

Analysis of Vibrational–Rotational Spectra with Optimal Fitting Parameters for Born–Oppenheimer Corrections to Dunham's Y_{ij}: An Application to Spectral Data of HCl

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Analytic expressions for Born–Oppenheimer corrections to Dunham's Y_{ij} with optimal fitting parameters, i.e., determinable clusters of expansion coefficients, are applied in analysis of data of reported vibrational–rotational and rotational transitions of HCl. In this method of analysis the choices of a set of fitting parameters and also a corresponding set of Y_{ij} that connects the fitting parameters with the term values are unique. A layered structure for empirical parameters Δ_{ij} is revealed. All spectral lines of four isotopomers of HCl are simultaneously fitted to a single set of molecular constants well within the experimental errors. The approach thus provides a better fit of smaller standard deviations with fewer number of adjustable parameters than from other methods of analysis. The determined values for the coefficients of adiabatic effects $s_1{}^{H}$ and $s_1{}^{Cl}$ reveal the wobble-stretch term to be unimportant in the adiabatic correction for HCl.

Contemporary infrared and microwave spectrometers enable accurate measurements of many spectral lines for diatomic molecules for several vibrational states and various isotopomers. In a simultaneous analysis of extensive spectral data for various isotopomers, one must take into account adiabatic and nonadiabatic corrections to the Born–Oppenheimer approximation.[1–9] A conventional method was to fit the spectral lines to levels v, J of a molecule AB, expressed as

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

in which U_{ij} and Δ_{ij} are mass-invariant constants. Correction parameters Δ_{ij} are treated as empirical parameters without direct physical significance.[3,5,10]

Following an analytic approach by Fernandez and Ogilvie[6] for the Born–Oppenheimer corrections, we modified the Δ_B and Δ_ω scheme by Thompson et al.,[11] with which we analyzed the spectra of molecules,[12–14] to obtain a compact expression for the contributions of the expansion coefficients for the correction terms in the Hamiltonian to Dunham Y_{ij} coefficients.[15–17] We applied the results to molecules LiH[15,16] and CaH,[17] but since estimated values of the fitting parameters for the corrections were effective we could not proceed[15–17] to relate those values of the fitting parameters to physical quantities, such as the molecular g_J values, electric dipole moments, and matrix elements of operators.

An examination of the determinacy of the fitting parameters has revealed optimal clusters of expansion coefficients in a set that is essential to relate the experimental values to the Born–Oppenheimer corrections.[18] Thus, a method to determine the functions of the corrections for adiabatic, nonadiabatic vibrational, and nonadiabatic rotational effects separately has been found:[18] if nonadiabatic rotational functions are obtained according to the method of Herman and Ogilvie[20] from the electric dipole moment and molecular g_J functions, the values of the optimal clusters of parameters enable an evaluation of adiabatic and nonadiabatic vibrational functions. One can determine three types of corrections separately only through this approach. An experimental determination of the optimal parameters, i.e., determinable clusters of expansion coefficients, has so far been made only for LiH.[18]

The purpose of this paper is to apply the analysis with optimal parameters[18] to another example, HCl. Reported 1110 rotational and vibrational–rotational spectral data for four isotopomeres of HCl were simultaneously fitted with only 21 adjustable parameters, among which eleven are optimal parameters. In contrast, 140 Dunham Y_{ij} coefficients in total, 35 Y_{ij} for each isotopomer, must be retained as adjustable parameters if the spectral data are directly fitted with the Dunham Y_{ij} coefficients. The determined values of the optimal parameters with the reported dipole moment and g_J values provided values of expansion coefficients $s_1{}^{H}$ and $s_1{}^{Cl}$ for the adiabatic corrections. Those values of the expansion coefficients indicate the wobble-stretch term to be unimportant in HCl.

Method of Analysis

A method of analysis based on the Δ_B and Δ_ω scheme with optimal fitting parameters has been reported.[18] An original effective Hamiltonian,[1,5,19,20] ignoring terms of order higher than $O(m_e/M_i)$, e.g., by Watson,[5] in electronic state $^1\Sigma$ yields a Schrödinger equation[18] in terms of a variable, $\xi = (r - r_e)/r_e$, as

$$\left[-\frac{h^2}{8\pi^2\mu r_e{}^2}\frac{d}{d\xi}\{1 + (m_e/M_a)Q_a(\xi) + (m_e/M_b)Q_b(\xi)\}\frac{d}{d\xi} + \frac{h^2}{8\pi^2\mu r_e{}^2(1+\xi)^2}\{1 + (m_e/M_a)R_a(\xi)\right.$$

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Table 1. Levels of Sets of $Y_{ij}{}^{*(0)}$ and Participating Determinable Optimal Parameters

Levels of sets of $Y_{ij}{}^{*(0)}$	Optimal parameters included
$Y_{01}{}^{*(0)}$	$\delta\Delta_B$
$Y_{10}{}^{*(0)}$	$\delta\Delta_\omega$
$Y_{01}{}^{*(0)}$, $Y_{02}{}^{*(0)}$, $Y_{10}{}^{*(0)}$	$\delta\Delta_B$, δr_{1q}, $\delta\Delta_\omega$
$Y_{01}{}^{*(0)}$, $Y_{02}{}^{*(0)}$, $Y_{03}{}^{*(0)}$, $Y_{10}{}^{*(0)}$, $Y_{11}{}^{*(0)}$	$\delta\Delta_B$, δr_{1q}, δr_{2q}, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$
$Y_{01}{}^{*(0)}$, $Y_{02}{}^{*(0)}$, $Y_{03}{}^{*(0)}$, $Y_{04}{}^{*(0)}$, $Y_{10}{}^{*(0)}$, $Y_{11}{}^{*(0)}$, $Y_{12}{}^{*(0)}$, $Y_{20}{}^{*(0)}$	$\delta\Delta_B$, δr_{1q}, δr_{2q}, δr_{3q}, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$, $\delta\Delta_{a2q}$

$$+ (m_e/M_b)R_b(\xi)\}J(J+1)$$
$$+ V(\xi) + (m_e/M_a)S_a(\xi) + (m_e/M_b)S_b(\xi)\Big]\psi_{vJ}(\xi)$$
$$= E_{vJ}\psi_{vJ}(\xi), \quad (2)$$

in which μ is the reduced mass of a molecule and M_a, M_b, and m_e are the masses of atoms A and B and the electron, respectively. Mass-independent functions $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$, are correction terms for nonadiabatic vibrational, nonadiabatic rotational, and adiabatic effects, respectively.

Similar to Dunham's original function for potential energy,[21]

$$V(\xi) = (1/2)kr_e{}^2\xi^2(1 + a_1\xi + a_2\xi^2 + \ldots), \quad (3)$$

functions $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$ are expressed,[18] after Fernandez and Ogilvie,[6] as series expansions of ξ as

$$Q_{a,b}(\xi) = \sum_{i=0} q_i^{a,b}\xi^i, \quad (4)$$

$$R_{a,b}(\xi) = \sum_{i=0} r_i^{a,b}\xi^i, \quad (5)$$

and

$$S_{a,b}(\xi) = \sum_{i=1} s_i^{a,b}\xi^i, \quad (6)$$

we confine our attention formally to a region with $|\xi| < 1$. Terms of $s_0{}^{a,b}$ are removed from Eq. 6 because they yield no effect on Eq. 2 in the electronic ground state.

We derived the Schrödinger equation written in the scheme of Δ_B and Δ_ω and then applied[15,18] a Dunham-like treatment[21–23] to it to yield the vibrational–rotational energy F_{vJ} eventually as

$$F_{vJ} = \sum_{ij} Y_{ij}^*(v + 1/2)^i[J(J+1)]^j. \quad (7)$$

Eight modified Dunham coefficients, $Y_{ij}{}^{*(0)}$ ($ij = 01$, 02, 03, 04, 10, 11, 12, and 20), expressed by seven clusters of the expansion coefficients for corrections, i.e., by seven optimal parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$, $\delta\Delta_{a2q}$, δr_{1q}, δr_{2q}, and δr_{3q}, are presented in Eqs. 36–43 of Ref. 18. A notation δx_i is used[18] for a pair of arbitrary quantities, $x_i{}^a$ and $x_i{}^b$:

$$\delta x_i = (m_e/M_a)x_i{}^a + (m_e/M_b)x_i{}^b. \quad (8)$$

At a level of a modified single Dunham coefficient, $Y_{01}{}^{*(0)}$ or $Y_{10}{}^{*(0)}$, only one correction parameter, $\delta\Delta_B$ or $\delta\Delta_\omega$, appears, respectively. In the next level of a set of three $Y_{ij}{}^{*(0)}$, $Y_{01}{}^{*(0)}$, $Y_{02}{}^{*(0)}$, and $Y_{10}{}^{*(0)}$, three correction parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, and δr_{1q}, are included. In two succeeding sets of five and eight $Y_{ij}{}^{*(0)}$, five and seven correction parameters are included, respectively. Therefore, in the level of a set of eight $Y_{ij}{}^{*(0)}$ there exists a redundancy among eight $Y_{ij}{}^{*(0)}$ or eight $\delta\Delta_{ij}{}^{adnad}$;[18] this redundancy is presented in Eq. 44 in Ref. 18. Those levels of sets of $Y_{ij}{}^{*(0)}$ and the participating optimal correction parameters are listed in Table 1.

The relation between $Y_{ij}{}^{*(0)}$ and the conventional parameter Δ_{ij} is

$$Y_{ij}{}^{*(0)} + Y_{ij}{}^{(2)} = Y_{ij}{}^{(0)}\{1 + (m_e/M_a)\Delta_{ij}^{adnad,a} + (m_e/M_b)\Delta_{ij}^{adnad,b}\} + Y_{ij}{}^{(2)}$$
$$= Y_{ij}{}^{(0)}\{1 + (m_e/M_a)\Delta_{ij}^{a} + (m_e/M_b)\Delta_{ij}^{b}\}. \quad (9)$$

$Y_{ij}{}^{(2)}$ is the Dunham correction, which is defined in Eq. 17 of Ref. 18. Dunham corrections $Y_{01}{}^{(2)}$, $\{Y_{02}{}^{(2)}, Y_{10}{}^{(2)}\}$, $\{Y_{03}{}^{(2)}, Y_{11}{}^{(2)}\}$, and $\{Y_{04}{}^{(2)}, Y_{12}{}^{(2)}, Y_{20}{}^{(2)}\}$ include potential constants of up to a_3, a_4, a_5, and a_6, respectively. Therefore, from Eq. 9, Table 1 indicates a layered structure, i.e., Δ_{01}, Δ_{10}, Δ_{02}, $\{\Delta_{03}, \Delta_{11}\}$, $\{\Delta_{04}, \Delta_{12}, \Delta_{20}\}$, …, for the conventional empirical parameters, Δ_{ij}. A simple way to take the redundancy for Δ_{ij} into account is to evaluate $Y_{ij}{}^{(2)}$ from the values of U_{ij}, and then to use Eq. 44 in Ref. 18 for Δ_{ij}^{adnad}. If one fits spectral data to a set of empirical parameters, Δ_{ij}, one should take into account the level of a set of Δ_{ij} and the redundancy.

Application to Spectral Data of HCl

Table 1 indicates the levels of the analysis of correction parameters. For a level through 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 $Y_{20}{}^{*(0)}$, only seven optimal parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, δr_{1q}, δr_{2q}, δr_{3q}, $\delta\Delta_{a1q}$, and $\delta\Delta_{a2q}$, participate. A set of $Y_{ij}{}^{*(0)}$ and the participating optimal parameters that are taken into the analysis should not be chosen arbitrarily, but be confined to those given in Table 1; an incorrect evaluation for the parameters might otherwise result.

The present method of analysis shows that the choices of the fitting parameters and the corresponding Y_{ij} in sets that connect those parameters with term values are unique. For example, if Dunham potential constants up to a_4 and correction parameters up to a level of three $Y_{ij}{}^{*(0)}$, i.e., $\delta\Delta_B$, $\delta\Delta_\omega$, and δr_{1q}, are required for a spectral fit, a set of Y_{ij} that connects the fitting parameters with energy levels should be $Y_{01}{}^{*(0)} + Y_{01}{}^{(2)}$, $Y_{02}{}^{*(0)} + Y_{02}{}^{(2)}$, $Y_{03}{}^{(0)}$, $Y_{04}{}^{(0)}$, $Y_{05}{}^{(0)}$, $Y_{06}{}^{(0)}$, $Y_{10}{}^{*(0)} + Y_{10}{}^{(2)}$, $Y_{11}{}^{(0)}$, $Y_{12}{}^{(0)}$, $Y_{13}{}^{(0)}$, $Y_{14}{}^{(0)}$, $Y_{20}{}^{(0)}$, $Y_{21}{}^{(0)}$, $Y_{22}{}^{(0)}$, and $Y_{30}{}^{(0)}$. According to the conventional method utilizing empirical parameters Y_{ij} and Δ_{ij}, to choose the best set of those parameters is difficult because the choice is not unique when spectral data for several vibrationally excited states for multiple isotopomers are included.

Spectral data of HCl in the electronic ground state $^1\Sigma$ were taken from the following papers: 403 transitions of the $v \rightarrow v - 1$ band sequence, with $v = 1$ to 6 for $H^{35}Cl$ and $v = 1$ to 5 for $H^{37}Cl$, by Clayton et al.;[24] 71 transitions of the rota-

tional and the $v = 1$–0 vibrational–rotational ones both for $H^{35}Cl$ and $H^{37}Cl$ by Rinsland et al.[25] excluding $v = 1$–0 transitions given by Ref. 24; 270 transitions of the rotational and the $v = 1$–0, 2–1, and 3–2 vibrational–rotational ones both for $H^{35}Cl$ and $H^{37}Cl$ by LeBranc et al.,[26] excluding rotational transitions listed in Ref. 25, 6 TuFIR rotational transitions of $H^{35}Cl$ and $H^{37}Cl$ by Odashima et al.;[27] and 360 transitions of the $v = 0$ and 1 rotational and the $v = 1$–0, 2–1, and 3–2 vibrational–rotational ones, both for $D^{35}Cl$ and $D^{37}Cl$ plus the $v = 4$–3 band of $D^{35}Cl$ by Parekunnel et al.[28]

Spectral data set of Rinsland et al.[25] includes rotational transitions for $H^{35}Cl$ and $H^{37}Cl$ given by Nolt et al.[29] Data set of Parekunnel et al.[28] includes rotational transitions by Fusina et al.[30] and by Klaus et al.[31] and $v = 1$–0 transitions by Klee and Ogilvie[32] for $D^{35}Cl$ and $D^{37}Cl$.

With reduced weight assigned to 15 outliers for vibrational–rotational transitions among the 1110 spectral data in total, 67 and 26 rotational transitions for $H^{35,37}Cl$ and $D^{35,37}Cl$ plus 683 and 334 vibrational–rotational transitions for $H^{35,37}Cl$ and $D^{35,37}Cl$, respectively, were simultaneously fitted with 21 adjustable parameters: U_ω ($= \mu^{1/2}\omega_e$), U_B ($= \mu B_e$), a_1, a_2, a_3, a_4, a_5, a_6, a_7, a_8, $\Delta_\omega{}^{H}$, $\Delta_\omega{}^{Cl}$, Δ_B^{H}, Δ_B^{Cl}, $\Delta_{a1q}{}^{H}$, $\Delta_{a1q}{}^{Cl}$, $\Delta_{a2q}{}^{H}$, $\Delta_{a2q}{}^{Cl}$, $r_{1q}{}^{H}$ ($= r_{1q}{}^{Cl}$), $r_{2q}{}^{H}$ ($= r_{2q}{}^{Cl}$), and $r_{3q}{}^{H}$ ($= r_{3q}{}^{Cl}$). Among these, eleven latter ones are optimal parameters. We assumed a theoretical relation, $r_{iq}{}^{a} = r_{iq}{}^{b}$.[18] The other parameters were set to zero.

An analysis was made connecting these parameters with the vibrational–rotational energy levels through $Y_{ij}{}^{*(0)}$, $Y_{ij}{}^{(0)}$, and $Y_{ij}{}^{(2)}$. The level of correction of eight $Y_{ij}{}^{*(0)}$, which were given in Eqs. 36–43 in Ref. 18, was found to be sufficient. Higher-order contributions $Y_{ij}{}^{(2)}$ for each $Y_{ij}{}^{*(0)}$ and other $Y_{ij}{}^{(0)}$ were taken from Bouanich,[33] Woolley,[34] Ogilvie and Bouanich,[35] Ogilvie and Tipping,[36] and Uehara,[16] or calculated for those not found explicitly in the literature; explicitly, eight $Y_{ij}{}^{(2)}$, i.e., 01, 02, 03, 04, 10, 11, 12, and 20 and 27 $Y_{ij}{}^{(0)}$, i.e., $ij = 05$, 06, 07, 08, 09, 010, 13, 14, 15, 16, 17, 18, 21, 22, 23, 24, 25, 26, 30, 31, 32, 33, 34, 40, 41, 42, and 50 were added $Y_{ij}{}^{*(0)}$ in the analysis. Expressions for $Y_{010}{}^{(0)}$, $Y_{18}{}^{(0)}$, $Y_{26}{}^{(0)}$, and $Y_{34}{}^{(0)}$ that are necessary for fitting a_8 were calculated with Dunham's approach.[15,21] Although a computer file[37] to calculate $Y_{ij}{}^{(n)}$ in terms of a_k or a deposited result[38] of the calculated $Y_{ij}{}^{(n)}$ may be available elsewhere, we present these in the Appendix, as well as an expression of $Y_{04}{}^{(2)}$, to make our approach reproducible. Other terms of greater order with $Y_{ij}{}^{(n\geqq 4)}$ are ignored.

The spectral uncertainties, δ_{obs}, are those given in each paper. The weights for the spectral fit of the data were assumed to be proportional to $(1/\delta_{obs})^2$. With 21 parameters the normalized standard deviation is 1.16. The molecular parameters determined in the fit are given in Table 2.

Discussion

In Table 2, the values of the molecular parameters, U_B ($= U_{01}$), U_ω ($= U_{10}$), and a_i ($i = 1, 2, \ldots$, and 8), for HCl reported by Coxon and Ogilvie[39] are also given. Our approach provides a better ($\sigma = 1.16$ to 1.41) fit for many more (1110 to 896) spectral lines with fewer numbers (21 to 23) of adjustable parameters compared to those by Coxon and Ogilvie.[39] The present values of ten comparable parameters, U_B ($= U_{01}$), U_ω ($= U_{10}$), and a_i ($i = 1, 2, \ldots$, and 8), were deter-

Table 2. Dunham Potential Constants and Optimal Parameters for Corrections for Hydrogen Chloride

Parameters	This work	Coxon and Ogilvie[39,a)]
U_B/cm^{-1} u^1	10.37638602(235)[b)]	10.3763962(273)
U_ω/cm^{-1} u$^{1/2}$	2960.323100(736)	2960.31403(208)
a_1	−2.3634893(138)	−2.3633725(352)
a_2	3.6607877(879)	3.660576(194)
a_3	−4.746415(424)	−4.74921(133)
a_4	5.44328(245)	5.45290(995)
a_5	−5.56137(889)	−5.5160(320)
a_6	4.6621(397)	4.284(127)
a_7	−3.798(240)	−1.726(415)
a_8	15.55(102)	−0.027(392)
$\Delta_B{}^{H}$	0.1678263(558)	0.1676(7)[c)]
$\Delta_B{}^{Cl}$	−0.1307(145)	−0.214(17)
$\Delta_\omega{}^{H}$	−0.005481(201)	−0.00612(88)
$\Delta_\omega{}^{Cl}$	0.2157(153)	0.1857(158)
$\Delta_{a1q}{}^{H}$	−0.2315(128)	
$\Delta_{a1q}{}^{Cl}$	−1.335(354)	
$\Delta_{a2q}{}^{H}$	−0.2128(498)	
$\Delta_{a2q}{}^{Cl}$	−6.09(144)	
$r_{1q}{}^{H} = r_{1q}{}^{Cl}$	−0.13145(326)	
$r_{2q}{}^{H} = r_{2q}{}^{Cl}$	−1.7004(948)	
$r_{3q}{}^{H} = r_{3q}{}^{Cl}$	0.999(287)	
Reduced standard deviation	1.16	1.41

a) Only comparable values for 14 parameters are listed among 23 ones. b) The uncertainty (one standard error) in the last digits is given in parentheses. c) See text.

mined with smaller standard errors than their values. The value of a_8 may be affected by truncation errors.

Removing the calculated values for the Dunham correction, −0.03558 and −0.05770, the values of $\Delta_{01}{}^{H,Cl}$ and $\Delta_{10}{}^{H,Cl}$ given by Coxon and Ogilvie result in $\Delta_B{}^{H,Cl}$ and $\Delta_\omega{}^{H,Cl}$, respectively, which are also listed in Table 2. Except for the value of $\Delta_B{}^{Cl}$, the agreement is satisfactory. We fitted the present data set with their parameter set[39] to determine $\Delta_{01}{}^{Cl}$. A value of −0.137(12), in contrast to −0.250(17) by them, was obtained for $\Delta_{01}{}^{Cl}$, which resulted in a calculated value of −0.101(12) for $\Delta_B{}^{Cl}$. Therefore, the discrepancy in $\Delta_B{}^{Cl}$ in Table 2 arises from disparate spectral data in both studies; other correction parameters are not comparable because the definitions differ. For similar reasons, our present parameters cannot be compared with those of Coxon and Hajigeorgiou.[40]

To facilitate calculations or predictions of the spectral frequencies, the values of 35 Y_{ij} for each isotopomer, through which 21 molecular parameters are connected with the energy values, were back-calculated with the values of the parameters given in Table 2. They are listed in Table 3. All of the 140 Y_{ij} are significantly determined in smaller standard errors. Therefore, if we fit the present set of spectral data with adjustable Dunham's Y_{ij}, 140 Y_{ij} are required to reproduce the data, but only 21 parameters are necessary in the present approach.

The optimal parameters expressed with expansion coefficients are given in Eqs. 22 and 29–34 of Ref. 18. Those clusters of coefficients can be resolved to yield expansion coefficients $q_i{}^{a,b}$ and $s_i{}^{a,b}$ if nonadiabatic coefficients $r_i{}^{a,b}$ are estimated by a method of Herman and Ogilvie[20] by use of an electric dipole moment function $M(\xi)$ and a function for the rotational g factor $g_J(\xi)$. With values of $r_i{}^{H,Li}$ ($i = 0$, 1, 2, and 3), the coefficients $s_1{}^{H,Cl}$, $q_0{}^{H,Cl}$, $s_2{}^{H,Cl}$, $q_1{}^{H,Cl}$, $s_3{}^{H,Cl}$, $q_2{}^{H,Cl}$, and $s_4{}^{H,Cl}$ can be determined successively from the observed values of $\Delta_B^{H,Cl}$, $r_{1q}^{H,Cl}$, $\Delta_\omega{}^{H,Cl}$, $r_{2q}^{H,Cl}$, $\Delta_{a1q}{}^{H,Cl}$, $r_{3q}{}^{H,Cl}$, and $\Delta_{a2q}{}^{H,Cl}$, respectively.[18]

Only in this way can one resolve clusters of expansion coefficients. For HCl, an accurate electric dipole moment function has been reported by Ogilvie and Lee[41] but an accurate

Table 3. Values of Dunham Coefficiens Y_{ij} Back-Calculated from 21 Molecular Constants Given in Table 2

Coefficients	Back-calculated from potential function given in Table 2			
/cm^{-1}	$H^{35}Cl$	$D^{35}Cl$	$H^{37}Cl$	$D^{37}Cl$
Y_{10}	2990.896820(424)[a)]	2145.119845(247)	2988.632373(421)	2141.961590(245)
Y_{20}	−52.766973(457)	−27.145796(224)	−52.687068(455)	−27.065904(223)
Y_{30}	0.200728(216)	0.0740449(796)	0.200273(215)	0.0737184(793)
10^3Y_{40}	−7.2725(453)	−1.9239(120)	−7.2505(452)	−1.9126(119)
10^4Y_{50}	−3.8144(335)	−0.72369(636)	−3.8000(334)	−0.71838(631)
Y_{01}	10.593286129(455)	5.448781562(164)	10.577255818(455)	5.432751100(168)
Y_{11}	−0.30695645(138)	−0.113227258(452)	−0.30626048(139)	−0.112728144(454)
10^3Y_{21}	1.59902(128)	0.423020(339)	1.59418(128)	0.420535(337)
10^5Y_{31}	−7.0500(459)	−1.33757(872)	−7.0233(458)	−1.32775(865)
10^6Y_{41}	−4.8360(542)	−0.65802(737)	−4.8141(539)	−0.65223(730)
10^4Y_{02}	−5.3161553(104)	−1.40630645(145)	−5.3000793(103)	−1.39804416(143)
10^6Y_{12}	7.209591(836)	1.367771(131)	7.182608(838)	1.357782(130)
10^7Y_{22}	−2.61454(450)	−0.35575(102)	−2.60269(747)	−0.35262(101)
10^8Y_{32}	−1.1942(301)	−0.11653(294)	−1.1879(300)	−0.11533(291)
$10^{10}Y_{42}$	−8.203(348)	−0.5741(244)	−8.153(346)	−0.5673(241)
10^8Y_{03}	1.696427(108)	0.23091708(781)	1.688735(107)	0.22888466(770)
$10^{10}Y_{13}$	−4.87428(617)	−0.475646(602)	−4.84852(614)	−0.470766(596)
$10^{11}Y_{23}$	−2.2090(412)	−0.15459(288)	−2.1957(410)	−0.15278(285)
$10^{12}Y_{33}$	−6.5045(869)	−0.32646(436)	−6.4604(863)	−0.32216(430)
$10^{13}Y_{04}$	−8.51319(209)	−0.5960757(807)	−8.46160(207)	−0.5890800(794)
$10^{14}Y_{14}$	−2.3321(221)	−0.11705(111)	−2.3163(219)	−0.11551(109)
$10^{15}Y_{24}$	−4.223(193)	−0.15200(695)	−4.191(192)	−0.14978(685)
$10^{16}Y_{34}$	6.810(288)	0.17580(744)	6.754(286)	0.17297(732)
$10^{17}Y_{05}$	3.21463(235)	0.1157095(847)	3.19039(234)	0.1140176(835)
$10^{18}Y_{15}$	−1.2147(537)	−0.03136(139)	−1.2046(533)	−0.03085(136)
$10^{18}Y_{25}$	−1.6768(474)	−0.031043(877)	−1.6616(470)	−0.030499(862)
$10^{21}Y_{06}$	−2.82385(588)	−0.052278(109)	−2.79832(583)	−0.051363(107)
$10^{22}Y_{16}$	−5.250(196)	−0.06971(260)	−5.199(194)	−0.06839(255)
$10^{22}Y_{26}$	3.1924(828)	0.030398(788)	3.1588(819)	0.029778(772)
$10^{25}Y_{07}$	1.03463(910)	0.0098516(866)	1.02371(900)	0.0096506(849)
$10^{26}Y_{17}$	−8.826(444)	−0.06027(303)	−8.726(439)	−0.05895(296)
$10^{29}Y_{08}$	−1.7242(242)	−0.008444(119)	−1.7034(239)	−0.008247(116)
$10^{29}Y_{18}$	1.8478(679)	0.006489(239)	1.8241(670)	0.006329(233)
$10^{34}Y_{09}$	−3.381(496)	−0.00851(125)	−3.335(489)	−0.00829(122)
$10^{38}Y_{010}$	7.938(708)	0.010284(917)	7.819(697)	0.009985(890)

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

value of the rotational g factor is available only for $^1H^{35}Cl$ in $v = 0$.[42,43] Therefore, we can only determine $s_1^{H,Cl}$ in this case. With $r_0^H = 0.456728(88)$ and $r_0^{Cl} = 0.099665(91)$ calculated from the values $M_0 = 3.64587(25) \times 10^{-30}$ C m and $g_J = 0.45935(9)$ taken for r_e, expansion coefficients of adiabatic effects, $s_1^H = -0.61051(33) \times 10^5$ cm^{-1} and $s_1^{Cl} = -0.510(36) \times 10^5$ cm^{-1}, were determined with the values of Δ_B^H and Δ_B^{Cl} listed in Table 2.

For LiH,[18] the expansion coefficients of adiabatic corrections $S_{H,Li}(\xi)$ agree satisfactorily with those predicted simply by wobble-stretch theory.[18,44] Assuming wobble-stretch theory, for HCl, a value of $\langle 0|L_x^2 + L_y^2|0\rangle = 1.61(h/2\pi)^2$, obtained from $s_1^H = -0.610 \times 10^5$ cm^{-1} ($\cong s_1^{Cl}$), yields $s_2^H = s_2^{Cl} = 0.915 \times 10^5$ cm^{-1}, and then with experimental values of Δ_ω^H and Δ_ω^{Cl}, $q_0^H = 0.578$ and $q_0^{Cl} = 1.058$. With Eq. 10 given below those wobble-stretch values of q_0^H and q_0^{Cl} lead to a coefficient of the electric dipole moment, $M_1 = -0.490 \times 10^{-29}$ C m, which is comparable with a value $M_1 = 0.412334(147) \times 10^{-29}$ C m presented by Ogilvie and Lee.[41] This discrepancy indicates that the wobble-stretch term is not important in the adiabatic correction for HCl, as is a theoretical result by Colbourn and Wayne,[45] in contrast with the experimental result for LiH.

It has been shown analytically, in Ref. 18, that the electric dipole moments and rotational g factors cannot be determined from an analysis of the vibrational–rotational spectra alone without external fields if the adiabatic corrections, $s_i^{a,b}$ ($i = 1, 2, \ldots$), are not evaluated independently by some other means.

Also, it has been shown[18] that a relation for the electric dipole moment given by Herman and Ogilvie,[20]

$$\frac{d}{d\xi}M(\xi) = (er_e/2)\sum_{i=0}(q_i^b - q_i^a)\xi^i, \tag{10}$$

cannot serve to resolve clusters of expansion coefficients, but provides constraints between the optimal parameters, $r_{iq}^H = r_{iq}^{Cl}$ for $i = 1, 2, \ldots$. Only clusters of the expansion coefficients are determinable. Individual expansion coefficients cannot be determined, even partially.

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Appendix

Here are Dunham's Y_{010}, Y_{18}, Y_{26}, Y_{34}, and $Y_{04}^{(2)}$ coefficients expressed in terms of potential constants a_i, B_e, and ω_e.

$$\begin{aligned}
Y_{010} = {} & 2048(B_e^{19}/\omega_e^{18})(-938223a_1^8 - 9382230a_1^7 \\
& + 2918916a_1^6a_2 - 45243198a_1^6 + 23351328a_1^5a_2 \\
& - 972972a_1^5a_3 - 137884032a_1^5 - 2594592a_1^4a_2^2 \\
& + 86177520a_1^4a_2 - 6949800a_1^4a_3 + 277992a_1^4a_4 \\
& - 291677760a_1^4 - 14826240a_1^3a_2^2 + 1235520a_1^3a_2a_3 \\
& + 188559360a_1^3a_2 - 22096800a_1^3a_3 + 1710720a_1^3a_4 \\
& - 66528a_1^3a_5 - 440757504a_1^3 + 658944a_1^2a_2^3 \\
& - 35354880a_1^2a_2^2 + 5702400a_1^2a_2a_3 - 228096a_1^2a_2a_4 \\
& + 259269120a_1^2a_2 - 118800a_1^2a_3^2 - 39283200a_1^2a_3 \\
& + 4419360a_1^2a_4 - 332640a_1^2a_5 + 12672a_1^2a_6 \\
& - 467470080a_1^2 + 2027520a_1a_2^3 - 253440a_1a_2^2a_3 \\
& - 41902080a_1a_2^2 + 9820800a_1a_2a_3 - 760320a_1a_2a_4 \\
& + 29568a_1a_2a_5 + 213700608a_1a_2 - 396000a_1a_3^2 \\
& + 31680a_1a_3a_4 - 39283200a_1a_3 + 5713920a_1a_4 \\
& - 624960a_1a_5 + 46080a_1a_6 - 1728a_1a_7 - 320550912a_1 \\
& - 22528a_2^4 + 1745920a_2^3 - 422400a_2^2a_3 + 16896a_2^2a_4 \\
& - 20951040a_2^2 + 17600a_2a_3^2 + 6348800a_2a_3 \\
& - 714240a_2a_4 + 53760a_2a_5 - 2048a_2a_6 + 83105792a_2 \\
& - 372000a_3^2 + 57600a_3a_4 - 2240a_3a_5 - 17808384a_3 \\
& - 1152a_4^2 + 3142656a_4 - 444416a_5 + 47616a_6 \\
& - 3456a_7 + 128a_8 - 109818368) \\
& + \text{higher-order terms},
\end{aligned}$$

$$\begin{aligned}
Y_{18} = {} & 18(B_e^{16}/\omega_e^{15})(-94616181a_1^8 - 756929448a_1^7 \\
& + 349383456a_1^6a_2 - 2976321348a_1^6 + 2271758400a_1^5a_2 \\
& - 146214720a_1^5a_3 - 7563816936a_1^5 - 369048960a_1^4a_2^2 \\
& + 6956738784a_1^4a_2 - 866816640a_1^4a_3 + 54297216a_1^4a_4 \\
& - 13700672910a_1^4 - 1740787200a_1^3a_2^2 \\
& + 220492800a_1^3a_2a_3 + 12936336768a_1^3a_2 \\
& - 2339418240a_1^3a_3 + 283627008a_1^3a_4 - 17224704a_1^3a_5 \\
& - 18291196440a_1^3 + 111716352a_1^2a_2^3 \\
& - 3504031488a_1^2a_2^2 + 857364480a_1^2a_2a_3 \\
& - 52918272a_1^2a_2a_4 + 15544252512a_1^2a_2 \\
& - 26496000a_1^2a_3^2 - 3621534720a_1^2a_3 \\
& + 637168896a_1^2a_4 - 74769408a_1^2a_5 + 4399104a_1^2a_6 \\
& - 17776808100a_1^2 + 288239616a_1a_2^3 \\
& - 54005760a_1a_2^2a_3 - 3596524032a_1a_2^2 \\
& + 1274496000a_1a_2a_3 - 151990272a_1a_2a_4 \\
& + 9117696a_1a_2a_5 + 11565972288a_1a_2 - 75878400a_1a_3^2 \\
& + 9154560a_1a_3a_4 - 3247145280a_1a_3 + 736154112a_1a_4 \\
& - 125174784a_1a_5 + 14204928a_1a_6 - 811008a_1a_7 \\
& - 11646924120a_1 - 4575232a_2^4 + 213223424a_2^3 \\
& - 77045760a_2^2a_3 + 4694016a_2^2a_4 - 1604168064a_2^2 \\
& + 4710400a_2a_3^2 + 731013120a_2a_3 - 126302208a_2a_4 \\
& + 14622720a_2a_5 - 851968a_2a_6 + 4215991968a_2 \\
& - 62873600a_3^2 + 14622720a_3a_4 - 860160a_3a_5 \\
& - 1365091200a_3 - 430080a_4^2 + 373189248a_4 \\
& - 81679360a_5 + 13410304a_6 - 1474560a_7 \\
& + 81920a_8 - 3995947365) + \text{higher-order terms},
\end{aligned}$$

$$\begin{aligned}
Y_{26} = {} & 384(B_e^{13}/\omega_e^{12})(-933120a_1^8 - 5598720a_1^7 \\
& + 3941379a_1^6a_2 - 17184960a_1^6 + 19293714a_1^5a_2 \\
& - 1903365a_1^5a_3 - 35582490a_1^5 - 4841820a_1^4a_2^2 \\
& + 46211310a_1^4a_2 - 8496900a_1^4a_3 + 829170a_1^4a_4 \\
& - 54768150a_1^4 - 17357760a_1^3a_2^2 + 3415200a_1^3a_2a_3 \\
& + 70093440a_1^3a_2 - 17896680a_1^3a_3 + 3275640a_1^3a_4 \\
& - 317940a_1^3a_5 - 64518840a_1^3 + 1730880a_1^2a_2^3
\end{aligned}$$

$$
\begin{aligned}
&- 27588384a_1{}^2a_2{}^2 + 10173600a_1{}^2a_2a_3 - 984816a_1{}^2a_2a_4 \\
&+ 71776080a_1{}^2a_2 - 500400a_1{}^2a_3{}^2 - 22533600a_1{}^2a_3 \\
&+ 5765040a_1{}^2a_4 - 1058400a_1{}^2a_5 + 101920a_1{}^2a_6 \\
&- 57115440a_1{}^2 + 3442176a_1a_2{}^3 - 1008640a_1a_2{}^2a_3 \\
&- 23339520a_1a_2{}^2 + 12036000a_1a_2a_3 - 2192256a_1a_2a_4 \\
&+ 209664a_1a_2a_5 + 47536752a_1a_2 - 1118400a_1a_3{}^2 \\
&+ 214960a_1a_3a_4 - 17222400a_1a_3 + 5446320a_1a_4 \\
&- 1411200a_1a_5 + 258720a_1a_6 - 24528a_1a_7 \\
&- 35051520a_1 - 84992a_2{}^4 + 2042112a_2{}^3 \\
&- 1125120a_2{}^2a_3 + 107776a_2{}^2a_4 - 8991840a_2{}^2 \\
&+ 109200a_2a_3{}^2 + 5744000a_2a_3 - 1469136a_2a_4 \\
&+ 265776a_2a_5 - 25088a_2a_6 + 16095472a_2 - 753400a_3{}^2 \\
&+ 273840a_3a_4 - 25760a_3a_5 - 6503920a_3 - 13040a_4{}^2 \\
&+ 2378640a_4 - 768880a_5 + 200480a_6 - 36288a_7 \\
&+ 3360a_8 - 11612320) + \text{higher-order terms},
\end{aligned}
$$

$$
\begin{aligned}
Y_{34} = (5B_e{}^{10}/32\omega_e{}^9)(&-159014583a_1{}^8 - 636058332a_1{}^7 \\
&+ 747564552a_1{}^6a_2 - 1428607206a_1{}^6 \\
&+ 2424873024a_1{}^5a_2 - 404593920a_1{}^5a_3 \\
&- 2333591316a_1{}^5 - 1034779824a_1{}^4a_2{}^2 \\
&+ 4229176320a_1{}^4a_2 - 1192959360a_1{}^4a_3 \\
&+ 201000960a_1{}^4a_4 - 2984513175a_1{}^4 \\
&- 2437454016a_1{}^3a_2{}^2 + 827554560a_1{}^3a_2a_3 \\
&+ 5059842720a_1{}^3a_2 - 1831849920a_1{}^3a_3 \\
&+ 523307520a_1{}^3a_4 - 89134080a_1{}^3a_5 - 3036118848a_1{}^3 \\
&+ 424947456a_1{}^2a_2{}^3 - 2787189984a_1{}^2a_2{}^2 \\
&+ 1605830400a_1{}^2a_2a_3 - 277079040a_1{}^2a_2a_4 \\
&+ 4311029880a_1{}^2a_2 - 138758400a_1{}^2a_3{}^2 \\
&- 1834870080a_1{}^2a_3 + 670510080a_1{}^2a_4 \\
&- 193729536a_1{}^2a_5 + 33589248a_1{}^2a_6 - 2404222272a_1{}^2 \\
&+ 552752640a_1a_2{}^3 - 286932480a_1a_2{}^2a_3 \\
&- 1839511872a_1a_2{}^2 + 1351810560a_1a_2a_3 \\
&- 400997376a_1a_2a_4 + 70404096a_1a_2a_5 \\
&+ 2446931712a_1a_2 - 198182400a_1a_3{}^2 \\
&+ 70471680a_1a_3a_4 - 1177272480a_1a_3 + 505409280a_1a_4 \\
&- 184859136a_1a_5 + 54878208a_1a_6 - 9805824a_1a_7 \\
&- 1357226496a_1 - 24566784a_2{}^4 + 233680128a_2{}^3 \\
&- 208266240a_2{}^2a_3 + 36584448a_2{}^2a_4 - 584617584a_2{}^2 \\
&+ 36864000a_2a_3{}^2 + 499001600a_2a_3 - 190373376a_2a_4 \\
&+ 58189824a_2a_5 - 10379264a_2a_6 + 719257344a_2 \\
&- 91974400a_3{}^2 + 57108480a_3a_4 - 10465280a_3a_5 \\
&- 377807360a_3 - 5191680a_4{}^2 + 186075840a_4 \\
&- 78887424a_5 + 29560832a_6 - 9289728a_7 \\
&+ 1720320a_8 - 412452096) + \text{higher-order terms},
\end{aligned}
$$

and

$$
\begin{aligned}
Y_{04}{}^{(2)} = 4(B_e{}^9/\omega_e{}^8)(&-18144a_1{}^6 - 72576a_1{}^5 + 64197a_1{}^4a_2 \\
&- 155736a_1{}^4 + 196308a_1{}^3a_2 - 36435a_1{}^3a_3 \\
&- 237252a_1{}^3 - 50652a_1{}^2a_2{}^2 + 291996a_1{}^2a_2 \\
&- 99000a_1{}^2a_3 + 18450a_1{}^2a_4 - 277674a_1{}^2 \\
&- 90432a_1a_2{}^2 + 32260a_1a_2a_3 + 259760a_1a_2 \\
&- 117800a_1a_3 + 40800a_1a_4 - 7280a_1a_5 - 241520a_1 \\
&+ 5024a_2{}^3 - 53216a_2{}^2 + 34800a_2a_3 - 6200a_2a_4 \\
&+ 121080a_2 - 2900a_3{}^2 - 63920a_3 + 30320a_4 \\
&- 10080a_5 + 1680a_6 - 125504).
\end{aligned}
$$

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