

Far-Infrared Rotational Spectra of ZnH and ZnD in the $X^2\Sigma^+$ ($v = 0$) State¹

F. Akif Tezcan,^{*2} Thomas D. Varberg,^{*3} Fred Stroh,^{†4} and Kenneth M. Evenson[†]

^{*}Department of Chemistry, Macalester College, 1600 Grand Avenue, St. Paul, Minnesota 55105; and [†]Time and Frequency Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303

Received April 22, 1997; in revised form August 7, 1997

Several rotational transitions of zinc hydride and deuteride within the $v = 0$ level of the $X^2\Sigma^+$ state have been measured in both electron spin components over the ranges $N'' = 2$ to 10 for ZnH and $N'' = 9$ to 21 for ZnD. A least-squares fit to these data in combination with low- N microwave data measured by other workers has resulted in improved values of the rotational, fine, and hyperfine structure constants. The values of the proton hyperfine constants are discussed in the context of a molecular orbital analysis of zinc hydride. © 1997 Academic Press

INTRODUCTION

In this paper we describe the measurement of the pure rotational spectrum of six isotopomers of zinc hydride in its $X^2\Sigma^+$ ($v = 0$) level by tunable far-infrared spectroscopy. Diatomic metal hydrides are of particular interest to astronomers, as several species of this group including zinc hydride have been detected in the optical spectra of the sun and cool stars (1). Ground state zinc hydride and deuteride were investigated in the infrared region by Jones and co-workers (2, 3), who used tunable diode laser spectroscopy to observe vibrational transitions of four isotopic forms (⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, and ⁶⁸Zn) of ZnH and ZnD. They determined a complete set of Dunham and spin-rotation parameters for each isotopomer and a set of mass-independent parameters for ZnH and ZnD separately. Bernath and co-workers (4) measured the $A^2\Pi-X^2\Sigma^+$ electronic transition of ZnD by Fourier transform emission spectroscopy and determined values of the rotational and spin-rotation constants in both states. Very recently, Goto *et al.* (5) measured the $N = 1-0$ transition of ZnH and the $N = 1-0$ and $2-1$ transitions of ZnD and successfully fitted the observed fine and hyperfine structure.

We recorded the far-infrared spectrum of several isotopic forms of zinc hydride in order to determine the isotopic dependence of the spin-rotation parameter and compare experimental observations with the theoretical predictions of Brown and Watson (6). However, as we discuss later, a

meaningful comparison with theory on this issue will require additional accurate measurements of pure rotational transitions of several isotopomers in excited vibrational levels. In the present work, we report improved values for the rotational, spin-rotation, and magnetic hyperfine parameters of the ⁶⁴Zn, ⁶⁶Zn, and ⁶⁸Zn isotopomers of ZnH and ZnD. We also discuss the fitted values of the proton hyperfine parameters of ZnH in relation to the molecular orbital in which the unpaired electron resides.

EXPERIMENTAL DETAILS

A detailed description of the NIST tunable far-infrared (TuFIR) spectrometer has been given elsewhere (7, 8), so only a brief description is presented here. Far-infrared radiation is generated by mixing the mid-infrared output of two CO₂ lasers (with frequencies ν_1 and ν_2) and a microwave synthesizer (with frequency ν_{MW}) on a metal-insulator-metal (MIM) diode. Two sidebands of frequency $\nu_{FIR} = |\nu_1 - \nu_2| \pm \nu_{MW}$ are generated in this way, and these can be tuned by scanning the frequency of the synthesizer, typically over the range 10–20 GHz. This radiation is then collimated with a parabolic mirror, passed through an absorption cell, and focused onto a liquid-helium-cooled bolometer or photodetector. The first derivatives of the molecular spectra are observed by frequency-modulating one of the two CO₂ lasers at 1 kHz and digitally recording the absorption signals with a lock-in amplifier and a computer. Calculated lineshapes are then fitted to the experimental spectra with an equation containing five adjustable parameters: the transition frequency and intensity, the Gaussian and Lorentzian linewidths, and the spectrometer baseline. For those ZnH spectra with resolvable ¹H hyperfine structure, the transition frequencies of the two observed components were independently varied, but the intensity of the weaker component

¹ The U.S. Government's right to retain a nonexclusive royalty-free license in and to the copyright covering this paper, for governmental purposes, is acknowledged.

² Present address: Division of Chemistry and Chemical Engineering, Caltech, 127-72, Pasadena, CA 91125.

³ To whom correspondence should be addressed. E-mail: varberg@macalester.edu.

⁴ Present address: Institute for Stratospheric Chemistry, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany.

was fixed relative to that of the stronger using the standard intensity formula (9).

Zinc hydride or deuteride was generated in a 112-cm long quartz tube with an outside diameter of 22 mm. The quartz tube had two 1-cm deep depressions spaced 15 cm apart in its center, into which were placed 15 g of zinc powder. A wire electrode was located 6 cm from each end of the tube. During operation, the central portion of the quartz tube was heated to 380°C by placing it in a 33-mm diameter, 30-cm long tube furnace. A dc positive-column electric discharge was ignited and maintained in a 10:1 mixture of Ar and H₂ (or D₂) at a total pressure of 100 Pa (0.8 Torr). An operating temperature of 380°C was chosen to slow the condensation of zinc metal on the cold cell walls at the ends of the tube furnace, since this condensation obstructs the path of the FIR radiation. The tube required cleaning and reloading every 15 hr of operation. The molecular signal intensity increased with discharge current, but the current was held at 60 mA to prevent the cathode from getting too hot. Comparable signals were also obtained with a discharge in pure hydrogen at a pressure of 50 Pa (0.4 Torr).

RESULTS

Several rotational transitions including resolved electron spin fine structure of zinc hydride and deuteride within the $v = 0$ level of the $X^2\Sigma^+$ state were measured over the ranges $N'' = 2$ to 10 for ZnH and $N'' = 9$ to 21 for ZnD (see Tables 1 and 2). Transitions involving the three most abundant isotopes of zinc (⁶⁴Zn, natural abundance of 49%; ⁶⁶Zn, 28%; and ⁶⁸Zn, 19%) were observed. The magnetic hyperfine structure arising from the ¹H nuclear spin ($I = \frac{1}{2}$) was resolved in the lowest three rotational lines of ZnH observed (originating from $N'' = 2, 3,$ and 4). A typical spectrum displaying this hyperfine structure is shown in Fig. 1. The hyperfine structure in all higher rotational transitions in ZnH (and in all lines of ZnD) was obscured by the Doppler broadening of the lines.

During our work, we learned of contemporary measurements of the microwave spectrum of zinc hydride and deuteride by Goto *et al.* (5). We have included their data, which consist of fine and hyperfine components of the $N = 1-0$ transition of ZnH and the $N = 1-0$ and $2-1$ transitions of ZnD, in our data set. The observed transition frequencies of each isotopomer were fitted by least squares using the standard Hamiltonian for a $2\Sigma^+$ state including hyperfine structure. The matrix elements of this Hamiltonian have been given in spherical tensor form by Ryzlewicz *et al.* (10). In fitting the frequencies of transitions which did not display resolved hyperfine structure, the parametrized Hamiltonian contained only the rotational and spin-rotation matrix elements.

Each transition frequency was weighted in the least-squares fit by the square of the inverse of its experimental uncertainty. The FIR transitions measured in the present work were weighted by an experimental uncertainty of 250

kHz. This uncertainty is considerably larger than we reported in earlier work at NIST on the TuFIR spectrum of carbon monoxide, where the uncertainty in the CO₂ laser difference frequency was about 10 kHz (8). We think that the larger experimental uncertainties in the present work may be due to a degradation in the electronics used to lock the CO₂ lasers to line center (which have since been replaced). For the microwave transitions, the experimental uncertainties given in Ref. (5) were used to weight each data point; these uncertainties are listed in Tables 1 and 2 of the present paper.

The results of the least-squares fits for each of the six isotopomers are given in Table 3. We determined values of the rotational constants B and the centrifugal distortion constants D , H , and L . To reduce the number of varied parameters, the parameter L for ⁶⁴ZnH was allowed to vary independently, while the values of L for the ⁶⁶ZnH and ⁶⁸ZnH isotopomers were isotopically scaled in a combined fit to all of the ZnH data. The isotopic scaling chosen was $L^i = \rho^8 L$, where $\rho^2 = \mu/\mu^i$ is the ratio of the reduced masses of two isotopomers (11). An identical procedure was employed for the ZnD data. Similarly for the spin-rotation interaction, the highest-order distortion constant that we could determine (γ_L for ZnH, γ_H for ZnD) was varied for the ⁶⁴Zn isotopomer only and constrained to isotopically scaled values for the ⁶⁶Zn and ⁶⁸Zn isotopomers. We think that this procedure leads to better values of these poorly determined, high-order parameters.

With respect to the hyperfine parameters, the Fermi-contact constant b_F of the ¹H (and ²D) nucleus was well determined for each isotopomer. All three Zn isotopes studied have a nuclear spin of 0. We also included in our hyperfine Hamiltonian the magnetic dipole-dipole coupling constant c and the nuclear spin-rotation coupling constant C_I . For these interactions a single parameter was varied for the three Zn isotopomers of either ZnH or ZnD; given the relative error of the fitted constants, the neglect of any small isotope effect is justified. Goto *et al.* (5) found that these latter parameters were not determinable from their microwave data. However, we found that for ZnH, the inclusion of c and C_I significantly decreases the variance of the least-squares fit relative to the experimental uncertainty (from 4.86 to 1.07), and that the parameters are fairly well determined, judging from their relative uncertainties (about 10%; see Table 3). For ZnD, the inclusion of c also reduced the variance of the fit. The nuclear spin-rotation constant C_I for ZnD was not determinable, which is not surprising, since the highest rotational level providing resolvable hyperfine structure is $N = 2$ for ZnD (compared to $N = 6$ for ZnH). The ratio of c in ZnH to that in ZnD (7.1 ± 3.0) is equal, within the large experimental uncertainty, to the ratio of the nuclear g values of ¹H and ²D (6.5). Our values of b_F are essentially identical to those of Ref. (5), with a modest improvement in precision.

DISCUSSION

Knight and Weltner (12) determined the hyperfine constants of ZnH in an electron spin resonance (ESR) study in

TABLE 1
Observed Rotational Frequencies of ZnH in MHz

$N'-N''$	$J'-J''$	$F'-F''$	^{64}ZnH		^{66}ZnH		^{68}ZnH	
			Observed ^a	O-C ^b	Observed	O-C	Observed	O-C
1-0	0.5-0.5	1-1	384773.741(18) ^c	9	384595.142(20) ^c	-5	384427.123(35) ^c	23
		0-1	384946.053(9) ^c	-2	384767.550(54) ^c	96	384599.437(59) ^c	-4
		1-0	385275.605(9) ^c	-1	385096.963(18) ^c	-5	384929.006(34) ^c	-2
	1.5-0.5	1-1	395991.303(13) ^c	-5	395807.522(21) ^c	7	395634.175(26) ^c	-8
		2-1	396321.009(5) ^c	1	396137.161(18) ^c	-17	395963.903(8) ^c	3
		1-0	396493.180(13) ^c	-2	396309.362(23) ^c	26		
3-2	2.5-1.5	3-2	1172456.166(250)	-170				
		2-1	1172469.758(250)	28				
		3-2	1179993.758(250)	109	1179447.106(250)	191		
4-3	3.5-2.5	4-3	1180006.936(250)	-114	1179459.966(250)	-349		
		3-2	1562978.318(250)	-146	1562254.832(250)	-19	1561572.665(250)	-558
		3-2	1562986.089(250)	228	1562262.209(250)	-38	1561580.642(250)	22
	4.5-3.5	5-4	1570460.136(250)	117	1569733.040(250)	-40	1569048.002(250)	-196
		4-3	1570467.205(250)	-214	1569739.943(250)	-536	1569055.179(250)	-419
		5-4	1952145.768(250)	31	1951242.934(250)	-157	1950392.542(250)	-206
5-4	4.5-3.5	4-3	1952150.772(250)	354	1951247.948(250)	176	1950397.725(250)	296
		6-5	1959561.059(250)	238	1958655.147(250)	224	1957801.429(250)	-21
		5-4	1959565.537(250)	33	1958659.817(250)	212	1957806.079(250)	-53
8-7	7.5-6.5		3108151.271(250)	-231	3106722.366(250)	-153	3105375.991(250)	-147
			3115287.664(250)	103	3113855.456(250)	-25	3112506.500(250)	208
9-8	8.5-7.5		3488530.396(250)	33	3486930.876(250)	195	3485423.798(250)	334
			3865872.112(250)	44	3864104.604(250)	-64	3862439.344(250)	-146
10-9	9.5-8.5		3872755.715(250)	-252			3869317.322(250)	-60
			4246578.709(250)	131				

^aValues in parentheses denote the estimated uncertainty (1σ) of the observed frequencies in kHz.

^bResiduals (Observed - Calculated) in kHz.

^cFrom Ref. (5).

an argon matrix. They found $b_F = A_{\text{iso}} = 478(3)$ or $495(4)$ MHz and $c = 3A_{\text{dip}} = -3(3)$ or $-3(6)$ MHz, depending on the matrix sites. These values of b_F and c agree well with the values reported here.

The small size of the ^1H dipolar coupling constant, $c = -0.28 \pm 0.03$ MHz, deserves some explanation. This parameter may be evaluated as an average over the coordinates of all unpaired electrons in the molecule,

$$c = \frac{3}{2} g \mu_B g_N \mu_N \sum_i \langle (3 \cos^2 \theta_i - 1) r_i^{-3} \rangle, \quad [1]$$

where (r_i, θ_i) are spherical polar coordinates of electron i , defined with respect to the ^1H nucleus (13). To a first approximation, we can write the $X^2\Sigma^+$ electronic configuration as $\cdots 6\sigma^2 3\pi^4 1\delta^4 7\sigma^2 8\sigma$, where the 6σ , 3π , and 1δ orbitals are nearly pure Zn $3d$ atomic orbitals, the 7σ molecular orbital is a filled bonding orbital, and the 8σ orbital containing the unpaired electron can be written as

$$|8\sigma\rangle = c_{4s}|Zn\ 4s\rangle + c_{4p}|Zn\ 4p\sigma\rangle + c_{1s}|H\ 1s\rangle. \quad [2]$$

The hydrogen character of the unpaired electron in the 8σ orbital can be estimated by comparing the fitted value of the ^1H Fermi contact parameter in ZnH to that of a free H atom (14):

$$c_{1s}^2 = \frac{b_F(\text{ZnH } X^2\Sigma^+)}{b_F(\text{free H})} = \frac{501.9 \text{ MHz}}{1420 \text{ MHz}} = 0.353. \quad [3]$$

The coefficients c_{4s} and c_{4p} cannot be determined directly in this way. However, we can write the normalization condition for the 8σ orbital as

$$\begin{aligned} \langle 8\sigma | 8\sigma \rangle &= c_{4s}^2 \langle 4s | 4s \rangle + c_{4p}^2 \langle 4p\sigma | 4p\sigma \rangle \\ &\quad + c_{1s}^2 \langle 1s | 1s \rangle + 2c_{4s}c_{4p} \langle 4s | 4p\sigma \rangle \\ &\quad + 2c_{4s}c_{1s} \langle 4s | 1s \rangle \\ &\quad + 2c_{4p}c_{1s} \langle 4p\sigma | 1s \rangle \\ &= c_{4s}^2 + c_{4p}^2 + c_{1s}^2 \\ &\quad + 2c_{4s}c_{1s} \langle 4s | 1s \rangle \\ &\quad + 2c_{4p}c_{1s} \langle 4p\sigma | 1s \rangle = 1. \end{aligned} \quad [4]$$

TABLE 2
Observed Rotational Frequencies of ZnD in MHz

$N'-N''$	$J'-J''$	$F'-F''$	^{64}ZnD		^{66}ZnD		^{68}ZnD	
			Observed ^a	O-C ^b	Observed	O-C	Observed	O-C
1-0	0.5-0.5	1.5-1.5	196921.446(11) ^c	15	196740.718(14) ^c	27		
		0.5-1.5	196959.862(17) ^c	39	196779.105(3) ^c	-1	196608.948(17) ^c	1
		1.5-0.5	197035.524(6) ^c	-20	196854.883(10) ^c	13	196684.689(14) ^c	18
	1.5-0.5	1.5-1.5	202752.807(7) ^c	-29	202566.857(15) ^c	9	202391.675(31) ^c	48
		2.5-1.5	202815.683(2) ^c	-2	202629.760(8) ^c	27	202454.479(4) ^c	1
		0.5-0.5	202828.581(3) ^c	0	202642.592(16) ^c	-44	202467.372(9) ^c	-3
2-1	1.5-0.5	1.5-0.5	202866.978(11) ^c	29	202681.051(15) ^c	24		
		0.5-0.5	399717.465(21) ^c	30	399350.922(27) ^c	-16	399005.649(71) ^c	-7
		1.5-1.5	399732.814(20) ^c	33	399366.270(17) ^c	-22	399020.931(27) ^c	-72
	2.5-1.5	2.5-2.5	403540.848(8) ^c	13	403170.826(43) ^c	14	402822.167(78) ^c	-18
		1.5-1.5					402846.836(51) ^c	-39
		3.5-2.5	403593.788(11) ^c	28	403223.763(5) ^c	-5	402875.117(14) ^c	6
10-9	9.5-8.5	1992404.332(250)	-74	1990590.432(250)	-127	1988881.675(250)	43	
	10.5-9.5	1996119.042(250)	70	1994301.916(250)	21	1992589.844(250)	-59	
16-15	15.5-14.5			3150014.601(250)	8	3147342.227(250)	-31	
17-16	16.5-15.5		3341909.889(250)	91	3338911.242(250)	240		
	17.5-16.5		3345285.242(250)	-179	3342283.675(250)	-212	3339456.186(250)	91
19-18	18.5-17.5		3715530.799(250)	84	3712215.488(250)	-4	3709091.906(250)	-72
	19.5-18.5		3718778.796(250)	-134	3715461.197(250)	45	3712335.431(250)	23
20-19	19.5-18.5		3899922.845(250)	31	3896453.723(250)	-145	3893185.582(250)	110
	20.5-19.5		3903102.411(250)	1	3899631.184(250)	177	3896360.402(250)	-102
22-21	21.5-20.5		4263446.071(250)	-108				
	22.5-21.5		4266479.060(250)	136	4262710.023(250)	-47		

^aValues in parentheses denote the estimated uncertainty (1σ) of the observed frequencies in kHz.

^bResiduals (Observed - Calculated) in kHz.

^cFrom Ref. (5).

We calculated the overlap integrals in Eq. [4] by numerical integration, in the manner employed by Varberg *et al.* (13) in analyzing the hyperfine structure in MnH, and found that $\langle 4s|1s\rangle = -0.468$ and $\langle 4p\sigma|1s\rangle = 0.545$. The radial functions

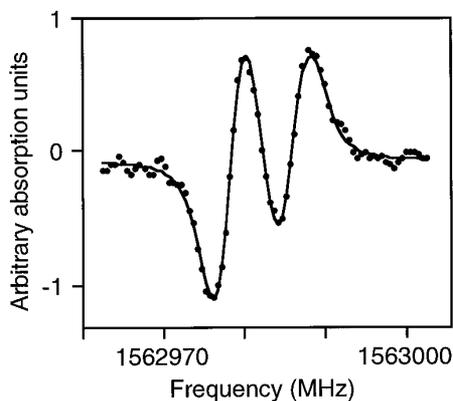


FIG. 1. First-derivative absorption spectrum of the two proton hyperfine components of the $N = 4-3$, $J = 3.5-2.5$ rotational transition of ^{64}ZnH . The circles are the observed data and the solid line is a calculated lineshape. A total of eight scans were recorded and averaged using a 300-msec output time constant on the lock-in amplifier.

of the Zn $|4s\rangle$ and $|4p\sigma\rangle$ orbitals were calculated using a self-consistent field program written by Herman and Skillman (15).

We can also write an expression for the matrix element of the dipolar hyperfine Hamiltonian \hat{H} within the 8σ molecular orbital as

$$\begin{aligned} \langle 8\sigma|\hat{H}|8\sigma\rangle = & c_{4s}^2\langle 4s|\hat{H}|4s\rangle + c_{4p}^2\langle 4p\sigma|\hat{H}|4p\sigma\rangle \\ & + c_{1s}^2\langle 1s|\hat{H}|1s\rangle + 2c_{4s}c_{4p}\langle 4s|\hat{H}|4p\sigma\rangle \\ & + 2c_{4s}c_{1s}\langle 4s|\hat{H}|1s\rangle + 2c_{4p}c_{1s}\langle 4p\sigma|\hat{H}|1s\rangle. \end{aligned} \quad [5]$$

The $\langle 1s|\hat{H}|1s\rangle$ integral is zero by symmetry, because the Hamiltonian has a $(3\cos^2\theta - 1)$ angular dependence and is operating between two spherically symmetric, hydrogen $1s$ orbitals (13). The other integrals appearing in Eq. [5] were evaluated numerically using Herman-Skillman radial functions (15). We found that

$$\begin{aligned} \langle 4s|\hat{H}|4s\rangle &= 23.0 \text{ MHz}, \\ \langle 4p\sigma|\hat{H}|4p\sigma\rangle &= 10.6 \text{ MHz}, \\ \langle 4s|\hat{H}|4p\sigma\rangle &= -7.5 \text{ MHz}, \\ \langle 4s|\hat{H}|1s\rangle &= -12.7 \text{ MHz}, \\ \langle 4p\sigma|\hat{H}|1s\rangle &= 6.4 \text{ MHz}. \end{aligned} \quad [6]$$

TABLE 3
Molecular Parameters of ZnH and ZnD in the $X^2\Sigma^+$ ($v = 0$) State

Parameter	Values in MHz ^a		
	⁶⁴ ZnH	⁶⁶ ZnH	⁶⁸ ZnH
B	196 292.995 2 (22)	196 201.926 1 (49)	196 116.140 8 (50)
D	14.168 02 (33)	14.155 25 (35)	14.143 45 (31)
H	$2.005 (48) \times 10^{-4}$	$2.026 (48) \times 10^{-4}$	$2.059 (44) \times 10^{-4}$
L	$-7.7 (21) \times 10^{-8}$	$[-7.7 \times 10^{-8}]$	$[-7.7 \times 10^{-8}]$
γ	7 588.063 (11)	7 584.569 (16)	7 581.047 (20)
γ_D	-2.384 0 (45)	-2.380 0 (46)	-2.373 9 (44)
γ_H	$3.84 (71) \times 10^{-4}$	$3.66 (64) \times 10^{-4}$	$3.42 (68) \times 10^{-4}$
γ_L	$-1.16 (34) \times 10^{-6}$	$[-1.16 \times 10^{-6}]$	$[-1.16 \times 10^{-6}]$
b_F	501.874 (14)	501.821 (21)	501.908 (34)
c	-0.281 (30)	$[-0.281]$	$[-0.281]$
C_I	0.061 7 (63)	$[0.061 7]$	$[0.061 7]$
	⁶⁴ ZnD	⁶⁶ ZnD	⁶⁸ ZnD
B	100 441.305 1 (15)	100 349.189 3 (18)	100 262.397 4 (36)
D	3.646 521 (77)	3.639 800 (72)	3.633 443 (68)
H	$3.186 (25) \times 10^{-5}$	$3.182 (24) \times 10^{-5}$	$3.175 (22) \times 10^{-5}$
L	$-6.74 (24) \times 10^{-9}$	$[-6.71 \times 10^{-9}]$	$[-6.69 \times 10^{-9}]$
γ	3 896.535 5 (62)	3 893.038 2 (66)	3 889.643 1 (141)
γ_D	-0.609 61 (85)	-0.608 71 (77)	-0.607 61 (78)
γ_H	$1.82 (12) \times 10^{-5}$	$[1.82 \times 10^{-5}]$	$[1.81 \times 10^{-5}]$
b_F	76.075 (8)	76.119 (13)	76.078 (29)
c	-0.039 (16)	$[-0.039]$	$[-0.039]$

^aNumbers in parentheses denote 1σ uncertainties of the last reported digits. Values in square brackets were isotopically scaled relative to the ⁶⁴ZnH(D) value in a manner described in the text. Variance of the least-squares fit relative to the experimental uncertainties: $\sigma^2 = 1.07$ (ZnH) and 2.70 (ZnD).

While the diagonal $c_{4s}^2 \langle 4s | \hat{H} | 4s \rangle$ and $c_{4p}^2 \langle 4p\sigma | \hat{H} | 4p\sigma \rangle$ terms give rise to large positive contributions to the hyperfine parameter c , the cross terms in Eq. [5] will tend to cancel these.

Now, from Eq. [3] we know the magnitude, but not the sign, of the c_{1s} coefficient: $c_{1s} = \pm\sqrt{0.353} = \pm 0.594$. Either choice of sign for c_{1s} leads via Eq. [4] to a separate quadratic equation in c_{4s} and c_{4p} . Each of these two equations gives two solution sets for (c_{4s}, c_{4p}) ; thus we obtain in total four solution sets for (c_{4s}, c_{4p}, c_{1s}) . For any point (c_{4s}, c_{4p}, c_{1s}) in one of these solution sets, we can evaluate Eq. [5] to find the expectation value of the hyperfine parameter c . In Table 4 we have done this over a range of points (c_{4s}, c_{4p}, c_{1s}) for which $0 \leq c_{4s} \leq 1$. While none of the four solution sets anywhere reproduces the observed value of $c = -0.28$ MHz, it is nonetheless satisfying to observe that Solution Set 1 (for which all three coefficients c_{4s} , c_{4p} , and c_{1s} are positive) leads to calculated values of c as small as 1.4 MHz. This result is roughly in agreement with the small experimental

value of the parameter, especially considering that a full unpaired Zn 4s electron would give rise to a much larger value of $c = 23$ MHz in ZnH (Eq. [6]). With all of the coefficients positive, the Zn 4s–4p hybrid orbital is polarized away from the hydrogen atom, giving the 8σ molecular orbital significant nonbonding character.

The proton nuclear spin–rotation parameter C_I in ZnH has been determined here for the first time: $C_I = 62 \pm 6$ kHz. This interaction contains both nuclear (first-order) and electronic (second-order) contributions, and Mizushima (16) has pointed out that for all diatomic molecules except H₂, the second-order terms are nonnegligible and difficult to evaluate. The value we observe in ZnH is consistent in magnitude (ca. 100 kHz or less) with those determined for several other diatomic hydrides (16).

Brown and Watson (6) have shown from theoretical considerations that the spin–rotation coupling constant γ_e is proportional to μ , the reduced mass of the molecule. It would be interesting to test this result using the rather precise data

TABLE 4
Calculated Values of the Proton Dipolar
Hyperfine Parameter c^a

c_{1s}	c_{4s}	c_{4p}	c	c_{4p}	c
			<u>Solution Set 1</u>	<u>Solution Set 2</u>	
0.594	0.000	0.543	7.3	-1.191	6.0
0.594	0.100	0.569	5.6	-1.217	7.0
0.594	0.200	0.583	4.2	-1.231	8.3
0.594	0.300	0.587	3.0	-1.234	9.9
0.594	0.400	0.579	2.1	-1.226	11.6
0.594	0.500	0.559	1.6	-1.207	13.5
0.594	0.600	0.528	1.4	-1.176	15.5
0.594	0.700	0.483	1.8	-1.131	17.5
0.594	0.800	0.422	2.7	-1.070	19.5
0.594	0.900	0.341	4.3	-0.989	21.2
0.594	1.000	0.231	6.8	-0.879	22.6
			<u>Solution Set 3</u>	<u>Solution Set 4</u>	
-0.594	0.000	1.191	6.0	-0.543	7.3
-0.594	0.100	1.152	5.3	-0.505	9.0
-0.594	0.200	1.099	5.1	-0.451	10.9
-0.594	0.300	1.027	5.4	-0.380	12.7
-0.594	0.400	0.932	6.2	-0.284	14.4
-0.594	0.500	0.797	8.0	-0.149	15.8
-0.594	0.600 ^b	0.565	11.3	0.083	16.0

^aValues of c (in MHz) are calculated from Eqs. [5] and [6] using values of (c_{4s} , c_{4p} , c_{1s}) which simultaneously satisfy Eqs. [3] and [4]. The two columns labeled c_{4p} indicate the two solutions for c_{4p} which are possible for the given values of c_{1s} and c_{4s} . Each of these results in a different value of the hyperfine parameter c .

^bFor $c_{4s} \geq 0.700$, Eq. [4] gives no real roots for c_{4p} .

set presented here for six isotopomers of zinc hydride. Essentially, we would try fitting all of the data to a single set of mass-independent Dunham parameters and see whether a mass-scaling factor is required in accurately fitting the spin-rotation interaction (analogous to the mass-scaling factors Δ_{kl} introduced by Watson (17) for describing the isotopic dependence of the Dunham vibration-rotation coefficients Y_{kl}). This scheme was employed by Birk *et al.* (3) in fitting the infrared spectra of ZnH and ZnD. They showed that no such mass-scaling factors for the spin-rotation interaction

were required at the precision of their infrared data set. We have not attempted a similar fit to a combined data set composed of the infrared (2, 3), far-infrared, and microwave (5) measurements, because we think that the accuracy of such a fit will be limited by the less precise infrared data, which provide the only direct information on the higher vibrational levels.

ACKNOWLEDGMENTS

We thank Lyndon Zink and John Brown for helpful discussions. This research was supported at NIST by NASA Grant W-18, 913 and at Macalester by a William and Flora Hewlett Foundation Award of Research Corporation. F.A.T. acknowledges support in the form of a summer undergraduate research stipend from the Violet Olson Beltmann Fund of Macalester College. F.S. is grateful for a Feodor-Lynen Fellowship given by the Alexander von Humboldt Foundation.

REFERENCES

1. R. F. Wing, J. Cohen, and J. W. Brault, *Astrophys. J.* **216**, 659-664 (1977).
2. R.-D. Urban, U. Magg, H. Birk, and H. Jones, *J. Chem. Phys.* **92**, 14-21 (1990).
3. H. Birk, R.-D. Urban, P. Polomsky, and H. Jones, *J. Chem. Phys.* **94**, 5435-5442 (1991).
4. L. C. O'Brien, W. T. M. L. Fernando, and P. F. Bernath, *J. Mol. Spectrosc.* **139**, 424-431 (1990).
5. M. Goto, K. Namiki, and S. Saito, *J. Mol. Spectrosc.* **173**, 585-590 (1995).
6. J. M. Brown and J. K. G. Watson, *J. Mol. Spectrosc.* **65**, 65-74 (1977).
7. L. R. Zink, M. Prevedelli, K. M. Evenson, and M. Inguscio, in "Applied Laser Spectroscopy" (W. Demtröder and M. Inguscio, Eds.), pp. 141-148. Plenum, New York, 1990.
8. T. D. Varberg and K. M. Evenson, *Astrophys. J.* **385**, 763-765 (1992).
9. W. Gordy and R. L. Cook, "Microwave Molecular Spectra," Eq. (15.139), p. 832, Wiley-Interscience, New York, 1984.
10. Ch. Ryzlewicz, H.-U. Schütze-Pahlmann, J. Hoeft, and T. Törring, *Chem. Phys.* **71**, 389-399 (1982).
11. G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., pp. 141-145. Van Nostrand-Reinhold, New York, 1950.
12. L. B. Knight, Jr. and W. Weltner, Jr., *J. Chem. Phys.* **55**, 2061-2070 (1971).
13. T. D. Varberg, R. W. Field, and A. J. Merer, *J. Chem. Phys.* **95**, 1563-1576 (1991).
14. W. Weltner, Jr., "Magnetic Atoms and Molecules," pp. 57-58. Van Nostrand-Reinhold, New York, 1983.
15. F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, 1963.
16. M. Mizushima, "The Theory of Rotating Diatomic Molecules," pp. 174-185. Wiley, New York, 1975.
17. J. K. G. Watson, *J. Mol. Spectrosc.* **80**, 411-421 (1980).