

Rotational Spectrum of Hydrogen Fluoride: Frequencies and Linewidths*

ARTHUR A. MASON† AND ALVIN H. NIELSEN

In many ways, this experimental effort was of an exploratory nature. There was the question of the availability of window materials which could resist the corrosive effect of HF and at the same time provide the required mechanical, thermal, and optical properties. The polyethylene and the silver chloride proved satisfactory chemically and optically but barely adequate mechanically and thermally. The many experimental difficulties of the far infrared make precision measurements extremely arduous. When the work began it was not known if transmittance measurements could be made across the breadth of a single absorption line in the far infrared; certainly there was little realization of the extreme intensity of these pure rotational lines of hydrogen fluoride.

The rotational term values in the ground-state vibrational level can be written

$$F_0(J) = B_0J(J+1) - D_0J^2(J+1)^2 + H_0J^3(J+1)^3 + \dots, \quad (1)$$

where B_0 , D_0 , and H_0 are the rotational constants. The absorption frequency for a given line is then

$$\nu(J) = 2B_0(J+1) - 2(2D_0 - H_0)(J+1)^3 + 6H_0(J+1)^5 + \dots \quad (2)$$

TABLE I. Collected values of HF pure-rotation line centers.

Transition (J)	Rothschild ^a (cm ⁻¹)	Smith and Nielsen ^b (cm ⁻¹)	Present work (cm ⁻¹)
0	41.30		41.08
1	82.35		82.19
2	122.83		123.15
3	163.97		164.00
4	204.59		204.62
5	245.09		244.93
6	285.14		285.01
7	324.75		324.65
8	364.17		363.93
9	403.06		402.82
10	441.28		441.13
11		441.21	441.13
12		479.00	478.94
13		516.27	516.20
14			552.85
15		588.90	588.82
16		624.13	624.07
			658.54

TABLE II. Rotational constants of hydrogen fluoride.

Constant	Herget <i>et al.</i> ^a (cm ⁻¹)	Rothschild ^b (cm ⁻¹)	Present work (cm ⁻¹)
B_0	20.558	20.567	20.561
D_0	0.00215	0.00208	0.00213
H_0	1.75×10^{-7} ^c		1.418×10^{-7}

^a Ref. 1.
^b Ref. 9.
^c Ref. 11.

The strength of an individual line may be evaluated by means of the Einstein coefficients and the Boltzmann distribution of molecules among the rotational energy levels. The resulting expression is

$$S^0 = \frac{8\pi^3}{3hc} \nu |\mu|^2 N (1 - e^{-\nu hc/kT}) \times \frac{(2J+1) \exp[-B_0J(J+1)hc/kT]}{\sum (2n+1) \exp[-B_0n(n+1)hc/kT]}, \quad (13)$$

The dipole-moment matrix element $|\mu|$ is evaluated on the basis of rigid-rotor wave functions.

The absorption coefficient is given by the Lorentz line-shape formula as

$$k_\nu = S\gamma_L / \pi [(\nu - \nu_0)^2 + \gamma_L^2], \quad (8)$$

where γ_L is the Lorentz half-width. The half-width is proportional to the frequency of collisions and hence approximately to the total pressure of the gas

$$\gamma_L \approx \gamma^0 P. \quad (9)$$

It was also assumed throughout this study that Doppler broadening made no measurable contribution to the linewidth. The half-width of a Doppler-broad-

TABLE IV. Lorentz half widths.

Transition (J)	Measured γ^0 (cm ⁻¹ /atm)	RDBM γ^0 (cm ⁻¹ /atm)
1	0.565	0.586
2	0.574	0.605
3	0.436	0.499
4	0.351	0.351
5	0.219	0.227
6	0.156	0.153
7	0.096	0.118
8	0.093	0.105
9		0.101
10	0.069	0.081
11	0.030	0.079
12	0.046	0.078
13	0.054	0.078
14	0.091	0.078
15	0.083	0.078

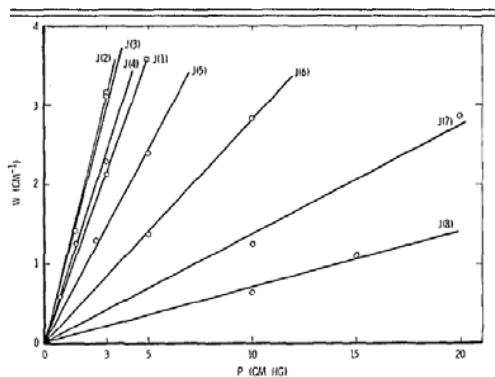


FIG. 1. Equivalent width vs pressure for lines $J(1)$ - $J(8)$.

^a Ref. 9.
^b Ref. 10.

Pure Rotational Absorption Spectrum of Hydrogen Fluoride Vapor between 22 and 250 μ

WALTER G. ROTHSCHILD

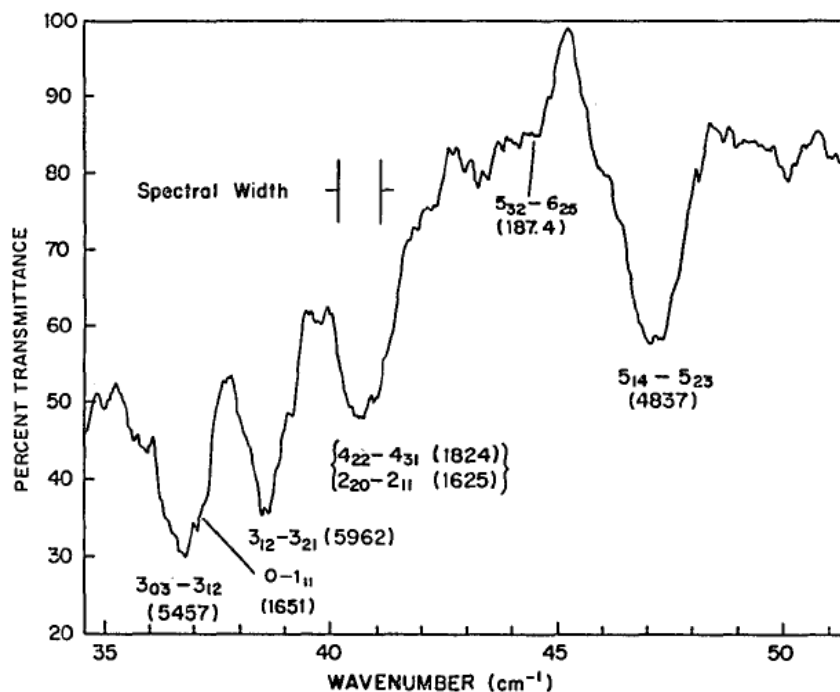


FIG. 1. Rotational spectrum of atmospheric water vapor between 50 and 35 cm^{-1} obtained by means of a modified Perkin-Elmer 301 (see text). The numbers in parentheses are the line strengths at 300°K in $\text{g}\cdot\text{cm}^{-2}$. The level assignment is given in the $K_{-1}K_1$ notation.

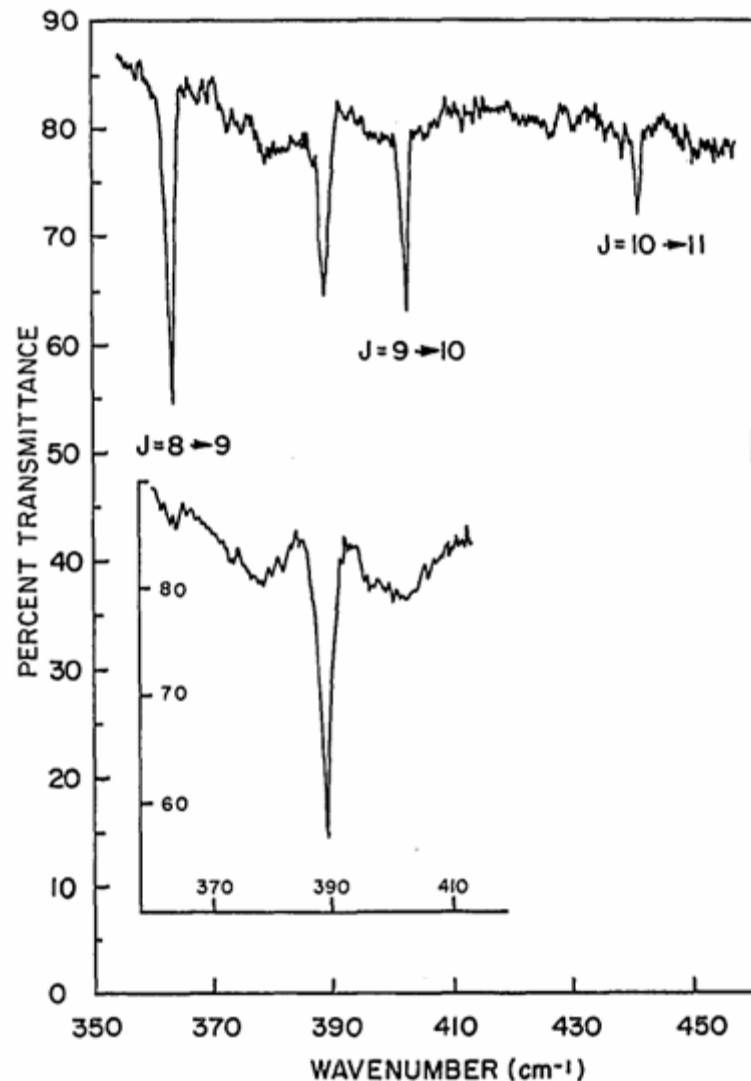


FIG. 2. The rotational transitions $J=8, 9,$ and 10 of hydrogen fluoride and the extraneous vibrational band at 389.1 cm^{-1} .

An identification of the band is not within the scope of this paper. Apparently, it belongs to a decomposition product due to the attack of HF or a reactive impurity contained in it, on polyethylene.

Infrared Spectrum of Hydrogen Fluoride*

G. A. KUIPERS AND D. F. SMITH, *Technical Division Oak Ridge Gaseous Diffusion Plant, Union Carbide Nuclear Company, Oak Ridge, Tennessee,*

AND

A. H. NIELSEN, *Department of Physics, The University of Tennessee, Knoxville, Tennessee*

The energy expression which contains sufficient terms to represent the data satisfactorily is given below as Eq. (1).

$$E/hc(\text{cm}^{-1}) = E_0/hc + \{\omega_e - x_e\omega_e(v + \frac{1}{2}) + y_e\omega_e(v + \frac{1}{2})^2 - z_e\omega_e(v + \frac{1}{2})^3\}(v + \frac{1}{2}) + B_e J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 - \{\alpha_e - \gamma_e(v + \frac{1}{2})\}(v + \frac{1}{2})J(J+1). \quad (1)$$

TABLE IV. Collected constants for HF from present investigation.

Constant	K, S, and N	Ref.
$\bar{\nu}_0(0\leftarrow-1)$	$3961.641 \pm 0.065 \text{ cm}^{-1}$	a
$\bar{\nu}_0(0\leftarrow-2)$	7751.238 ± 0.136	b
B_0	20.5534 ± 0.0060	a
B_1	19.7819 ± 0.0074	a
B_2	19.0279 ± 0.0146	b
D_0	0.002114 ± 0.000049	a
D_1	0.002069 ± 0.000093	a
D_2	0.002038 ± 0.000151	b
H_0	$(1.757 \pm 1.05) \times 10^{-7}$	a
H_1	$(2.144 \pm 3.75) \times 10^{-7}$	a
ω_e	4137.25_3	c
$x_e\omega_e$	88.72_6	c
$y_e\omega_e$	0.533_4	c
$z_e\omega_e$	-0.021_1	c
B_e	20.945_6	
D_e	0.00213_1	
α_e	0.788_3	
γ_e	0.0087_3	
β_e	-0.00003_3	

* Calculated using 23 lines from fundamental and 5 pure rotational lines. 95% confidence interval.

^b Calculated from first overtone. 95% confidence interval.

^c Calculated from $\bar{\nu}_0(0\leftarrow-1)$, $\bar{\nu}_0(0\leftarrow-2)$ this paper, and $\bar{\nu}_0(0\leftarrow-3)$, $\bar{\nu}_0(0\leftarrow-4)$, reference 3.

Because the hydrogen fluoride molecule is extremely anharmonic, it is necessary to include terms in $(v + \frac{1}{2})$ and $J(J+1)$ of higher power than the square in the energy in order to represent the data satisfactorily.

TABLE I. Vacuum wave numbers of the vibration-rotation lines of $0\leftarrow-1$ of HF (band center 3961.64 cm^{-1}).

Assignment	Obs $\bar{\nu} \text{ cm}^{-1}$	Calc $\bar{\nu} \text{ cm}^{-1}$	$\Delta(\text{O}-\text{C})$	Assignment	Obs $\bar{\nu} \text{ cm}^{-1}$	Calc $\bar{\nu} \text{ cm}^{-1}$	$\Delta(\text{O}-\text{C})$
R(0)	4001.27	4001.196	+0.074	P(1)	3920.45	3920.542	-0.092
R(1)	4039.23	4039.159	+0.071	P(2)	3877.89	3877.952	-0.062
R(2)	4075.51	4075.482	+0.028	P(3)	3833.96	3833.915	+0.045
R(3)	4110.16	4110.110	+0.050	P(4)	3788.47	3788.502	-0.032
R(4)	4143.01	4143.017	-0.007	P(5)	3741.71	3741.748	-0.038
R(5)	4174.11	4174.142	-0.032	P(6)	3693.75	3693.714	+0.036
R(6)	4203.35	4203.442	-0.092	P(7)	3644.44	3644.454	-0.014
R(7)	4230.97	4230.898	+0.072	P(8)	3594.00	3594.024	-0.024
R(8)	4256.45	4256.455	-0.005	P(9)	3542.49	3542.479	+0.011
R(9)	4279.98	4280.085	-0.105	P(10)	3489.97	3489.878	+0.092
R(10)	4301.70	4301.760	-0.060	P(11)	3436.36	3436.277	+0.083
R(11)	4321.48	4321.453	+0.027				

The wave number of a spectral line may be determined by application of the Bohr wave-number condition with the selection rules $\Delta v = \pm 1, 2, \dots$, etc., and $\Delta J = \pm 1$. For example, the wave number of any line in the R and P branch of the fundamental is given by

$$\begin{aligned} \bar{\nu}(R) = & \bar{\nu}_0(\text{band center}) + (B_0 + B_1)(J+1) \\ & + [(B_1 - B_0) - (D_1 - D_0)](J+1)^2 \\ & - [2(D_1 + D_0) - (H_1 + H_0)](J+1)^3 \\ & - [(D_1 - D_0) - 3(H_1 - H_0)](J+1)^4 \\ & + 3(H_1 + H_0)(J+1)^5 + (H_1 - H_0)(J+1)^6 \quad (2) \end{aligned}$$

$$\begin{aligned} \bar{\nu}(P) = & \bar{\nu}_0(\text{band center}) - (B_0 + B_1)J \\ & + [(B_1 - B_0) - (D_1 - D_0)]J^2 \\ & + [2(D_1 + D_0) - (H_1 + H_0)]J^3 \\ & - [(D_1 - D_0) - 3(H_1 - H_0)]J^4 \\ & - 3(H_1 + H_0)J^5 + (H_1 - H_0)J^6. \end{aligned}$$

In Eq. (2) J is the rotational quantum number of the $v=0$ state. Similar expressions may be written for the overtone transitions.

**Diagrammatic perturbation theory
Potential curves for the hydrogen fluoride molecule**

by STEPHEN WILSON†

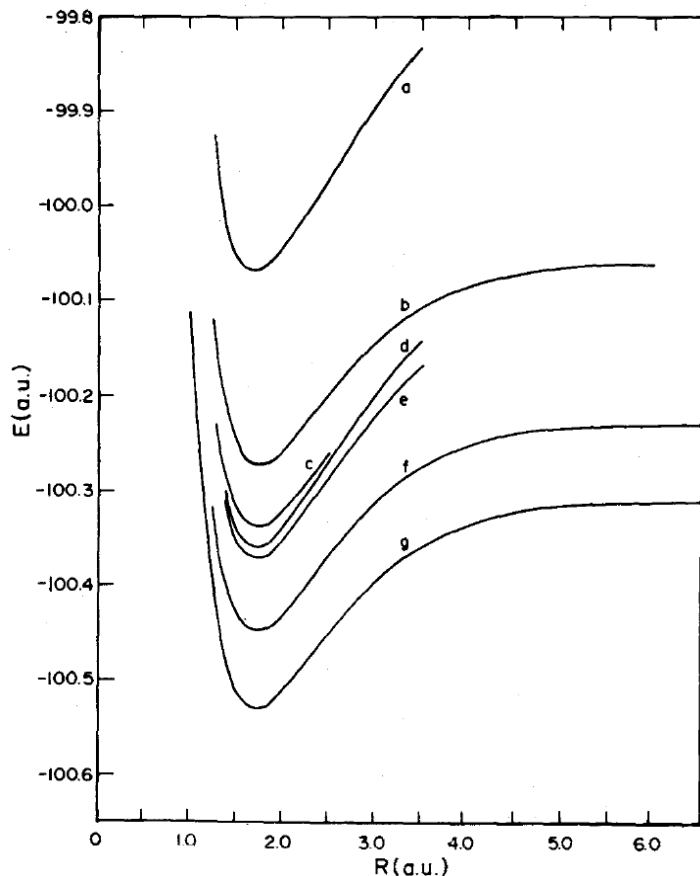


Fig. 2. Potential curves for the $X^1\Sigma^+$ state of the hydrogen fluoride molecule. Curve (a) is the Hartree-Fock potential energy function. Curve (b) is the function calculated by Dunning using the generalized valence-bond method. Curve (c) is that obtained by Meyer and Rosmus using the coupled electron pair method. Curve (d) corresponds to the $E_{\text{var}}(\gamma_{\text{opt}})$ energy values reported in this work, while curve (e) is the Padé approximant $E[2/1]$. Curves (f) and (g) are derived from experimental data. The latter is the Morse function determined by the experimental r_e , D_e , ω_e , while the former includes an empirical correction for the relativistic energies.

In this paper we report calculated potential energy curves for the $X^1\Sigma^+$ state of the hydrogen fluoride molecule. Diagrammatic perturbation theory [1-3] is employed through third order in the energy and through first order in the wave function. The Hartree-Fock independent electron model is used to generate the reference wave function. Since this function does not describe the dissociation of hydrogen fluoride correctly, we shall limit our study to that part of the potential curve close to the equilibrium configuration.