Determination of Radial Functions from the Vibration-rotational Energies of the Ground Electronic State $X^1\Sigma^+$ of Hydrogen Fluoride

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Résumé

Les fonctions radiales de l'énergie potentielle internucléaire et de celle des effets adiabatiques et non-adiabatiques pour l'atome d'hydrogène (ainsi que d'autres effets mineurs) ont été déterminées pour l'état fondamental $X^1\Sigma^+$ du fluorure d'hydrogène, dans l'intervalle de distances internucléaires $0.65 \leqslant R/10^{-10}$ m $\leqslant 1.65$ et un domaine d'énergie s'étendant jusqu'à environ le tiers de l'énergie de dissociation, et ce, à partir d'une analyse (incluant des tests complets de signification statistique) des fréquences de lignes spectrales dans une région allant des micro-ondes à l'UV lointain. Les tests internes de cohérence confirment la signification physique des résultats.

Abstract

For the ground electronic state $X^1\Sigma^+$ of hydrogen fluoride in the range of internuclear distance $0.65 \leqslant R/10^{-10}$ m $\leqslant 1.65$ and for the energy range up to almost two thirds the dissociation energy, the radial functions for both the internuclear potential energy and (for the hydrogen atomic centre) the adiabatic and nonadiabatic (as well as other minor) effects have been determined from an analysis, with full tests of statistical significance, of the frequencies and wavenumbers of spectral lines from the millimetre-wave region to the vacuum ultraviolet. The internal tests of consistency confirm the physical significance of the results.

Introduction

Hydrogen fluoride is the active medium of an important laser system operating on vibration-rotational transitions. Any extension of the range of such transitions as well as other molecular properties important in some collisional processes depend on an accurate knowledge of the energies of the vibration-rotational states and the radial functions for internuclear potential energy and the nonmechanical effects (collectively the adiabatic and nonadiabatic effects) that determine those energies within the Born-Oppenheimer approximation of the separation of electronic and nuclear motions.

The information from spectroscopic experiments necessary for the derivation of either these functions in various representations or the coefficients of a representation of the energy in terms of the vibrational v and rotational J (in the absence of other important contributions to the total molecular angular momentum) quantum numbers exists in the form of published measurements of frequencies and wavenumbers of spectral lines from the submillimetre (or far infrared) range to the vacuum ultraviolet region. These lines encompass all three types of transitions, namely pure rotational, vibration-rotational and rovibronic transitions, including both absorption and emission spectra, and involving the three sets of nuclides $^1H^{19}F$, $^2H^{19}F$ and $^3H^{19}F$. In a previous study of hydrogen chloride (1), we have described a procedure developed for an analysis of such extensive and diverse data from disparate sources, of variable extent and precision. In the present work we have employed this procedure to take account of the similarly extensive set of data available for HF. As in the previous work (1), we have succeeded in effecting a global analysis of the data found to be consistent within the numerical precision of the analytical treatment, specifically up to $v = 9$ and $J = 34$ in the ground electronic state. Not only has a potential-energy function of great precision been derived, but

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also the values of the coefficients Δ^{H}_{kl} that in part take into account the deviations from mechanical behaviour have been used, for the first time in a complete analysis, in order to determine a second radial function to describe these nonmechanical effects. The latter effects include contributions from nonadiabatic effects, related to the fact that the electrons imperfectly follow the nuclei during the vibrational and rotational motions, relativistic, radiative and other less important effects that have the same mass dependence, but mostly from adiabatic effects, related to the finite nuclear kinetic energies.

Of the two principal objectives of the present investigation, one has been to determine a potential-energy function of HF, specifically the values of the coefficients c_j in the general flexible function V(z) (2,3)

$$V(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j) \qquad [1]$$

in which the reduced displacement variable z is defined in terms of the instantaneous R and equilibrium R_e internuclear separations

$$z \equiv 2\,(R - R_e)/(R + R_e) \qquad [2]$$

The theoretically most meaningful potential energy is that which is independent of nuclear mass; in order to derive such a function it is necessary also to determine the nonmechanical effects on the wavenumbers and frequencies of the pertinent spectral lines. We may consider these effects in a diatomic molecule to be the sum of independent contributions from the two atomic centres. With data for $^{1}H^{19}F$, $^{2}H^{19}F$ and $^{3}H^{19}F$, we have the means to determine, according to our second objective, a further radial function $K^H(z)$ (4)

$$K^H(z) = \sum_{j=1} h^H_j z^j \qquad [3]$$

that includes collectively the contributions for H from all the forementioned effects. Because $K^F(z)$ cannot be determined, V(z) is therefore obtained as a potential energy independent of hydrogen mass but specifically applicable to isotopic species containing ^{19}F.

The vibration-rotational terms $E^i(v,J)$ of a particular isotopic molecule may be represented according to the equation

$$E^i(v,J) = \sum_{k=0} \sum_{l=0} U_{kl}\, \mu_i^{-(k+2l)/2} (v+1/2)^k (J^2+J)^l \, [1 + m_e(\Delta^a_{kl}/M_a + \Delta^b_{kl}/M_b)] \qquad [4]$$

in which $\mu_i = M_a M_b/(M_a + M_b)$ is the atomic reduced mass of a particular isotopic species. The analytic expressions of U_{kl} in terms of the potential-energy coefficients c_j have been published in machine-readable form (5). Relations to connect the $\Delta^{a,b}_{kl}$ coefficients to the coefficients $h^{a,b}_j$ through the quantities $Z^{a,b}_{kl}$ have also been proposed (4) and are discussed further herein. Although it is possible to derive the values of the potential-energy c_j and further $h^{a,b}_j$ coefficients directly from the spectral wavenumbers and frequencies, in this work we used the approach of stepwise merging, in which the numerical estimates of the U_{kl} and $\Delta^{a,b}_{kl}$ coefficients are fitted in one stage, followed by a further stage to derive the values of the coefficients in the fundamental radial functions, with a full treatment of statistical weights of the data at each stage (1). However, because of the lack of stable fluorine isotopes, no values of the coefficients Δ^{F}_{kl} (and hence also h^F_j) could be determined from the present set of spectral data.

In this report we outline the essential aspects of the procedure, and then present the results from the analysis of all the spectra. Finally we conclude with a discussion of the significance of these results and the problems encountered in such analyses.

Procedure

The process of the determination of the potential-energy function of HF has consisted of several steps of data selection and reduction within two principal stages. At the end of the first stage, a set of the coefficients U^{eff}_{kl} and Δ^{H}_{kl} was obtained. During the second stage, the latter data U^{eff}_{kl} and Δ^{H}_{kl} were further analysed in order to extract the physically meaningful functions for the potential energy and adiabatic (and related) effects. The notation U^{eff}_{kl} is employed to emphasize that the fitted coefficients are not strictly those pertaining to the Born-Oppenheimer potential energy but are instead effective values for isotopic species containing the ^{19}F nuclide. It is implicit hereinafter that the U_{kl} parameters are U^{eff}_{kl}.

During the course of several decades, many measurements have been made of spectra of HF involving the rotational and vibrational states of the ground electronic state. In addition to the many publications containing frequency or wavenumber data from rotational or vibration-rotational transitions of HF, DF and TF, an important source of information about the higher vibration-rotational states of the ground electronic state is the electronic emission spectrum of HF (6). First of all, a selection of all the data published before 1986 served to eliminate spectra of such poor resolution that they were unlikely to be useful for our present purposes. Of the remaining data (6-20), the preliminary fits of individual data bands by the method of least squares of residuals achieved three purposes: the determination whether the quality of the data sufficed for their inclusion in the subsequent global fit; the rejection of particular measurements having anomalously large fitting errors, and the estimation of the precision of the measurements as indicated by the standard errors of the fits after deletion of suspect measurements (outliers). In these fits according to the conventional representation of the wavenumbers of bands involving different vibrational quantum numbers,

$$\begin{aligned}\nu(J) = \nu_0 &+ [B'J'(J'+1) - D'J'^2(J'+1)^2 + H'J'^3(J'+1)^3 \\ &+ L'J'^4(J'+1)^4 + M'J'^5(J'+1)^5] - [B''J''(J''+1) \\ &- D''J''^2(J''+1)^2 + H''J''^3(J''+1)^3 + \\ &L''J''^4(J''+1)^4 + M''J''^5(J''+1)^5] \qquad [5]\end{aligned}$$

some band parameters (B, D, H, L, M) were constrained at approximate values so that realistic standard errors could be obtained even in the cases of sparse data. In other cases there were too few data even to permit such constrained fits; in these cases the precision of the data was estimated by comparison with other data measured by the same authors. The electronic data (6) were truncated at v = 9 and J = 34 because further data required rotational parameters of order greater than M, the handling of which caused computational problems due to divergent representations. The data in table I specify the sets of transitions, 1456 lines in total, from fifteen publications that were included in the global fit. The fourth column of this table is a list of the estimated standard errors of each data set, consisting of N lines up to the maximum value J_{max} of J″ specified in the sixth and seventh columns; the rejected data, relatively few, are indicated in the final column.

For the analysis (1) of the HCl data we used a normal stepwise merge procedure; however both the sparse data in some sets and the excessively large number of parameters that would have been required precluded such an approach for the HF data set. We therefore employed a modified program of the 'merge' type to accomplish a global fitting by least squares in order to decrease the described data to a small set of output parameters that included the coefficients U_{kl} of the ground electronic state. By this means, the frequencies and wavenumbers of the measured lines were progressively included in a series of fits; each fit blended the previously estimated set of parameters (with its variance-covariance matrix) with additional data of

Table I. Sources of Data for the Analysis.

species	band	ref.	σ/m⁻¹	rms/σ	N	J_{max}	origin	excluded lines
HF	3*–9	6	3.4	1.71	44	34		P(18,21,35,36),R(35–37)
	4*–9	6	3.2	1.74	54	34		P(18,35–38),R(8,15,29,35–38)
	5*–9	6	3.3	1.65	56	34		P(35–37),R(8,15,17,35–37)
	6*–9	6	2.1	1.41	37	23		
	7*–9	6	2.4	1.29	39	24		P(3) R(7)
	8*–9	6	2.6	1.05	35	22		P(20)
	6*–8	6	2.5	1.21	47	27		P(6)
	7*–8	6	2.7	1.09	49	27		P(1) R(27)
	8*–8	6	3.4	1.14	47	30		P(4,9,21),R(8)
	7*–7	6	2.8	1.06	42	30		P(6) R(6,7,16)
	8*–7	6	3.7	1.09	44	30		P(12,13)
	1 –0	7	.025	0.72	22	11	*	P(11)
	1 –0	8	.44	0.91	10	15		
	1 –0	9	7.0	1.05	14	27		P(5–15) R(7–11,26)
	2 –0	7	.037	0.74	16	8	*	P(1,9)
	2 –0	9	11.	0.93	28	27		P(1–9,28),R(2–14,23,25)
	2 –0	10	.80	1.00	15	9		R(8)
	2 –1	8	.58	0.93	12	13	*	
	2 –1	9	5.9	0.92	11	24		P(1–12) R(0–11,20)
	3 –0	9	2.8	1.24	37	20		P(2) R(1,21)
	3 –0	11	.44	1.69	15	8	*	R(0,9)
	3 –2	8	.32	0.94	8	13	*	P(5)
	3 –2	9	3.7	0.99	26	22		P(4,9) R(10)
	4 –0	11	.56	0.99	33	6		
	4 –1	9	1.3	1.01	25	14		P(8,14) R(0)
	4 –2	9	12.	0.99	46	24		P(1)
HF	4 –3	8	.58	0.85	9	14	*	
	5 –0	9	5.9	0.97	16	14		
	5 –0	11	.71	1.62	8	4	*	R(0)
	5 –1	9	1.6	0.98	41	23		P(6,14) R(0)
	5 –2	9	2.2	1.19	25	19		P(1,8) R(4,20)
	5 –3	9	6.4	0.98	29	19		P(4,5,12,14),R(1,6,20)
	5 –4	8	.50	0.82	7	9	*	
	6 –1	9	6.2	0.93	29	16		
	6 –2	9	2.2	0.70	42	21	*	P(1) R(13,18)
	6 –3	9	.55	1.53	10	13	*	R(2,3,5)
	6 –4	9	11.	0.99	32	18	*	
	6 –5	8	0.6	0.46	3	9		P(10)
	7 –2	9	2.8	0.94	29	17	*	P(12,15,18),R(14,18)
	7 –3	9	1.7	1.03	32	19	*	P(16) R(0,16)
	8 –3	9	2.9	1.00	29	21	*	P(1–4,8)
	8 –4	9	2.9	0.67	21	16	*	P(8) R(8,9)
	v=0	8	.19	1.20	5	21		
	v=0	12	10.	1.44	10	32		R(28,30)
	v=0	13	35.	1.22	8	24		
	v=0	14	26.	0.99	32	40		R(15)
	v=0	15	4.3	1.00	10	9		R(10–16)
	v=0	15	10.	1.01	7	16		R(1–9)
	v=1	8	.28	0.65	6	23		
	v=1	12	9.6	0.84	7	28		
	v=1	14	29.	0.98	21	34		R(16,20,30,31)
	v=2	8	.67	0.47	6	23		
	v=2	14	25.	0.92	13	26		R(17,21,24,28)
	v=3	8	.67	0.33	3	22		
DF	1 –0	8	.34	1.06	29	17	*	
	1 –0	16	8.0	1.20	3	16		
	1 –0	17	1.3	1.42	20	12	*	P(6,7,9,10),R(7)
	2 –0	17	1.1	0.89	19	10	*	
	2 –1	8	.36	0.62	13	16	*	
	2 –1	16	4.9	0.80	9	12		P(3,13,16,17)
DF	3 –2	8	.25	0.94	11	14	*	
	3 –2	16	6.2	0.83	10	14		P(10)
	4 –3	8	.48	1.08	5	8	*	
	4 –3	16	8.0	0.35	3	7		
	v=0	18	.002	0.25	1	0		
	v=0	19	8.6	1.36	13	15		R(6,14)
TF	1 –0	20	12.	1.02	21	14	*	P(5,12–14),R(12–14)
	2 –0	20	4.3	1.02	17	10	*	P(5,7) R(5,9)

* An asterisk beside the vibrational quantum number of the upper state denotes the B $^1\Sigma^+$ state, but all other bands are either vibration-rotational or pure rotational (within the indicated vibrational state) within the ground electronic state $X^1\Sigma^+$.

Table II. Lists of parameters and coefficients in fits A, B1 and B2.

Fit A		Fit B1		Fit B2	
$U^{HF}_{0,1}$, $U^{DF}_{0,1}$, $U^{TF}_{0,1}$	3		3	$U_{0,1}$, $\Delta^{H}_{0,1}$	2
$U^{HF}_{1,1}$, $U^{DF}_{1,1}$, $U^{TF}_{1,1}$	3		3	$U_{1,1}$, $\Delta^{H}_{1,1}$	2
$U_{k,1}$, $2 \leq k \leq 5$	4		4		4
$U^{HF}_{0,2}$, $U^{DF}_{0,2}$, $U^{TF}_{0,2}$	3		3	$U_{0,2}$, $\Delta^{H}_{0,2}$	2
$U_{k,2}$, $1 \leq k \leq 3$	3		3		3
$U_{k,3}$, $0 \leq k \leq 2$	3		3		3
$U_{0,4}$, $U_{1,4}$	2		2		2
ν_0 (origins for HF, DF, TF)	43	$U^{HF}_{1,0}$, $U^{DF}_{1,0}$, $U^{TF}_{1,0}$	3	$U_{1,0}$, $\Delta^{H}_{1,0}$	2
				$U^{TF}_{1,0}$	1
		$U^{HF}_{2,0}$, $U^{DF}_{2,0}$, $U^{TF}_{2,0}$	3	$U_{2,0}$, $\Delta^{H}_{2,0}$	2
				$U^{TF}_{2,0}$	1
		$U_{k,0}$, $3 \leq k \leq 6$	4		4
		ν_0 (origins, HF,DF)	20		20
ν_0 (origins, HF, B—X)	11		11		11
D''_v, $7 \leq v \leq 9$, HF	3		3		3
H''_v, $7 \leq v \leq 9$, HF	3		3		3
L''_v, $7 \leq v \leq 9$, HF	3		3		3
B'_v, $3 \leq v \leq 8$, HF	6		6		6
$U'_{k,2}$, $0 \leq k \leq 2$, HF	3		3		3
$U'_{k,3}$, $0 \leq k \leq 2$, HF	3		3		3
$U'_{0,4}$, $U'_{1,4}$, HF	2		2		2
$U'_{0,5}$, HF	1		1		1
total	99		86		83

several bands or sets of transitions (with their estimated variances). In all cases the mass-reduced parameters $\mu_1^5 M''_v$ were constrained to values for the three isotopic species HF, DF and TF calculated from the coefficients $U_{0,5}$, $U_{1,5}$ and $U_{2,5}$ derived from a preliminary fit that generated values of the potential-energy coefficients.

During a later step of the first stage, the ninety-nine output parameters specified as fit A in Table II were produced. Of particular note are (i) the separate U_{kl} coefficients for the three isotopic species retained for $U^i_{0,1}$, $U^i_{1,1}$ and $U^i_{0,2}$, and (ii) the exclusion of data for HF with $v>6$ in estimates of $U_{k,2}$, $U_{k,3}$ and $U_{k,4}$. The reason for the latter omission is that in the earlier series of fits the inclusion of the band paramaters D_v, H_v and L_v for $7 \leqslant v \leqslant 9$ with values of k larger than that specified in Table II led to either poor fits or problems in matrix inversion due to divergent fits. However, the parameters of fit A reproduce well the input data: in the fifth column of Table I, the ratios of the root-mean-square residuals to the standard errors of the frequencies or wavenumbers of lines calculated by means of these parameters are almost all near unity; the principal exceptions are some bands in the electronic spectra involving $v = 9$ that should perhaps have suffered truncation even before $J = 34$. We estimate the variance of the equivalent single-step merge to produce the parameters in fit A to be $\sigma^2_M \sim 1.76^2$.

In the succeeding step, fit B1, we reduced the ninety-nine input parameters to a smaller set comprising eighty-six parameters by incorporating a selected set of the band origins in terms of the coefficients $U_{k,0}$, $1<k<6$, but still retaining separately the values of $U^i_{1,0}$ and $U^i_{2,0}$ of the three isotopic species. Many band origins were known to be subject to serious systematic errors; of the forty-three available origins, we used in the determination of all the $U_{k,0}$ parameters those twenty-three (denoted by asterisks in the eighth column of Table I) with the least systematic error. In the final step of the first stage, all the U^i_{kl} parameters of particular isotopic species were converted to the molecular parameters U_{kl} and Δ^H_{kl}. The comparatively large absolute errors in the measurements of the vibration-rotational bands of TF precluded the use of $U^{TF}_{1,0}$ and $U^{TF}_{2,0}$ in the process of reduction to $U_{1,0}$, $\Delta^H_{1,0}$, $U_{2,0}$ and $\Delta^H_{2,0}$. Thus the variance of the equivalent single-step merge of the eighty-three parameters of this fit B2 is estimated to be $\sigma^2_M \sim 2.27^2$, larger than for fit A but still acceptable for a fit that depends on many absolute measurements of line wavenumbers. We performed all subsequent fitting with the upper set (in Table II) of twenty-eight parameters from fit B2 and the corresponding variance-covariance submatrix; the parameter values and standard errors (in parentheses) are listed in the column of Table III labeled "obs".

From the latter data set during the second stage, a series of fits, designated C1, C2 and C3, employed selected values of U_{kl} parameters; in fits C2 and C3, some RKR turning points were also used, as in our previous work on HCl (1). In fit C1, the values of the parameters $U_{2,0}$, $U_{3,0}$, $U_{4,0}$, $U_{5,0}$, $U_{1,1}$, $U_{2,1}$, $U_{3,1}$, $U_{4,1}$, $U_{1,2}$, $U_{2,2}$, $U_{0,3}$, $U_{1,3}$, $U_{2,3}$, $U_{0,4}$ and $U_{1,4}$ were used to generate values of the coefficients c_j, $1 \leqslant j \leqslant 8$; in addition new estimates of $U_{1,0}$ and $U_{0,1}$ were found; the values of $U_{6,0}$, $U_{5,1}$ and $U_{3,2}$ (as well as Δ^H_{kl} and $U^{TF}_{1,0}$ and $U^{TF}_{2,0}$ of TF) were retained as single-valued parameters for which new estimates were obtained (in the column labeled "fitted"). In fit C2, the values of the parameters $U_{5,0}$ and $U_{4,1}$ were removed from the above list, and in their place the values of the turning points R_{max} for $v = 8$ and $v = 9$ of HF from the RKR program were introduced as the means to determine c_7 and c_8. As expected, the variances ($\sigma^2_M = 2.26^2$) of fits C1 and C2 are identical, as are the corresponding values of the coefficients c_j, $1 \leqslant j \leqslant 6$. In fit C3, the values of $U_{4,0}$ and $U_{3,1}$ were also removed from the list for fit C1; the RKR turning points R_{min} for $v = 9$ and R_{max} for $7 \leqslant v \leqslant 9$ were incorporated into this fit. The merge variance of the fit C3 is $\sigma^2_M = 2.95^2$.

Results

The principal results of this work comprise the values in Table III of the coefficients c_j, $1 \leqslant j \leqslant 8$, $U_{1,0}$, $U_{0,1}$,

Table III. Values of Parameters Generated in Fits C1, C2 and C3.

Parameter	C1	C2	C3
c_1	−1.2464852(1300)	−1.2464852(1300)	−1.2464954(1400)
c_2	0.8245851(6100)	0.8245851(6100)	0.8243035(6000)
c_3	−0.426432 (1900)	−0.426432 (1900)	−0.421960 (3000)
c_4	0.165491 (6300)	0.165491 (6300)	0.153653 (7800)
c_5	−0.26365 (3000)	−0.26365 (3000)	−0.23836 (2900)
c_6	−0.03260 (6000)	−0.03260 (6000)	−0.01822 (5900)
c_7	2.3956 (3100)	1.15308 (17000)	0.9265 (2300)
c_8	−7.145 (860)	−1.25412 (17000)	−0.9907 (2400)

coef[a]	obs	fitted	back	fitted	back	fitted	back
$U_{1,0}$	404846.6(15)	404846.93(86)		404846.93(86)		404847.45(112)	
$U_{2,0}$	−8612.2(16)	−8612.8			−8612.8		−8613.8
$U_{3,0}$	88.7(8)		88.9		88.9		89.4
$U_{4,0}$	−2.05(18)		−2.11		−2.11	−2.21(12)	−2.06
$U_{5,0}/10^{-2}$	4.9(19)		5.6	5.6(10)	−0.3	6.6(13)	−1.2
$U_{6,0}/10^{-3}$	−4.6(8)	−4.85(42)		−4.85(42)		−5.2(5)	
$U_{0,1}$	2004.810(9)	2004.8099(82)		2004.8099(82)		2004.8093(82)	
$U_{1,1}$	−74.2501(10)		−74.2496		−74.2496		−74.2500
$U_{2,1}$	0.997(6)		0.998		0.998		1.004
$U_{3,1}/10^{-2}$	−1.89(23)		−1.89		−1.89	−2.07(14)	−1.89
$U_{4,1}/10^{-4}$	−3.1(33)		−3.4	−3.4(6)	−13.	−0.7(11)	−12.
$U_{5,1}/10^{-5}$	−4.3(16)	−4.18(30)		−4.18(30)		−5.5(9)	
$U_{0,2}$	−0.19665(13)		−0.19665		−0.19665		−0.19665
$U_{1,2}/10^{-3}$	5.180(18)		5.216		5.216		5.213
$U_{2,2}/10^{-5}$	−6.4(7)		−7.4		−7.4		−7.5
$U_{3,2}/10^{-6}$	−8.5(6)	−7.85(30)	−12.	−7.85(30)	−12.	−7.86(30)	−11.
$U_{0,3}/10^{-5}$	1.454(5)		1.453		1.453		1.453
$U_{1,3}/10^{-7}$	−3.3(5)		−3.7		−3.7		−3.6
$U_{2,3}/10^{-8}$	−2.9(4)		−2.2		−2.2		−2.2
$U_{0,4}/10^{-9}$	−1.34(4)		−1.31		−1.31		−1.31
$U_{1,4}/10^{-12}$	9(43)		15		15		12
$U_{2,4}/10^{-10}$			−0.08		−0.08		−0.07
$U_{3,3}/10^{-9}$			5.9		1.0		0.6
$U_{4,2}/10^{-6}$			1.2		1.0		0.8
$\Delta^{H}_{1,0}$	.0494(37)	.0512(34)		.0512(34)		.0534(34)	
$\Delta^{H}_{2,0}$	−.154(45)	−.143(43)		−.143(43)		−.126(42)	
$\Delta^{H}_{0,1}$	.5250(93)	.5270(76)		.5270(76)		.5295(76)	
$\Delta^{H}_{1,1}$	.63(19)	.76(15)		.76(15)		.65(11)	
$\Delta^{H}_{0,2}$	1.4(12)	1.547(46)		1.547(46)		1.565(50)	
$U^{TF}_{1,0}$	404777.(28)	404777.(28)		404777.(28)		404778.(28)	
$U^{TF}_{2,0}$	−8557.(15)	−8556.(15)		−8556.(15)		−8557.(15)	

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[a] The units of U_{kl} are $m^{-1}amu^{(k+2l)/2}$ but Δ^{H}_{kl} are dimensionless. Atomic masses/amu used are: $^1H = 1.007825037$, $^2H = 2.0014101787$, $^3H = 3.016049286$, and $^{19}F = 18.99840325$; 1 amu = $1.660565472 \times 10^{-27}$ kg; $m_e = 5.485802368 \times 10^{-4}$ amu. Values in parentheses are estimated (one) standard errors in units of the last significant digits quoted.

Table IV. Values of the Coefficients h^{H}_{j}/B_e for $^1H^{19}F$.

j	h^{H}_{j}/B_e
1	3.066(40)
2	−7.477(12)
3	10.36(72)
4	0.078(3000)

Table V. RKR Turning Points of the Potential Energy of HF $X^1\Sigma^+$, Calculated from the Parameters $U_{k,0}$ and $U_{k,1}$ So Applicable to a Hypothetical Isotopic Species Having a Reduced Mass Equal to 1 amu; $R_e = 0.916984 \times 10^{-10}$ m.

v	$G(v)/m^{-1}$	$R_{min}/10^{-10}$ m	$R_{max}/10^{-10}$ m
0	200280.6	0.835181	1.019325
1	588181.0	0.785853	1.110568
2	959598.5	0.756314	1.183200
3	1314974.1	0.734688	1.249184
4	1654703.5	0.717585	1.312014
5	1979133.1	0.703476	1.373347
6	2288552.9	0.691526	1.434180
7	2583185.6	0.681221	1.495233
8	2863172.8	0.672220	1.557110
9	3128558.0	0.664279	1.620399

and the coefficients Δ^{H}_{kl}. In Table IV we present the set of coefficients h^{H}_{j}, $1 \leq j \leq 4$, determined from the Δ^{H}_{kl} coefficients. For this purpose we removed the contribution of the second-order mechanical effects $Y^{(2)}_{kl}$ according to the relation

$$Z^{H}_{kl} = U_{kl}\mu_i^{-(k+2l)/2}\, m_e\, \Delta^{H}_{kl}/M_H - Y^{(2)}_{kl}\, \mu_i/M \qquad [6]$$

In this equation these second-order terms $Y^{(2)}_{kl}$ are apportioned between the ^1H and ^{19}F atomic centres (in $^1H^{19}F$) in the ratio of the reciprocal masses M_H^{-1} and M_F^{-1}. This procedure differs from that previously proposed (4) in which the scaling factors $\Delta^{a,b}_{kl}/M_{a,b}$ were employed for atoms a and b; in the latter case no apportionment could be applied when $\Delta^{a,b}_{kl}$ is known for only one atom. Moreover equation 6 defines the contributions to the vibration-rotational terms $Z_{kl}(v + 1/2)^k (J^2 + J)^l$) in the approximation that all nonmechanical effects related to the breakdown of the Born-Oppenheimer approximation are represented by an effective hamiltonian that contains the function $K^{a,b}(z)$ of equation 3. Although this approximation may not always be appropriate, as found in recent work on HCl (21), it is satisfactory for the truncated rotational range of the relatively low vibrational states of HF considered in the present work. It is straightforward to show that equation 6 is consistent with the form of the energy corrections given by Watson (22). Because the effects represented in the values of the coefficients h^{H}_{j} are relative to those at the equilibrium internuclear distance (4), no value of h^{H}_{0} can be determined. The error on h^{H}_{4} is relatively large because of the uncharacteristically small magnitude of the value of this coefficient, like the case of c_6. The classical turning points according to the numerical RKR method are also presented, in Table V; as explained above, these values are not quite those of the Born-Oppenheimer potential energy because a small dependence on the F mass is inextricably contained in the effective values of $U_{k,0}$ and $U_{k,1}$.

From the value of the coefficient $U_{0,1}$ one can calculate the value of an equilibrium internuclear separation that is expected to have a value close to that of R_e^{BO}, corresponding to the Born-Oppenheimer separation of electronic and nuclear motions; of the standard error attached to this estimate $(0.9169839 \pm .0000023) \times 10^{-10}$ m of R_e^{BO}, one fifth is due to the uncertainty in the fundamental physical constants (23). Likewise from $U_{1,0}$, one can calculate the value $(965.680 \pm .20)$ N m^{-1} of the harmonic force coefficient ($\sim k_e^{BO}$) through the value of $c_0 \equiv U_{1,0}{}^2/(4U_{0,1}) \equiv (2.043853 \pm 0.00042) \times 10^7 m^{-1}$.

Discussion

By means of frequencies and wavenumbers of spectral lines from a broad range and for three isotopic species of hydrogen fluoride, we have succeeded in determining both a potential-energy function V(z) and another radial function $K^H(z)$ mostly attributable to adiabatic effects, both for the ground electronic state X $^1\Sigma^+$. Both functions are valid within the range $0.65 \leqslant R/10^{-10}\ m \leqslant 1.65$ of internuclear separation, corresponding approximately to the classical turning points for $v = 9$, and within the range of energy up to almost two thirds the dissociation limit of this electronic state.

The physical significance of the potential-energy function is confirmed by the consistency of the values of the energy coefficients U_{kl} back-calculated from the values of the parameters c_j, in the final column of table 3, for fit C3, in comparison with the observed values from the direct fit of the frequency and wavenumber data with the U_{kl} coefficients; despite the sensitivity of many higher-order values of U_{kl} to the effects of truncation of power series, the agreement is generally within two standard errors. Likewise, a test of the physical significance of the h_j^H coefficients is available from the value -7.76 ± 0.26 of h_2^H/B_e calculated from $\Delta^H_{0,2}$ (and h_1^H); the agreement is most satisfactory, resulting from the care taken to constrain the value of $U_{0,2}$ as required by its relation to $U_{0,1}$ and $U_{1,0}$. The fact that it has proved impossible to determine any values of the Δ_{kl}^F (and consequently the h_j^F coefficients) means that the values of the U_{kl} coefficients contain, by default, the corresponding perturbations from the adiabatic, nonadiabatic etc. effects for the fluorine atomic centre, but these effects are relatively small, much smaller than those due to the hydrogen atomic centre according to the precedent of HCl (1). After the calculations were completed, the values of $\mu_1^5 M_v$ for $0 \leqslant v \leqslant 9$ were calculated by means of Hutson's program (24); these values agree poorly with those of the preliminary estimate, but this condition is of little consequence, because, as shown in Table III, even $U_{1,4}$ could not be determined significantly.

The values of the potential-energy coefficients c_j have already proved useful in the determination of the electric dipole-moment function of HF (25) from an analysis of the expectation values of the dipole moment from the Stark effect and the matrix elements from infrared intensities, for which accurate values of these quantities c_j are essential. Doubtless they, as well as the values of the coefficients h_j^H, can also prove useful in the future as tests of the accuracy of computations of 'ab initio' quantum mechanics, for which hydrogen fluoride is an attractive model.

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