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Herman–Wallis Factors for Higher Overtone Bands: Application to HCl

R. H. TIPPING[1]

Air Force Geophysics Laboratory, Hanscom Air Force Base, Bedford, Massachusetts 01731

AND

J. F. OGILVIE

Research School of Chemistry, Institute for Advanced Studies, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia

Theoretical expressions for the Herman–Wallis factors in terms of the Dunham potential-energy parameters and dipole-moment coefficients were derived for higher overtone bands by the method of computer algebra. These results were applied to an analysis of the vibration-rotational intensities of HCl, leading to a good fit of the data and a dipole-moment function that is improved and extended by comparison with previous results.

1. INTRODUCTION

In the past few years, numerous experimental papers have appeared (*1–4*) reporting accurate vibration–rotational line intensities for higher overtone bands. These data, consisting of the absolute values of the rotationless dipole-moment matrix elements and the corresponding Herman–Wallis coefficients (*5, 6*), are necessary in order that one can obtain an accurate representation of the dipole-moment function in the vicinity of the equilibrium internuclear separation. However, in order to accomplish this objective, one needs accurate theoretical expressions (or numerical values) for these quantities.

2. HERMAN–WALLIS COEFFICIENTS

Theoretical expressions based on the Dunham potential-energy function correct to terms of order a_1^6 have been published (*7–9*) for vibrational matrix elements for powers of the reduced displacement from the equilibrium internuclear separation, $x = (R - R_e)/R_e$, for $v' = 0$–7. If one represents the dipole-moment function $M(x)$ as a truncated series expansion

$$M(x) = \sum_{j=0}^{v'} M_j x^j, \tag{1}$$

one can write

$$\langle 0|M(x)|v'\rangle = \sum_{j=0}^{v'} M_j \langle 0|x^j|v'\rangle. \tag{2}$$

[1] Permanent address: Department of Physics and Astronomy, University of Alabama, University, Alabama 35486.

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TABLE I

Theoretical Expressions for the Herman–Wallis Coefficients $C_v^{v'}$

v'-v	$C_v^{v'}$
0	0
1	$\gamma[-4\theta_o] + \left(\frac{v'+v+1}{2}\right)\gamma^2\left[\left(\frac{-41}{4}a_1^2 - 15a_1 + 9a_2 - 12\right)\theta_o + \left(\frac{13}{2}a_1 + \frac{3}{2}\right)\theta_1 - 2\theta_2\right]$
2	$\gamma\left[(-a_1 + 3)\phi_o - 4\phi_1\right] + \left(\frac{v'+v+1}{3}\right)\gamma^2\left[\left(\frac{-333}{32}a_1^3 + \frac{279}{32}a_1^2 + \frac{129}{8}a_1a_2\right.\right.$
	$\left.+ 18a_1 - \frac{99}{8}a_2 - 5a_3 + 15\right)\phi_o + \left(\frac{-135}{8}a_1^2 - \frac{111}{4}a_1 + \frac{37}{2}a_2 - 20\right)\phi_1$
	$\left.+ \left(\frac{33}{2}a_1 + \frac{9}{2}\right)\phi_2 - 6\phi_3\right]$
3	$\gamma\left[\left(\frac{-1}{4}a_1^2 + 2a_1 - \frac{1}{3}a_2 - \frac{8}{3}\right)\mu_o + (-3a_1 + 3)\mu_1 - 4\mu_2\right] + \left(\frac{v'+v+1}{4}\right)\gamma^2$
	$\left[\left(\frac{-363}{64}a_1^4 + \frac{57}{2}a_1^3 + \frac{37}{8}a_1^2a_2 - 2a_1^2 - 48a_1a_2 + \frac{3}{4}a_1a_3 - 20a_1 + \frac{17}{4}a_2^2\right.\right.$
	$\left.+ 16a_2 + 14a_3 - \frac{5}{2}a_4 - 20\right)\mu_o + \left(\frac{-717}{16}a_1^3 - \frac{69}{16}a_1^2 + \frac{283}{4}a_1a_2 + 17a_1\right.$
	$\left.- \frac{81}{4}a_2 - \frac{39}{2}a_3 + \frac{45}{2}\right)\mu_1 + \left(-14a_1^2 - 41a_1 + \frac{88}{3}a_2 - \frac{88}{3}\right)\mu_2$
	$\left.+ (27a_1 + 9)\mu_3 - 12\mu_4\right]$
4	$\gamma\left[\left(\frac{-1}{16}a_1^3 + \frac{15}{16}a_1^2 - \frac{1}{4}a_1a_2 - 3a_1 + \frac{3}{4}a_2 - \frac{1}{6}a_3 + \frac{5}{2}\right)\rho_o + \left(\frac{-3}{2}a_1^2 + \frac{7}{2}a_1\right.\right.$
	$\left.\left.- \frac{4}{3}a_2 - \frac{8}{3}\right)\rho_1 + (-5a_1 + 3)\rho_2 - 4\rho_3\right] + \left(\frac{v'+v+1}{5}\right)\gamma^2\left[\left(\frac{-315}{128}a_1^5 + \frac{3525}{128}a_1^4\right.\right.$
	$- \frac{25}{8}a_1^3a_2 - \frac{405}{8}a_1^3 - \frac{135}{4}a_1^2a_2 - \frac{55}{48}a_1^2a_3 - \frac{175}{16}a_1^2 + \frac{75}{8}a_1a_2^2 + \frac{195}{2}a_1a_2$
	$+ \frac{25}{8}a_1a_3 + \frac{3}{4}a_1a_4 + \frac{75}{4}a_1 - \frac{105}{8}a_2^2 + \frac{3}{4}a_2a_3 - \frac{75}{4}a_2 - \frac{55}{2}a_3 + \frac{15}{2}a_4$

As is well known (*5*, *6*), these matrix elements alone do not enable one to deduce a unique set of dipole-moment coefficients M_j because of the uncertainty of the relative signs of the experimental dipole-moment matrix elements. If, in addition, one knows the (approximate) values of the Herman–Wallis coefficients $C_v^{v'}$ defined

TABLE I—*Continued*

v'-v	$C_v^{v'}$
	$-\frac{7}{4}a_5 + \frac{105}{4}\Big)\rho_o + \Big(\frac{-2865}{64}a_1^4 + \frac{3535}{64}a_1^3 + \frac{2365}{48}a_1^2a_2 + \frac{131}{12}a_1^2 - \frac{1917}{16}a_1a_2$
	$-\frac{73}{24}a_1a_3 - \frac{135}{8}a_1 + 24a_2^2 + 16a_2 + \frac{61}{2}a_3 - 12a_4 - 28\Big)\rho_1 + \Big(\frac{-2965}{32}a_1^3$
	$-\frac{1045}{32}a_1^2 + \frac{3905}{24}a_1a_2 + \frac{55}{6}a_1 - \frac{225}{8}a_2 - \frac{505}{12}a_3 + \frac{125}{4}\Big)\rho_2 + \Big(\frac{5}{2}a_1^2$
	$-\frac{105}{2}a_1 + 40a_2 - 40\Big)\rho_3 + (35a_1 + 15)\rho_4 - 20\rho_5\Big]$
5	$\gamma\Big[\Big(\frac{-1}{64}a_1^4 + \frac{3}{8}a_1^3 - \frac{1}{8}a_1^2a_2 - \frac{21}{10}a_1^2 + \frac{9}{10}a_1a_2 - \frac{11}{60}a_1a_3 + 4a_1 - \frac{1}{20}a_2^2$
	$-\frac{6}{5}a_2 + \frac{2}{5}a_3 - \frac{1}{10}a_4 - \frac{12}{5}\Big)\varepsilon_o + \Big(\frac{-5}{8}a_1^3 + \frac{5}{2}a_1^2 - \frac{5}{3}a_1a_2 - \frac{13}{3}a_1$
	$+\frac{3}{2}a_2 - \frac{5}{6}a_3 + \frac{5}{2}\Big)\varepsilon_1 + \Big(\frac{-15}{4}a_1^2 + 5a_1 - \frac{7}{3}a_2 - \frac{8}{3}\Big)\varepsilon_2 + (-7a_1 + 3)\varepsilon_3$
	$-4\varepsilon_4\Big] + \left(\frac{v'+v+1}{6}\right)\gamma^2\Big[\Big(\frac{-1935}{2048}a_1^6 + \frac{585}{32}a_1^5 - \frac{2271}{512}a_1^4a_2 - \frac{297}{4}a_1^4 + \frac{9}{16}a_1^3a_2$
	$-\frac{337}{64}a_1^3a_3 + \frac{285}{4}a_1^3 + \frac{891}{128}a_1^2a_2^2 + \frac{441}{4}a_1^2a_2 + \frac{57}{16}a_1^2a_3 + \frac{3}{160}a_1^2a_4$
	$+\frac{117}{4}a_1^2 - \frac{171}{4}a_1a_2^2 + \frac{629}{80}a_1a_2a_3 - 165a_1a_2 - \frac{69}{4}a_1a_3 + \frac{27}{40}a_1a_4$
	$+\frac{3}{10}a_1a_5 - \frac{63}{5}a_1 + \frac{51}{32}a_2^3 + 27a_2^2 + \frac{3}{10}a_2a_3 + \frac{9}{8}a_2a_4 + \frac{99}{5}a_2 - \frac{23}{12}a_3^2 + 46a_3$
	$-\frac{153}{10}a_4 + \frac{27}{5}a_5 - \frac{7}{5}a_6 - \frac{168}{5}\Big)\varepsilon_o + \Big(\frac{-7857}{256}a_1^5 + \frac{22143}{256}a_1^4 - \frac{277}{32}a_1^3a_2$
	$-\frac{6119}{80}a_1^3 - \frac{21873}{160}a_1^2a_2 - \frac{171}{20}a_1^2a_3 - \frac{951}{32}a_1^2 + \frac{6343}{80}a_1a_2^2 + \frac{3503}{20}a_1a_2$
	$+\frac{2137}{160}a_1a_3 + \frac{111}{80}a_1a_4 + \frac{54}{5}a_1 - \frac{549}{16}a_2^2 + \frac{65}{24}a_2a_3 - \frac{145}{8}a_2 - \frac{160}{3}a_3$

by

$$F_v^{v'}(m) \equiv \langle vJ|M(x)|v'J'\rangle^2/\langle v0|M(x)|v'0\rangle^2 = 1 + C_v^{v'}m + D_v^{v'}m^2 + \cdots, \quad (3)$$

in which $m = 1/2[J'(J'+1) - J(J+1)]$ and v, J denote the standard vibrational and rotational quantum numbers, respectively, one can determine the coefficients M_j unambiguously (*6*).

TABLE I—*Continued*

$v'-v$	$C_v^{v'}$
	$+ \frac{285}{16} a_4 - 10a_5 + 35)\varepsilon_1 + (\frac{-4389}{32} a_1^4 + \frac{2361}{32} a_1^3 + \frac{373}{2} a_1^2 a_2 + \frac{131}{5} a_1^2$
	$- \frac{8967}{40} a_1 a_2 - \frac{997}{40} a_1 a_3 - \frac{27}{4} a_1 + \frac{551}{10} a_2^2 + \frac{62}{5} a_2 + \frac{537}{10} a_3 - \frac{531}{20} a_4$
	$- \frac{186}{5})\varepsilon_2 + (\frac{-4575}{32} a_1^3 - \frac{2475}{32} a_1^2 + \frac{2361}{8} a_1 a_2 - \frac{15}{2} a_1 - \frac{279}{8} a_2 - \frac{295}{4} a_3$
	$+ \frac{165}{4})\varepsilon_3 + (\frac{135}{4} a_1^2 - 60a_1 + 49a_2 - 52)\varepsilon_4 + (\frac{75}{2} a_1 + \frac{45}{2})\varepsilon_5 - 30\varepsilon_6]$
6	$\gamma[(-\frac{1}{256} a_1^5 + \frac{35}{256} a_1^4 - \frac{5}{96} a_1^3 a_2 - \frac{7}{6} a_1^3 + \frac{21}{32} a_1^2 a_2 - \frac{1}{8} a_1^2 a_3 + \frac{15}{4} a_1^2$
	$- \frac{1}{16} a_1 a_2^2 - 2a_1 a_2 + \frac{5}{8} a_1 a_3 - \frac{3}{20} a_1 a_4 - 5a_1 + \frac{3}{16} a_2^2 - \frac{1}{15} a_2 a_3 + \frac{5}{3} a_2$
	$- \frac{2}{3} a_3 + \frac{1}{4} a_4 - \frac{1}{15} a_5 + \frac{7}{3})\delta_0 + (- \frac{15}{64} a_1^4 + \frac{45}{32} a_1^3 - \frac{5}{4} a_1^2 a_2 - \frac{41}{10} a_1^2$
	$+ \frac{101}{40} a_1 a_2 - \frac{27}{20} a_1 a_3 + \frac{21}{4} a_1 - \frac{23}{60} a_2^2 - \frac{28}{15} a_2 + \frac{9}{10} a_3 - \frac{3}{5} a_4 - \frac{12}{5})\delta_1$
	$+ (\frac{-35}{16} a_1^3 + \frac{77}{16} a_1^2 - \frac{49}{12} a_1 a_2 - \frac{17}{3} a_1 + \frac{9}{4} a_2 - \frac{3}{2} a_3 + \frac{5}{2})\delta_2 + (-7a_1^2$
	$+ \frac{13}{2} a_1 - \frac{10}{3} a_2 - \frac{8}{3})\delta_3 + (-9a_1 + 3)\delta_4 - 4\delta_5]$

In extending the Dunham formalism by means of computer algebra (*10*, *11*), we have recently obtained extensive new results (correct to higher powers of a_1) for the energy term-value coefficients Y_{kl}, wavefunctions, expectation values, and vibration–rotational matrix elements of x^j; these will be published elsewhere (*11*, *12*). Here we report theoretical expressions for the Herman–Wallis coefficients $C_v^{v'}$ and $D_v^{v'}$ for $0 \leqslant (v' - v) \leqslant 6$, correct through terms of order a_1^6. Some of these results are new (the correction term proportional to γ^2 ($\gamma \equiv 2B_e/\omega_e$) in C_v^{v+5} and the $(v' - v) = 6$ results); in addition, as a result of the present work, a few minor misprints and mistakes[2] have been detected in published expressions (*13*, *14*). For convenience we list in Tables I and II all the results for $C_v^{v'}$ and $D_v^{v'}$ expressed in terms of the notation

[2] The coefficient of $\gamma^2\phi_0 a_1 a_2$ in Ref. (*13*) should read 129/8 not 127/8; the coefficients of $\gamma^2\rho_0 a_1^5$, $\gamma^2\rho_0 a_1 a_4$, and $\gamma^2\rho_1 a_4$ in Ref. (*14*) should read −63/32, 3/5, and −6, respectively, not 63/32, 1/10, and −45/8.

TABLE II

Theoretical Expressions for the Herman–Wallis Coefficients $D_v^{v'}$

v'-v	$D_v^{v'}$
0	$\gamma^2[2\nu_1]$
1	$\left(\frac{1}{2}C_v^{v+1}\right)^2 + \gamma^2\left[\left(-\frac{3}{2}a_1 - \frac{3}{2}\right)\theta_1 + 4\theta_2\right]$
2	$\left(\frac{1}{2}C_v^{v+2}\right)^2 + \gamma^2\left[4\phi_0 + \left(-\frac{9}{2}a_1^2 - \frac{9}{2}a_1 + 4a_2 - 4\right)\phi_1 + (-a_1 - 3)\phi_2 + 6\phi_3\right]$
3	$\left(\frac{1}{2}C_v^{v+3}\right)^2 + \gamma^2\Big[(2a_1 - 6)\mu_0 + \Big(\frac{-99}{32}a_1^3 - \frac{99}{32}a_1^2 + \frac{3}{8}a_1a_2 - 3a_1 - \frac{21}{8}a_2$
	$+ \frac{5}{2}a_3 + \frac{13}{2}\Big)\mu_1 + \left(-\frac{39}{4}a_1^2 - \frac{21}{2}a_1 + 9a_2 - 8\right)\mu_2 + \left(\frac{3}{2}a_1 - \frac{9}{2}\right)\mu_3 + 8\mu_4\Big]$
4	$\left(\frac{1}{2}C_v^{v+4}\right)^2 + \gamma^2\Big[\left(\frac{3}{4}a_1^2 - \frac{11}{2}a_1 + \frac{2}{3}a_2 + \frac{91}{12}\right)\rho_0 + \Big(-\frac{3}{2}a_1^4 - \frac{3}{2}a_1^3 - 3a_1^2a_2 -$
	$\frac{3}{2}a_1^2 - \frac{9}{2}a_1a_2 + \frac{1}{2}a_1a_3 + \frac{13}{2}a_1 + 2a_2^2 - 2a_2 - 2a_3 + 2a_4 - 8\Big)\rho_1 + \Big(-11a_1^3$
	$- \frac{45}{4}a_1^2 + 5a_1a_2 - 10a_1 - 6a_2 + \frac{17}{3}a_3 + 9\Big)\rho_2 + \Big(-\frac{57}{4}a_1^2 - 18a_1$
	$+ 15a_2 - 12\Big)\rho_3 + (6a_1 - 6)\rho_4 + 10\rho_5\Big]$
5	$\left(\frac{1}{2}C_v^{v+5}\right)^2 + \gamma^2\Big[\left(\frac{1}{4}a_1^3 - \frac{13}{4}a_1^2 + \frac{2}{3}a_1a_2 + \frac{31}{3}a_1 - 2a_2 + \frac{1}{3}a_3 - 9\right)\varepsilon_0$
	$+ \Big(-\frac{315}{512}a_1^5 - \frac{315}{512}a_1^4 - \frac{215}{64}a_1^3a_2 - \frac{5}{8}a_1^3 - \frac{255}{64}a_1^2a_2 - \frac{93}{32}a_1^2a_3 + \frac{65}{16}a_1^2$
	$+ \frac{41}{32}a_1a_2^2 - \frac{5}{2}a_1a_2 - \frac{143}{32}a_1a_3 + \frac{17}{16}a_1a_4 - \frac{45}{4}a_1 - \frac{39}{32}a_2^2 + \frac{37}{12}a_2a_3$
	$+ \frac{35}{12}a_2 - \frac{11}{6}a_3 - \frac{27}{16}a_4 + \frac{7}{4}a_5 + \frac{28}{3}\Big)\varepsilon_1 + \Big(\frac{-505}{64}a_1^4 - \frac{255}{32}a_1^3 - \frac{13}{2}a_1^2a_2$

TABLE II—*Continued*

v'-v	$D_v^{v'}$
	$- \frac{15}{2} a_1^2 - \frac{117}{8} a_1a_2 + \frac{47}{12} a_1a_3 + \frac{27}{2} a_1 + \frac{25}{4} a_2^2 - 6a_2 - \frac{9}{2} a_3 + \frac{9}{2} a_4$
	$- 10\Big)\varepsilon_2 + \Big(\frac{-759}{32} a_1^3 - \frac{819}{32} a_1^2 + \frac{123}{8} a_1a_2 - 21a_1 - \frac{81}{8} a_2 + \frac{19}{2} a_3 + \frac{23}{2}\Big)\varepsilon_3$
	$+ \Big(- \frac{33}{2} a_1^2 - 27a_1 + 22a_2 - 16\Big)\varepsilon_4 + \Big(\frac{25}{2} a_1 - \frac{15}{2}\Big)\varepsilon_5 + 12\varepsilon_6\Big]$
6	$\left(\frac{1}{2} C_v^{v+6}\right)^2 + \gamma^2\Big[\Big(\frac{5}{64} a_1^4 - \frac{25}{16} a_1^3 + \frac{5}{12} a_1^2a_2 + \frac{4051}{480} a_1^2 - \frac{173}{60} a_1a_2 + \frac{9}{20} a_1a_3$
	$- \frac{197}{12} a_1 + \frac{23}{180} a_2^2 + \frac{1429}{360} a_2 - \frac{21}{20} a_3 + \frac{1}{5} a_4 + \frac{1859}{180}\Big)\delta_0 + \Big(\frac{-117}{512} a_1^6$
	$- \frac{117}{512} a_1^5 - \frac{75}{32} a_1^4a_2 - \frac{15}{64} a_1^4 - \frac{165}{64} a_1^3a_2 - \frac{137}{32} a_1^3a_3 + \frac{65}{32} a_1^3 - \frac{21}{32} a_1^2a_2^2$
	$- \frac{15}{8} a_1^2a_2 - \frac{81}{16} a_1^2a_3 - \frac{99}{40} a_1^2a_4 - \frac{75}{8} a_1^2 - \frac{81}{32} a_1a_2^2 + \frac{111}{40} a_1a_2a_3 + \frac{35}{8} a_1a_2$
	$- 3a_1a_3 - \frac{189}{40} a_1a_4 + \frac{33}{20} a_1a_5 + \frac{691}{40} a_1 + \frac{3}{4} a_2^3 - \frac{3}{4} a_2^2 - \frac{21}{10} a_2a_3 + 3a_2a_4$
	$- \frac{47}{10} a_2 + a_3^2 + 2a_3 - \frac{9}{5} a_4 - \frac{3}{2} a_5 + \frac{8}{5} a_6 - \frac{53}{5}\Big)\delta_1 + \Big(\frac{-1149}{256} a_1^5 - \frac{1155}{256} a_1^4$
	$- \frac{417}{32} a_1^3a_2 - \frac{35}{8} a_1^3 - \frac{567}{32} a_1^2a_2 - \frac{93}{16} a_1^2a_3 + \frac{189}{16} a_1^2 + \frac{111}{16} a_1a_2^2$
	$- \frac{21}{2} a_1a_2 - \frac{105}{8} a_1a_3 + \frac{93}{20} a_1a_4 - 19a_1 - \frac{63}{16} a_2^2 + \frac{183}{20} a_2a_3 + \frac{77}{12} a_2$
	$- 5a_3 - \frac{15}{4} a_4 + \frac{39}{10} a_5 + \frac{133}{12}\Big)\delta_2 + \Big(\frac{-2919}{128} a_1^4 - \frac{189}{8} a_1^3 - \frac{105}{16} a_1^2a_2$
	$- 21a_1^2 - \frac{63}{2} a_1a_2 + \frac{45}{4} a_1a_3 + 23a_1 + \frac{105}{8} a_2^2 - 12a_2 - \frac{15}{2} a_3 + \frac{15}{2} a_4$
	$- 12\Big)\delta_3 + \Big(\frac{-161}{4} a_1^3 - \frac{189}{4} a_1^2 + 33 a_1a_2 - 36a_1 - 15a_2 + 14a_3 + 14\Big)\delta_4$
	$+ \Big(-15a_1^2 - \frac{75}{2} a_1 + 30a_2 - 20\Big)\delta_5 + (21a_1 - 9)\delta_6 + 14\delta_7\Big]$

TABLE III

Experimental Potential-Energy Parameters and Rotationless Dipole-Moment Matrix Elements

j	a_j	$\langle 0\|M(x)\|j\rangle$/Debye
1	$-2.3633725 \pm 3.5 \times 10^{-5}$	$7.12 \times 10^{-2} \pm 2.5 \times 10^{-3}$
2	$3.6605756 \pm 1.9 \times 10^{-4}$	$-7.75 \times 10^{-3} \pm 2.5 \times 10^{-4}$
3	$-4.74921 \pm 1.3 \times 10^{-3}$	$5.15 \times 10^{-4} \pm 2.0 \times 10^{-5}$
4	$5.4529 \pm 9.9 \times 10^{-3}$	$-3.063 \times 10^{-5} \pm 1.0 \times 10^{-7}$
5	$-5.516 \pm 3.2 \times 10^{-2}$	$-8.42 \times 10^{-6} \pm 3.6 \times 10^{-8}$
6	4.284 ± 0.13	$6.61 \times 10^{-6} \pm 2.4 \times 10^{-8}$
	$\gamma = 7.083694 \times 10^{-3} \pm 1.7 \times 10^{-8}$	$\langle 0\|M(x)\|0\rangle = 1.10847 \pm 5 \times 10^{-4}$

$$\begin{aligned}
\nu_j &= M_j/\langle 0|M(x)|0\rangle, \\
\theta_j &= \sqrt{\gamma}M_j/\sqrt{2}\langle 0|M(x)|1\rangle, \\
\phi_j &= \gamma M_j/\sqrt{2}\langle 0|M(x)|2\rangle, \\
\mu_j &= \gamma^{3/2}\sqrt{3}M_j/2\langle 0|M(x)|3\rangle, \\
\rho_j &= \gamma^2\sqrt{6}M_j/2\langle 0|M(x)|4\rangle, \\
\epsilon_j &= \gamma^{5/2}\sqrt{15}M_j/2\langle 0|M(x)|5\rangle, \\
\delta_j &= 3\gamma^3\sqrt{5}M_j/2\langle 0|M(x)|6\rangle.
\end{aligned} \tag{4}$$

Because of the form of these expressions a large amount of cancellation can occur in determining both the individual coefficients of M_j and the final numerical values. Consequently, in order to obtain consistent results, one must retain all the contributions to the same power of γ. For this reason, the correction term to C_v^{v+6} is not given because it contains contributions of the order of a_1^7. Finally, higher-order corrections (higher powers of γ) to the C and D coefficients, as well as the coefficients of m^3, m^4, etc., in Eq. [3] can be derived by identical methods. Such extensions, however, are not warranted at present in light of the accuracy of the experimental results.

3. APPLICATION TO HCl

As an example to illustrate the use of the Herman–Wallis coefficients in extracting the dipole-moment coefficients M_j from the experimental data, we have reanalyzed (*15*) the vibration–rotational intensities of HCl incorporating both the recent results

TABLE IV

Coefficients of the Dipole-Moment Function

j	M_j/Debye
0	$1.09333 \pm 8.6 \times 10^{-4}$
1	1.20538 ± 0.039
2	0.03842 ± 0.060
3	-1.4882 ± 0.10
4	-0.9881 ± 0.14
5	-0.6476 ± 0.19
6	-0.9358 ± 0.41

for the higher overtone bands (*4*) and the accurate Dunham potential-energy parameters obtained from a global analysis of the transition frequencies (*16*). These data are assembled in Table III, including estimates of the experimental uncertainties

TABLE V

Comparison of Calculated and Measured Herman–Wallis Coefficients

	Experiment	Theory
C_0^0	-	0
D_0^0	-	$1.1 \times 10^{-4} \pm 3.7 \times 10^{-6}$
C_0^1	$-2.60 \times 10^{-2} \pm 2.0 \times 10^{-3}$	$-2.66 \times 10^{-2} \pm 9.3 \times 10^{-4}$
D_0^1	$4.5 \times 10^{-4} \pm 2.0 \times 10^{-4}$	$2.8 \times 10^{-4} \pm 7.7 \times 10^{-6}$
C_0^2	$-8.60 \times 10^{-3} \pm 1.5 \times 10^{-3}$	$-5.67 \times 10^{-3} \pm 7.9 \times 10^{-4}$
D_0^2	$4.1 \times 10^{-4} \pm 2.0 \times 10^{-4}$	$3.1 \times 10^{-4} \pm 8.5 \times 10^{-6}$
C_0^3	1.70×10^{-2}	$1.07 \times 10^{-2} \pm 2.2 \times 10^{-3}$
D_0^3	-	$3.7 \times 10^{-4} \pm 1.7 \times 10^{-5}$
C_0^4	$2.77 \times 10^{-2} \pm 1.1 \times 10^{-3}$	$1.20 \times 10^{-2} \pm 7.3 \times 10^{-3}$
D_0^4	$1.42 \times 10^{-3} \pm 1.7 \times 10^{-4}$	$7.9 \times 10^{-4} \pm 2.5 \times 10^{-5}$
C_0^5	$1.74 \times 10^{-2} \pm 1.3 \times 10^{-3}$	$3.21 \times 10^{-2} \pm 7.0 \times 10^{-3}$
D_0^5	$4.61 \times 10^{-4} \pm 2.4 \times 10^{-4}$	$1.4 \times 10^{-3} \pm 3.2 \times 10^{-4}$
C_0^6	$3.35 \times 10^{-2} \pm 1.1 \times 10^{-3}$	$4.99 \times 10^{-2} \pm 2.9 \times 10^{-3}$
D_0^6	$7.99 \times 10^{-4} \pm 1.8 \times 10^{-4}$	$1.3 \times 10^{-3} \pm 1.8 \times 10^{-4}$

(*4*, *13*, 16, *17*). With the choice of signs for the dipole-moment matrix elements indicated in Table III, we obtained the best overall fit. The corresponding theoretical values of the dipole-moment and Herman–Wallis coefficients are given in Tables IV and V. The accompanying error estimates were obtained by a Monte-Carlo sampling method, according to which the input parameters (a_j, γ, and $\langle 0|M(x)|v'\rangle$) were subjected to random variation within one (nominal) standard deviation of their published values, and the variation of the M_j, $C_0^{v'}$, and $D_0^{v'}$ coefficients correspondingly determined. These estimates are equivalent to one standard deviation, and thus are indicative of the relative uncertainties. A detailed comparison of the present results with the previous analysis (*15*) based on $0 \leqslant v' \leqslant 5$ demonstrates that the addition of the $6 \leftarrow 0$ results and the improved potential-energy parameters improves the overall fit; all the C and D coefficients have the correct signs and approximately the correct magnitudes. We are thus led to believe that the present dipole-moment function is correspondingly better.

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