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Vibration-rotational Einstein coefficients for HF/DF and HCl/DCI

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The experimentally based dipole-moment functions have been combined with the best Rydberg-Klein-Rees potentials to calculate the vibration-rotational Einstein coefficients for HF, DF, HCl, and DCI. Calculations were done for the $\Delta v = 1, 2$, and 3 transitions for $v \leq 6$ for HF and $v \leq 7$ for HCl, which are in the range of the internuclear distance, r , for which the dipole moment functions are valid. The calculations were done for $J \leq 25$ for each v level. The higher v levels of HF were investigated using a Padé extrapolation of the experimental dipole function and a recently published *ab initio* function. Our $\Delta v = 1$ Einstein coefficients for HF agree closely with those from an earlier experimentally based dipole function and with the new *ab initio* results for $v \leq 6$. Our results for HCl, however, represent a significant improvement over the Einstein coefficients currently in the literature. The isotopic ratio of Einstein coefficients for the $\Delta v = 1$ transitions, $A_{\text{DX}}/A_{\text{HX}}$, were not changed significantly. Also, the changes in the ratios of the Einstein coefficients, $A_{v,v-1}/A_{1,0}$, were less significant than the changes in the absolute magnitudes. The effect of high rotational energy on the Einstein coefficients for HF(v, J) is discussed.

I. INTRODUCTION

In 1985 Oba *et al.*¹ published vibration-rotational Einstein coefficients for HF, DF, HCl, and DCI for a wide range of v and J , which were calculated using Rydberg-Klein-Rees (RKR) potential functions and the best dipole moment functions available at that time. The dipole function of Sileo and Cool² seemed to provide reliable results for HF up to $v = 9$. The situation for HCl was less satisfactory in that significant differences in the Einstein coefficients existed between the experimentally based dipole functions of Smith³ and Herbelin and Emanuel⁴ and the *ab initio* calculations of Werner and Rosmus.⁵ New more accurate dipole-moment functions of HF (Ref. 6) and HCl (Ref. 7) are now available. These are based on experimental data with careful definition of the range of internuclear distances, r , for which the functions are reliable. Improved potential energy curves for HF (Ref. 8) and HCl (Ref. 9) have also been reported, but the dipole moment function has a greater influence on the Einstein coefficients than does the potential.^{1,3} In this work we have used Ogilvie's dipole moment functions for HF and HCl with the best potentials to calculate the Einstein coefficients for HF, DF, HCl, and DCI; the new results provide some improvement over the Einstein coefficients of Oba *et al.*, especially for HCl and DCI. Our objective was to provide reliable Einstein coefficients for the v and J levels corresponding to the range of Ogilvie's functions, which are $v \leq 6$ for HF and $v \leq 7$ for HCl. After our calculations were completed, Zemke *et al.*¹⁰ reported Einstein coefficients for HF from a new *ab initio* dipole function. The goal of their work was to examine all v levels up to the dissociation limit. We took the opportunity to compare their new theoretical re-

sults with those based upon Ogilvie's dipole function. The results closely agree which provides confidence in the HF Einstein coefficients for levels $v \leq 6$. (In this paper, v and J refer to the vibrational and rotational quantum numbers of the upper state. The " and ' are used to distinguish the lower and upper states when needed.)

The historical interest of the K.S.U. laboratory in Einstein coefficients has been for the conversion of emission spectra into vibration-rotational distributions¹¹⁻¹⁵ of HF, DF, HCl, and DCI. We have observed high rotational states of HF ($8 \leq J \leq 25$) from several reactions,¹³⁻¹⁵ and also from $v \rightarrow R$ energy transfer following collisions of HF(v) with CO and CO₂.¹⁶ Conventional formulations of the Einstein coefficients failed to give self-consistent results for the high rotational state populations derived from the P and R -branch line intensities of HF(v).¹¹ Therefore, we developed a numerical integration method using potentials and wave functions that explicitly included rotation.^{1,11} This method gives reliable Einstein coefficients for the P and R -branch lines, provided that the dipole function is accurate for the necessary range of r . Since Zemke *et al.*¹⁰ have provided an *ab initio* dipole function for a wide range of r , we have used this function and the Padé function of Ogilvie^{6,7} to examine the unusual dependence of the Einstein coefficients on rotational energy for levels $1 \leq v \leq 14$ and $0 \leq J \leq 25$ of HF.

II. METHODOLOGY

The computational method has been described previously in detail.¹ The Einstein coefficients for spontaneous emission, $A_{v',v''}(m)$, where $m = J'' + 1$ for an R -branch and $-J''$ for a P -branch line, are given by Eq. (1),

$$A_{v',v''}(m) = \frac{64\pi^4}{3h} \nu^3 \frac{|m|}{2J' + 1} |R_{v',v''}(m)|^2. \quad (1)$$

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The transition matrix elements, $R_{v',-v''}(m)$, are calculated by numerical integration of Eq. (2),

$$R_{v',-v''}(m) = \int_0^\infty \Psi_{v'',J''}(r) \mu(r) \Psi_{v',J'}(r) r^2 dr, \quad (2)$$

for selected values of J , such that $m = \pm 1, \pm 6, \pm 11, \pm 21$, and ± 26 , for each v and interpolated smoothly to give results for all $m = 0-26$ as given below,

$$R_{v',-v''}(m) = a_0 + a_1 m + a_2 m^2 + a_3 m^3. \quad (3)$$

In Eq. (2) $\mu(r)$ is the dipole moment function, which was expressed as a truncated Taylor series about the equilibrium internuclear separation,

$$\mu(r) = \sum_i M_i (r - r_e)^i. \quad (4)$$

The wave function is determined by solving the radial Schrödinger equation numerically,

$$\frac{d^2}{dr^2} \Psi(r) + [V(r) - E] \Psi(r) = 0, \quad (5)$$

where $V(r)$ is the sum of the internuclear potential energy for stretching the diatomic bond and the centrifugal potential.

Table I gives the M_i coefficients for the dipole moment expansion for HF and HCl from Refs. 6 and 7. These were calculated using recently measured experimental intensities of both fundamental and overtone spectra and older data in the literature, critically combined; the functions are accurate over the range of r up to $v = 6(9)$ for HF(DF) and $v = 7(10)$ for HCl(DCl). As dipole functions have no dependence on nuclear mass, they apply equally well to the deuterated molecules. Details of the calculation and evaluation of the reliability appear in Refs. 6 and 7. Ogilvie's functions include a thorough analysis of the propagation of errors from the original experimental measurements. We have used these error limits to estimate the probable uncertainty of the calculated Einstein coefficients. This was done by duplicating the calculations with the maximum positive and negative deviations given for the terms in Table I. These calculated Einstein coefficients are included in the tables of rotationless Einstein coefficients as the expected deviation from the recommended values. Inspection of Table I shows that the uncertainty is larger for the dipole function of HF than for HCl and, indeed, the deviations in the Einstein coefficients for HCl are smaller than for HF. These dipole functions must be used cautiously for levels beyond the specified range of r . In particular, the expansion given by Eq. (4) with the coefficients in Table I does not approach the correct limit as r becomes larger for either HF or HCl. We extended the calculations to $v = 7$ and 8 for HF, but the results indicate serious deviation for $v = 8$, by comparison to Refs. 2 and 10. For HCl, DCl, and DF the calculations were done up to $v = 8$ and the results appear reasonable. Ogilvie^{6,7} also specified Padé functions for HF and HCl that matched the experimentally defined parts of the dipole function. These Padé functions provide a better basis for extrapolation to higher v levels and extension to the $v \geq 8$ levels for HF is considered in the Discussion.

TABLE I. Expansion coefficients for the dipole moment function.^a

| i | HF ^b | HCl ^c |
|-----|---------------------------|---------------------------|
| 0 | 1.802 784 \pm 0.000 076 | 1.093 004 \pm 0.000 012 |
| 1 | 1.535 9 \pm 0.000 5 | 0.969 830 \pm 0.000 098 |
| 2 | -0.033 8 \pm 0.000 2 | 0.012 70 \pm 0.003 3 |
| 3 | -1.097 \pm 0.012 | -0.739 75 \pm 0.006 3 |
| 4 | -0.674 2 \pm 0.040 | -0.348 12 \pm 0.001 0 |
| 5 | -1.46 \pm 0.25 | -0.104 6 \pm 0.017 |
| 6 | 4.09 \pm 4 | -0.101 9 \pm 0.017 |
| 7 | ... | 0.064 3 \pm 0.038 |

^a Units in Debye Å⁻¹.

^b Taken from Ref. 6; this expansion is valid for the range of r corresponding to $0 < v \leq 6$ of HF.

^c Taken from Ref. 7; this expansion is valid for the range of r corresponding to $0 < v \leq 7$ of HCl.

The RKR potentials for HF (Ref. 8) and HCl (Ref. 9) were taken from the recent literature. The improvements in the RKR potentials are relatively minor for $v \leq 8$. In fact, changes in the potential for the same dipole moment function altered the Einstein coefficients insignificantly ($< 1\%$). Also, the RKR potential calculated using HF or DF and HCl or DCl spectral parameters' could be interchangeably used. These spectral parameters were used to calculate the term values and transition wave numbers.

III. RESULTS AND DISCUSSION

A. General trends

The hypothetical rotationless vibrational Einstein coefficients for transition from $v', J' = 0$ to $v'', J'' = 0$, are presented in Tables II (HCl and DCl) and III (HF and DF) for the $\Delta v = 1, 2$, and 3 transitions. These coefficients are defined according to Eq. (6),

$$A_{v'-v''} = \frac{64\pi^4}{3h} \nu^3 \times \left| \int \Psi_{v'',J''=0}(r) \mu(r) \Psi_{v',J'=0}(r) r^2 dr \right|^2. \quad (6)$$

These vibrational Einstein coefficients, which were calculated with accurate RKR potentials and the most recent experimentally based dipole moment function, supersede the values presented in Ref. 1. For comparison, the results from the dipole functions of Smith for HCl and of Sileo and Cool for HF are reproduced in Tables II and III. For all four molecules considered here, the magnitudes of the new $\Delta v = 1$ Einstein coefficients are somewhat higher than those given by Oba *et al.*¹ The change in the relative ratios of the $\Delta v = 1$ Einstein coefficients, i.e., A_v/A_1 for $v \leq 4$ is within 1% for HF and within 1.6% for HCl. This ratio is the most important for interpretation of infrared chemiluminescence measurements to obtain relative populations of vibrational levels. The isotopic ratio of $\Delta v = 1$ Einstein coefficients, $A_{\text{DCl}}/A_{\text{HCl}}$, is nearly the same for both experimental dipole functions; the change in this ratio is $< 1\%$ for DF/HF and $< 3\%$ for DCl/HCl. Thus, the new Einstein coefficients do not lead to significant changes in the relative vibrational distributions from chemiluminescence intensity measurements. The

TABLE II. Vibrational Einstein coefficients (s^{-1}) for HCl and DCl, $\Delta v = 1, 2$, and 3 .^{a,b}

| v' | HCl | | | DCl | | |
|------|-----------------------------|----------------------------|------------------------------|------------------------------|-----------------------------|--------------------------------|
| | $\Delta v = 1$ | $\Delta v = 2$ | $\Delta v = 3$ | $\Delta v = 1$ | $\Delta v = 2$ | $\Delta v = 3$ |
| 1 | 40.21 ± 0.01 (38.2) | ... | ... | 11.038 ± 0.003 (10.5) | ... | ... |
| 2 | 70.02 ± 0.02 (66.6) | 3.74 ± 0.02 (3.4) | ... | 20.096 ± 0.006 (19.0) | 0.705 ± 0.003 (0.66) | ... |
| 3 | 89.67 ± 0.02 (85.7) | 11.45 ± 0.04 (10.4) | 0.064 ± 0.003 (0.048) | 27.185 ± 0.007 (25.6) | 2.139 ± 0.008 (2.05) | 0.0083 ± 0.0004 (0.005) |
| 4 | 99.66 ± 0.05 (96.3) | 23.42 ± 0.03 (21.0) | 0.280 ± 0.010 (0.250) | 32.359 ± 0.008 (30.4) | 4.36 ± 0.10 (4.21) | 0.036 ± 0.001 (0.022) |
| 5 | 100.75 ± 0.12 (99.2) | 39.8 ± 0.03 (34.8) | 0.764 ± 0.025 (0.767) | 35.699 ± 0.009 (33.3) | 7.38 ± 0.11 (7.22) | 0.095 ± 0.004 (0.064) |
| 6 | 93.85 ± 0.17 (95.5) | 60.87 ± 0.10 (51.5) | 1.658 ± 0.047 (1.821) | 37.262 ± 0.026 (34.5) | 11.21 ± 0.03 (11.1) | 0.200 ± 0.007 (0.146) |
| 7 | 80.29 ± 0.26 (86.3) | 86.65 ± 0.25 (70.4) | 3.186 ± 0.072 (3.677) | 37.177 ± 0.049 (34.2) | 15.94 ± 0.05 (15.9) | 0.372 ± 0.012 (0.290) |
| 8 | 61.88 ± 0.33 (72.9) | 117.0 ± 0.4 (90.6) | 5.652 ± 0.092 (6.634) | 35.597 ± 0.076 (32.3) | 21.54 ± 0.08 (21.6) | 0.637 ± 0.018 (0.520) |

^a The values in parentheses are based on Smith's dipole function, Ref. 3.

^b For HCl, $v = 8$ is outside the range of validity for the dipole function, but the $A_{u,v}$ values still are useful for converting emission intensities to relative populations.

A_{DX}/A_{HX} ratios of coefficients for the $\Delta v = 2$ and 3 transitions, have changed more significantly for DF/HF compared to the $\Delta v = 1$ ratio; the change is 20% for $A_{2,0}$ and 75% for $A_{3,0}$. The corresponding changes for DCl/HCl are 3.5% and 20%. The new Einstein coefficients are discussed in more detail in the following sections with comparison to other results in the literature.

B. Einstein coefficients for HCl and DCl

The HCl and DCl Einstein coefficients calculated from the experimental dipole moment functions of Smith³ and Herbelin and Emanuel⁴ were significantly different.¹ The results in Table II from Ogilvie's dipole moment function closely agree with the Einstein coefficients from Smith's di-

TABLE III. Vibrational Einstein coefficients (s^{-1}) for HF and DF, $\Delta v = 1, 2$, and 3 .^{a,b}

| v' | HF | | | DF | | |
|----------------|-----------------------------|-----------------------------|----------------------------|-----------------------------|----------------------------|-------------------------------|
| | $\Delta v = 1$ | $\Delta v = 2$ | $\Delta v = 3$ | $\Delta v = 1$ | $\Delta v = 2$ | $\Delta v = 3$ |
| 1 | 194.5 ± 0.1 (190.0) | ... | ... | 55.96 ± 0.03 (54.5) | ... | ... |
| 2 | 333.9 ± 0.6 (324.8) | 23.54 ± 0.04 (23.8) | ... | 100.7 ± 0.1 (98.1) | 4.844 ± 0.002 (4.1) | ... |
| 3 | 422.8 ± 2.2 (411.0) | 65.89 ± 0.72 (66.8) | 1.52 ± 0.03 (1.62) | 134.7 ± 0.2 (131.5) | 13.74 ± 0.04 (12.2) | 0.2324 ± 0.0008 (0.14) |
| 4 | 467.7 ± 7.6 (454.6) | 123.5 ± 4.0 (124.8) | 5.53 ± 0.35 (6.15) | 158.8 ± 0.7 (155.1) | 26.38 ± 0.28 (23.9) | 0.859 ± 0.021 (0.54) |
| 5 | 477.2 ± 20.0 (461.6) | 191.2 ± 14.1 (194.4) | 13.1 ± 1.7 (14.49) | 174.2 ± 1.8 (169.7) | 41.9 ± 1.1 (39.2) | 2.04 ± 0.12 (1.34) |
| 6 | 459.8 ± 43.4 (437.7) | 262.3 ± 37.5 (272.6) | 25.4 ± 5.5 (27.11) | 181.6 ± 4.1 (175.8) | 59.7 ± 2.9 (57.8) | 3.82 ± 0.40 (2.65) |
| 7 ^c | 425.4 ± 82.6 (388.3) | 328.0 ± 83.5 (357.4) | 44.9 ± 14.2 (44.04) | 182.3 ± 8.0 (174.3) | 79.4 ± 6.8 (79.5) | 6.48 ± 1.07 (4.59) |
| 8 | ... | ... | ... | 177.9 ± 14.4 (166.0) | 99.4 ± 13.9 (104.0) | 10.32 ± 2.43 (7.29) |

^a The values in parentheses are based on the dipole function of Sileo and Cool (Ref. 2).

^b The $\Delta v = 1$, Einstein coefficients from the *ab initio* dipole function of HF (Ref. 10) are 203.5, 348.4, 439.9, 484.1, 487.2, 455.9, and 397.7 for $v = 1-7$.

^c The large error limits reflect the extrapolation of the dipole function outside the specified range of validity. However, comparison to the *ab initio* Einstein coefficient shows that this value (and the $A_{u,v}$ of Table VI) will be useful for converting emission intensities to relative populations.

pole function. Thus, the situation for HCl is clarified and the calculated results from Ogilvie's function are to be recommended. In fact, the uncertainty associated with the entries in Table II are extremely small. The Einstein coefficients for the $\Delta v = 1$ transitions changed relative to Smith's results, by $+5\%$ at $v = 1$ to -7% at $v = 7$ for HCl, whereas the coefficients for DCI increased by 5% – 10% for $v = 1$ – 8 . The Einstein coefficients from the Werner and Rosmus⁵ *ab initio* dipole function are significantly lower than those calculated from Ogilvie's function, even though the ratios (A_v/A_1) are in close agreement. The $\Delta v = 2$ Einstein coefficients for HCl increased by $>9\%$, whereas the change for DCI was from $+6.1\%$ to -0.5% for $v = 1$ – 8 , relative to Smith's results. The $A_{v,v-1}/A_{v,v-2}$ ratios from both Smith's and Ogilvie's dipole functions are in close agreement with the experimental intensity ratios up to $v = 5$.¹ The Einstein coefficient becomes larger for the $\Delta v = 2$ transition than for the $\Delta v = 1$ for $v > 7$ for HCl. This trend also is observed for HF. (See Sec. III D and Ref. 10.) For DCI this change has not occurred for $v = 9$, but presumably it occurs at higher v levels.

Tables IV and V give the expansion coefficients for transition matrix elements for HCl and DCI for $\Delta v = 1, 2$, and 3 and $J < 25$. By means of these coefficients and Eqs. (1) and (3), the user can generate the Einstein coefficients for $\Delta v = 1, 2$, and 3 for $v < 8$ and $J < 25$. The results for DCI should be accurate for all these v and J levels. According to the specified range of the dipole for HCl, the results are valid up to $v = 7$ only; however, the extrapolation to $v = 8$ should

TABLE V. Transition matrix elements expansion coefficients for DCI.^a

| v' | $a(0)$ | $a(1)$ | $a(2)$ | $a(3)$ |
|----------------|------------|------------|------------|------------|
| $\Delta v = 1$ | | | | |
| 1 | 6.204e-20 | -5.738e-22 | 1.423e-24 | -1.955e-26 |
| 2 | 8.706e-20 | -8.284e-22 | 1.494e-24 | -2.781e-26 |
| 3 | 1.054e-19 | -1.035e-21 | 1.224e-24 | -3.436e-26 |
| 4 | 1.198e-19 | -1.219e-21 | 5.561e-25 | -3.962e-26 |
| 5 | 1.312e-19 | -1.389e-21 | -4.832e-25 | -4.462e-26 |
| 6 | 1.398e-19 | -1.552e-21 | -1.887e-24 | -4.869e-26 |
| 7 | 1.459e-19 | -1.707e-21 | -3.833e-24 | -5.315e-26 |
| 8 | 1.495e-19 | -1.858e-21 | -6.377e-24 | -5.781e-26 |
| $\Delta v = 2$ | | | | |
| 2 | -5.650e-21 | 1.021e-23 | -5.096e-25 | 1.236e-27 |
| 3 | -1.024e-20 | 1.925e-23 | -9.278e-25 | 3.282e-27 |
| 4 | -1.520e-20 | 3.078e-23 | -1.410e-24 | 4.595e-27 |
| 5 | -2.060e-20 | 4.447e-23 | -1.997e-24 | 7.214e-27 |
| 6 | -2.652e-20 | 6.085e-23 | -2.637e-24 | 1.092e-26 |
| 7 | -3.301e-20 | 8.135e-23 | -3.368e-24 | 1.485e-26 |
| 8 | -4.013e-20 | 1.058e-22 | -4.240e-24 | 2.075e-26 |
| $\Delta v = 3$ | | | | |
| 3 | 3.396e-22 | 1.355e-24 | 4.737e-26 | 3.253e-28 |
| 4 | 7.320e-22 | 2.869e-24 | 8.482e-26 | 8.364e-28 |
| 5 | 1.251e-21 | 4.950e-24 | 1.465e-25 | 1.119e-27 |
| 6 | 1.887e-21 | 7.695e-24 | 2.452e-25 | 1.288e-27 |
| 7 | 2.691e-21 | 1.060e-23 | 3.392e-25 | 2.093e-27 |
| 8 | 3.678e-21 | 1.464e-23 | 4.949e-25 | 1.835e-27 |

^aSee footnote a in Table IV.

TABLE IV. Transition matrix-element expansion coefficients for HCl.^a

| v' | $a(0)$ | $a(1)$ | $a(2)$ | $a(3)$ |
|----------------|------------|------------|------------|------------|
| $\Delta v = 1$ | | | | |
| 1 | 7.308e-20 | -9.525e-22 | 2.656e-24 | -6.398e-26 |
| 2 | 1.019e-19 | -1.386e-21 | 2.038e-24 | -9.039e-26 |
| 3 | 1.221e-19 | -1.744e-21 | -4.386e-26 | -1.126e-25 |
| 4 | 1.365e-19 | -2.069e-21 | -3.667e-24 | -1.320e-25 |
| 5 | 1.459e-19 | -2.375e-21 | -9.183e-24 | -1.476e-25 |
| 6 | 1.503e-19 | -2.671e-21 | -1.716e-23 | -1.582e-25 |
| 7 | 1.488e-19 | -2.958e-21 | -2.837e-23 | -1.635e-25 |
| 8 | 1.406e-19 | -3.235e-21 | -4.417e-23 | -1.574e-25 |
| $\Delta v = 2$ | | | | |
| 2 | -8.086e-21 | 2.083e-23 | -1.484e-24 | 6.107e-27 |
| 3 | -1.494e-20 | 4.168e-23 | -2.879e-24 | 1.425e-26 |
| 4 | -2.265e-20 | 6.894e-23 | -4.517e-24 | 2.604e-26 |
| 5 | -3.135e-20 | 1.045e-22 | -6.549e-24 | 4.360e-26 |
| 6 | -4.124e-20 | 1.507e-22 | -9.028e-24 | 6.924e-26 |
| 7 | -5.253e-20 | 2.115e-22 | -1.198e-23 | 1.046e-25 |
| 8 | -6.536e-20 | 2.907e-22 | -1.551e-23 | 1.548e-25 |
| $\Delta v = 3$ | | | | |
| 3 | 5.934e-22 | 3.291e-24 | 1.483e-24 | 1.464e-27 |
| 4 | 1.308e-21 | 7.368e-24 | 3.281e-25 | 3.002e-27 |
| 5 | 2.292e-21 | 1.283e-23 | 6.090e-25 | 4.599e-27 |
| 6 | 3.587e-21 | 1.975e-23 | 1.071e-24 | 6.100e-27 |
| 7 | 5.293e-21 | 2.786e-23 | 1.736e-24 | 7.454e-27 |
| 8 | 7.527e-21 | 3.747e-23 | 2.720e-24 | 7.265e-27 |

^aThe coefficients in Tables IV–VII are in c.g.s. units. These coefficients can be used in Eqs. (1) and (3), with v in cm^{-1} and h in erg s to yield Einstein coefficients in s^{-1} for $J < 25$. Exponential notation is used and $1.000e-19$ is to be read as 1.000×10^{-19} .

be satisfactory. Figure 1 shows the J dependence of several $\Delta v = 1$ transitions for HCl. This plot and others (not shown) for DCI are similar to those presented by Oba *et al.*¹ For all the v levels considered in this paper, the Einstein coefficients for the $\Delta v = 1$ transitions gradually decrease with increasing J for P -branch transitions, whereas the R -branch transitions show a broad maximum followed by a decrease with increasing J . This decline for the R -branch transitions becomes more pronounced as v increases and for very high v levels the situation resembles that of mid- v levels of HF, *vide infra*.

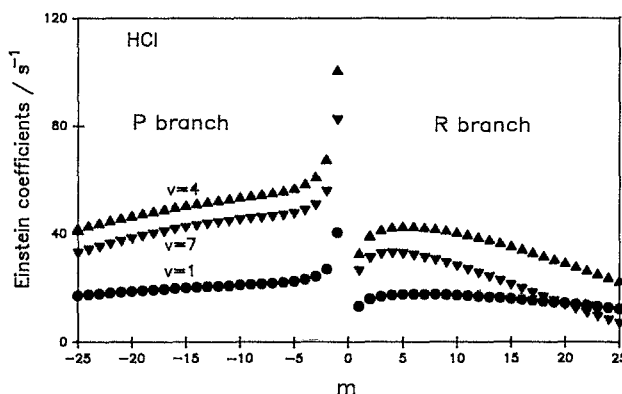


FIG. 1. The $\Delta v = 1$ Einstein coefficients (s^{-1}) for HCl as a function of m . ($m = J' + 1$ for the R -branch and $-J'$ for the P -branch.) circles, $v = 1$; triangles, $v = 4$; inverted triangles, $v = 7$.

C. Einstein coefficients for HF and DF

The increase in $A_{v,v-1}$ for HF relative to Sileo and Cool's values was only 2.3%–4.8% for $v = 1$ –6; the difference increases to 8.7% for $v = 7$, which requires extrapolation of the dipole function. Comparison (see footnote in Table III) can be made with the calculations of Zemke *et al.*,¹⁰ which also gave values slightly larger than the Einstein coefficients of Sileo and Cool.² The differences between our Einstein coefficients and those of Zemke *et al.*'s decrease from 4.4% to 0.9% for $v = 1$ –6. Thus, the Einstein coefficients calculated using Ogilvie's dipole function agree slightly better with the *ab initio* calculated results than the results from the dipole function of Sileo and Cool up to $v = 6$. Of course, all the differences are quite small, and we conclude that the $\Delta v = 1$ Einstein coefficients for HF are well established for $v < 7$. Inspection of Table III shows that the uncertainty in the HF and DF Einstein coefficients increases with v and is 8%–9% for $v = 6$ of HF and $v = 9$ of DF (not shown). For levels above $v = 7$ of HF, the Padé form of dipole function given by Ogilvie or the *ab initio* dipole function of Zemke *et al.* should be employed, *vide infra*.

The $A_{v,v-2}$ values from Ogilvie's dipole function are $\sim 1.5\%$ smaller than those from the function of Sileo and Cool for $v = 2$ –4; the differences increase for higher v and become 3.9% and 8.9% for $v = 6$ and 7. The $A_{v,v-3}$ values from Ogilvie's function are $\sim 6\%$ smaller than the values of Sileo and Cool for $v = 3$ –7. In fact, the two sets of Einstein coefficients are within the uncertainty associated with the dipole function of Ogilvie. The $\Delta v = 2$ Einstein coefficients

from the *ab initio* dipole are slightly larger than those from Sileo and Cool, whereas the $\Delta v = 3$ results lie between the two sets of numbers given in Table II.

The $\Delta v = 1$ Einstein coefficients for DF from Ogilvie's dipole moment functions are 2.4% larger than those from Sileo and Cool for $v = 1$ –6; the difference increases to 4.4% and 6.7% for $v = 7$ and 8. The $\Delta v = 2$ coefficients are $\sim 10\%$ larger, but the difference decreases with v ; for the $8 \rightarrow 6$ transition our Einstein coefficient actually is 5% smaller than the value from Sileo and Cool. In contrast with HF, the $\Delta v = 3$ coefficients for DF from the two dipole functions differ significantly, with the values from Ogilvie's function being 40%–30% larger for $v = 3$ –8. Although these large differences are surprising relative to the HF results, they illustrate the sensitivity of the Einstein coefficients to the dipole function.

Tables VI and VII give the expansion coefficients for the matrix elements for HF ($v \leq 7$) and DF ($v \leq 8$) and the *P* and *R*-branch Einstein coefficients for $\Delta v = 1$ transitions have been plotted in Fig. 2 for HF ($v = 1, 4$, and 7). The results resemble the plots for HCl, except that the decline in the transition probability of the *R*-branch with increasing J is more marked. In fact, the $v = 7$ Einstein coefficients for the *R*-branch transitions with $J > 20$ are nearly zero. The experimental ratios of the *R* and *P*-branch line intensities are compared to the ratios of Einstein coefficients in Fig. 3, as a test of the trends shown in Fig. 2. The spectra were obtained in a flow reactor from the $F + HBr$ ($v = 1$ and 2) [Ref. 17(a)] and $H + F + Ar$ ($v = 3$ and 4) [Ref. 17(b)] reactions. The agreement between the experimental and calculated ratios is

TABLE VI. Transition matrix-element expansion coefficients for HF.^{a,b}

| v' | $a(0)$ | $a(1)$ | $a(2)$ | $a(3)$ |
|----------------|------------|------------|------------|------------|
| $\Delta v = 1$ | | | | |
| 1 | 1.000e-19 | -2.681e-21 | 6.899e-24 | -2.181e-25 |
| 2 | 1.401e-19 | -3.876e-21 | 6.250e-24 | -2.809e-25 |
| 3 | 1.688e-19 | -4.848e-21 | 3.393e-24 | -3.263e-25 |
| 4 | 1.902e-19 | -5.700e-21 | -5.726e-25 | -3.822e-25 |
| 5 | 2.061e-19 | -6.490e-21 | -4.619e-24 | -4.462e-25 |
| 6 | 2.174e-19 | -7.242e-21 | -6.495e-24 | -5.201e-25 |
| 7 | 2.250e-19 | -7.961e-21 | -2.106e-24 | -6.486e-25 |
| $\Delta v = 2$ | | | | |
| 2 | -1.268e-20 | 1.528e-22 | -1.015e-24 | 1.868e-26 |
| 3 | -2.268e-20 | 2.720e-22 | -2.073e-24 | 4.271e-26 |
| 4 | -3.328e-20 | 4.004e-22 | -2.854e-24 | 7.586e-26 |
| 5 | -4.447e-20 | 5.437e-22 | -2.994e-24 | 1.170e-25 |
| 6 | -5.610e-20 | 7.058e-22 | -1.489e-24 | 1.671e-25 |
| 7 | -6.780e-20 | 8.944e-22 | 3.524e-24 | 2.118e-25 |
| $\Delta v = 3$ | | | | |
| 3 | 1.817e-21 | -1.579e-23 | -1.886e-26 | 2.079e-27 |
| 4 | 3.690e-21 | -2.921e-23 | 2.008e-25 | 2.061e-27 |
| 5 | 6.065e-21 | -4.365e-23 | 8.536e-25 | -1.105e-27 |
| 6 | 9.043e-21 | -5.926e-23 | 2.392e-24 | -1.286e-26 |
| 7 | 1.288e-20 | -7.687e-23 | 5.138e-24 | -4.150e-26 |

^a The HF dipole moment function is valid only in the range $0.69 < r/\text{\AA} < 1.45$. Thus, for $1 < v < 4$ the expansion is valid for all J ($J < 25$). For $v = 5$ and 6, the function is valid up to $J \approx 20$ and 10, respectively. The $v = 7$ is outside the range of validity.

^b See footnote a in Table IV.

TABLE VII. Transition matrix elements expansion coefficients for DF.^a

| v' | $a(0)$ | $a(1)$ | $a(2)$ | $a(3)$ |
|----------------|------------|------------|------------|------------|
| $\Delta v = 1$ | | | | |
| 1 | 8.524e-20 | -1.644e-21 | 3.730e-24 | 7.126e-26 |
| 2 | 1.200e-19 | -2.365e-21 | 4.191e-24 | 8.931e-26 |
| 3 | 1.456e-19 | -2.942e-21 | 3.973e-24 | 1.070e-25 |
| 4 | 1.660e-19 | -3.442e-21 | 3.108e-24 | -1.232e-25 |
| 5 | 1.826e-19 | -3.907e-21 | 1.631e-24 | -1.272e-25 |
| 6 | 1.961e-19 | -4.341e-21 | 5.933e-26 | -1.367e-25 |
| 7 | 2.070e-19 | -4.749e-21 | -1.460e-24 | -1.576e-25 |
| 8 | 2.153e-19 | -5.147e-21 | -2.890e-24 | -1.741e-25 |
| $\Delta v = 2$ | | | | |
| 2 | -9.075e-21 | 7.965e-23 | -3.337e-25 | 3.948e-27 |
| 3 | -1.603e-20 | 1.400e-22 | -6.795e-25 | 8.684e-27 |
| 4 | -2.331e-20 | 2.035e-22 | -9.430e-25 | 1.324e-26 |
| 5 | -3.088e-20 | 2.708e-22 | -1.390e-24 | 2.062e-26 |
| 6 | -3.874e-20 | 3.422e-22 | -1.758e-24 | 3.128e-26 |
| 7 | -4.698e-20 | 4.206e-22 | -1.789e-24 | 4.211e-26 |
| 8 | -5.540e-20 | 5.073e-22 | -1.514e-24 | 5.439e-26 |
| $\Delta v = 3$ | | | | |
| 3 | 1.106e-21 | -7.262e-24 | 4.520e-28 | 4.172e-28 |
| 4 | 2.234e-21 | -1.361e-23 | -3.804e-26 | 7.640e-28 |
| 5 | 3.618e-21 | -2.107e-23 | -2.217e-26 | 1.608e-27 |
| 6 | 5.203e-21 | -2.866e-23 | 2.001e-25 | 1.366e-27 |
| 7 | 7.110e-21 | -3.649e-23 | 4.873e-25 | -1.590e-28 |
| 8 | 1.485e-20 | -4.583e-23 | 9.342e-25 | -2.030e-27 |

^a See footnote a in Table IV.

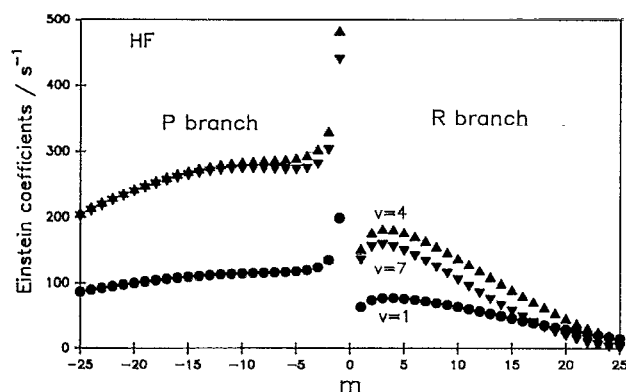


FIG. 2. The $\Delta v = 1$ Einstein coefficients (s^{-1}) for HF as a function of m . circles, $v' = 1$; triangles, $v' = 4$; inverted triangles, $v' = 7$.

good up to the highest levels observed, which was $J = 18$ – 20 . The recombination reaction, $H + F + Ar$, gives a broad distribution of HF (v, J) and P -branch emission from high J levels can be observed for $v \leq 5$. According to the calculations, the intensities of the R -branch lines for $v = 4$ and 5 , $10 < J < 20$ would have been within the experimental noise level relative to the observed intensities of the P -branch lines. Indeed, the R -branch lines could not be clearly observed. Thus, the enormous decline in the intensities of the R -branch lines for $J > 10$ is experimentally verified for $v = 1$ – 5 .

D. HF Einstein coefficients for $v \geq 8$

As shown in Fig. 2, the $\Delta v = 1$ Einstein coefficients for the R -branch of HF $\Delta v = 1$ transitions approach zero for $v > 7$ at certain J , which is a consequence of the transition matrix elements [Eq. (2)] crossing zero.¹ In order to investigate this trend, as well as to consider the HF (v) Einstein coefficients for $v > 7$, we did calculations using the *ab initio* dipole function¹⁰ and the Padé form of the dipole function, given by Eq. (7),

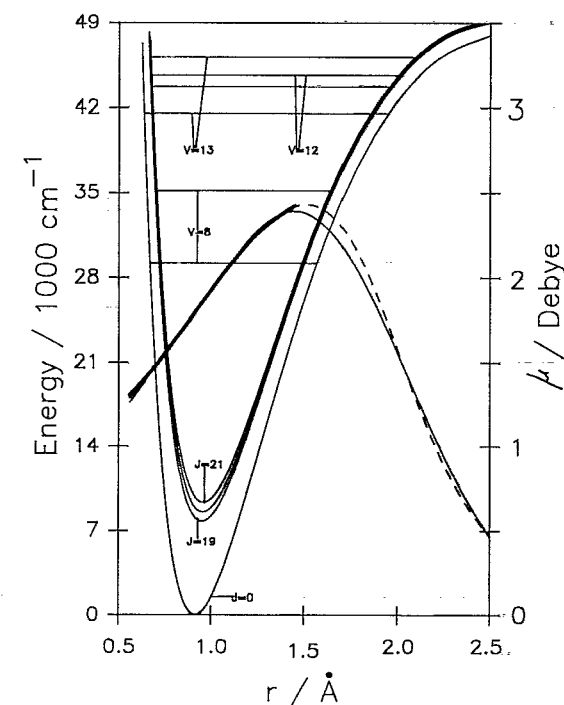


FIG. 4. The RKR potential ($J = 0$) for HF and the potentials for $J = 19$, 20 , and 21 with the dipole moment function; thick line, Ogilvie power series; dashed line, Ogilvie Padé form; continuous line, Zemke *et al.*'s *ab initio* calculation. The $v = 8$ and 13 energy levels have been drawn on $J = 0$ and 20 potentials. The $v = 12$ energy level has been drawn on $J = 19$ and 21 potentials. For $J' = 20$, observe the difference in the range of integration for a P -branch ($J'' = 21$) and an R -branch ($J'' = 19$) Einstein coefficients.

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

As shown in Fig. 4, the two functions have similar shape, but the maximum in the Padé function occurs at somewhat larger r . Perhaps fortuitously, given the experimental uncertainty, the function of Sileo and Cool agrees with the *ab initio* dipole function up to the region of the maximum. The Padé function exactly matches the experimentally based function (Table I) in the range $0.69 < r/\text{\AA} < 1.45$, and it has qualitatively the correct form in the extrapolated region; both functions are equally experimentally based within the specified range of r given in Table I. The *ab initio* dipole function probably should be preferred for large r . We have used both functions to explore the rotational dependence of the $A_{v,J}$ values for HF (high v). The calculated rotationless Einstein coefficients are presented in Table VIII, for $v' = 7$ – 14 . The calculated coefficients from the Padé function match the trend from the *ab initio* function. The maximum value for the $\Delta v = 1$ and 2 transitions occur at $v = 5$ and 12 , respectively, for both functions, but the minimum in the $\Delta v = 1$ transition is at $v = 13$ for the *ab initio* function and at $v = 14$ for the Padé function. The $\Delta v = 1$ Einstein coefficients calculated with the Padé function are within 7% of the *ab initio* values up to $v' = 7$ but for higher v the Padé function gave significantly greater Einstein coefficients.

The $\Delta v = 1$ $A_{v,J}$ values for $v' = 8$, 11 , and 14 are plotted in Fig. 5 for $J' \leq 25$. Both functions gave similar results even

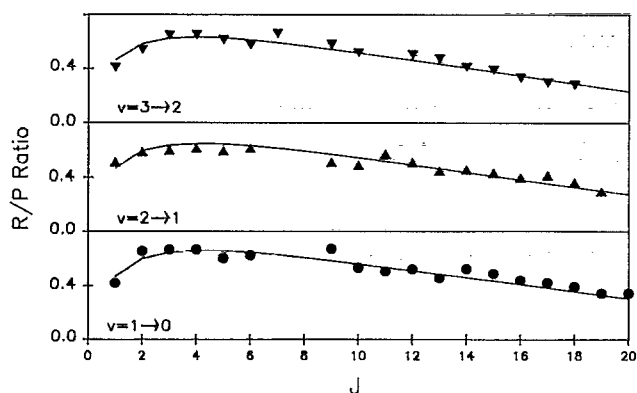


FIG. 3. Experimental ratio of intensities of R and P -branch lines (symbols) compared with the corresponding ratio of Einstein coefficients (lines) for HF(v). The $v' = 1$ and 2 data are from $F + HBr$ experiments and $v' = 3$ data are from $H + F + Ar$ reaction.

TABLE VIII. HF($8 \leq v \leq 14$) Einstein coefficients (s^{-1}) for the $\Delta v = 1$ ($\Delta v = 2$) transitions.

| v' | <i>ab initio</i> ^a | Padé form ^b |
|------|-------------------------------|------------------------|
| 8 | 320.9(501.3) | 354.6(429.1) |
| 9 | 235.2(599.8) | 269.8(531.9) |
| 10 | 150.8(685.2) | 182.0(628.1) |
| 11 | 78.1(745.4) | 102.0(704.9) |
| 12 | 26.4(763.8) | 40.5(746.7) |
| 13 | 1.82(724.6) | 6.0(738.4) |
| 14 | 5.19(617.7) | 2.1(668.6) |

^aDipole function from Ref. 10.^bPadé representation of dipole function from Ref. 6.

though the minimum $A_{v,J}$ value occurs at different J for each function. In fact for sufficiently high v levels, the minimum moves to the P -branch, as shown for $v = 14$. Both the minimum $A_{v,J}$ and the minimum value for the rotationless Einstein coefficients (see Table VIII) appear to depend on the location of the maximum in the transition dipole function (see Fig. 4). However, the extreme dependence of the $A_{v,J}$ values on m is general and exists for the Sileo and Cool function, the Padé function and the *ab initio* function. The situation for $v = 14$ is especially noteworthy in that the R -branch intensities are predicted to be much larger than the P -branch intensities, a reversal of the trend for lower v levels.

The minimum $A_{v,J}$ occurs around the m value at which the transition dipole matrix elements $R_{v,m}$ change sign. Figure 6 shows the matrix elements as a function of m for var-

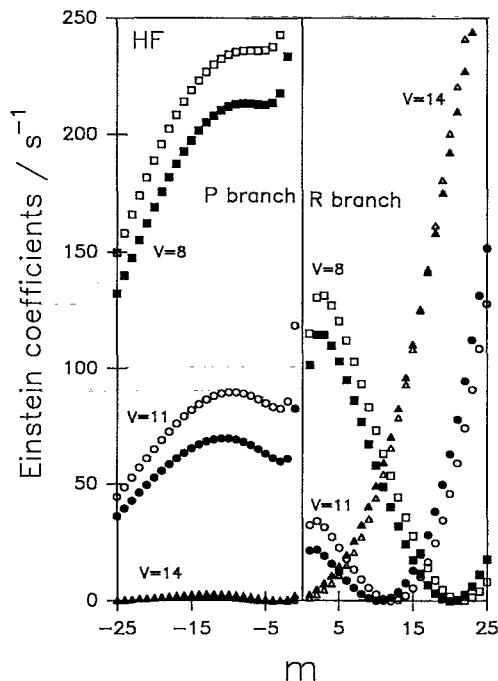


FIG. 5. The $\Delta v = 1$ Einstein coefficients for $v = 8$ (squares), 11 (circles), and 14 (triangles) for HF calculated using Ogilvie's Padé form [Eq. (7) and Ref. 6] dipole function (open symbols) and *ab initio* (Ref. 10) dipole function (closed symbols) as a function of m .

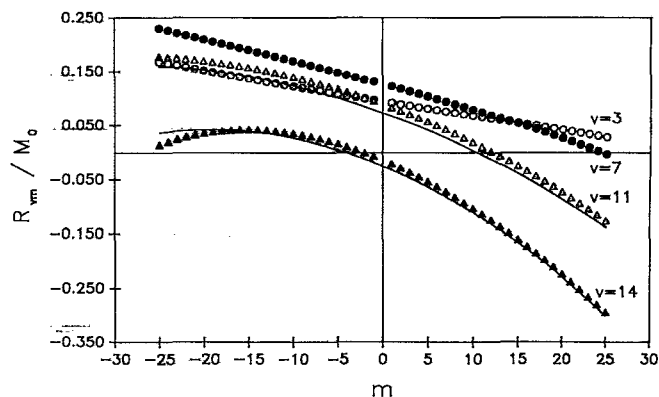


FIG. 6. Transition matrix elements, $R_{v,m}/M_0$, calculated using the Padé form (symbols) of dipole moment function as a function of m for $v = 3$ (open circles), 7 (closed circles), 11 (open triangles), and 14 (closed triangles) for HF. The calculated results from the *ab initio* function are shown for $v = 11$ and 14 by the solid curves.

ious v levels, calculated with the Padé and the *ab initio* functions. For $v' = 3$, the transition matrix elements are positive for $m \leq 25$ and the absolute value smoothly decreases as m increases. For $v' = 7$, the matrix element crosses zero near $m = 24$, which is the minimum $A_{v,J}$ in the R -branch. For $v' = 11$, the zero crossing occurs at $m = 12$ for the Padé function and the Einstein coefficients reach a minimum and start to increase, because they depend on the square of the transition matrix elements. For $v' = 14$, the zero crossing occurs at $m = -2$; hence, the irregular intensity variation occurs in the P -branch. For the *ab initio* function (solid lines in Fig. 6), the zero crossing occurs at $m = 10$ and -4 for $v' = 11$ and 14, respectively. This difference, relative to the Padé function, is a consequence of the location of the maximum for the dipole function. The same trends, as shown in Fig. 6 exist for the $\Delta v = 1$ coefficients of HCl, but these effects occur at only very high v levels because the integral samples the maximum in the dipole function only for vibrational levels that have large r .

The strong dependence of the matrix elements upon whether the lower state wave function is for a P -branch ($\Delta J = -1$) or an R -branch ($\Delta J = +1$) transition has been discussed by Zemke *et al.*¹⁰ and Oba *et al.*¹ The former extracted empirical Herman-Wallis factors^{18,19} and based their discussion on these factors. There is no need to repeat their conclusions here, but as they point out, only for low v levels (where the dipole function is almost linear) do the separated Herman-Wallis factors give useful results. In our approach the Herman-Wallis factors are not separated from the $A_{v,J}$ values. However, our calculated $A_{v,J}$ values are exactly the same (for the same dipole function) as Zemke *et al.* and we agree with their conclusions. We did a few additional exploratory calculations to understand the dependence of the matrix elements on the dipole function and the influence of rotation. A linear dipole function (with positive slope) gave matrix elements that can be described in terms of straightforward Herman-Wallis factors, i.e., the $A_{v,J}$ values increase with m for the P -branch lines and decrease with m for the R -branch lines for all v levels.¹⁹ This difference for

the P and R -branches arises from the integration over the lower state wave functions for $J - 1$ and $J + 1$. Figure 4 includes the potential curves for $J = 0, 19, 20$, and 21 . The potential for $J = 19$ is outside and the one for $J = 21$ is inside the $J = 20$ potential. Thus, the ranges for the two integrals are different and the degree of overlap of the two wave functions decides the Einstein coefficients. A linear dipole function (with a positive slope) favors the P -branch over R -branch.¹⁹ The question becomes, what is the effect of the actual dipole function on these integrals?

Examination of Fig. 4 suggests a possible explanation for the trends in $A_{v,J}$ values. The turning points for the $v = 13$ level in the $J = 0$ potential are approximately at $r = 0.64$ and 1.93 Å and in the $J = 20$ potential they are at 0.67 and 2.11 Å. The dipole function is nearly symmetric over the range of the $J = 0$ potential and the value of the integral is nearly 0 ($A_{13,12} = 1.82$ s⁻¹). For the Padé function the maximum position is shifted slightly towards higher r and the minimum $A_{v,v-1}$ is at $v = 14$ rather than $v = 13$. For the integration range of the $J = 20$ potential, both dipole functions sample a wider-range of r and the values of the integrals are not zero. Both functions have a negative slope for $r > 1.5$ Å. The Einstein coefficient for the R branch of $v = 13, J = 20$ (155.5 and 149.3 s⁻¹ for *ab initio* and Padé form) is much larger than that of the P -branch for $J = 20$ (9.8 and 7.9 s⁻¹, respectively). Clearly the numerical value of the integral is extremely sensitive to the shift of the wave functions in the $J'' = J' - 1$ and $J'' = J' + 1$ potentials of the v'' state. For $v = 8$, the dipole function is asymmetric but the function has a positive slope over most of the range of r . In the $J = 0$ potential, the dipole function reaches the maximum and just starts turning down, whereas for the $J = 20$ potential it extends into the region of negative slope. The rotationless Einstein coefficient for $v = 8$ is 320.9(354.6) s⁻¹ and for $J = 20$, the values for the R and P -branches are 0.02(1.9) and 162.1(181.5) s⁻¹ for the *ab initio* (Padé) function.

The shape of the dipole function in the range of integration (in r) clearly affects the relative intensities of P and R -branch lines. Herman and Wallis¹⁸ have, in fact, proved this dependence analytically even though they considered only linear dipole functions. They showed that the sign of the M_1/M_0 ratio of the dipole moment function [Eq. (4)] determines whether the P or the R -branch will be stronger in the spectrum. If M_1/M_0 is positive the P -branch is stronger and if it is negative the R -branch is stronger. Conversely, the spectral intensities can be used to determine the sign of this ratio, but this procedure is formally practicable for only the fundamental band. As is evident from Fig. 4, the dipole functions are not linear over the full range of r and either the P or the R -branch will be stronger, depending on the shape of the dipole function in the integration range.

IV. CONCLUSIONS

The vibrational-rotational Einstein coefficients for HF, DF, HCl, and DCI have been calculated for the range of v and J levels for which the experimentally based transition

dipole functions are reliable. The uncertainty in the Einstein coefficients arising from the uncertainty associated with the dipole functions have been estimated. We believe that the $\Delta v = 1, 2$, and 3 Einstein coefficients are reliable up to $v = 6, J = 25$ for HF and up to $v = 8, J = 25$ for DF, HCl, and DCI. The Einstein coefficients for higher v levels of HF were calculated using the Padé extrapolation of the experimental dipole function and a recent *ab initio* dipole function.¹⁰ The rotational dependence of the HF Einstein coefficients for the high v' levels have been analyzed using these two functions. The difference in the potentials for $J'' = J' + 1$ and $J' - 1$ for the HF molecule interacts with the shape of the dipole function to give $A_{v,J}$ values that have strong and nonmonotonic dependence on J . The same phenomena can be expected for DF and HCl for sufficiently high vibrational levels.

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