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The electric dipole moment function of HF

J F Ogilvie

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

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Abstract. Based on recently published experimental data with improved accuracy, a new determination of the electric dipole moment function of the molecule HF in the X ${}^{1}\Sigma^{+}$ electronic state has been made. The new results are presented in the forms both of a power series, valid within the range of internuclear separation $0.69 < R/10^{-10}$ m < 1.45, and of a rational function at least qualitatively valid at all larger internuclear distances. The rotational dependence of expectation values of the electric dipole moment operator is also investigated.

1. Introduction

Recently new experimental information about the expectation values and matrix elements of the dipole moment operator M(x) of the hydrogen fluoride molecule in the $X^{1}\Sigma^{+}$ electronic state has become available. A value of the matrix element $\langle 0 | M(x) | 1 \rangle$ has been determined from the measurement of the linestrengths in the fundamental vibration-rotational band (Pine et al 1985) under greatly improved conditions of spectral resolution compared with previous measurements. The expectation values $\langle 0 | M(x) | 0 \rangle$ and $\langle 1 | M(x) | 1 \rangle$ have been measured with great precision by means of the Stark effect on a molecular beam on radiofrequency transitions (Bass et al 1987). The analysis of these data requires information about the potential energy function of HF, and new results have been obtained (Coxon and Ogilvie 1987) from an analysis similar in scope and accuracy to the earlier one for HCl (Coxon and Ogilvie 1982). Therefore it seems timely to revise the former analysis of the dipole moment function of HF (Ogilvie et al 1980) to take account of the new data, especially as the function proposed by Bass et al (1987) failed to make use of all the available experimental data. In another recent publication, Huffaker et al (1987) used none of the specified new experimental data, but based all their calculations on the rough but extensive data of Sileo and Cool (1976) consisting of ratios of intensities of emission spectra, normalised with the old value of $\langle 0 | M(x) | 0 \rangle$ from Muenter and Klemperer (1970). In the present work we demonstrate that our new dipole moment function fits satisfactorily all the new experimental data in addition to the data of Sileo and Cool. We also investigate quantitatively the rotational dependence of the electric dipole moment.

2. Treatment of data

We first assume the radial dependence of the electric dipole moment of the HF molecule

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to be of the form of the power series

$$M(x) = \sum_{j=0}^{\infty} M_j x^j \qquad x \equiv (R - R_e) / R_e$$
(1)

including as many terms as are appropriate to fit the available experimental data; in the reduced internuclear displacement variable x, R is the instantaneous internuclear separation and R_e is the equilibrium distance. Because the experimental intensity data of the absorption spectra are available up to the fourth overtone $(v' = 5 \leftarrow v'' = 0)$, the upper limit of the sum is first taken to be five, although the use of emission spectra enables later a further coefficient M_6 to be determined. With this choice of dipole moment function, the experimental expectation value $|\langle 0|M(x)|0\rangle|$ and matrix elements $|\langle 0|M(x)|v'\rangle|$, $1 \le v' \le 5$, can be written as a series of linear equations

$$\langle 0 | M(x) | v' \rangle = \sum_{j=0}^{5} M_{j} \langle 0 | x^{j} | v' \rangle \qquad 0 \le v' \le 5.$$

$$\tag{2}$$

Because this set of equations requires the signs of the expectation value and matrix elements in addition to the magnitudes defined directly from experimental intensities and Stark shifts of spectral transitions, further information is required to enable a unique solution of the values of the coefficients M_i . We assume M_0 to be positive; then the Herman-Wallis factors, specifically the coefficients $C_0^{v'}$ therein, permit the relative determination of the other signs, as previously explained in detail (Ogilvie and Tipping 1983). The experimental intensities of HF on which the matrix elements are based are relatively few (Pugh and Rao 1976, Smith et al 1985). Only single values of $|\langle 0|M(x)|v' \rangle|$, $3 \le v' \le 5$, are known (Spellicy *et al* 1972, Rimpel 1974). For the first overtone, one value has been obtained (Atwood et al 1972) from measurements under conditions of broadening by means of large pressures, whereas the only other value has been obtained (Meredith 1972) from the measurements of the strengths of individual lines in the band. The published experimental data from the latter work and from the other overtone intensities have been re-analysed. According to a standard statistical test, specifically the value of the F statistic (Ogilvie and Abu-Elgheit 1981), the accuracy of the measurements of these line intensities warrants fitting of the squares of the vibration-rotational matrix elements to only a linear function of the running number m = [J'(J'+1) - J''(J''+1)]/2; thus only the magnitude of the pure vibrational transition moment $|\langle 0|M(x)|v'\rangle|$ and the value of the first coefficient $C_0^{v'}$ in the Herman-Wallis factor can be significantly determined. Although a few values of the matrix element $|\langle 0|M(x)|1\rangle|$ have been published, the precision of the recent value (Pine et al 1985) is greatly superior to that of previous values. These values of the matrix elements and of the expectation values (Bass et al 1987) for v = 0 and 1 are presented in table 1.

The matrix elements $\langle 0|x^{j}|v'\rangle$ of the coordinate x to various powers have been calculated directly from the general analytic expressions already published (Bouanich *et al* 1986). For substitution therein for the purpose of evaluation for HF, the values of the potential energy coefficients a_{i} in the Dunham (1932) function

$$V(x) = a_0 x^2 \left(1 + \sum_{j=1}^{n} a_j x^j \right)$$
(3)

and the expansion parameter $\gamma = 2B_e/\omega_e$ are required; the values (Coxon and Ogilvie 1987) used are given in table 1. The coefficients M_j , together with their standard errors estimated by a Monte Carlo method (Ogilvie 1984), thereby determined from the set

Table 1. Basic data for the analysis.

$\gamma/10^{-2} = 1.012628 \pm 1.9 \times 10^{-6}$	$/10^{-30} \text{ C m}$	
$a_{1} = -2.246 \ 4874 \pm 1.4 \times 10^{-4}$ $a_{2} = 3.444 \ 0485 \pm 7.6 \times 10^{-4}$ $a_{3} = -4.441 \ 091 \pm 2.7 \times 10^{-3}$ $a_{4} = 5.144 \ 466 \pm 7.6 \times 10^{-3}$ $a_{5} = -5.721 \ 46 \pm 0.035$ $a_{6} = 5.9093 \pm 0.11$ $a_{7} = -4.3686 \pm 0.14$ $B_{e}/m^{-1} = 2095.429 \ 44 \pm 0.0082$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	

^a Bass et al (1987).

^b Pine et al (1985).

^c Recalculated from data of Meredith (1972).

^d Recalculated from data of Spellicy et al (1972).

^e Recalculated from data of Rimpel (1974).

of linear equations are listed in table 2 as set B. The Herman-Wallis coefficients $C_0^{\nu'}$ and $D_0^{\nu'}$ calculated therefrom (Tipping and Ogilvie 1982) are compared with the experimental values in table 3.

Table 2. Dipole moment coefficients for HF.

	$M_j/10^{-30} \mathrm{C} \mathrm{m}$		
j	set A	set B	e _{,i}
0	$6.013\ 438 \pm 0.000\ 040$	$6.013\ 592 \pm 0.000\ 058$	1
1	4.6970 ± 0.0015	4.7006 ± 0.0016	2.2189 ± 0.00035
2	-0.0948 ± 0.0067	-0.1274 ± 0.0108	1.2826 ± 0.0011
3	-2.819 ± 0.030	-2.896 ± 0.037	0.5019 ± 0.0050
4	-1.589 ± 0.095	-1.683 ± 0.100	0.9326 ± 0.0016
5	-3.15 ± 0.53	-3.26 ± 0.57	0.9912 ± 0.09
6	(8.10 ± 8)	(8.30 ± 8)	-0.3694 ± 1.4
7	· · ·	. ,	1.5 ± 0.5

Table 3. Herman-Wallis coefficients.

	Experiment	Set A	Set B
$\overline{C_0^0}$		0	0
$D_0^{0}/10^{-4}$		1.6000 ± 0.0005	1.6000 ± 0.0005
$C_0^1/10^{-2}$	-5.2103 ± 0.0194	-5.3316 ± 0.0013	-5.3317 ± 0.0013
$D_0^1/10^{-4}$	4.91 ± 0.61	8.63 ± 0.0075	8.60 ± 0.0098
$C_0^2 / 10^{-2}$	-1.98 ± 0.09	-2.34 ± 0.0009	-2.34 ± 0.0056
$D_0^2/10^{-4}$		2.31 ± 0.03	2.38 ± 0.03
$C_0^3/10^{-2}$	-1.74 ± 0.29	-1.72 ± 0.013	-1.69 ± 0.015
$D_0^3/10^{-4}$		-0.45 ± 0.10	-0.48 ± 0.10
$C_0^4/10^{-2}$	-1.30 ± 0.095	-2.15 ± 0.029	-2.12 ± 0.029
$D_0^4/10^{-4}$		1.47 ± 0.62	1.50 ± 0.67
$C_0^5/10^{-2}$	-6.1 ± 1.1	-3.03 ± 0.05	-3.00 ± 0.05
$D_0^5/10^{-4}$		5.1 ± 1.5	5.2 ± 1.2

Because the relative precision (Bass *et al* 1987) of the expectation value $|\langle 1|M(x)|1\rangle|$ is much greater than that (Meredith 1972) of the matrix element $|\langle 0|M(x)|2\rangle|$, an alternative determination of the dipole moment coefficients M_j was made by replacing in the set of linear equations (1) the equation for $\langle 0|M(x)|2\rangle$ by that for $\langle 1|M(x)|1\rangle$. The corresponding coefficients in table 2 are denoted set A, and the related Herman-Wallis coefficients are also listed in table 3.

In general, the use of these infrared intensities limits the value of the subscript k of the last coefficient M_k that can be determined to the maximum value Δv of the change of vibrational quantum numbers of bands for which intensity data are available. The maximum value of v' and therefore Δv for the absorption intensities is five, but in the emission spectra (Sileo and Cool 1976) the relative intensities of some bands in the sequence $\Delta v = 6$ have been measured. By comparing the calculated ratios of the squares of matrix elements with the experimental ratios of Sileo and Cool (1976), we have roughly determined a value of M_6 , also given in table 2 within both sets A and B.

In order to avoid the divergence of the power series expansion M(x) so as to permit some predictive power of properties dependent on the dipole moment function beyond the range $0.69 < R/10^{-10}$ m < 1.45 corresponding to the classical turning points for the vibrational state v = 6, a rational function has been formed as in the earlier work (Ogilvie *et al* 1980). Because the six coefficients M_j , $1 \le j \le 6$, enable the calculation (Kirschner *et al* 1977) of the corresponding six coefficients e_j , $1 \le j \le 6$, only one further calculated value of the dipole moment at large separation R is required in order to form the Padé function

$$M(x) = M_0 (1+x)^3 \left(1 + \sum_{j=1}^7 e_j x^j \right)^{-1}.$$
 (4)

The value $M = 6.67 \times 10^{-35}$ C m at $R = 1.6 \times 10^{-9}$ m, from the *ab initio* computations of Ogilvie *et al* (1980), was thus used to determine e_7 with the values of M_j , $1 \le j \le 6$, taken from set A. These results for the coefficients e_j are given in table 2.

In this work the International System of units is used exclusively. The values of the fundamental physical constants used (Cohen and Taylor 1986) and the atomic masses (Wapstra and Audi 1985) are the latest available. All stated uncertainties beside the values of derived quantities correspond to one standard error, propagated ultimately from stated uncertainties in experimental measurements.

3. Discussion

Because the estimated standard errors of the coefficients M_j in set A are slightly smaller than those in set B, therefore set A is preferred. By means of this set, the matrix element $\langle 0 | M(x) | 2 \rangle$ is calculated to be $(-0.041 \ 257 \pm 4.1 \times 10^{-5}) \times 10^{-30}$ C m, in reasonable agreement with the experimental value given in table 1. Analogously, the expectation value $\langle 1 | M(x) | 1 \rangle$ is calculated by means of set B to be $(6.249 \ 446 \pm 0.000 \ 16) \times 10^{-30}$ C m, in much worse agreement in terms of the standard deviation given (Bass *et al* 1987) for this expectation value. For these reasons also, set A of the coefficients M_j is considered superior to set B.

The values of the coefficients M_j , $0 \le j \le 4$, of either set A or set B appear to differ significantly from those determined by Bass *et al* (1987), although the latter authors failed to indicate any measure of the accuracy of their results. The reason for this

difference is unclear. The analytic expressions (Bouanich et al 1986) for the matrix elements of x^{j} used in the present calculations were determined separately by two distinctly different methods, either through the analytic wavefunctions or by means of Rayleigh-Schrödinger perturbation theory with a basis set of a harmonic oscillator; both methods gave identical analytic results (Bouanich et al 1986). The wavefunctions that Bass et al (1987) used were the same as those used in the former method to derive the matrix elements of x^{i} (Ogilvie and Tipping 1987). Furthermore one can easily prove formally that the 'wavefunction approximation' used by Bass et al (1987) is absolutely equivalent to the use of the analytic matrix elements of x^{i} . The contention of these authors that the results for the coefficients M_i are strongly dependent on the number of equations used in their calculation is inaccurate, at least in the case of HCl (Ogilvie and Tipping 1985) for which there is found, on the whole, a remarkable resilience of these coefficients over the years and despite the different degrees of the polynomial M(x), the different methods of calculation and the improving quality and extent of experimental data. Bass et al (1987) also alluded to a purported problem related to numerical ill conditioning of the direct method with the matrix elements $\langle 0|x_i|v' \rangle$; however the fact that the determinant of the matrix (implied by the set of linear equations in (1)) to be inverted is of the order of 10^{-9} is irrelevant both because the range of powers of ten carried by the computer processors of the data far exceeds nine and because the number of significant digits carried through the calculation also far exceeds nine. In any case, because the wavefunction method is formally equivalent to the matrix technique in this work, there almost certainly exists in the former method a numerical limitation corresponding to the determinant of the matrix. It can also be noted that the use of the values (Bass et al 1987) of the coefficients M_i with the accurate values of the matrix elements of x^{i} in the present work fails to reproduce satisfactorily the experimental values of the matrix elements $\langle 0 | M(x) | v' \rangle$ and of even their own expectation values $\langle 0 | M(x) | 0 \rangle$ and $\langle 1 | M(x) | 1 \rangle$ (Bass *et al* 1987). The differences far exceed what result from the set of slightly different values of the potential energy coefficients a_i and the extended expressions of the wavefunctions inherent in the matrix elements of the present work.

In the course of the use of the experimental data from the HF emission spectrum (Sileo and Cool 1976), it was discovered that the dipole moment function, set A or B, fitted the measured ratios of the squares of the matrix elements $\langle v'' | M(x) | v' \rangle$ better (by half, in terms of the sum of the squares of the residuals, experimental ratios minus calculated ratios, with values of v'' and v' < 8 for which the explicit analytic expressions (Bouanich *et al* 1986) for the matrix elements of x^j are available) than the dipole moment function of Sileo and Cool (1976) for which no indication of the accuracy was provided. The values of their coefficients M_j for HF are very different from those in table 2. Because their dipole moment functions of HF and DF differ from each other, reflecting the relatively inaccurate experimental data, far more than would be expected to result from the partial failure of the Born-Oppenheimer approximation, it must be concluded that these functions (Sileo and Cool 1976) have little physical significance.

Within the stated range of validity, the electric dipole moment function in power series form of HF derived above (specifically set A) should be the most accurate available that is based primarily upon experimental data, and according to which the accuracy of theoretical dipole moments can be judged. Beyond this range, the function in the form of the Padé approximant should offer qualitative accuracy, perhaps semiquantitative accuracy, because the Padé function mimics the series function closely

within the defined range and then tends to approach the limits of the united atom $({}^{20}\text{Ne}\,{}^{1}\text{S}_{0})$ and the separate atoms $({}^{1}\text{H}\,{}^{2}\text{S}_{1/2} + {}^{19}\text{F}\,{}^{2}\text{P})$ according to the correct behaviour, namely proportional to R^3 as $R \to 0$ and proportional to R^{-4} as $R \to \infty$ (Ogilvie et al 1980). However, two caveats about the use of this Padé function require to be stated. First, because of a root of the polynomial in the denominator, the Padé function has a pole near $R \sim 3.5 \times 10^{-11}$ m; this flaw is of no practical importance because this internuclear separation is much smaller than those distances accessible in molecular states of discrete energy. In numerical integrations involving this Padé function, one must simply take care that the limit of integration at small R is at least $R \sim 6 \times 10^{-11}$ m. However the accuracy of the Padé function at large values of R is of much greater interest. The value of the coefficient e_7 has been defined through the use of a computed dipole moment (Ogilvie et al 1980) at $R = 1.6 \times 10^{-9}$ m; the accuracy of this computational method has been previously discussed in detail (Ogilvie et al 1980). We note here that the approximate value of M_6 newly derived from the emission spectra makes the dipole moment more positive in the region $R \sim 1.4 \times 10^{-10}$ m, and therefore in worse agreement with the computed function (Ogilvie et al 1980). One may then expect that the computed value of dipole moment at $R = 1.6 \times 10^{-9}$ m might similarly be an underestimate. Nevertheless the present Padé function represents the best available estimate of the electric dipole moment function beyond the range defined directly from experiment.

One envisages that a dipole moment function of the form of a power series based on the alternative reduced displacement variable $z \equiv 2(R - R_e)/(R + R_e)$ (Ogilvie 1981)

$$M(z) = \sum P_j z^j \tag{5}$$

lacks this problem of a possible pole in the region of positive R. Obviously, the lack of a denominator precludes the possibility of such a divergence, while the finite range of z, $-2 \le z \le 2$, corresponding to the entire range of molecular existence, $0 \le R < \infty$, makes possible the application of boundary conditions (Ogilvie 1988a) in order to generate additional coefficients P_j beyond those determined from experiment, so as to bestow the proper limiting behaviours specified above. Unfortunately, just as the Padé function is debased by its pole resulting from the circumstantial values of the coefficients e_j , so the function M(z) expanded to about the fifteenth order of the polynomial suffers adventitiously from two finite (in fact shallow) but unphysical minima, in the regions $R/10^{-10}$ m ~ 0.16 and 5.0. For this reason, the Padé function is more useful than the polynomial because the region of interest can extend to $R \sim 5 \times 10^{-10}$ m at which the Padé function maintains physically acceptable behaviour.

Although the rotational dependence of the expectation values of the electric dipole moment may not have been experimentally detected for diatomic molecules, in polyatomic molecules this effect has been observed (Dyke and Muenter 1973, Freund *et al* 1974, Tanaka and Tanaka 1978). It is worthwhile to examine the extent of such an effect for HF. To proceed, we express the expectation value of the dipole moment operator for a particular vibration-rotational state as a double summation (Schlier 1959) in terms of the functionals $(v + \frac{1}{2})$ and J(J+1) of the vibrational and rotational quantum numbers v and J respectively:

$$\langle vJ | M(x) | vJ \rangle = \sum_{j=0}^{N} M_j \langle vJ | x^j | vJ \rangle$$

= $\sum_{k=0}^{N} \sum_{l=0}^{N} \mu_{kl} (v + \frac{1}{2})^k [J(J+1)]^l.$ (6)

The rotational dependence is given to a good approximation by only a few terms, from the difference:

$$\langle vJ | M(x) | vJ \rangle - \langle v, 0 | M(x) | v, 0 \rangle$$

= $\mu_{0,1}J(J+1) + \mu_{0,2}[J+(J+1)]^2 + \mu_{1,1}(v+\frac{1}{2})J(J+1)$
+ $\mu_{2,1}(v+\frac{1}{2})^2J(J+1).$ (7)

Then these dipole moment coefficients μ_{kl} can be expressed in terms of the potential energy coefficients a_j and the other dipole moment coefficients M_j . Alternatively, in order to gain the advantage of the useful properties of the variable z mentioned above, one can express these coefficients μ_{kl} in terms of the potential energy coefficients c_j (Ogilvie 1981) and the related dipole moment coefficients P_j defined in equation (5). In that case the expressions for μ_{kl} are exactly equivalent to those for Z_{kl} used for other radial functions (Ogilvie 1987, 1988b) of diatomic molecules with the coefficients P_j replacing those denoted h_j . The pertinent expressions for μ_{kl} , including some terms not previously published in their equivalent form as Z_{kl} , required in the present context are given in table 4. The relation for the conversion of the potential energy coefficients (Ogilvie 1981) is

$$c_{j} = 2^{-j}(j+1) + \sum_{k=0}^{j-1} 2^{-k}(j+1)! a_{j-k} / [k!(j+1-k)!]$$
(8)

whereas the relations for the conversion of the dipole moment coefficients (Ogilvie 1988a) are

$$P_0 = M_0$$

$$P_j = \sum_{k=1}^{j} (j-1)! 2^{k-j} M_k / [(j-k)!(k-1)!]$$

$$j > 0.$$
(9)

With these relations and the numerical values of the coefficients for potential energy from table 1 and for the dipole moment (set A) from table 2, we obtain the desired rotational dependence of vibration-rotational expectation values of the electric dipole moment operator as in equation (7) specifically applicable to HF:

$$(\langle vJ | M(x) | vJ \rangle - \langle v, 0 | M(x) | v, 0 \rangle) / 10^{-34} \text{ C m}$$

= (4.814±0.0015)J(J+1)+1.726×10^{-4}[J(J+1)]²
+0.1104(v+¹/₂)J(J+1)-0.0239(v+¹/₂)²J(J+1). (10)

Even for J = 1 and v = 0, we see that the change in expectation value is $\sim 10^{-33}$ C m, about forty times as large as the nominal inaccuracy of the measurements on the

Table 4. Expressions for the coefficients μ_{kl} .

$$\begin{split} \mu_{0,1} &= \gamma^2 P_1 + \gamma^4 [P_1(\frac{97}{32}c_1 - \frac{37}{2}c_1c_2 + \frac{205}{16}c_1c_3 - \frac{191}{32}c_2 + \frac{35}{4}c_3 - \frac{45}{8}c_4 + \frac{105}{16}c_1^2 - \frac{333}{16}c_1^2c_2 + \frac{327}{32}c_1^3 \\ &\quad + \frac{63}{8}c_1^4 + \frac{23}{4}c_2^2 + \frac{163}{128}) + P_2(-\frac{35}{16}c_1 + \frac{69}{8}c_1c_2 + 4c_2 - \frac{15}{4}c_3 - \frac{81}{16}c_1^2 - \frac{21}{4}c_1^3 - \frac{1}{2}) + P_3(\frac{27}{8}c_1 - \frac{23}{4}c_2 + \frac{35}{16}c_1^2 + \frac{23}{2}c_2 + \frac{35}{2}c_1 - \frac{23}{4}c_2 + \frac{35}{2}c_1 + \frac{29}{8}c_1 - 2) + \frac{15}{8}P_5] \\ \mu_{0,2} &= \gamma^4(P_2 - 2P_1 - \frac{3}{2}c_1P_1) \\ \mu_{1,1} &= \gamma^3 [P_1(\frac{27}{4}c_1^2 + \frac{9}{2}c_1 - 6c_2 + \frac{3}{4}) - \frac{9}{2}c_1P_2 + 3P_3] \\ \mu_{2,1} &= \gamma^4 [P_1(\frac{33}{8}c_1 - 66c_1c_2 + \frac{285}{4}c_1c_3 - \frac{15}{8}c_2 + 15c_3 - \frac{45}{2}c_4 + \frac{63}{4}c_1^2 - \frac{621}{4}c_1^2c_2 + \frac{423}{4}c_1^3 + \frac{135}{2}c_1^4 + 39c_2^2 + \frac{3}{32}) \\ &\quad + P_2(-\frac{3}{4}c_1 + \frac{117}{2}c_1c_2 - 15c_3 - \frac{81}{4}c_1^2 - 45c_1^3) + P_3(\frac{27}{2}c_1 - \frac{39}{2}c_2 + \frac{135}{4}c_1^2 + \frac{3}{8}) - \frac{39}{2}c_1P_4 + \frac{15}{2}P_5] \end{split}$$

molecular beams made by Bass *et al* (1987). Therefore with larger values of *J*, the effect becomes even more significant, in fact increasing quadratically with *J*, and thus an effective method of determining some parameters M_j or P_j in the dipole moment function. Taken with the numerical values of the coefficients in equation (10), the expressions for μ_{kl} in table 4 make plain that the parameter most sensitive to such a rotational dependence is $P_1 = M_1$. The optical selection rule $\Delta J = \pm 1$ limits the sensitivity of measurements of the Stark effect on vibration-rotational transitions to such rotational effects, but for the most accurate work this phenomenon should be taken into account.

In some cases (for instance, Kaiser 1970 and Muenter 1972), the electric dipole moment of diatomic molecules has been supposed to have no rotational dependence. This supposition is artificial and unphysical for the following reason: the dipole moment is always assumed to have a functional dependence on internuclear distance, according to the Born-Oppenheimer procedure, such that the expectation value, the observable value, of the dipole moment represents an average or effective value over the range of the internuclear distance in a particular vibrational state (essentially between the classical turning points of the vibrational amplitude). However it is always accepted that the effective potential energy function, and thus the range of oscillation in a particular vibrational state, depends on the quantum number J for angular momentum in the centrifugal term $R_e^2 B_e J(J+1)/R^2$. In order to take into account to some extent this centrifugal effect, the molecular Hamiltonian used by Kaiser (1970) and Muenter (1972) in the analysis of their data contains a term proportional to $\gamma^2 P_1 = \gamma^2 M_1$, the leading term in $\mu_{0,1}$, but the proportionality factor in their work seems to differ from that given by Charifi et al (1978). It may be that the purported residual isotopic effect in the values of $P_0 = M_0$ deduced for ¹H³⁵Cl and ²H³⁵Cl, attributed by Kaiser (1970) to a failure of the Born-Oppenheimer approximation, in fact results from the inadequate treatment of the rotational dependence of the electric dipole moment.

4. Conclusions

A new function for the electric dipole moment of HF has been determined from published experimental data, and is in satisfactory agreement with other data not used in its derivation. The rotational dependence of the electric dipole moment should be taken into effect in accurate work, and such measurements of the rotational dependence would provide an alternative method to the use of infrared intensities for the determination of coefficients in the dipole moment function, principally M_1 or P_1 .

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