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Analysis of Rotational and Vibrational−Rotational Spectra of HF Based on the Non-Born−Oppenheimer Effective Hamiltonian

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Rotational transitions of HF that are important as a wavenumber standard have been analyzed by simultaneous fitting of the reported rotational and vibrational−rotational transitions plus rotational measurements of the present study with the non-Born−Oppenheimer effective Hamiltonian expressed with the optimal parameters, i.e., the determinable clusters of the expansion coefficients of the correction functions for the breakdown of the Born−Oppenheimer approximation. Since the spectral fit is made with the analytical solution of the Schrödinger equation, one can easily reproduce the fitting procedure. This is the first example of the non-Born−Oppenheimer analysis of a single isotopologue with physically meaningful parameters based on the traditional concept of the molecular constants. Fitting of a data set for HF has generated 15 independent parameter values that include 4 determinable clusters of the expansion coefficients. These 15 parameters are sufficient to generate 41 Y_{ij} coefficients and 72 rotational constants, which provide comprehensive sets of molecular constants of HF.

1. Introduction

HF is an important gas molecule often used for an absolute wavenumber standard. In particular, a series of the rotational transitions from $J = 1-0$ up to $J = 33-32$ that are interspersed in the far-infrared and mid-infrared ranges up to 1100 cm^{-1} are useful and convenient for calibration of spectral lines of molecules measured at high temperature. Sengupta et al.[1] reported 20 pure rotational laser transitions of HF in the $v = 0-3$ levels with an accuracy of ±0.002 cm^{-1}. Four rotational transitions of $J = 1-0$ to $4-3$ observed with a TuFIR spectrometer with an uncertainty of 1 part in 10^7 have provided benchmark calibration standards.[2] An additional 14 measurements of rotational transitions up to $J = 33-32$ have also been reported with uncertainties of ±0.0002 to ±0.0025 cm^{-1}.[2] Guelachvili[3] and Sengupta et al.[1] reported vibrational−rotational transitions of HF in the $v = 1-0$ and $2-0$ bands and in the $v = 1-0$ up to $6-5$ laser emission bands, respectively. Mann et al.[4] studied vibrational−rotational emission spectrum up to the $v = 9-4$ band at 670 nm from a hydrogen−fluorine diffusion flame.

In 1991 and 1994, Hedderich et al.[5] and LeBranc et al.[6] published measurements of rotational transitions at 1600 K and vibrational−rotational transitions at 1350 K of HF, respectively. Combining accurately measured lower rotational transitions up to 300 cm^{-1}, the latter authors analyzed the vibrational−rotational and pure rotational transitions to determine the rotational constants for each vibrational band. Subsequently, Ram et al.[7] observed the rotational and vibrational−rotational transitions below 2670 K up to $J'' = 34$ and $v = 5-4$ band, respectively. Again, their analysis gave the rotational constants of each vibrational band.

A set of rotational and vibrational−rotational spectral data of diatomic molecules has usually been analyzed by fitting a single set of molecular parameters to multiple vibrational bands of various isotopologues, if any, simultaneously. Typically, the fitting has been made with an energy level expressed by

$$E_{vJ}/hc = \sum_{i,j} \mu^{-(i+2j)/2} U_{ij}[1 + (m_e/M_a)\Delta_{ij}^a + (m_e/M_b)\Delta_{ij}^b] \times (v + 1/2)^i [J(J+1)]^j \quad (1)$$

in which U_{ij} and Δ_{ij} are mass-invariant constants.[8–10] For the HF single isotopologue, however, the spectral fit with a set of parameters for different vibrational bands has never been made even with the expression 1 except for the theoretical studies by Coxon's group,[11–13] who analyzed a spectral data set of HF and DF. Their numerical direct fitting method has generated a precise, effective potential function over a wide range of the internuclear distance R, and extensive sets of rotational constants for the X and B states were calculated.[13]

Although an analysis with eq 1 is conventional,[14] it has obvious drawbacks. The parameters Δ_{ij} for corrections of the breakdown of the Born−Oppenheimer approximation are empirical ones and have redundancies.[15] The parameters U_{ij} also have redundancies.[16,17] We presented an effective non-Born−Oppenheimer Hamiltonian[18] of diatomic molecules in the $^1\Sigma$ electronic states expressed with determinable parameters[15] for the corrections of the breakdown of the Born−Oppenheimer approximation, Δ_B, r_{iq}, Δ_ω, and Δ_{aiq}, which are the clusters of the expansion coefficients of the correction functions[8,9,19–21] $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$ for the adiabatic and nonadiabatic vibrational and rotational effects. An analytical approach to obtain the eigenvalues of the Schrödinger equation given by the effective non-Born−Oppenheimer Hamiltonian generated expressions of Y_{ij}* in terms of the determinable parameters Δ_B, r_{iq}, Δ_ω, and Δ_{aiq}.[15] This line of approach has been applied to analyses of reported spectral data sets of LiH[15] and HCl.[22,23]

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The recent trend to determine non-Born−Oppenheimer parameters is a numerical approach.[24−29] Although Watson[24,25] suggested that only combinations of Q_i, R_i, and S_i could be determined from the energy levels, the mainstream[26−29] of the numerical approach proposes the individual expansion coefficients of the non-Born−Oppenheimer correction functions as the fitting parameters by treating them as though they were determinable physical quantities. Only clusters, i.e., combinations of the expansion coefficients, are determinable quantities.[15,24] The values obtained by the direct fit to the individual expansion coefficients are effective ones, and they have neither well-founded physical significance nor internal consistency.[23] We found in ref 15 that, if we rewrote Watson's Schrödinger equation[9] in terms of the variable ξ, the equation gave exactly the same analytical expressions for $Y_{ij}{}^*$ as those expressed with the determinable parameters Δ_B, r_{iq}, Δ_ω, and Δ_{aiq}. Note that this finding never justifies the premise that the individual expansion coefficients are determinable physical quantities but merely confirms the correctness of Watson's idea[9,24] that only combinations of the expansion coefficients are determinable.

In the present study, we have remeasured the important rotational transitions with a Fourier transform spectrometer with slightly better resolution than that of the reported study to confirm their accuracy associated with the spectral lines in the range from 600 to 1000 cm^{-1}. The reported rotational and vibrational−rotational transitions for several vibrational levels plus the present rotational measurements for a single isotopologue of HF have been analyzed simultaneously by an analytical approach with a non-Born−Oppenheimer effective Hamiltonian. The analytical expressions of the Dunham coefficients Y_{ij} including the potential constants up to a_9 and an extended set of the modified Dunham coefficients $Y_{ij}{}^*$ that are necessary for the spectral fit have been calculated. The analysis has yielded the molecular parameters of HF that satisfactorily represent the whole energy levels studied in high resolution.

2. Overview of the Approach for the Spectral Analysis Presented in This Paper

To enable readers to follow the approach presented in this paper, key items for the descriptions in the following sections from 3 to 7 are summarized here as a to e:

a. Theoretical Basis. The Schrödinger equation is given in eq 2 with the original non-Born−Oppenheimer effective Hamiltonian written in terms of the variable ξ.

An analytical solution is given in eq 10 for the eigenvalue of eq 2 in terms of the modified Dunham coefficients $Y_{ij}{}^{*(0)}$ that are expressed with optimal correction parameters, i.e., clusters of the expansion coefficients of the non-Born−Oppenheimer correction functions.

Non-Born−Oppenheimer effective Hamiltonian is expressed in eq 11 with the optimal parameters generated from eq 2. Equation 11 is identical to Dunham's Hamiltonian if all the optimal parameters are ignored.

b. Extended Calculations of Modified Dunham Coefficients and a_9 Potential Terms. Modified Dunham coefficients $Y_{05}{}^{*(0)}$, $Y_{13}{}^{*(0)}$, and $Y_{21}{}^{*(0)}$ (eqs 13−15) for an extended level of eleven $Y_{ij}{}^{*(0)}$ are derived from eq 11.

The calculated Dunham corrections $Y_{05}{}^{(2)}$ and $Y_{13}{}^{(2)}$ (Supporting Information) are the same orders of the corrections in the level of eleven $Y_{ij}{}^{*(0)}$.

Expressions (eqs 21, 22) in terms of the expansion coefficients are derived for the optimal parameters δr_{4q} and $\delta\Delta_{a3q}$ that appear in the level of eleven $Y_{ij}{}^{*(0)}$.

The higher-order Dunham coefficients $Y_{011}{}^{(0)}$, $Y_{19}{}^{(0)}$, $Y_{27}{}^{(0)}$, $Y_{35}{}^{(0)}$, $Y_{43}{}^{(0)}$, and $Y_{51}{}^{(0)}$ (Supporting Information) that include potential constants up to a_9 are calculated by use of an extended Dunham's expression (eq 23).

The quantities derived in this section are required to fit the spectral transitions of HF except that eqs 21 and 22 are necessary to discuss the physical significance of the optimal parameters.

c. Experimental Section. Remeasured rotational transitions of HF, listed in Table 1 and indicated by superscript *g*, have been calibrated against the OCS spectral standards.

d. Analysis and Results. The rotational and vibrational−rotational transitions of a single isotopologue of HF are analyzed using the analytical solution (eq 10) for the non-Born−Oppenheimer Hamiltonian (eq 11).

A set of the reported transitions plus the present measurements, in total 302 transitions (Table 1), are fitted to 15 adjustable parameters (Table 2) through the modified Dunham coefficients in the level of eleven $Y_{ij}{}^{*(0)}$ and the higher-order Dunham coefficients $Y_{ij}{}^{(0)}$ that include the potential constants up to a_9.

e. Discussion. The present results are compared with the reported ones in section *7.3 Y_{ij} values* (Table 3) back-calculated from the 15 parameters (Table 2) and section *7.5. Rotational Constants of Each Vibrational State* (Table 4) derived from the Y_{ij} values (Table 3).

3. Theoretical Basis

The reported analytical approach[15,18,22] is briefly reproduced below. A non-Born−Oppenheimer appropriate original effective Hamiltonian[9,20,21,30,31] in the electronic state $^1\Sigma$, where terms higher than O($m_e/M_{a,b}$) are ignored, yields a Schrödinger equation in terms of the variable $\xi = (r - r_e)/r_e$ as[15]

$$\left[-\frac{h^2}{8\pi^2\mu r_e^2}\frac{d}{d\xi}\{1 + (m_e/M_a)Q_a(\xi) + (m_e/M_b)Q_b(\xi)\}\frac{d}{d\xi} + \frac{h^2}{8\pi^2\mu r_e^2(1+\xi)^2}\{1 + (m_e/M_a)R_a(\xi) + (m_e/M_b)R_b(\xi)\}J(J+1) + V(\xi) + (m_e/M_a)S_a(\xi) + (m_e/M_b)S_b(\xi)\right]\psi_{vJ}(\xi) = E_{vJ}\psi_{vJ}(\xi) \quad (2)$$

where μ is the reduced mass of a molecule and M_a, M_b, and m_e are masses of atoms A and B and the electron, respectively. Mass-independent functions, e.g., after Watson,[9] $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$ are non-Born−Oppenheimer terms for nonadiabatic vibrational, nonadiabatic rotational, and adiabatic effects, respectively.

Functions $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$ are expressed as series expansion of ξ; similarly to Dunham's potential function,[16] and the expansion coefficients of the ξ^i terms of $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$ are $q_i^{a,b}$, $r_i^{a,b}$, and $s_i^{a,b}$, respectively.[15] The treatments below are applicable to local representations near r_e, in the region of $|\xi| < 1$. With appropriate manipulation of a Strum−Liouville-type operator in eq 2 for the vibrational kinetic energy followed by removal of adiabatic correction terms linear in ξ, the Schrödinger eq 2 is rewritten in wavenumber units as[15]

TABLE 1: Fitted Rotational and Vibrational−Rotational Transitions of HF

J'	J''	obs./cm^{-1}
$v = 0$		
1	0	41.1109832(2)[a,b]
2	1	82.1711179(−3)[b]
3	2	123.1296703(−52)[b]
4	3	163.9361645(49)[b]
5	4	204.54045(2)[b]
6	5	244.892784(−10)[c]
7	6	284.944158(−3)[c]
13	12	516.28061(−5)[d]
14	13	552.92047(17)[d]
15	14	588.89912(11)[d]
16	15	624.17735(13)[d]
17	16	658.71685(3)[d]
18	17	692.48118(−3)[d]
19	18	725.43521(12)[d]
20	19	757.54563(−6)[d]
21	20	788.78038(−9)[d]
22	21	819.10934(−13)[d]
23	22	848.50403(−13)[d]
24	23	876.93760(−11)[d]
25	24	904.38479(−17)[d]
26	25	930.82215(−31)[d]
27	26	956.228158(−268)[e]
28	27	980.58255(−19)[d]
29	28	1003.86689(−3)[d]
30	29	1026.06399(−14)[f]
31	30	1047.15883(−25)[f]
32	31	1067.13753(−52)[f]
33	32	1085.98903(24)[e]
34	33	1103.69963(−90)[f]
35	34	1120.26465(80)[f]
18	17	692.48114(−7)[g]
19	18	725.43529(−4)[g]
20	19	757.54560(−9)[g]
21	20	788.78041(−6)[g]
22	21	819.10927(−20)[g]
23	22	848.50401(−15)[g]
24	23	876.93745(−26)[g]
25	24	904.38525(29)[g]
$v = 1$		
13	12	496.68517(−5)[d]
14	13	531.89851(−4)[d]
15	14	566.46812(−15)[d]
16	15	600.35572(−9)[d]
17	16	633.52402(2)[d]
18	17	665.93707(−5)[d]
19	18	697.56091(−2)[d]
20	19	728.36279(5)[d]
21	20	758.31128(−10)[d]
22	21	787.37827(96)[d]
23	22	815.53356(102)[f]
24	23	842.75135(63)[f]
25	24	869.00760(53)[f]
26	25	894.27869(27)[f]
27	26	918.54337(17)[f]
28	27	941.78139(3)[f]
29	28	963.97457(15)[f]
30	29	985.10526(−10)[f]
31	30	1005.15850(−14)[f]
32	31	1024.11993(−17)[f]
33	32	1041.97689(−5)[f]
34	33	1058.71676(−86)[f]
35	34	1074.33221(39)[f]
17	16	633.52367(−33)[g]
18	17	665.93696(−16)[g]
19	18	697.56079(−14)[g]
$v = 2$		
15	14	544.59319(0)[d]
16	15	577.12112(−31)[d]
17	16	608.94862(24)[d]
18	17	640.03793(−118)[d]
19	18	670.36020(11)[d]
20	19	699.87946(20)[f]
21	20	728.56627(23)[f]
22	21	756.39145(10)[f]
23	22	783.32767(5)[f]
24	23	809.34869(−8)[f]
25	24	834.43023(−3)[f]
26	25	858.54898(−1)[f]
27	26	881.68349(15)[f]
28	27	903.81340(26)[f]
29	28	924.91981(24)[f]
30	29	944.98541(22)[f]
32	31	981.93152(105)[f]
33	32	998.78249(114)[f]
$v = 3$		
15	14	523.22033(3)[f]
16	15	554.41615(8)[f]
17	16	584.92745(22)[f]
18	17	614.71996(50)[f]
19	18	643.75983(−2)[f]
20	19	672.01718(37)[f]
21	20	699.46074(55)[f]
22	21	726.06171(51)[f]
23	22	751.79253(3)[f]
24	23	776.62827(16)[f]
25	24	800.54360(15)[f]
26	25	823.51454(−75)[f]
27	26	845.52163(−7)[f]
28	27	866.54127(−79)[f]
29	28	886.55639(−53)[f]
30	29	905.54697(−103)[f]
$v = 4$		
16	15	532.17449(172)[f]
17	16	561.39016(203)[f]
18	17	589.89959(−52)[f]
19	18	617.67742(125)[f]
20	19	644.68549(39)[f]
21	20	670.89627(−66)[f]
22	21	696.28180(−122)[f]
$v = 1-0$		
27	28	2427.08679(−2)[f]
26	27	2489.12609(−26)[f]
25	26	2551.07579(−56)[f]
24	25	2612.89090(−85)[f]
23	24	2674.52490(−109)[f]
22	23	2735.93044(−72)[f]
21	22	2797.05753(−48)[f]
20	21	2857.85601(−9)[f]
19	20	2918.27442(59)[f]
18	19	2978.25993(134)[f]
14	15	3212.78712(316)[h]
13	14	3269.78406(−36)[h]
12	13	3326.01911(−39)[h]
11	12	3381.43162(−37)[h]
10	11	3435.96386(−54)[h]
9	10	3489.55896(−21)[h]
8	9	3542.15785(−85)[h]
7	8	3593.70541(−12)[h]
6	7	3644.14227(−14)[h]
5	6	3693.41248(−1)[h]
4	5	3741.45946(8)[h]
3	4	3788.22725(−6)[h]
2	3	3833.66122(−2)[h]
1	2	3877.70704(3)[h]
0	1	3920.31155(13)[h]
1	0	4000.98919(8)[h]
2	1	4038.96214(10)[h]
3	2	4075.29321(7)[h]
4	3	4109.93606(9)[h]
5	4	4142.84579(8)[h]
6	5	4173.97944(7)[h]
7	6	4203.29592(13)[h]
8	7	4230.75584(3)[h]
9	8	4256.32233(4)[h]
10	9	4279.96021(2)[h]
11	10	4301.63671(1)[h]
12	11	4321.32121(2)[h]
13	12	4338.98544(6)[h]
14	13	4354.60375(48)[h]
15	14	4368.15167(43)[h]
16	15	4379.60851(47)[h]
18	17	4396.17661(148)[f]
19	18	4401.25544(59)[f]
20	19	4404.18235(9)[f]
21	20	4404.94794(−1)[f]
22	21	4403.54427(−52)[f]
23	22	4399.96736(−50)[f]
24	23	4394.21427(−15)[f]
25	24	4386.28323(−54)[f]
26	25	4376.17732(9)[f]
27	26	4363.89811(14)[f]
5	6	3693.412419(−73)[i]
4	5	3741.459370(−11)[i]
3	4	3788.227307(−3)[i]
2	3	3833.661267(24)[i]
1	2	3877.707068(58)[i]
$v = 2-1$		
25	26	2427.19891(8)[f]
24	25	2487.04762(62)[f]
23	24	2546.70559(30)[f]
22	23	2606.12848(9)[f]
20	21	2724.08059(−27)[f]
19	20	2782.51324(25)[f]
18	19	2840.51520(−43)[f]
17	18	2898.03796(50)[f]
16	17	2955.02693(74)[f]
15	16	3011.42992(115)[f]
14	15	3067.19327(188)[f]
13	14	3122.26159(192)[f]
11	12	3230.09348(25)[h]
10	11	3282.74768(2)[h]
9	10	3334.48637(6)[h]
8	9	3385.25340(1)[h]
7	8	3434.99221(−102)[h]
6	7	3483.65039(4)[h]
5	6	3531.16959(3)[h]
4	5	3577.49618(2)[h]
3	4	3622.57625(28)[h]
2	3	3666.35554(2)[h]
1	2	3708.78181(−36)[h]
0	1	3749.80427(9)[h]
1	0	3827.43237(−42)[h]
2	1	3863.94158(−8)[h]
3	2	3898.85045(−24)[h]
4	3	3932.11370(−86)[h]
5	4	3963.68952(−3)[h]
6	5	3993.53346(−19)[h]
7	6	4021.60672(9)[h]
8	7	4047.87022(7)[h]
9	8	4072.28778(2)[h]
10	9	4094.82538(19)[h]
11	10	4115.45038(36)[h]
13	12	4150.84558(215)[f]
14	13	4165.55980(159)[f]
15	14	4178.25404(119)[f]
16	15	4188.90695(94)[f]
17	16	4197.49942(84)[f]
18	17	4204.01435(66)[f]
19	18	4208.43735(70)[f]
20	19	4210.75635(137)[f]
21	20	4210.95978(150)[f]
22	21	4209.03841(17)[f]
23	22	4204.99067(212)[f]
$v = 3-2$		
23	24	2421.77333(−141)[f]
22	23	2479.33060(−41)[f]
21	22	2536.59693(−49)[f]
20	21	2593.52794(−65)[f]
19	20	2650.07663(−118)[f]
18	19	2706.19585(−137)[f]
17	18	2761.83623(−161)[f]
16	17	2816.94772(−200)[f]
15	16	2871.47977(−226)[f]
14	15	2925.38191(−125)[f]
13	14	2978.59941(−143)[f]
12	13	3031.08114(−110)[f]
11	12	3082.77325(−85)[f]
10	11	3133.62210(−73)[f]
9	10	3183.57399(−61)[f]
8	9	3232.57485(−68)[f]
7	8	3280.57165(−9)[f]
6	7	3327.50933(−16)[f]
5	6	3373.33549(16)[f]
4	5	3417.99648(31)[f]
3	4	3461.44017(70)[f]
2	3	3503.61335(7)[f]
1	2	3544.46655(12)[f]
0	1	3583.94832(−30)[f]
1	0	3658.60418(27)[f]
2	1	3693.68123(−57)[f]
3	2	3727.20008(158)[f]
5	4	3789.37342(60)[f]
6	5	3817.94683(27)[f]
7	6	3844.78930(−224)[f]
9	8	3893.14641(1)[f]
10	9	3914.58613(−41)[f]
12	11	3951.83185(−60)[f]
13	12	3967.57974(−60)[f]
14	13	3981.37559(−75)[f]
15	14	3993.19492(−173)[f]
16	15	4003.01911(−42)[f]
17	16	4010.82500(−33)[f]
18	17	4016.59619(−22)[f]
19	18	4020.31703(−12)[f]
$v = 4-3$		
21	22	2410.50038(51)[f]
20	21	2465.66443(29)[f]
19	20	2520.43978(56)[f]
18	19	2574.78062(76)[f]
17	18	2628.64051(91)[f]
16	17	2681.97169(75)[f]
15	16	2734.72601(62)[f]
14	15	2786.85413(48)[f]
13	14	2838.30615(51)[f]
12	13	2889.03104(33)[f]
11	12	2938.97789(24)[f]
10	11	2988.09512(22)[f]
9	10	3036.33059(0)[f]
8	9	3083.63280(8)[f]
7	8	3129.94949(23)[f]
6	7	3175.22827(4)[f]
5	6	3219.41883(95)[f]
4	5	3262.46678(0)[f]
3	4	3304.32400(6)[f]
2	3	3344.93901(8)[f]
1	2	3384.26078(−125)[f]
0	1	3422.24209(−220)[f]
1	0	3493.99560(39)[f]
2	1	3527.67136(36)[f]
3	2	3559.81985(−56)[f]
4	3	3590.40062(49)[f]
6	5	3646.68385(−60)[f]
7	6	3672.30985(−2)[f]
8	7	3696.20931(192)[f]
9	8	3718.34136(−24)[f]
11	10	3757.18805(77)[f]
12	11	3773.83739(44)[f]
13	12	3788.60019(45)[f]
15	14	3812.36316(139)[f]
17	16	3828.28684(54)[f]
$v = 5-4$		
16	17	2549.52543(−392)[f]
15	16	2600.60105(−136)[f]
14	15	2651.04911(−87)[f]
15	14	2700.82405(−28)[f]
12	13	2749.87993(293)[f]
11	12	2798.15934(38)[f]
10	11	2845.62142(72)[f]
9	10	2892.21285(49)[f]
8	9	2937.88447(61)[f]
7	8	2982.58526(26)[f]
5	6	3068.87592(31)[f]
4	5	3110.36629(107)[f]
3	4	3150.68542(43)[f]
2	3	3189.78430(−168)[f]
1	2	3227.62045(61)[f]
3	2	3396.14489(−130)[f]
4	3	3425.40935(−20)[f]
5	4	3453.09161(−167)[f]
6	5	3479.15768(9)[f]
8	7	3526.27593(−26)[f]

[a] Observed−Calculated in parentheses. [b] Ref 2. [c] Ref 38. [d] Ref 5. [e] Ref 39. [f] Ref 7. [g] This work. [h] Ref 6. [i] Ref 40.

$$\Bigg[-B_e\{1+\delta q_0+(4B_e/\omega_e^2)\delta s_1'\}\frac{d^2}{d\eta^2}+\frac{B_e\{1+\delta r_0+(4B_e/\omega_e^2)\delta s_1'\}}{(1+\eta)^2}\left(1+\sum_{i=1}\delta r_i'\eta^i\right)J(J+1)+\frac{\omega_e^2}{4B_e}(1-(2B_e/\omega_e^2)\{(2+3a_1)\delta s_1'-2\delta s_2'\})\eta^2\times\left(1+\sum_{i=1}k_i\eta^i\right)\Bigg]\psi_{vJ}(\eta)=F_{vJ}\psi_{vJ}(\eta) \quad (3)$$

in which

$$\eta=\{1+(2B_e/\omega_e^2)\delta s_1'\}\xi+(2B_e/\omega_e^2)\delta s_1' \quad (4)$$

$$\delta r_i'=(m_e/M_a)(r_i^a-q_i^a)+(m_e/M_b)(r_i^b-q_i^b) \quad (5)$$

$$\delta s_i'=(m_e/M_a)(s_i^a+q_i^aF_{vJ})+(m_e/M_b)(s_i^b+q_i^bF_{vJ}) \quad (6)$$

$$k_1=a_1-\delta q_1-(2B_e/\omega_e^2)\{(a_1-3a_1^2+4a_2)\delta s_1'+2a_1\delta s_2'-2\delta s_3'\} \quad (7)$$

$$k_2=a_2-a_1\delta q_1-\delta q_2-(2B_e/\omega_e^2)\{(2a_2-3a_1a_2+5a_3)\delta s_1'+2a_2\delta s_2'-2\delta s_4'\} \quad (8)$$

and

$$k_3=a_3-a_2\delta q_1-a_1\delta q_2-\delta q_3-(2B_e/\omega_e^2)\{(3a_3-3a_1a_3+6a_4)\delta s'_1+2a_3\delta s'_2-2\delta s'_5\} \quad (9)$$

A Dunham-like treatment of eq 3 provides, after appropriate manipulations and a replacement of F_{vJ} in eq 6 with a known power series expansion in $(v + 1/2)$ and $J(J + 1)$, an eigenvalue

$$F_{vJ}=\sum_{i,j}Y_{ij}^*(v+1/2)^i[J(J+1)]^j \quad (10)$$

in which Y_{ij}^* ($=Y_{ij}^{*(0)}+Y_{ij}^{(2)}+\cdots$) includes Born−Oppenheimer corrections to Dunham's original notation Y_{ij}. The $Y_{ij}^{*(0)}$ coefficients that are expressed with optimal correction parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$, $\delta\Delta_{a2q}$, δr_{1q}, δr_{2q}, and δr_{3q}, are given for $Y_{01}^{*(0)}$, $Y_{02}^{*(0)}$, $Y_{03}^{*(0)}$, $Y_{04}^{*(0)}$, $Y_{10}^{*(0)}$, $Y_{11}^{*(0)}$, $Y_{12}^{*(0)}$, and $Y_{20}^{*(0)}$ in eqs 36−43 of ref 15. For a pair of quantities x_i^a and x_i^b, symbol δx_i denotes $\delta x_i = (m_e/M_a)x_i^a + (m_e/M_b)x_i^b$ in which x_i stands for Δ_B, Δ_ω, r_{iq}, or Δ_{aiq}, etc. It is notable that the correction terms in $Y_{ij}^{*(0)}$ coefficients are the quantities on the order of $Y_{ij}^{(2)}$, i.e., the Dunham correction.[16] The optimal correction

TABLE 2: Dunham Potential Constants and Correction Parameters of HF

parameters	fitted
$U_B(1 + \delta\Delta_B)$/cm^{-1} u	20.05443107(102)[a]
$U_\omega(1 + \delta\Delta_\omega)$/cm^{-1} u$^{1/2}$	4048.732948(789)
$a_1(1 + \delta\Delta_{a1q})$	−2.2459742(122)
$a_2(1 + \delta\Delta_{a2q})$	3.4440963(722)
$a_3(1 + \delta\Delta_{a3q})$	−4.452458(234)
a_4	5.161233(816)
a_5	−5.54541(467)
a_6	5.5075(162)
a_7	−4.8301(357)
a_8	3.527(125)
a_9	−3.055(598)
$r_{1q}^H = r_{1q}^F$	−0.11113(357)
$r_{2q}^H = r_{2q}^F$	−0.8322(494)
$r_{3q}^H = r_{3q}^F$	0.4921(753)
$r_{4q}^H = r_{4q}^F$	−0.557(385)
reduced standard deviation	1.22

[a] The uncertainty (one standard error) in the last digits is given in parentheses.

TABLE 3: Values of the Dunham Coefficients Y_{ij} (in units of cm^{-1}) Back-Calculated from 15 Molecular Constants Given in Table 2

coeff.	back-calculated	reference 11	coeff.	back-calculated	reference 11
Y_{10}	4138.38519(105)[a]	4138.411(17)[b]	$10^{12}Y_{43}$	−0.1181(503)	
Y_{20}	−89.94347(100)	−89.979(17)	$10^{10}Y_{04}$	−0.1562996(109)	−0.1597(48)
Y_{30}	0.924646(387)	0.9474(85)	$10^{13}Y_{14}$	0.9664(254)	1.1(52)
$10Y_{40}$	−0.155316(658)	−0.224(20)	$10^{13}Y_{24}$	−0.39014(897)	
10^3Y_{50}	−0.43614(411)	0.55(21)	$10^{14}Y_{34}$	0.1786(249)	
10^4Y_{60}		−0.525(91)	$10^{14}Y_{05}$	0.1607012(612)	
Y_{01}	20.95368788(125)	20.95368(14)	$10^{16}Y_{15}$	−0.2097(137)	
Y_{11}	−0.79328883(305)	−0.793305(83)	$10^{17}Y_{25}$	−0.5028(729)	
$10Y_{21}$	0.1084489(208)	0.10885(66)	$10^{17}Y_{35}$	−0.1733(136)	
10^3Y_{31}	−0.186648(529)	−0.211(26)	$10^{18}Y_{06}$	−0.201417(167)	
10^5Y_{41}	−0.89331(479)	−0.35(38)	$10^{19}Y_{16}$	−0.12859(315)	
10^6Y_{51}	−0.12851(311)	−0.50(19)	$10^{20}Y_{26}$	0.1713(356)	
10^2Y_{02}	−0.214890475(498)	−0.214858(200)	$10^{22}Y_{07}$	0.244195(797)	
10^4Y_{12}	0.5840064(625)	0.5781(20)	$10^{23}Y_{17}$	0.1589(137)	
10^5Y_{22}	−0.103187(371)	−0.0730(80)	$10^{23}Y_{27}$	−0.1279(146)	
10^7Y_{32}	−0.50479(920)	−0.991(70)	$10^{26}Y_{08}$	−0.37591(185)	
10^8Y_{42}	−0.22049(821)		$10^{27}Y_{18}$	−0.2511(734)	
10^6Y_{03}	0.16605888(470)	0.16586(57)	$10^{30}Y_{09}$	0.53011(392)	
10^8Y_{13}	−0.444397(392)	−0.385(58)	$10^{30}Y_{19}$	0.5198(289)	
$10^{10}Y_{23}$	−0.9375(231)	−3.46(48)	$10^{34}Y_{010}$	−0.8101(185)	
$10^{10}Y_{33}$	−0.17800(601)		$10^{38}Y_{011}$	0.9402(719)	

[a] The uncertainty (one standard error) in the last digits is given in parentheses. [b] Calculated from U_{ij} and Δ_{ij}^H in ref 11.

TABLE 4: Rotational Constants (in units of cm^{-1}) for HF Calculated from 41 Y_{ij} Given in Table 3

v	G_v	G_v-G_0	B_v	10^3D_v	10^7H_v	$10^{11}L_v$
0	2050.762276(584)[a]	0.0	20.55973079(204)	2.11996885(595)	1.6381123(513)	−1.559117(169)
	2050.761082	0.0	20.559730458	2.119962810	1.63803772	−1.5587674
		0.0	20.55973066(42)	2.119960(15)	1.63793(64)	−1.5528(111)
1	6012.18467(306)	3961.42239(312)	19.78747950(690)	2.0638070(139)	1.5912131(937)	−1.556675(453)
	6012.183537	3961.422455	19.787476946	2.06379542	1.5910548	−1.555203
		3961.422490(19)	19.7874717(13)	2.0637007(102)	1.58711(29)	−1.4840(32)
2	9801.55554(945)	7750.79326(946)	19.0349685(173)	2.0102272(320)	1.540803(205)	−1.560429(938)
	9801.55456	7750.79348	19.034963756	2.01019848	1.5403308	−1.556565
		7750.793323(75)	19.0349598(25)	2.010084(20)	1.53556(57)	−1.4754(66)
3	13423.5660(233)	11372.8037(233)	18.3006163(365)	1.9596381(654)	1.485757(416)	−1.56931(177)
	13423.56507	11372.80399	18.300604183	1.95957337	1.4847830	−1.564264
		11372.80411(17)	18.3006000(51)	1.959512(42)	1.4821(13)	−1.508(16)
4	16882.4037(496)	14831.6414(496)	17.5825887(686)	1.912501(121)	1.424921(771)	−1.58224(313)
	16882.40268	14831.64160	17.582569664	1.91238665	1.423507	−1.58553
		14831.64203(24)	17.5825644(81)	1.912272(70)	1.4172(22)	−1.442(21)
5	20181.7001(956)	18130.9378(956)	16.878783(119)	1.869331(207)	1.35712(132)	−1.59815(515)
	20181.70002	18130.93894	16.878770194	1.8692437	1.354870	−1.6256
		18130.93866(39)	16.878753(21)	1.86896(34)	1.344(19)	−1.50(35)

v	$10^{15}M_v$	$10^{19}N_v$	$10^{23}O_v$	$10^{27}P_v$	$10^{31}Q_v$	$10^{35}R_v$	$10^{39}S_v$
0	1.595053(937)	−2.07418(246)	2.4894(111)	−3.8847(411)	7.900(150)	−8.101(185)	9.402(719)
	1.592244	−2.05007	2.35884	−3.2821	3.555	5.51	2
	1.480(85)	−1.23(24)					
1	1.55840(274)	−2.16851(945)	2.3925(396)	−4.136(112)	13.098(435)	−8.101	9.402
	1.544336	−2.07143	2.1219	−3.287	4.90	7.99	−227
	0.950(12)						
2	1.49608(611)	−2.2286(237)	2.0398(978)	−4.387(184)	18.296(724)	−8.101	9.402
	1.47013	−2.0945	2.2395	−4.181	−17.3	208.7	−1168
	0.834(26)						
3	1.3977(117)	−2.2544(450)	1.431(185)	−4.638(258)	23.49(101)	−8.101	9.402
	1.38819	−2.2783	1.538	6.74	−111.8	649	−2.45 × 10^3
	0.829(74)						
4	1.2529(202)	−2.2459(735)	0.567(302)	−4.889(331)	28.69(130)	−8.101	9.402
	1.2760	−2.327	−2.38	37.8	−287	1.19 × 10^3	−3.0 × 10^3
5	1.0513(325)	−2.203(109)	−0.553(448)	−5.140(404)	33.89(159)	−8.101	9.402
	1.0771	−1.870	−11.64	90.2	−505	1.50 × 10^3	−1.1 × 10^3

[a] The uncertainty (one standard error) in the last digits is given in parentheses. The second- and third-row entries are values of References 13 and 7 respectively.

parameters are determinable clusters of the expansion coefficients of $q_i^{a,b}$, $r_i^{a,b}$, and $s_i^{a,b}$.[15]

The fact that optimal parameters $\delta\Delta_B$, $\delta\Delta_\omega$, and $\delta\Delta_{aiq}$ in the expressions of $Y_{ij}{}^{*(0)}$ appear as the factors of $B_e(1 + \delta\Delta_B)$, $\omega_e(1 + \delta\Delta_\omega)$, and $a_i(1 + \delta\Delta_{aiq})$, respectively, in eqs 36−43 of ref 15 indicates that the effective non-Born−Oppenheimer Hamiltonian can be expressed by the parameters $B_e(1 + \delta\Delta_B)$, $\omega_e(1 + \delta\Delta_\omega)$, and $a_i(1 + \delta\Delta_{aiq})$, instead of B_e, ω_e, and a_i, respectively, for the Dunham Hamiltonian. In fact, a manipulation of the Hamiltonian in eq 3 has generated an effective non-Born−Oppenheimer Hamiltonian expressed with a set of optimal parameters as[18]

$$H = -B_e(1 + \delta\Delta_B)\frac{d^2}{d\xi'^2} + \frac{B_e(1 + \delta\Delta_B)}{(1 + \xi')^2} \times \left(1 + \sum_{i=1} \delta r_{iq}\xi'^i\right)J(J + 1) + \frac{[\omega_e(1 + \delta\Delta_\omega)]^2}{4B_e(1 + \delta\Delta_B)} \times \xi'^2\left(1 + \sum_{i=1} a_i(1 + \delta\Delta_{aiq})\xi'^i\right) \qquad (11)$$

where

$$\xi' = (1 + \delta\Delta_B/2)\xi + \delta\Delta_B/2 = (1 + \delta\Delta_B/2)\frac{r - r_e}{r_e} + \delta\Delta_B/2 \qquad (12)$$

Equation 11 has formally the same form as the Dunham Hamiltonian[16] except the corrections for the successive ξ'^i terms of a series expansion of the rotational parameter $B(\xi')$. This indicates that the minimum of the effective potential function occurs at $(1 - \delta\Delta_B/2)r_e$, which is equal to the internuclear distance determined from $B_e(1 + \delta\Delta_B)$. Note that terms of orders higher than $O(m_e/M_{a,b})$ should be ignored throughout. The eigenvalue of the Schrödinger equation given in eq 11 is exactly identical[18] to that of eq 3 and is written as eq 10 in units of cm^{-1}, in which eight modified Dunham coefficients $Y_{ij}{}^{*(0)}$ are given in eqs 36−43 of ref 15, as stated above.

4. Extended Calculations of Modified Dunham Coefficients and a_9 Potential Terms

HF has a high degree of potential anharmonicity, which has prevented a reliable simultaneous fit of multiple vibrational bands. We have extended the level set of eight $Y_{ij}{}^{*(0)}$[22] for the correction of the Born−Oppenheimer approximation to a set of eleven $Y_{ij}{}^{*(0)}$ and also the analytical expressions of the Dunham Y_{ij} coefficients to those including the potential constants up to a_9.

In the level set of eight $Y_{ij}{}^{*(0)}$, i.e., $Y_{01}{}^{*(0)}$, $Y_{02}{}^{*(0)}$, $Y_{03}{}^{*(0)}$, $Y_{04}{}^{*(0)}$, $Y_{10}{}^{*(0)}$, $Y_{11}{}^{*(0)}$, $Y_{12}{}^{*(0)}$, and $Y_{20}{}^{*(0)}$, seven correction parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$, $\delta\Delta_{a2q}$, δr_{1q}, δr_{2q}, and δr_{3q}, are participating.[22] One redundancy exists among eight $Y_{ij}{}^{*(0)}$.[15] In the next level set of eleven $Y_{ij}{}^{*(0)}$, i.e., the set of eight $Y_{ij}{}^{*(0)}$ plus $Y_{05}{}^{*(0)}$, $Y_{13}{}^{*(0)}$, and $Y_{21}{}^{*(0)}$, nine correction parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$, $\delta\Delta_{a2q}$, $\delta\Delta_{a3q}$, δr_{1q}, δr_{2q}, δr_{3q}, and δr_{4q}, are included.

The set of eleven $Y_{ij}{}^{*(0)}$ has two redundancies. Since the analytical expressions for $Y_{05}{}^{*(0)}$, $Y_{13}{}^{*(0)}$, and $Y_{21}{}^{*(0)}$ have not been reported, we have calculated those expressions with Maple applying Dunham's treatment that is equivalent to a perturbation approach by Kilpatick[32] to the Schrödinger equation given by the effective Hamiltonian (eq 11). In ref 15, expressions for a set of $Y_{ij}{}^{*(0)}$ have been obtained by an involved process of the calculation applying a Dunham-like treatment to eq 3, but in this study, the use of the Hamiltonian (eq 11) has significantly simplified the calculation. Analytical expressions for three $Y_{ij}{}^{*(0)}$ are as follows:

$$\begin{aligned} Y^{*(0)}_{05} = {} & [32\{B_e(1+\delta\Delta_B)\}^9/\{\omega_e(1+\delta\Delta_\omega)\}^8]\times \\ & [544+576a_1(1+\delta\Delta_{a1q})-96a_2(1+\delta\Delta_{a2q})+ \\ & 8a_3(1+\delta\Delta_{a3q})+270\{a_1(1+\delta\Delta_{a1q})\}^2- \\ & 48\{a_1(1+\delta\Delta_{a1q})\}\{a_2(1+\delta\Delta_{a2q})\}+ \\ & 54\{a_1(1+\delta\Delta_{a1q})\}^3-(1600+1620a_1- \\ & 256a_2+20a_3+720a_1^2-120a_1a_2+135a_1^3)\delta r_{1q}+ \\ & (480+360a_1-320a_2+90a_1^2)\delta r_{2q}-(88+36a_1)\delta r_{3q}+8\delta r_{4q}] \end{aligned} \tag{13}$$

$$\begin{aligned} Y^{*(0)}_{13} = {} & [2\{B_e(1+\delta\Delta_B)\}^6/\{\omega_e(1+\delta\Delta_\omega)\}^5]\times \\ & [1398+1674a_1(1+\delta\Delta_{a1q})-720a_2(1+\delta\Delta_{a2q})+ \\ & 160a_3(1+\delta\Delta_{a3q})+1134\{a_1(1+\delta\Delta_{a1q})\}^2- \\ & 528\{a_1(1+\delta\Delta_{a1q})\}\{a_2(1+\delta\Delta_{a2q})\}+ \\ & 378\{a_1(1+\delta\Delta_{a1q})\}^3-(2628+2997a_1-1200a_2+ \\ & 240a_3+1890a_1^2-792a_1a_2+567a_1^3)\delta r_{1q}+ \\ & (1062+972a_1-240a_2+378a_1^2)\delta r_{2q}-(408+216a_1)\delta r_{3q}+ \\ & 96\delta r_{4q}] \end{aligned} \tag{14}$$

$$\begin{aligned} Y^{*(0)}_{21} = {} & [3\{B_e(1+\delta\Delta_B)\}^3/2\{\omega_e(1+\delta\Delta_\omega)\}^2]\times \\ & [20+40a_1(1+\delta\Delta_{a1q})-12a_2(1+\delta\Delta_{a2q})+ \\ & 20a_3(1+\delta\Delta_{a3q})+30\{a_1(1+\delta\Delta_{a1q})\}^2- \\ & 52\{a_1(1+\delta\Delta_{a1q})\}\{a_2(1+\delta\Delta_{a2q})\}+ \\ & 30\{a_1(1+\delta\Delta_{a1q})\}^3-(16+30a_1-8a_2+ \\ & 10a_3+20a_1^2-26a_1a_2+15a_1^3)\delta r_{1q}+(12+ \\ & 20a_1-4a_2+10a_1^2)\delta r_{2q}-(8+10a_1)\delta r_{3q}+4\delta r_{4q}] \end{aligned} \tag{15}$$

The corresponding Dunham correction $Y_{ij}{}^{(2)}$ has to be added to each of the eleven $Y_{ij}{}^{*(0)}$ when expressions of $Y_{ij}{}^{*(0)}$ are applied to a spectral analysis. Although expressions of $Y_{01}{}^{(2)}$,[16] $Y_{02}{}^{(2)}$,[16] $Y_{03}{}^{(2)}$,[33] $Y_{04}{}^{(2)}$,[22] $Y_{10}{}^{(2)}$,[16] $Y_{11}{}^{(2)}$,[16] $Y_{12}{}^{(2)}$,[33] $Y_{20}{}^{(2)}$,[16] and $Y_{21}{}^{(2)}$,[33] have been reported in references, as indicated by superscripts for the reference numbers, no expressions for $Y_{05}{}^{(2)}$ and $Y_{13}{}^{(2)}$ have yet been registered. The calculated values with Maple in this work are given as Supporting Information.

Optimal parameters, $\delta\Delta_{a3q}$ and δr_{4q}, introduced in eqs 13−15, should be expressed with the expansion coefficients. Since the process to express the optimal parameters with the expansion coefficients reported in ref 15 is lengthy, we follow the method given in ref 18. Changing the variable r of Watson's correction functions $\tilde{R}_{a,b}(r)$ and $\tilde{S}_{a,b}(r)$ to the reduced variable ξ and expanding them as a power series in ξ, we obtain the following relations

$$\tilde{R}_{a,b}(\xi) = R_{a,b}(\xi) - \frac{1}{1+\xi}\int_{\xi_0}^{\xi} Q_{a,b}(\xi)\,\mathrm{d}\xi = \sum_{i=0} \tilde{r}_i^{a,b}\xi^i \tag{16}$$

$$\tilde{S}_{a,b}(\xi) = S_{a,b}(\xi) + \frac{1}{2}\frac{\mathrm{d}V(\xi)}{\mathrm{d}\xi}\int_{\xi_0}^{\xi} Q_{a,b}(\xi)\,\mathrm{d}\xi = \sum_{i=1} \tilde{s}_i^{a,b}\xi^i \tag{17}$$

in which

$$\begin{aligned} \{\tilde{r}_0^{a,b}, \tilde{r}_1^{a,b}, \tilde{r}_2^{a,b}, \tilde{r}_3^{a,b}, \tilde{r}_4^{a,b}\} = {} & \{r_0^{a,b} - P^{a,b}(\xi_0), r_1^{a,b} + P^{a,b}(\xi_0) - \\ & q_0^{a,b}, r_2^{a,b} - P^{a,b}(\xi_0) + q_0^{a,b} - q_1^{a,b}/2, r_3^{a,b} + P^{a,b}(\xi_0) - q_0^{a,b} + \\ & q_1^{a,b}/2 - q_2^{a,b}/3, r_4^{a,b} - P^{a,b}(\xi_0) + q_0^{a,b} - q_1^{a,b}/2 + q_2^{a,b}/3 - \\ & q_3^{a,b}/4\} \end{aligned} \tag{18}$$

and

$$\begin{aligned} \{\tilde{s}_1^{a,b}, \tilde{s}_2^{a,b}, \tilde{s}_3^{a,b}, \tilde{s}_4^{a,b}, \tilde{s}_5^{a,b}\} = {} & \{s_1^{a,b} + (hc\omega_e^2/4B_e)P^{a,b}(\xi_0), s_2^{a,b} + \\ & (hc\omega_e^2/4B_e)(3a_1P^{a,b}(\xi_0)/2 + q_0^{a,b}), s_3^{a,b} + \\ & (hc\omega_e^2/2B_e)(a_2P^{a,b}(\xi_0) + 3a_1q_0^{a,b}/4 + q_1^{a,b}/4), s_4^{a,b} + \\ & (hc\omega_e^2/2B_e)(5a_3P^{a,b}(\xi_0)/4 + a_2q_0^{a,b} + 3a_1q_1^{a,b}/8 + \\ & q_2^{a,b}/6), s_5^{a,b} + (hc\omega_e^2/4B_e)(3a_4P^{a,b}(\xi_0) + 5a_3q_0^{a,b}/2 + \\ & a_2q_1^{a,b} + a_1q_2^{a,b}/2 + q_3^{a,b}/4\} \end{aligned} \tag{19}$$

The quantity $P^{a,b}(\xi_0)$ is the definite integral of $Q_{a,b}(\xi)$ from ξ_0 to 0. Setting $P^{a,b}(\xi_0)$ to $r_0{}^{a,b}$, a replacement of

$$\begin{aligned} & \{\delta q_0, \delta q_1, \delta q_2, \delta q_3, \delta r_0, \delta r_1, \delta r_2, \delta r_3, \delta r_4, \delta s_1, \delta s_2, \delta s_3, \delta s_4, \delta s_5\} \\ & \rightarrow \{0, 0, 0, 0, 0, \delta\tilde{r}_1, \delta\tilde{r}_2, \delta\tilde{r}_3, \delta\tilde{r}_4, \delta\tilde{s}_1, \delta\tilde{s}_2, \delta\tilde{s}_3, \delta\tilde{s}_4, \delta\tilde{s}_5\} \end{aligned} \tag{20}$$

applied to $\delta r_i'$ and k_3 of eqs 5 and 9, respectively, yields

$$\delta r_{4q}(=\delta\tilde{r}_4) = \delta r_4 - \delta r_0 + \delta q_0 - \delta q_1/2 + \delta q_2/3 - \delta q_3/4 \tag{21}$$

and

$$\begin{aligned} \delta\Delta_{a3q} = {} & -(2B_e/\omega_e^2)\{(3 - 3a_1 + 6a_4/a_3)\delta s_1 + 2\delta s_2 - \\ & 2\delta s_5/a_3\} - 3(\delta r_0 - \delta q_0)/2 + a_2\delta q_1/a_3 + \\ & a_1\delta q_2/2a_3 + \delta q_3/4a_3 \end{aligned} \tag{22}$$

Since the eigenvalue of eq 3 is defined in units of cm^{-1}, units of s_i and $\tilde{s}_i$ in the replacement (eq 20) are in cm^{-1} and the factor $hc\omega_e{}^2/B_e$ in eq 19 is changed to $\omega_e{}^2/B_e$ when the replacement (eq 20) is applied. Expressions for the lower-order optimal parameters, $\Delta_B{}^{a,b}$, $\Delta_\omega{}^{a,b}$, $\Delta_{aiq}{}^{a,b}$ (i = 1 and 2), and $r_{iq}{}^{a,b}$ (i = 1, 2, and 3) are given in ref 15.

Although expressions of $Y_{ij}{}^{*(0)}$ and $Y_{ij}{}^{(0)}$ including the potential constants of up to a_8 have been reported so far in references indicated by superscripts for $Y_{ij}{}^{*(0)}$ and $Y_{ij}{}^{(0)}$ as $Y_{01}{}^{*(0)}$,[15] $Y_{02}{}^{*(0)}$,[15] $Y_{03}{}^{*(0)}$,[15] $Y_{04}{}^{*(0)}$,[15] $Y_{05}{}^{(0)}$,[33] $Y_{06}{}^{(0)}$,[34] $Y_{07}{}^{(0)}$,[36] $Y_{08}{}^{(0)}$,[36] $Y_{09}{}^{(0)}$,[37] $Y_{010}{}^{(0)}$,[22] $Y_{10}{}^{*(0)}$,[15] $Y_{11}{}^{*(0)}$,[15] $Y_{12}{}^{*(0)}$,[15] $Y_{13}{}^{(0)}$,[16] $Y_{14}{}^{(0)}$,[33] $Y_{15}{}^{(0)}$,[34] $Y_{16}{}^{(0)}$,[36] $Y_{17}{}^{(0)}$,[37] $Y_{18}{}^{(0)}$,[22] $Y_{20}{}^{*(0)}$,[15] $Y_{21}{}^{(0)}$,[16] $Y_{22}{}^{(0)}$,[16] $Y_{23}{}^{(0)}$,[33] $Y_{24}{}^{(0)}$,[34] $Y_{25}{}^{(0)}$,[37] $Y_{26}{}^{(0)}$,[22]

$Y_{30}^{(0)}$,[16] $Y_{31}^{(0)}$,[16] $Y_{32}^{(0)}$,[33] $Y_{33}^{(0)}$,[35] $Y_{34}^{(0)}$,[22] $Y_{40}^{(0)}$,[16] $Y_{41}^{(0)}$,[33] $Y_{42}^{(0)}$,[35] and $Y_{50}^{(0)}$,[33] none of the expressions of $Y_{ij}^{(0)}$'s, i.e., $Y_{011}^{(0)}$, $Y_{19}^{(0)}$, $Y_{27}^{(0)}$, $Y_{35}^{(0)}$, $Y_{43}^{(0)}$, and $Y_{51}^{(0)}$, that are necessary for fitting a_9 have appeared. We have calculated them in the present study with Dunham's approach.[16]

Extending Dunham's analytical solution for the eigenvalue F in units of cm^{-1} to higher terms as

$$\begin{aligned}F = {} & B_eA_1A_3/16 + A_1B_e^{1/2}(v + 1/2) + (B_e^{3/2}A_1^2/32) \times \\ & (5A_5 - B_2A_3)(v + 1/2) - (B_eB_2A_1^2/4)(v + 1/2)^2 + \\ & (B_e^2A_1^3/128)(35A_7 - 15B_2A_5 + 3A_3B_2^2 - 3A_3B_4)(v + 1/2)^2 + \\ & (B_e^{3/2}A_1^3/8)(B_2^2 - B_4)(v + 1/2)^3 + (B_e^2A_1^4/64)(10B_2B_4 - \\ & 5B_2^3 - 5B_6)(v + 1/2)^4 + (B_e^{5/2}A_1^5/128)(15B_2B_6 - 21B_2^2B_4 + \\ & 7B_2^4 + 6B_4^2 - 7B_8)(v + 1/2)^5 + (B_e^3A_1^6/512)(35B_4B_6 + \\ & 49B_2B_8 - 56B_2B_4^2 - 70B_2^2B_6 + 84B_2^3B_4 - 21B_2^5 - 21B_{10}) \times \\ & (v + 1/2)^6 + \cdots \end{aligned} \tag{23}$$

we have obtained expressions of $Y_{011}^{(0)}$, $Y_{19}^{(0)}$, $Y_{27}^{(0)}$, $Y_{35}^{(0)}$, $Y_{43}^{(0)}$, and $Y_{51}^{(0)}$ with Maple, which are presented as Supporting Information to make our approach reproducible.

5. Experimental Section

So far, we have applied with success the present analytical method of the spectral fit (universal fit[23]) to LiH[15] and HCl.[22,23] However, an initial attempt to fit the reported rotational and vibrational−rotational spectral lines of a data set of HF showed a slight (less than 0.0007 cm^{-1}) but systematic deviation of the calculated rotational transitions from the observed ones in the range 750−1000 cm^{-1}. The data set consists of the benchmark rotational transitions observed by Tu-FIR,[2,38] higher rotational transitions observed by FTIR,[5,7] vibrational−rotational transitions by FTIR,[6,7] and several heterodyne measurements.[39,40] The deviation may originate from inconsistency among those categories of the measured transitions and/or inadequacy of the fitting model. To improve the accuracy of the fitting model, we have extended, as described above, a set of seven correction parameters for the breakdown of the Born−Oppenheimer approximation to nine parameters. Although a deviation appears in the range of the higher rotational transitions, it does not necessarily mean that the reported higher rotational transitions include errors. However, since the high-J rotational lines interspersed in wide ranges of far-infrared and mid-infrared up to 1100 cm^{-1} are important as calibration standards with claimed accuracy of $\pm$0.0002 cm^{-1},[5] we decided to re-measure the rotational transitions of HF in the range 600−950 cm^{-1}. Moreover, refs 5 and 41 reported that those transitions were calibrated against CO_2. Since the calibration standards of the CO_2 lines in the book of Guelachvili and Rao[42] cover only the range 592−716 cm^{-1}, the calibration procedures in refs 5 and 40 in the range 750−1000 cm^{-1} are not clear. We have calibrated the observed rotational transitions against the OCS calibration standards given by the NIST table[43] in the range 820−890 cm^{-1} that are located at the central portion of the region from 750 to 1000 cm^{-1}.

A high-temperature cell[44] that was made with a stainless steel tube of 50 mm in inner diameter was loaded with 13 g of AlF_3 at its central portion and 18 hPa of Ar buffer gas. The rotational emission spectrum of HF that was generated by the reaction of hot AlF_3 with residual water in the cell was observed by heating the cell to 1550 K. The total sample pressure was maintained at ~21 hPa during the measurements. One end of the high-temperature cell was sealed with a KRS-5 window, through which the emission from HF gas was transmitted. The radiation was focused onto an emission port of a Fourier transform spectrometer (Bruker IFS-125HR). With a KCl beam splitter and an MCT detector, the rotational spectra of the $v = 0$ and 1 states of HF were detected at the unapodized resolution of 0.0040 cm^{-1}, in contrast to 0.0053 cm^{-1} in refs 5 and 41, in the range 600−910 cm^{-1}. Sixty-four scans were accumulated in 60 min of integration.

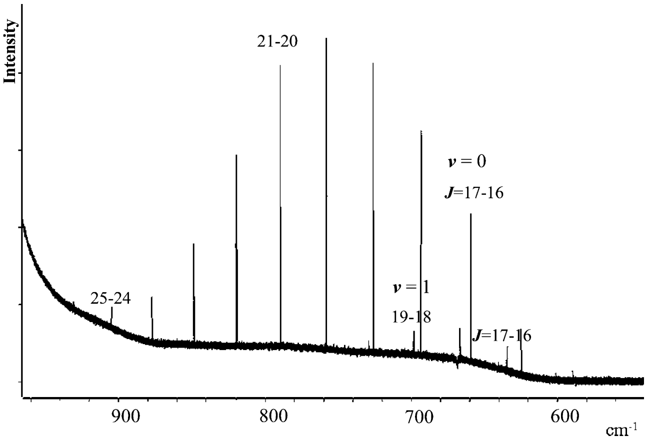

Figure 1. Rotational emission spectrum of HF measured to confirm spectral accuracy.

The OCS absorption spectrum was observed for the spectral calibration at 0.4 hPa in a 12-cm-long cell at room temperature. Eighty-one scans were added with the unapodized resolution of 0.0040 cm^{-1}. The observed rotational emission spectrum of HF is shown in Figure 1 and the transition wavenumbers are listed in Table 1 indicated by a superscript *g*. Spectral lines from $J = 15-14$ to $17-16$ of the $v = 0$ level have been observed but are not listed in the table because accurate measurements of these transitions suffered from self-absorptions. Estimated uncertainties in our measurements are $\pm$0.0002 cm^{-1} and $\pm$0.0005 cm^{-1} for the $v = 0$ and the weaker $v = 1$ transitions, respectively. The previously reported rotational transitions are also listed in the table. The sources of those transitions that are listed below are indicated in the table by the superscript. Our measurements of the high-J rotational lines in the $v = 0$ and 1 states agree well with those in ref 5 and have confirmed their measurements.

6. Analysis and Results

The spectral data of HF in the electronic ground state $^1\Sigma^+$ that have been included in the analysis are four benchmark TuFIR spectral lines studied by Jennings et al.[2] plus two additional TuFIR lines by Odashima et al.[38] and one FTFIR rotational transitions for the $v = 0$ state studied by Jennings et al.;[2] 11 FTIR rotational transitions for the $v = 0$ and 1 states remeasured in this work; 31 and 54 FTIR rotational transitions studied by Hedderich et al.[5] for the $v = 0$ to 2 states and by Ram et al.[7] for the $v = 0$ to 4 states, respectively; two diode laser heterodyne measurements of $v = 0$ rotational lines studied by Jennings and Wells;[39] 54 and 138 vibrational−rotational lines studied by Le Blanc et al.[6] for the $v = 1-0$ and $2-1$ transitions and by Ram et al.[7] for the $v = 1-0$ to $5-4$ transitions, respectively; and 5 heterodyne measurements of the $v = 1-0$ vibrational−rotational lines studied by Goddon et al.[40]

With reduced weights assigned to 9 outliers for the vibrational−rotational transitions among the 302 data in total, 105 rotational plus 197 vibrational−rotational transitions were simultaneously fitted with 15 adjustable parameters: $U_\omega(1 + \delta\Delta_\omega)$, $U_B(1 + \delta\Delta_B)$, $a_1(1 + \delta\Delta_{a1q})$, $a_2(1 + \delta\Delta_{a2q})$, $a_3(1 + \delta\Delta_{a3q})$, a_4, a_5, a_6, a_7, a_8, a_9, $r_{1q}{}^{\mathrm{H}}$ $(=r_{1q}{}^{\mathrm{F}})$, $r_{2q}{}^{\mathrm{H}}$ $(=r_{2q}{}^{\mathrm{F}})$, $r_{3q}{}^{\mathrm{H}}$ $(=r_{3q}{}^{\mathrm{F}})$, and $r_{4q}{}^{\mathrm{H}}$ $(=r_{4q}{}^{\mathrm{F}})$, where $U_\omega = \mu^{1/2}\omega_{\mathrm{e}}$, $U_B = \mu B_{\mathrm{e}}$, and $\delta x_i = (m_{\mathrm{e}}/M_{\mathrm{H}})x_i{}^{\mathrm{H}} + (m_{\mathrm{e}}/M_{\mathrm{F}})x_i{}^{\mathrm{F}}$ in which x_i stands for Δ_ω, Δ_B, or Δ_{akq} ($k =$ 1, 2, and 3) and μ is in units of u (atomic mass constant). The parameters $r_{iq}{}^{\mathrm{H,F}}$ (i = 1, 2, 3, and 4) denote the non-Born−Oppenheimer ones, which must be included explicitly in the spectral analysis even for the single isotopologue. A theoretical relation $r_{iq}{}^{\mathrm{H}} = r_{iq}{}^{\mathrm{F}}$ is assumed.[15]

An analysis has been made connecting these parameters with the vibrational−rotational energy levels through $Y^*_{ij}{}^{(0)} + Y_{ij}{}^{(2)}$ and $Y_{ij}{}^{(0)}$. The level of correction of a set of eleven $Y^*_{ij}{}^{(0)}$ and the Dunham potential constants up to a_9 are found to be sufficient for the present analysis, i.e., a set of 41 Y_{ij} that connected the fitting parameters with the energy levels is that of $Y^*_{ij}{}^{(0)} + Y_{ij}{}^{(2)}$ for ij = 01, 02, 03, 04, 05, 10, 11, 12, 13, 20, and 21 and $Y_{ij}{}^{(0)}$ for ij = 06, 07, 08, 09, 010, 011, 14, 15, 16, 17, 18, 19, 22, 23, 24, 25, 26, 27, 30, 31, 32, 33, 34, 35, 40, 41, 42, 43, 50, and 51. The spectral uncertainties, δ_{obs}, are those given in each paper. The weights for the spectral fit of the data are assumed to be proportional to $(1/\delta_{\mathrm{obs}})^2$. The fundamental physical constants are taken from the 2006 CODATA recommended values.[45] The fit is satisfactory: with 15 parameters, the normalized standard deviation is 1.22. The spectral data set and the obs − calc values are listed in Table 1 to show the quality of the present analysis. The molecular parameters determined in the fit are given in Table 2.

To facilitate calculations or predictions of the spectral frequencies, the values of 41 Y_{ij}, through which 15 molecular parameters are connected with the energy values, have been back-calculated with the values of the parameters given in Table 2. They are listed in Table 3. All of the 41 Y_{ij} are significantly determined with smaller standard errors. Therefore, if one attempts to fit the present set of spectral data with adjustable Dunham's Y_{ij}, 41 Y_{ij} parameters are required to reproduce the data, whereas only 15 parameters are needed in the present approach.

7. Discussion

7.1. Non-Born−Oppenheimer Analysis for a Single Isotopologue. We have presented in this paper the analytical approach of the non-Born−Oppenheimer analysis for a single isotopologue in case of HF; this is the first example of the non-Born−Oppenheimer analysis of a single isotopologue with physically meaningful parameters based on the conventional molecular constants. Since the spectral fit was made with the analytical solution of the Schrödinger equation, anyone can easily reproduce the fitting procedure.

In a recent trend of the numerical approach of the non-Born−Oppenheimer analysis, even in the reliable method by Watson,[24,25] it is not clear how to find correct fitting parameters to be used for an analysis of a spectral data set of a single isotopologue. The parameters determined in Table 2 have well-defined physical significance. The values of $B_{\mathrm{e}}(1 + \delta\Delta_B)$, $r_{\mathrm{e}}(1 - \delta\Delta_B/2)$, $\omega_{\mathrm{e}}(1 + \delta\Delta_\omega)$, and $k(1 - 2\delta\Delta_\omega)$, instead of B_{e}, r_{e}, ω_{e}, or k, from the present fit are 20.954 308 01(107) cm^{-1}, 91.683 898 91(233) pm, 4138.573 005(806) cm^{-1}, and 965.802 732(376) N m^{-1}, respectively.

Coxon and Hajigeorgiou[13] defined the Hamiltonian for a particular isotopologue i on the basis of the theoretical work by Watson.[9] Their numerical approach[13] that utilizes the analytical potential model with an iterative direct potential-fit method works well to reproduce the spectral data extending over a large internuclear distance. However, it differs from our analytical approach not only by the procedure but also by the goal. Watson's Hamiltonian[9] aims at the separate determination of the isotopically invariant μB_{e} $(=U_{01})$, $\mu^{1/2}\omega_{\mathrm{e}}$ $(=U_{10})$, Dunham's potential constants a_k (the Born−Oppenheimer potential), and two functions $\tilde{R}_{a,b}(\xi)$ and $\tilde{S}_{a,b}(\xi)$ by simultaneous fitting of the spectral lines of multiple isotopologues, and cannot be used for a single isotopologue without considering conversions of the original fitting parameters to those determinable by fitting transitions of only one isotopologue. The consideration has been made in ref 18 based on the generally accepted concept of the molecular constants that correspond to the Dunham series expansion.[46]

In contrast, Coxon and Hajigeorgiou[13] utilized $\tilde{R}_{a,b}(\xi)$ as $q_i(x)$ in which x is identical to ξ but did not use $\tilde{S}_{a,b}(R)$ to construct $U_{\mathrm{HF}}{}^{\mathrm{eff}}(R)$, an overall effective potential function of HF. They introduced an effective potential function $U_{\mathrm{HF}}{}^{\mathrm{eff}}(R)$ for HF and used $U^{\mathrm{H}}(R)$, which corresponds to $\tilde{S}_H(R)$, to generate $U_{\mathrm{DF}}{}^{\mathrm{eff}}(R)$ from $U_{\mathrm{HF}}{}^{\mathrm{eff}}(R)$. Thus, in a fit of all the HF and DF data together, they determined the functions $U_{\mathrm{HF}}{}^{\mathrm{eff}}(R)$ and $U^{\mathrm{H}}(R)$, simultaneously. It should be noted that the functions $\tilde{R}_{a,b}(\xi)$ and $\tilde{S}_{a,b}(\xi)$ are tightly coupled through a constant term $r_0{}^{a,b}$ of $R_{a,b}(\xi)$.[15] The constant term $r_0{}^{a,b}$ is the major part of $R_{a,b}(\xi)$. In ref 15, we presented relations that generated $r_0{}^{a,b}$ from the rotational g factor and the electric dipole moment by eqs 52 and 53, in both of which '$i = 1$' under the symbol Σ was a typing error and should read '$i = 0$'.

The $\tilde{S}_{a,b}(\xi)$ function is especially important, contrary to $\tilde{R}_{a,b}(\xi)$ or $q_{a,b}(x)$, because the expansion coefficients $\tilde{s}_1{}^{a,b}$, $\tilde{s}_2{}^{a,b}$, $\tilde{s}_3{}^{a,b}$, and $\tilde{s}_4{}^{a,b}$, ..., of $\tilde{S}_{a,b}(\xi)$ define isotopically invariant μB_{e}, i.e., r_{e}, $\mu^{1/2}\omega_{\mathrm{e}}$, i.e., the force constant k, a_1, and a_2, ..., respectively. This is easily verified by applying a replacement in eq 20 of the expressions of the optimal parameters given in Table 2 of ref 15.

The physical significance of the isotopically invariant R_{e}, $\mu^{1/2}\omega_{\mathrm{e}}$, and Dunham's potential constants a_1, a_2, ..., which are the important concept of spectroscopy, is presented as the goal of the present non-Born−Oppenheimer analysis of the analytical approach.

7.2. Combined Fit for HF and DF Spectral Data. Since the purpose of the present study is to apply the analytical approach to transitions of a single isotopologue, we show only a fraction of the results of a simultaneous fit for HF and DF spectral data that advance understanding of the molecular parameters obtained for HF written above. The details of the simultaneous fit will be published elsewhere. The spectral data of DF have been taken from the reported papers.[7,47,48] The 302 and 294 spectral transitions for HF and DF, respectively, have simultaneously been fitted with 20 molecular parameters that are invariant for HF and DF: $U_\omega(1 + m_{\mathrm{e}}\Delta_\omega{}^{\mathrm{F}}/M_{\mathrm{F}})$, $U_B(1 + m_{\mathrm{e}}\Delta_B{}^{\mathrm{F}}/M_{\mathrm{F}})$, $a_1(1 + m_{\mathrm{e}}\Delta_{a1q}{}^{\mathrm{F}}/M_{\mathrm{F}})$, $a_2(1 + m_{\mathrm{e}}\Delta_{a2q}{}^{\mathrm{F}}/M_{\mathrm{F}})$, $a_3(1 + m_{\mathrm{e}}\Delta_{a3q}{}^{\mathrm{F}}/M_{\mathrm{F}})$, a_4, a_5, a_6, a_7, a_8, a_9, $\Delta_\omega{}^{\mathrm{H}}$, $\Delta_B{}^{\mathrm{H}}$, $\Delta_{a1q}{}^{\mathrm{H}}$, $\Delta_{a2q}{}^{\mathrm{H}}$, $\Delta_{a3q}{}^{\mathrm{H}}$, $r_{1q}{}^{\mathrm{H}}$ $(=r_{1q}{}^{\mathrm{F}})$, $r_{2q}{}^{\mathrm{H}}$ $(=r_{2q}{}^{\mathrm{F}})$, $r_{3q}{}^{\mathrm{H}}$ $(=r_{3q}{}^{\mathrm{F}})$, and $r_{4q}{}^{\mathrm{H}}$ $(=r_{4q}{}^{\mathrm{F}})$. The fit is satisfactory; the normalized standard deviation is 1.23.

The values of $U_B(1 + m_{\mathrm{e}}\Delta_B{}^{\mathrm{F}}/M_{\mathrm{F}})$, $r_{\mathrm{e}}(1 - m_{\mathrm{e}}\Delta_B{}^{\mathrm{F}}/2M_{\mathrm{F}})$, $U_\omega(1 + m_{\mathrm{e}}\Delta_\omega{}^{\mathrm{F}}/M_{\mathrm{F}})$, and $k(1 - 2m_{\mathrm{e}}\Delta_\omega{}^{\mathrm{F}}/M_{\mathrm{F}})$ are 20.048 112 94(103) cm^{-1} u, 91.698 344 78(236) pm, 4048.449 190(711) cm^{-1} u$^{1/2}$, and 965.667 359(339) N m^{-1}, respectively. The value of $r_{\mathrm{e}}(1 - m_{\mathrm{e}}\Delta_B{}^{\mathrm{F}}/2M_{\mathrm{F}})$ is significantly different from the R_{e} value of 91.683 896(2) pm of ref 13 given for HF by a simultaneous analysis of HF and DF data.

We have shown in ref 18 that δr_{iq} (i = 1, 2, ···) can be determined for each isotopologue. Therefore, just identical values of $r_{1q}{}^{\mathrm{H}}$ $(=r_{1q}{}^{\mathrm{F}})$, $r_{2q}{}^{\mathrm{H}}$ $(=r_{2q}{}^{\mathrm{F}})$, $r_{3q}{}^{\mathrm{H}}$ $(=r_{3q}{}^{\mathrm{F}})$, and $r_{4q}{}^{\mathrm{H}}$ $(=r_{4q}{}^{\mathrm{F}})$

TABLE 5: Reported Rotational Transitions Accurately Measured up to 1000 cm^{-1} and obs − calc Values Evaluated in this Work and Ref 13 (Units are in cm^{-1})

				obs − calc	
J'	J''	obs	uncertainties	this work	ref 13
$v = 0$					
1	0	41.1109832^a	3.0×10^{-6}	2.0×10^{-7}	8.0×10^{-7}
2	1	82.1711179^a	6.0×10^{-6}	-3.0×10^{-7}	-2.0×10^{-7}
3	2	123.1296703^a	9.0×10^{-6}	-5.2×10^{-6}	-3.8×10^{-6}
4	3	163.9361645^a	1.2×10^{-5}	4.9×10^{-6}	6.1×10^{-6}
5	4	204.54045^a	2.0×10^{-4}	2.0×10^{-5}	2.0×10^{-5}
6	5	244.892784^b	1.2×10^{-5}	-1.0×10^{-5}	-1.1×10^{-5}
7	6	284.944158^b	3.3×10^{-5}	-3.0×10^{-6}	-6.0×10^{-6}
13	12	516.28061^c	2.0×10^{-4}	-5.0×10^{-5}	-8.0×10^{-5}
14	13	552.92047^c	2.0×10^{-4}	1.7×10^{-4}	1.3×10^{-4}
15	14	588.89912^c	2.0×10^{-4}	1.1×10^{-4}	7.0×10^{-5}
16	15	624.17735^c	2.0×10^{-4}	1.3×10^{-4}	8.0×10^{-5}
17	16	658.71685^c	2.0×10^{-4}	3.0×10^{-5}	-3.0×10^{-5}
18	17	692.48118^c	2.0×10^{-4}	-3.0×10^{-5}	-9.0×10^{-5}
19	18	725.43521^c	2.0×10^{-4}	-1.2×10^{-4}	-1.8×10^{-4}
20	19	757.54563^c	2.0×10^{-4}	-6.0×10^{-5}	-1.3×10^{-4}
21	20	788.78038^c	2.0×10^{-4}	-9.0×10^{-5}	-1.5×10^{-4}
22	21	819.10934^c	2.0×10^{-4}	-1.3×10^{-4}	-1.9×10^{-4}
23	22	848.50403^c	2.0×10^{-4}	-1.3×10^{-4}	-1.8×10^{-4}
24	23	876.93760^c	2.0×10^{-4}	-1.1×10^{-4}	-1.5×10^{-4}
25	24	904.38479^c	2.0×10^{-4}	-1.7×10^{-4}	-2.1×10^{-4}
26	25	930.82215^c	2.0×10^{-4}	-3.1×10^{-4}	-3.3×10^{-4}
27	26	956.228158^d	2.7×10^{-4}	-2.7×10^{-4}	-2.6×10^{-4}
28	27	980.58255^c	2.0×10^{-4}	-1.9×10^{-4}	-1.5×10^{-4}
29	28	1003.86689^c	2.0×10^{-4}	-3.0×10^{-5}	3.0×10^{-5}
33	32	1085.98903^d	2.7×10^{-4}	2.4×10^{-4}	5.5×10^{-4}
18	17	692.48114^e	2.0×10^{-4}	-7.0×10^{-5}	-1.3×10^{-4}
19	18	725.43529^e	2.0×10^{-4}	-4.0×10^{-5}	-1.0×10^{-4}
20	19	757.54560^e	2.0×10^{-4}	-9.0×10^{-5}	-1.6×10^{-4}
21	20	788.78041^e	2.0×10^{-4}	-6.0×10^{-5}	-1.2×10^{-4}
22	21	819.10927^e	2.0×10^{-4}	-2.0×10^{-4}	-2.6×10^{-4}
23	22	848.50401^e	2.0×10^{-4}	-1.5×10^{-4}	-2.0×10^{-4}
24	23	876.93745^e	2.0×10^{-4}	-2.6×10^{-4}	-3.0×10^{-4}
25	24	904.38525^e	2.0×10^{-4}	2.9×10^{-4}	2.5×10^{-4}
$v = 1$					
13	12	496.68517^c	2.0×10^{-4}	-5.0×10^{-5}	-6.0×10^{-5}
14	13	531.89851^c	2.0×10^{-4}	-4.0×10^{-5}	-5.0×10^{-5}
15	14	566.46812^c	2.0×10^{-4}	-1.5×10^{-4}	-1.7×10^{-4}
16	15	600.35572^c	2.0×10^{-4}	-9.0×10^{-5}	-1.2×10^{-4}
17	16	633.52402^c	2.0×10^{-4}	2.0×10^{-5}	-3.0×10^{-5}
18	17	665.93707^c	2.0×10^{-4}	-5.0×10^{-5}	-1.0×10^{-4}
19	18	697.56091^c	2.0×10^{-4}	-2.0×10^{-5}	-8.0×10^{-5}
20	19	728.36279^c	2.0×10^{-4}	5.0×10^{-5}	-1.0×10^{-5}
21	20	758.31128^c	2.0×10^{-4}	-1.0×10^{-4}	-1.7×10^{-4}
22	21	787.37827^c	2.0×10^{-4}	9.6×10^{-4}	8.9×10^{-4}
17	16	633.52367^e	5.0×10^{-4}	-3.3×10^{-4}	-3.8×10^{-4}
18	17	665.93696^e	5.0×10^{-4}	-1.6×10^{-4}	-2.1×10^{-4}
19	18	697.56079^e	5.0×10^{-4}	-1.4×10^{-4}	-2.0×10^{-4}

[a] Ref 2. [b] Ref 38. [c] Ref 5. [d] Ref 39. [e] This work.

should be obtained in all the cases of the fit for a single isotopologue and the simultaneous fit for HF and DF. The theoretical relation $r_{iq}{}^{\mathrm{H}} = r_{iq}{}^{\mathrm{F}}$, i.e., $\tilde{r}_i{}^{\mathrm{H}} = \tilde{r}_i{}^{\mathrm{F}}$, ($i = 1, 2, \cdots$) has been given in ref 15. Excellent agreement with the theory and the experimental results has been obtained, since the values of $r_{1q}{}^{\mathrm{H}}$ ($= r_{1q}{}^{\mathrm{F}}$), $r_{2q}{}^{\mathrm{H}}$ ($= r_{2q}{}^{\mathrm{F}}$), and $r_{3q}{}^{\mathrm{H}}$ ($= r_{3q}{}^{\mathrm{F}}$) determined from the simultaneous fit, −0.106 00(331), −0.9149(526), and 0.521(105), respectively, agree with those given in Table 2 within the mutual error limits. The value for $r_{4q}{}^{\mathrm{H}}$ ($= r_{4q}{}^{\mathrm{F}}$), 0.654(331), does not agree with the value listed in Table 2, but since it carries large error limits and/or truncation errors, this deviation is acceptable. The values of $q_1{}^{\mathrm{H}}$, $q_2{}^{\mathrm{H}}$, and $q_3{}^{\mathrm{H}}$ reported by Coxon and Hajigeorgiou[13] do not agree, in conflict with the relation $\tilde{r}_i{}^{\mathrm{H}} = \tilde{r}_i{}^{\mathrm{F}}$, with those of $q_1{}^{\mathrm{F}}$, $q_2{}^{\mathrm{F}}$, and $q_3{}^{\mathrm{F}}$, respectively. The reason their values of $q_i{}^{\mathrm{H}}$ and $q_i{}^{\mathrm{F}}$ ($i = 1, 2, \cdots$) do not satisfy the relation $q_i{}^{\mathrm{H}} = q_i{}^{\mathrm{F}}$ is unknown, but the physical significance of $q_i{}^{\mathrm{H,F}}$ is not clear since they arbitrarily introduced switching functions as factors for H and F.

7.3. Y_{ij} Values. Coxon and Ogilvie[11] made a simultaneous analysis of a spectral data set of HF, DF, and TF from the millimeter-wave region to the vacuum ultraviolet, but they did not include accurate TuFIR, FTFIR, and FTIR measurements. The Y_{ij} values for ref 11 included in Table 3 were those calculated from the obs values of U_{ij} and $\Delta_{ij}{}^{\mathrm{H}}$ that were given by Coxon and Ogilvie[11] after a rather complicated process of fitting. In contrast, our data set consists of only the high-resolution rotational and vibrational−rotational spectra excluding those with much larger uncertainties such as the electronic spectra, which smear out the effect of the breakdown of the Born−Oppenheimer approximation due to larger line widths.

Table 3 shows that the agreement of our Y_{ij} values with those of Coxon and Ogilvie[11] is in general good, but the present values have much higher precision and consistency. The present analysis has revealed that the potential expansion up to the a_9 term, which corresponds to 41 Y_{ij} values, must be included to fit the vibrational−rotational transitions up to the $v = 5{-}4$ band. In contrast, although Coxon and Ogilvie[11] included transitions of up to $v = 9$ they determined only 21 U_{ij} values, which correspond to 21 Y_{ij} for HF. Their analysis was limited by much larger uncertainties of the spectral data included.

An easy and straightforward procedure of the single fit to the whole vibrational states with only the 15 parameters, instead of the 41Y_{ij}, corroborates the merit of the present physical model for application to an analysis of the spectra of $^1\Sigma$ diatomic molecules.

7.4. Clusters of the Expansion Coefficients as Determinable Parameters. Although the present report has focused the attention on the spectral analysis of a single isotopologue, this analytical approach is more general.[18,23] If a molecule AB has multiple isotopic nuclides for both atoms A and B, the only change is the choice of fitting parameters, which should be U_ω, U_B, a_i ($i = 1, 2, \cdots$), $\Delta_\omega{}^{a,b}$, $\Delta_B{}^{a,b}$, $\Delta_{aiq}{}^{a,b}$ ($i = 1, 2, \cdots$), and $r_{iq}{}^{a,b}$ ($i = 1, 2, \cdots$). A notable feature of the present analysis is that the choice of the fitting parameters and the corresponding set of Y_{ij} that connects the fitting parameters with term values are all unique.[22]

In any kind of analyses[26–28,49] including studies[26–28] based on numerical approaches, where expansion coefficients of the individual correction functions $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, or $S_{a,b}(\xi)$ are chosen as independent fitting parameters, the lack of correct physical significance of the determined numerical values of the coefficients hinders transferability of the parameter values.[23] One would often assume that a naive numerical fitting of individual expansion coefficients could result in a reasonably accurate set of lower-order coefficients under any circumstances, but this is *not* the case. The expressions of $Y^*{}_{ij}{}^{(0)}$, which are experimentally determinable, are simple combinations[15] of the expansion coefficients of $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$. Therefore, there is no priority of the lower-order individual expansion coefficients for their determinations from the expressions of $Y^*{}_{ij}{}^{(0)}$. This is the key issue of the fact that the determinable parameters are only the clusters,[15,18,23] i.e., the combinations after Watson,[9,24,25] of the expansion coefficients as explicitly demonstrated in the effective Hamiltonian (eq 11), which is equivalent to the original effective Hamiltonian (eq 2). The point is entirely ignored in recent analyses with numerical approaches.[26–28]

7.5. Rotational Constants of Each Vibrational State and the Merit of the Analytical Approach. It is easy for the analytical approach to confine the calculation up to the order of O(m_e/M_i). In a recent style of the numerical approach[26] to get eigenvalues of the Schrödinger equation of diatomic molecules in $^1\Sigma$, the order of the calculation is not confined to O(m_e/M_i), but the basic requirement for the original Hamiltonian is the neglect of terms of orders higher than O(m_e/M_i). The numerical calculation[24,25,27] that includes higher order(s) than O(m_e/M_i) cannot improve the accuracy of the determination of the fitting parameters but may end up with unexpected systematic errors.

Coxon and Hajigeorgiou[13] ignored the traditional concept of the molecular constants for fitting parameters but adopted an overall analytical potential function $U_{\mathrm{HF}}^{\mathrm{eff}}(R)$ with the iterative fitting over large internuclear distances. They calculated the vibrational term values and the rotational constants a posteriori using the radial effective functions thus determined. We compare the molecular constants of HF that they calculated from their radial operators with our values listed in Table 4 calculated with Y_{ij}'s shown in Table 3.

Notations of the rotational and the distortion constants in Table 4 are given by the equation for the energy levels as

$$\begin{aligned}F_v(J) = G_v + B_vJ(J+1) - D_v[J(J+1)]^2 + \\ H_v[J(J+1)]^3 + L_v[J(J+1)]^4 + M_v[J(J+1)]^5 + \\ N_v[J(J+1)]^6 + O_v[J(J+1)]^7 + P_v[J(J+1)]^8 + \\ Q_v[J(J+1)]^9 + R_v[J(J+1)]^{10} + S_v[J(J+1)]^{11} \quad (24)\end{aligned}$$

A term $Y_{00} = (B_e/8)(3a_2 - 7a_1^2/4)$, which is not listed in Table 3, is included in the calculation of G_v. The molecular constants of Coxon and Hajigeorgiou[13] are given at the second row entries.

Spectral analyses by Bernath's group[5–7] provided the rotational constants for each vibrational state. Their values can also be compared with our values in Table 4. Their rotational constants[7] that have been determined from the most extensive compilation of the rotational and the vibrational−rotational spectral lines of HF are listed at the third row entries.

Our values of $G_v - G_0$, B_v, and D_v agree well with those of Ram et al.[7] and Coxon and Hajigeorgiou,[13] but the agreements of the higher-order rotational constants, H_v, L_v, and M_v, are much better with those of Coxon and Hajigeorgiou[13] than those of Ram et al.,[7] although the former did not give error limits for those values of the molecular constants. Our error limits are larger than those of Ram et al.,[7] because our limits reflect the uncertainty in the potential function at a high-energy range. The error limits given by Ram et al.[7] contain no such effects.

The terms up to $S_v[J(J+1)]^{11}$ need be included in this analysis, in which the potential expansion up to a_9 is necessary to reproduce the spectral transitions. Although the vibrational terms of this study agree well with those of ref 13, the agreement of the rotational constants of the orders higher than P_v of this study with those of ref 13 is not satisfactory, presumably because our constants include the truncation errors; the present study does not intend to determine the potential function that extends over highly excited vibrational states that can be observed in the electronic spectra.

The values of the constants with error limits can be easily obtained from G_v up to S_v in this study from a set of the fitted molecular parameters through the values of Y_{ij}, but it is not the case for the numerical approach. By the merit of the analytical approach, it is easy to reproduce the numerical values of the present potential function and the eigenvalues including the effect of the breakdown of the Born−Oppenheimer approximation. It is notable that only the 15 molecular parameters determined experimentally have generated the 72 rotational constants in Table 4.

In Table 5, the reported rotational transitions accurately measured up to 1000 cm^{-1} that provide useful absolute wavelength standards are compared with the calculated values of the present study and those of ref 13 calculated by using the rotational constants listed in Table 4. Table 5 shows that there may still be a slight but uniform shift up to 0.0002 cm^{-1} in the obs − calc values of the rotational transitions in the range 800−1050 cm^{-1}. The amount of the shift for the calculated values of ref 13 is larger than that of the present study. Although we anticipated that the shift might originate from the reported measurements, our present measurements confirmed the accuracy of those reported in ref 5. The origin is unknown at present, but further study of the accuracy of the vibrational−rotational transitions is needed to confirm whether the observed slight shift arises from an inconsistency in the data set.

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Supporting Information Available: Dunham's $Y_{011}^{(0)}$, $Y_{19}^{(0)}$, $Y_{27}^{(0)}$, $Y_{35}^{(0)}$, $Y_{43}^{(0)}$, $Y_{51}^{(0)}$, $Y_{05}^{(2)}$, and $Y_{13}^{(2)}$ coefficients expressed in terms of the potential constants a_i, B_e, and ω_e. This material is available free of charge via the Internet at http://pubs.acs.org.

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