

Experimental Vibrational Zero-Point Energies: Diatomic Molecules

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Vibrational zero-point energies (ZPEs), as determined from published spectroscopic constants, are derived for 85 diatomic molecules. Standard uncertainties are also provided, including estimated contributions from bias as well as the statistical uncertainties propagated from those reported in the spectroscopy literature. This compilation will be helpful for validating theoretical procedures for predicting ZPEs, which is a necessary step in the *ab initio* prediction of molecular energetics. © 2007 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.. [DOI: 10.1063/1.2436891]

Key words: molecular energetics; uncertainty; vibrational spectroscopy; zero-point energy.

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1. Introduction

One of the most popular uses of computational quantum chemistry models is to predict molecular energetics, which is required for applications such as thermochemistry and reaction kinetics. As a result of steady progress in electronic structure theory and computational efficiency, the precision of *ab initio* molecular energetics has improved by a factor of

about 10 every 10 years. With the advent of basis-set extrapolation methods and highly correlated theories, the energetics of small molecules can now be computed to high precision almost routinely.¹ As the uncertainties in electronic energy fall away, other sources of uncertainty become increasingly noticeable. Vibrational zero-point energy (ZPE) has emerged as one of the principal remaining sources of uncertainty in calculations of molecular energetics. In careful work, it is necessary to go beyond the harmonic approximation to obtain a reliable ZPE.²⁻⁵ However, the most common practice is simply to scale the computed harmonic ZPE by a multiplicative correction factor. The empirical scaling factor carries uncertainty. We have recently quantified the uncertainties associated with scaling factors for fundamental vibrational frequencies.⁶ The uncertainties associated with the experimental vibrational frequencies were required in the analysis, although in the end their contribution was small enough to be neglected. Similar work is underway to provide scaling factors, with their associated uncertainties, appropriate for routine predictions of ZPE. Unfortunately, we have been unable to locate any recent compilations of experimentally derived ZPEs, or compilations of any age that include uncertainties. Moreover, existing compilations include few data for polyatomic molecules. We are now working to fill this gap by providing benchmark, experimental ZPEs along with the associated uncertainties. The present list, restricted to diatomic molecules, is not intended to be exhaustive. Nevertheless, it is the largest such list yet assembled, the first to employ spectroscopic data more recent than those compiled by Huber and Herzberg,⁷ and the first to include uncertainties.

2. Definition of Zero-Point Energy

In quantum chemistry, the Born-Oppenheimer approximation (BOA) is almost⁸ always accepted. Thus, the most common definition of the molecular ZPE is the energy difference between the vibrational ground state and the lowest point on the Born-Oppenheimer potential energy surface. Unfortu-

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nately, this definition is not convenient for experimental ZPEs, as the BOA is never adopted by real molecules. Experimental spectra are generally analyzed, however, as if the BOA were followed by real molecules; explicit Born-Oppenheimer corrections are only made when simultaneously fitting different isotopologs to the same effective potential. Thus, in the present compilation, the experimental ZPE is defined as the difference between the molecular ground state and the lowest point on its isotope-specific effective potential. The small difference between this definition and that used by quantum chemists must be absorbed by the empirical scaling factor that is typically applied to theoretically determined ZPEs.

The ZPE cannot be measured directly since no molecule can be observed below its ground state. Instead, the term “experimental ZPE” describes a value that is usually (but not necessarily⁹) derived by combining experimental spectroscopic constants with standard theoretical or empirical models for anharmonic oscillators. Thus, “experimental” ZPE values are actually hybrids of experiment and theoretical modeling.

Most available experimental ZPEs are for diatomic molecules, because far fewer spectroscopic constants are needed for diatomic molecules than for polyatomic molecules. Although the field of molecular spectroscopy is home to crowds of molecular constants, among nonspecialists the most common expression for the vibrational energy levels of a diatomic molecule, relative to the minimum on the potential energy curve, is

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2. \quad (1)$$

In Eq. (1), ω_e and $\omega_e x_e$ are the harmonic frequency and the first anharmonicity constant, respectively, and v is the vibrational quantum number, which can assume nonnegative integer values.¹⁰ Note that the symbol $\omega_e x_e$ represents a single constant, not a product. Thus, the most popular expression for diatomic ZPE is, to second order in $(v + \frac{1}{2})$,

$$\text{ZPE} = G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e. \quad (2)$$

This expression is derived by extrapolating Eq. (1) to $v_i = -\frac{1}{2}$, which corresponds to the lowest point on the effective potential, to a good approximation.¹¹ Contributions from higher-order anharmonicities are generally negligible (e.g., 0.1 cm⁻¹ for H₂, 0.07 cm⁻¹ for OH, and 0.0013 cm⁻¹ for CO). Unfortunately, as has been pointed out recently,²⁻⁵ the popular expression is incorrect.

In addition to the linear and quadratic terms in Eq. (1), there is a constant term that is usually overlooked. This was demonstrated by Dunham in his classic power-series analysis.¹² The resulting energy levels, to second order, are given by

$$G(v) = Y_{00} + Y_{10} \left(v + \frac{1}{2} \right) + Y_{20} \left(v + \frac{1}{2} \right)^2, \quad (3)$$

where $Y_{10} \approx \omega_e$ and $Y_{20} \approx -\omega_e x_e$ to good approximations. The constant Y_{00} does not influence the line positions (i.e., energy intervals) in a spectrum but contributes to the ZPE. In this

paper we include Y_{00} and even the third-order term (second anharmonicity constant) when available. Thus, ZPEs of diatomic molecules are taken to be

$$\text{ZPE} = G(0) = Y_{00} + \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + \frac{1}{8} \omega_e y_e, \quad (4)$$

where $Y_{30} \approx \omega_e y_e$. To a good approximation, Y_{00} can be expressed in terms of conventional spectroscopic constants as¹³

$$Y_{00} \approx \frac{B_e}{4} + \frac{\alpha_e \omega_e}{12B_e} + \frac{\alpha_e^2 \omega_e^2}{144B_e^3} - \frac{\omega_e x_e}{4}. \quad (5)$$

The Dunham constants that correspond to the conventional rotational constants here are $Y_{01} \approx B_e$ and $Y_{11} \approx -\alpha_e$. The value of Y_{00} is largest for H₂ ($Y_{00} = 8.9$ cm⁻¹), smaller for hydrides such as OH ($Y_{00} = 3.0$ cm⁻¹), and less than one wavenumber for nonhydrides such as CO ($Y_{00} = 0.2$ cm⁻¹).

3. Selection of Molecules

An initial list of molecules and associated ground-state spectroscopic constants was culled from the classic compilation by Huber and Herzberg⁷ and from the NIST Diatomic Spectral Database.¹⁴ For compatibility with the NIST Computational Chemistry Comparison and Benchmark Database,¹⁵ only molecules composed of elements lighter than argon (i.e., atomic number $Z < 18$) were included. More recent values of constants were taken from the spectroscopic literature as available. Since our goal is a list of reliable ZPEs, diatomic molecules were excluded if their ZPEs obviously (upon cursory analysis) had standard uncertainties of about 0.5 cm⁻¹ or more. Our final list of diatomic molecules, with their spectroscopic constants, is provided in Table 1. (In Table 1, and throughout this paper, H refers specifically to protium and D to deuterium.) Standard uncertainties are listed in the spectroscopic style. For example, the quantity 12.345 ± 0.067 would be written 12.345(67). When the ground state is classically degenerate (usually ²Π), averaged constants are used, as reported in the experimental sources cited. This choice was made for convenient comparison with conventional, non-relativistic quantum chemistry calculations. For Cl₂⁺, only separate constants for ²Π_{3/2} and ¹Π_{3/2} were reported.⁷

4. Contributions to Uncertainties

The spectroscopic constants have both statistical uncertainty (i.e., uncertainty from random effects) and bias (i.e., systematic error). As we are interested in the ZPE, it is necessary to determine how the uncertainties in the constants contribute to the uncertainty in the corresponding ZPE. For this purpose, we accept the common linearized propagation of uncertainties¹⁶ given by

$$\sigma_y^2 \approx \sum_i \sigma_{ii} (\partial y / \partial x_i)^2 + 2 \sum_{i < j} \sigma_{ij} (\partial y / \partial x_i) (\partial y / \partial x_j), \quad (6)$$

for a quantity $y = f(x_1, x_2, \dots, x_i, \dots)$, where σ_y^2 is the estimated variance of y and $\sigma_{ij} = \langle (x_i - \bar{x}_i)(x_j - \bar{x}_j) \rangle$ is the element of the covariance matrix that corresponds to the pair of vari-

TABLE I. Spectroscopic constants for selected diatomic molecules. Standard uncertainties (1σ) are between parentheses and refer to the least significant digits. Values are in wavenumber units (cm^{-1}).

Molecule	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	Reference
First-row elements only						
H ₂	4401.213(18)	121.336(18)	0.8129(18)	60.8530(18)	3.0622(18)	7
HD	3813.15(18)	91.65(9)	0.723(9)	45.655(9)	1.986(9)	7
D ₂	3115.50(9)	61.82(9)	0.562(9)	30.4436(18)	1.0786(9)	7
Second-row elements						
BeH	2061.235(15)	37.327(22)	0.084(17)	10.31992(5)	0.3084(2)	22
BeD	1529.986(11)	20.557(12)	0.035(7)	5.68830(3)	0.1261(1)	22
Be ¹⁸ O	1457.09(22)	11.311(74)	0.0143(83)	1.5847(5)	0.01784(15)	33
BF	1402.15865(26)	11.82106(15)	0.051595(35)	1.51674399(21)	0.01904848(22)	23
BH	2366.7296(16)	49.33983(99)	0.362(10)	12.025755(45)	0.421565(22)	34
BO	1885.286(41)	11.694(11)	-0.00952(83)	1.781110(31)	0.016516(17)	35
C ₂	1855.0663(63)	13.6007(54)	-0.116(2)	1.820053(11)	0.0179143(44)	36
C ₂ ⁻	1781.189(18)	11.6717(48)	0.009981(28)	1.74666(32)	0.01651(46)	37
CF	1307.93(37)	11.08(12)	0.093(15)	1.41626(48)	0.01844(17)	38
CH	2860.7508(98)	64.4387(85)	0.3634(27)	14.45988(20)	0.53654(33)	39
CD	2101.05193(55)	34.72785(58)	0.14147(10)	7.8079823(55)	0.212240(11)	40
CN	2068.648(11)	13.0971(68)	-0.0124(17)	1.89978316(67)	0.0173720(12)	41
CO	2169.75589(8)	13.28803(2)	0.0104109(14)	1.9316023(7)	0.01750513(14)	42
CO ⁺	2214.127(35)	15.094(21)	-0.0117(34)	1.976941(39)	0.018943(34)	43 and 44
F ₂	916.929(10)	11.3221(10)	-0.10572(67)	0.889294(11)	0.0125952(24)	45
HF	4138.3850(7)	89.9432(7)	0.92449(31)	20.953712(2)	0.7933704(65)	46
Li ₂	351.4066(10)	2.58324(41)	-0.00583(7)	0.6725297(50)	0.0070461(16)	47 and 48
LiF	910.57272(10)	8.207956(46)	0.569166(82)	1.34525715(57)	0.02028749(19)	49
LiH	1405.49805(76)	23.1679(7)	0.17093(28)	7.5137315(9)	0.2163911(24)	50
LiD	1054.93973(32)	13.05777(21)	0.075478(50)	4.23308131(46)	0.09149428(84)	50
LiO	814.62(15)	7.78(15)	NA	1.21282948(11)	0.0178990(25)	27
N ₂	2358.57(9)	14.324(9)	-0.00226(9)	1.998241(18)	0.017318(9)	7
N ₂ ⁺	2207.0115(60)	16.0616(23)	-0.04289(25)	1.93176(9)	0.01881(9)	vib, ⁵¹ rot ⁷
NF	1141.37(9)	8.99(9)	NA	1.205679(53)	0.014889(53)	vib, ⁷ rot ⁵²
NH	3282.72(10)	79.04(8)	0.367(23)	16.66792(6)	0.65038(17)	53
ND	2399.126(30)	42.106(21)	0.1203(54)	8.90867(15)	0.25457(19)	54
NO	1904.1346(18)	14.08836(89)	0.01005(20)	1.7048885(21)	0.0175416(14)	55
NO ⁺	2376.72(11)	16.255(18)	-0.01562(92)	1.997195(89)	0.018790(69)	56
O ₂	1580.161(9)	11.95127(9)	0.0458489(9)	1.44562(9)	0.0159305(9)	57
O ₂ ⁺	1905.892(82)	16.489(13)	0.02057(90)	1.689824(91)	0.019363(37)	58
FO	1053.0138(12)	9.9194(13)	-0.06096(59)	1.05870763(81)	0.0132951(23)	59
OH	3737.761(18)	84.8813(18)	0.5409(18)	18.9108(18)	0.7242(9)	7
OD ⁺	2271.80(9)	44.235(9)	0.4267(18)	8.9116(18)	0.2896(9)	7
Third-row elements						
AlCl	481.77466(20)	2.101811(88)	0.006638(15)	0.243930066(12)	0.001611082(12)	60
AlF	802.32447(11)	4.849915(44)	0.0195738(68)	0.552480208(65)	0.004984261(44)	23
AlH	1682.37474(31)	29.05098(29)	0.24762(12)	6.3937842(17)	0.1870527(15)	61
AlD	1211.77402(15)	15.06477(11)	0.09244(4)	3.3183929(8)	0.0698773(4)	61
AlO	979.4852(50)	7.0121(32)	-0.00206(56)	0.6413856(54)	0.0057796(8)	62
AlS	617.1169(33)	3.3310(19)	-0.00924(32)	0.2800368(33)	0.00178225(55)	63
BCl	840.29472(63)	5.49170(33)	0.02995(7)	0.684282(12)	0.0068124(14)	17
BeS	997.94(9)	6.137(9)	NA	0.79059(9)	0.00664(9)	7
BS	1179.91(3)	6.25(3)	-0.0083(58)	0.79478(5)	0.00578(4)	64
CCl	876.89749(69)	5.44698(54)	0.02607(15)	0.697137(34)	0.00685277(45)	25
Cl ₂	559.751(20)	2.69427(20)	-0.003325(2)	0.24415(20)	0.001516(20)	65
Cl ₂ ⁺	645.61(9)	3.015(9)	0.007(9)	0.26950(18)	0.00164(9)	7
($\Omega=1/2$)	644.77(9)	2.988(9)	NA	0.2697(9)	0.00167(9)	7
ClF	783.4534(24)	4.9487(6)	-0.0176(1)	0.5164805(31)	0.0043385(8)	66
ClO	853.64268(13)	5.51828(6)	-0.01256(30)	0.62345797(4)	0.0059357(1)	28
CP	1239.79924(8)	6.833769(46)	-0.001377(7)	0.79886775(8)	0.00596933(19)	67
CS	1285.15464(10)	6.502605(53)	0.003887(9)	0.82004356(4)	0.00591835(5)	68
HCl	2990.9248(15)	52.8000(15)	0.21803(55)	10.5933002(13)	0.3069985(41)	69

TABLE 1. Spectroscopic constants for selected diatomic molecules. Standard uncertainties (1σ) are between parentheses and refer to the least significant digits. Values are in wavenumber units (cm^{-1}).—Continued

Molecule	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	Reference
DCI	2145.1326(11)	27.1593(7)	0.07993(20)	5.4487838(6)	0.1132345(15)	69
HCl ⁺	2673.69(9)	52.537(9)	NA	9.95661(18)	0.32716(18)	7
LiCl	642.95453(93)	4.47253(40)	0.020118(49)	0.70652247(20)	0.00801019(32)	70
NaLi	256.5412(19)	1.62271(96)	-0.00495(22)	0.3758620(89)	0.0031465(15)	30
Mg ₂	51.121(18)	1.645(9)	0.01624(18)	0.09287(9)	0.003776(18)	7
MgH	1492.7763(36)	29.847(4)	-0.3048(20)	5.8255229(41)	0.177298(14)	71
MgD	1077.2976(26)	15.521(2)	-0.1184(7)	3.0343436(21)	0.066607(5)	71
MgO	785.2183(6)	5.1327(3)	0.01649(7)	0.5748414(3)	0.0053223(3)	72
MgS	528.74(9)	2.704(9)	NA	0.26797(9)	0.00176(9)	7
Na ₂	159.08548(44)	0.70866(29)	-0.004632(77)	0.15473537(29)	0.00086375(11)	29
NaCl	364.6842(4)	1.7761(2)	0.005937(35)	0.21806302(8)	0.00162479(6)	73
NaF	535.65805(21)	3.57523(13)	0.018453(34)	0.43690153(7)	0.00455918(7)	74
NaH	1171.968(12)	19.703(10)	0.175(2)	4.90327(13)	0.1370(4)	75
NCl	827.95767(75)	5.30015(61)	-0.00480(19)	0.649767390(85)	0.00641432(20)	76
P ₂	780.77(9)	2.835(18)	-0.00462(9)	0.30362(9)	0.00149(9)	7
P ₂ ⁺	672.20(9)	2.74(9)	NA	0.27600(18)	0.00151(9)	7
PF	846.75(9)	4.489(9)	0.019(9)	0.5667427(35)	0.00456(9)	7 but B_e^{77}
PH	2363.774(36)	43.907(27)	0.1059(73)	8.53904(19)	0.25339(28)	54
PN	1336.948(20)	6.8958(57)	-0.00605(48)	0.7864844(28)	0.0055337(36)	78
PO	1233.34(9)	6.56(9)	NA	0.733223657(22)	0.005466162(50)	vib, ⁷ rot ⁷⁹
S ₂	725.7102(97)	2.8582(25)	NA	0.29539516(30)	0.00159754(59)	80
SF	837.6418(5)	4.46953(18)	NA	0.555173(4)	0.004459(10)	81
SH	2696.2475(58)	48.7420(28)	0.1124(6)	9.600247(51)	0.27990(10)	82
Si ₂	510.98(9)	2.02(9)	NA	0.2390(9)	0.00135(18)	7
SiCl	535.59(2)	2.1757(50)	0.00604(36)	0.256103(14)	0.0015817(72)	83
SiF	837.32507(22)	4.83419(9)	0.019807(16)	0.58125735(21)	0.00503859(39)	84
SiH	2042.5229(8)	36.0552(5)	0.1254(1)	7.503898(30)	0.21814(2)	85
SiH ⁺	2157.17(9)	34.24(9)	NA	7.6603(9)	0.2096(9)	7
SiN	1151.284(43)	6.455(21)	-0.0069(20)	0.730927(15)	0.005685(30)	86 but $\omega_e y_e^{87}$
SiO	1241.54388(7)	5.97437(2)	0.006090(3)	0.72675206(2)	0.00503784(1)	88
SiS	749.64559(7)	2.58623(4)	0.001048(9)	0.303527856(6)	0.001473130(3)	88
SO	1150.7913(10)	6.4096(5)	0.01306(11)	0.72082210(2)	0.00575080(2)	vib, ⁸⁹ rot ⁹⁰

ables x_i and x_j . For the problem at hand, y is the ZPE and the x_i are generic spectroscopic constants. The required derivatives, summarized in Table 2, are straightforward but do not

TABLE 2. Derivatives of ZPE with respect to spectroscopic constants, c .

c	$\partial(\text{ZPE})/\partial c$
	$\text{ZPE} = \frac{\omega_e}{2} - \frac{\omega_e x_e}{2} + \frac{\omega_e y_e}{8} + \frac{B_e}{4} + \frac{\alpha_e \omega_e}{12B_e} + \frac{\alpha_e^2 \omega_e^2}{144B_e^3}$
ω_e	$1/2 + \frac{B_e}{\omega_e} s(2s+1)$, where $s \equiv \frac{\alpha_e \omega_e}{12B_e^2}$
$\omega_e x_e$	-1/2
$\omega_e y_e$	1/8
B_e	$1/4 - s(3s+1)$
α_e	$\frac{B_e}{\alpha_e} s(2s+1)$

appear to have been compiled previously.

Typically, only the diagonal elements, σ_{ii} , of the covariance matrix (i.e., the variances of the fitting constants) are reported and available to us. Omitting the off-diagonal contributions in Eq. (6) yields the estimate

$$\sigma_y^2 \approx \sum_i \sigma_i^2 (\partial y / \partial x_i)^2, \quad (7)$$

where the standard uncertainties of the x_i are $\sigma_i = \sqrt{\sigma_{ii}}$. This diagonal approximation introduces a bias in the estimated uncertainty, which will be different for different molecules. To estimate the magnitude of the bias, we consider the situation for BCl, for which the covariance matrix has been published.¹⁷ Using the derivatives in Table 2 and the parameter values and statistical uncertainties from Table 1, the standard uncertainty (i.e., the square root of the variance) for the ZPE is 0.00065 cm^{-1} . When only the diagonal terms are included, the resulting standard uncertainty is only slightly smaller, 0.00057 cm^{-1} . Given only the variances, the most pessimistic scenario for the correlation coefficients r_{ij} ($-1 \leq r_{ij} \equiv \sigma_{ij} / \sigma_i \sigma_j \leq 1$) leads to the upper bound

TABLE 3. Estimated standard uncertainties associated with some diatomic ZPEs (cm^{-1} units) as determined using the full [Eq. (6)], diagonal [Eq. (7)], and pessimistic [Eq. (8)] approximations.

Molecule	Full	Diagonal ^a	Pessimistic
BCl	0.00065	0.00057 (-12%)	0.00098 (+51%)
CS	0.00044	0.00045 (+2%)	0.00050 (+14%)
SiO	0.00033	0.00052 (+58%)	0.00082 (+148%)
SiS	0.00036	0.00037 (+3%)	0.00041 (+14%)

^aPercentage deviation from “full” value given between parentheses.

$$\sigma_y \leq \sum_i \sigma_i |\partial y / \partial x_i|, \quad (8)$$

or $\sigma_y \leq 0.00098 \text{ cm}^{-1}$ for the BCl example. This is 50% larger than the result from Eq. (6) and appears inferior to the diagonal approximation. These various estimates are summarized in Table 3, along with analogous estimates for three other diatomic molecules, based upon unpublished fitting data generously provided by Dr. F. J. Lovas. Based upon the data for these four molecules, the diagonal approximation appears reasonable and in this paper we use Eq. (7) to estimate the statistical contribution to the standard uncertainty of the diatomic ZPEs.

Most of the standard uncertainties presented in Table 1 are from the experimental papers in which the constants were reported. In some cases, uncertainties were reported but not described; they have been assumed to represent standard uncertainties (1σ). When uncertainties have been described as 95% confidence intervals, they have been divided by 2 to estimate standard uncertainties. Other special cases are described in Sec. 5.

The uncertainties associated with spectroscopic constants only reflect the statistical uncertainties resulting from fitting the observed line positions to a model Hamiltonian. In this context, a Hamiltonian is a physically motivated fitting function involving selected spectroscopic constants and various quantum numbers. In some cases, the uncertainties were propagated from ν -dependent fitting constants or from estimated [type B (Ref. 18)] uncertainties in line positions.

In addition to the statistical uncertainties, there are sources of bias (“systematic error”) which may dominate the combined uncertainties. True bias cannot be known, since that requires knowledge of true values. When ancillary information is available about the possible values of bias, we can make a correction for bias, as recommended in the *Guide to the Expression of Uncertainty in Measurement*, published by the International Organization for Standardization.¹⁹ There is uncertainty associated with the correction for bias, corresponding to the uncertainty of the ancillary information. If we have no information, we choose the value of the correction to be zero, but there is still an uncertainty associated with this (null) value. This uncertainty is combined with the statistical uncertainties to obtain the combined uncertainty.

One source of bias derives from the truncation in Taylor-series expansions such as Eq. (1). Such model-dependent uncertainties are seldom discussed.^{20–22} The fitted values of

low-order constants are affected when higher-order constants are included in the fitting procedure. Further, our ZPE computation [Eq. (4)] includes terms only through third order. For diatomic molecules, we estimate the uncertainty due to truncation using the simplified analytical model described in the following paragraph.

Assume, for this approximate model, that the diatomic vibrational energy levels are perfectly described by the sextic polynomial

$$G(\nu) = \sum_{i=0}^6 b_i \left(\nu + \frac{1}{2}\right)^i, \quad (9)$$

where ν is the quantum number, $G(\nu)$ is the energy of the associated level, and the b_i are constants. The exact zero-point energy within this model is

$$\text{ZPE} = b_0 + \frac{1}{2}b_1 + \frac{1}{4}b_2 + \frac{1}{8}b_3 + \frac{1}{16}b_4 + \frac{1}{32}b_5 + \frac{1}{64}b_6. \quad (10)$$

Also suppose that n transition frequencies, $y_j = G(j) - G(0)$, are observed and are fitted to the empirical expression

$$G(\nu) \approx \sum_{i=0}^n a_i \left(\nu + \frac{1}{2}\right)^i, \quad (11)$$

where $a_i = Y_{i0}$ or the equivalent conventional constant and $n \leq 6$. This is an exact fit because we have assumed, for mathematical convenience, that the number of free parameters is equal to the number of data. Then the apparent zero-point energy is

$$\text{ZPE}_{\text{app}} = a_0 + \frac{1}{2}a_1 + \frac{1}{4}a_2 + \frac{1}{8}a_3. \quad (12)$$

ZPE_{app} depends upon the number, n , of fitted constants even though the higher-order constants are not explicit in Eq. (12). The difference ($\text{ZPE}_{\text{app}} - \text{ZPE}$), determined from Eqs. (10) and (12), is the truncation bias in this simple model; its absolute value is an estimate for the uncertainty arising from truncation of the spectroscopic Hamiltonian. The biases in the cubic approximation (12), for different orders n of the fitting polynomial (11), are listed in the second column of Table 4. The value for $n=2$ uses the more severely truncated quadratic expression $\text{ZPE}_{\text{app}} = a_0 + \frac{1}{2}a_1 + \frac{1}{4}a_2$ instead of Eq. (12), because a_3 is undefined. The differences ($a_0 - b_0$), which appear in the expressions for estimated bias, require evaluation. If we identify a_0 and b_0 with Y_{00} , we can use Eq. (5) to estimate that

$$\begin{aligned} (a_0 - b_0) &\approx \nabla Y_{00} \cdot (\mathbf{a} - \mathbf{b}) \\ &= \frac{\alpha_e}{12B_e} \left(1 + \frac{\alpha_e}{6B_e^2} \omega_e \right) (a_1 - b_1) - \frac{1}{4} (a_2 - b_2). \end{aligned} \quad (13)$$

The expressions for $(a_1 - b_1)$ and for $(a_2 - b_2)$ are given in the last two columns of Table 4. To obtain numerical values for the uncertainty arising from truncation for a particular diatomic molecule, we determine n based upon the order of the experimental fit, choose $b_i \approx Y_{i0}$, and combine Eq. (13) with the expressions in Table 4. However, frequently the higher

TABLE 4. Truncation bias with respect to sextic diatomic vibrational model [Eqs. (9)–(13)]. The order of the fitting polynomial is n .

n	$ZPE_{\text{app}} - ZPE$	$(a_1 - b_1)$	$(a_2 - b_2)$
6	0	0	0
5	$(a_0 - b_0) - \frac{1}{16}b_4 - \frac{1}{32}b_5 + \frac{679}{4}b_6$	$\frac{4881}{8}b_6$	$-\frac{12139}{16}b_6$
4	$(a_0 - b_0) - \frac{1}{16}b_4 - \frac{485}{16}b_5 - \frac{6005}{16}b_6$	$-\frac{1689}{16}b_5 - 1290b_6$	$\frac{475}{4}b_5 + \frac{22061}{16}b_6$
3	$(a_0 - b_0) + \frac{105}{16}b_4 + \frac{105}{2}b_5 + \frac{8925}{32}b_6$	$22b_4 + \frac{2711}{16}b_5 + \frac{1765}{2}b_6$	$-\frac{43}{2}b_4 - 150b_5 - \frac{11909}{16}b_6$
2	$(a_0 - b_0) - \frac{15}{8}b_3 - \frac{135}{16}b_4 - \frac{435}{16}b_5 - \frac{2475}{32}b_6$	$-\frac{23}{4}b_3 - 24b_4 - \frac{1199}{16}b_5 - 210b_6$	$\frac{9}{2}b_3 + \frac{29}{2}b_4 + \frac{165}{4}b_5 + \frac{1771}{16}b_6$

Y_{i0} are unknown. As typically $|Y_{i+1,0}| < |Y_{i0}|$, we estimate the missing Y_{i0} crudely by geometric extrapolation from the two highest measured Y_{i0} . As pointed out by a referee, Y_{i0} and $Y_{i+1,0}$ usually differ in sign. Thus, an alternating sign is assumed in the present work. However, for about one-third of the data at hand, the sign does not change, i.e., $Y_{i0}Y_{i-1,0} > 0$ (for $i > 3$). To test the sensitivity of the results to the choice of sign, we consider a positive sign in the extrapolation. This changes the magnitude of $(ZPE_{\text{app}} - ZPE)$ by a mean factor of 1.8 (standard deviation = 1.5). Thus, we multiply the truncation bias values by 1.8 to reflect the uncertainty of the extrapolation.

Among the remaining sources of uncertainty, the most important is probably that Dunham's canonical treatment is itself an approximation that leads to bias. In particular, any perturbations from electronically or vibrationally excited states will displace some rovibrational levels, skewing the values of the fitting constants. These effects are specific to individual molecules. We do not attempt to quantify the associated uncertainties. However, they are probably small for the ground states of diatomic molecules. Dunham's analysis is also for non-degenerate electronic states ($^1\Sigma$) and must be considered more approximate in other cases.

To illustrate the current procedure, consider BF as an example. Constants from Table 1 are substituted into Eq. (5) to obtain $Y_{00} = 0.3111 \text{ cm}^{-1}$. Applying Eq. (4) yields $ZPE = 698.4416 \text{ cm}^{-1}$, as listed in Table 5. The associated uncertainty is computed by propagating the uncertainties in the spectroscopic constants, estimating the uncertainty associated with the (null) correction for truncation bias, and combining these two quantities to obtain a combined standard uncertainty. To propagate uncertainties, substitute values from Table 1 into the formulas in Table 2 to obtain the partial derivatives $\partial(ZPE)/\partial(\omega_e) = 0.50307$, $\partial(ZPE)/\partial(\omega_e x_e) = -0.5$, $\partial(ZPE)/\partial(\omega_e y_e) = 0.125$, $\partial(ZPE)/\partial(B_e) = -3.5257$, and $\partial(ZPE)/\partial(\alpha_e) = 226.11$. The intermediate quantity s

$= 0.96750$ (Table 2). The standard uncertainties for the spectroscopic constants, from Table 1, are combined with these derivatives according to Eq. (7) to obtain the estimated statistical contribution to the variance of the ZPE. Taking the square root gives $u_{\text{stat}} \approx 0.000159 \text{ cm}^{-1}$, as listed in Table 5 (rounded to two digits). To estimate the uncertainty associated with the (null correction for) truncation bias, check the literature (Zhang *et al.*²³) to find the available Dunham constants Y_{n0} . In this case, $Y_{40} = 0.0003464 \text{ cm}^{-1}$ and no higher constants are available. Thus, the appropriate row in Table 4 is that for $n=4$. Values of b_j in Table 4 are approximated as $b_j \approx Y_{j0}$. The missing constants are estimated by geometric extrapolation with sign alternation as $Y_{i+1,0} \approx -|Y_{i,0}^2/Y_{i-1,0}|(Y_{i,0}/|Y_{i,0}|)$, so $Y_{50} \approx -2.33 \times 10^{-6} \text{ cm}^{-1}$ and $Y_{60} \approx 1.56 \times 10^{-8} \text{ cm}^{-1}$. Then from the third column of Table 4, $(a_1 - b_1) = 0.000225 \text{ cm}^{-1}$ and from the fourth column of Table 4, $(a_2 - b_2) = -0.000255 \text{ cm}^{-1}$. Substituting these values into Eq. (13) then gives $(a_0 - b_0) = 6.435 \times 10^{-5} \text{ cm}^{-1}$. Finally the expression in the second column of Table 4 evaluates to $(ZPE_{\text{app}} - ZPE) = 0.000107 \text{ cm}^{-1}$. Multiplying by 1.8 to account for sensitivity to guessed Y_{i0} values, and taking the absolute value, $u_{\text{trunc}} \approx 0.000193 \text{ cm}^{-1}$. The final, estimated, combined standard uncertainty is then $\sigma = (u_{\text{stat}}^2 + u_{\text{trunc}}^2)^{1/2} = 0.000250 \text{ cm}^{-1}$, which is rounded to a single digit in Table 5.

5. Analyses for Individual Molecules

In their classic compilation, Huber and Herzberg (H&H) did not attempt to estimate the uncertainties associated with the reported spectroscopic constants.⁷ Instead, they provided the following guidance. "...we hope that the number of digits quoted may serve as a *very* rough indication of the estimated order of magnitude of the error, generally ± 9 units of the last decimal place. Where the last digit is given as a subscript, we expect that the uncertainty may considerably

TABLE 5. Experimental vibrational zero-point energies (cm^{-1}) for selected diatomic molecules. Combined standard uncertainties (1σ) are between parentheses and refer to the least significant digit. The combined uncertainties include both the estimated statistical uncertainties (u_{stat}) and the estimated uncertainties arising from truncation bias (u_{trunc}).

Molecule	State designation	ZPE	u_{stat}	u_{trunc}
H ₂	$1^1\Sigma_g^+$	2179.3(1)	0.022	0.11
HD	$1^1\Sigma^+$	1890.3(2)	0.14	0.13
D ₂	$1^1\Sigma_g^+$	1546.50(8)	0.065	0.049
⁹ BeH	$2^2\Sigma^+$	1022.23(1)	0.015	0
⁹ BeD	$2^2\Sigma^+$	760.372(9)	0.009	0
⁹ Be ¹⁸ O	$1^1\Sigma^+$	725.8(1)	0.12	0.00039
¹¹ B ¹⁹ F	$1^1\Sigma^+$	698.4416(3)	0.00016	0.00019
¹¹ BH	$1^1\Sigma^+$	1172.64(5)	0.0018	0.055
¹¹ B ¹⁶ O	$2^2\Sigma^+$	939.89(2)	0.022	0.00017
¹² C ₂	$1^1\Sigma_g^+$	924.0(5)	0.0043	0.52
¹² C ₂ ⁻	$2^2\Sigma_g^+$	887.7(1)	0.10	0.00018
¹² C ¹⁹ F	$2^2\Pi$	651.6(2)	0.20	0.0011
¹² CH	$2^2\Pi$	1416.07(4)	0.014	0.033
¹² CD	$2^2\Pi$	1042.792(9)	0.00068	0.0091
¹² C ¹⁴ N	$2^2\Sigma^+$	1031.133(7)	0.0065	0.00089
¹² C ¹⁶ O	$1^1\Sigma^+$	1081.74682(5)	0.000054	0
¹² C ¹⁶ O ⁺	$2^2\Sigma^+$	1103.36(2)	0.022	0.00019
¹⁹ F ₂	$1^1\Sigma_g^+$	455.41(2)	0.0051	0.020
H ¹⁹ F	$1^1\Sigma^+$	2050.77(1)	0.00055	0.010
⁷ Li ₂	$1^1\Sigma_g^+$	175.0259(6)	0.00056	0.00021
⁷ Li ¹⁹ F	$1^1\Sigma^+$	453.70762(7)	0.000063	0.000017
⁷ LiH	$1^1\Sigma^+$	697.952(5)	0.00053	0.0050
⁷ LiD	$1^1\Sigma^+$	524.762(1)	0.00019	0.0012
⁷ Li ¹⁶ O	$2^2\Pi$	405.6(4)	0.11	0.39
¹⁴ N ₂	$1^1\Sigma_g^+$	1175.78(5)	0.045	0.00079
¹⁴ N ₂ ⁺	$2^2\Sigma_g^+$	1099.40(2)	0.025	0.0024
¹⁴ N ¹⁹ F	$3^3\Sigma^-$	568.8(4)	0.065	0.37
¹⁴ NH	$3^3\Sigma^-$	1623.6(6)	0.065	0.55
¹⁴ ND	$3^3\Sigma^-$	1190.13(5)	0.021	0.046
¹⁴ N ¹⁶ O	$2^2\Pi$	948.647(1)	0.0011	0
¹⁴ N ¹⁶ O ⁺	$1^1\Sigma^+$	1184.33(6)	0.059	0.00032
¹⁶ O ₂	$3^3\Sigma_g^-$	787.380(6)	0.0045	0.0040
¹⁶ O ₂ ⁺	$2^2\Pi_g$	948.91(4)	0.043	0.0016
¹⁹ F ¹⁶ O	$2^2\Pi$	524.053(1)	0.0011	0
¹⁶ OH	$2^2\Pi$	1850.69(5)	0.035	0.042
¹⁶ OD ⁺	$3^3\Sigma^-$	1126.5(1)	0.065	0.083
²⁷ Al ³⁵ Cl	$1^1\Sigma^+$	240.4516(1)	0.00011	0.0000042
²⁷ Al ¹⁹ F	$1^1\Sigma^+$	400.13958(6)	0.000062	0.0000024
²⁷ AlH	$1^1\Sigma^+$	835.024(8)	0.00023	0.0081
²⁷ AlD	$1^1\Sigma^+$	602.685(1)	0.00010	0.0011
²⁷ Al ¹⁶ O	$2^2\Sigma^+$	487.976(3)	0.0030	0.000013
²⁷ Al ³² S	$2^2\Sigma^+$	307.672(2)	0.0019	0.00054
¹¹ B ³⁵ Cl	$1^1\Sigma^+$	418.984(3)	0.00057	0.0034
⁹ Be ³² S	$1^1\Sigma^+$	497.4(2)	0.052	0.20
¹¹ B ³² S	$2^2\Sigma^+$	588.39(3)	0.025	0.00024
¹² C ³⁵ Cl	$2^2\Pi$	437.3613(6)	0.00048	0.00035
³⁵ Cl ₂	$1^1\Sigma_g^+$	279.22(2)	0.016	0
³⁵ Cl ₂ ⁺	$2^2\Pi_{3/2g}$	322.09(8)	0.077	0.00034
³⁵ Cl ₂ ⁺	$2^2\Pi_{1/2g}$	321.7(1)	0.077	0.074
³⁵ Cl ¹⁹ F	$1^1\Sigma^+$	390.510(2)	0.0013	0.0013
³⁵ Cl ¹⁶ O	$2^2\Pi$	425.6295(6)	0.000090	0.00061
¹² C ³¹ P	$2^2\Sigma^+$	618.20033(9)	0.000086	0.0000060
¹² C ³² S	$1^1\Sigma^+$	641.03295(6)	0.000060	0.0000010
H ³⁵ Cl	$1^1\Sigma^+$	1483.89(2)	0.0011	0.023

TABLE 5. Experimental vibrational zero-point energies (cm^{-1}) for selected diatomic molecules. Combined standard uncertainties (1σ) are between parentheses and refer to the least significant digit. The combined uncertainties include both the estimated statistical uncertainties (u_{stat}) and the estimated uncertainties arising from truncation bias (u_{trunc}).—Continued

Molecule	State designation	ZPE	u_{stat}	u_{trunc}
D ³⁵ Cl	$1^1\Sigma^+$	1066.607(7)	0.00067	0.0065
H ³⁵ Cl ⁺	$2^2\Pi$	1326.(5)	0.047	5.2
⁷ Li ³⁵ Cl	$1^1\Sigma^+$	320.550(2)	0.00051	0.0019
²³ Na ⁷ Li	$1^1\Sigma^+$	127.817(1)	0.0011	0
²⁴ Mg ₂	$1^1\Sigma_g^+$	25.26(1)	0.011	0.0013
²⁴ MgH	$2^2\Sigma^+$	739.1(9)	0.0028	0.89
²⁴ MgD	$2^2\Sigma^+$	534.9(1)	0.0017	0.14
²⁴ Mg ¹⁶ O	$1^1\Sigma^+$	391.433(1)	0.00035	0.0011
²⁴ Mg ³² S	$1^1\Sigma^+$	263.7(1)	0.065	0.073
²³ Na ₂	$1^1\Sigma_g^+$	79.3359(3)	0.00026	0
²³ Na ³⁵ Cl	$1^1\Sigma^+$	181.9709(2)	0.00022	0.0000013
²³ Na ¹⁹ F	$1^1\Sigma^+$	267.1154(1)	0.00013	0.000018
²³ NaH	$1^1\Sigma^+$	581.63(2)	0.017	0.014
¹⁴ N ³⁵ Cl	$3^3\Sigma^-$	412.886(2)	0.00049	0.0021
³¹ P ₂	$1^1\Sigma_g^+$	389.70(8)	0.075	0.00016
³¹ P ₂ ⁺	$2^2\Pi_u$	335.4(1)	0.087	0.060
³¹ P ¹⁹ F	$3^3\Sigma^-$	422.41(6)	0.057	0.0017
³¹ PH	$3^3\Sigma^-$	1171.9(4)	0.028	0.40
³¹ P ¹⁴ N	$1^1\Sigma^+$	666.79(1)	0.011	0.00011
³¹ P ¹⁶ O	$2^2\Pi$	615.1(2)	0.064	0.19
³² S ₂	$3^3\Sigma_g^-$	362.19(6)	0.0050	0.060
³² S ¹⁹ F	$2^2\Pi$	417.9(1)	0.0038	0.13
³² SH	$2^2\Pi$	1337.2(2)	0.0064	0.19
²⁸ Si ₂	$3^3\Sigma_g^-$	255.0(1)	0.12	0.043
²⁸ Si ³⁵ Cl	$2^2\Pi$	267.34(1)	0.011	0.00035
²⁸ Si ¹⁹ F	$2^2\Pi$	417.6275(2)	0.00019	0.000021
²⁸ SiH	$2^2\Pi$	1013.336(9)	0.0012	0.0092
²⁸ SiH ⁺	$1^1\Sigma^+$	1071.(3)	0.080	2.8
²⁸ Si ¹⁴ N	$2^2\Sigma^+$	574.10(3)	0.027	0.00016
²⁸ Si ¹⁶ O	$1^1\Sigma^+$	619.39217(4)	0.000036	0.00000090
²⁸ Si ³² S	$1^1\Sigma^+$	374.21174(4)	0.000038	0.0000051
³² S ¹⁶ O	$3^3\Sigma^-$	573.9499(6)	0.00057	0.00019

exceed ± 10 units of that last decimal place.” Although rarely explicit, the implicit assumption of normal distributions pervades the literature of molecular spectroscopy, with coverage factors^{18,19} (i.e., multipliers of the standard uncertainty) ranging from 1 to 3. To accommodate the “very rough” quality of the estimated uncertainties, we assume a coverage factor of 1 for the uncertainty estimates from H&H. Where we have taken spectroscopic constants from H&H, we have thus assumed the associated standard uncertainties to be 9 in the last digit except when printed as a subscript, in which cases we assumed 18 in that last, subscripted digit.

A few spectroscopic constants were reported without associated uncertainties. In such cases we estimated the uncertainties. This was done for Be¹⁸O (ω_e), BH ($\omega_e y_e$, taken equal to that estimated for the corresponding constant in the A state²⁴), O₂ (all constants), BS [all (deperturbed) constants, estimated from effect of deperturbation], CCl (B_e , based upon the discrepancy between Jin *et al.*²⁵ and Endo *et al.*²⁶), Cl₂ (all constants), and ClO ($\omega_e y_e$). For LiO, we derived a

value for α_e from published²⁷ values of B_0 and B_1 . In some reports of isotopic studies, uncertainties $u(Y_{l,m})$ are reported only for the Dunham constants of the most common isotopolog. In such cases, uncertainties for the Dunham constants of the rarer isotopologs are estimated by using Eq. (14), where μ is the reduced nuclear mass and the primed quantities refer to the rarer isotopolog:¹²

$$u(Y'_{l,m}) \approx u(Y_{l,m})(\mu/\mu')^{m+l/2}. \quad (14)$$

For ClO, there is an apparent transcription error; Y_{11} ($\approx -\alpha_e$) should be negative.²⁸ For BeO, note that the tabulated values are for the rare isotopolog $^9\text{Be}^{18}\text{O}$.

6. Results and Discussion

Table 5 lists our recommended values for ZPE as derived from experimental spectroscopic constants. The uncertainties listed are combined standard uncertainties (i.e., coverage factor $k=1$) that include both statistical uncertainties (u_{stat}) and uncertainties arising from (null) corrections for bias (u_{trunc}). For nearly half the molecules, $u_{\text{trunc}} > u_{\text{stat}}$. As expected, cases truncated most severely, at $n=2$ (i.e., for which Y_{20} is the highest Y_{n0} measured), tend to have high values of the ratio $u_{\text{trunc}}/u_{\text{stat}}$ (mean=18 and standard deviation=32, for 12 values). In contrast, this mean ratio equals 3 (for 26 values; standard deviation=6) and 4 (for 28 values; standard deviation=7) for $n=3$ and 4, respectively. Surprisingly, the highest mean ratio (50, for 12 values; standard deviation=93) is for the most lightly truncated nontrivial case, $n=5$. Upon inspection, we find that the highest values of the ratio $u_{\text{trunc}}/u_{\text{stat}}$ are associated with low values of the ratio $Y_{n-1,0}/Y_{n,0}$. That is, truncation bias is expected to be large when the polynomial expansion [compare Eq. (11)] converges slowly. Log-log linear regression yields a correlation coefficient of -0.64 with slope= -1.12 and intercept= 4.75 . This corresponds crudely to $u_{\text{trunc}}/u_{\text{stat}} \approx 100Y_{n,0}/Y_{n-1,0}$, with substantial scatter. Note that our estimate of u_{trunc} (second column of Table 4) is identically zero for $n=6$ only because the model is based upon a sextic polynomial approximation. This may underestimate the final, combined uncertainties significantly when $n=6$ and convergence is slow. For example, BeH, BeD, FO, Na₂, and NaLi have rather low values of Y_{50}/Y_{60} (6, 8, 16, 16, and 19 respectively). BeH, BeD, Na₂, and NaLi have been measured to $n=8$,²² 8,²² 12,²⁹ and 9,³⁰ respectively, but FO could have significant uncertainty arising from the (null correction for) polynomial truncation bias.

The present study is limited to 85 diatomic molecules, some of them isotopologs. In contrast, earlier work has included polyatomic molecules, which is clearly essential if bending vibrations are to be represented. This was important because the focus of the earlier work was to determine empirical scaling factors for ZPEs obtained from *ab initio* calculations. Among the many previous studies, the most heavily cited is that by Scott and Radom.³¹ In that study, experimental ZPEs were computed by using Eq. (2) (or its polyatomic analog) for a set of 29 diatomic and 10 poly-

atomic molecules. The reference data were not reported but literature references were provided. The earlier, classic paper by Grev *et al.*³² included 12 diatomic and 12 polyatomic molecules. Reference data and citations were both provided. The present work is the first to include uncertainty analyses and to include copious, recent spectroscopic data.

The principal utility of the present compilation is for developing empirical corrections for ZPEs obtained from *ab initio* calculations. However, only stretching vibrations are represented by diatomic molecules, so reference ZPEs for polyatomic molecules are still needed. Data evaluation and uncertainty analysis are substantially more complicated for polyatomic molecules than for diatomic. For example, vibrational resonances (i.e., perturbations) are common, the analog of Y_{00} is not readily determined, and far more spectroscopic constants are required for characterization. Furthermore, adequate spectroscopic data are available for fewer than 20 polyatomic molecules. Despite these challenges, such an evaluation is currently underway at NIST.

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