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

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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.

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 (\( ^{64}\text{Zn}, \ ^{66}\text{Zn}, \ ^{67}\text{Zn}, \text{ and} \ ^{68}\text{Zn} \)) 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 \( A''\Pi-X^2\Sigma^+ \) 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 isotopomers 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 \( ^{64}\text{Zn}, \ ^{66}\text{Zn}, \text{ and} \ ^{68}\text{Zn} \) 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 CO\(_2\) lasers (with frequencies \( \nu_1 \) and \( \nu_2 \)) and a microwave synthesizer (with frequency \( \nu_{\text{MW}} \)) on a metal–insulator–metal (MIM) diode. Two sidebands of frequency \( \nu_{\text{FIR}} = |\nu_1 - \nu_2| \pm \nu_{\text{MW}} \) 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 photoductor. The first derivatives of the molecular spectra are observed by frequency-modulating one of the two CO\(_2\) 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 \( ^1\text{H} \) hyperfine structure, the transition frequencies of the two observed components were independently varied, but the intensity of the weaker component
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 \( \nu = 0 \) 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 (\(^{66}\)Zn, natural abundance of 49%; \(^{68}\)Zn, 28%; and \(^{64}\)Zn, 19%) were observed. The magnetic hyperfine structure arising from the \(^1\)H 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 \( N = 1 \rightarrow 0 \) transition of ZnH and the \( N = 1 \rightarrow 0 \) and \( 2 \rightarrow 1 \) 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 \( \Sigma^+ \) 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 \(^{64}\)ZnH was allowed to vary independently, while the values of \( L \) for the \(^{66}\)ZnH and \(^{68}\)ZnH isotopomers were isotopically scaled in a combined fit to all of the ZnH data. The isotopic scaling chosen was \( L' = \rho^8 L \), where \( \rho^2 = \mu^2 / \mu'^2 \) 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 (\( \gamma_5 \) for ZnH, \( \gamma_4 \) for ZnD) was varied for the \(^{64}\)Zn isotopomer only and constrained to isotopically scaled values for the \(^{66}\)Zn and \(^{68}\)Zn 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 \( b_x \) of the \(^1\)H (and \(^3\)D) 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 \(^1\)H and \(^3\)D (6.5). Our values of \( b_x \) 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

<table>
<thead>
<tr>
<th>(N' - N'')</th>
<th>(J' - J'')</th>
<th>(F' - F'')</th>
<th>(6^{6})ZnH</th>
<th>(6^{6})ZnH</th>
<th>(6^{8})ZnH</th>
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<tr>
<td></td>
<td>Observed&lt;sup&gt;a&lt;/sup&gt;</td>
<td>O-C&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Observed</td>
<td>O-C</td>
<td>Observed</td>
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<tr>
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<td>0.5-0.5</td>
<td>1-1</td>
<td>384773.741(18)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>9</td>
<td>384595.142(20)&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
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<td>1-0</td>
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<td>-2</td>
<td>384767.550(54)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
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<td>1-1</td>
<td>385275.605(9)&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
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<td>2-1</td>
<td>396321.009(5)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-1</td>
<td>396137.161(18)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>1-0</td>
<td>2-1</td>
<td>396493.180(13)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-2</td>
<td>396309.362(23)&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>1179447.106(250)</td>
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<td>1562254.832(250)</td>
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<td>1951242.934(250)</td>
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<td>5-4</td>
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<td>354</td>
<td>1951247.948(250)</td>
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<td>5-4</td>
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<td>-231</td>
<td>3106722.366(250)</td>
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<td>3488530.396(250)</td>
<td>33</td>
<td>3486920.876(250)</td>
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<td>3865872.112(250)</td>
<td>44</td>
<td>3864104.604(250)</td>
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<td>110-10-10.5</td>
<td>4246657.709(250)</td>
<td>131</td>
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<sup>a</sup>Values in parentheses denote the estimated uncertainty (1σ) of the observed frequencies in kHz.

<sup>b</sup>Residuals (Observed – Calculated) in kHz.

<sup>c</sup>From Ref. (5).

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 \( ^1\)H 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,

\[
c = \frac{3}{2} g \mu_B g_N \mu_N \sum_i \left( 3 \cos^2 \theta_i - 1 \right) r_i^{-3}, \tag{1}
\]

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

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

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

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

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

\[
\langle 8\sigma | 8\sigma \rangle = c_{4s}^2 \langle 4s | 4s \rangle + c_{4p}^2 \langle 4p \sigma | 4p \sigma \rangle + 2c_{1s}c_{4s} \langle 4s | 1s \rangle + 2c_{4p}c_{1s} \langle 4p \sigma | 1s \rangle \quad [4]
\]

\[
= c_{4s}^2 + c_{4p}^2 + c_{1s}^2 + 2c_{4s}c_{1s} \langle 4s | 1s \rangle + 2c_{4p}c_{1s} \langle 4p \sigma | 1s \rangle = 1.
\]
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
\[
\langle 4s | 1s \rangle = -0.468 \quad \text{and} \quad \langle 4p \sigma | 1s \rangle = 0.545.
\]
The radial functions 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 8$\sigma$ molecular orbital as
\[
\langle 8\sigma | \hat{H} | 8\sigma \rangle = c_{4s}^2 \langle 4s | \hat{H} | 4s \rangle + 2c_{4s}c_{4p\sigma} \langle 4p \sigma | \hat{H} | 4p \sigma \rangle + c_{4p\sigma}^2 \langle 4p \sigma \sigma | \hat{H} \sigma | 4p \sigma \sigma \rangle.
\]

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
\[
\langle 4s | \hat{H} | 4s \rangle = 23.0 \text{ MHz},
\]
\[
\langle 4p \sigma | \hat{H} | 4p \sigma \rangle = 10.6 \text{ MHz},
\]
\[
\langle 4s | \hat{H} | 1s \rangle = -7.5 \text{ MHz},
\]
\[
\langle 4p \sigma | \hat{H} | 1s \rangle = -12.7 \text{ MHz},
\]
\[
\langle 4p \sigma | \hat{H} | 1s \rangle = 6.4 \text{ MHz}.
\]
While the diagonal $c_z^2(4s|\hat{H}|4s)$ and $c_y^2(4p\sigma|\hat{H}|4p\sigma)$
terms give rise to large positive contributions to the hyper-
fine 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: $c_{1s} = \pm 0.353 = \pm 0.594$. Either
choice of sign for $c_{1s}$ leads via Eq. [4] to a separate quadratic
equation in $c_{2s}$ and $c_{4p}$. Each of these two equations gives
two solution sets for $(c_{2s}, c_{4p})$; thus we obtain in total four
solution sets for $(c_{2s}, c_{4p}, c_{1s})$. In some 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 $(c_{2s}, c_{4p}, c_{1s})$
for which $0 \leq c_{2s} \leq 1$. 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 $c_{2s}$, $c_{4p}$, 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

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<tr>
<th>Parameter</th>
<th>$^{64}$ZnH</th>
<th>$^{66}$ZnH</th>
<th>$^{68}$ZnH</th>
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</thead>
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<tr>
<td>B</td>
<td>196 292.995 (22)</td>
<td>196 201.926 1 (49)</td>
<td>196 116.140 8 (50)</td>
</tr>
<tr>
<td>D</td>
<td>14.168 02 (33)</td>
<td>14.155 25 (35)</td>
<td>14.143 45 (31)</td>
</tr>
<tr>
<td>H</td>
<td>2.005 (48) × 10^{-4}</td>
<td>2.026 (48) × 10^{-4}</td>
<td>2.059 (44) × 10^{-4}</td>
</tr>
<tr>
<td>L</td>
<td>-7.7 (21) × 10^{-8}</td>
<td>[-7.7 × 10^{-8}]</td>
<td>[-7.7 × 10^{-8}]</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>7 588.063 (11)</td>
<td>7 584.569 (16)</td>
<td>7 581.047 (20)</td>
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<td>-2.380 0 (46)</td>
<td>-2.373 9 (44)</td>
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<td>501.874 (14)</td>
<td>501.821 (21)</td>
<td>501.908 (34)</td>
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<tr>
<td>c</td>
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<td>$C_l$</td>
<td>0.061 7 (63)</td>
<td>[0.061 7]</td>
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<th>$^{66}$ZnD</th>
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<td>100 349.189 3 (18)</td>
<td>100 262.397 4 (36)</td>
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<td>D</td>
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<td>3.639 800 (72)</td>
<td>3.633 443 (68)</td>
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<tr>
<td>H</td>
<td>3.186 (25) × 10^{-5}</td>
<td>3.182 (24) × 10^{-5}</td>
<td>3.175 (22) × 10^{-5}</td>
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<td>L</td>
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<td>[-6.69 × 10^{-9}]</td>
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<td>3 893.038 2 (66)</td>
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<td>-0.608 71 (77)</td>
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<td>c</td>
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<td>[-0.039]</td>
<td>[-0.039]</td>
</tr>
</tbody>
</table>

$^a$Numbers in parentheses denote 1σ uncertainties of the last reported digits. Values in
square brackets were isotopically scaled relative to the $^{64}$ZnH(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).

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

The proton nuclear spin–rotation parameter $C_l$ in ZnH
has been determined here for the first time: $C_l = 62 \pm 6$
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
$H_2$, 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
which 0

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 8s
molecular orbital significant nonbonding character.

Brown and Watson (6) have shown from theoretical con-
siderations that the spin–rotation coupling constant $\gamma_c$
is proportional to $\mu$, the reduced mass of the molecule. It would
be interesting to test this result using the rather precise data
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.

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