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A Reexamination of the Spin–Rotation Constant for $^2\Pi$ States: The A–X Band System of HCl^+

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Using the line positions measured by Sheasley and Mathews, we have reanalyzed the $A\ ^2\Sigma^+$–$X^2\Pi$ emission spectrum of $H^{35}Cl^+$, $H^{37}Cl^+$, $D^{35}Cl^+$, and $D^{37}Cl^+$ employing the Hamiltonians and "direct approach" described by Zare, Schmeltekopf, Harrop, and Albritton. The new values for the molecular constants now show the expected isotope relations. Attention is concentrated on the centrifugal distortion correction to the spin–orbit splitting, A_D, and the spin–rotation constant, γ, of the $^2\Pi$ state. Fixing A_D to values calculated using an algorithm by Coxon, a value for γ is derived. This compares poorly to the value of γ expected from an approximation suggested by Van Vleck. The source for this discrepancy is suggested to be the inadequacy of the Van Vleck approximation for the spin–rotation constant and/or the fact that the experimentally derived value is, in general, only an effective parameter containing both the "true" spin–rotation interaction and pseudo-spin–rotation interactions caused by electronic perturbations, such as simultaneous interaction with $^2\Sigma^+$ and $^2\Sigma^-$ states or interactions with $^2\Delta$ or other $\Lambda \neq 0$ states with different multiplicity.

I. INTRODUCTION

The work described in this paper was initiated to resolve a discrepancy between observed and predicted isotope effects on the centrifugal distortion correction to the spin–orbit constant, A_D, reported by Sheasley and Mathews (*1*) in their analysis of the $A\ ^2\Sigma^+$–$X^2\Pi$ emission spectrum of $H^{35}Cl^+$, $H^{37}Cl^+$, $D^{35}Cl^+$, $D^{37}Cl^+$. The present investigation developed along two lines: (1) an evaluation of the procedure used to determine molecular constants from the assigned spectral lines and (2) an evaluation and extension of the theoretical description of the molecular constants. In both approaches, attention quickly focussed on the constants A_D (the centrifugal distortion correction to the spin–orbit splitting constant), γ (the spin–rotation constant), and the Λ-doubling constants, p and q.

The analysis of $^2\Pi$ states has its theoretical origins in the works of Hill and Van Vleck (*2*) Van Vleck (*3*), and Mulliken and Christy (*4*). However, as more spectroscopic

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information has become available on $^2\Pi$ states through the analysis of high-resolution $^2\Sigma$–$^2\Pi$ optical spectra and through advances in microwave spectroscopy, it has become apparent that centrifugal distortion effects, neglected in the original theoretical treatment, had to be included to explain the observed fine structure splittings. An early refinement in this area was the work of Almy and Horsfall (*5*) in which the effects of rotational stretching on the B_v constant were introduced but its effects on the spin–orbit constant A_v were omitted. The first consideration of vibration–rotation interaction on the spin–orbit constant appears to be the work of James (*6*). He found that A_v had a J dependence and should be replaced by $A_v + A_{Dv}(J + \frac{1}{2})^2$ in the secular determinant for the energy levels of the $^2\Pi$ state. He also noticed that the spin–rotation constant of the $^2\Pi$ state, denoted here as γ^Π, entered the expressions for the $^2\Pi$ energy levels in such a way that there is "no clearcut method" for distinguishing between the contributions from A_D and γ^Π.

The HCl^+ and DCl^+ molecules provide a particularly fertile proving ground for testing our understanding of the fine structure splittings in $^2\Pi$ diatomics. Not only are those molecules very light, so that the effects of centrifugal distortion are accentuated, but the spin–orbit interaction is unusually large (A is on the order of -650 cm^{-1}), so that small J-dependent variations in the spin-orbit constant should readily manifest themselves in the analysis of the optical spectra. It is with the goal of obtaining a deeper insight into the centrifugal distortion of the $^2\Pi$ energy level structure that we examine here at some length the results of the new analysis of the HCl^+ and DCl^+ $A\ ^2\Sigma^+$–$X\ ^2\Pi$ band system using the measurements and assignments given by Sheasley and Mathews (*1*).

It will be of some interest to review briefly the fitting procedure used by Sheasley and Mathews (*1*). The constants for the $v = 0$ level of the $X\ ^2\Pi$ state were obtained first by fitting all possible combination differences (e.g., about 1400 differences for $D^{35}Cl^+$ from 9 bands, $v' = 0$–8) to differences calculated from the following energy expression for a $^2\Pi$ state,

$$F_i^{e,f}(J) = Bx - Dx^2 + Hx^3 \pm \left[\frac{(A^* - 2B^*)^2}{4} + B^{*2}x\right]^{\frac{1}{2}} \pm \tfrac{1}{2}\varphi_i^{e,f}. \tag{1}$$

Here the upper signs refer to the F_2 component, the lower signs refer to the F_1 component, and

$$x = (J + \tfrac{1}{2})^2 - 1, \tag{2}$$

$$B^* = B - 2Dx + 3Hx^2, \tag{3}$$

and

$$A^* = A + A_D x. \tag{4}$$

The Λ-doubling expressions $\varphi_i^{e,f}$ are:

$$\varphi_1^{e,f}(J) = \pm\,[Q(J + \tfrac{1}{2})^3 + QQ(J + \tfrac{1}{2})^5] \tag{5}$$

and

$$\varphi_2^{e,f}(J) = \pm\,[P(J + \tfrac{1}{2}) + PP(J + \tfrac{1}{2})^3 + PPP(J + \tfrac{1}{2})^5 + PPPP(J + \tfrac{1}{2})^7], \tag{6}$$

where in Eqs. (5) and (6) the plus sign is for the e component and the minus sign is for the f component. Formerly, the e and f components were denoted by c and d (*7*).

These $^2\Pi$ state constants were used to calculate term values for the $v'' = 0$ level, which were added to observed transitions (spectral lines) terminating on $v'' = 0$ to generate term values for the $^2\Sigma^+$ state. Upper state constants were then obtained by fitting these term values to the $^2\Sigma^+$ Hamiltonian,

$$F_1(N) = BN(N+1) - DN^2(N+1)^2 + HN^3(N+1)^3 + \tfrac{1}{2}[\gamma + \gamma_D N(N+1)]N \quad (7)$$

and

$$F_2(N) = BN(N+1) - DN^2(N+1)^2 + HN^3(N+1)^3 - \tfrac{1}{2}[\gamma + \gamma_D N(N+1)](N+1). \quad (8)$$

A fit of the term values for the $v'' = 1$ and $v'' = 2$ levels of the $^2\Pi$ state, obtained by subtracting the appropriate spectral lines from the $^2\Sigma^+$ term values, gave the remaining constants for the $^2\Pi$ state.[2]

It was pointed out by Watson (see footnote 3 of Ref. (*1*)) that the observed ratio of A_D (deuteride)/A_D (hydride) $\cong 0.23$ obtained in the previous analysis differed considerably from the expected isotope ratio of 0.51. In addition, the values of A_D obtained for HCl^+ and DCl^+ respectively, were -6.7 and -3.0 times the values predicted from an expression given by Veseth (*8*).[3] This interesting discrepancy was suggested by Sheasley and Mathews as a topic meriting further study. It was additionally suggested by Sheasley (*9*) that a reanalysis of the data using a different mathematical model and fitting procedure might provide a useful check of the physical interpretation of the constants.

II. REANALYSIS

A. Procedure

Each band was first reduced to a set of upper and lower state constants by an equally weighted least-squares fit of the measured line positions to line positions calculated from numerically diagonalizing upper and lower state Hamiltonians having adjustable molecular constants (*10*). The upper state ($^2\Sigma^+$) Hamiltonian contained the following adjustable constants: ν_0, B, D, H, γ, and γ_D; the lower state ($^2\Pi$) Hamiltonian contained A, A_D, B, D, and H plus the Λ-doubling constants, p, p_D, q, and q_D. A detailed descrip-

[2] A difficulty encountered in a term value analysis such as the one described above is the dependence of the experimental term values upon the absolute wavenumbers of the spectral lines. A wavenumber difference between two spectral lines can be reproduced much more accurately from plate to plate than can the absolute wavenumber value of the line positions. In the previous analysis it was found that the wavenumbers of the same lines recorded on different plates differed by as much as ± 0.05 cm^{-1}. To correct for this shift between plates, the average of the residuals for each set of calculated term values was subtracted from each experimental term value in that set. These corrections were incorporated into the present reanalysis by subtracting a correction term, calculated separately for each band and F component, from each of the observed lines. The only constants noticeably affected by these corrections are the band origin, ν_0, the spin–orbit constant A_v and the Λ-doubling constant o_v. To first order, the remaining constants, whose contribution to the energy is J-dependent, remain unchanged.

[3] Our molecular constant A_D is the same as the A_J used by Sheasley and Mathews (*1*) but equals $2A_J$ as used by Veseth (*8*).

TABLE I

Molecular Constants[a] (in cm^{-1}) for the X $^2\Pi$ State of $H^{35}Cl^+$ and $H^{37}Cl^+$

	$H^{35}Cl^+$			$H^{37}Cl^+$		
v =	0	1	2	0	1	2
B	9.793698(78)	9.471858(100)	9.15534(25)	9.778679(130)	9.457999(170)	9.14257(80)
$D\times10^4$	5.4768(45)	5.3906(62)	5.3582(220)	5.4473(99)	5.3860(140)	5.418(120)
$H\times10^8$	1.524(78)	1.407(110)	2.82(90)	1.367(220)	1.37(32)	3.8(36)
A	-648.1290(31)	-647.7107(46)	-647.2566(160)	-648.1279(47)	-647.7178(74)	-647.240(39)
$A_D\cdot10^3$	2.0881(160)	2.803(25)	3.545(120)	2.126(28)	2.794(51)	3.40(37)
$Q\times10^2$	-1.1178(62)	-1.0630(110)	-1.027(48)	-1.0923(120)	-1.0977(200)	-1.142(140)
$Q_D\cdot10^6$	1.569(200)	0.58(41)	0.5(33)	0.69(51)	2.75(110)	14.3(130)
p	0.60907(39)	0.59886(56)	0.59361(200)	0.60807(61)	0.59888(99)	0.5922(49)
$P_D\cdot10^6$	-3.253(170)	-3.11(33)	-6.27(170)	-3.13(35)	-3.42(68)	-6.9(50)
T_v	0.0	2568.6198(33)	5032.1666(95)	0.0	2566.7504(51)	5028.5786(210)

[a]The numbers in parentheses are the uncertainty in the last digits that corresponds to one standard deviation, computed using all the (weighted) line positions (11). The standard deviation of the residuals (each line equally weighted) is 0.016 cm^{-1} for the 1839 lines of $H^{35}Cl^+$ and 0.017 cm^{-1} for the 1384 lines of $H^{37}Cl^+$.

tion of this approach and explicit definitions of these constants as matrix elements is given elsewhere (*10*).[4]

The constants obtained from our band-by-band fit were then combined to obtain a single set of constants for each vibrational level (*11*) using a program called MERGE. The MERGE program employs the variance-covariance matrix associated with the constants of each band in such a way as to make our final constants equivalent to those that would be obtained from a simultaneous weighted least-squares fit of the lines of all the bands (*12*).

Our final constants are listed in Tables I–IV, Tables I and II for the HCl^+ and DCl^+ $^2\Pi$ states, Tables III and IV for the HCl^+ and DCl^+ $^2\Sigma^+$ states. The molecular constants for the $^2\Sigma^+$ state are in excellent agreement with those obtained previously (*1*), while the constants for the $^2\Pi$ state differ appreciably for A_D and the Λ-doubling parameters. In particular, the values for A_D now agree in sign with those predicted from the Veseth relation (*8*) but differ in magnitude by approximately a factor of two.

The different results for the $^2\Pi$ state might be attributed to the use of a different statistical approach (i.e., "direct" as compared to the "combination difference" approach). This possibility was tested by using the combination differences and statistical package used by Sheasley and Mathews (*1*) after replacing the energy expressions in Eq. (1) by the Hamiltonian-diagonalization of the present analysis. This procedure gave results nearly identical to those in Tables I and II. Consequently the differences must be attributed to the different Hamiltonians rather than to the use of combination differences. These data as well as the correlation coefficients discussed in the next

[4] There is a typographical error in the second entry ot Table II of Ref. (*10*); the sign in front of $A_{Dv}\Lambda(\Sigma \pm \frac{1}{2})f_v(\Omega\Sigma)$ should be changed from minus to plus.

TABLE II

Molecular Constants[a] (in cm^{-1}) for the X $^2\Pi$ State of $D^{35}Cl^+$ and $D^{37}Cl^+$

	$D^{35}Cl^+$			$D^{37}Cl^+$		
v =	0	1	2	0	1	2
B	5.061609(52)	4.942457(58)	4.824526(75)	5.046722(110)	4.928191(130)	4.810339(260)
$D \times 10^4$	1.45911(210)	1.4452(23)	1.4330(28)	1.4522(63)	1.4457(70)	1.4262(130)
$H \times 10^9$	2.883(220)	2.83(25)	3.21(37)	4.20(98)	5.27(110)	4.75(140)
A	-648.1693(48)	-647.8881(63)	-647.5355(81)	-648.1695(84)	-647.8573(120)	-647.5270
$A_D \times 10^3$	0.9518(170)	1.2209(180)	1.466(27)	1.004(41)	1.240(47)	1.677(170)
$Q \times 10^3$	-2.929(55)	-2.949(110)	-2.687(110)	-2.842(140)	-2.895(170)	-2.21(41)
$Q_D \times 10^7$	0.43(140)	3.14(160)	-0.2(29)	-2.6(51)	3.6(49)	-4.1(140)
P	0.31402(31)	0.31123(39)	0.30624(48)	0.31340(54)	0.30923(77)	0.30586(160)
$P_D \times 10^6$	-8.53(110)	-11.47(120)	-8.63(170)	-11.58(260)	-10.9(31)	-26.7(98)
T_v	0.0	1864.0307(41)	3673.5351(50)	0.0	1861.3324(77)	3668.3453(140)

[a]The numbers in parentheses are the uncertainty in the last digits that corresponds to one standard deviation, computed using all the (weighted) line positions (11). The standard deviation of the residuals (each line equally weighted) is 0.015 cm^{-1} for the 2979 lines of $D^{35}Cl^+$ and 0.018 cm^{-1} for the 1696 lines of $D^{37}Cl^+$.

section, provide additional support of the reliability of combination differences obtained from several bands, as discussed by Plíva and Telfair (*13*).

B. Correlation of Molecular Constants

The correlation matrices for all our merged constants are rather large, 71 × 71 for both $H^{35}Cl^+$ and $H^{37}Cl^+$, and 89 × 89 for both $D^{35}Cl^+$ and $D^{37}Cl^+$. They are available

TABLE III

Molecular Constants[a] (in cm^{-1}) for the A $^2\Sigma^+$ State of $H^{35}Cl^+$ and $H^{37}Cl^+$

v	B	$D \times 10^4$	$H \times 10^8$	γ	$\gamma_D \times 10^6$	T_v
			$H^{35}Cl^+$			
0	7.341503(73)	6.4351(38)	2.300(62)	0.59421(28)	-3.369(130)	28 095.9720(23)
1	7.023208(95)	6.1935(95)	1.833(95)	0.58683(48)	-3.094(180)	29 623.6501(31)
2	6.716136(90)	6.0144(53)	1.881(84)	0.57951(35)	-3.473(150)	31 075.2665(34)
3	6.417195(120)	5.8396(100)	1.39(23)	0.57070(56)	-4.59(33)	32 452.7800(32)
4	6.124706(100)	5.7209(73)	0.986(150)	0.55890(54)	-5.49(36)	33 757.4086(29)
5	5.835770(90)	5.6630(62)	0.632(120)	0.54091(38)	-7.551(200)	34 989.4479(25)
6	5.544452(150)	5.701(20)	-3.49(78)	0.51145(56)	-17.32(52)	36 148.3377(27)
			$H^{37}Cl^+$			
0	7.330339(130)	6.4064(110)	2.103(240)	0.59334(48)	-3.43(28)	28 096.3356(35)
1	7.012871(190)	6.1753(210)	1.91(68)	0.58565(74)	-3.31(62)	29 622.9350(40)
2	6.706349(170)	5.9786(140)	1.38(29)	0.57927(62)	-3.79(40)	31 073.5531(52)
3	6.408526(170)	5.8623(170)	2.46(45)	0.57015(68)	-4.87(48)	32 450.1920(41)
4	6.116502(140)	5.7164(120)	1.25(27)	0.55678(62)	-4.61(47)	33 754.0549(37)
5	5.827751(140)	5.6293(120)	0.40(30)	0.54032(53)	-6.98(36)	34 985.4444(33)
6	5.53717(26)	5.629(39)	-6.18(170)	0.50999(93)	-15.70(110)	36 143.7938(43)

[a]The numbers in parentheses are the uncertainty in the last digits that corresponds to one standard deviation, computed using all the (weighted) line positions (11). The standard deviation of the residuals (each line equally weighted) is 0.016 cm^{-1} for the 1839 lines of $H^{35}Cl^+$ and 0.017 cm^{-1} for the 1384 lines of $H^{37}Cl^+$.

TABLE IV

Molecular Constants[a] (in cm^{-1}) for the A $^2\Sigma^+$ State of $D^{35}Cl^+$ and $D^{37}Cl^+$

v	B	D × 10^4	H × 10^9	γ	γ_D × 10^6	T_v
			$D^{35}Cl^+$			
0	3.799062(47)	1.71657(180)	3.981(220)	0.306046(170)	-0.858(47)	28 247.6458(28)
1	3.680562(51)	1.67127(210)	3.67(24)	0.30347(26)	-0.765(86)	29 359.3570(29)
2	3.565140(57)	1.6323(27)	3.51(37)	0.30066(29)	-0.703(120)	30 431.5605(29)
3	3.452458(69)	1.6023(42)	4.62(69)	0.29862(36)	-1.219(180)	31 464.9986(32)
4	3.341616(86)	1.5413(42)	-1.66(120)	0.29479(45)	-1.09(24)	32 460.2842(33)
5	3.232923(86)	1.5249(48)	1.14(69)	0.29081(54)	-1.243(210)	33 417.8740(39)
6	3.125778(92)	1.5127(54)	2.25(86)	0.28560(63)	-1.20(34)	34 338.1223(37)
7	3.019429(69)	1.5049(40)	2.31(69)	0.27997(37)	-2.167(200)	35 221.1356(30)
8	2.912448(100)	1.4652(200)	-12.3(69)	0.27113(75)	-3.33(69)	36 066.6438(39)
9	2.803160(160)	1.5421(170)	-6.9(49)	0.25284(69)	-6.38(47)	36 873.6898(42)
			$D^{37}Cl^+$			
0	3.787936(98)	1.7089(57)	5.23(98)	0.30461(31)	-0.634(120)	28 248.1771(49)
1	3.670046(110)	1.6683(77)	5.27(150)	0.30284(40)	-0.843(200)	29 358.3035(49)
2	3.555097(130)	1.6308(110)	6.14(240)	0.29983(51)	-0.67(32)	30 429.0516(57)
3	3.443075(180)	1.6214(150)	13.9(39)	0.29847(91)	-1.88(56)	31 461.1331(59)
4	3.332179(270)	1.5064(260)	-6.9(70)	0.29389(130)	-0.90(98)	32 455.1861(77)
5	3.224332(180)	1.5199(130)	1.8(24)	0.28966(84)	-0.72(39)	33 411.6313(67)
6	3.117186(270)	1.467(37)	-4.0(150)	0.28440(110)	-0.56(110)	34 330.8727(61)
7	3.011580(160)	1.4826(170)	-1.2(49)	0.27814(70)	-1.40(61)	35 212.9641(53)
8	2.90605(35)	1.602(58)	48.9(260)	0.27053(130)	-3.79(140)	36 057.6546(67)
9	2.79782(49)	1.734(91)	91.(47)	0.25158(150)	-1.17(180)	36 864.0103(77)

[a]The numbers in parentheses are the uncertainty in the last digits that corresponds to one standard deviation, computed using all the (weighted) line positions (11). The standard deviation of the residuals (each line equally weighted) was 0.015 cm^{-1} for the 2979 lines of $D^{35}Cl^+$ and 0.018 cm^{-1} for the 1696 lines of $D^{37}Cl^+$.

elsewhere,[5] along with the results of our band-by-band analysis and a listing of the program MERGE. Excerpted portions, however, of the $H^{35}Cl^+$ correlation matrix can be found in the upper triangle of Table V, which shows the relation between the merged rotational constants B_0^Π, D_0^Π, H_0^Π, B_0^Σ, D_0^Σ, H_0^Σ, B_1^Π, D_1^Π, and H_1^Π. The lower triangle of this table gives the correlation coefficients for the same constants obtained in the initial band-by-band fits of the (0, 0) and (0, 1) bands.

It can be seen from Table V that the correlation between the upper and lower state constants is less in the merged constants than in the constants obtained in the band-by-band analysis. This result is expected since the dependence within a band of one constant on another is reduced by considering additional bands with common upper or lower vibrational states. Note however that the correlation between the constants of any one vibrational state remains roughly the same, since this depends more on the model Hamiltonian and the extent of the data than on what other bands are included. Although Table V only shows a small portion of the correlation matrix, it is characteristic of other portions of the same matrix as well as the correlation matrix for the constants of the other isotopes of HCl^+.

C. *Isotope Dependence of Selected* $^2\Pi$ *State Molecular Constants*

The isotope ratios, $A_D(DCl^+)/A_D(HCl^+)$, obtained in this analysis are 0.46(2), 0.44(2), and 0.41(5) for $v = 0$, 1, and 2, respectively, where the error estimates are

[5] This material is on deposit in the Editorial Office of the *Journal of Molecular Spectroscopy* and can be made available on request.

TABLE V

CORRELATION MATRIX FOR SELECTED MERGED CONSTANTS (UPPER TRIANGLE) AND BAND-BY-BAND CONSTANTS (LOWER TRIANGLE) OF $H^{35}Cl^+$

	B_0^π	D_0^π	H_0^π	B_0^Σ	D_0^Σ	H_0^Σ	B_1^π	D_1^π	H_1^π
B_0^π	1.00	0.87	0.68	0.80	0.74	0.64	0.59	0.48	0.35
D_0^π	0.89	1.00	0.92	0.67	0.80	0.81	0.54	0.56	0.48
H_0^π	0.78	0.96	1.00	0.52	0.72	0.83	0.45	0.55	0.53
B_0^Σ	0.93	0.79	0.67	1.00	0.89	0.73	0.62	0.45	0.29
D_0^Σ	0.90	0.95	0.89	0.88* 0.89*	1.00	0.94	0.58	0.56	0.43
H_0^Σ	0.80	0.95	0.96	0.73* 0.76*	0.95* 0.96*	1.00	0.50	0.57	0.51
B_1^π				0.91	0.87	0.77	1.00	0.89	0.69
D_1^π				0.79	0.93	0.93	0.91	1.00	0.90
H_1^π				0.68	0.89	0.95	0.79	0.96	1.00

* The upper entry is from the (0,0) band and the lower entry is from the (0,1) band.

based on two standard deviations. This should be compared to 0.23(2), 0.21(2), and 0.17(6) obtained previously (*1*). In the present analysis the (deuteride)/(hydride) ratio of the Λ-doubling constants is expected to be 0.51 for p, 0.26 for q, 0.26 for p_D and 0.14 for q_D. With error estimates based on two standard deviations, the $v'' = 0$ isotope ratios are: 0.52(1) for p, 0.26(1) for q, 0.26 (+11, −9) for p_D, and 0.03(+25, −15) for q_D. The isotope ratios are well satisfied for all the constants within their stated errors.

We conclude that the anomalous A_D values obtained previously were the result of a fit to a $^2\Pi$ state Hamiltonian that appreciably mixed the mechanical and magnetic meanings of the $^2\Pi$ state constants. More specifically, the particular Λ-doubling expressions given in Eqs. (5) and (6) affect substantially the centrifugal distortion correction to A as well as the isotopic dependence of the Λ-doubling constants. The high correlation between A_D and the Λ-doubling constants is an additional indication of this interdependence.

III. DISCUSSION AND THEORETICAL INTERPRETATION

We may now consider in more detail the orgins of the constants, A_D and γ^Π, as well as the difficulty of separating their effects.

First, let us review briefly the origin of the centrifugal distortion correction to the spin–orbit interaction. According to the Van Vleck transformation (*10*), the perturbation H' connecting different vibrational levels $v\Omega\Sigma$ in the same electronic state may be taken into account through fourth order in the energy by adding to the secular matrix for the $^2\Pi$ energy levels a correction matrix of the form

$$H_{ij} = \sum_{v' \neq v} \sum_{\Omega', \Sigma'} \frac{\langle v\Omega_i\Sigma_i | H' | v'\Omega'\Sigma' \rangle \langle v'\Omega'\Sigma' | H' | v\Omega_j\Sigma_j \rangle}{E_v - E_{v'}}. \tag{9}$$

In the case at hand,

$$H' = H_{so} + H_{rot}. \tag{10}$$

If one neglects terms that connect to other electronic states (*14*), then

$$H_{so} = A(r)L_zS_z \tag{11}$$

and

$$H_{rot} = B(r)\mathbf{R}^2. \tag{12}$$

Here

$$\mathbf{R}^2 = \mathbf{J}^2 - 2J_zS_z + \mathbf{S}^2 - L_z^2 - J_+S_- - J_-S_+, \tag{13}$$

J is the total angular momentum, **S** the electronic spin angular momentum, **L** the electronic orbital angular momentum, and the z axis coincides with the internuclear axis.

Substitution of Eqs. (10)–(12) into Eq. (9) leads to three types of centrifugal distortion correction terms. The first type involves only the spin–orbit Hamiltonian. It has the form

$$H_{ij} = a_D\Lambda^2\Sigma^2\delta_{ij} \tag{14}$$

where

$$a_{Dv} = \sum_{v'\neq v} \frac{\langle v|A(r)|v'\rangle\langle v'|A(r)|v\rangle}{E_v - E_{v'}}. \tag{15}$$

Because this correction is independent of J, it is incorporated into the band origin. The second type involves only the rotational Hamiltonian and has the form

$$H_{ij} = -D_v\langle\Omega_i\Sigma_i|\mathbf{R}^4|\Omega_j\Sigma_j\rangle, \tag{16}$$

where

$$D_v = -\sum_{v'\neq v} \frac{\langle v|B(r)|v'\rangle\langle v'|B(r)|v\rangle}{E_v - E_{v'}}. \tag{17}$$

This is recognized as the familiar centrifugal distortion correction to B_v. Finally, the third type contains the cross terms resulting from the joint interaction of the spin–orbit Hamiltonian and the rotational Hamiltonian. It has the form

$$H_{ij} = A_{Dv}\Lambda\Sigma\langle\Omega_i\Sigma_i|\mathbf{R}^2|\Omega_j\Sigma_j\rangle, \tag{18}$$

where

$$A_{Dv} = 2\sum_{v'\neq v} \frac{\langle v|A(r)|v'\rangle\langle v'|B(r)|v\rangle}{E_v - E_{v'}}. \tag{19}$$

This is the so-called centrifugal distortion correction to the spin–orbit constant. Equation (19) has been derived previously by Veseth (*8*) and by Merer (*15*) who first noted that A_D has its origin in the simultaneous variation of $A(r)$ and $B(r)$ with internuclear distance.

Both these workers attempted to estimate the value of A_D for the $v = 0$ level. Based on the assumption that the molecular potential is harmonic, Veseth finds

$$A_{Dv=0} = \frac{2(A_{v+1} - A_v)D_{v=0}}{(B_v - B_{v+1}) + 6B_e^2/\omega_e} \tag{20}$$

and Merer finds

$$A_{Dv=0} = \frac{-2D_e\alpha_A}{\alpha_e + 6B_e^2/\omega_e}, \tag{21}$$

where in Eq. (21) α_A is defined by $A_v = A_e - \alpha_A(v + \frac{1}{2})$.

Recently, a different approach for evaluating A_D has been developed by Coxon (*16*) which is not limited to the lowest vibrational level or to a harmonic potential. Molecular wavefunctions are first obtained numerically from the RKR potential for the $^2\Pi$ state. The radial part of the spin–orbit operator is then expanded as a power series in r

$$A(r) = A(r_e) + (\partial A/\partial r)_{r_e}(r - r_e) + \tfrac{1}{2}(\partial^2 A/\partial r^2)_{r_e}(r - r_e)^2 + \cdots, \tag{22}$$

which may be rewritten as

$$A(r) = A^{(0)} + A^{(1)}r + A^{(2)}r^2 + \cdots, \tag{23}$$

where

$$A^{(0)} = A(r_e) - r_e(\partial A/\partial r)_{r_e} + \tfrac{1}{2}r_e^2(\partial^2 A/\partial r^2)_{r_e} - \cdots, \tag{24}$$

$$A^{(1)} = (\partial A/\partial r)_{r_e} - r_e(\partial^2 A/\partial r^2)_{r_e} + \cdots, \tag{25}$$

$$A^{(2)} = \tfrac{1}{2}(\partial^2 A/\partial r^2)_{r_e} - \cdots, \text{etc.} \tag{26}$$

Substitution of Eq. (23) into Eq. (19) gives

$$A_{Dv} = 2A^{(1)} \sum_{v' \neq v} \frac{\langle v|B(r)|v'\rangle\langle v'|r|v\rangle}{E_v - E_{v'}} \tag{27}$$

where $A^{(2)}$ and higher-order terms have been neglected. Since in this approximation

$$A_v = A^{(0)} + A^{(1)}\langle v|r|v\rangle, \tag{28}$$

$A^{(1)}$ can be determined from a least-squares fit of A_v to $\langle v|r|v\rangle = \bar{r}_v$, the expectation value of r in the vibrational level v. Then A_{Dv} may be found from Eq. (27) by explicity evaluating the summation shown in Eq. (27), much in the same manner as the centrifugal distortion constants D_v, H_v, etc., can be calculated from the RKR potential (*17*).

Our data for HCl^+ and DCl^+ can be used to compare the results for A_D obtained from the Veseth relation [Eq. (20)] or the Merer relation [Eq. (21)] with those given by the Coxon approach [Eqs. (27) and (28)]. Table VI lists the calculated values of A_D. It is apparent that there is substantial agreement between all three procedures. We adopt the values of the Coxon approach as the values of A_D(true) in what follows.

As has been shown elsewhere (*16, 18*), A_D and γ^Π are *nearly totally correlated*. Although the spin–rotation Hamiltonian

$$H_{sr} = \gamma(r)\mathbf{N}\cdot\mathbf{S} \tag{29}$$

has slightly different matrix elements than the centrifugal distortion correction to the spin–orbit constant, it is virtually impossible to obtain these constants independently from optical data. Instead, we have attempted to find γ_v^Π by fixing the value of A_{Dv} to those values of A_{Dv}(true) obtained from the Coxon approach (see Table VI). The same approach was used previously by Coxon to find values of γ_v^Π from an analysis

TABLE VI

CALCULATED VALUES[a] OF $A_D \times 10^4$ (IN cm^{-1})

v	Coxon Approach	Veseth Relation	Merer Relation
		$H^{35}Cl^+$	
0	8.78(66)	8.42(29)	8.87(37)
1	9.23(70)		
2	9.70(74)		
		$D^{35}Cl^+$	
0	4.48(34)	4.08(34)	4.65(33)
1	4.65(35)		
2	4.82(37)		

[a] The numbers in parentheses are the uncertainty in the last digits that corresponds to one standard deviation.

of the OD $A\ ^2\Sigma$–$X\ ^2\Pi$ band system. The resulting values of γ_v^{Π} for HCl^+ and its isotopes are listed in Table VII. The theoretical isotope ratios for γ_v^{Π} are the same as those for A_{Dv} (*19*). However, Table VII shows this condition is not met. Moreover, the vibrational dependence of the γ_v^{Π} values is larger than might be expected.

To check the possibility that these discrepancies are caused by the neglect of γ_D^{Π} (the centrifugal distortion correction to γ^{Π}), we tried several fits in which both γ^{Π} and γ_D^{Π} were free to vary. Our results are inconclusive. While the isotope ratios of γ^{Π}(deuteride)/γ^{Π}(hydride) improve, the high correlation between γ^{Π} and the barely determined γ_D^{Π} substantially increase the error estimate of γ^{Π}.

An alternative check on our values of γ^{Π} is provided by work of Veseth (*20*). In a second study on the corrections to the spin–orbit splitting in $^2\Pi$ states, Veseth deduced an approximate linear relationship between γ^{Π} and A_D of the form

$$\gamma^{\Pi} = \tfrac{1}{2}A_D(A_v - 2B_v)/B_v + \tfrac{1}{2}\Gamma - s \tag{30}$$

where Γ is a function of the known constants A_v, $\nu(\Pi, \Sigma)$, B_v^{Σ}, B_v^{Π}, p_v, and q_v and s can

TABLE VII

DERIVED VALUES[a] OF $\gamma^{\pi} \times 10^2$ (IN cm^{-1})

v	$D^{35}Cl^+$	$H^{35}Cl^+$	$\gamma^{\pi}(D^{35}Cl^+)/\gamma^{\pi}(H^{35}Cl^+)$
0	3.4(4)	4.1(3)	0.83(16)
1	4.8(4)	6.6(4)	0.72(10)
2	6.3(5)	9.8(8)	0.64(10)

[a] This is based on fixing the values of A_{Dv} to those given in TABLE VI by the Coxon approach. The error estimates (one standard deviation) include an uncertainty of one standard deviation in the value of A_D. The bands used to obtain γ^{π} are as follows for $D^{35}Cl^+$, (0,0), (1,0), (2,0), (0,1), (1,1), and (0,2); and for $H^{35}Cl^+$, (0,0), (1,0), (0,1), and (2,2).

be found by making a least-squares fit of the square of the "combination difference"

$$y(J) = F_{2e}(J) - F_{1e}(J) + F_{2f}(J) - F_{1f}(J) - K(J) \tag{31}$$

to a polynomial in $(J + \frac{1}{2})^i$ where $i = 0$, 2, and 4. The parameter s is the coefficient of the $(J + \frac{1}{2})^2$ term. In Eq. (31) $K(J)$ is a complex expression involving known constants of the $^2\Pi$ and $^2\Sigma$ states, given by Veseth (*20*). Using Veseth's values $s = -9.0(2) \times 10^{-2}$ cm^{-1} for the (0, 0) band of HCl^+ and $s = -8.5(6) \times 10^{-2}$ cm^{-1} from the (1, 0) band of DCl^+, combined with the A_D values calculated with Coxon's approach, we find γ_0^{Π} to be $4.0(8) \times 10^{-2}$ cm^{-1} for HCl^+ and γ_0^{Π} to be $4.1(4) \times 10^{-2}$ cm^{-1} for DCl^+. Our own values of $\gamma_0^{\Pi} = 3.7(5) \times 10^{-2}$ cm^{-1} for HCl^+ and $\gamma_0^{\Pi} = 4.4(3) \times 10^{-2}$ cm^{-1} for DCl^+ are judged to be in excellent agreement. Consequently, we believe we have determined a value for the spin–rotation constant in these $^2\Pi$ states. We conclude that fixing the value of A_D using Coxon's approach provides an attractive and practical means of estimating γ^{Π}, a constant which heretofore has largely escaped determination.

We are led to look more closely at the meaning of the *spin–rotation constant*, γ^{Π}. The phenomenological spin–rotation and spin–orbit Hamiltonians, given in Eqs. (11) and (29), have their origins in the interaction between the individual electron spins and the ambient magnetic field produced by the orbital motions of the electrons and nuclei. Let $\mathbf{r}$ denote the position vector and $\mathbf{v}$ the velocity vector. The indices i and j will refer to electrons and k to nuclei. Then the microscopic fine structure Hamiltonian may be written (*21*).

$$H_{\text{fine}} = H_{\text{so}}^{(e)} + H_{\text{soo}}^{(e)} + H_{\text{so}}^{(n)} + H_{\text{soo}}^{(n)} \tag{32}$$

where

$$H_{\text{so}}^{(e)} = -\tfrac{1}{2} \sum_{i<j} \left(\frac{-e_i}{mc}\right) \mathbf{s}_i \cdot \left[\left(\frac{-e_j}{r_{ij}^3}\right)(\mathbf{r}_i - \mathbf{r}_j) \times \frac{\mathbf{v}_i}{c}\right] \tag{33}$$

is the electronic contribution to the spin–orbit interaction,

$$H_{\text{soo}}^{(e)} = \sum_{i<j} \left(\frac{-e_i}{mc}\right) \mathbf{s}_i \cdot \left[\left(\frac{-e_j}{r_{ij}^3}\right)(\mathbf{r}_i - \mathbf{r}_j) \times \frac{\mathbf{v}_j}{c}\right] \tag{34}$$

is the electronic contribution to the spin–other–orbit interaction,

$$H_{\text{so}}^{(n)} = -\tfrac{1}{2} \sum_{i,k} \left(\frac{-e_i}{mc}\right) \mathbf{s}_i \cdot \left[\left(\frac{Z_k e}{r_{ik}^3}\right)(\mathbf{r}_i - \mathbf{r}_k) \times \frac{\mathbf{v}_i}{c}\right] \tag{35}$$

is the nuclear contribution to the spin–orbit interaction and

$$H_{\text{soo}}^{(n)} = \sum_{i,k} \left(\frac{-e_i}{mc}\right) \mathbf{s}_i \cdot \left[\left(\frac{Z_k e}{r_{ik}^3}\right)(\mathbf{r}_i - \mathbf{r}_k) \times \frac{\mathbf{v}_k}{c}\right] \tag{36}$$

is the nuclear contribution to the spin–other–orbit interaction. In Eqs. (33)–(36) $\mathbf{s}_i$ is the spin operator of electron i, having a charge $-e_i$ and a mass m, and $Z_k e$ is the charge of nucleus k. Note that in each case the nuclear contribution is obtained from the corresponding electronic contribution by replacing electron j by nucleus k and appropriately relabelling the summation indices.

It is traditional to combine Eqs. (33)–(35) and call them the microscopic spin–orbit Hamiltonian

$$H_{so}^{(m)} = H_{so}^{(n)} + H_{so}^{(e)} + H_{soo}^{(e)} \tag{37}$$

and to rename Eq. (36) the microscopic spin–rotation Hamiltonian

$$H_{sr}^{(m)} = H_{soo}^{(n)}. \tag{38}$$

The spin–orbit interaction is dominated by the term $H_{so}^{(n)}$. Comparing $H_{so}^{(n)}$ to $H_{soo}^{(n)}$ we see that they differ primarily by the replacement of the electronic velocity $\mathbf{v}_i$ by the nuclear velocity $\mathbf{v}_k$. Since these velocities are inversely related to the characteristic masses of electronic and nuclear motion, i.e., m and μ (the reduced mass), we are led to the approximation, first stated by Van Vleck (*3*), that "γ is of the order m/μ times A." Indeed, closer inspection of Eqs. (35) and (36) indicates that

$$\gamma^{\Pi}(\text{true}) \approx -\tfrac{1}{2}(m/\mu)A. \tag{39}$$

We shall refer to Eq. (39) as the Van Vleck approximation for the "true value" of the spin–rotation constant. Using the spin–orbit constant obtained for the HCl^+ $^2\Pi$ state, we estimate $\gamma^{\Pi}(\text{true}) \approx 18 \times 10^{-2}$ cm^{-1}, a factor of about *4 times larger* than the values of γ^{Π} given in Table VII. For the analogous OD X $^2\Pi$ state, the disagreement is even more marked. The value of $\gamma^{\Pi}(\text{true})$ calculated from Eq. (39) is about *12 times larger* than the mean value of γ_0^{Π} and γ_1^{Π}, reported by Coxon (*16*). Moreover, in both cases the variation of γ_v^{Π} with v is much more rapid than A_v with v. These disparities might be caused by two possibilities. First, the value of γ^{Π} found by using the Coxon approach to fix the value of A_D might contain other contributions that have the same J dependence as $\gamma^{\Pi}(\text{true})$ but arise from different sources. Second, the Van Vleck approximation as given in Eq. (39) might be no better than an order-of-magnitude estimate of $\gamma^{\Pi}(\text{true})$. We consider these possibilities in turn.

It is well-known that the value of the spin–rotation constant for $^2\Sigma$ states arises primarily from off-diagonal spin–orbit interaction, rather than the true spin–rotation interaction (*10*, *22*). Accordingly, perturbations of the $^2\Pi$ state with other electronic states suggest themselves as a possible origin of a pseudo-spin–rotation interaction. Indeed, this hypothesis is confirmed, as the following analysis shows.

Let us consider the effect of a $^2\Sigma^+$ state on the $^2\Pi$ energy level structure. That part of the Hamiltonian causing Λ-doubling is given by

$$H_{\Lambda} = -B(r)(J_+L_- + J_-L_+) + [B(r) + \tfrac{1}{2}A(r)](L_+S_- + L_-S_+). \tag{40}$$

The H_{Λ} perturbation may be treated once again by applying a Van Vleck transformation. This causes a 2×2 correction matrix, denoted by $H_{\Omega\Omega'}^{p}$, to be added to the otherwise identical parity blocks, p. Using the Λ-doubling parameters o_v, p_v, and q_v defined elsewhere (*10*), this correction matrix has the form

$$H_{\frac{3}{2}\frac{3}{2}}^{\pm} = \tfrac{1}{2}q_v[(J + \tfrac{1}{2})^2 - 1] \tag{41}$$

$$H_{\frac{1}{2}\frac{1}{2}}^{\pm} = \tfrac{1}{2}q_v[(J + \tfrac{1}{2})^2 \pm 2(J + \tfrac{1}{2}) + 1] + \tfrac{1}{2}p_v[\pm(J + \tfrac{1}{2}) + 1] + o_v \tag{42}$$

and

$$H_{\frac{1}{2}\frac{3}{2}}^{\pm} = H_{\frac{3}{2}\frac{1}{2}}^{\pm} = \tfrac{1}{2}q_v[(J + \tfrac{1}{2})^2 - 1]^{\frac{1}{2}}[\pm(J + \tfrac{1}{2}) + 1] + \tfrac{1}{4}p_v[(J + \tfrac{1}{2})^2 - 1]^{\frac{1}{2}}. \tag{43}$$

From Eqs. (41)–(43) it is seen that *both* parity blocks are affected by interaction with the $^2\Sigma^+$ state, but in an *unequal* manner. This differential interaction causes the Λ components to be split.

Now let us consider the effect of a $^2\Sigma^-$ state on the $^2\Pi$ energy level structure. The same analysis leads to the new correction matrices.

$$H_{\frac{3}{2}\frac{3}{2}}^{\pm} = \tfrac{1}{2}q_v'[(J+\tfrac{1}{2})^2 - 1], \tag{44}$$

$$H_{\frac{1}{2}\frac{1}{2}}^{\pm} = \tfrac{1}{2}q_v'[(J+\tfrac{1}{2})^2 \mp 2(J+\tfrac{1}{2}) + 1] + \tfrac{1}{2}p_v'[\mp (J+\tfrac{1}{2}) + 1] + o_v', \tag{45}$$

$$H_{\frac{1}{2}\frac{3}{2}}^{\pm} = H_{\frac{3}{2}\frac{1}{2}}^{\pm} = \tfrac{1}{2}q_v'[(J+\tfrac{1}{2})^2 - 1]^{\frac{1}{2}}[\mp (J+\tfrac{1}{2}) + 1] + \tfrac{1}{4}p_v'[(J+\tfrac{1}{2})^2 - 1]^{\frac{1}{2}}, \tag{46}$$

where the Λ-doubling parameters o_v', p_v', and q_v' are the $^2\Sigma^-$ counterparts of o_v, p_v, and q_v. Thus the two parity blocks are again both affected but in an unequal manner which is formally opposite to that of interaction with the $^2\Sigma^+$ state.

Since the $^2\Pi$ state under study is the ground state, any perturbing electronic state must lie above in energy, causing the signs of o_v', p_v', and q_v' to be the same as o_v, p_v, and q_v, respectively. Suppose interactions with both $^2\Sigma^+$ and $^2\Sigma^-$ states are present. Then the resulting correction to the $^2\Pi$ energy level structure is found by combining Eqs. (41)–(43) with the corresponding Eqs. (44)–(46). Consequently, both Λ components are shifted downwards, and to the extent to which the $^2\Sigma^+$ and $^2\Sigma^-$ states act in consort this combined interaction does not result in a splitting of the Λ components but rather in a J-dependent shift of the fine structure which behaves as the spin–rotation interaction. Thus the introduction of the adjustable Λ-doubling parameters p_v and q_v in this case cannot fully account in general for the combined action of the $^2\Sigma^+$ and $^2\Sigma^-$ perturbations but does account for the differential shift of the Λ components, i.e., the Λ-doubling.

In the limit that the $^2\Sigma^+$ states and $^2\Sigma^-$ states have the same interaction with the $^2\Pi$ ground state, $o_v = o_v'$, $p_v = p_v'$, $q_v = q_v'$, and the Λ-doubling disappears. The sum of the correction matrices then have the form

$$H_{\frac{3}{2}\frac{3}{2}}^{+} = H_{\frac{3}{2}\frac{3}{2}}^{-} = q_v[(J+\tfrac{1}{2})^2 - 1], \tag{47}$$

$$H_{\frac{1}{2}\frac{1}{2}}^{+} = H_{\frac{1}{2}\frac{1}{2}}^{-} = q_v[(J+\tfrac{1}{2})^2 + 1] + p_v - \gamma_v^{\Pi}(\text{true}) + 2o_v, \tag{48}$$

$$H_{\frac{1}{2}\frac{3}{2}}^{+} = H_{\frac{3}{2}\frac{1}{2}}^{+} = H_{\frac{1}{2}\frac{3}{2}}^{-} = H_{\frac{3}{2}\frac{1}{2}}^{-} = q_v[(J+\tfrac{1}{2})^2 - 1]^{\frac{1}{2}} + \tfrac{1}{2}p_v[(J+\tfrac{1}{2})^2 - 1]^{\frac{1}{2}} - \tfrac{1}{2}\gamma_v^{\Pi}(\text{true})[(J+\tfrac{1}{2})^2 - 1]^{\frac{1}{2}}, \tag{49}$$

where the "true" spin–rotation contribution from Eq. (29) to the secular matrix for the $^2\Pi$ energy levels has also been displayed in Eqs. (47)–(49) for comparison. It is seen that in this limit the q_v contribution is absorbed into the effective B_v rotational constant and the p_v contribution arising from the concerted interaction with $^2\Sigma^+$ and $^2\Sigma^-$ states is indistinguishable from the γ_v^{Π} contribution arising from the true spin–rotation interaction. Thus, p_v is totally correlated with γ_v^{Π}(true). Moreover, p_v and γ_v^{Π} have the same theoretical isotope dependence. However, Eqs. (47)–(49) show that the p_v contribution enters with an opposite sign to γ_v^{Π}(true) [both p_v and γ_v^{Π}(true) are positive quantities). This causes the effective γ_v^{Π} value found from the analysis of the optical spectra to be smaller than the γ_v^{Π} value predicted by the Van Vleck approximation, in accord with our findings for HCl^+ and DCl^+ as well as Coxon's findings for OD.

The above limiting case also serves to show that the interaction of $a\,^2\Delta$ state with $a\,^2\Pi$ state causes the same effect. Here interaction with $^2\Delta$ states leaves the Λ splitting virtually unchanged but contributes a J-dependent shift to the $^2\Pi$ energy level structure which acts once again as a pseudo-spin–rotation interaction.

We conclude then that the spin–rotation constant γ^{Π} derived for a $^2\Pi$ state from an analysis of its optical spectra in which the A_D constant is fixed, is nevertheless an effective constant containing the "pure" spin–rotation interaction as well as electronic perturbation contributions that have the same functional dependence as the spin–rotation interaction. It is tempting, then, to think that this may be the explanation why the value of γ^{Π}(true) obtained from the Van Vleck approximation differs so markedly from the experimentally derived value of γ^{Π}(true). However, at least in the case of OD, the following considerations forcefully argue against this conclusion. Coxon and Hammersley (*23*) have carried out ab initio calculations of the electronic matrix elements $\langle X\,^2\Pi | L_+ | A\,^2\Sigma^+\rangle$ and $\langle X\,^2\Pi | A(r) L_+ | A\,^2\Sigma^+\rangle$ and compared their values with those determined from the Λ-doubling constants p_v^{Π} and q_v^{Π}, assuming that *only* the $A\,^2\Sigma^+$ state is responsible for causing the Λ-doubling in the $^2\Pi$ state. They find that the agreement between the experimental and ab initio matrix elements is better than 1%. Unfortunately, a similar analysis for the HCl^+ $X\,^2\Pi$ state is lacking, although Raftery and Richards (*24*) have predicted that in the neighborhood of the $A\,^2\Sigma^+$ state is both a $^4\Sigma^-$ and a $^4\Pi$ state. Moreover, a $^2\Sigma^-$ state is also expected to be found since the lowest energy dissociation products of HCl^+, $H(^2S)$ and $Cl^+(^3P)$, correlate with $X\,^2\Pi$, $^4\Pi$, $^2\Sigma^-$, and $^4\Sigma^-$. While we are not presently able to dismiss the possibility that some pseudo-spin–rotation interaction of electronic origin is (partly) responsible in HCl^+ for the deviation between the experimental and theoretical values of γ_v(true), in the case of OD we are forced to suspect the validity of Eq. (39).

In order to bring this problem to rest, we recommend an ab initio calculation of γ_v^{Π}. In addition, we recommend that the analogous $A\,^2\Sigma^+$–$X\,^2\Pi$ band systems of HF^+ and DF^+ be reexamined so that the theoretically and experimentally derived values of γ_v(true) can be compared. Already there has been an excellent analysis of the HF^+ band system by Gerwutz, Lew ,and Flainek (*25*) using the Johns-Lepart program (*26*) and this comparison would be most desirable since $HF^+(DF^+)$ is at the same time isoelectronic to OH(OD) and a homologue of $HCl^+(DCl^+)$.

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