GHz region while reacting zinc vapor with BrCH_3 resulted in the appearance of a series of doublets, varying in intensity, with a doublet separation of about 120 MHz. The lines were found to require both zinc and bromomethane. The strongest harmonic pattern yielded a rotational constant within $\sim 200\text{ MHz}$ of that predicted by theory²⁴ for ZnBr. The set of harmonic doublets lying highest in frequency in the pattern were assigned to $^{64}\text{Zn}^{79}\text{Br}$, the least massive isotopologue. The heavier species, resulting from all combinations of ^{64}Zn , ^{66}Zn , and ^{68}Zn , with ^{79}Br

FIG. 1. Stick diagram illustrating the pattern of the $N = 53 \leftarrow 52$ rotational transition for $^{64}\text{Zn}^{79}\text{Br}$, $^{64}\text{Zn}^{81}\text{Br}$, $^{66}\text{Zn}^{79}\text{Br}$, $^{66}\text{Zn}^{81}\text{Br}$, $^{68}\text{Zn}^{79}\text{Br}$, and $^{68}\text{Zn}^{81}\text{Br}$ in the $v = 0$ –3 states, showing the spin-rotation doublets. For clarity, transitions for $^{67}\text{Zn}^{79}\text{Br}$ have been omitted. Approximate observed intensities are given, which reflect the natural abundances for zinc-64, 66, 68 and bromine-79, 81, and the increased energies of the vibrational states.

TABLE I. Selected transition frequencies for ZnBr: $X^2\Sigma^+$ ($v = 0-3$).^a

$N' \leftarrow N''$	$J' \leftarrow J''$	$^{64}\text{Zn}^{79}\text{Br}$			$^{64}\text{Zn}^{81}\text{Br}$			$^{66}\text{Zn}^{79}\text{Br}$			$^{66}\text{Zn}^{81}\text{Br}$			$^{68}\text{Zn}^{79}\text{Br}$			$^{68}\text{Zn}^{81}\text{Br}$		
		ν_{obs}	$\nu_0 - \nu_c$		ν_{obs}	$\nu_0 - \nu_c$		ν_{obs}	$\nu_0 - \nu_c$		ν_{obs}	$\nu_0 - \nu_c$		ν_{obs}	$\nu_0 - \nu_c$		ν_{obs}	$\nu_0 - \nu_c$	
v = 0																			
52 $\leftarrow$ 51	51.5 $\leftarrow$ 50.5	287 808.384	-0.049	284 638.915	0.012	283 008.534	0.018	279 838.652	-0.007	278 486.135	-0.007	275 315.900	-0.063						
	52.5 $\leftarrow$ 51.5	287 926.758	0.019	284 755.881	0.011	283 124.905	0.014	279 953.660	-0.033	278 600.745	0.041	275 429.223	0.032						
53 $\leftarrow$ 52	52.5 $\leftarrow$ 51.5	293 318.364	0.009	290 088.416	-0.007	288 426.957	-0.026	285 196.721	0.015	283 818.514	0.097	280 587.852	0.045						
	53.5 $\leftarrow$ 52.5	293 436.523	0.004	290 205.274	0.008	288 543.246	0.045	285 311.631	0.027	283 932.872	0.029	280 700.904	-0.001						
54 $\leftarrow$ 53	53.5 $\leftarrow$ 52.5	298 826.780	-0.008	295 536.476	-0.011	293 844.003	-0.007	290 553.331	-0.015	289 149.306	0.006	285 858.320	0.031						
	54.5 $\leftarrow$ 53.5	298 944.812	0.004	295 653.176	-0.029	293 960.000	-0.069	290 668.088	-0.018	289 263.508	-0.078	285 971.229	-0.025						
v = 1																			
52 $\leftarrow$ 51	51.5 $\leftarrow$ 50.5	286 492.491	0.004	283 344.664	-0.080	281 725.530	0.010	278 577.207	0.039										
	52.5 $\leftarrow$ 51.5	286 606.661	0.039	283 457.604	-0.022	281 837.891	0.040	278 688.268	-0.021										
53 $\leftarrow$ 52	52.5 $\leftarrow$ 51.5	291 977.045	0.023	288 769.291	-0.010	287 119.226	0.007	283 910.962	0.065										
	53.5 $\leftarrow$ 52.5	292 091.016	0.013	288 882.118	0.080	287 231.358	-0.042	284 021.932	0.074										
54 $\leftarrow$ 53	53.5 $\leftarrow$ 52.5	297 460.079	0.012	294 192.439	0.040	292 511.485	0.009	289 243.154	-0.063										
	54.5 $\leftarrow$ 53.5	297 573.882	-0.009	294 304.938	-0.051	292 623.516	0.011	289 354.063	0.047										
v = 2																			
52 $\leftarrow$ 51	51.5 $\leftarrow$ 50.5	285 174.955	-0.033	282 049.034	-0.018														
	52.5 $\leftarrow$ 51.5	285 284.774	-0.081	282 157.744	0.045														
53 $\leftarrow$ 52	52.5 $\leftarrow$ 51.5	290 634.078	-0.007	287 448.718	0.097														
	53.5 $\leftarrow$ 52.5	290 743.798	-0.006	287 557.106	-0.006														
54 $\leftarrow$ 53	53.5 $\leftarrow$ 52.5	296 091.695	0.006	292 846.728	-0.003														
	54.5 $\leftarrow$ 53.5	296 201.281	0.024	292 955.084	0.023														
v = 3																			
52 $\leftarrow$ 51	51.5 $\leftarrow$ 50.5			280 751.655	0.103														
	52.5 $\leftarrow$ 51.5			280 855.882	-0.031														
53 $\leftarrow$ 52	52.5 $\leftarrow$ 51.5			286 125.975	-0.084														
	53.5 $\leftarrow$ 52.5			286 230.283	0.038														
54 $\leftarrow$ 53	53.5 $\leftarrow$ 52.5			291 499.069	-0.032														
	54.5 $\leftarrow$ 53.5			291 603.133	0.023														

^aIn MHz; full data set given in the [supplementary material](#).

FIG. 2. Individual spectra of the $N = 53 \leftarrow 52$ rotational transition ($v = 0$) for six $\text{ZnBr} (X^2\Sigma^+)$ isotopologues measured in the range 280–293 GHz. The top panels show $^{64}\text{Zn}^{81}\text{Br}$ and $^{64}\text{Zn}^{79}\text{Br}$, the middle panels are $^{66}\text{Zn}^{81}\text{Br}$ and $^{66}\text{Zn}^{79}\text{Br}$, and the lower panels present $^{68}\text{Zn}^{81}\text{Br}$ and $^{68}\text{Zn}^{79}\text{Br}$. Each spectrum contains a frequency break in order to show the respective spin-rotation doublets, labeled by $J = 52.5 \leftarrow 51.5$ and $J = 53.5 \leftarrow 52.5$. The arrows indicate the doublets when contaminating features are present. Each spectrum was created from two, 70 s, 110 MHz-wide scans, which were truncated and spliced to produce the shown figures.

and ^{81}Br were then located by simple mass-scaling of the rotational constants. The remaining doublets were found to exhibit patterns with uniformly decreasing intensities that readily identified them as arising from excited vibrational states. Thereafter, the $^{67}\text{Zn}^{79}\text{Br}$ species was found, which exhibited a complex hyperfine pattern due to the ^{67}Zn nuclear spin of $I = 5/2$. In total, 255 lines were measured between seven isotopologues and three vibrational states. The data clearly indicate that the ground state for ZnBr is $^2\Sigma^+$, as found for ZnF^{19} and ZnCl^{15} . There was no evidence of bromine hyperfine splitting in the spectra; both bromine nuclei have spins of $I = 3/2$.

Figure 1 illustrates the spectral pattern observed for the $N = 53 \leftarrow 52$ rotational transition of $\text{ZnBr} (X^2\Sigma^+)$. This stick spectrum shows the lines originating from $^{64}\text{Zn}^{79}\text{Br}$, $^{64}\text{Zn}^{81}\text{Br}$, $^{66}\text{Zn}^{79}\text{Br}$, $^{66}\text{Zn}^{81}\text{Br}$, $^{68}\text{Zn}^{79}\text{Br}$, and $^{68}\text{Zn}^{81}\text{Br}$; for clarity, $^{67}\text{Zn}^{79}\text{Br}$ was not included. The vibrational satellite lines identified in the data are also indicated, which varied with isotopologue.

Select transition frequencies are presented in Table I for $^{64}\text{Zn}^{79}\text{Br}$, $^{64}\text{Zn}^{81}\text{Br}$, $^{66}\text{Zn}^{79}\text{Br}$, $^{66}\text{Zn}^{81}\text{Br}$, $^{68}\text{Zn}^{79}\text{Br}$, and $^{68}\text{Zn}^{81}\text{Br}$ for the $v = 0$ and $v = 1$ –3 vibrational states. A complete set is available in the supplementary material. The spin-rotation doublets, labeled by quantum number J , where $J = N + S$, were

measured for all transitions. In total, eight rotational transitions, $N \rightarrow N + 1$, were observed for each species in the frequency range of 259–310 GHz. Vibrational satellite lines were observed for $^{64}\text{Zn}^{79}\text{Br}$ ($v = 1$ and 2), $^{64}\text{Zn}^{81}\text{Br}$ ($v = 1, 2$, and 3), $^{66}\text{Zn}^{79}\text{Br}$ ($v = 1$), and $^{66}\text{Zn}^{81}\text{Br}$ ($v = 1$).

Figure 2 presents spectra of the $N = 53 \leftarrow 52$ rotational transition ($v = 0$) for six isotopologues of ZnBr. Each spectrum has a frequency break in order to show the spin-rotation doublets ($J = 52.5 \leftarrow 51.5$ and $53.5 \leftarrow 52.5$), split by about 120 MHz. The top, middle, and bottom panels display the ^{64}Zn , ^{66}Zn , and ^{68}Zn species, respectively, with Zn^{81}Br on the left and Zn^{79}Br on the right. The varying line intensities reflect the zinc isotope abundances. Contaminant lines are present in the $^{66}\text{Zn}^{81}\text{Br}$ and $^{68}\text{Zn}^{79}\text{Br}$ data; the arrows identify the ZnBr features.

The transitions measured for $^{67}\text{Zn}^{79}\text{Br}$ are presented in Table II. Five rotational transitions, $N \rightarrow N + 1$, were recorded for this isotopologue. Each transition consists of fine structure doublets, which are further split into sextets by hyperfine interactions of the ^{67}Zn nucleus. Quantum number F labels the hyperfine lines, where $F = J + I$. In the lower J spin-rotation component, the lowest F value transition is lowest in frequency, followed by the highest F value line,

and then with decreasing F to higher frequency. The two highest frequency components are blended together. In the higher spin-rotation component, the hyperfine transitions increase in frequency in sequence with the F value. The two lowest frequency hyperfine components are blended in this case, creating a mirror image of the other sextet. This overall pattern is clearly seen in the $N = 52 \leftarrow 51$ and $53 \leftarrow 52$ transitions, as shown in Table II. In other transitions, a few hyperfine components were also heavily blended with each other and could not reliably be included in the analysis.

Figure 3 displays the spectrum of the $N = 54 \leftarrow 53$ transition of $^{67}\text{Zn}^{79}\text{Br}$ near 291 GHz. The hyperfine pattern is displayed under the data, and the individual features are indicated by quantum number F . The spin-rotation doublets each exhibit a sextet pattern with two hyperfine lines closely blended in each set near the center of the pattern. For the higher frequency $J = 54.5 \leftarrow 53.5$ spin doublet, F increases with frequency, as mentioned; for the other doublet, the pattern wraps around, with the lowest F value transition lying lowest in frequency, followed by the highest F component and then decreasing monotonically thereafter.

TABLE II. Observed transition frequencies for $^{67}\text{Zn}^{79}\text{Br}$: $X^2\Sigma^+$ ($v = 0$).^a

$N' \leftarrow N''$	$J' \leftarrow J''$	$F' \leftarrow F''$	ν_{obs}	$\nu_o - \nu_c$	$J' \leftarrow J''$	$F' \leftarrow F''$	ν_{obs}	$\nu_o - \nu_c$
48 $\leftarrow$ 47	47.5 $\leftarrow$ 46.5	45 $\leftarrow$ 44	259 197.664	−0.051	48.5 $\leftarrow$ 47.5	46 $\leftarrow$ 45	259 302.831	0.017
		50 $\leftarrow$ 49	259 200.011	−0.037		47 $\leftarrow$ 46	259 303.522	...
		49 $\leftarrow$ 48	259 202.652	0.006		48 $\leftarrow$ 47	259 305.890	−0.020
		48 $\leftarrow$ 47	...	...		49 $\leftarrow$ 48	259 308.422	−0.055
		47 $\leftarrow$ 46	...	...		50 $\leftarrow$ 49	259 311.093	0.022
		46 $\leftarrow$ 45	259 208.322	−0.001		51 $\leftarrow$ 50	259 313.609	0.005
52 $\leftarrow$ 51	51.5 $\leftarrow$ 50.5	49 $\leftarrow$ 48	280 709.926	0.007	52.5 $\leftarrow$ 51.5	50 $\leftarrow$ 49	280 816.428	−0.023
		54 $\leftarrow$ 53	280 712.038	0.063		51 $\leftarrow$ 50	280 816.778	−0.005
		53 $\leftarrow$ 52	280 714.325	0.062		52 $\leftarrow$ 51	280 818.639	0.053
		52 $\leftarrow$ 51	280 716.468	0.009		53 $\leftarrow$ 52	280 820.716	−0.063
		51 $\leftarrow$ 50	280 718.270	0.003		54 $\leftarrow$ 53	280 823.053	−0.010
		50 $\leftarrow$ 49	280 718.567	−0.035		55 $\leftarrow$ 54	280 825.324	−0.009
53 $\leftarrow$ 52	52.5 $\leftarrow$ 51.5	50 $\leftarrow$ 49	286 084.626	0.061	53.5 $\leftarrow$ 52.5	51 $\leftarrow$ 50	286 191.310	−0.064
		55 $\leftarrow$ 54	286 086.568	0.011		52 $\leftarrow$ 51	286 191.694	0.083
		54 $\leftarrow$ 53	286 088.842	0.066		53 $\leftarrow$ 52	286 193.354	0.036
		53 $\leftarrow$ 52	286 090.852	−0.038		54 $\leftarrow$ 53	286 195.442	0.014
		52 $\leftarrow$ 51	286 092.584	−0.017		55 $\leftarrow$ 54	286 197.647	0.004
		51 $\leftarrow$ 50	286 092.880	0.038		56 $\leftarrow$ 55	286 199.910	0.056
54 $\leftarrow$ 53	53.5 $\leftarrow$ 52.5	51 $\leftarrow$ 50	291 457.824	0.029	54.5 $\leftarrow$ 53.5	52 $\leftarrow$ 51	291 564.878	0.025
		56 $\leftarrow$ 55	291 459.673	−0.054		53 $\leftarrow$ 52	...	...
		55 $\leftarrow$ 54	291 461.169	...		54 $\leftarrow$ 53	291 566.742	...
		54 $\leftarrow$ 53	291 463.852	−0.063		55 $\leftarrow$ 54	291 568.626	−0.029
		53 $\leftarrow$ 52	291 465.590	0.056		56 $\leftarrow$ 55	291 570.864	0.061
		52 $\leftarrow$ 51	...	...		57 $\leftarrow$ 56	291 572.967	0.010
55 $\leftarrow$ 54	54.5 $\leftarrow$ 53.5	52 $\leftarrow$ 51	296 829.528	−0.055	55.5 $\leftarrow$ 54.5	53 $\leftarrow$ 52	296 936.878	0.014
		57 $\leftarrow$ 56	296 831.470	0.014		54 $\leftarrow$ 53	296 936.878	−0.064
		56 $\leftarrow$ 55	296 833.541	−0.003		55 $\leftarrow$ 54	296 938.512	0.039
		55 $\leftarrow$ 54	296 835.420	−0.087		56 $\leftarrow$ 55	296 940.365	−0.066
		54 $\leftarrow$ 53	296 837.096	0.055		57 $\leftarrow$ 56	296 942.485	−0.031
		53 $\leftarrow$ 52	296 837.096	−0.025		58 $\leftarrow$ 57	296 944.589	−0.026

^aIn MHz.

FIG. 3. Measured spectrum of the $N = 54 \leftarrow 53$ rotational transition of $^{67}\text{Zn}^{79}\text{Br}$ near 291 GHz. The two spin-rotation doublets, labeled by J and separated by a frequency break, each consist of a hyperfine sextet, arising from the ^{67}Zn nuclear spin of $I = 5/2$. The pattern of the hyperfine lines, which are denoted by F , is shown under the spectrum. The $F = 53 \leftarrow 52$ and $F = 52 \leftarrow 51$ components are blended in each doublet. The sextet spectra were created from an average of 60, 30 MHz wide scans, each scan lasting 60 s in duration. Each spectrum has been truncated to 14 MHz.

IV. ANALYSIS

The data were analyzed using a Hund's case ($b_{\beta 1}$) effective Hamiltonian comprised of rotation, spin-rotation, and zinc

magnetic hyperfine terms (applicable only to $^{67}\text{ZnBr}$)

$$\hat{H}_{\text{eff}} = \hat{H}_{\text{rot}} + \hat{H}_{\text{sr}} + \hat{H}_{\text{mhf}(\text{Zn})}. \tag{1}$$

Specific forms of these Hamiltonian terms are given in Ref. 34. Centrifugal distortion corrections are included in the three terms. The non-linear least squares fitting program SPFIT³⁵ was used to fit the data. The seven isotopologues of ZnBr were fitted separately, as were the various vibrational states. The resulting spectroscopic constants are given in Table III ($v = 0$) and Table IV ($v = 1-3$).

As shown in Table III, with the exception of $^{67}\text{ZnBr}$, all isotopologues of ZnBr were fit with a rotational constant (B), centrifugal distortion constant (D), spin-rotation parameter (γ), and centrifugal distortion correction to spin-rotation (γ_D). The rms of the fits lies in the range 19–41 kHz. The same set of constants successfully fit the $v = 1-3$ states, as shown in Table IV. Here the rms of the fits was somewhat larger (36–67 kHz) because of a lower signal-to-noise ratio. For $^{67}\text{Zn}^{79}\text{Br}$, the hyperfine structure was successfully modeled with the Fermi contact term, b_F , its centrifugal distortion correction, b_{FD} , and the dipolar constant, c , resulting in an rms to the fit of 41 kHz (see Table III). The parameter c had to be fixed in the final analysis because it was defined only to a 2σ uncertainty, not 3σ , as for all other constants. An attempt to fit the quadrupole parameter, eqQ , was not successful, and it was therefore not used in the final fit.

From molecular constants determined in the $v = 0-3$ states, equilibrium parameters were calculated using the following equations:³⁶

TABLE III. Spectroscopic constants for ZnBr: $X^2\Sigma^+$ ($v = 0$).^a

Parameter	$^{64}\text{Zn}^{79}\text{Br}$	$^{64}\text{Zn}^{81}\text{Br}$	$^{66}\text{Zn}^{79}\text{Br}$	$^{66}\text{Zn}^{81}\text{Br}$	$^{67}\text{Zn}^{79}\text{Br}$	$^{68}\text{Zn}^{79}\text{Br}$	$^{68}\text{Zn}^{81}\text{Br}$
B_0	2774.2898(41)	2743.6679(41)	2727.9180(41)	2697.2954(41)	2705.7114(25)	2684.2292(41)	2653.6069(41)
$D \times 10^3$	1.170 91(74)	1.145 18(74)	1.132 18(74)	1.106 90(74)	1.113 84(44)	1.096 01(74)	1.071 33(74)
γ	121.95(86)	120.16(83)	120.40(86)	118.53(86)	118.64(52)	118.08(86)	116.58(86)
$\gamma_D \times 10^4$	−4.5(1.1)	−3.94(99)	−5.0(1.1)	−4.3(1.1)	−3.97(62)	−4.3(1.1)	−4.1(1.1)
b_F (Zn)					1133.9(5.4)		
b_{FD} (Zn)					0.000 66(26)		
c (Zn)					21.06 ^b		
rms	0.025	0.024	0.030	0.019	0.041	0.041	0.030

^aParameters in MHz; quoted uncertainties are 3σ .

^bHeld fixed.

TABLE IV. Spectroscopic Constants for ZnBr: $X^2\Sigma^+$ ($v = 1-3$).^a

Parameter	$v = 1$				$v = 2$		$v = 3$
	$^{64}\text{Zn}^{79}\text{Br}$	$^{64}\text{Zn}^{81}\text{Br}$	$^{66}\text{Zn}^{79}\text{Br}$	$^{66}\text{Zn}^{81}\text{Br}$	$^{64}\text{Zn}^{79}\text{Br}$	$^{64}\text{Zn}^{81}\text{Br}$	$^{64}\text{Zn}^{81}\text{Br}$
B_v	2761.6274(41)	2731.2158(44)	2715.5747(41)	2685.1549(44)	2748.9526(43)	2718.7454(46)	2706.2680(53)
$D_v \times 10^3$	1.172 96(74)	1.147 29(78)	1.134 53(74)	1.108 39(78)	1.175 53(76)	1.148 87(84)	1.152 40(99)
γ	118.10(86)	116.61(91)	116.17(86)	115.23(91)	113.68(88)	112.68(96)	108.8(1.1)
$\gamma_D \times 10^4$	−4.9(1.1)	−4.6(1.1)	−4.7(1.1)	−5.1(1.1)	−4.7(1.1)	−5.0(1.2)	−5.5(1.4)
rms	0.043	0.045	0.038	0.047	0.036	0.042	0.067

^aParameters in MHz; quoted uncertainties are 3σ .

TABLE V. Equilibrium parameters for ZnBr ($X^2\Sigma^+$).^a

Parameter	⁶⁴ Zn ⁷⁹ Br	⁶⁴ Zn ⁸¹ Br	⁶⁶ Zn ⁷⁹ Br	⁶⁶ Zn ⁸¹ Br
B_e (MHz)	2780.626(18)	2749.908(28)	2734.0897(22)	2703.3657(22)
α_e (MHz)	12.669(11)	12.467(12)	12.3433(20)	12.1405(21)
$D_e \times 10^3$ (MHz)	1.169 67(77)	1.1438(20)	1.131 005 0(40)	1.106 155 0(40)
$\beta_e \times 10^6$ (MHz)	2.31(45)	2.32(85)	2.3500(35)	1.4900(36)
γ_e (MHz)	124.11(84)	122.15(39)	122.52(46)	120.18(46)
γ_e' (MHz)	−4.14(49)	−3.79(17)	−4.23(41)	−3.30(42)
ω_e (cm ^{−1})	286	284	284	282
$\omega_e x_e$ (cm ^{−1})	1.04	1.03	1.02	1.01
D_E (eV)	2.45	2.45	2.45	2.45
r_e (Å)	2.268 48(90)	2.268 5(14)	2.268 48(11)	2.268 48(11)

^aQuoted uncertainties are 3 σ .

$$B_v = B_e - \alpha_e(v + 1/2), \quad (2)$$

$$D_v = D_e + \beta_e(v + 1/2), \quad (3)$$

$$\gamma_v = \gamma_e + \gamma_e'(v + 1/2). \quad (4)$$

A least-squares analysis was performed to determine the constants for ⁶⁴Zn⁷⁹Br and ⁶⁴Zn⁸¹Br, as more than one vibrationally excited state was observed. For the other isotopologues, a simple algebraic solution was found. The resulting equilibrium constants are given in Table V. The vibrational frequency (ω_e), anharmonicity constant ($\omega_e x_e$), and dissociation energy (D_E) were then calculated using

$$\omega_e = (4B_e^3/D_e)^{1/2}, \quad (5)$$

$$\omega_e x_e = B_e(\alpha_e \omega_e / 6B_e^2 + 1)^2, \quad (6)$$

$$D_E = (\omega_e^2 / 4\omega_e x_e). \quad (7)$$

The resulting constants, as well as the equilibrium bond length calculated to be 2.268 48(90) Å, are also given in

Table V. From these equations, a Morse potential (plotted in Fig. 4) was made using the following expression, where $k_e = \omega_e^2 \mu$:

$$V(r) = D_e(1 - e^{-\sqrt{k_e/2D_e}(r-r_e)})^2. \quad (8)$$

V. DISCUSSION

This study demonstrates that ZnBr has a $^2\Sigma^+$ ground state, as indicated by previous optical data and predicted by theory.^{20,24} It therefore follows the pattern established by ZnF and ZnCl.^{19,15} The equilibrium bond length, $r_e = 2.268 48(90)$ Å, however, is shorter than the best theoretical value of 2.341 Å.²⁴ It is also significantly shorter than the Zn–Br bond length of 2.42(1) Å, derived from the ZnBr₂ crystal structure.³⁷ Bond lengths have been established for four other 3d diatomic bromides: ScBr ($X^1\Sigma$), TiBr ($X^4\Phi_r$), CuBr ($X^1\Sigma$), and NiBr ($X^2\Pi_i$).^{26–29,31} TiBr has the longest bond length of the series with $r_e = 2.411$ Å, closely followed by ScBr ($r_e = 2.381$ Å), whereas CuBr has the shortest ($r_e = 2.173$ Å), with a similar value for NiBr ($r_0 = 2.178$ Å).

The bond lengths for the 3d bromides appear to follow the trend established by the corresponding chlorides, as plotted in Fig. 5. Here experimental bond lengths of the chlorides^{15,38–46} and the known bromides^{26–29,31} are given as a function of the 3d metal. The bond lengths are r_e , except for the case of VCl, FeCl, NiCl, and NiBr, where it is r_0 . Unfortunately, the bond distances have only been measured accurately for a few of the bromides, as mentioned, while the chloride series is complete. Nevertheless, the variation in bromide bond lengths closely resembles that of the chlorides. The scandium compounds have one of the longest values of the 3d series, with a small increase of ~0.03 Å at titanium. The bond lengths then decrease by ~0.2 Å going to copper and nickel. They subsequently increase at zinc by almost 0.1 Å. The negligible change in the bond length from Ni to Cu for both sets of halides suggests that the additional electron adds to a non-bonding π orbital. Conversely, the distinct increase from Cu to Zn is a likely result of the addition to an anti-bonding (primarily σ) orbital.

FIG. 4. Morse potential curves generated empirically from experimental equilibrium parameters of ZnF¹⁹ (dotted-dashed line), ZnCl¹⁵ (dotted line), and ZnBr (solid line), as well as the theoretical curve for zinc bromide from Ref. 24 (dashed line). The theoretical and empirical curves for ZnBr are in reasonable agreement. The curves show the expected increase in the bond length and well anharmonicity from ZnF to ZnBr.

FIG. 5. A plot of the bond lengths as a function of 3d metals for the chloride and bromide series. Experimental bond lengths have been measured for all chlorides, but only for five bromides (ScBr, TiBr, NiBr, CuBr, and ZnBr). Bond lengths are typically r_e , except in the cases where only r_0 values are available (VCl, FeCl, NiCl, and NiBr). The trend established by the chlorides appears to be replicated in the bromides. The titanium halide has the longest bond length of the 3d series, but only slightly longer (~ 0.03 Å) than that of the scandium species. The bond length shortens by ~ 0.2 Å for copper and nickel, and then increases by almost 0.1 Å at zinc.

The calculated values of the vibrational constants found in this work are $\omega_e = 286$ cm^{-1} and $\omega_e x_e = 1.04$ cm^{-1} . In comparison, the best theoretical value²⁴ is $\omega_e \approx 267.2$ cm^{-1} , roughly similar. The past experimental gas-phase measurement²⁰ of this parameter was $\omega_e \approx 319$ cm^{-1} , closer to our value than the Raman estimate²¹ of $\omega_e \approx 198$ cm^{-1} . This work here resolves the 30-year discrepancy between the reported experimental numbers for ω_e and confirms the theoretical estimate as the most accurate value prior to this study.

The dissociation energy, D_e , determined here from a simple Morse potential model is ~ 2.448 eV [Eq. (7)]. The most accurate theory value is ~ 2.049 eV,²⁴ in reasonable agreement. As shown in Fig. 4, the empirical Morse potential curve and that established by multireference configuration interaction (MRCI) calculations are qualitatively similar. The potential curves for ZnF¹⁹ and ZnCl,¹⁵ derived from equilibrium parameters and a Morse potential, are also displayed in Fig. 4. As expected, there is an increase in the bond length and a decrease in the dissociation energy from ZnF to ZnBr.

The equilibrium spin-rotation parameter, γ_e , for the known zinc halides are ~ 150 , 126 , and 122 MHz for ZnF, ZnCl, and ZnBr, respectively. For these three species, γ_e/B_e is ~ 0.014 , 0.026 , and 0.045 , indicating that the spin-rotation constant does not scale directly with mass, as would be expected to first order. Second-order spin-orbit coupling clearly plays an important role here in determining the value of γ .⁴⁷ The nearest perturber influencing this interaction may be the $A^2\Pi$ state, which results from the promotion of the unpaired σ electron to the nearest π orbital. Elmoussaoui et al.^{24,25} calculate that this state drops in energy from $\sim 38\,000$ cm^{-1} in ZnF to $\sim 33\,000$ and $\sim 32\,000$ cm^{-1} for ZnCl

and ZnBr. Furthermore, there could be other low-lying electronic states that are coupled to the ground $^2\Sigma$ state through H_{so} operator, contributing to the value of γ . Theory suggests there are 19 doublet and quartet excited states in ZnBr lying less than $59\,000$ cm^{-1} in energy.²⁴ New experimental electronic measurements of the zinc halides are clearly needed to confirm their excited state manifolds.

The ^{67}Zn , ^{79}Br , and ^{81}Br nuclei all have nuclear spins, as mentioned, with magnetic moments of 0.87, 2.1, and 2.3 Bohr magnetons, respectively.⁴⁸ In $^{67}\text{Zn}^{79}\text{Br}$, however, the observed hyperfine pattern clearly arises from the ^{67}Zn spin, indicating that the unpaired electron resides primarily on the zinc nucleus, likely in the 15σ orbital chiefly $4s$ in character. The Fermi contact constant (b_F) can give an estimate of the s -character of the orbital of the unpaired electron by comparing it with the atomic value for the $^{67}\text{Zn}^+$ nucleus. As discussed by Flory et al.,¹⁹ a gas-phase value of the Fermi contact term for this nucleus does not exist, but a value of 1425.6 MHz has been established in calcite.⁴⁹ Using this number, $b_F(^{67}\text{ZnBr})/b_F(^{67}\text{Zn}) \approx 0.80$, suggesting the orbital of the unpaired electron is $\sim 80\%$ s character. Alternatively, calculations done by Koh and Miller⁵⁰ using the Roothaan-Hartree-Fock method predict the Fermi contact term of Zn^+ to be 1683.96 MHz. In this case, the percent s character is $\sim 69\%$ for ZnBr.

The s character of the orbital containing the unpaired electron has also been calculated for ZnF and ZnCl.^{19,15} For comparison, these values are listed in Table VI, along with those for ZnBr. Independent of the chosen value of the atomic Fermi contact constant for the $^{67}\text{Zn}^+$ nucleus, the trend is clear. The greatest s contribution to the orbital of the unpaired electron is found for ZnF, followed by ZnCl, and then ZnBr. Therefore, the ionic character of the metal halide bond decreases down the halogen column, as predicted by theory.²⁵ This decrease is thought to arise from the decline in the electronegativity of the halide atom from fluorine to bromine.

The dipolar constant, c , indicates the non-spherical or angular character of the orbital with the unpaired electron, namely, the π and δ contributions. There are no experimental or computational values available for the atomic $^{67}\text{Zn}^+$ dipolar term. Therefore, it is difficult to evaluate the angular part of the orbital with any reliability. However, an estimate of the atomic $^{67}\text{Zn}^+$ dipolar term can be made by the Goudsmit method^{51,52} of analyzing nuclear magnetic moments; see Flory et al.¹⁹ This method yields a value of the dipolar term of ~ 500 MHz, suggesting the non-spherical character in the

TABLE VI. Fermi contact values for ZnF, ZnCl, and ZnBr.^a

Parameter	ZnF ^b	ZnCl ^c	ZnBr
b_F (Zn)	1291.4(1.6)	1192.9(2.6)	1133.9(1.8)
% Zn(4s)	90, ^d 77 ^e	83, ^d 71 ^e	80, ^d 69 ^e

^aIn MHz.

^bReference 19.

^cReference 15.

^dUsing the estimate for $b_F(^{67}\text{Zn}^+)$ derived in calcite; see the text.

^eUsing the theoretical estimate for $b_F(^{67}\text{Zn}^+)$; see the text.

orbital of the unpaired electron in ZnBr is ~4%. This result suggests that the total orbital contribution from the bromine atom in ZnBr is ~16%.

VI. CONCLUSIONS

These measurements constitute the first in-depth spectroscopic study of the ZnBr radical. From this work, molecular properties for zinc bromide have been derived that allow direct comparison with the other zinc halides that have been investigated spectroscopically. ZnBr appears to be less ionic than either ZnCl or ZnF, with more bonding contribution from the bromine atom, in agreement with theoretical predictions. In addition, the bond length in ZnBr appears to increase significantly from neighboring CuBr, in a trend also seen in the 3d chlorides. This study helps to benchmark recent theoretical calculations for zinc bromide. It also lays the foundation for future optical and infrared measurements of this radical.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the complete list of measured transition frequencies for $^{64}\text{Zn}^{79}\text{Br}$, $^{64}\text{Zn}^{81}\text{Br}$, $^{66}\text{Zn}^{79}\text{Br}$, $^{66}\text{Zn}^{81}\text{Br}$, $^{68}\text{Zn}^{79}\text{Br}$, and $^{68}\text{Zn}^{81}\text{Br}$ ($X^2\Sigma^+$) for the $v = 0-3$ vibrational states.

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