

THE FAR-INFRARED ROTATIONAL SPECTRUM OF THE CF RADICAL

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The rotational spectrum of CF in its ground electronic state was studied around 1000 GHz, using a tunable far-infrared source. Seven transitions were observed originating from the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ substates. The hyperfine and Λ -type splittings were resolved. The results were combined with gas-phase electron resonance and infrared diode laser spectra to determine all pertinent molecular constants

1. Introduction

The spectrum of the CF radical has been studied in the past by electronic [1,2] and infrared diode laser spectroscopy [3], by gas-phase electron-paramagnetic (EPR) [4], and laser magnetic resonance (LMR) [5], and by microwave spectroscopy [6]. However, since the Λ -doubling parameter q was still undetermined and of the magnetic hyperfine constants only a linear combination was known [4], it was felt necessary to investigate in more detail the rotational spectra of CF in the ground vibronic state. Several rotational transitions $J+1 \leftarrow J$ for J ranging from 17/2 to 23/2 in both the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sublevels fall within the range of our FIR side-band spectrometer. These spectra have been studied with high resolution in zero magnetic field. Both the Λ -doubling and hyperfine structure was resolved. Besides the normal rotational constants B and D , we determined the two Λ -doubling constants p and q and the four magnetic hyperfine parameters a , b , c and d of Frosh and Foley.

2. Experiment and results

The FIR side-band spectrometer has been described in detail elsewhere [7,8]. The radiation of a fixed-frequency HCN laser and that of a tunable millimeter wave klystron were mixed on a diode. The diode generated two beams of tunable far-infrared

radiation with a frequency equal to the sum and difference of the fundamental frequencies of laser and klystron (laser side-bands). The diode which was of the Schottky barrier type was mounted in a mixer with semi-open structure, i.e. the microwave radiation was transmitted to the diode via a normal closed rectangular waveguide penetrated by the diode stud, whereas far-infrared radiation was transported towards and from the diode via a whisker antenna mounted in free space. A Michelson-type interferometer [9] separated the side-bands from fundamental laser radiation and a simple monochromator was used to select the side-band beam corresponding to either the sum or difference frequency. The tunable side-band radiation then passed through a 1 m long absorption cell and was detected by a helium-cooled bolometer.

For each required side-band frequency the HCN laser was free running at one of its strongest lines at 890.7603 and 964.3127 GHz [8]. During the measurements the laser was set manually at the top of the gain profile. It was found that by this procedure the accuracy of the laser frequency setting was ± 0.8 MHz.

The CF radicals were produced by a dc glow discharge in a gas mixture rapidly flowing through the absorption cell. Several combinations of gases have been investigated. The best signals were obtained with a mixture of either argon and CF₄ or argon, CF₄ and methyl fluoride. The total pressure was in the region below 75 mbar and the discharge current be-

Table 1
Observed and calculated rotational transition ($J+1, F$) \leftarrow (J, F') (in MHz) of CF in its ground vibrational state

| Ω | $J+1$ | F^a | F' | Label | Observed frequency | Obs. - calc. | | |
|----------|-------|-------|------|-----------------------|--------------------|--------------|-----------------|------|
| 1/2 | 19/2 | 9e | 8e | ν_1 | 786 742.7(8) | -0.3 | | |
| | | 10e | 9e | ν_2 | 786 745.8(8) | -0.6 | | |
| | | 10f | 9f | ν_3 | 786 974.1(8) b) | - | | |
| | | 9f | 8f | ν_4 | 786 976.6(8) | 0.3 | | |
| 1/2 | 21/2 | | | $\nu_3 - \nu_2$ | 228.3(8) | -0.2 | | |
| | | 10e | 9e | ν_5 | 869 612.7(8) | 0.5 | | |
| | | 11e | 10e | ν_6 | 869 616.7(8) b) | - | | |
| | | 10f | 9f | ν_7 | 869 840.0(8) b) | - | | |
| | | 11f | 10f | | | | | |
| | | | | $\nu_6 - \nu_5$ | 4.0(4) | 0.1 | | |
| | | | | $\nu_7 - \nu_5$ | 223.3(8) | 0.2 | | |
| 1/2 | 23/2 | 11e | 10e | ν_8 | 952 484.6(8) | 0.7 | | |
| | | 12e | 11e | ν_9 | 952 488.7(8) b) | - | | |
| | | 11f | 10f | ν_{10} | 952 705.8(8) b) | - | | |
| | | 12f | 11f | | | | | |
| | | | | $\nu_9 - \nu_8$ | 4.1(4) | -0.2 | | |
| | | | | $\nu_{10} - \nu_8$ | 217.1(8) | -0.1 | | |
| 1/2 | 25/2 | 12e | 11e | ν_{11} | 1035 354.2(8) | 0.4 | | |
| | | 13e | 12e | ν_{12} | 1035 359.0(8) b) | - | | |
| | | 12f | 11f | ν_{13} | 1035 569.9(8) b) | - | | |
| | | 13f | 12f | | | | | |
| | | | | $\nu_{12} - \nu_{11}$ | 4.8(3) | 0.3 | | |
| | | | | $\nu_{13} - \nu_{11}$ | 210.9(8) | -0.2 | | |
| | | 3/2 | 19/2 | 10e | 9e | ν_{14} | 815 230.5(8) | -0.0 |
| | | | | 9e | 8e | ν_{15} | 815 248.4(8) b) | - |
| 10f | 9f | | | ν_{16} | 815 261.0(8) b) | - | | |
| 9f | 8f | | | ν_{17} | 815 274.3(8) b) | - | | |
| | | | | $\nu_{15} - \nu_{14}$ | 17.9(2) | 0.2 | | |
| | | | | $\nu_{16} - \nu_{15}$ | 12.7(2) | -0.2 | | |
| | | | | $\nu_{17} - \nu_{16}$ | 13.3(2) | -0.0 | | |
| 3/2 | 21/2 | | | 11e | 10e | ν_{18} | 900 671.8(8) | 0.1 |
| | | 10e | 9e | ν_{19} | 900 687.3(8) b) | - | | |
| | | 11f | 10f | ν_{20} | 900 708.2(8) b) | - | | |
| | | 10f | 9f | ν_{21} | 900 719.1(8) b) | - | | |
| | | | | $\nu_{19} - \nu_{18}$ | 15.5(2) | -0.1 | | |
| | | | | $\nu_{20} - \nu_{19}$ | 20.9(8) | 0.4 | | |
| | | | | $\nu_{21} - \nu_{20}$ | 10.9(2) | -0.0 | | |
| 3/2 | 25/2 | 13e | 12e | ν_{22} | 1071 239.7(8) | -0.1 | | |
| | | 12e | 11e | ν_{23} | 1071 252.2(8) b) | - | | |
| | | 13f | 12f | ν_{24} | 1071 287.9(8) b) | - | | |
| | | 12f | 11f | ν_{25} | 1071 294.9(8) b) | - | | |
| | | | | $\nu_{23} - \nu_{22}$ | 12.6(6) | -0.2 | | |
| | | | | $\nu_{24} - \nu_{23}$ | 35.0(3) | 0.2 | | |
| | | | | $\nu_{25} - \nu_{24}$ | 7.7(3) | 0.1 | | |

a) The *e/f* convention for labeling the levels suggested by Brown et al. [10] has been followed.

b) This line was left out of the fit; as indicated below, the difference of this line with another of the same rotational transition has been included.

tween 50 and 200 mA. Under these conditions it was possible to observe spectra of CF for several hours before cleaning of the cell became necessary.

To facilitate phase-sensitive detection Zeeman modulation has been applied. The modulation field was generated by a coil wrapped around the absorption cell, which produced a sine wave magnetic field alternating between 0 and ≈ 7.5 mT. The signal-to-noise ratio under optimum conditions varied between 10 and 50 at an integration time of 1 s. The full linewidth of the observed absorption lines was 2–3 MHz which is the Doppler limit at these frequencies. A list of the observed transition frequencies is given in table 1. The $\Pi_{3/2}$, $J = 23/2 \leftarrow 21/2$ transition is missing from this list, because it was unobservable due to strong absorption by atmospheric water vapour at 986 GHz. The accuracy in the absolute frequency of each line was limited by the uncertainty to which the HCN laser frequency could be set (0.8 MHz). The drift in the frequency of the free running laser was negligible during the short time interval of measurement of a single rotational transition. Consequently small splittings between the hyperfine Λ -doubling components of a rotational transition could be measured more accurately. The uncertainties in the splittings were dominated by the accuracy to which the peak frequencies of the individual components could be determined. Table 1 also lists these splittings.

3. Analysis and discussion

In order to obtain an accurate and as complete as possible set of the molecular parameters of CF we combined the present FIR spectra with most of the data available in the literature. The hamiltonian discussed in ref. [8] provides an adequate description of the fine structure contributions to the energy of a molecule in a $^2\Pi$ electronic state ‡ . This hamiltonian is based on a power-series expansion in R^2 , where R is the angular momentum of the nuclei. However, it was shown [11] on theoretical grounds that a hamiltonian expanded as a power series in N^2 is to be

‡ Eqs. (1) and (2) of the hamiltonian presented in ref. [8] contain two unfortunate misprints. In both equations the diagonal element for $\Omega = 1/2$ of A_D should read $-(X + 1)$, while the off-diagonal matrix element of the parity dependent Λ -doubling should read $\frac{1}{2}qX^{1/2}$.

Table 2

The molecular constants of CF($X^2\Pi$) in the $v = 0$ and $v = 1$ vibrational states. All values are in MHz, except A_{eff} and ν_0 , which are in cm^{-1}

| | $v = 0$ | $v = 1$ |
|-----------------------------|---------------|----------------|
| $A_{\text{eff}}^{\text{a)}$ | 77.11(1) | 76.46(1) |
| $A_{D,\text{eff}}$ | -7.94(22) | -7.98(30) |
| B_{eff} | 42197.031(59) | 41651.42(17) |
| D | 0.19870(23) | 0.19629(56) |
| P | 255.60(35) | 253.6(1.5) |
| q | 0.760(14) | |
| a | 633(29) | |
| b | 261(6) | |
| $b + \frac{1}{3}c$ | 195(18) | |
| d | 772(27) | |
| $c(\text{calc})$ | -200(61) | |
| $h(\text{calc})^{\text{a)}$ | 663.5(3.0) | |
| ν_0 | | 1286.14639(24) |

$^{\text{a)}$ $A_{\text{eff}}(v = 0)$ and h were restrained to 77.11(1) cm^{-1} [1] and 662.9(30) MHz [4], respectively (see text).

preferred; here $N = R + L$, with L being the electronic orbital momentum. We decided to follow this recommendation and the resulting molecular constants for CF given in table 2 are from a fit to the N^2 -type hamiltonian. Explicit expressions for matrix elements of the N^2 -type hamiltonian were recently published by Amiot et al. (ref. [12], table 2). The expansion in powers of the quantum number J of the total angular momentum is only slightly different for the R^2 - and N^2 -type hamiltonian and the only two major changes involve the rotational constant B and the vibrational energy spacing ν_0 :

$$B_{\text{eff},v}(N^2) - B_{\text{eff},v}(R^2) = 2D_v, \quad (1)$$

$$\nu_0(N^2) - \nu_0(R^2) = B_{\text{eff},1}(N^2) - B_{\text{eff},0}(N^2). \quad (2)$$

The hyperfine structure in CF can properly be described by the four parameters a , b , c and d of Frosh and Foley (for matrix elements see e.g. ref. [13]).

Recently Kawaguchi et al. [3] analyzed their diode laser spectra of the $v = 0 \rightarrow 1$ vibrational transition in CF using the R^2 -type hamiltonian. The parameter A_J^{eff} they use to describe the centrifugal distortion effect in the spin-orbit differs slightly from our $A_{D,\text{eff}}$. It can easily be shown that

$$A_{D,\text{eff}} = 2A_J^{\text{eff}} + Bp/(A - 2B). \quad (3)$$

As a check we reanalysed the data of Kawaguchi et al.

and found perfect agreement taking into account the relations (1)–(3). In the next step we added the present FIR data from table 2. For each rotational transition (except $\Pi_{1/2}$, $J = 19/2 \leftarrow 17/2$) we included in the fit the absolute frequency of one of the hyperfine Λ -doubling components and the frequency distances of the others, as indicated in table 1. In the cases of unresolved transitions the calculated average of these transitions was fitted to the observed frequency. This allowed us to reduce the uncertainty in some of the fine structure constants, and in addition to determine the Λ -doubling constant q and all the hyperfine structure parameters.

Two further steps were undertaken to improve the accuracy of the parameters of CF. Since the correlation between $A_{\text{eff},0}$ and $A_{\text{eff},1}$ has been removed in the combined set of FIR and IR data both parameters could be obtained. The results were in excellent agreement with those of Porter et al. [1]. However, the accuracy for $A_{\text{eff},0}$ of Porter et al. was still about a factor of five higher. We therefore restricted $A_{\text{eff},0}$ to the value $77.11(1) \text{ cm}^{-1}$ of Porter et al. and allowed this constant to vary within the given accuracy.

A similar situation occurred with the hyperfine parameters. The present FIR data allow an independent determination of all four hyperfine parameters. Carrington and Howard [4] obtained from their EPR studies of CF $b = 190(50) \text{ MHz}$ and a linear combination between a , b and c .

$$\tilde{h} = a + \frac{1}{2}(b + c) = 662.9(3.0) \text{ MHz} . \quad (4)$$

The value for h we derived purely from the FIR spectra was in agreement with that of Carrington and Howard. However, their uncertainty in this constant was about a factor of 10 smaller than ours. We therefore restrained h to $662.9(3.0) \text{ MHz}$, again free to vary within its error limits. This procedure considerably improved the accuracy of the four independent hyperfine structure parameters. The constants obtained from the final least-squares fit are in table 2. The agreement between the results of the best fit calculation and the experimental frequencies is excellent as can be seen from table 2.

Since all four hyperfine structure parameters for the ground vibrational state are now known, an independent determination of the expectation values associated with the unpaired electron is made possible. Using relations given before [14] we find $\langle 1/r^3 \rangle_{\text{U}} = 8.50(40)$, $\langle (3 \cos^2\theta - 1)/r^3 \rangle_{\text{U}} = -1.78(57)$,

$\langle \sin^2\theta/r^3 \rangle_{\text{U}} = 6.94(24)$ and $\langle \Psi^2(0) \rangle_{\text{U}} = 0.313(29)$, all in units of 10^{24} cm^{-3} . It follows that the ratios between the first three quantities is not equal to that of a pure p-orbital centered at the fluorine atom $(4/5) : (-2/5) : 1$. It also follows that the assumption of Carrington and Howard [4] that the contribution to the Fermi contact term $\langle \Psi^2(0) \rangle_{\text{U}}$ arises mainly from the fluorine s atomic orbital is too simple.

The prediction from SCF calculations by Hall and Richards [15] is: $\langle 1/r^3 \rangle = 8.5$ and $\langle (3 \cos^2\theta - 1)/r^3 \rangle = -2.9$, in units of 10^{24} cm^{-3} . Although the authors claim that their method of calculation predicts the spin distributions poorly, their results are in quite good agreement with the present experimental values.

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References

- [1] T.L. Porter, D.E. Mann and N. Aquista, *J. Mol. Spectry.* **16** (1965) 228.
- [2] D.K. Carroll and T.P. Grennan, *J. Phys.* **B3** (1970) 865.
- [3] K. Kawaguchi, C. Yamada, Y. Hamada and E. Hirota, *J. Mol. Spectry.* **86** (1981) 136.
- [4] A. Carrington and B.J. Howard, *Mol. Phys.* **18** (1970) 225.
- [5] R.J. Saykally and K.M. Evenson, 34th Symposium on Molecular Spectroscopy, Columbus, Ohio, 1979, paper TG4.
- [6] S. Saito, Y. Endo and E. Hirota, 41st Annual Meeting of the Chemical Society of Japan, Osaka, 1980, paper ID31.
- [7] D.D. Bićanić, *Intern. J. Infrared Millimeter Waves* **2** (1981) 247.
- [8] G.C. van den Heuvel, W.L. Meerts and A. Dymanus, *J. Mol. Spectry.* **84** (1980) 162.
- [9] N.R. Erickson, *IEEE Trans. MTT* **25** (1977) 865.
- [10] J.M. Brown, J.T. Hougan, K.-P. Huber, J.W.C. Johns, I. Kopp, H. Lefebvre-Brion, A. J. Merer, D.A. Ramsay, J. Rostas and R.N. Zare, *J. Mol. Spectry.* **55** (1975) 500.
- [11] J.M. Brown, E.A. Colbourn, J.K.G. Watson and F.D. Wayne, *J. Mol. Spectry.* **74** (1979) 294.
- [12] C. Amiot, J.-P. Maillard and J. Chauville, *J. Mol. Spectry.* **87** (1981) 196.
- [13] W.L. Meerts, J.P. Bekooij and A. Dymanus, *Mol. Phys.* **37** (1979) 425.
- [14] W.L. Meerts and A. Dymanus, *Can. J. Phys.* **53** (1975) 2123.
- [15] J.A. Hall and W.G. Richards, *Mol. Phys.* **23** (1972) 331.