Vibration-Rotation Interaction in the HF Molecule

II. Evaluation of the r-Centroids and the Higher Terms of the Electric Dipole Moment for Some Vibration-Rotation Bands

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The wave functions, calculated by the method described in a preceding article, are used for the evaluation of the r-centroids relative to the $1-0$ transition of the $X\,^1\Sigma^+$ state. By means of experimental line intensities, it is shown that in the expansion of the electric dipole moment, the quadratic and higher terms are not negligible.

Introduction

The intensity of an emitted line is given by the formula [1]

$$I_J = C\,P_1\,\nu_J^4\,R^2$$

where C is a constant, P_1 the population in the initial state, ν_J the frequency of the transition from the superior $(v', J+1)$ to the inferior (v'', J) levels, expressed in wave numbers, R the matrix element for the transition.

By definition, we have

$$R = \int_0^\infty \Psi_1\,M\,\Psi_2\,\mathrm{d}r$$

where Ψ_1 and Ψ_2 are the wave functions of the initial and final states, respectively, r the nuclear separation, M the electric dipole moment.

We can expand M with respect [2] to r

$$M = M_0 + M_1\,r + M_2\,r^2 + M_3\,r^3 + M_4\,r^4 + \dots\ .$$

For an accurate calculation of the infrared band intensities, it is necessary to consider the fact that M does not a priori vary linearly with r. It follows that

$$\begin{aligned} R = {} & M_0 \int_0^\infty \Psi_1\,\Psi_2\,\mathrm{d}r + M_1 \int_0^\infty \Psi_1\,r\,\Psi_2\,\mathrm{d}r \\ & + M_2 \int_0^\infty \Psi_1\,r^2\,\Psi_2\,\mathrm{d}r + M_3 \int_0^\infty \Psi_1\,r^3\,\Psi_2\,\mathrm{d}r \\ & + M_4 \int_0^\infty \Psi_1\,r^4\,\Psi_2\,\mathrm{d}r + \dots\ . \end{aligned}$$

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If $\overline{r^k_{1-2}}$ represents the k-th order r-centroid of the transition, we have

$$R = \sum_k M_k\,\overline{r^k_{1-2}}$$

with

$$\overline{r^k_{1-2}} = \int_0^\infty \Psi_1\,r^k\,\Psi_2\,\mathrm{d}r\ .$$

We have to calculate the r-centroids from the wave function curves plotted, as explained in a former article, with the help of an analogue computer [3]. The different terms of the electric dipole moment will be determined afterwards by means of the measured intensities.

Determination of the r-Centroids

The values of the wave functions are required for the evaluation of the r-centroids. Therefore, they are read on the plotted curves by means of a coordinograph. In order to have a good precision, we give to the abscissae increments of 2 mm, which correspond to $\Delta r = 0.00918$ Å. Tables 1 and 2 give the values of Ψ needed in this paper, corresponding to $v=0$ with $7 \leqq J \leqq 11$, and $v=1$ with $8 \leqq J \leqq 12$, respectively.

For the calculation of the r-centroids relative to the $1-0$ infrared emission band, we put (the wave functions being not normalized)

$$\overline{r^k_{1-2}} = \left(\sum_r \Psi_{v'',J}\,\Psi_{v',J+1}\,r^k\right) \Big/ \left(\sum_r \Psi^2_{v'',J} \sum_r \Psi^2_{v',J+1}\right)^{1/2}$$

where $v'=1$, $v''=0$.

Table 1. Values of wave functions for $v=0$.

r (Å)	Wave functions $J=7$	$J=8$	$J=9$	$J=10$	$J=11$
0.66034	+ 0.02				
0.66952	+ 0.04		+ 0.02		
0.67870	+ 0.05	+ 0.02	+ 0.04	+ 0.02	+ 0.02
0.68788	+ 0.07	+ 0.04	+ 0.06	+ 0.04	+ 0.04
0.69706	+ 0.08	+ 0.06	+ 0.08	+ 0.05	+ 0.06
0.70624	+ 0.10	+ 0.08	+ 0.10	+ 0.07	+ 0.09
0.71542	+ 0.12	+ 0.10	+ 0.13	+ 0.10	+ 0.11
0.72460	+ 0.17	+ 0.13	+ 0.16	+ 0.13	+ 0.14
0.73378	+ 0.21	+ 0.17	+ 0.20	+ 0.17	+ 0.16
0.74296	+ 0.26	+ 0.20	+ 0.25	+ 0.22	+ 0.20
0.75214	+ 0.33	+ 0.26	+ 0.30	+ 0.30	+ 0.26
0.76132	+ 0.39	+ 0.33	+ 0.38	+ 0.40	+ 0.32
0.77050	+ 0.50	+ 0.42	+ 0.45	+ 0.49	+ 0.40
0.77968	+ 0.58	+ 0.50	+ 0.57	+ 0.60	+ 0.50
0.78886	+ 0.70	+ 0.60	+ 0.67	+ 0.73	+ 0.60
0.79804	+ 0.80	+ 0.70	+ 0.78	+ 0.86	+ 0.70
0.80722	+ 0.93	+ 0.82	+ 0.93	+ 1.00	+ 0.82
0.81640	+ 1.08	+ 0.97	+ 1.06	+ 1.17	+ 0.95
0.82558	+ 1.27	+ 1.12	+ 1.22	+ 1.33	+ 1.12
0.83476	+ 1.38	+ 1.28	+ 1.36	+ 1.50	+ 1.26
0.84394	+ 1.53	+ 1.41	+ 1.42	+ 1.68	+ 1.40
0.85312	+ 1.70	+ 1.60	+ 1.58	+ 1.88	+ 1.60
0.86230	+ 1.88	+ 1.77	+ 1.75	+ 2.08	+ 1.76
0.87148	+ 2.01	+ 1.94	+ 1.90	+ 2.24	+ 1.93
0.88066	+ 2.16	+ 2.09	+ 2.06	+ 2.40	+ 2.09
0.88984	+ 2.27	+ 2.24	+ 2.20	+ 2.56	+ 2.23
0.89902	+ 2.38	+ 2.36	+ 2.29	+ 2.69	+ 2.33
0.90820	+ 2.46	+ 2.46	+ 2.38	+ 2.80	+ 2.43
0.91738	+ 2.53	+ 2.54	+ 2.44	+ 2.89	+ 2.50
0.92656	+ 2.55	+ 2.58	+ 2.50	+ 2.94	+ 2.56
0.93574	+ 2.55	+ 2.60	+ 2.53	+ 2.99	+ 2.59
0.94492	+ 2.55	+ 2.61	+ 2.54	+ 3.00	+ 2.61
0.95410	+ 2.55	+ 2.61	+ 2.54	+ 3.00	+ 2.60
0.96328	+ 2.50	+ 2.58	+ 2.54	+ 2.99	+ 2.59
0.97246	+ 2.43	+ 2.54	+ 2.50	+ 2.93	+ 2.55
0.98164	+ 2.33	+ 2.46	+ 2.40	+ 2.85	+ 2.47
0.99082	+ 2.22	+ 2.35	+ 2.32	+ 2.75	+ 2.38
1.00000	+ 2.09	+ 2.23	+ 2.23	+ 2.60	+ 2.28
1.00918	+ 1.97	+ 2.11	+ 2.09	+ 2.26	+ 2.13
1.01836	+ 1.85	+ 1.96	+ 1.94	+ 2.30	+ 1.98
1.02754	+ 1.69	+ 1.83	+ 1.80	+ 2.15	+ 1.84
1.03672	+ 1.55	+ 1.70	+ 1.66	+ 2.00	+ 1.71
1.04590	+ 1.41	+ 1.54	+ 1.53	+ 1.82	+ 1.55
1.05508	+ 1.28	+ 1.40	+ 1.38	+ 1.65	+ 1.41
1.06426	+ 1.16	+ 1.28	+ 1.25	+ 1.49	+ 1.27
1.07344	+ 1.03	+ 1.14	+ 1.13	+ 1.34	+ 1.15
1.08262	+ 0.91	+ 1.00	+ 1.00	+ 1.21	+ 1.03
1.09180	+ 0.78	+ 0.90	+ 0.91	+ 1.08	+ 0.92
1.10098	+ 0.70	+ 0.78	+ 0.80	+ 0.95	+ 0.80
1.11016	+ 0.62	+ 0.68	+ 0.68	+ 0.84	+ 0.70
1.11934	+ 0.52	+ 0.61	+ 0.60	+ 0.75	+ 0.63
1.12852	+ 0.45	+ 0.52	+ 0.50	+ 0.65	+ 0.52
1.13770	+ 0.40	+ 0.44	+ 0.44	+ 0.55	+ 0.46
1.14688	+ 0.31	+ 0.38	+ 0.37	+ 0.48	+ 0.40
1.15606	+ 0.28	+ 0.31	+ 0.32	+ 0.40	+ 0.35
1.16524	+ 0.24	+ 0.28	+ 0.27	+ 0.35	+ 0.29
1.17442	+ 0.19	+ 0.23	+ 0.23	+ 0.30	+ 0.23
1.18360	+ 0.17	+ 0.19	+ 0.19	+ 0.26	+ 0.20
1.19278	+ 0.13	+ 0.15	+ 0.16	+ 0.22	+ 0.18
1.20196	+ 0.10	+ 0.12	+ 0.13	+ 0.20	+ 0.14
1.21114	+ 0.06	+ 0.10	+ 0.09	+ 0.17	+ 0.10
1.22032	+ 0.04	+ 0.07	+ 0.05	+ 0.14	+ 0.08
1.22950	+ 0.01	+ 0.05	+ 0.03	+ 0.11	+ 0.08
1.23868		+ 0.02	+ 0.01	+ 0.09	+ 0.05
1.24786				+ 0.05	+ 0.04
1.25704				+ 0.03	+ 0.02
1.26622				+ 0.02	

J, corresponding to the final state, varies from 7 to 11. As M will be expanded up to the fourth order, k takes integer values from 0 to 4.

This formula permits us to calculate, with the help of an IBM 1620 computer, the r-centroids from the values of the wave functions. The results are listed in Table 3.

Evaluation of the Initial State Populations

The population of a level characterized by v' and $J+1$ is given by Boltzmann's formula [1]

$$P_1 = A\{2(J+1)+1\}\exp\{-(E_v+E_r)/KT\}$$

where E_v and E_r represent the vibrational and rotational energies, respectively, K is Boltzmann's constant, T the absolute temperature, A a constant.

For a given band, and at constant temperature, the rotational state sum as well as E_v and

$$A_1 = A\exp\{-E_v/KT\}$$

remain unchanged. Hence

$$P_1 = A_1(2J+3)\exp\{-B_{v'}(J+1)(J+2)/KT\}$$

where $B_{v'} = B_e - \alpha_e(v'+\frac{1}{2})$.

The rotational line intensity measurements, listed in Table 4, have been carried out at various temperatures by CHEVALEYRE [4, 5]. A monochromator fitted with a lead sulfide photocell was used, after being calibrated against a tungsten ribbon standard lamp. The precision is better than 1%.

We have then

$$\sum_{k=0}^{n} \overline{r_{1-2}^{k}}\, M_k = D\left(\frac{I_J}{(2J+3)\,\nu_J^4}\exp\{B_{v'}(J+1)(J+2)/KT\}\right)^{1/2} \quad (1)$$

where D is a constant. For a given band, the r-centroids remain constant, but the second member changes with the temperature. Table 4 shows that the number of equations like Eq. (1) is 5, whereas there are only $(n+1)$ homogeneous unknowns M_k/D.

Table 2. Values of wave functions for $v=1$.

r (Å)	Wave functions $J=8$	$J=9$	$J=10$	$J=11$	$J=12$	r (Å)	Wave functions $J=8$	$J=9$	$J=10$	$J=11$	$J=12$
0.63280		+ 0.02	+ 0.02	+ 0.01		1.02754	− 2.48	− 2.45	− 2.86	− 2.42	− 2.44
0.64198	+ 0.02	+ 0.03	+ 0.04	+ 0.03		1.03672	− 2.56	− 2.55	− 2.96	− 2.53	− 2.56
0.65116	+ 0.03	+ 0.04	+ 0.06	+ 0.05		1.04590	− 2.60	− 2.61	− 3.00	− 2.60	− 2.62
0.66034	+ 0.04	+ 0.07	+ 0.08	+ 0.06	+ 0.03	1.05508	− 2.60	− 2.63	− 3.03	− 2.63	− 2.64
0.66952	+ 0.05	+ 0.10	+ 0.10	+ 0.08	+ 0.05	1.06426	− 2.58	− 2.63	− 3.02	− 2.63	− 2.64
0.67870	+ 0.09	+ 0.12	+ 0.12	+ 0.10	+ 0.08	1.07344	− 2.50	− 2.60	− 2.98	− 2.62	− 2.63
0.68788	+ 0.12	+ 0.15	+ 0.17	+ 0.13	+ 0.11	1.08262	− 2.40	− 2.52	− 2.90	− 2.54	− 2.56
0.69706	+ 0.14	+ 0.20	+ 0.22	+ 0.17	+ 0.16	1.09180	− 2.27	− 2.41	− 2.77	− 2.46	− 2.45
0.70624	+ 0.19	+ 0.26	+ 0.29	+ 0.21	+ 0.20	1.10098	− 2.11	− 2.24	− 2.61	− 2.32	− 2.32
0.71542	+ 0.27	+ 0.33	+ 0.35	+ 0.29	+ 0.26	1.11016	− 1.95	− 2.08	− 2.44	− 2.17	− 2.17
0.72460	+ 0.34	+ 0.41	+ 0.46	+ 0.36	+ 0.35	1.11934	− 1.80	− 1.93	− 2.25	− 2.02	− 2.00
0.73378	+ 0.44	+ 0.52	+ 0.55	+ 0.48	+ 0.44	1.12852	− 1.65	− 1.75	− 2.07	− 1.84	− 1.85
0.74296	+ 0.55	+ 0.64	+ 0.67	+ 0.58	+ 0.56	1.13770	− 1.47	− 1.58	− 1.88	− 1.68	− 1.68
0.75214	+ 0.68	+ 0.77	+ 0.83	+ 0.70	+ 0.68	1.14688	− 1.32	− 1.41	− 1.70	− 1.52	− 1.50
0.76132	+ 0.89	+ 0.93	+ 0.99	+ 0.84	+ 0.84	1.15606	− 1.19	− 1.26	− 1.54	− 1.38	− 1.35
0.77050	+ 1.05	+ 1.10	+ 1.19	+ 1.01	+ 0.98	1.16524	− 1.04	− 1.11	− 1.36	− 1.21	− 1.20
0.77968	+ 1.22	+ 1.25	+ 1.40	+ 1.18	+ 1.16	1.17442	− 0.90	− 0.99	− 1.20	− 1.07	− 1.06
0.78886	+ 1.42	+ 1.38	+ 1.58	+ 1.36	+ 1.32	1.18360	− 0.78	− 0.85	− 1.06	− 0.95	− 0.92
0.79804	+ 1.67	+ 1.58	+ 1.79	+ 1.53	+ 1.50	1.19278	− 0.66	− 0.74	− 0.93	− 0.84	− 0.80
0.80722	+ 1.86	+ 1.77	+ 2.00	+ 1.73	+ 1.69	1.20196	− 0.58	− 0.65	− 0.81	− 0.73	− 0.68
0.81640	+ 2.02	+ 1.93	+ 2.20	+ 1.93	+ 1.87	1.21114	− 0.50	− 0.53	− 0.70	− 0.64	− 0.59
0.82558	+ 2.20	+ 2.08	+ 2.39	+ 2.10	+ 2.05	1.22032	− 0.40	− 0.45	− 0.60	− 0.55	− 0.50
0.83476	+ 2.32	+ 2.24	+ 2.55	+ 2.23	+ 2.20	1.22950	− 0.36	− 0.37	− 0.53	− 0.46	− 0.42
0.84394	+ 2.40	+ 2.35	+ 2.65	+ 2.33	+ 2.31	1.23868	− 0.30	− 0.31	− 0.45	− 0.39	− 0.37
0.85312	+ 2.45	+ 2.39	+ 2.73	+ 2.39	+ 2.38	1.24786	− 0.22	− 0.23	− 0.40	− 0.33	− 0.27
0.86230	+ 2.47	+ 2.40	+ 2.75	+ 2.40	+ 2.42	1.25704	− 0.20	− 0.18	− 0.35	− 0.28	− 0.22
0.87148	+ 2.42	+ 2.39	+ 2.75	+ 2.40	+ 2.42	1.26622	− 0.16	− 0.13	− 0.31	− 0.23	− 0.14
0.88066	+ 2.30	+ 2.29	+ 2.64	+ 2.35	+ 2.35	1.27540	− 0.11	− 0.09	− 0.26	− 0.18	− 0.10
0.88984	+ 2.10	+ 2.13	+ 2.45	+ 2.23	+ 2.19	1.28458	− 0.10	− 0.04	− 0.24	− 0.16	− 0.06
0.89902	+ 1.87	+ 1.90	+ 2.19	+ 2.01	+ 2.00	1.29376	− 0.06		− 0.22	− 0.12	
0.90820	+ 1.55	+ 1.64	+ 1.86	+ 1.78	+ 1.75	1.30294	− 0.04		− 0.18	− 0.07	
0.91738	+ 1.23	+ 1.33	+ 1.52	+ 1.47	+ 1.46	1.31212	− 0.02		− 0.17	− 0.04	
0.92656	+ 0.86	+ 1.01	+ 1.13	+ 1.13	+ 1.10	1.32130	− 0.01		− 0.15		
0.93574	+ 0.43	+ 0.63	+ 0.68	+ 0.75	+ 0.70	1.33048			− 0.14		
0.94492	+ 0.02	+ 0.24	+ 0.22	+ 0.38	+ 0.37	1.33966			− 0.12		
0.95410	− 0.37	− 0.14	− 0.24	− 0.02	− 0.06	1.34884			− 0.11		
0.96328	− 0.75	− 0.52	− 0.68	− 0.42	− 0.45	1.35802			− 0.10		
0.97246	− 1.14	− 0.92	− 1.09	− 0.82	− 0.82	1.36720			− 0.10		
0.98164	− 1.46	− 1.27	− 1.53	− 1.20	− 1.21	1.37638			− 0.09		
0.99082	− 1.77	− 1.58	− 1.86	− 1.50	− 1.50	1.38556			− 0.07		
1.00000	− 2.00	− 1.86	− 2.21	− 1.83	− 1.82	1.39474			− 0.06		
1.00918	− 2.22	− 2.09	− 2.47	− 2.07	− 2.05	1.40392			− 0.05		
1.01836	− 2.35	− 2.30	− 2.68	− 2.27	− 2.28	1.41310			− 0.04		

Table 3. Values of the r-centroids for the 1−0 band of the $X\,^1\Sigma^+$ state.

k	$J=7$	$J=8$	$J=9$	$J=10$	$J=11$
0	− 0.51276986 E − 2	− 0.31793041 E − 1	− 0.38446958 E − 1	− 0.17416820 E − 1	− 0.26240043 E − 1
1	− 0.72540959 E − 1	− 0.97667310 E − 1	− 0.10531831 E 0	− 0.85566315 E − 1	− 0.92705551 E − 1
2	− 0.13346420 E 0	− 0.15808097 E 0	− 0.16653078 E 0	− 0.14841648 E 0	− 0.15398668 E 0
3	− 0.18930406 E 0	− 0.21432141 E 0	− 0.22343116 E 0	− 0.20728298 E 0	− 0.21134765 E 0
4	− 0.24126750 E 0	− 0.26750903 E 0	− 0.27718794 E 0	− 0.26332373 E 0	− 0.26589889 E 0

Calculation of the Terms of the Electric Dipole Moment

Let X be the column matrix

$$X=\{M_k/D\} \quad \text{with} \quad 0 \leqq k \leqq n\,.$$

The system to be solved has the following form [6]

$$U\,X=V$$

where U is a rectangular matrix having in general more rows than columns. This system becomes a

Table 4. Experimental line intensities of the 1−0 transition in arbitrary units.

J	ν_J (cm^{-1})	$T = 3257$ °K	$T = 3616$ °K	$T = 3890$ °K
7	4230.85	9.9_6	9.2_0	8.6_6
8	4256.32	9.4_5	8.8_4	8.3_6
9	4279.91	8.3_2	8.0_4	7.5_2
10	4301.55	7.3_2	7.1_8	6.9_4
11	4321.28	6.2_4	6.2_4	6.5_2

quadratic set when we multiply on the left by the transposed matrix U^T

$$U^T U X = U^T V$$

and its resolution gives the least-squared values of X.

When we supply the computer program, based on the Gauss' method, with the elements of the square matrix $U^T U$ and the second member $U^T V$, we obtain the values of the unknowns. These, in turn, permit us to evaluate the residuals δ, namely the differences between the five calculated first members of Eq. (1) and the "measured" second members.

In order to estimate the influence of the degree of the polynomial representing the electric dipole moment on the precision of the results, we allowed n to take values from 1 to 4. Table 5 shows that the sum of the squares of the residuals decreases with increasing n, and the error is comparatively large if a first order expansion is retained.

Table 5. Values of $\Sigma(\delta)^2$ in arbitrary units.

n	$T = 3257$ °K	$T = 3616$ °K	$T = 3890$ °K
1	2.58	2.04	1.46
2	0.90	0.64	0.66
3	0.81	0.59	0.48
4	0.67	0.50	0.20

The best results are thus obtained with $n = 4$, whatever the temperature may be. The precision is better than 4% in this case. Table 6 gives the relative values of the corresponding dipole moment terms, averaged over the temperature range under consideration.

Table 6. Mean relative values of the terms of the electric dipole moment.

M_1/M_0	M_2/M_0	M_3/M_0	M_4/M_0
− 2.20	0.14	2.27	− 1.21

Summary

For the plotting of the potential energy curves relative to the HF molecule, we have taken into account the vibration-rotation interaction term. The Schrödinger equation has been solved from these curves by an analogue computation method, which permitted us to calculate the matrix elements of the 1 − 0 transition belonging to the $X\,^1\Sigma^+$ state.

Comparison of experimental line intensities with their theoretical values results in the fact that the different terms of the electric moment expansion are of the same order of magnitude. There is thus electrical anharmonicity for the involved transition of hydrogen fluoride, and the dipole moment does not vary linearly with the internuclear distance.

The proposed method gives a fourth-order representation of the dipole moment. It is obviously possible to increase the number of expansion terms without prohibitive complication, when experimental line intensities are available.

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