

High-Resolution Spectroscopy of HF from 40 to 1100 cm^{-1} : Highly Accurate Rotational Constants¹

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Highly accurate spectra of ground state rotational transitions in HF have been combined with earlier spectra to yield accurate rotational constants and frequencies of HF from 1 to 33 THz (40 to 1100 cm^{-1}). These lines can be used for accurate secondary frequency references for IR and FIR spectroscopy. Direct frequency measurements provided the references for the most accurate of these data. © 1987 Academic Press, Inc.

EXPERIMENTAL DETAILS

The HF spectra were recorded in four different laboratories with four different high-resolution experimental techniques. The first four rotational lines ($J = 1 \leftarrow 0$ to $4 \leftarrow 3$) were observed with a tunable far-infrared (TuFIR) spectrometer (1) at the National Bureau of Standards, Boulder, laboratory and were referred to frequency-measured CO_2 lines. The next three lines were observed using a commercial high-resolution Fourier transform spectrometer (FTS) at the National Research Council, Ottawa, Canada. The five lines from $J = 17$ to $J = 21$ were measured with a vacuum grating spectrograph using CO , CO_2 , and N_2O reference lines and were obtained from a pulsed HF laser (2). The highest-frequency set ($J = 26$ to $J = 32$) was measured in a dc glow discharge with a tunable diode laser spectrometer at the University of Lille, France (3).

The frequencies of the first four rotational transitions lie in the 1- to 6-THz region of the spectrum (300 to 50 μm). These lines, with an uncertainty of 1 part in 10^7 , provide benchmark frequency calibration standards in this region and reduce the uncertainty of these transitions by more than two orders of magnitude.

The complete TuFIR spectrometer is shown in Fig. 1 and the generation technique

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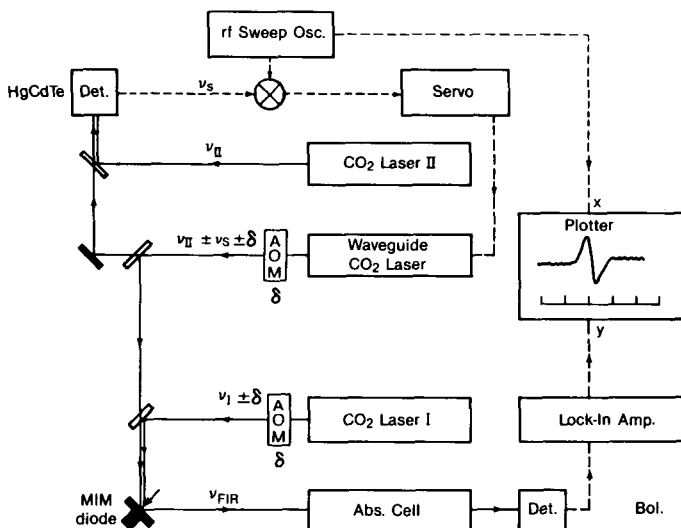


FIG. 1. Schematic of the TuFIR spectrometer.

is described elsewhere (1). The two drive lasers CO₂ laser I and CO₂ waveguide laser, were combined on the beam splitter and then focused on the metal-insulator-metal (MIM) diode where the far-infrared radiation was generated. Laser I was frequency modulated and the derivative of the absorption signal was observed following lock-in detection. Laser II was used to control the frequency of the waveguide laser by using frequency offset locking techniques. Both CO₂ lasers I and II were frequency stabilized with an accuracy of better than 25 kHz using the saturated fluorescence technique (4). The tunable far-infrared radiation was controlled by the rf sweep oscillator in the frequency offset lock loop. Opto-acoustic modulators operating to 90 MHz were used to isolate the lasers from the MIM point-contact diode and to provide an additional 180 MHz of tunability.

The detector used in this experiment was a Ge bolometer with a NEP of 10^{-13} W/(Hz)^{1/2} cooled to less than 1 K by a ³He cryostat. The overall noise level of the system corresponds to a fractional absorption of about 1×10^{-4} with a 1-sec time constant.

HF gas was maintained at a pressure of less than 1.33 Pa and all data were taken at room temperature, approximately 300 K. The first four rotational transitions of the HF ground state were observed and are listed in Table I.

The 200-cm⁻¹ transitions ($J = 4$ to $J = 6$) were observed with a FTS with a resolution of about 0.004 cm⁻¹ and an uncertainty of 3×10^{-4} cm⁻¹. Absorption spectra were observed at a pressure between 0 and 133 Pa with a 15-cm path length. Lower-frequency lines of HF and HCl were used to calibrate the spectrometer. The overall experimental uncertainty is about an order of magnitude greater than for the first four lines, but the set provides frequencies in a part of the spectrum not yet reached with laser techniques. The set from $J = 17$ to $J = 21$ is even less accurate; however, it furnishes the best available data in the 15- μ m region.

The highest-frequency set ($J = 26$ to $J = 32$) was observed in absorption in a dc

TABLE I
Measured and Calculated Frequencies of HF Rotational Lines

| J+1+J | Observed (cm ⁻¹) | Calculated ^a (cm ⁻¹) | Obs. - Calc. (cm ⁻¹) | Calculated ^a (THz) |
|-------|---------------------------------|------------------------------------------------|-------------------------------------|----------------------------------|
| 1 0 | 41.1109832(30) ^b | 41.1109816(46) | 1.6 E-6 | 1.23247622(14) |
| 2 1 | 82.1711179(60) ^b | 82.1711168(71) | 1.1 E-6 | 2.46342811(21) |
| 3 2 | 123.1296703(90) ^b | 123.1296765(95) | -6.2 E-6 | 3.69133484(28) |
| 4 3 | 163.9361645(120) ^b | 163.936166(20) | -1.3 E-6 | 4.91468261(62) |
| 5 4 | 204.54045(20) ^c | 204.540440(44) | 1.0 E-5 | 6.1319681(13) |
| 6 5 | 244.89283(20) ^c | 244.892817(80) | 1.3 E-5 | 7.3417019(24) |
| 7 6 | 284.94444(30) ^c | 284.94419(13) | 2.5 E-4 | 8.5424119(38) |
| 8 7 | | 324.64614(18) | | 9.7326464(55) |
| 9 8 | | 363.95103(25) | | 10.9109774(75) |
| 10 9 | | 402.81212(33) | | 12.0760035(98) |
| 11 10 | | 441.18365(41) | | 13.226353(12) |
| 12 11 | | 479.02095(50) | | 14.360687(15) |
| 13 12 | | 516.28050(61) | | 15.477700(18) |
| 14 13 | | 552.92004(72) | | 16.576126(22) |
| 15 14 | | 588.89862(86) | | 17.654737(26) |
| 16 15 | | 624.1767(10) | | 18.712346(30) |
| 17 16 | | 658.7161(12) | | 19.747813(35) |
| 18 17 | 692.4842(20) ^d | 692.4804(13) | 3.8 E-3 | 20.760040(40) |
| 19 18 | 725.4373(20) ^d | 725.4344(15) | 2.9 E-3 | 21.747975(45) |
| 20 19 | 757.5486(20) ^d | 757.5446(17) | 4.0 E-3 | 22.710616(50) |
| 21 20 | 788.7776(20) ^d | 788.7793(18) | -1.7 E-3 | 23.647009(53) |
| 22 21 | 819.1002(20) ^d | 819.1083(19) | -8.1 E-3 | 24.556249(55) |
| 23 22 | | 848.5030(19) | | 25.437480(55) |
| 24 23 | | 876.9366(18) | | 26.289899(53) |
| 25 24 | | 904.3841(16) | | 27.112752(49) |
| 26 25 | | 930.8218(14) | | 27.905334(43) |
| 27 26 | 956.2281(10) ^e | 956.2280(13) | 1.4 E-4 | 28.666993(39) |
| 28 27 | 980.5832(15) ^e | 980.5825(13) | 7.0 E-4 | 29.397124(39) |
| 29 28 | 1003.8672(10) ^e | 1003.8669(14) | 3.3 E-4 | 30.095172(42) |
| 30 29 | | 1026.0642(15) | | 30.760630(46) |
| 31 30 | 1047.1570(25) ^e | 1047.1591(15) | -2.1 E-3 | 31.393040(46) |
| 32 31 | 1067.1377(10) ^e | 1067.1378(17) | -1.4 E-4 | 31.991987(51) |
| 33 32 | 1085.9890(25) ^e | 1085.9881(33) | 8.5 E-4 | 32.557106(98) |

a) The uncertainty in the last digits (2σ) is given in parentheses;

b) Tunable Far Infrared Spectroscopy;

c) Fourier Transform Spectroscopy;

d) Ref. [3];

e) Diode laser measurement.

glow discharge modulated at 10 kHz. The glow discharge was necessary to heat the molecules to populate the high rotational levels, the highest being $18.5 \times 10^3 \text{ cm}^{-1}$ above the ground state. A 60-cm-long discharge cell with a 12-mm internal diameter and a mixture of 13.3 Pa of CF_4 , 5.3 Pa of H_2 , and 33.3 Pa of Ar was used. The apparatus was identical to that of Ref. (4), with the glow modulated at 10 kHz. Reference lines in C_2H_4 and OCS were used to provide accurate calibrations on each line. This set was crucial in providing the centrifugal distortion constants.

ANALYSIS OF THE DATA

The energy levels were fitted to the expression (5)

$$E_v(J) = B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 - L_v [J(J+1)]^4 + M_v [J(J+1)]^5.$$

TABLE II
Rotational Constants of Ground State HF

| | MHz | cm ⁻¹ |
|----------------|---------------------------|-----------------------------|
| B ₀ | 616365.199(75) | 20.5597300(25) |
| D ₀ | 63.5532(41) | 2.11991(14)10 ⁻³ |
| H ₀ | 4.897(15)10 ⁻³ | 0.16334(50)10 ⁻⁶ |
| L ₀ | 4.41(20)10 ⁻⁷ | 0.1473(66)10 ⁻¹⁰ |
| M ₀ | 2.82(80)10 ⁻¹¹ | 0.94(27)10 ⁻¹⁵ |

The uncertainty in the last digits (2σ) is given in parentheses.

In each fit each line was weighted according to the reciprocal squared of its respective uncertainty. Even though the highest-frequency lines were less accurate, they were nevertheless extremely important in determining the complete set of rotational constants.

The resulting rotational constants are presented in Table II and 2σ uncertainties are given. The wavenumbers and frequencies calculated from these constants are listed in Table I in the second and fourth columns along with a 2σ uncertainty. As a check on the fit either data set in the middle could be omitted with only a slight degradation of the observed minus calculated wavenumbers shown in column 3.

Although HF does not provide a high density of calibration lines, it is often present as an impurity spectrum in the most sensitive spectrometers and can now provide highly accurate lines over a wide region of the electromagnetic spectrum.

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